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REACTIONS OF MOLYBDENUM AND TUNGSTEN HYDRAZIDO(2-) COMPLEXES WITH ALKENES

by

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ABSTRACT

The reaction between transition metal hydrazido(2-) complexes and alkenes by Stephen Alan Taylor

The reactions between cyanoalkenes and dinitrogen derived hydrazido(2-) complexes of molybdenum and tungsten were investigated. Two types of reaction were observed, either the formation of vinyldiazenido(1-) complexes or a reaction with loss of the hydrazido(2-) ligand and formation of nitrile-derived methyleneamino complexes. A single crystal-X-ray study has characterised the bromotricyanoprop-2-enylideneamino ligand. The kinetics and mechanism of the former reaction have been investigated.

Protonation of the vinyldiazenido(1-) complexes with HBF_4 in thf produced vinylhydrazido(2-) complexes, which were reduced electrochemically via a four electron reduction to give aminocyanopyrazoles and the starting hydrazido(2-) complex. A cyclic process for the formation of aminocyanopyrazole is described.

The reaction between the hydrazido(2-) complex and alkenes activated by either palladium or mercury salts was investigated, and attempted intramolecular cyclisation reactions to form heterocyclic ring structures on the terminal nitrogen atom of alkenylhydrazido(2-) complexes are described. The reaction between the hydrazido(2-) complex and alkenes in strong acid solution was also briefly investigated.

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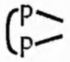
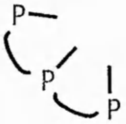
ABBREVIATIONS

1. General

acac = 3,5 pentanedionate
b.p. = boiling point
Bu^n = n-butyl
Bu^t = tertiary-butyl
Cp = cyclopentadienyl
DDQ = dichloro-dicyano-quinodimethane
dme = 1,2 dimethoxyethane
dec. = decomposed
depe = 1,2 bis(diethylphosphino)ethane
dmf = dimethylformamide
dppe = 1,2 bis(diphenylphosphino)ethane = 
Et = ethyl
i.r. = infra-red
Me = methyl
m.p. = melting point
n.m.r. = nuclear magnetic resonance
Ph = phenyl
Pr^i = iso-propyl
Pr^n = n-propyl
TCNQ = 7,7,8,8-tetracyanoquinodimethane
TCQ = tetrachloro-o-benzoquinone
thf = tetrahydrofuran
triphos = Bis(2-diphenylphosphinoethyl)phenylphosphine = 

2. Electrochemical

Ep^1 = primary peak potential
Ep^2 = secondary peak potential
ip = peak current
n = number of electrons
ox = oxidation
red = reduction

3. Spectroscopic

i.r. spectra

s = strong

m = medium
w = weak
br = broad

n.m.r. spectra

br = broad
d = doublet
m = multiplet
q = quartet
qn = quintet
s = singlet
t = triplet
v = very

CHAPTER ONE

INTRODUCTION

(i) AIM OF THE PROJECT

The broad aim of the project is to investigate the production of amino- or hydrazino- alkenes from gaseous dinitrogen, coordinated to a transition metal, and a relatively available alkene. Necessarily this involves investigating reactivities and properties of the intermediate transition metal complexes, the nature of the organic product, and the possibility of generating a cyclic process. The work presented here discusses the synthetic, kinetic and electrochemical aspects of such a system.

(ii) HISTORICAL BACKGROUND

Although it was realised as early as 1930 that molybdenum is necessary for the fixation of atmospheric dinitrogen by the nitrogenase enzyme, it was not until 1969 that the first molybdenum-dinitrogen complex was reported (1). Indeed, prior to 1965 transition metal - dinitrogen complexes were unknown. The known reactions of the dinitrogen molecule were very few, being limited to:

1. Rection with metallic lithium to give lithium nitride, Li_3N.
2. Reactions at elevated temperatures and pressures, for example,

$$N_2 + 3Mg \rightarrow Mg_3N_2$$
$$N_2 + 3H_2 \rightarrow 2NH_3$$
$$N_2 + CaC_2 \rightarrow C + CaNCN$$

3. Enzymic reduction to ammonia.

Since dinitrogen is isoelectronic with carbon monoxide, it may be expected that dinitrogen could act as a ligand to transition metals, bonding in a linear manner (M-NN) analogous to the well known transition metal-carbonyls (M-CO).

In 1965, Allen and Senoff described the first transition metal-dinitrogen complex $[Ru(NH_3)_5(N_2)]^{2+}$, prepared from aqueous ruthenium (III) chloride and hydrazine (2). This complex was later prepared directly from dinitrogen (3).

The first molybdenum-dinitrogen complex was $[(CH_3Ph)Mo(PPh_3)_2(N_2)]$ reported in 1969 (4), followed in the same year by the trans bis(dinitrogen) complex trans $[Mo(N_2)_2(dppe)_2]$ (1).

Since that time, a greater understanding of the nature of the transition metal-dinitrogen bond and the properties of the metal centre which facilitiate dinitrogen coordination, combined with improved inert atmosphere techniques, have produced a large number and wide variety of transition metal-dinitrogen complexes. A comprehensive review of such complexes has been published by Chatt and his co-workers, covering the work in this area up to 1978 (5).

Recent work has placed emphasis on further analysis and characterisation of the many transition metal-dinitrogen derivatives already prepared, including ^{15}N n.m.r. spectroscopy, X-ray single crystal studies and electrochemical studies.

The interest in transition metal-dinitrogen chemistry has centred on two areas:

1. The protonation and reduction of ligating dinitrogen, to form nitrogen hydrides.
2. Carbon-nitrogen bond formation (in which the carbon fragment is ideally derived from a cheap feedstock), as a method of producing organo-nitrogen chemicals.

Both areas are of obvious economic and industrial importance, the former as an alternative to the energy intensive Haber process, the latter as a source of organo-nitrogen chemicals directly from dinitrogen, possibly catalytically. Both areas are likely to be of increasing importance as the world's energy resources are consumed.

(iii) THE TRANSITION METAL-DINITROGEN BOND

Before the discovery of the first metal-dinitrogen complex, several theories were put forward as to why dinitrogen did not coordinate to transition metals (6). However, with the report of $[Ru(NH_3)_5(N_2)]^{2+}$, a revision of ideas was needed to explain the bonding in this and, subsequently, many other dinitrogen complexes.

By far the most common bonding mode between dinitrogen and a transition metal is a linear, or "end-on" mode ($M \leftarrow N \equiv N$), in which the electron-distribution may be described as follows. Electrons are donated from the dinitrogen $3\sigma_g$ orbital to a hybrid acceptor orbital or d orbital of suitable symmetry on the metal, and there is back donation from a d (or hybrid) orbital on the metal to the antibonding $1\pi^*_g$ orbital on the dinitrogen ligand. The overall result is that electron density is removed from the bonding σ orbital on the dinitrogen ligand and electrons are supplied to the antibonding orbital from the metal. This synergic effect produces a build up of negative charge on the terminal nitrogen atom, and a considerable weakening of the nitrogen-nitrogen bond. The valence-bond interpretation of this effect is illustrated diagramatically in figure 1.

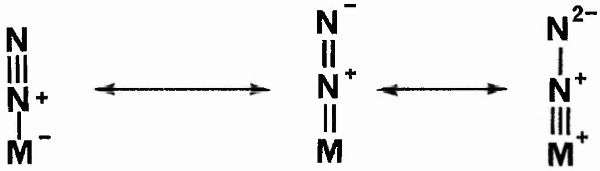


Figure 1

A comparison of the complexes formed by dinitrogen ligand with the isoelectronic carbonyl ligand shows that the dinitrogen complexes are relatively unstable and scarce, whereas the corresponding carbonyl complexes are more stable and abundant. This difference is ascribed to the relative σ donor/π acceptor properties of the ligands. The use of Mössbauer spectroscopy enables a comparison of the σ donor/π acceptor properties of dinitrogen with other ligands. For the complex trans[FeH(L)(ddpe)$_2$]BPh$_4$ (L = N_2, CO, PhNC, MeCN, etc) the ^{57}Fe isomer shifts are dependent upon the s electron density at the metal nucleus, which is affected by the σ donor/π acceptor properties of L (7). The results indicate that the dinitrogen ligand has a σ donor ability which is less than that of any other ligand, and a π acceptor ability which is moderate and lies between carbon monoxide and organic cyanides. Hence the overall effect for dinitrogen is to withdraw electrons from the metal to an extent that is similar to carbon monoxide, but the total electron transfer in both directions is less than for carbon monoxide and the corresponding metal-ligand bond is weaker.

The above bonding scheme is supported by data from other physical techniques.

1. Infra red spectroscopy : the lowered frequency of the N-N stretching vibrations of transition metal-dinitrogen complexes (compared with gaseous N_2 at 2331 cm^{-1} (Raman)), indicating strong π electron back donation from metal to ligand, and a general weakening and slight lengthening of the N-N bond, (the latter is further supported by X-ray crystallography).
2. X-ray photoelectron spectroscopy : results indicate a build up of negative charge on the ligand, with the terminal nitrogen carrying a higher charge than the metal bound nitrogen e.g. for $[ReCl(N_2)(dppe)_2]$ the spectrum shows two peaks at 28.6 MJ (metal bound nitrogen) and 38.4 MJ (terminal nitrogen) (8). For gaseous dinitrogen a single peak appears at 39.7 MJ.

The linear configuration of metal and dinitrogen ligand represents the most favourable end-on bonding mode. Any bending of the $M \leftarrow N \equiv N$ bonding system results in decreased orbital overlap between metal and dinitrogen, thereby reducing the stability of the metal-nitrogen bond.

Several other bonding modes are found, but are much less common, for example;

1. the lateral or "side on" mode (9), proposed for $[(Cp)_2\ Zr(CH\ SiMe_3)_2\ \ N_2]$;
2. the "end on bridging" mode (10), found for $[(C_5Me_5)_2\ Zr(N_2)]_2\mu(N)_2$;
3. the "sideon bridging" mode (11), the only example being $[(PhLi)_6Ni_2\ (N_2)\ (Et_2O)_2]$.

A characteristic of all stable transition metal-dinitrogen complexes is the presence of strong σ donor co-ligands (phosphine, amine, hydrido, for example) and a metal in a low oxidation state (-1 to +2), implying that a high electron density on the metal centre is necessary for coordination of dinitrogen. This is consistent with dinitrogen acting primarily as an electron acceptor.

The bonding scheme for the "end on bridging" mode has been reviewed by Sellmann (12).

(iv) GENERAL CHEMISTRY OF MOLYBDENUM AND TUNGSTEN-DINITROGEN COMPLEXES

Dinitrogen complexes of molybdenum and tungsten, and their derivatives are probably the most thoroughly studied and best characterised of all the transition metal-dinitrogen complexes prepared to date. Much of this work has been carried out by Chatt and his co-workers at the A.R.C. Unit of Nitrogen Fixation, University of Sussex, with contributions from George at the University of Lincoln, Nebraska, Hidai at the University of Tokyo, Sellmann at the Technical University of Munich and Colquhoun at I.C.I. New Science Group.

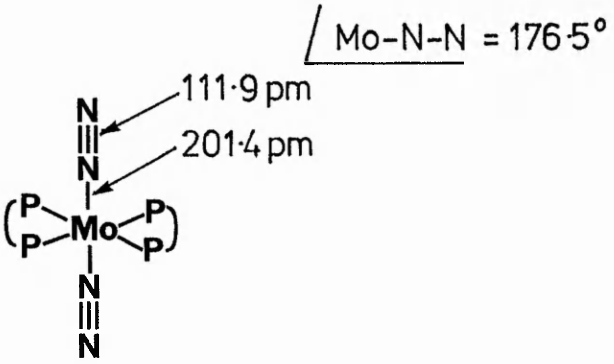
The major reasons for the interest in this group of dinitrogen complexes are:

1. the presence of molybdenum in the nitrogenase enzyme, and its possible role in the nitrogen fixation process, and
2. both molybdenum and tungsten (particularly the latter) form relatively stable dinitrogen complexes, hence facilitating investigation of the reactivity of dinitrogen coordinated to a metal centre.

The brief review which follows describes the synthesis and properties of molybdenum and tungsten dinitrogen complexes and derivatives containing phosphine co-ligands which have been prepared and investigated up to July 1982. Additionally, recent work at the University of Sussex has produced a series of hydrazido (2-) complexes of molybdenum containing dithiocarbamate co-ligands. The nitrogen ligands are, however, obtained from hydrazine derivatives and not from free dinitrogen (13, 14, 15). A dinitrogen complex derived directly from dinitrogen containing the dithiocarbamate ligand is, as yet, unknown.

A. Synthesis of molybdenum and tungsten bis(dinitrogen) complexes containing bi- and tridentate phosphine ligands

The first preparation of trans $[Mo(N_2)_2(dppe)_2]$, reported in 1969 (1), involved the use of $[Mo(acac)_3]$, tri-isobutylaluminium, and dppe in toluene under N_2. The dinitrogen complex was obtained in 30% yield after a reaction time of five days. Several other methods have appeared for the preparation of this complex (16, 17, 18, 19) culminating in perhaps the most convenient synthesis from $[MoCl_5]_2$ and dppe in thf under N_2 with 1% sodium amalgam as the reducing agent (20). A single crystal X-ray structure of this complex shows the centrosymmetric structure (21);



(where  represents dppe)

Figure 2

The tungsten analogue may be prepared from the magnesium reduction of $[WCl_4(dppe)]$ in the presence of dppe in thf under N_2 to give 70-80% yield of product (22). The most convenient synthesis of trans$[W(N_2)_2(dppe)_2]$ is that of Colquhoun (23; see Chapter 2 section (i)) a single-vessel preparation giving a yield of ca. 80% after 60 hours.

Other bidentate ligands used in the synthesis of molybdenum and tungsten bis(dinitrogen) complexes include $Ph_2P(CH_2)_nPPh_2$ (where n=1,3) (24), $Ph_2PCH{=}CHPPh_2$ (24) and $Ph_2As(CH_2)_2AsPh_2$ (25), though these are very much less commonly used than the stable, readily available dppe ligand.

Complexes containing a mixture of either bidentate and monodentate or tridentate and monodentate phosphines have been reported. Complexes of the type $[M(N_2)_2(PMe_2Ph)_2(dppe)]$ (M = Mo, W) have been prepared in moderate yield by reduction of $[MCl_4(dppe)]$ or cis $[M(N_2)_2(PMePh_2)_4]$

in thf under N_2 in the presence of the appropriate phosphine (26). Recently, molybdenum bis(dinitrogen) complexes of the type trans$[Mo(N_2)_2(triphos)(PR_3)]$ (R = Ph, mPhMe, pPhMe) have been prepared (27). The tungsten analogues have not been reported.

The action of a variety of oxidising agents on $[M(N_2)_2(dppe)_2]$ (M = Mo, W), will produce the M(I) cation trans $[M(N_2)_2(dppe)_2]^+$. These include I_2 (28, 29; M = Mo, W), $FeCl_3$ (29; M = W), tetracyanoethene (29; M = W) and other organic electron acceptor molecules (for example T.C.N.Q., T.C.Q.; 30). The cation may also be generated electrochemically (28, 31). Protonation of trans$[W(N_2)_2(dppe)_2]$ with HCl produces the hydride complex $[WH(N_2)_2(dppe)_2]^+HCl_2^-$ (16).

B. Synthesis of molybdenum and tungsten mono(dinitrogen) complexes containing bidentate phosphine ligands

The Mo(I) complex $[MoX(N_2)(dppe)_2]$ (X = Cl, Br) has been reported by two groups of workers (17, 32). However, this complex has been shown to consist of a co-crystallised mixture of trans$[Mo(N_2)_2(dppe)_2]$ and trans$[MoX_2(dppe)_2]$ by raman spectroscopy (29), cyclic voltammetry and electron spin resonance spectroscopy (33).

Mono(dinitrogen) complexes may be prepared by a ligand exchange reaction via the parent bis(dinitrogen) complexes. Reaction between trans$[Mo(N_2)_2(dppe)_2]$ and organic nitriles in toluene produces complexes of the type trans $[Mo(N_2)(RCN)(dppe)_2]$ where R = Me, Ph, p-C_6H_4Cl, p-C_6H_4OMe, p-$C_6H_4NH_2$ for example (34, 35). The analogous tungsten complexes, where R = Me, Ph have also been reported (33, 36).

The complex trans$[Mo(N_2)(CO)(dppe)_2]$ may be prepared via the reaction sequence (37, 38):

$$\begin{array}{c} \text{trans }[Mo(N_2)_2(dppe)_2] \\ \downarrow \text{ d.m.f., benzene, reflux} \\ [Mo(\text{d.m.f.})(CO)(dppe)_2] \\ \downarrow N_2\text{, benzene} \\ [Mo(N_2)(CO)(dppe)_2] \end{array}$$

The dinitrogen ligand in $[Mo(N_2)(CO)(dppe)_2]$ is labile and may be replaced by a variety of nitrogen donor ligands, for example, amines, nitriles, pyridines, or imidazoles (38).

Anionic complexes of the type trans$[M(N_2)X(dppe)_2]^-$ (M = Mo, W; X = SCN^-, CN^-, N_3^-) may be prepared from the parent bis(dinitrogen) complex and the appropriate tetraalkylammonium salt. The complexes are sensitive to oxidation and readily lose one electron to form the analogous neutral complex (39). The higher oxidation states of these complexes (generated electrochemically) are more stable, compared with those of the bis(dinitrogen) complexes. This enhanced stability is attributed to the greater net donor effect of the anionic ligand compared with N_2, thereby strengthening the M-N_2 bonding interaction (39). Thus, where X is the neutral ligand RCN, the following oxidation states may be generated (36);

$$\begin{array}{ll} [M(N_2)(RCN)(dppe)_2] & M(0) \\ \quad -e \downarrow\uparrow +e & \\ [M(N_2)(RCN)(dppe)_2]^+ & M(I) \\ \quad -e \downarrow\uparrow +e & \\ [M(N_2)(RCN)(dppe)_2]^{2+} & M(II) \end{array}$$

C. Reactivity of molybdenum and tungsten bis(dinitrogen) complexes containing bi and tridentate phosphine ligands

Many reagents cause complete loss of dinitrogen on reaction with trans$[M(N_2)_2(dppe)_2]$ (M = Mo, W) especially where M = Mo. Examples of reagents which displace coordinated dinitrogen include CO, forming cis$[M(CO)_2(dppe)_2]$ via a trans intermediate (M = Mo; 28, 40, 41); H_2, forming $[MH_4(dppe)_2]$ (M = Mo; 42); isocyanides, forming trans$[M(CNR)_2(dppe)_2]$ (M = Mo, W; R = Me, Ph, Bu^t; 43, 44); and thiols, forming trans $[M(SR)_2(dppe)_2]$ (M = Mo; R = Et, Ph, Pr^n, Bu^n; 45).

Perhaps the simplest reaction of coordinated dinitrogen is the formation of an adduct with a Lewis acid. The Lewis base properties of the terminal nitrogen result from the build up of negative charge at this atom (on complexation) as discussed earlier. Adducts with trialkylaluminium complexes have been prepared, (46) for example trans-$[M(N_2)(N_2AlR_3)(dppe)_2]$ (M = Mo, W; R = Me, Ph). Since the simplest Lewis acid is the proton, it would be expected that this would also react with the terminal nitrogen, thereby providing a method for the direct reduction of ligating dinitrogen. However, since the transition metal centre is in a low oxidation state and must be considered electron rich, despite any electron donation to the dinitrogen ligand, it is also a potential site for protonation. In the reaction between trans$[W(N_2)_2(dppe)_2]$ and anhydrous HCl, protonation occurs at the metal, producing the seven coordinate species $[WH(N_2)_2(dppe)_2]^+$ mentioned earlier. However, the use of other acids, eg. HBr leads to protonation at the terminal nitrogen.

The reaction between trans $[M(N_2)_2(dppe)_2]$ (M = Mo, W) and HBr in thf produces hydrazido(2-) complexes (16);

$$\text{trans}[M(N_2)_2(dppe)_2]$$
$$\downarrow \text{HBr}$$
$$\text{trans}[MBr(N_2H_2)(dppe)_2]^+Br^- + N_2$$

An analogous reaction occurs where M = W and the acid is HCl (>5 molar excess), and where M = Mo, W and the acid is HBF_4 (30, 47) or H_2SO_4 (48). Crystal structures for $[MX(N_2H_2)(dppe)_2]^+$, where M = W, X = Cl (49) and M = Mo, X = F (47) show the following bond lengths and angles:

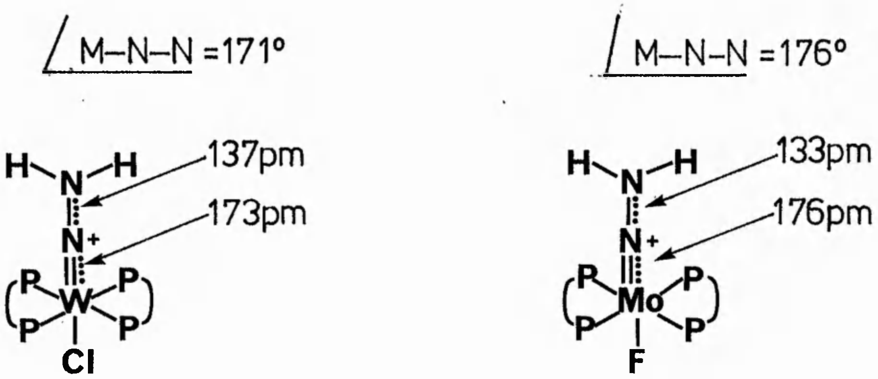


Figure 3

The M-N-N unit is essentially linear. The M-N bond lengths indicate considerable multiple bonding, and the N-N bond lengths indicate a bond order of 1.5-2.

Complex	M-N/pm	N-N/pm	Ref.
$[MoF(N_2H_2)(dppe)_2]^+BF_4^-$	176.2	133.3	47
$[WCl(N_2H_2)(dppe)_2]^+BPh_4^-$	173.1	137.2	49
$[WBr(N_2Me_2)(dppe)_2]^+Br^-$	172.4	135.5	50
$[WBr(N_2CH(CH_2)_3OH)(dppe)_2]^+PF_6^-$	178.0	131.0	50
$[WBr(N_2HMe)(dppe)_2]^+$	176.8	132.2	51
$[Mo(N_2)_2(dppe)_2]$	201.4	111.9	21
N_2	-	109.8	-
trans PhN=NPh	-	124.4	-

The valence bond representation of the structure may be considered as two extreme forms;

(i) (ii)

Figure 4

with cannonical form (ii) providing the main contribution to the structure.

The uncoordinated anion may undergo metathetical exchange reactions with suitable anions, for example, PF_6^-, ClO_4^- and BPh_4^-. The reaction between trans$[Mo(N_2)_2(dppe)_2]$ and aqueous HCl produces loss of dinitrogen, with the formation of $[MoCl_2H_2(dppe)_2]$ (16).

Kinetic studies of the protonation of coordinated dinitrogen in trans$[M(N_2)_2(dppe)_2]$ (M = Mo, W) indicate the following ionic mechanism (106);

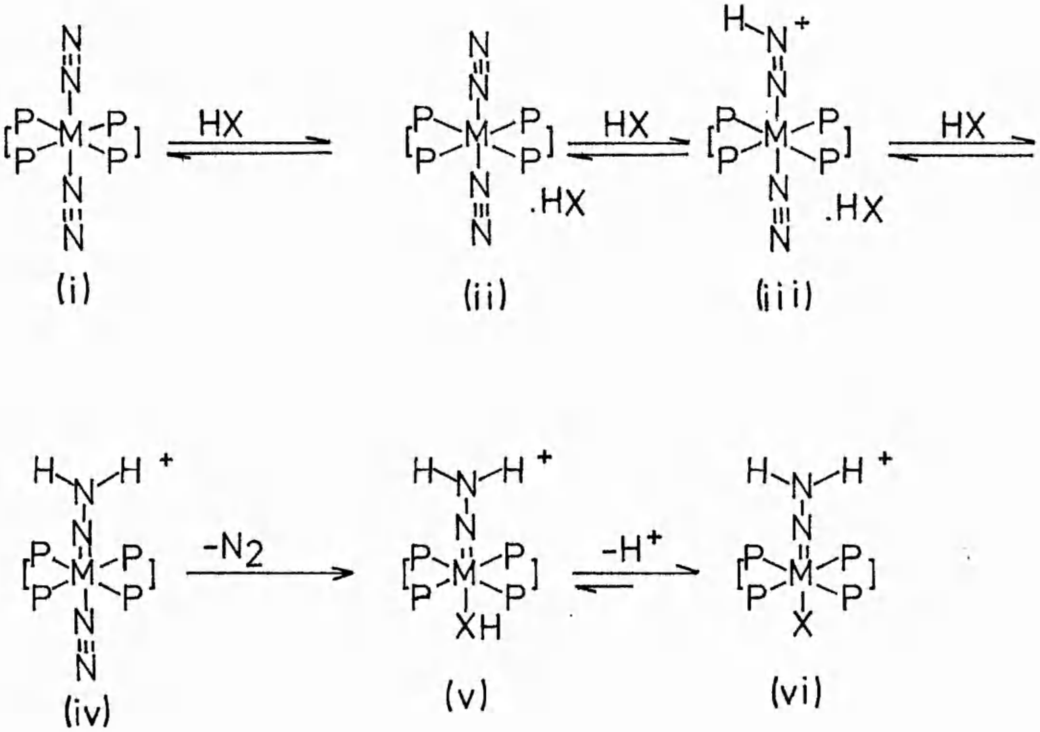


Figure 5

An initial adduct (ii) is formed between the bis(dinitrogen) complex and the acid. Protonation of the terminal nitrogen then occurs via (iii) and (iv) to give the hydrazido(2-) ligand. This labilises the trans dinitrogen ligand, since it withdraws electron density from the metal to a greater extent than dinitrogen. Rate limiting loss of dinitrogen then occurs followed by coordination of HX to the vacant site on the metal. Cleavage of the H-X bond produces the hydrazido(2-) complex.

Attempts at further protonation of the coordinated dinitrogen ligand beyond the hydrazido(2-) stage, using a variety of reagents (16), does not produce a stable complex with the ligand still coordinated. The diazenium complex $[MX(N_2H_3)(dppe)_2]^{2+}$ and the hydrazido(1-) complex $[MX(NHNH_2)(dppe)_2]^{2+}$ are unknown, although the former may exist in solution since the yellow-brown hydrazido(2-) complex gives a deep purple solution when dissolved in strong acids (eg. CF_3CO_2H/cH_2SO_4). Attempts to isolate this complex have only resulted in recovery of the

the starting material (30). When [$WBr(N_2H_2)(dppe)_2]^+Br^-$ is heated at 80°C in a sealed tube in the presence of CH_2Cl_2 and HBr for 15 hours, moderate yields of ammonia (0.4 mol/W atom) and hydrazine (0.44 mol/W atom) are obtained (52). If a mixture of trans[$Mo(N_2)_2(dppe)_2$] and [$MoBr(N_2H_2)(dppe)_2]^+Br^-$ is treated with HBr in a high boiling solvent such as propylene carbonate or N-methylpyrrolidone, removal of solvent and Kjeldahl distillation produces ammonia (0.24 mol/Mo atom) (48). In both this and the previous process, the phosphine ligands are displaced and the metal complex is irreversibly destroyed.

In contrast, the complex trans[$Mo(N_2)_2(PPh_3)$(triphos)] can be protonated by excess HBr to produce free ammonia (0.8 mol/Mo atom) and [$MoBr_3$(triphos)], the latter being a precursor to the parent bis(dinitrogen) complex (27, 53).

The hydrazido(2-) complexes containing dppe may be dehydrohalogenated with weak bases, for example Et_3N or aqueous K_2CO_3, to give diazenido complexes ((ii) figure 6). Addition of acid to a diazenido complex regenerates the hydrazido(2-) complex ((i) figure 6) (48).

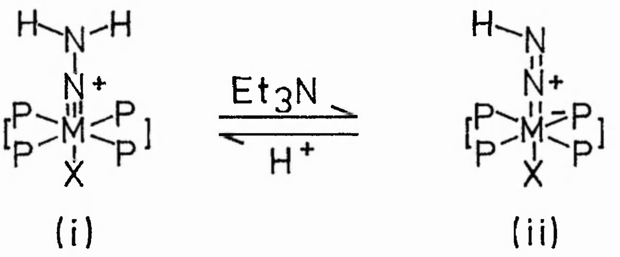


Figure 6

Deprotonation enhances the nucleophilicity of the terminal nitrogen, and facilitates nucleophilic attack at suitable electrophilic centres.

From the above, it can be seen that the dinitrogen ligand acts as a two electron donor, the diazenido ligand acts as a three electron donor and the hydrazido(2-) ligand acts as a four electron donor to the metal centre.

Until quite recently, the carbon-nitrogen bond forming reactions of the bis(dinitrogen) and hydrazido(2-) complexes were essentially limited to;

1. free radical reactions between the bis(dinitrogen) complexes and suitable alkyl, aroyl or acyl halides (32, 33, 34, 54-62), and
2. condensation reactions between the hydrazido(2-) complexes and aldehydes and ketones (59, 63-65).

The first example of carbon-nitrogen formation involving the terminal nitrogen was reported in 1972 (51, 66):

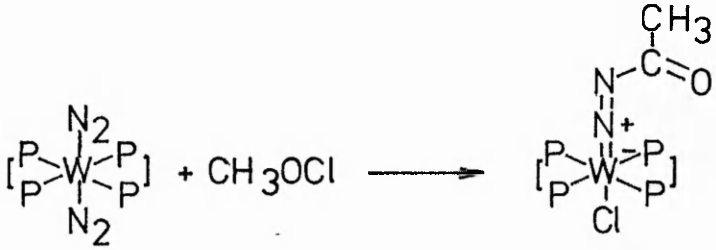
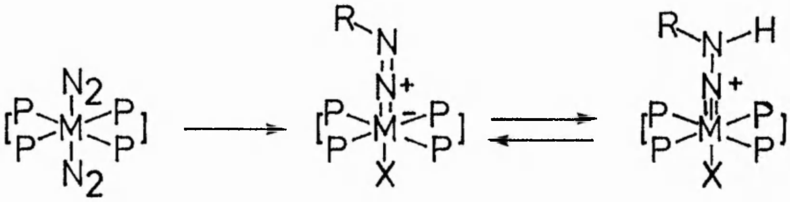


Figure 7

Analogous reactions are observed with appropriate alkyl halides. In each case, the alkyl-, aroyl- or acyldiazenido ligands may be reversibly



M = Mo, W   X = Br, I

R = Me, Et, Pr, Pr , C_6H_{11}, C_8H_{17}, EtCO, PhCO, for example.

Figure 8

protonated with aqueous acid to form the corresponding alkyl-, aroyl- or acylhydrazido(2-) complexes. (32, 34, 54, 55, 57).
The reactions are accelerated by tungsten filament irradiation for M = Mo, and this irradiation is essential where M = W. Suitable solvents include toluene and benzene for example. For simple alkyl bromides (particularly MeBr), the use of thf, dioxan, tetrahydrothiophene or related solvents (33) leads to an organonitrogen ligand derived from the solvent, for example;

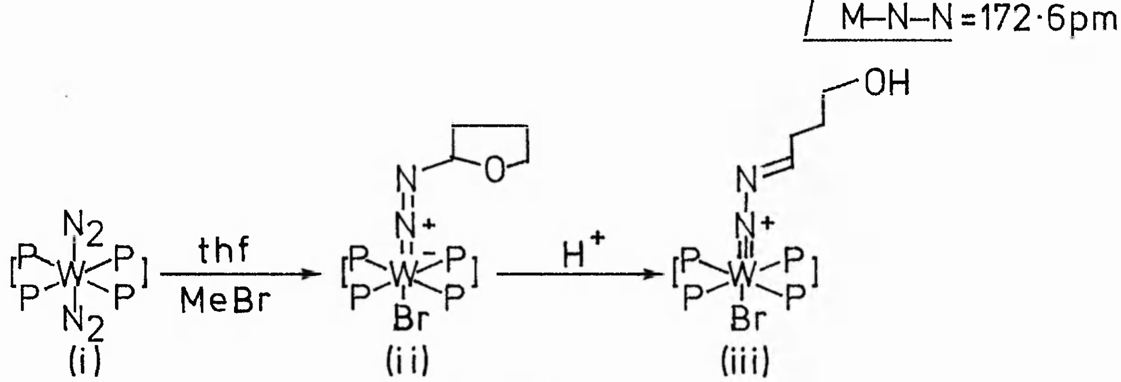


Figure 9

Addition of acid ring-opens the heterocyclic ligand to produce a diazobutanol complex (eg. (iii) Figure 9), the structure of which was determined by a single crystal X-ray study (50, 67). The use of excess MeBr, where M = W, in an inert solvent yield $[WBr(N_2Me_2)(dppe)_2]^+Br^-$ (54). α,ω-dibromides, $(CH_2)_nBr_2$, react in an analogous manner, though the nature of the product is dependent upon the value of n. Thus, where n = 1, a diazomethane complex is formed (59) $[WBr(NNCH_2)(dppe)_2]^+Br^-$. Where n = 4, 5 heterocyclic ring structures are formed on the terminal nitrogen (62);

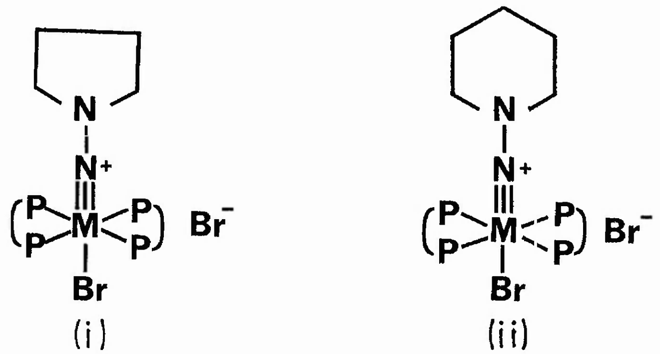


Figure 10

presumably via the corresponding bromoalkyldiazenido complex, the ring being formed by nucleophilic displacement of the second bromine by the terminal nitrogen. When n > 5, a mixture of long chain bromoalkyldiazenido and bridged dimeric species are obtained, and when n = 2, all nitrogen is lost and [$MBr_2(dppe)_2$] is formed.

The free radical mechanism invoked in the description of the formation of these complexes is as follows;

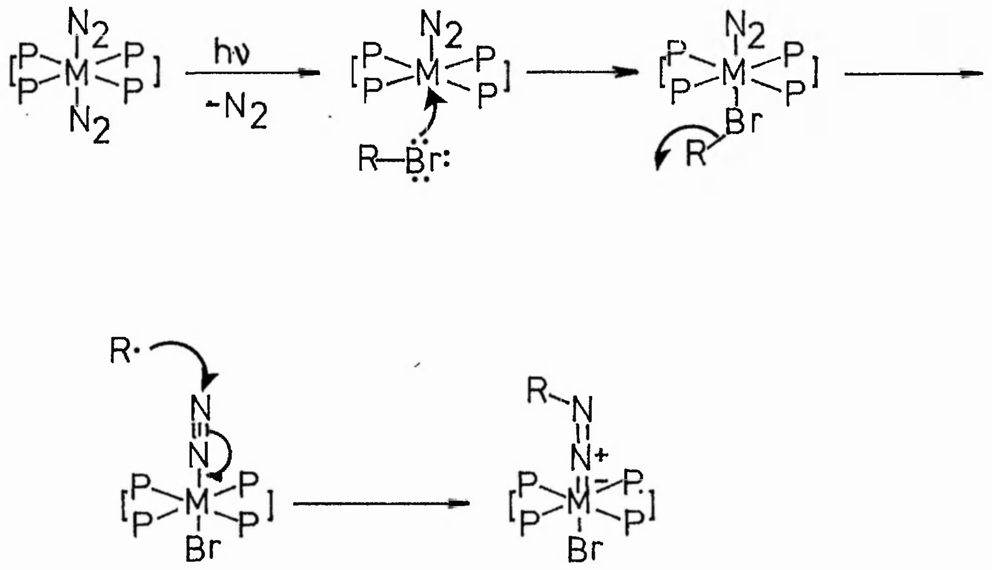


Figure 11

The involvement of free radicals was confirmed by the use of bromohex-5-ene, giving the hex-5-enyl radical which rapidly cyclises to the cyclopentylmethyl radical. This reacts to produce a cyclopentylmethyldiazenido complex with none of the linear analogue detected (68).

The acylation of trans[$M(N_2)_2(dppe)_2$] using trifluoroacetic anhydride, has been reported (69), to produce complexes of the type [$M(OCOCF_3)$-(N_2COCF_3)($dppe)_2$]. The mechanism for the formation of these complexes is probably analogous to that determined for protonation of the bis-

(dinitrogen) complex by acid.

A second general method for the formation of carbon-nitrogen bonds in these systems is the condensation of the hydrazido(2-) group with aldehydes and ketones. The former are generally more reactive than the latter, and indeed acid catalysis is preferred for ketones (63).

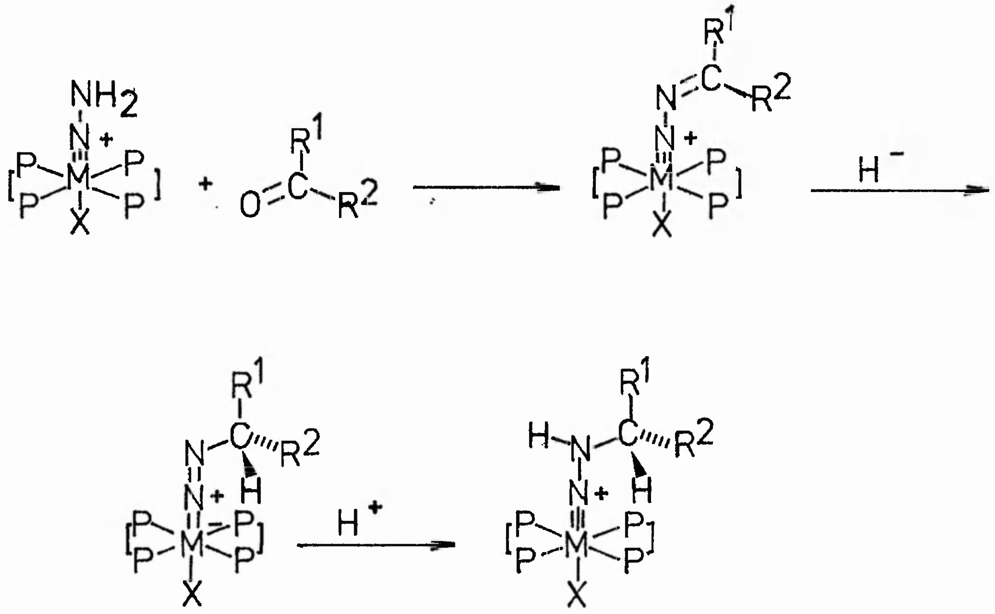


Figure 12

Reduction of the first-formed diazoalkane complexes by borohydride produces the neutral alkyldiazenido analogues (30, 59) (Figure 12).

The production of organonitrogen species from the hydrazido(2-) complexes is limited, and vigorous conditions are necessary to cleave the M-N or N-N bond. Heating dialkylhydrazido(2-) complexes and $LiAlH_4$ to 80°C in diethyl ether in sealed tubes produces secondary amines in yields of up to 95%. Lower yields were obtained by direct distillation from 40% KOH (70). Sodium borohydride reduction of $[MoBr(N_2Bu)(dppe)_2]$ in methanol/benzene in an autoclave for 10 hours at various temperatures produces a mixture of n-butylamine (53-57%) and ammonia (49-55%) (61,71). Optimum yields were obtained at elevated temperatures. Similar conditions with $[\mathrm{MoI(N_2C_6H_{11})(dppe)_2}]$ produces a mixture of ammonia cyclohexylamine and N-methylcyclohexylamine. Cleavage reactions of this type usually produce free dppe and an uncharacterised metal product, although $[\mathrm{MoH_4(dppe)_2}]$ has been reported to form in low yield (61). Electrochemical cleavage of the Mo-N bond of complex (i) figure 13 under N_2 in thf produces the free hydrazine in yields of 60-70% and regenerates the bis (dinitrogen) complex in 45% yield. The following mechanism is postulated (72):

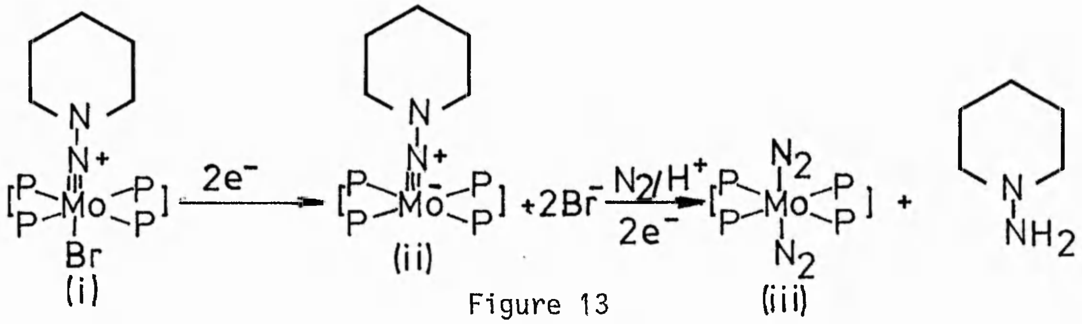


Figure 13

The analogous trans dicarbonyl complex is obtained when the electrolysis is carried out under carbon monoxide. Oxidation of (i) Figure 13 under argon in acetonitrile generates

$$[\mathrm{Mo(MeCN)(N\overline{NCH_2(CH_2)_3CH_2})(dppe)_2}]^{2+}$$

More recent work on the tungsten hydrazido(2-) complex has demonstrated the nucleophilicity of the terminal nitrogen in either the hydrazido(2-) complex, or the more reactive diazenido analogue. Reaction between $[\mathrm{WF(N_2H_2)(dppe)_2}]^+\mathrm{BF_4}^-$ and succinyl dichloride produces the heterocyclic structure (73):

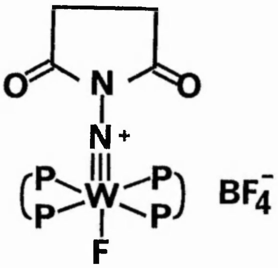


Figure 14

Reaction between $[MBr(N_2H_2)(dppe)_2]^+Br^-$ (M = Mo, W) and phenyl isocyanate produces the complexes $[MBr(N_2HCONHPh)(dppe)_2]$, which may be deprotonated to give the diazenido analogue (73).

The diazenido ligand, generated in. situ. from $[WX(N_2H_2)(dppe)_2]^+$ (X = Br, F, CF_3CO_2) reacts with 2,4 dinitrofluorobenzene to produce 2,4 dinitrophenyldiazenido complexes (74). Reaction of the hydrazido (2-) complex $[WBr(N_2H_2)(dppe)_2]^+Br^-$ with a diphenyliodonium salt in a two phase aqueous base/organic solvent system, gives products derived from the organic solvent. Thus, with CH_2Cl_2 as solvent, a formyl-diazenido complex is formed (75) and the mechanism for its formation is illustrated in Figure 15. With $CHCl_3$ or $CBrCl_3$ as solvent, a dichlorodiazomethane ligand is formed (Figure 16).

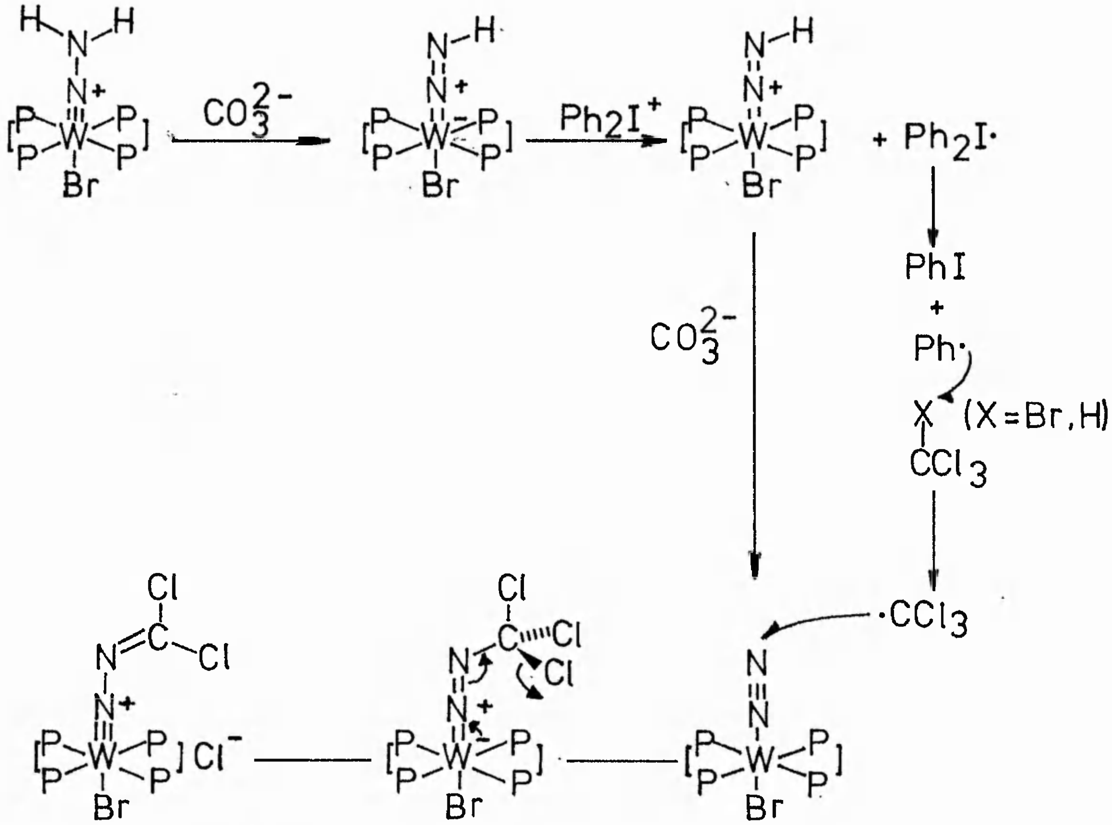


Figure 16

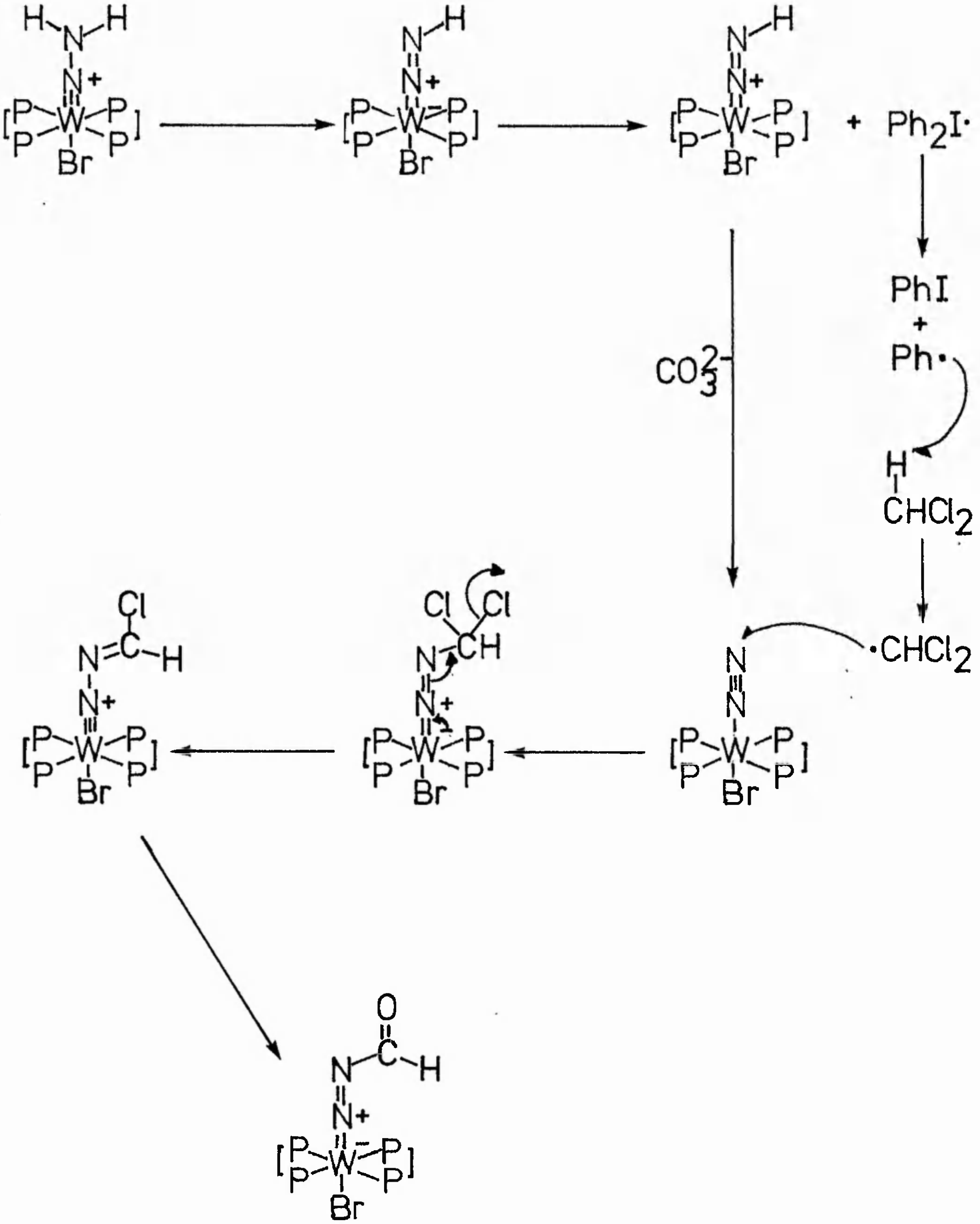


Figure 15

This ligand will react with a variety of reagents to produce a range of novel organodinitrogen ligands, as illustrated in Figure 17 (76).

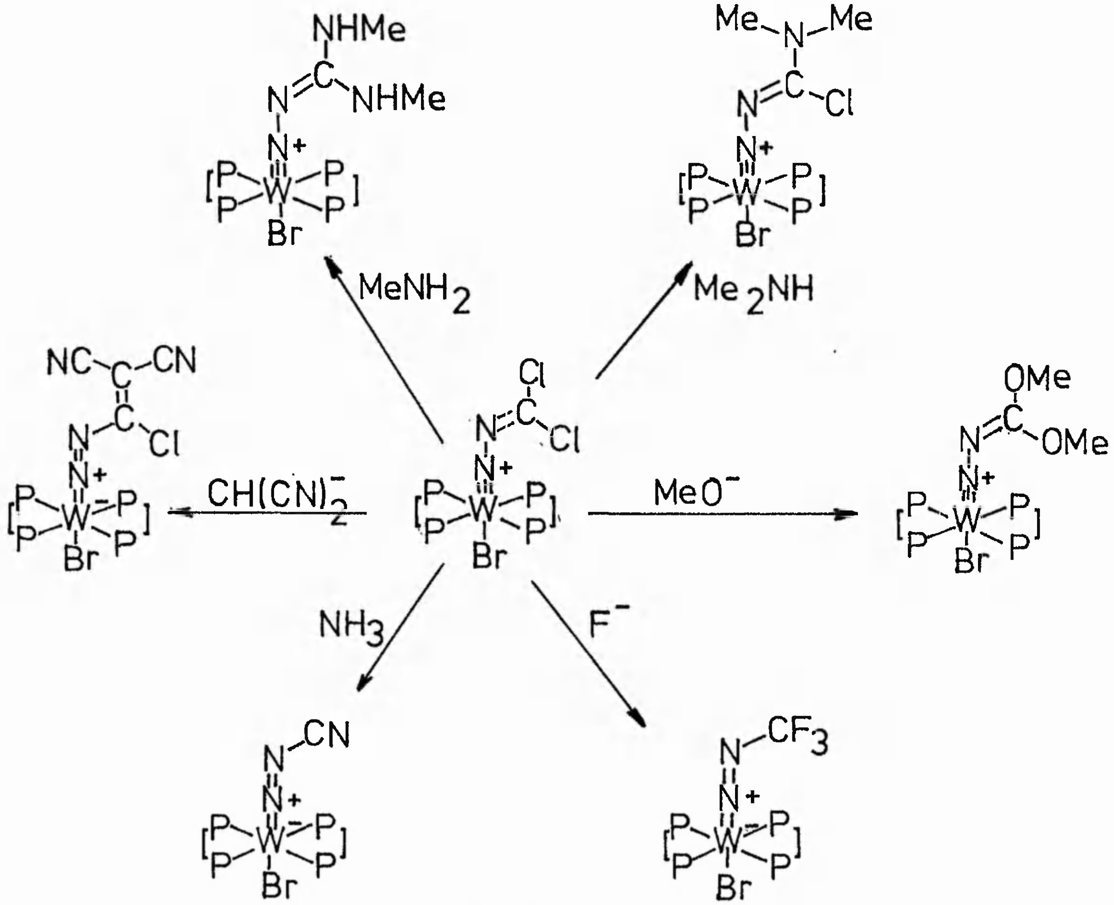


Figure 17

Crystal structures are available for the dichlorodiazomethane complex and the product from its reaction from malonitrile (77). Using $CHFBr_2$ as solvent, a dimeric structure containing a bridging formazanido(3-) ligand, $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+Br^-$, is obtained (78).

Electrochemical studies on tungsten and molybdenum diazoalkane complexes of the type $[MF(N_2CR_1R_2)(dppe)_2]^+BF_4^-$ (M = Mo, W; R_1 = H, CH_3; R_2 = Ph, pMePh, p NH_2Ph etc), have shown that consecutive one- and two- electron oxidations and reductions occur at a platinum electrode in acetonitrile/ 0.1 mol dm^{-3} $[Bu^n_4N]^+BF_4^-$ (79); for example,

$$\begin{array}{c} [MF(N_2CHPh)(dppe)_2]^+ \\ -e \downarrow\uparrow +e \\ [MF(N_2CHPh)(dppe)_2]^{2+} \\ -e \downarrow \\ \text{unstable complex} \end{array}$$

and

$$\begin{tikzcd} {[MF(N_2CHPh)(dppe)_2]^+} \arrow[d, shift right, "+e"'] \\ {[MF(N_2CHPh)(dppe)_2]} \arrow[u, shift right, "-e"'] \arrow[d, "+e"'] \\ \text{unstable complex} \end{tikzcd}$$

Further discussion on kinetic and electrochemical properties of the tungsten hydrazido(2-) and diazenido complexes are included in Chapter 3 section (ii) and (iii).

D. Preparation, properties and chemical reactivities of molybdenum and tungsten bis(dinitrogen) complexes and their derivatives, containing exclusively monodentate phosphine ligands

This group of bis(dinitrogen) complexes have been extensively investigated by Chatt and his co-workers with particular emphasis on nitrogen hydride formation.

The bis(dinitrogen) complexes may be prepared by the reduction of $[MoCl_5]_2$ or trans $[WCl_4(PPh_3)_2]$ in thf under N_2 in the presence of the appropriate phosphine ligand, to produce cis$[M(N_2)_2[PMe_2Ph)_4]$ or trans-$[M(N_2)_2(PMePh_2)_4]$ (M = Mo, W) for example (18, 16, 26, 20, 48).

The protonation reactions with acids are complex and produce a variety of products dependent upon the nature of the metal, ligand, acid and solvent (80). Protonation of cis$[M(N_2)_2(PMe_2Ph)_4]$ with halogen acids in methanol produces the hydrazido(2-) complex $[MX_2(N_2H_2)(PMe_2Ph)_3]$ (M = Mo, W; X = Cl, Br, I) (80, 81, 82). In contrast, the use of H_2SO_4 produces ammonia (M = Mo, W) and hydrazine (M = W) after base distillation (48). The reaction between $[MoCl_2(N_2H_2)(PMe_2Ph)_3]$, cis$[M(N_2)_2(PMe_2Ph)_4]$ or $[MBr_2(N_2H_2)(PMe_2Ph)_3]$ (M = Mo, W) and HCl in d.m.e. produces both ammonia and hydrazine (83, 84).

Hydride hydrazido(2-) complexes, $[WX_3H(N_2H_2)(PMe_2Ph)_2]$, may be prepared by the reaction of HX (X = Cl, Br) with $[WX_2(N_2H_2)(PMe_2Ph)_3]$ in thf (85). The hydride hydrazido(2-) complex $[WHClBr(N_2H_2)(PMe_2Ph)_3]^+Br^-$ is obtained from the reaction between one mole equivalent of gaseous HCl and $[WBr_2(N_2H_2)(PMe_2Ph)_3]$ in dme. This complex reacts with $NaBPh_4$ to produce the triphenylboron adduct of a diazenido complex [WHClBr-(N_2(BPh_3)H)(PMe_2Ph_3] in low yield (86).

In general, the above complexes will produce free nitrogen hydrides in varying yields on treatment with a suitable acid (H_2SO_4, HCl for example) in the appropriate solvent (MeOH, dme for example).

A proposed mechanism for the formation of ammonia/hydrazine from these complexes is: (86)

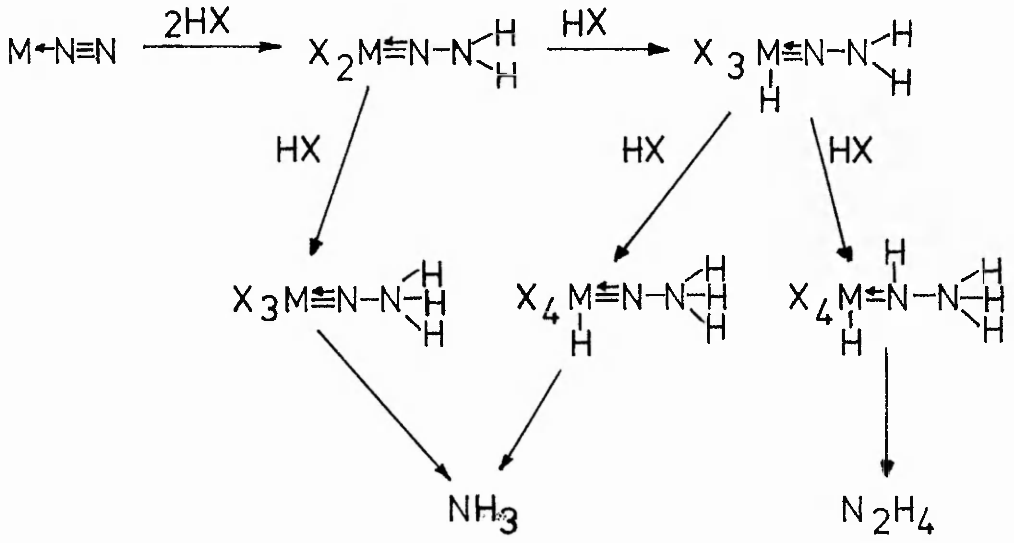


Figure 18

However, a greater understanding of the further reduction of the hydrazido(2-) group bonded to molybdenum or tungsten is required before a mechanism can be proposed with any certainty (80). Recently, a mechanism for the protonation of the dinitrogen complex cis[M(N_2)$_2$-(PMe_2Ph)$_4$] (M = Mo, W) in MeOH with acids HX (X = Cl, Br, HSO_4) has been described, (87) to give [M(N_2H_2)(OCH_3)$_2$(PMe_2Ph)$_3$] via the sequence;

$$\mathrm{cis[M(N_2)_2(PMe_2Ph)_4]}$$
$$2H^+ \downharpoonleft\upharpoonright$$
$$\mathrm{[M(N_2H_2)(N_2)(PMe_2Ph)_4]^{2+}}$$
$$\downharpoonleft\upharpoonright$$

$$\begin{gathered}
[M(N_2H_2)(N_2)(PMe_2Ph)_4]^{2+} \\
CH_3OH \downarrow\uparrow \\
[M(N_2H_2)(OCH_3)(PMe_2Ph)_4]^{+} \\
\downarrow\uparrow \\
[M(N_2H_2)(OCH_3)(PMe_2Ph)_3]^{+} + PMe_2Ph \\
\downarrow\uparrow \\
[M(N_2H_2)(OCH_3)_2(PMe_2Ph_3)]
\end{gathered}$$

The carbon-nitrogen bond forming reactions of this class of bis-(dinitrogen) and hydrazido(2-) complexes are extremely limited. Unlike the analogous bis(dinitrogen) complexes containing bidentate phosphine ligands, reaction with alkyl, acyl or aroyl halides produces complete loss of dinitrogen with no alkyldiazenido complex formed (70). The hydrazido(2-) complexes of both molybdenum and tungsten will undergo condensation reactions with suitable aldehydes and ketones (88, 89). Of particular interest is the condensation of acetophenone to give $[WBr_2(N_2CMePh)(PMe_2Ph)_3]$, a reaction which does not occur with the analogous hydrazido(2-) complex containing bidentate phosphine ligands (see Chapter 3, section (i)).

(v) OUTLINE OF PROJECT

A variety of nucleophiles has been shown to react with alkenes coordinated to a suitable transition metal salt (90). Of particular importance is the Wacker process for the industrial manufacture of ethanal, where the attacking nucleophile is water, the alkene is ethene and the metal salt is $PdCl_2$ (91, 92, 93).

Reaction between amines and alkenes (94, 95, 96, 97) dienes (98, 99) and allylic compounds (100, 101, 102) have been demonstrated, producing the corresponding aminated addition product. In each case, palladium (II) salts were used to activate the double bond towards nucleophilic attack by the amine. Common palladium(II) salts used in this process are $PdCl_2$, $Pd(OAC)_2$, $PdCl_2(RCN)_2$ (R = Ph, Me).

Alkenes are normally unreactive towards nucleophiles, more commonly undergoing electrophilic attack. However, if the alkene (1) contains highly electron withdrawing groups on the β unsaturated (negatively polarised) carbon atom of the double bond, or (2) is coupled to a transition metal salt, particularly palladium(II) salts, then in both cases, electron density is removed from the alkene double dond, hence facilitating the attack of the nucleophile.

For case (1), the use of unsaturated electron withdrawing substituents facilitates stabilisation of the intermediate carbanion via electron delocalisation, viz:

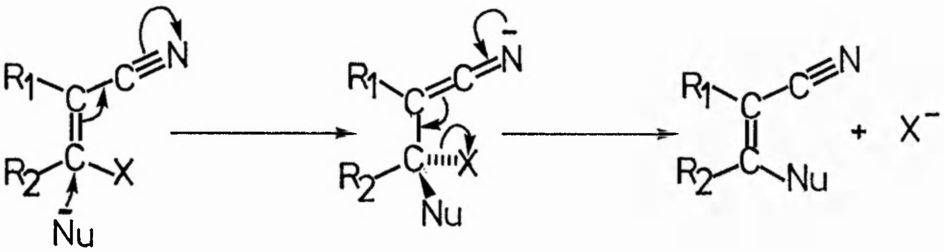


Figure 19

This mesomeric electron withdrawal is much more effective than simple inductive electron withdrawal, for example with -F, -CF_3. A partial order of effectiveness in promoting nucleophilic attack is found to be (103)

$$-NO_2 > -CHO > -CN > -CO_2R > -CO_2NH_2$$

For case (2), coordination of the alkene results from the following shift in electron density, eg. for palladium;

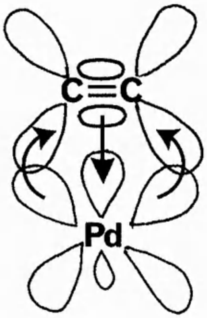


Figure 20

according to the well known Chatt-Dewar-Duncanson molecular orbital description, the net donation of electron density rendering the double bond electron deficient. Attack by a nucleophile results in the formation of a carbon-palladium σ bond

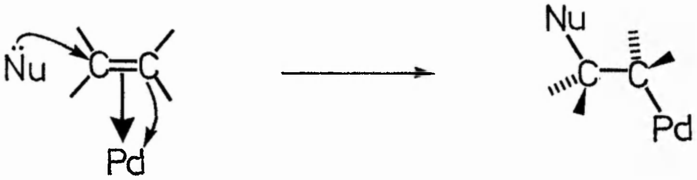


Figure 21

Two possible processes may then occur depending upon the nature of the reactants and reaction conditions;

(1) Elimination

Figure 22

(2) Nucleophilic substitution

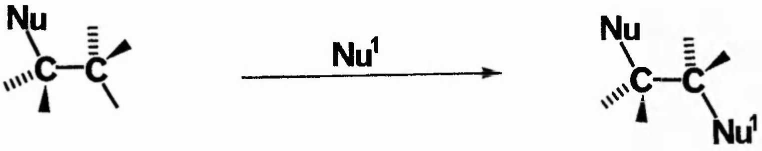


Figure 23

The reaction between an alkene activated towards nucleophilic attack and a ligand derived from dinitrogen coordinated to a transition metal may lead ultimately to the formation of free amino- or hydrazino-alkenes. If the initial transition metal-dinitrogen complex can be conveniently regenerated the possibility of a cyclic process becomes apparent. The production of amino- or hydrazino-alkenes from dinitrogen and a cheap, readily available alkene is obviously an attractive industrial process, providing a route to valuable synthetic intermediates via a potentially cheap and versatile method.

Recently, Sellmann has demonstrated that, in principle, azomethane may be synthesised in a cyclical process from dinitrogen according to the following scheme; (104, 105).

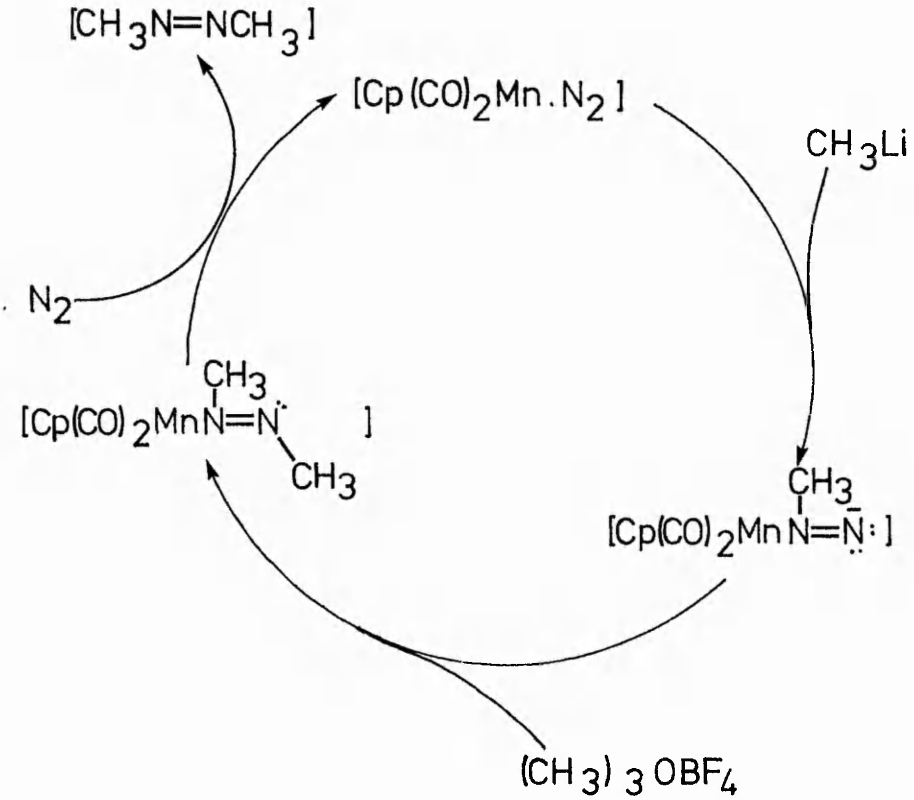
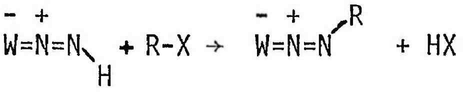


Figure 24

Unfortunately, the catalyst is destroyed after a short time by side reactions, and the cycle is not workable in its present form.

The nucleophilic behaviour of the terminal nitrogen atom in $[WX(N_2H_2)(dppe)_2]^+$ has been described in the previous section. The nucleophile is thought to be the diazenido derivative of the ligand,



$$\overset{-}{W}=\overset{+}{N}=\underset{H}{N} + R\text{-}X \rightarrow \overset{-}{W}=\overset{+}{N}=N{-}R + HX$$

formed in situ by the addition of an excess of weak base to a mixture of the hydrazido(2-) complex and reactant (see section (iv)).

Thus, a cyclic process involving trans$[M(N_2)_2(dppe)_2]$ (M=Mo, W) and a suitably activated alkene may be envisaged as follows;

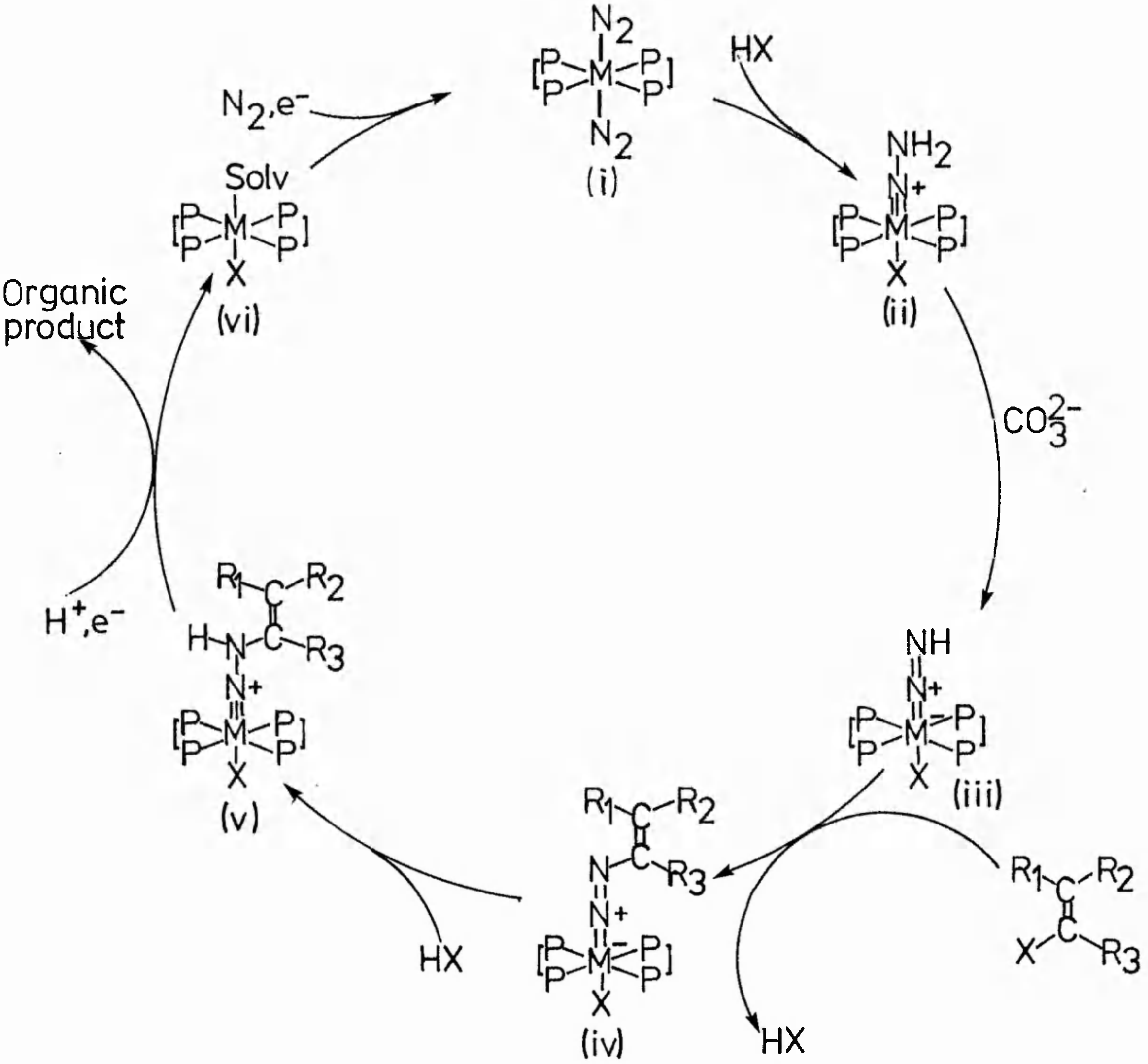
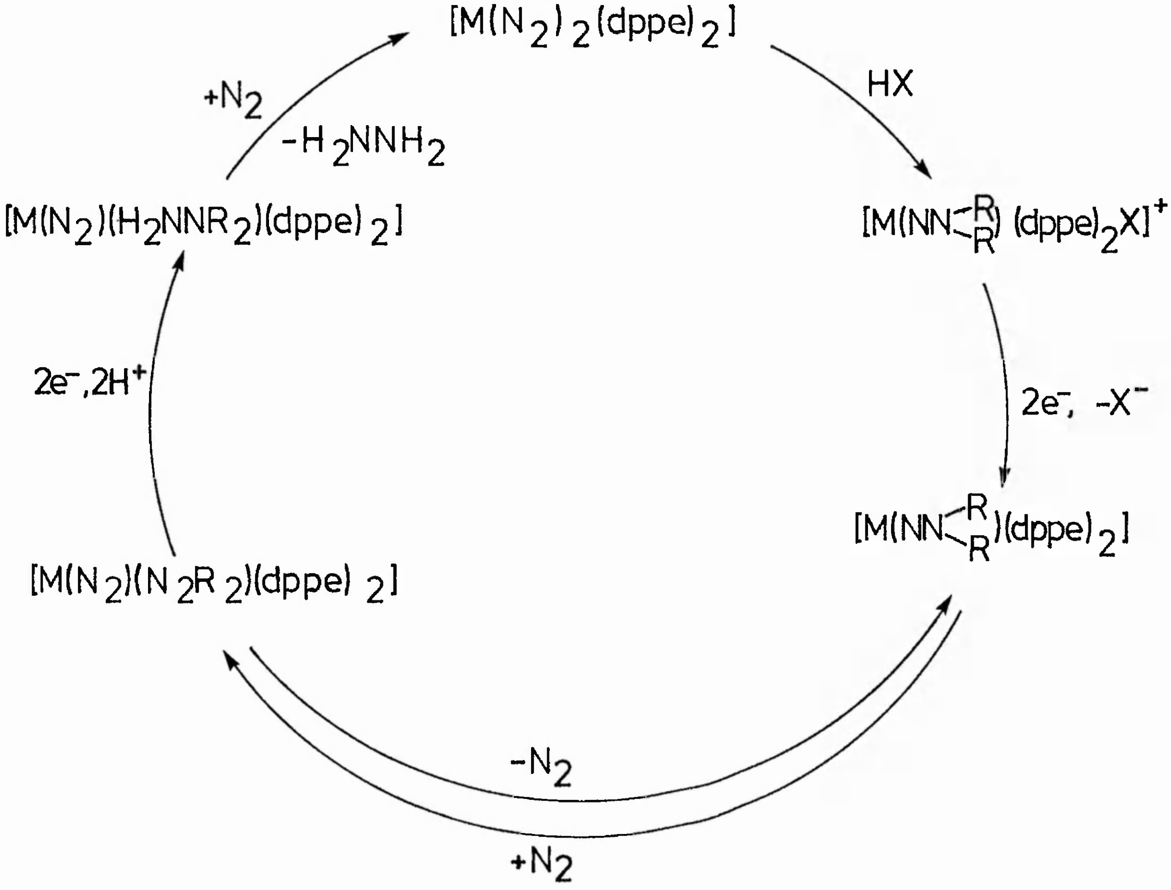


Figure 25

Step (iii) to (iv) is supported by recent work of Bäckvall demonstrating external attack by the nucleophile on the alkene (93). The intermediate (vi) is represented as a 5-coordinate species for convenience, and the exact nature of steps (v) to (vi) is discussed in Chapter 3, section (iii).

Several variations based on this cycle are possible, including intramolecular nucleophilic attack on an alkene already coordinated to the terminal nitrogen via an alkyl chain, forming heterocyclic ring structures; viz (i) and (ii) Figure 10, and will be discussed in Chapter 3, section (i).

The possibility of a cyclic process similar to that in Figure 25 for generating N-aminopiperidine and trans$[Mo(N_2)_2(dppe)_2]$ has been reported for the electrochemical reduction of complex (ii) Figure 10 (72); the cycle is illustrated in Figure 26.



M = Mo or W; X = Br or I; R = alkyl.

Figure 26

The work contained in this thesis describes the synthesis, properties and reactivities of complexes (i) - (vi) Figure 25, (in particular, steps (iii) → (iv) → (v) → (i)) and considers the possibility of producing a workable cyclic process.

CHAPTER TWO

EXPERIMENTAL PROCEDURES

A. PREPARATIVE STUDIES

(1) INSTRUMENTAL METHODS

Melting points were recorded on a Gallenkamp melting point apparatus in open capillaries and are uncorrected. Literature values of known compounds are written in parentheses. Ultra violet/visible spectra were recorded on a Perkin Elmer 402 instrument using 10mm silica cells, and dichloromethane as solvent. Infra-red spectra were obtained on a Perkin Elmer 157G instrument (4000-625cm^{-1}) or a Perkin Elmer 683 instrument (4000-200cm^{-1}) as KBr/CsI discs, nujol mulls or evaporated/thin films between NaCl plates as indicated. Nuclear magnetic resonance spectra were recorded on a Jeol FX 100 spectrometer using $CDCl_3$, CD_2Cl_2 or d_6-acetone as solvents. ^1H and ^{13}C n.m.r. spectra were recorded at 100 MHz and 25.1 MHz respectively using t.m.s. as reference ($\delta_{tms} = 0$) ^{19}F spectra were recorded at 94 MHz using $CFCl_3$ as reference. ^{31}P n.m.r. spectra were recorded at 40.3 MHz using 85% H_3PO_4 as external reference. Elemental analyses were performed at I.C.I. New Science Group, Runcorn, Cheshire.

(2) SOLVENT AND REAGENT PRETREATMENTS

Where necessary, the following solvents were distilled and degassed with dinitrogen (B.O.C. white spot) for at least 30 min. prior to use. The following drying agents and conditions were used before distillation:

(i) Acetone : $CaCl_2$ or 4A molecular sieves;
(ii) Acetonitrile : 4A molecular sieves;
(iii) Dichloromethane : Phosphorus pentoxide, K_2CO_3, reflux;
(iv) Ethanol : Magnesium ethoxide, reflux;
(v) Diethyl ether : Sodium hydroxide pellets or sodium wire.
(vi) Hexane : 4A molecular sieves;

(vii) Tetrahydrofuran : sodium (using benzophenone as an indicator), reflux;

(viii) Toluene : sodium (using benzophenone as an indicator), reflux;

(ix) Methanol : Magnesium methoxide, reflux;

(x) Petroleum ether : 4A molecular sieves;

(xi) 1,2-dichloroethane : Phosphorus pentoxide, reflux.

WCl_6 was obtained from B.D.H. and Mo_2Cl_{10} was obtained from Aldrich Chemical Co. Ltd. Both were used without further purification. Unless otherwise indicated, commercial grade chemicals were used without further purification.

(3) PREPARATION OF BIS(DINITROGEN) COMPLEXES AND THEIR DERIVATIVES

trans-Bis[bis(1,2-diphenylphosphino)ethane] bis(dinitrogen)tungsten(0). $[W(N_2)_2(dppe)_2]$

(Complex I)

To zinc wool (10g), dppe (21g, 50 mmol) and thf (500 cm³) in a 3 necked 1 litre flask was added WCl_6 (10g, 25 mmol). The mixture was stirred for 12 hours under dinitrogen to produce an orange precipitate of $[WCl_3(dppe)_2]$ (23). Grignard magnesium turnings (10g) and a crystal of iodine were added and the mixture stirred under dinitrogen for a further 36 hours. The orange-brown suspension was filtered through "Hy-flow" filter aid and the filtrate reduced to an oil *in vacuo*. Addition of acetone (100 cm³) to this produced a red-orange precipitate, which was collected by filtration. This solid was combined with the solid from the initial filtration and recrystallised from CH_2Cl_2/acetone as red crystals. Yield = 18g (68%); m.p. = 152-155°C (dec.); i.r. spectrum (nujol mull) $\nu(N\equiv N)$ 1956 cm^{-1} (s) (22).

trans-Bis[bis(1,2-diphenylphosphino)ethane]-bromo-hydrazido(2-)-tungsten (IV) bromide. $[WBr(N_2H_2)(dppe)_2]^+Br^-$.

(Complex II)

Trans$[W(N_2)_2(dppe)_2]$ (3g) was dissolved in CH_2Cl_2 (50 cm³) and aqueous HBr (5 cm³, 48%) was added dropwise with rapid stirring. The solution darkened and N_2 was evolved. This solution was stirred for 20 min. and then washed with water (2 x 50 cm³). The organic layer was separated and dried over anhydrous $MgSO_4$ before filtration. Addition of diethyl ether to the filtrate precipitated the product as an orange-brown crystalline solid, which was filtered off, washed with diethyl ether and dried. Yield = 3.1g (91%); m.p. = 220-223°C, (224-227°C (16)); i.r. spectrum (nujol mull) ν(N-H) 3300 cm^{-1} (w) (16).

trans-Bis[bis(1,2-diphenylphosphino) ethane]-fluoro-hydrazido(2-)-tungsten (IV) tetrafluoroborate. $[WF(N_2H_2)(dppe)_2]^+BF_4^-$

(Complex III)

This was prepared analogously to $[WBr(N_2H_2)(dppe)_2]^+Br^-$, using HBF_4 (40% aq. sol.) as the acid. Yield = 95%. m.p. = 251-253°C (254-258°C (133)); i.r. spectrum (nujol mull) ν(N-H) 3335 cm^{-1} (w), 3255 cm^{-1} (w), ν(B-F) 1060 cm^{-1} (s).

Bis(2-diphenylphosphinoethyl)phenylphosphine-triphenylphosphine-bis(dinitrogen)-molybdenum (0). $[Mo(N_2)_2(PPh_3)(triphos)]$

(Complex IV)

a) Preparation of $[MoCl_3(thf)_3]$

To zinc wool (5g) in thf (50 cm³) at 0°C was added $[MoCl_5]_2$ (3g). The mixture was shaken vigorously under dinitrogen and allowed to warm to room temperature. After one hour the product was filtered off, washed with t.h.f. (200 cm³), diethyl ether (50 cm³) and dried *in vacuo*

b) Preparation of $[Mo(N_2)_2(PPh_3)(triphos)]$

$[MoCl_3(thf)_3]$ (4.06g, 10 mmol) was suspended in thf (100 cm³) under dinitrogen and triphos (5.35g, 10 mmol) was added. The mixture was stirred for 48 hrs, to produce a precipitate of yellow $MoCl_3$ (triphos). Triphenylphosphine (2.6g, 10 mmol) and sodium amalgam (0.7g sodium in 70g mercury) were added and the mixture stirred vigorously for 4 hours to produce a dark orange-brown solution. (I.r. spectrum (evaporated film) $\nu(N{\equiv}N)$ 1970 cm^{-1}(s)). The following manipulations were carried out under a dinitrogen atmosphere using dried and degassed solvents. Filtration of the orange-brown solution through "Hy-flow" filter-aid and addition of methanol (100 cm³) precipitated the product as an orange-brown solid, which was filtered off, washed with methanol (20 cm³) and dried. Yield = 1.05g, 11%. The complex is very air sensitive in the solid state.

Bis(2-diphenylphosphinoethyl)phenylphosphine-triphenylphosphine-hydrazido(2-)-fluoro-molybdenum(IV)-tetrafluoroborate. $[MoF(N_2H_2)(PPh_3)(triphos]^+BF_4^-$

(Complex V)

To $[Mo(N_2)_2(PPh_3)(triphos)]$ (0.92g, 1 mmol) in thf (50 cm³) under dinitrogen was added HBF_4 (0.183g, 1 mmol) with vigorous stirring. The dark brown mixture was stirred for 30 min. and reduced to approximately

10 cm³ in vacuo. The orange solid which precipitated was filtered off under dinitrogen, washed with diethyl ether (10 cm³) and dried in vacuo. Yield = 0.29g (29%); m.p. 164-170°C i.r. spectrum (nujolmull) : ν(N-H) 3260 cm^{-1} (vw) ν(B-F) 1050 cm^{-1}(s).

The material is very air sensitive and decomposes rapidly on contact with air.

trans-Bis[bis(1,2-diphenylphosphino)ethane]-bromo-diazenido-tungsten(II). $[WBr(N_2H)(dppe)_2]$.

(Complex VI)

$[WBr(N_2H_2)(dppe)_2]^+Br^-$ (1.17g, 1 mmol) was partially dissolved in methanol (50 cm³) and triethylamine (0.25 cm³) added dropwise. After stirring for 30 min, the precipitated yellow solid was filtered off, washed with water (30 cm³), methanol (30 cm³), and diethyl ether (10 cm³) and dried in vacuo. Yield = 0.9-1.0g, 83-93%; m.p. = 190-195°C (ded) (>180°C (dec.)(133)); i.r. spectrum (nujolmull) ν(N≡N) 1880 cm^{-1}(s), 1850 cm^{-1}(m).

trans-Bis[bis(1,2-diphenylphosphino)ethane]-fluoro-diazenido-tungsten (II). $[WF(N_2H)(dppe)_2]$

(Complex VII)

Prepared by a method analogous to that for complex VI. Yield = 80-90%; m.p. = 183-187°C dec. (>176°C(dec.)(133)); i.r. spectrum (nujol mull) ν(N≡N) 1825 cm^{-1}(s).

trans-Bis[1,2-bis(diphenylphosphino)ethane]-(methyldiazenido)-bromotungsten(II). [WBr(N_2Me)(dppe)$_2$].

(Complex VIII)

Prepared by the method of Chatt et. al. (54) using toluene as the solvent, and two 150 watt tungsten filament lamps for irradiation. m.p. = 259-262°C (257-260°C (54)); i.r. spectrum (KBr disc) ν(N=N) 1520 cm^{-1} (s) ν(C-N) 1355 cm^{-1} (s).

trans-Bis[1,2-bis(diphenylphosphino)ethane]-(methylhydrazido(2-)-bromotungsten (IV) tetrafluoroborate. $[WBr(N_2HMe)(dppe)_2]^+BF_4^-$

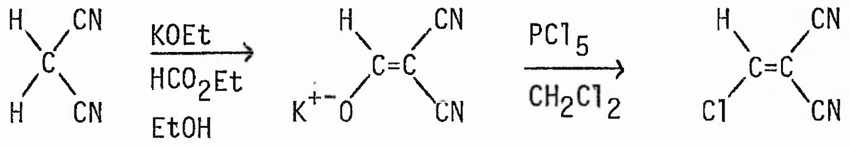
(Complex IX)

To [WBr(N_2Me)(dppe)$_2$] (0.28g, 0.25 mmol) dissolved in CH_2Cl_2 (20 cm³) was added HBF_4 (0.5 cm³) dropwise with rapid stirring. The mixture was stirred vigorously for 20 min., washed with water (2 x 30 cm³), dried over 3A molecular sieves and filtered. Slow addition of hexane to the filtrate precipitated the product as orange crystals, which were filtered off, washed with diethyl ether and dried *in vacuo*. Yield = 0.17g, 57%; m.p. = 248-250°C (dec.) (>253°C (dec.) (54)).

(4) PREPARATION OF CYANO- AND ETHOXYCARBONYL-SUBSTITUTED ALKENES

2-Chloro- 1,1-dicyanoethene

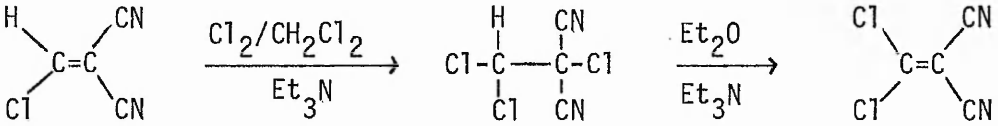
Prepared by the method of Josey et. al. (107) *via* the following reaction sequence;



and obtained as an off white solid (0°C), light yellow liquid (25°C). Yield = 50%; b.p. = 100-110°C @ 25 mm Hg (73°C @ 10 mmHg); i.r. spectrum (thin film) ν(C-H) 3070 cm^{-1} (m), ν(C≡N) 2240 cm^{-1} (m), ν(C=C) 1570 cm^{-1} (s).

1,1-dichloro-2,2-dicyanoethene

Prepared by the method of reference (107) via the following reaction sequence:



The product was recrystallised twice from hexane (sublimation produced decomposition) and was obtained as white needles. Yield = 80%; m.p. = 65-65.5°C (63-64°C) i.r. spectrum (thin film) ν(C≡N) 2245 cm^{-1} (m), ν(C=C) 1541 cm^{-1} (m).

2-chloro-1-cyano-1-ethoxycarbonylethene

Prepared by an adaptation of the method described by Friedrich and Thieme (108). To the potassium salt of hydroxymethylene-ethyl cyanoacetate (prepared from potassium ethoxide, ethyl formate and ethanol) (19.3g, 0.1 mol) in 1,2-dichloroethane (2.0 cm³) at room temperature was added $POCl_3$ (15.4g, 0.1 mol) via a reflux condenser. The mixture was refluxed for six hours, allowed to cool and the solid residue filtered off. This was washed with 1,2-dichloroethane (3 x 50 cm³) and the combined washings and original filtrate were distilled in vacuo to remove the solvent and 1,2-dichloroethane. Further distillation in vacuo gave the product as a clear liquid which solidified on cooling to give white crystals. Yield = 10.6g 72%; m.p. = 64-66°C; i.r. spectrum (nujol mull) ν(C≡N) 2240 cm^{-1} (m) ν(C=O) 1735 cm^{-1} (s), ν(C=C) 1600 cm^{-1} (s), ν(C-O) 1255, 1095 cm^{-1} (s).

1,1-dicyano-2-ethoxyethene

Prepared by the method of Diels, et al. (109). A mixture of malononitrile (2.0g 30 mmol), ethyl orthoformate (4.6g 62 mol) and freshly distilled acetic anhydride (20 cm^3) was refluxed for 7 hours. The solvent was reduced to approximately 7 cm^3 *in vacuo* with gentle heating. The residue crystallised on standing for 24 hours, the crystals were filtered off and dried *in vacuo*. The material was recrystallised from toluene to give white crystals. Yield = 2.0g 54%; m.p. = 67-68°C (66°C); i.r. spectrum (nujol mull) ν(C≡N) 2230 cm^{-1} (s).

1-cyano-2-ethoxy-1-ethoxycarbonylethene

Prepared by a method analogous to that for 1,1-dicyano-2-ethoxyethene, using ethyl cyanoacetate (3.49g 30 mmol), ethyl orthoformate (4.6g 62 mmol) and acetic anhydride (30 cm^3), and obtained as off-white crystals after recrystallisation from toluene. Yield = 2.4g 46%; m.p. = 52-53°C; b.p. = 180-185°C @ 25 mmHg; i.r. spectrum (nujol mull) ν(C-H) 3030 cm^{-1} (m), ν(C≡N) 2225 cm^{-1} (s), ν(C=O) 1720 cm^{-1} (s). ν(C=C) 1620 cm^{-1} (s), ν(C-O) 1250/1120 cm^{-1} (vs).

1-cyano-2-ethoxy-1-ethoxycarbonyl-2-methylethene

Prepared by a method analogous to that for 1,1-dicyano-2-ethoxyethene, using ethyl cyanoacetate (30 mmol), ethyl orthoacetate (60 mmol) and freshly distilled acetic anhydride. Obtained as an off-white solid. Yield = 56%; m.p. = 72-75°C; i.r. spectrum (nujol mull) ν(C≡N) 2230 cm^{-1} (s), ν(C=O) 1720 cm^{-1} (s), ν(C=C) 1575 cm^{-1} (s).

1,1-dicyano-2-ethoxy-2-methylethene

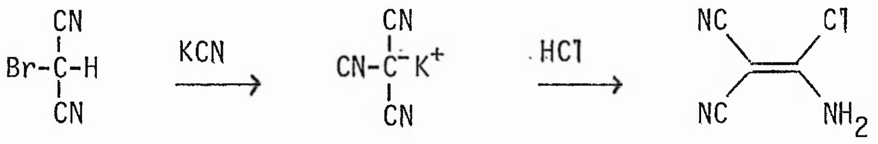
Prepared by a method analogous to that for 1,1-dicyano-2-ethoxyethene, using malononitrile (30 mmol), ethyl orthoacetate (60 mmol), and freshly distilled acetic anhydride (30 cm^3). Recrystallised from toluene and obtained as white crystals. Yield = 30%; m.p. = 90-91.5°C (90-92°C); i.r. spectrum (nujol mull) ν(C≡N) 2220 cm^{-1} (m), ν(C=C) 1580 cm^{-1} (s), ν(C-O) 1230/1020 cm^{-1} (s).

1,1-dicyano-2-ethoxy-2-ethylethene

Prepared by a method analogous to that for 1,1-dicyano-2-ethoxyethene from malononitrile (30 mmol), ethyl orthopropionate (60 mmol) and freshly distilled acetic anhydride. Obtained as a yellow liquid at o° b.p. = 100-105°C @ 25 mmHg; i.r. spectrum (thin film) ν(C≡N) 2240 cm^{-1} (s), ν(C=C) 1570 cm^{-1} (s), ν(C-O) 1220, 1040 cm^{-1} (s).

1-amino-1-chloro-2,2-dicyanoethene

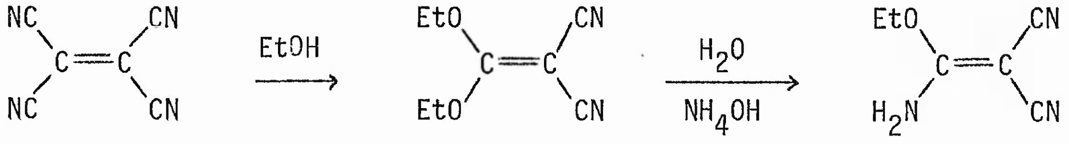
Prepared by the method of Middleton et. al. (110) via the following reaction sequence:



and obtained as a yellow crystalline solid after recrystallisation from diethyl ether. Yield = 66%; m.p. = 212-214°C; i.r. spectrum (nujol mull) ν(N-H) 3320/3170 cm^{-1} (s), ν(C$\equiv$N) 2220 cm^{-1} (s), δ(N-H) 1650 cm^{-1} (s) ν(C=C) 1550 cm^{-1} (s).

1-amino-2,2-dicyano-1-ethoxyethene

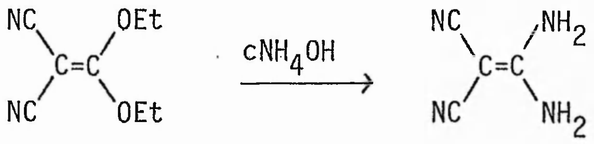
Prepared by the method of reference (111) via the following reaction sequence:



and obtained as white crystals. Yield = 80%; m.p. = 227-229°C (225-226°C); i.r. spectrum (nujol mull) ν(N-H) 3350; 3220 cm^{-1} (s), ν(C$\equiv$N) 2225, 2220 cm^{-1} (s), δ(N-H) 1660 cm^{-1} (s), ν(C=C) 1550 cm^{-1} (s), ν(C-O) 1040 cm^{-1} (vs).

1,1-diamino-2,2-dicyanoethene

Prepared by the method of reference (111) via the sequence:



Recrystallised from water to give white needles. Yield = 48%; m.p. =

236-238.5°C (236-238°C); i.r. spectrum (nujol mull) ν(N-H) 3450, 3340, 3230 cm^{-1} (s), ν(C≡N) 2210, 2190 cm^{-1} (s), δ(N-H) 1650 cm^{-1} (s), ν(C=C) 1550 cm^{-1} (s).

1,1-dicyano-2,2-diethoxyethene

Prepared by the method of reference (111) from tetracyanoethene, urea and ethanol. Recrystallised from isopropanol and obtained as white needles. Yield = 56%; m.p. = 58-59°C (58-59°C; i.r. spectrum (nujol mull) ν(C≡N) 2205 cm^{-1} (s), ν(C=C) 1550 cm^{-1} (s), ν(C-O) 1220, 1010 cm^{-1} (s).

1-chloro-1,2,2-tricyanoethene

Prepared by the method of Dickenson et. al. (112) from tetramethylammonium tricyanoethanolate (113) and oxalyl chloride. Recrystallised from toluene to give the product as off-white needles. Yield = 28%; m.p. = 73-75.5°C (70-72°C); i.r. spectrum (nujol mull) ν(C-H) 3030 cm^{-1} (m), ν(C≡N) 2220 cm^{-1} (s), ν(C=C) 1500 cm^{-1} (m).

1,1-diethoxycarbonyl-2-ethoxyethene

A mixture of diethylmalonate (1.6g 10 mmol), ethyl orthoformate (1.48g 20 mmol) and acetic anhydride (20 cm^3) were refluxed for 2 hours. The solvent was removed by distillation in vacuo and the product obtained by vacuum distillation as a light yellow liquid. Yield 0.8g 37%; b.p. = 110-120°C @ 15 mmHg; i.r. spectrum (thin film) ν(C=O) 1750 cm^{-1} (vs) ν(C=C) 1640 cm^{-1} (m), ν(C-O) 1190/1040 cm^{-1} (s).

1,1-diethoxycarbonyl-2-chloroethene

To the potassium salt of hydroxymethylene-diethyl malonate (from potassium ethoxide, diethyl malonate, ethyl formate and ethanol) (1.8g 10 mmol) in 1,2 dichloroethane (20 cm³) was added $POCl_3$ (1.54g 10 mmol) in one portion. The mixture was refluxed for six hours and the solvent and excess $POCl_3$ distilled off. The residue was vacuum distilled to give the product as a yellow liquid. Yield = 1.0g, 63%; b.p. 116-123°C @ 15 mmHg (119°C @ 15 mmHg (108)) i.r. spectrum (thin film) ν(C=O) 1740 cm^{-1} (s); ν(C=C) 1620 cm^{-1} (s).

1,1-dicyano-2,2-dimethylethene

Prepared via a Knoevenagel condensation from malononitrile (3,3g 50 mmol), acetone (2.9g 50 mmol), acetic acid (0.5 cm³) and β alanine (trace) in toluene (50 cm³); the water was removed azeotropically. The solvent was removed *in vacuo* and the residue was vacuum distilled to give the product as a white solid. Yield = 5.1g 92%; b.p. = 100-105°C @ 15 mmHg (100-102°C @ 16 mmHg); i.r. spectrum (nujol mull) ν(C≡N) 2240 cm^{-1} (s), ν(C=C) 1610 cm^{-1} (s).

1-cyano-2,2-dimethyl-1-ethoxycarbonylethene

Prepared by a method analogous to that for 1,1-dicyano-2,2-dimethylethene, using ethyl cyanoacetate (3.4g 30 mmol), acetone (1.75g 30 mmol), acetic acid (0.5 cm³) and β alanine (trace) in toluene (50 cm³). Vacuum distillation gave the product as a white solid. Yield = 2.9g 63%; b.p. 115-119°C @ 15 mmHg (115-120°C @ 16mmHg); i.r. spectrum (mujol mull) ν(C≡N) 2225 cm^{-1} (m), ν(C=O) 1735 cm^{-1} (s),

ν(C=C) 1620 cm^{-1} (m), ν(C-O) 1230/1085 cm^{-1} (s).

(5) REACTIONS BETWEEN CYANO- AND ETHOXYCARBONYL- SUBSTITUTED ALKENES AND TUNGSTEN HYDRAZIDO(2-)/DIAZENIDO(1-) COMPLEXES

All reactions were carried out at room temperature.

trans-Bis[bis(1,2-diphenylphosphino)ethane]-1,1-dicyanovinyldiazenido-bromo-tungsten(II). $[WBr(N_2CH{:}C(CN)_2)(dppe)_2]\cdot 0.5\ CH_2Cl_2$.

(Complex X)

Method 1

$[WBr(N_2H_2)(dppe)_2]^+Br^-$ (3.0g 3.51 mmol) was dissolved in methanol (250 cm³) under dinitrogen and 1,1-dicyano-2-ethoxyethene (0.39g, 3.51 mmol) added. Triethylamine was added dropwise with stirring until the solution darkened (*ca.* 1 cm³). The product started to precipitate after a few minutes and the solution was stirred for a further 30 minutes. The brown crystalline product was filtered off, washed with diethyl ether and dried *in vacuo*. Yield = 2.52g, 84%.

Method 2

To a solution of $[WBr(N_2H_2)(dppe)_2]^+Br^-$ (1.17g, 1 mmol) in 100 cm³ CH_2Cl_2 was added 1,1-dicyano-2-chloroethene (0.112g, 1 mmol), followed by dropwise addition of Et_3N (0.5 cm³) with rapid stirring. The solution immediately darkened and was stirred for 30 minutes. After washing with water (2 x 100 cm³) and separating, the organic layer was dried over 3A molecular sieves. Methanol (50 cm³) was added and the solution reduced in volume under reduced pressure until a dark brown crystalline precipitate was formed. This was filtered off, washed with diethyl ether and dried in vacuo. Yield = 1.06g 90%; m.p. = 185-190°C (dec.); U.V. spectrum λ_{max} = 412 nm ε = 26,000; i.r. spectrum (KBr disc) $\nu(C{\equiv}N)$ 2220 cm^{-1} (s), 2190 cm^{-1} (m), $\nu(C{=}C)$ 1510 cm^{-1} (s); elemental analysis, found C = 55.8, H = 4.0, N = 4.6, Calc. for $C_{56.5}H_{50}N_4P_4WBrCl$ C = 56.2, H = 4.1, N = 4.6.

trans-Bis[bis(1,2-diphenylphosphino)ethane]-1,1-dicyanovinyldiazenido-fluoro-tungsten(II). $[WF(N_2CH{:}C(CN)_2)(dppe)_2]$. 0.5 CH_2Cl_2 (Complex XI)

Prepared analogously to method 1 from $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ (1.12g 1 mmol) and 2-chloro-1,1-dicyanoethene (0.113g, 1 mmol), and obtained as orange crystals from CH_2Cl_2/MeOH. Yield = 1.0g 91%; m.p. 136-139°C (dec.); U.V. spectrum λ_{max} 395 nm ε = 33,500; i.r. spectrum (nujol mull) $\nu(C{\equiv}N)$ 2195 cm^{-1} (s) $\nu(C{=}C)/\nu(N{=}N)$ 1470 cm^{-1} (vs, br) $\nu(C{-}N)$ 1265 cm^{-1} (m); elemental analysis, found C = 58.6, H = 4.2, N = 4.7, calc. for $C_{56.5}H_{50}N_4P_4WFCl$ C = 59.2 H = 4.4 N = 4.9; ^{13}C n.m.r. (CD_2Cl_2) -C≡N 118.5, 117.4 ppm. ^{19}F n.m.r. (CD_2Cl_2) W-F 157.7 ppm (qu, $J^{31}P\text{-}^{19}F$ = 40 Hz).

trans-Bis[bis(1,2-diphenylphosphino)ethane]-1,1-dicyano-2-chlorovinyl-diazenido-bromo-tungsten(II). $[WBr(N_2C(Cl){:}C(CN)_2)(dppe)_2].CH_2Cl_2$ (Complex XII)

Prepared by method 2 using $[WBr(N_2H_2)(dppe)_2]^+Br^-$ (1,17g 1 mmol) and 1,1-dichloro-2,2-dicyanoethene (0.147g, 1 mmol), to give the product as dark brown-green crystals. Yield = 1.1g, 88%; m.p. = 210°C (dec.); U.V. spectrum λ_{max} = 408 nm ε = 29,000; i.r. spectrum (KBr disc) $\nu(C\equiv N)$ 2205 cm^{-1} (s) 2195 cm^{-1} (m), $\nu(C=C)$ 1480 cm^{-1} (s); elemental analysis, found C = 53.8, H = 3.8, N = 4.3, calc. for C_{57} H_{50} N_4 P_4 WBr Cl_3 C = 53.3 H = 3.9 N = 4.4; ^{13}C nmr (CD_2Cl_2) -C N 118.9, 117.1 ppm; ^{31}P nmr (CD_2Cl_2) 24.5 ppm, singlet with ^{185}W satellites (J $^{185}W-^{31}P$ = 281 Hz).

trans-Bis[bis(1,2-diphenylphosphino)ethane]-1,1-dicyano-2-chlorovinyl-diazenido-fluoro-tungsten(II). (WF($N_2C(Cl):C(CN)_2$)(dppe)$_2$].CH_2Cl_2

(Complex XIII)

Prepared analogously from method 1, using $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ (1.12g, 1 mmol) and obtained as dark red crystals. Yield = 1.0g, 82%; m.p. = 172-174°C (dec.); U.V. spectrum λ_{max} = 390 nm ε = 30,000; i.r. spectrum (KBr disc) $\nu(C\equiv N)$ 2190 cm^{-1} (s), $\nu(C=C)/\nu(N=N)$ 1490 cm^{-1} (s,br); elemental analysis, found C = 56.6, H = 4.3 N = 4.4, calc. for C_{57} H_{50} N_4 $WFCl_3$ C = 55.9 H = 4.1 N = 4.6. ^{13}C n.m.r. (CD_2Cl_2) $-C\equiv N$ 118.6 120.1 ppm ^{19}F n.m.r. (CD_2Cl_2) W-F 157.6 ppm (qu, br).

trans-Bis[bis(1,2-diphenylphosphino)ethane]-1-cyano-1-ethoxycarbonyl-vinyldiazenido-bromo-tungsten(II). [WBr($N_2CH:C(CN)CO_2Et$(dppe)$_2$] 0.5 CH_2Cl_2

(Complex XIV)

Prepared by method 2 from $[WBr(N_2H_2)(dppe)_2]^+Br^-$ (1.17g, 1 mmol) and 2-chloro-1-cyano-1-ethoxycarbonylethene (0.16 g, 1 mmol) to give the product as brown crystals. Yield = 0.98g,81%; m.p. = 250-255°C (dec.); U.V. spectrum λ_{max} = 419 nm ε = 32,000; i.r. spectrum (KBr disc) $\nu(C\equiv N)$

2190 cm^{-1} (s), ν(C=O) 1680 cm^{-1} (m), ν(C=C) 1500 cm^{-1} (s); elemental analysis found C = 56.4, H = 4.5, N = 3.5, calc. for $C_{58.5}H_{55}N_4P_4WO_2BrCl$ C = 56.1 H = 4.3 N = 3.2. ^1H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.18 ppm (m, 40H), $-CH_2CH_3$ 3.84 ppm (q, 2H), $P(CH_2)_2P$ 2.65 ppm (d, 8H), $-CH_2CH_3$ 1.05 ppm (t, 3H); ^{13}C n.m.r. ($CDCl_3$) -C=O 160.9 ppm, -C≡N 118.8 ppm, $-OCH_2$ 58.9 ppm $-CH_3$ 14.7 ppm.

trans-Bis[bis(1,2 diphenylphosphino)ethane]-1-cyano-1-ethoxycarbonylvinyldiazenido-fluoro-tungsten(II). $[WF(N_2CH{:}C(CN)CO_2Et)(dppe)_2]$. (Complex XV)

Prepared *via* method 1 using $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ (1,12g, 1 mmol) and 2-chloro-1-cyano-1-ethoxycarbonylethene (0.16g, 1 mmol), obtained as red crystals. Yield = 1.1g 95%; m.p. = 184-189°C (dec.); U.V. spectrum λ_{max} = 403 nm ε = 31,000; i.r. spectrum (nujol mull) ν(C≡N) 2190 cm^{-1} (m) ν(C=O) 1-65 cm^{-1} (s) ν(C=C) 1500 cm^{-1} (s) ν(N=N) 1485 cm^{-1} (s) ν(C-O) 1255, 1090 cm^{-1} (s); elemental analysis, found C = 59.0, H = 4.4, N = 3.4, calc. for $C_{58}H_{56}N_3P_4WO_2F$ C = 56.5, H = 4.4, N = 3.4 ^{13}C n.m.r. (CD_2Cl_2) -C=O 172.6 ppm, -C≡N 128.1 ppm, $-OCH_2$ 58.6 ppm, $-CH_3$ 12.1 ppm. ^{19}F n.m.r. (CD_2Cl_2) W-F 176.3 ppm (s, vbr).

The reactions between $[WX(N_2H_2)(dppe)_2]^+$ (X = F, Br) and other cyanoalkenes.

In general, reactions were carried out at room temperature between equimolar quantities of the hydrazido(2-) complex and alkene in the presence of a weak base (Et_3N or $K_2CO_{3(aq)}$) with CH_2Cl_2, thf or methanol as solvents. The reaction solutions, and solid products obtained from the work-up of these solutions were examined by i.r. spectroscopy and U.V. spectroscopy. The alkenes which did not react with the hydrazido(2-) complex in the presence of base are listed in table 1.

Table 1

R_1	R_2	R_3	X
-CN	-CN	$-NH_2$	-Cl
-CN	-CN	$-CH_3$	-OEt
-CN	-CN	$-C_2H_5$	-OEt
-CN	-CN	$-CH_3$	$-CH_3$
-CN	-H	-H	-H
-CN	-CN	$-NH_2$	-OEt
-CN	-CN	$-NH_2$	$-NH_2$
-CN	-CN	-OEt	-OEt
-CN	$-CO_2Et$	-H	-OEt
-CN	$-CO_2Et$	$-CH_3$	$-CH_3$
$-CO_2Et$	$-CO_2Et$	-H	-OEt
-Cl	-Cl	-Cl	-Cl

Either the diazenido complex $[WX(N_2H)(dppe)_2]$ (X = Br, F) or a tungsten-phosphine decomposition product from the diazenido complex was all that could be isolated from the reaction mixtures.

The reaction between $[WBr(N_2H)(dppe)_2]$ and $Cl(X)C:C(CN)_2$ (X = H, Cl)

To a solution of $[WBr(N_2H)(dppe)_2]$ (1.09g, 1 mmol) in CH_2Cl_2 (30 cm³) under dinitrogen was added an equimolar quantity of the appropriate alkene. An immediate colour change occurred (yellow-orange to dark brown) and the solution was stirred for 15 min. Work up of this solution, as described for complex X, produced [WBr($N_2C(X):C(CN)_2$)-($dppe)_2$] (X = H, Cl), identified by comparison of its u.v. and i.r. spectrum with those of an authentic sample.

The reactions between [WX($N_2CH:C(CN)_2$)($dppe)_2$(X = Br, F) or [WX(N_2CCl:-$C(CN)_2$)($dppe)_2$] (X = Br, F) and acids.

To a solution of [WX($N_2CH:C(CN)_2$)($dppe)_2$] in CH_2Cl_2 was added CF_3CO_2H dropwise. A rapid colour change was observed (for X = Br, brown-yellow to green, for X = F orange-red to pale green). The mixture was stirred for 20 min, washed with water, the organic layer dried over anhydrous $MgSO_4$ and filtered. Addition of diethyl ether precipitated only the starting material (identified by its u.v. and i.r. spectra).

Addition of excess Et_3N to an acidified solution of [WX($N_2HCH:C(CN)_2$) ($dppe)_2$] in CH_2Cl_2 regenerated the starting diazenido complex.

Solutions of the hydrazido(2-) complexes may however be characterised by u.v. and i.r. spectroscopy. In the u.v. spectrum, a blue shift was observed in the λ_{max} of the diazenido complex on protonation, which reverts back to the λ_{max} for the diazenido complex on addition of Et_3N (Table 2). A similarly reversible shift to higher wavenumber of the nitrile stretching frequency was also observed in the i.r. spectrum on protonation (Table 2).

Analogous reactions occur in thf using aqueous HBF_4 as the acid. However, using CH_2Cl_2/HBF_4 a different reaction was observed.

Table 2

Solvent : CH_2Cl_2 Acid : CF_3CO_2H Base : NEt_3

$$\text{Diazenido} \underset{\text{BASE}}{\overset{\text{ACID}}{\rightleftharpoons}} \text{Hydrazido(2-)}$$

Diazenido complex	λ_{max}	$\nu(C\equiv N)$	Hydrazido(2-) complex	λ_{max}	$\nu(C\equiv N)$
$[WBr(N_2CH:C(CN)_2)(dppe)_2]$	414	2220	$[WBr(N_2HCH:C(CN)_2)(dppe)_2]^+$	348	2235
$[WBr(N_2CCl:C(CN)_2)(dppe)_2]$	412	2205	$[WBr(N_2HCCl:C(CN)_2)(dppe)_2]^+$	350	2235
$[WF(N_2CH:C(CN)_2)(dppe)_2]$	393	2195	$[WF(N_2HCH:C(CN)_2)(dppe)_2]^+$	350	2230
$[WF(N_2CCl:C(CN)_2)(dppe)_2]$	390	2190	$[WF(N_2HCCl:C(CN)_2)(dppe)_2]^+$	350	2225

Table 3

Solvent : CH_2Cl_2/HBF_4 Acid : HBF_4

$$\text{Diazenido} \overset{\text{Acid}}{\rightarrow} \text{Hydrazido(2-)} \rightarrow \text{final complex}$$

Hydrazido(2-) complex	λ_{max}	Final λ_{max}
$[WBr(N_2HCH{:}C(CN)_2)(dppe)_2]^+$	348	420
$[WBr(N_2HCCl{:}C(CN)_2)(dppe)_2]^+$	350	423
$[WF(N_2HCH{:}C(CN)_2)(dppe)_2]^+$	350	408
$[WF(N_2HCCl{:}C(CN)_2)(dppe)_2]^+$	350	407

Table 4

Solvent : CH_2Cl_2 Acid : HBF_4 or CF_3CO_2H Base : NEt_3

$$\text{Diazenido} \underset{\text{Base}}{\overset{\text{Acid}}{\rightleftharpoons}} \text{Hydrazido(2-)}$$

Diazenido complex	λ_{max}	Hydrazido(2-) complex	λ_{max}
$[WBr(N_2CH{:}C(CN)CO_2Et)(dppe)_2]$	419	$[WBr(N_2HCH{:}C(CN)CO_2Et)(dppe)_2]^+$	350
$[WF(N_2CH{:}C(CN)CO_2Et)(dppe)_2]$	404	$[WF(N_2HCH{:}C(CN)CO_2Et)(dppe)_2]^+$	345

Protonation of the diazenido complex initially gave a product with a u.v. spectrum characteristic of the hydrazido(2-) complex, but after a few seconds, the λ_{max} associated with the hydrazido(2-) complex disappeared and an absorption band several nanometers higher than that for the starting diazenido complex appeared (Table 3). The protonation was irreversible.

The reactions between $[WX(N_2CH:C(CN)CO_2Et)(dppe)_2]$ (X = Br, F) and acids.

These complexes were reversibly protonated in CH_2Cl_2 using HBF_4 or CH_3CO_2H. No evidence for irreversibility or decomposition of the hydrazido(2-) complex in acid solution was found (u.v. spectrum) over a period of several hours. Addition of excess Et_3N to acid solutions of the hydrazido(2-) complexes regenerated the starting diazenido complexes (Table 4).

trans-Bis[bis(1,2-diphenylphosphino)ethane]-1,1-dicyanovinyl-(N-methylhydrazido(2-))-bromo-tungsten(IV) hexafluorophosphate. $[WBr(N_2(CH_3)-CH:C(CN)_2)(dppe)_2]^+PF_6^-.0.5CH_2Cl_2$

(Complex XVI)

$[WBr(N_2HCH_3)(dppe)_2]^+BF_4^-$ (0.12g, 0.1 mmol) was dissolved in CH_2Cl_2 (10 cm³) under dinitrogen and 2-chloro-1-1 dicyanoethene (0.12g, 0.1 mmol) added. On addition of Et_3N (3 drops) the colour of the solution changed from light red to dark green, and was stirred for 30 min. The organic layer was washed with water (2 x 30 cm³), separated, dried over 3A molecular sieves, filtered and hexane added to give a green oil. The supernatant liquid was decanted off and the residue dissolved in methanol (5 cm³), to which NH_4PF_6 (1g) in methanol (10 cm³) was added dropwise. The suspension was stirred for 30 min. and the product filtered off. This was washed with diethyl ether (20 cm³) and dried in vacuo. Yield = 0.08g, 60%; m.p. 174-179°C (dec.); u.v. spectrum λ_{max} = 366 nm; i.r. spectrum (KBr disc) ν(C≡N) 2220, 2195, 2160 cm^{-1} (m), ν(C=C) 1525 cm^{-1} (s), ν(P-F) 840 cm^{-1} (s); elemental analysis, found C = 48.4, H = 4.2, N = 4.7, calc. for $C_{57.5} H_{53} N_4 P_5 WBr F_6 Cl$ C = 50.5 H = 3.9 N = 4.1. ^{13}C n.m.r. (CD_2Cl_2) -C≡N 111.7, 110.9 ppm, $-CH_3$ 45.0 ppm.

[Bis(2-diphenylphosphinoethyl)phenyl phosphine-triphenylphosphine]-1,1-dicyano-2-chlorovinyl diazenido-fluoro-molybdenum (II)

$[MoF(N_2H_2)(PPh_3)(triphos)]^+BF_4^-$ (0.52g, 0.5 mmol) was dissolved in dried and degassed CH_2Cl_2 (20 cm³) under dinitrogen. To this was added the alkene (0.074g, 0.5 mmol) and Et_3N (2 drops) with rapid stirring. The mixture was stirred for one hour and poured into hexane (50 cm³) under dinitrogen. This produced an oil, which, after decanting the supernatant, was dissolved in dry, degassed methanol (50 cm³) and filtered. Reduction in volume of this solution in vacuo to approximately 5 cm³ and cooling to 0°C produced a brown solid, which was filtered off in air, washed with ice-cold methanol (2-3 cm³) and diethyl ether (10 cm³) and dried in vacuo. Yield = 0.2g, 38%; m.p. 164-170°C (dec.); u.v. spectrum, λ_{max} = 400 nm; i.r. spectrum (KBr disc) ν(C≡N) 2195 cm^{-1} (s), ν(C=C) 1540 cm^{-1} (m), ν(N=N) 1475 cm^{-1} (s); elemental analysis, found C = 58.9 H = 4.5 N = 4.1, calc. for $C_{58} H_{52} N_4 P_4 MoF Cl_5$ C = 57.0 H = 4.3 N = 4.6.

The product appears to be moderately stable in air. Protonation of this complex in CH_2Cl_2 with HBF_4 gave a colour change in the solution from orange-brown to brown-green. The i.r. spectrum of a sample taken from the solution (evaporated film, NaCl plates) showed the disappearance of the band assigned to $\nu(N{=}N)$ at 1475 cm^{-1}, and the u.v. spectrum of the solution shows a shift in the λ_{max} to 340 nm, but no pure product could be isolated from the reaction mixture.

[Bis(2-diphenylphosphinoethyl)phenyl phosphine-triphenylphosphine]-1,1-dicyano-2-methylvinyl diazenido-fluoro-molybdenum(II). [$MoF(N_2C(CH_3){:}C(CN)_2)(PPh_3)$(triphos)]

(Complex XVIII)

The reaction was carried out as above, using equimolar (0.5 mmol) quantities of the hydrazido(2-) complex and alkene, with methanol as the solvent. The product precipitated from solution after stirring for one hour. Reduction in the volume of solvent *in vacuo* and cooling to 0°C gave the product, which was filtered off, washed with methanol and diethyl ether and dried *in vacuo*. Yield = 0.09g, 17.5%; M.pt. = not determined; u.v. spectrum, λ_{max} = 360 nm; i.r. spectrum (nujol mull) $\nu(C{\equiv}N)$ 2180 cm^{-1} (s), $\nu(C{=}C)$ 1530 cm^{-1} (m), $\nu(N{=}N)$ 1490 cm^{-1} (m). The complex could not be isolated pure, and elemental analyses were poor. No reaction was observed between [$MoF(N_2H_2)(PPh_3)$(triphos)]$^+BF_4^-$ and 1,1-dicyano-2-ethoxy-2-ethylethene, only decomposition of the hydrazido(2-) complex occurred.

The reaction between ($MoF(N_2H_2)(PPh_3)$(triphos)]$^+BF_4^-$ and 1-amino-1-chloro-2,2-dicyanoethene

(Complex XIX)

The reaction was carried out as above, using CH_2Cl_2 as solvent. The product was obtained as a dark orange-brown powder. Attempts to recrystallise this from methanol or CH_2Cl_2/diethyl ether did not improve the crystallinity of the product. The product is quite stable in air. The u.v. spectrum has no λ_{max} in the 350-450 nm region and the i.r. spectrum (KBr disc) has no band assignable to $\nu(N=N)$. A very strong band at 2160 cm^{-1} assigned to $\nu(C\equiv N)$ is present.

^{31}P n.m.r. (CD_2Cl_2) 105.6 ppm (t) ($^{185}W-{}^{31}P$ = 41 Hz),
64.2 ppm (d) ($^{185}W-{}^{31}P$ = 39 Hz);

^{13}C n.m.r. (CD_2Cl_2) 129.5, 129.6 ppm ($-\underline{C}\equiv N$).

trans-Bis[bis(1,2-diphenylphosphino)ethane](Bromotricyanoprop-2-enylideneamino)-bromo-tungsten (II). $[WBr(NC(Br)C(CN):C(CN)_2)(dppe)_2].CH_2Cl_2$ (Complex XX)

$[WBr(N_2H_2)(dppe)_2]^+Br^-$ (1.17g, 1 mmol) was partially dissolved in thf (100 cm³) under dinitrogen and tetracyanoethene (0.26g, 2 mmol) added in one portion with rapid stirring. The solution darkened slowly and was stirred for 20 min. After removal of solvent *in vacuo*, extraction of the red residue into CH_2Cl_2 (100 cm³), washing several times with water and drying the organic layer over 3A molecular sieves, the dark red solution was filtered and acetonitrile (50 cm³) added. Reduction in volume of this solution *in vacuo* precipitated a black-green crystalline solid, which was filtered off, washed with acetonitrile (10 cm³) and diethyl ether (50 cm³), and dried *in vacuo*. Yield = 0.65g, 71%; m.p. = 205-210°C (dec.); crystals suitable for a single crystal X-ray structure analysis were obtained by slow evaporation of CH_2Cl_2/acetonitrile mixtures under a flow of dinitrogen. U.V. spectrum, λ_{max} = 510 nm ε = 51,000; i.r. spectrum (KBr disc), $\nu(C\equiv N)$ 2180 cm^{-1} (s), 2150 cm^{-1} (m), ν(C=C) 1465 cm^{-1} (s); elemental analysis, found C = 52.8, H = 3.7, N = 4.4, P = 9.1, Br = 12.0, W = 14.0, Cl = 2.7, calc. for $C_{59}H_{50}N_4P_4Br_2Cl_2$ C = 53.5, H = 3.7, N = 4.3, P = 9.5, Br = 12.2, W = 14.2, Cl = 2.6; ^{13}C n.m.r. (CD_2Cl_2) -CN 119.6, 114.6 ppm $-\overset{|}{C}=\overset{|}{C}-$ 135.3 ppm; ^{31}P n.m.r. (CD_2Cl_2) 19.9 ppm (J $^{185}W-{}^{31}P$ = 278.3 Hz).

The reaction between $[WBr(NC(Br)C(CN):C(CN)_2)(dppe)_2]$ and CF_3CO_2H

To a small quantity of the complex dissolved in CH_2Cl_2 was added CF_3CO_2H dropwise. A colour change occurred (green to pale yellow), which was reversible on addition of excess Et_3N. An i.r. spectrum (CH_2Cl_2 solution) of the complex in acid solution showed complete disappearance of the nitrile ν(C≡N) bands. These reappeared on addition of weak base to the solution. Attempts to isolate the protonated complex were however unsuccessful, and the reason for the absence of ν(C≡N) bands in its solution spectrum is unclear.

trans-Bis[bis(1,2-diphenylphosphino)ethane]-(Bromo-2-chloro-dicyanoprop-2-enylideneamino-)bromo-tungsten (II). $[WBr(NC(Br)C(Cl):C(CN)_2)(dppe)_2].CH_2Cl_2$.

(Complex XXI)

To $[WBr(N_2H_2)(dppe)_2]^+Br^-$ (0.59g, 0.5 mmol) partially dissolved in thf (50 cm^3) under dinitrogen was added chlorotricyanoethene (0.14g, 1 mmol) with rapid stirring. The dark red-brown solution was stirred for two hours and the solvent removed *in vacuo*. The residue was extracted into CH_2Cl_2 (50 cm^3) and filtered. Methanol (30 cm^3) was added and the volume of the solution reduced *in vacuo* to precipitate a red-brown solid, which was filtered off, washed with diethyl ether and dried _in vacuo_. Yield = 0.09g, 14%; m.p. = 195-210°C (dec.); u.v. spectrum λ_{max} 410 nm; i.r. spectrum (KBr disc) $\nu(C{\equiv}N)$ 2190 cm^{-1} (s) $\nu(C{=}C)$ 1500 cm^{-1} (m); elemental analysis, found C = 50.4, H = 3.5, N = 3.1, calc. for $C_{58}H_{50}N_3P_4WBr_2Cl_3$, C = 51.1, H = 3.7, N = 3.1.

trans-Bis[bis(1,2 diphenylphosphino)ethane] (bromo-3-cyanoprop-2-enylideneamino)-bromo-tungsten(II). $[WBr(NC(Br)CH{:}C(CN)H)(dppe)_2].CH_2Cl_2$ (Complex XXII)

To $[WBr(N_2H_2)(dppe)_2]^+Br^-$ (1,17g, 1 mmol) dissolved in CH_2Cl_2 (50 cm³) under dinitrogen were added trans-1,2-dicyanoethene (0.16g, 1 mmol) and Et_3N (0.25 cm³) with rapid stirring. After 24 hours, the dark brown solution was washed with water (2 x 100 cm³), dried over 3A molecular sieves, filtered, and methanol added. Reduction in volume of this solution _in vacuo_ precipitated a dark red-brown powder, which was filtered off, washed with diethyl ether (50 cm³) and dried. This material was recrystallised from CH_2Cl_2/diethyl ether to give brown-red crystals. Yield = 0.97g, 79%; m.p. = 166-170°C (dec.); u.v. spectrum λ_{max} 410 nm; i.r. spectrum (KBr disc) $\nu(C{\equiv}N)$ 2170 cm^{-1} (m), $\nu(C{=}C)$ 1550 cm^{-1} (m); elemental analysis, found C = 52.6, H = 4.3, N = 2.5, calc. for $C_{57}H_{57}N_2P_4WBr_2Cl_2$, C = 52.4, H = 4.0, N = 2.0. ^{13}C n.m.r. (CD_2Cl_2) $-C{\equiv}N$ 122.4 ppm.

trans-Bis[bis(1,2-diphenylphosphino)ethane]-(bromo-(7, 7', 8-tricyanoquinododimethane) ideneamino-bromo-tungsten(II). $[WBr(NC(Br)C(CN){:}C_6H_4{:}C(CN)_2)(dppe)_2]$.
(Complex XXIII)

$[WBr(N_2H_2)(dppe)_2]^+Br^-$ (1.17g, 1 mmol) was partially dissolved in thf (50 cm³) under dinitrogen and T.C.N.Q. (0.41g, 2 mmol) dissolved in thf (10 cm³) added dropwise. After stirring for one hour, the green solution was filtered and the filtrate taken to dryness *in vacuo*. The residue was redissolved in methanol (100 cm³), filtered and the volume of the solution reduced *in vacuo* to approximately 10 cm³. Cooling to 0°C precipitated a green solid, which was filtered off, washed with ice-cold methanol (5 cm³) and diethyl ether (50 cm³) and dried *in vacuo*. Yield = 0.76g, 57%; m.p. = 184-190°C; u.v. spectrum (methanol) λ_{max} 420, 742 and 828 nm; i.r. spectrum (KBr disc) $\nu(C{\equiv}N)$ 2250, 2170, 2130 cm^{-1} (m), $\nu(C{=}C)$ 1510 cm^{-1} (m); elemental analysis, found C = 57.1, H = 3.9, N = 4.1, calc. for $C_{64}H_{52}N_4P_4WBr_2$, C = 57.1, H = 3.8, N = 4.0.

The reaction between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and tetracyanoethene

To $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ (0.56g, 0.5 mmol) dissolved in thf (50 cm³) under N_2, was added tetracyanoethene (0.13g, 1 mmol) with rapid stirring. The solution slowly became dark red in colour and was stirred for 30 min. Filtration and removal of solvent *in vacuo* gave a crude product, which was extracted into CH_2Cl_2 (50 cm³), filtered and acetonitrile added (30 cm³). The volume of the solvent was reduced to approximately 20 cm³ *in vacuo* and the solid product filtered off, washed with diethyl ether and dried *in vacuo*. Repeated recrystallisation form CH_2Cl_2/diethyl ether and CH_2Cl_2/acetonitrile mixtures failed to give a pure product. Attempted purification of an acetone solution of the complex by column chromatography on cellulose, using acetone as elutant again did not produce an identifiable complex. Elemental analysis, found C = 49.8, H = 3.5, N = 8.2; u.v. spectrum, no λ_{max} in 350-500 nm region.

(6) PREPARATION OF ALKENE AND ALLYL PALLADIUM- AND ALKENE-MERCURY COMPLEXES

bis(benzonitrile)palladium(II) chloride

Prepared by the method of Kharasch et. al. (114).

bis(1-hexene)dipalladium(II) tetrachloride (97)

To $[PdCl_2(PhCN)_2]$ (0.192g, 0.5 mmol) in thf (10 cm³) at -20°C under dinitrogen was added 1-hexene (0.042g, 0.5 mmol), the mixture was allowed to warm to 0°C and stirred for one hour. The yellow solution of the palladium-1-hexene complex was used in the reactions with $[WX(N_2H_2)(dppe)_2]^+$. No attempt was made to isolate the unstable π-alkene complex. Solutions of bis(cyclohexene)dipalladium(II) tetrachloride, bis(1-decene)dipalladium(II) tetrachloride, and bis(styrene)dipalladium(II) tetrachloride in thf were prepared and used analogously.

bis(η³-1-methylallyl)dipalladium(II) dichloride (115)

To a solution of K_2PdCl_4 (0.98g, 3 mmol) and crotyl chloride (0.17g, 3 mmol) in methanol (30 cm³) under dinitrogen was added anhydrous $SnCl_2$ (0.57g, 3 mmol). The mixture was stirred for 30 min, evaporated to dryness *in vacuo* and the residue extracted with several portions of CH_2Cl_2. The combined extracts were filtered and the volume of the solvent reduced to give the product as a yellow solid. Yield = 0.75g, 80%; m.p. = 135-138°C; i.r. spectrum (KBr disc) ν(C-H) 3160, 2980, 2950, 2910 cm^{-1} (m) ν(C=C) 1475 (m), 1425 (s).

bis(η^3-2-methylallyl)dipalladium(II) dichloride was prepared analogously, using 2-methylallyl chloride. Yield = 70%; m.p. = 166-168°C; i.r. spectrum (KBr disc) ν(C-H) 3160, 2990, 2940, 2900 cm^{-1} (m) ν(C=C) 1475 cm^{-1} (m), 1425 cm^{-1} (s).

Preparation of mercury-alkene complexes

To the appropriate mercury(II) salt ($HgCl_2$, $Hg(OAc)_2$, $HgNO_3$) partially dissolved in CH_2Cl_2 under dinitrogen was added the alkene (1-hexene or cyclohexene). The suspension was stirred for 3 hours. after which time the hydrazido(2-) complex $[WX(N_2H_2)(dppe)_2]^+$ (X = F, Br) was added (see section 7).

(7) REACTIONS BETWEEN TRANSITION METAL-ALKENE/ALLYL COMPLEXES AND TUNGSTEN HYDRAZIDO(2-)/DIAZENIDO COMPLEXES

The reaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and $[PdCl_2(1\text{-hexene})]_2$

To the pre-formed $[PdCl_2(1\text{-hexene})]_2$ (0.26g, 0.5 mmol) in thf (10 cm^3) at -78°C under dinitrogen, was added a suspension of $[WBr(N_2H_2)(dppe)_2]^+Br^-$ (0.59g, 0.5 mmol) in thf (30 cm^3) dropwise with rapid stirring. The mixture was stirred at -78°C for 4 hours. An i.r. sample removed from the reaction mixture showed only bands due to starting materials. The suspension was allowed to warm to room temperature and stirred for a further 12 hours. The solid material was filtered off, washed with diethyl ether and dried. An i.r. spectrum of this material showed ν(N-H) at 3210 cm^{-1} (w).

Recrystallisation of this material from CH_2Cl_2/diethyl ether produced a black residue, probably metallic palladium, and a dark brown powdery material, with an i.r. spectrum similar to that of the impure material before recrystallisation. Further recrystallisations removed all free Pd to give a dark red crystalline material. Yield = 0.72g 48%; m.p. = 203-210°C (dec.). The same product may be obtained in higher yield (∿60%) from the reaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and $[PdCl_2(PhCN)_2]$; i.r. spectrum (CsI disc) ν(N-H) 3210 cm^{-1} (m), ν(Pd-Cl) 335 cm^{-1} (m): elemental analysis, found C = 48.0, H = 3.4, N = 1.4, Cl = 6.1, Br = 14.0, W = 7.0, Pd = 4.9, calc. for $C_{105}H_{98}N_4P_8W_2PdBr_4Cl_4$ (including one mol of CH_2Cl_2) C = 48.4, H = 3.8, N = 2.1, Cl = 5.5, Br = 12.3, W = 7.1, Pd = 4.0; ^{1}Hn.m.r. (CD_2Cl_2) $-PPh_2$ 7.4 ppm (d, 80H) $-P(CH_2)_2P-$ 2-85 ppm (5, 16H). ^{31}P n.m.r. (CD_2Cl_2) 30.4 ppm ($J^{185}W-^{31}P$ = 147 Hz). The reaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and $[PdCl_2(alkene)]_2$ (alkene = 1-decene, cyclohexene, styrene) gave the same product.

The reaction between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and $[PdCl_2(alkene]_2$ (alkene = 1-hexene or cyclohexene)

The reactions were carried out according to the above procedure. Again, no reaction was observed at -78°C, and the mixture was allowed to warm to room temperature and stirred for 12 hours. Using the work up procedure described above, the product could only be obtained as a red-brown powder. Yield = 55%; m.p. = 198-205°C (dec.); i.r. spectrum (CsBr disc) ν(N-H) 3210 cm^{-1} (m), ν(Pd-Cl) 335 cm^{-1} (m); elemental analysis, found C = 46.9, H = 3.3, N = 1.7, W = 10.9, Ph = 7.6, calc. for $C_{53}H_{52}N_2P_4WPdFCl_5$ (including one mol of CH_2Cl_2) C = 48.0, H = 3.9, N = 2.1, W = 13.9, Pd = 7.9; ^{1}H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.4 ppm (m, 40H), $-P(CH_2)_2P-$ 2.75 ppm (d, 8H); ^{31}P n.m.r. (CD_2Cl_2) 30.4 ppm ($J^{185}W-^{31}P$ =

147 Hz) ^{19}F n.m.r. (CD_2Cl_2) 137.7 ppm (qu) ($J^{185}W-^{19}F$ = 44 Hz). The same product may be obtained from the reaction between $[WF(N_2H_2)(dppe)_2]^+$ BF_4^- and $[PdCl_2(PhCN)_2]$.

Addition of HBF_4 to CH_2Cl_2 solutions of the above complexes gave, after work up, high yields of the hydrazido(2-) complexes $[WX(N_2H_2)-(dppe)_2]^+BF_4^-$ (X = Br, F).

Addition of Et_3N to CH_2Cl_2 solutions of the complexes prepared above produced an immediate black precipitate of metallic palladium and a yellow solution. This mixture was filtered, and the filtrate washed several times with water, dried over anhydrous $MgSO_4$, filtered, and diethyl ether added to precipitate a dull yellow powder. This complex had no bands assignable to $\nu(N\equiv N)$ or $\nu(N-H)$ in its infra-red spectrum.

The reaction between $WBr(N_2H)(dppe)_2$ and $[PdCl_2(1\text{-hexene})]_2$

To a suspension of $[PdCl_2(1\text{-hexene})]_2$ (0.06g, 0.5 mmol) in thf (10 cm³) at -78°C under dinitrogen was slowly added a solution of $WBr(N_2H)(dppe)_2$ (0.52g, 0.5 mmol) in thf (30 cm³). The mixture was stirred for 4 hours at -78°C. No reaction was observed. The mixture was allowed to warm to room temperature, stirred for a further 2 hours and reduced to an oil *in vacuo*. Addition of hexane and scratching, crystallised the oil to give an impure solid, containing metallic palladium. An infra red spectrum (KBr) of this material showed no bands assignable to $\nu(N-H)$ or $\nu(N\equiv N)$ and an elemental analysis demonstrated complete loss of nitrogen had occurred.

The reaction between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$, $HgCl_2$ and 1-hexene

To a suspension of the $HgCl_2$/1-hexene complex (1 mmol) in CH_2Cl_2 (30 cm³) under dinitrogen, was added $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ (1 mmol) with rapid stirring. The mixture became green in colour after refluxing under dinitrogen for one hour. The green solution was filtered and diethyl ether added to produce a mixture of $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and a new hydrazido(2-) complex, (i.r. spectrum). Slow recrystallisation of the yellow mixture from CH_2Cl_2/diethyl ether produced $[WF(N_2H_2)(dppe)_2]^+HgCl_3^-$ as long yellow needles. Yield = 0.23g, 17%; m.p. = 169°C; i.r. spectrum (CsI disc) ν(N-H) 3245, 3150 cm^{-1} (w) νHg-Cl 435 cm^{-1} (m); elemental analysis, found C = 45.6, H = 3.4, N = 2.0, calc. for $C_{52.5}H_{49}N_2P_4WHgCl_4F$ (including 0.5 CH_2Cl_2) C = 45.7, H = 3.5, N = 2.0. Addition of diethyl ether to the filtrate from the above crystallisation produced $[WF(N_2H_2)(dppe)_2]^+BF_4^-$. Yield = 0.85g; i.r. spectrum (KBr disc) ν(N-H) 3335, 3255 cm^{-1} (w).

No evidence for the coordination of 1-hexene was found.

The reaction was repeated using cyclohexene with similar results.

The complex $[WF(N_2H_2)(dppe)_2]^+HgCl_3^-$ may be obtained from the reaction between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and $HgCl_2$ in CH_2Cl_2 in the absence of an alkene.

The reactions between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and other mercury(II) salts

The reaction between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and $Hg(OAc)_2$ in CH_2Cl_2 under dinitrogen in the presence or absence of an alkene, produces immediate decomposition of the hydrazido(2-) complex, with liberation of free dppe.

The reaction between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and $Hg(NO_3)_2$ in CH_2Cl_2 under dinitrogen produced, after a few seconds stirring, a lilac solution of the oxo-complex $[WF(O)(dppe)_2]^+BF_4^-$. This was isolated by filtering the solution and adding diethyl ether slowly to the filtrate. Any precipitated mercury salt was filtered off before the complex was precipitated as lilac crystals (m.p. = 240°C; i.r. spectrum (KBr disc) ν(W=O) 950 cm^{-1} (m), νB-F 1060 cm^{-1} (s); elemental analysis, calc. for $C_{52}H_{48}P_4WOBF_5$, C = 56.6, H = 4.4, expt. C = 56.6, H = 4.3). Prolonged contact (several minutes) with $Hg(NO_3)_2$ produces decomposition of the oxo-complexes, with liberation of free dppe.

The reaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and $[PdCl_2$ (η^3-1-methylallyl)$]_2$

To $[WBr(N_2H_2)(dppe)_2]^+Br^-$ (0.58g, 0.5 mmol) in CH_2Cl_2 (30 cm³) under dinitrogen was added $[PdCl_2$ (η^3-1-methylallyl)$]_2$ (0.23g, 0.5 mmol). The mixture was stirred for seven hours, with no obvious reaction. Addition of K_2CO_3 (1g) dissolved in water (10 cm³) produced an immediate black precipitate. This was stirred vigorously for one hour, filtered and the organic layer dried over 3A molecular sieves. Filtration and addition of diethyl ether produced a dark orange crystalline material, which was filtered off, redissolved in methanol, and $NH_4^+PH_6^-$ (1g) in methanol (10 cm³) added dropwise until crystallisation of the product commenced. The suspension was stirred for 30 min. the product filtered off washed with water, methanol and hexane, and dried *in vacuo*. Yield = 0.09g, 14%; m.p. = 219-223°C (dec.); i.r. spectrum (KBr disc) ν(P-F)

840 cm^{-1} (vs); elemental analysis, found C = 51.3, H = 4.0, N = 0.0, calc. for $C_{57}H_{57}P_5WBrF_6Cl_2$ (including one mol of CH_2Cl_2) C = 50.9, H = 4.2; ^{1}H n.m.r. (d_6 actone) $-PPh_2$ 7.6 ppm (m, 40H), allylic-H 5.97, 5.85, 5.75, 5.64 ppm (complex m, 4H), $-P(CH_2)_2P-$ 2.95 ppm (s, br, 8H), $-CH_3$ 1.79 ppm (q, 3H). A portion of the above complex was dissolved in CH_2Cl_2 and left in contact with air for several days. A purple colour developed in the solution, characteristic of the oxo-complex $[WBr(O)(dppe)_2]^+PF_6^-$

The reaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and $[PdCl_2(\eta^3\text{-2-methylallyl})]_2$

The reaction was carried out as described for the reaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and $[PdCl_2(\eta^3\text{-1-methylallyl})]_2$ (above), and the product obtained as brown crystals in low yield. Yield = 0.19g 30%; m.p. = 125-131°C (dec.); i.r. spectrum ν(P-F) 840 cm^{-1} (vs); elemental analysis found, C = 51.1, H = 4.2, N = 0.0, calc. for $C_{57}H_{57}P_5WBrF_6Cl_2$ (including one mol of CH_2Cl_2) C = 50.9, H = 4.2; ^{1}H n.m.r. (d_6 acetone) $-PPh_2$ 7.3 ppm (d), allylic-H 5.44, 5.13, 4.92, 4.76 ppm (q of t), $-CH_3$ 1.33 ppm (s).

The reaction between $[WBr(N_2H_2)(dppe)_2{}^+Br^-$ and $[Pd(PPh_3)_2(\eta^3\text{-1-methylallyl})]^+Cl^-$

Addition of triphenylphosphine (0.262g, 1 mmol) to $[PdCl_2(\eta^3\text{-1-methylallyl})]_2$ (0.232g, 0.5 mmol) in thf at 0°C under dinitrogen produced the cationic palladium complex $[Pd(PPh_3)_2(\eta^3\text{-1-methylallyl}(]^+Cl^-$ (101). To this was added a thf (50 cm³) solution of $[WBr(N_2H_2)(dppe)_2]^+Br^-$ (0.56g, 0.5 mmol) Et_3N (3 drops) was added with rapid stirring. No precipitation of palladium metal was observed and the red solution was stirred for one hour, taken to dryness in vacuo and the residue treated with 40-60 petroleum ether (500 cm³). This was filtered and the light yellow filtrate reduced in vacuo to give a yellow solid which was filtered off, washed with hexane and dried in vacuo. This yellow complex has the m.p. and i.r. spectrum of $[PdCl_2(PPh_3)_2]$. The red residue from the filtration (above), was recrystallised from CH_2Cl_2/diethyl ether but no pure complex could be obtained. No evidence for coordination of the allylic group to the tungsten-dppe complex could be found from i.r. or ^1H n.m.r. spectroscopy.

(8) ATTEMPTED INTRAMOLECULAR CYCLISATION REACTIONS

a) Preparation of starting hydrazido(2-) complexes

trans-Bis[bis(1,2-diphenylphosphino)ethane] (2-diazo-hex-5-ene)-bromo-tungsten(IV) hexafluorophosphate. $[WBr(N_2C(CH_3)(CH_2CH_2CH : CH_2)-(dppe)_2]^+PF_6^- . 0.5\ CH_2Cl_2$

(Complex XXIV)

$[WBr(N_2H_2)(dppe)]^+Br^-$ (1.17g, 1 mmol) was suspended in 5-hexene-2-one (40 cm³) and conc. HCl (1.0 cm³) was added with rapid stirring under dinitrogen. The suspension was warmed to 90°C, the solid material dissolved completely, and the brown solution was stirred for four hours. This was cooled to room temperature, filtered and poured into hexane (100 cm³), giving, on vigorous stirring, a green oil. The supernatant was decanted off and the remaining oil extracted into methanol (10 cm³). To this was added a filtered solution of $NH_4^+PF_6^-$ (1.0g) in methanol (10 cm³), to precipitate a grey-green solid. The solid was collected by filtration and washed with diethyl ether. The impure product was recrystallised from dichloromethane/diethyl ether to give a grey crystalline solid, which was filtered off, washed with methanol (10 cm³) and diethyl ether and dried *in vacuo*. Yield = 1.06g, 80%; m.p. = 182-184°C (dec.); i.r. spectrum (KBr disc) ν(C=N) 1570 cm^{-1} (m), ν(C=C) 1635 cm^{-1} (w) ν(P-F) 840 cm^{-1} (s); elemental analysis, found C = 51.7, H = 4.4, N = 1.9, calc. for $C_{58.5}H_{59}N_2P_5WBrClF_6$ C = 51.7, H = 4.4, N = 2.1; ^{1}H n.m.r. (CD_2Cl_2) -PPh$_2$ 7.3 ppm (s, 40H), =CH- 5.75 ppm (s, 1H), =CH$_2$ 5.08 ppm (t, 2H), -P(CH$_2$)$_2$P- 3.28 ppm (s, br, 8H), -(CH$_2$)$_2$- 1.63, 1.16 (d, m 4H), OCH$_3$ -0.77 (s, 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane]-(hex-5-enyl-2-diazenido)-bromo-tungsten(II). [WBr(N_2.CH(CH_3)CH_2CH_2CH:CH_2)(dppe)$_2$]. 3CH_2Cl_2 (Complex XXV)

To complex (XXIV) (1.0g, 0.76 mmol) suspended in 95% ethanol (20 cm³) was added $NaBH_4$ (1.5g) in approximately 0.2g portions. The mixture was stirred for two hrs, gradually forming a light-yellow suspension. The solid was filtered off, washed with water, hexane and dried. This material was redissolved in CH_2Cl_2 (50 cm³), washed with water (3 x 100 cm³) and the organic layer dried over 3A molecular sieves. Filtration, addition of hexane (10 cm³) and reduction of the volume of the solution *in vacuo* gave the product as yellow needles, which were filtered off, washed with hexane and dried. Yield = 0.75g 64%; m.p. = 106-110°C (dec.); i.r. spectrum (KBr disc) ν(C=C) 1635 cm^{-1} (w), ν(N=N) 1480 cm^{-1} (s), ν(C-N) 1300 cm^{-1} (m); elemental analysis, found C = 50.8, H = 4.2, N = 1.8 calc. for $C_{51}H_{64}N_2P_4BrCl_6$, C = 51.3, H = 4.6, N = 2.0; ^{1}H n.m.r. (CD_2Cl_2) -PPh$_2$ 7.1 ppm (d, 40H), = CH- 5.50 ppm (m, 1H), =CH$_2$ 4.74 (d, 2H), -P(CH$_2$)$_2$P- 2.65 ppm (s, br, 8H), -(CH$_2$)$_2$ 1.24, 0.72 ppm (t, m, 4H), -CH$_3$ 0.16 ppm (d, 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane](hex-5-enyl-2-hydrazido(2-))-bromo-tungsten(IV) hexafluorophosphate. $[WBr(N_2H.CH(CH_3)CH_2CH_2CH{:}CH_2)(dppe)_2]^+PF_6^-$. $0.5CH_2Cl_2$

(Complex XXVI)

Complex (XXV) (0.5g, 0.43 mmol) was dissolved in CH_2Cl_2 (30 cm³) and HBF_4 (1.0 cm³) added dropwise with rapid stirring under dinitrogen. The solution was stirred for 20 min, filtered, washed with water (2 x 30 cm³) and the organic layer dried over anhydrous $MgSO_4$. This was filtered and excess diethyl ether added to precipitate the crude complex, which was filtered off, washed with diethyl ether and dried. This material was dissolved in methanol (10 cm³), filtered, and a filtered solution of $NH_4^+PF_6^-$ (1.0g) in methanol (10 cm³) added dropwise to precipitate the product as yellow-orange crystals, which were filtered off, washed with diethyl ether and dried *in vacuo*. Yield = 0.42g 83%; m.p. = 179°C (dec.); i.r. spectrum (KBr disc) ν(N-H) 3280 cm^{-1} (w), ν(C=C) 1635 cm^{-1} (w), ν(P-F) 840 cm^{-1} (s); elemental analysis, found C = 51.9, H = 4.7, N = 2.1, calc. for $C_{58.5}H_{60}N_2P_5WBrClF_6$, C = 51.7 H = 4.5, N = 2.1; ^1H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.4 ppm (d, 40H), = CH- 5.50 ppm (m, 1H), $=CH_2$ 4.88 ppm (t, 2H), $-P(CH_2)_2P-$ 3.10 ppm (s, br, 8H), $(CH_2)_2$ 1.46, 0.72 ppm (s, t, 4H), $-CH_3$ -0.08 (d, 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane](2-diazo-prop-3-ene)-bromo-tungsten(IV) hexafluorophosphate. $[WBr(N_2CHC(CH_3){:}CH_2)(dppe)_2]^+ PF_6^-$. CH_2Cl_2.

(Complex XXVII)

$[WBr(N_2H_2)(dppe)_2]^+Br^-$ (1.17, 1 mmol) was stirred in trifluoroacetic acid (30 cm³) under dinitrogen and methacrylaldehyde (0.7g, 10 mmol) added dropwise. The green-brown solution was stirred for ten min. and then poured into water (100 cm³), vigorous stirring produced a brown oil. The supernatant was decanted and the oily residue dissolved in methanol (20 cm³). A filtered solution of $NH_4^+PF_6^-$ (1.0g) in methanol (10 cm³) was added dropwise to precipitate a grey solid. This was filtered off, washed with methanol (5 cm³) and diethyl ether and dried. This material was recrystallised from dichloromethane/diethyl ether and obtained as green crystals. Yield = 1.15g 89%; m.p. = 131-136°C; i.r. spectrum (KBr disc) ν(C=C) 1630 cm^{-1} (w), ν(C=N) 1580 cm^{-1} (m), ν(P-F) 840 cm^{-1} (s); elemental analysis, found C = 49.1, H = 4.0, N = 1.9, calc. for $C_{57}H_{56}N_2P_5WBrCl_2F_6$ C = 49.8, H = 4.0, N = 2.0; ^1H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.2 ppm (d, 40H), $=CH_2$ 6.47 (t, 2H), =CH- 5.95 (t, 1H), $-P(CH_2)_2P-$ 3.10 ppm (s, br, 8H), $-CH_3$ 1.12, 0.84 ppm (t, t, 2 x 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane] (1-diazo-hexa-2,4-diene)-bromo-tungsten(IV) tetrafluoroborate. $[WBr(N_2CHCH:CHCH:CH(CH_3))(dppe)_2]^+ BF_4^-$

(Complex XXVIII)

Prepared by a method analogous to that for Complex (XXVII) from $[WBr(N_2H_2(dppe)_2{}^+Br^-$ and 2,4-hexadienal. The complex was obtained as light green crystals. Yield = 85%; m.p. = 127-130°C (dec.); i.r. spectrum (KBr disc) ν(C=C) 1620 cm^{-1} (m), ν(C=N) 1595 cm^{-1} (s), ν(P-F) 840 cm^{-1} (s); elemental analysis, found C = 52.7, H = 4.3, N = 2.0, calc. for $C_{58}H_{56}N_2P_5WBrF_6$, C = 53.0, H = 4.3, N = 2.1; ^1H n.m.r. (d_6 acetone) $-PPh_2$ 7.3 ppm (s, 40H), olefinic-H 6.04, 6.25 ppm (d, s, 4H), N = CH- 5.64 (s, 1H), $-P(CH_2)_2P-$ 3.19 (s, br, 8H), $-CH_3$ 1.20 ppm (t, 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane] (prop-3-enyl-2-diazenido)-bromo-tungsten (II). $[WBr(N_2CH_2C(CH_3):CH_2)(dppe)_2].3CH_2Cl_2$ (Complex XXIX)

Complex (XXVII) (0.64g, 0.5 mmol) was suspended in i-propanol (10 cm^3) under dinitrogen and $NaBH_4$ (1.0g) added in small portions. The suspension was stirred rapidly for one hour, and the yellow solid filtered off, washed with water, methanol and hexane and dried. The crude product was dissolved in CH_2Cl_2 (20 cm^3), washed with water (2 x 20 cm^3), the organic layer dried over anhydrous $MgSO_4$ and filtered. Addition of hexane (10 cm^3) and slow reduction of solvent volume *in vacuo* to approx. 10 cm^3 precipitated the product as yellow needles, which were filtered off, washed with hexane and dried *in vacuo*. Yield = 0.41g 71%; m.p. = 121-125°C (dec.); i.r. spectrum (KBr disc), ν(C=C) 1660 cm^{-1} (m) ν(N=N) 1505 cm^{-1} (s) ν(C-N) 1310 cm^{-1} (m); elemental analysis, found C = 49.7, H = 4.3, N = 1.7, calc. for $C_{59}H_{61}N_2P_4WBrCl_6$ C = 49.1, H = 4.3, N = 1.9; ^{1}H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.3 ppm (m, 40H), $=CH_2$ 6.45 ppm (m, 2H), $-P(CH_2)_2P-$ 3.0 ppm (s, br, 8H), $-CH_2-$ 1.90 ppm (d, 2H), $-CH_3$ 0.60, 0.39 ppm (t, t, 2 x 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane](hexa-2,4-dienyl-1-diazenido)-bromo-tungsten (II). $[WBr(N_2CH_2CH:CHCH:CH(CH_3)(dppe)_2].0.5CH_2Cl_2$ (Complex XXX)

Prepared by a method analogous to that for complex (XXV) using complex (XXVIII) and $NaBH_4$ in 95% ethanol and obtained as yellow crystals. Yield = 85%; m.p. = 194-197°C (dec.); i.r. spectrum (KBr disc) ν(C=C) 1615 cm^{-1} (m), ν(N=N) 1530 cm^{-1} (m), ν(C-N) 1305 cm^{-1} (s); elemental analysis found C = 57.8, H = 4.7, N = 1.6, calc. for $C_{58.5}H_{58}N_2P_4WBrCl$, C = 57.6, H = 4.7, N = 2.3; ^{1}H n.m.r. ($CDCl_3$) (poor resolution) $-PPh_2$ 7.4 ppm (s, 40H), $-P(CH_2)_2P-$ 2.81 ppm (s, br, 8H), $-CH_2-$ 1.32 ppm (s, 2H) $-CH_3$ 0.88 ppm (t, 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane](prop-3-enyl-2-hydrazido(2-))-bromo-tungsten (IV) tetrafluoroborate. $[WBr(N_2HCH_2C(CH_3):CH_2(dppe)_2]^+BF_4^-$. $0.5CH_2Cl_2$

(Complex XXXI)

Complex (XXIX) (0.29g, 0.25 mmol) was dissolved completely in CH_2Cl_2 (20 cm³) and HBF_4 (1.0 cm³, 40%) added dropwise with rapid stirring under dinitrogen. A solid precipitated and the mixture was stirred for 20 min. The solid was filtered off, and the filtrate washed with water (2 x 20 cm³). The organic layer was dried over 3A molecular sieves, filtered and reduced to a red oil *in vacuo*. This was extracted into methanol (10 cm³), a solution of $NH_4^+BF_4^-$ (0.1g) in methanol (1 cm³) added, and the mixture cooled in ice. After two hours, the orange-red crystalline product was filtered off, washed with diethyl ether and dried *in vacuo*. Yield = 0.27g, 84%; m.p. = 167-169°C (dec.); i.r. spectrum (KBr disc) ν(N-H) 3280 cm^{-1} (m) ν(C=C) 1620 cm^{-1} (w), ν(B-F) 1050 cm^{-1} (s); elemental analysis, found C = 53.2, H = 4.4, N = 2.1, calc. for $C_{56.5}H_{57}N_2P_4WBF_4ClBr$. C = 53.2, H = 4.5, N = 2.2; ^{1}H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.3 ppm (d, 40H), $=CH_2$ 6.45 ppm (m, 2H), $-P(CH_2)_2P-$ 3.0 ppm (s, br, 8H), $-CH_3$ 0.16, 0.40 ppm (t, t, 2 x 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane](hexa-2,4-dienyl-1-hydrazido(2-))-bromo-tungsten (IV) tetrafluoroborate. $[WBr(N_2HCH_2CH:CHCH:CH-(CH_3)(dppe)_2]^+BF_4^-$. $0.5CH_2Cl_2$

(Complex XXXII)

Prepared by a method analogous to that from complex (XXXI) from complex (XXX). Obtained as orange crystals. Yield = 77%; m.p. = 183-186°C (dec.); i.r. spectrum (KBr disc) ν(N-H) 3280 cm^{-1} (m), ν(C=C) 1620 cm^{-1} (w); ν(B-F) 1050 cm^{-1} (s); elemental analysis, found C = 53.9, H = 4.5, N = 2.0, calc. for $C_{57.5}H_{57}N_2P_4WBrBClF_4$, C = 53.6, H = 4.5, N = 2.2; ^1H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.3 ppm (d, 40H), olefinic-H 5.7 ppm (m, 3H); $-P(CH_2)_2P-$ 2.93 ppm (s, br, 8H), $-CH_2-$ 1.68 ppm (d, 2H), $-CH_3$ 0.82 ppm (s, br, 3H).

trans-Bis[bis(1,2-diphenylphosphino)ethane]-(allyl-oxycarbonyl-diazenido)-fluoro-tungsten (II). $[WF(N_2CO.O.CH_2CH:CH_2)(dppe)_2]$ (Complex XXXIII)

$[WF(N_2H_2)(dppe)_2]^+BF_4^-$ (0.56g, 0.5 mmol) was dissolved in CH_2Cl_2 (30 cm³) at 0°C and allyl chloroformate (0.6g, 5 mmol) was added dropwise with rapid stirring. Et_3N (3 drops) was added, a vigorous reaction ensued, and the reaction mixture was stirred for 30 min. at room temperature. The red solution was washed with water (2 x 50 cm³), the organic layer dried over $MgSO_4$, filtered and methanol (15 cm³) added. Reduction in volume of this solution *in vacuo* to ≅5 cm³ gave the product as red crystals. Yield = 0.36g, 73%; m.p. = 203-210°C (dec.); i.r. spectrum (KBr disc) ν(C=O) 1600 cm^{-1} (s), ν(N=N) 1475 cm^{-1} (m), ν(C-N) 1365 cm^{-1} (s), ν(C-O) 1240/1228 cm^{-1} (s); elemental analysis, found C = 60.0, H = 5.2, N = 2.3, calc. for $C_{56}H_{53}N_2P_4WFO_2$, C = 60.0, H = 4.8, N = 2.5; ^1H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.2 ppm (s, 40H), olefinic-H 5.17, 5.08, 4.96 ppm (t, 2H), $-CH_2-$ 3.95 (d, 2H), $-P(CH_2)_2P-$ 2.8 ppm (d, 8H).

trans-Bis[bis(1,2-diphenylphosphino)ethane](allyl-oxycarbonyl-hydrazido-

(2-))-fluoro-tungsten (IV) tetrafluoroborate. $[WF(N_2HCO.O.CH_2CH:CH_2)-(dppe)_2]^+BF_4^-$

(Complex XXXIV)

Complex (XXXIII) (0.56g, 0.5 mmol) was dissolved in CH_2Cl_2 (30 cm³) and HBF_4 (1 cm³, 48% aq. solution) added dropwise with rapid stirring. The solution darkened and was stirred for a further 15 min. After washing with water, (2 x 50 cm³) drying over 3A molecular sieves, and filtering, slow addition of diethyl ether to the CH_2Cl_2 solution precipitated the product as an orange-brown powder. This was filtered off and recrystallised from dichloromethane/diethyl ether to give orange crystals. Yield = 0.51g 86%; m.p. = 184-185°C (dec.); i.r. spectrum (KBr disc) ν(N-H) 3240 cm^{-1} (w), ν(C=O) 1735 cm^{-1} (m-s), ν(C-N) 1210 cm^{-1} (s), ν(B-F) 1060 cm^{-1} (vs, br); elemental analysis, found C = 56.7, H = 4.7, N = 1.8, calc. for $C_{56}H_{49}N_2P_4WF_5O_2B$, C = 56.0, H = 4.5, N = 2.3; ^{1}H n.m.r. (CD_2Cl_2) $-PPh_2$ 7.3 ppm (s, 40H), olefinic-H 5.20, 5.00 ppm (d, s, 3H), $-CH_2-$ 4.03 ppm (d, 2H), $-P(CH_2)_2P-$ 2.8 ppm (d, 8H).

b) Attempted intramolecular cyclisation reactions

The following methods were general and were used for the hydrazido (2-) complex(es) indicated (see section 8a).

Reaction with K_2PtCl_4

To K_2PtCl_4 (1 mmol) in methanol (50 cm³) under N_2 was added the hydrazido(2-) complex (1 mmol equivalent, complexes (XXVI, XXXI, XXXIII) with stirring. The dark red suspension was stirred for 3 hrs, filtered, and the filtrate poured into water (300 cm³). The residue was filtered off, dissolved in CH_2Cl_2 (30 cm³), dried over $CaSO_4$ (anhydrous), filtered and diethyl ether added to precipitate the product. This was filtered off, washed with diethyl ether and dried. The infra red spectrum indicated unreacted starting materials.

Reaction with K_2PtCl_4/cHCl

The above method was followed, using methanol (40 cm³) of solvent and with cHCl (2 cm³). A similar work up and spectroscopic testing (i.r. spectroscopy) revealed only starting materials present.

Reaction with K_2PtCl_4/cHCl under reflux

A portion of the above reaction mixture was heated under reflux for 15 min. Again only starting materials were obtained (i.r. spectrum).

Reaction with $PdCl_2(PhCN)_2$

$PdCl_2(PhCN)_2$ (1 mmol) was dissolved in thf (20 cm³) under dinitrogen and the solution cooled to -10°C. A suspension of the hydrazido(2-) complex (1.32g, 1 mmol) complex (XXVI) in thf (50 cm³) was added. An immediate precipitate formed and the resulting dark brown suspension was stirred for two hours. The orange-brown solid was filtered off and washed with diethyl ether. This material was recrystallised several times from dichloromethane/diethyl ether. Yield = 0.35g; m.p. = 146-148°C (dec.); i.r. spectrum (KBr) ν(N-H) 3280 cm^{-1} (m), ν(C≡N) 2280 cm^{-1}

(m).

Reaction in strong acid solutions

The appropriate hydrazido(2-) complex (complexes XXVI, XXXI, XXXII 1 mmol) was added to a solution of 100% H_2SO_4 (10 cm³) in glacial acetic acid (40 cm³) under dinitrogen. The solid dissolved almost immediately and was stirred for ten min. The product was extracted with CH_2Cl_2, the CH_2Cl_2 layer separated, washed with several portions of water and dried over $CaSO_4$. Filtration and addition of diethyl ether precipitated a solid, which was filtered off, washed with diethyl ether and dried *in vacuo*.

The above procedure was repeated using CF_3SO_3H (few drops) in 40 cm³ CH_2Cl_2 as the acid medium, producing the same product at the end of the reaction, as that for cH_2SO_4/CH_3CO_2H. In both systems, only starting materials were isolated (identified by i.r. spectroscopy).

(9) THE REACTION BETWEEN TUNGSTEN HYDRAZIDO(2-) COMPLEXES AND ALKENES IN STRONG ACID SOLUTIONS

A solution of the hydrazido(2-) complex (complex II) was prepared by dissolving 0.57g (0.5 mmol) of the complex in cH_2SO_4 (1 cm³)/glacial acetic acid (10 cm³) under dinitrogen. A gaseous alkene (isobutene or propene) was bubbled slowly through this solution for up to 30 minutes or in the case of a liquid alkene (cyclohexene or styrene) it was added dropwise over a period of 20 minutes. The reaction mixtures were quenched by pouring into water (200 cm³) and the oil/solid thus formed extracted into CH_2Cl_2 (2 x 50 cm³). The CH_2Cl_2 was dried over anhydrous $MgSO_4$ and filtered. Addition of diethyl ether (200 cm³) precipitated the product, which was filtered off, washed with diethyl ether and dried. The products were identified by the N-H stretching bands in the infra-red spectrum.

Where necessary, the products were converted into their PF_6^- salts by dissolving the crude product in methanol, filtering, and adding of filtered solution of NH_4PF_6 in methanol to precipitate the product.

The above procedure was repeated using CH_3SO_3H (few drops)/CH_2Cl_2 (20 cm³) as the acid medium.

No evidence for the coordination of the alkene ligands was found from i.r. or ^1H n.m.r. spectroscopy.

The stability of various alkyl hydrazido(2-) complexes in strong acid solution

$[WBr(N_2HEt)(dppe)_2]^+PF_6^-$, $[WBr(N_2H\ ^iPr)(dppe)_2]^+PF_6^-$ and $[WBr(N_2H\text{-}^tBu)(dppe)_2]^+PF_6^-$ were prepared by tungsten filament light irradiation of a mixture of trans$[W(N_2)_2(dppe)_2]$ and the appropriate alkyl bromide in thf, according to the method of Chatt, et. al. (54) and identified by the ν(N-H) stretching band in the infra red spectrum.

The hydrazido(2-) complex and each of the alkylhydrazido(2-) complexes were dissolved in cH_2SO_4 (1 cm³)/glacial acetic acid (10 cm³) under dinitrogen and stirred for 30 minutes. The mixture was poured into water (200 cm³) and extracted into CH_2Cl_2 (2 x 50 cm³). The

CH_2Cl_2 layer was dried over anhydrous $MgSO_4$, filtered, and diethyl ether added to precipitate the product, which was filtered off, washed with diethyl ether and dried. The products were identified by the N-H stretching bands in the infra red spectrum.

(10) MISCELLANEOUS REACTIONS

trans-Bis[1,2 bis(diphenylphosphino)ethane]-bis(dinitrogen)-(tetracyanoquinododimethane)$^{\dot{-}}$ bis(tetracyanoquinododimethane)-tungsten(I). $[W(N_2)_2(dppe)_2]^+[TCNQ]^{\dot{-}}[TCNQ]_2(toluene)$

(Complex XXXV)

To a solution of trans$[W(N_2)_2(dppe)_2]$ (1.04g, 1 mmol) in toluene (150 cm^3) was added a solution of TCNQ (0.21g, 1 mmol) in toluene (10 cm^3). The orange solution became dark green almost immediately, and precipitated the product after a few minutes stirring. The dark green microcrystalline product was filtered off, washed with toluene (30 cm^3) and diethyl ether (30 cm^3) and dried *in vacuo*. Yield = 1.32g 80%; m.p. = 197-199°C (dec.); u.v. spectrum λ_{max} 398 nm ($\varepsilon = 2.6 \times 10^4$), 845 nm ($\varepsilon = 4.5 \times 10^3$); i.r. spectrum (KBr disc) $\nu(N\equiv N)$ 2005 cm^{-1} (vs), $\nu(C\equiv N)$ 2175 cm^{-1} (s), 2140 cm^{-1} (m), $\nu(C=C)$ 1470 cm^{-1}; elemental analysis, found C = 64.0, H = 3.5, N = 13.1, calc. for $C_{95}H_{68}N_{16}P_4W$, C = 64.1, H = 3.6, N = 13.6.

The complex $[W(N_2)_2(dppe)_2]^+[TCQ]^-.(toluene)$, (complex XXXVI) was prepared analogously and obtained as a light green crystalline solid. Yield = 1.05g 82%; m.p. 149-153°C (dec.); i.r. spectrum (KBr disc) $\nu(N\equiv N)$ 2000 cm^{-1} (s), $\nu(C=O)$ 1550 cm^{-1} (s), $\nu(C=C)$ 1528 cm^{-1} (m); elemental analysis, found C = 56.5, H = 4.1, N = 4.1, calc. for $C_{56}H_{56}N_4P_4WO_2Cl_4$, C = 56.8, H = 4.1, N = 4.1.

p-Benzoquinone and D.D.Q. produced unidentifiable materials (elemental analysis, u.v. and i.r. spectroscopy) which have no $\nu(N\equiv N)$ band assignable to tungsten (0) or tungsten (I) bis(dinitrogen) complexes. The latter possessed strong bands assignable to $\nu(C\equiv N)$.

trans-Bis[1,2-bis(diphenylphosphino)ethane]-(2,5-diketopyrrolidinylimido)-fluoro- tungsten (IV) tetrafluoroborate. $[WF(NNCO.(CH_2)_2CO)(dppe)_2]^+BF_4^-$ (Complex XXXVII)

To a mixture of $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ (0.52g, 0.5 mmol) and succinic anhydride (0.05g, 0.5 mmol) in CH_2Cl_2 (30 cm³) was added triethylamine (0.1 cm³) and the resulting red solution stirred for two hours. This was washed with water (2 x 30 cm³), the organic layer dried over 3A molecular sieves and filtered. Addition of methanol (30 cm³) and reduction in volume of the solution *in vacuo* gave the product as red crystals, which were filtered off, washed with diethyl ether and dried *in vacuo*. Yield = 0.48g, 84%; m.p. = 120°C (dec.) i.r. spectrum (KBr disc) $\nu(C{=}O)$ 1725 cm^{-1} (vs), $\nu(B{-}F)$ 1050 cm^{-1} (vs); elemental analysis, found C = 53.9, H = 4.1, N = 2.1, calc. for $C_{56}H_{52}N_2P_4WO_2BF_5$, C = 53.2, H = 4.0, N = 2.3.

trans-Bis[1,2-bis(diphenylphosphino)ethane](dicarbonyl)-tungsten (0). $[W(CO)_2(dppe)_2]$
(Complex XXXVIII)

$[W(N_2)_2(dppe)_2]$(1.04g, 1 mmol) was dissolved in thf (50 cm³) and CO bubbled through the solution with stirring. The solution was irradiated with two 150W tungsten filament lamps and the bubbling continued for five hours. The white precipitate was filtered off, and diethyl ether added to the filtrate to precipitate a yellow powder. This was filtered off, washed with diethyl ether dried and recrystallised from dichloromethane/diethyl ether to give a yellow solid. Yield = 0.68g 64%; m.p. = >300°C; i.r. spectrum (nujol) ν(C=O) 1850, 1780 cm^{-1} (s); (thf solution) ν(C=O) 1860, 1795 cm^{-1} (s).

B. KINETIC STUDIES

INSTRUMENTATION

Kinetic measurements were made using an Applied Photophysics Stopped-Flow Apparatus, Applied Photophysics Photometric Control Unit and a Telequipment DM 64 oscilloscope. Absorbance measurements were made using a Pye-Unicam SP600 spectrophotometer.

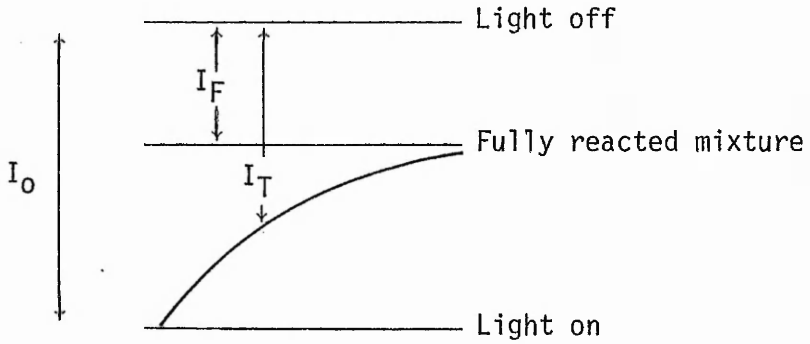
SOLVENT AND REAGENT PRETREATMENTS

$[WBr(N_2H_2)(dppe)_2]^+Br^-$ and 1,1-dichloro-2,2-dicyanoethene were prepared and purified as described in Section A. Commercial "Analar" triethylamine was used without further purification.

Dichloromethane was used as the solvent for all measurements. This was treated with K_2CO_3, refluxed over P_2O_5 and distilled immediately prior to use. This ensured any HCl present in the CH_2Cl_2 was removed and that the water content of the solvent was reduced to a minimum.

All solutions were used within one hour of their preparation, and freshly prepared for each kinetic run. The stopped-flow instrument contained two storage and delivery syringes, syringe 1 contained a dichloromethane solution of the base and syringe 2 contained a dichloromethane solution of the hydrazido(2-) complex and the alkene (which do not react in the absence of base).

The formation of the product was monitored at 415 nm, and traces of the following type were obtained on the oscilloscope;



where I_F = light transmitted by fully reacted solution

I_T = light transmitted by reacting solution

I_o = light transmitted before any product is formed.

The value for I_o was found from the absorbance of the reaction mixture and I_F using the equation;

$$A_{415} \times 2 = \log_{10} (I_o/I_F)$$

$$\therefore I_o = I_F \, [\text{antilog } (2 \times A_{415})]$$

The absorbance measure on the Pye Unicam SP600 is mulptiplied by a factor of 2 since the cells for absorption measurements have 1 cm cells, and the stopped flow apparatus has an optical pathlength of 2 cm. From the above trace, the concentration of product at time t, Cp^t, was calculated from the equation

$$Cp^t = \frac{1}{2\varepsilon} \cdot \left(\log_{10} I_o/I_T\right)$$

where ε = molar extinction coefficient.

From a plot of Cp^t against t, the initial rate of the reaction may be obtained by drawing a tangent to the curve at t = o, the slope of the tangent being equal to the initial rate (mol s^{-1}). From this and other measurements, the order and rate of the reaction may be obtained by the Initial Rate method, as indicated in the Results and Discussion section.

The results for the kinetic runs are summarised below:

$$[WBr(N_2H_2)(dppe)_2]^+Br^- + (CN)_2C:C(Cl)_2 + Et_3N \xrightarrow{CH_2Cl_2} [WBr(N_2C(Cl):C(CN)_2)(dppe)_2] + [Et_3NH]^+Br^-$$

Reagent	Molar Ratio Hydrazido(2-):Alkene:Base	Order of Reaction, n	Rate Constant, K
$[WBr(N_2H_2)(dppe)_2]^+Br^-$	1 : 1 : 100	1	1.6×10^5
Alkene	1 : 1 : 100	1	1.9×10^5
Base	1 : 1 : 100	0	1.0×10^5
Base	1 : 1 : 10	1	9.2×10^6

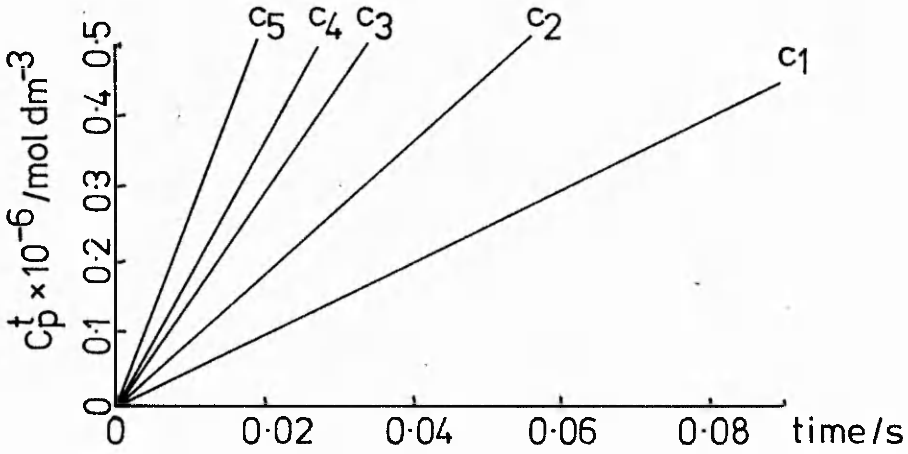
The results for each run are tabulated in tables 5 to 8.

Table 5

Determination of the order of reaction with respect to $[WBr(N_2H_2)(dppe)_2]^+ Br^-$

Concentration of alkene = 1.25×10^{-5} mol dm^{-3}

Concentration of base = 7.0×10^{-2} mol dm^{-3}



log [complex]	log Initial Rate	log k	k / 10 ^{5}
-5.602	-5.301	5.204	1.6
-5.301	-5.036	5.163	1.5
-5.125	-4.821	5.207	1.6
-5.000	-4.735	5.168	1.5
-4.903	-4.596	5.210	1.6

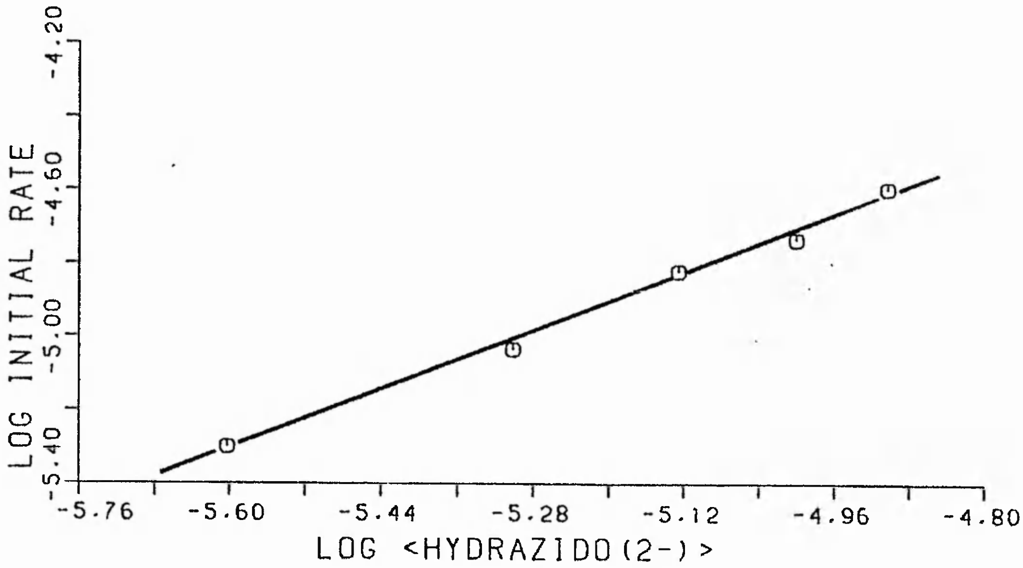
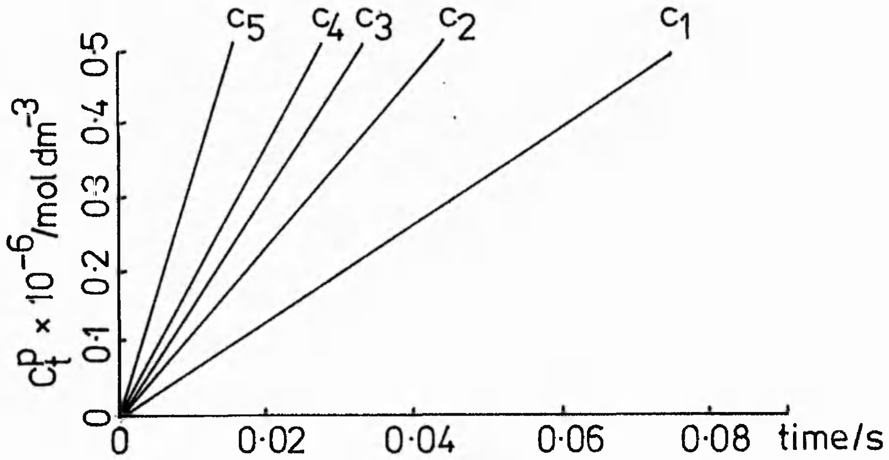


Table 6

Determination of the order of reaction with respect to 1,1-dichloro-2,2-dicyanoethene

Concentration of $[WBr(N_2H_2)(dppe)_2]^+ Br^-$ = 1.25×10^{-5} mol dm^{-3}

Concentration of base = 7.0×10^{-2} mol dm^{-3}



log [alkene]	log Initial Rate	log k	k / 10^5
-5.602	-5.177	5.328	2.1
-5.301	-4.914	5.290	2.0
-5.125	-4.799	5.229	1.7
-5.000	-4.730	5.173	1.5
-4.903	-4.493	5.313	2.1

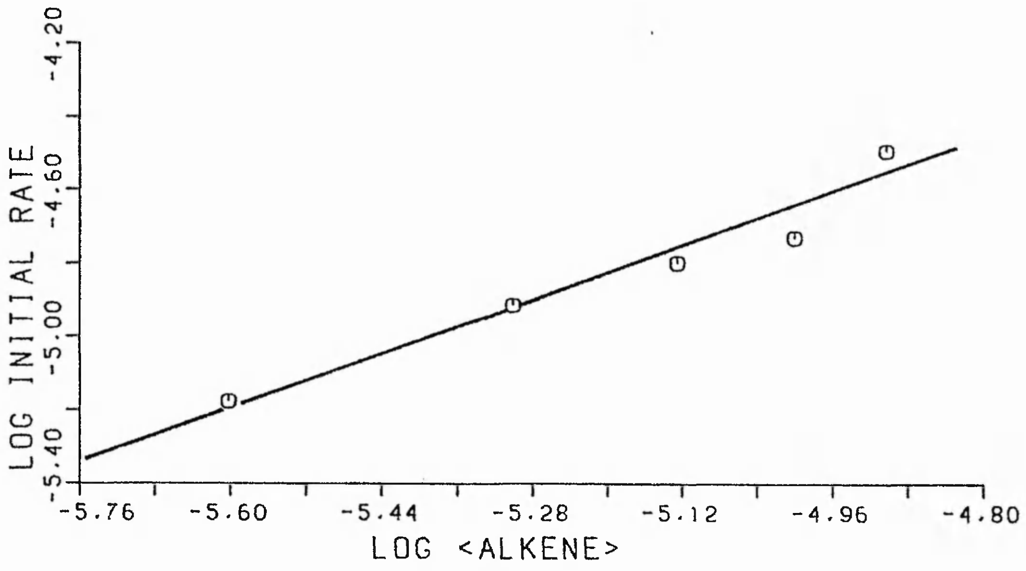
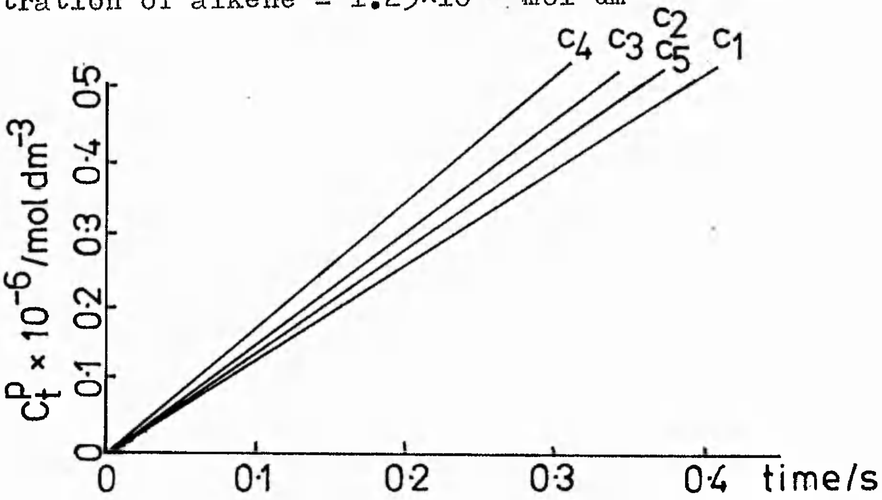


Table 7

Determination of the order of reaction with respect to base in high concentration

Concentration of $[WBr(N_2H_2)(dppe)_2]^+ Br^- = 1.25\times10^{-5}$ mol dm^{-3}

Concentration of alkene = 1.25×10^{-5} mol dm^{-3}



log [base]	log Initial Rate	log k	k / 10^5
-1.460	-4.84	4.966	0.9
-1.158	-4.82	4.986	1.0
-0.983	-4.88	4.926	0.8
-0.857	-4.75	5.056	1.1
-0.761	-4.82	4.986	1.0

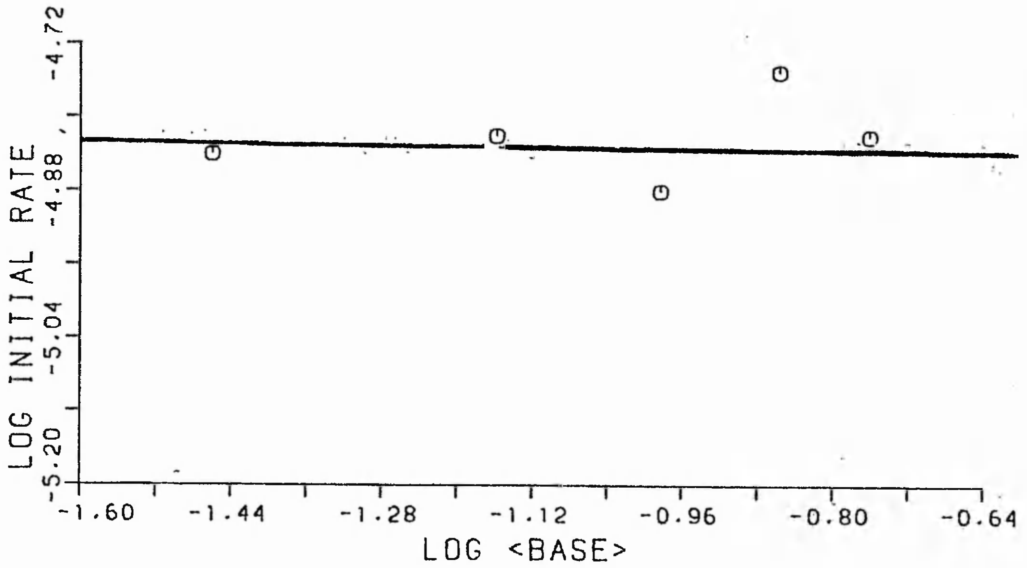
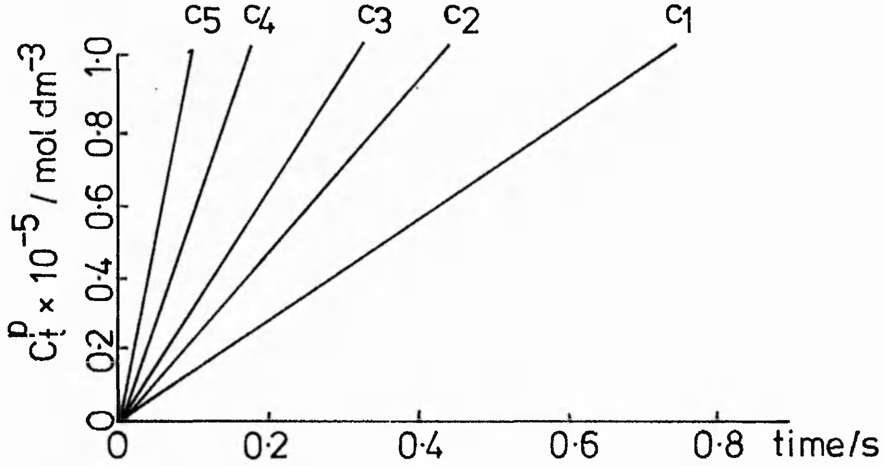


Table 8

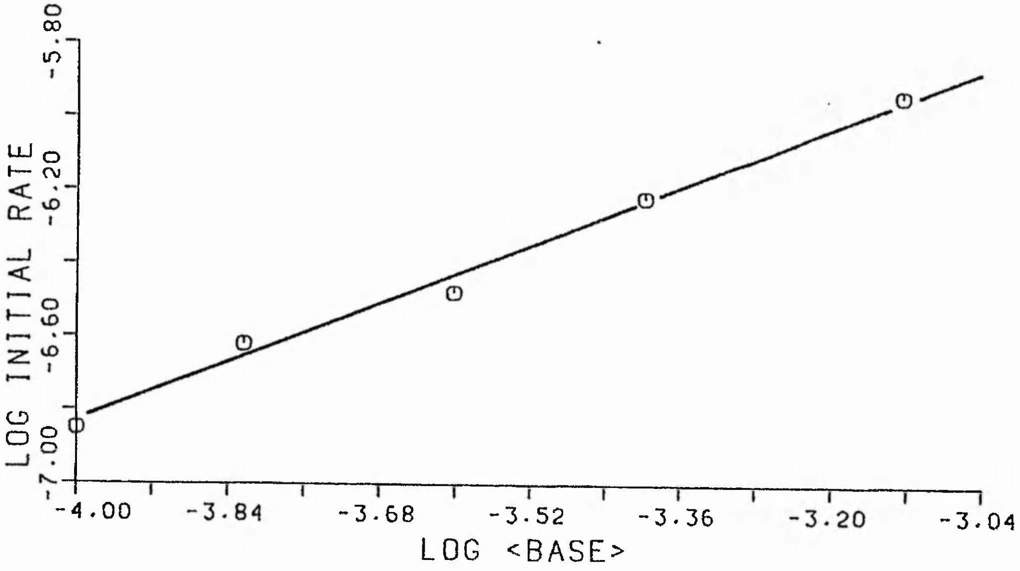
Determination of the order of reaction with respect to base in near stoichiometric concentration

Concentration of $[WBr(N_2H_2)(dppe)_2]^+ Br^-$ = 1.25×10^{-5} mol dm^{-3}

Concentration of alkene = 1.25×10^{-5} mol dm^{-3}



log [base]	log Initial Rate	log k	k / 10^6
-4.000	-6.851	6.955	9.0
-3.824	-6.620	7.010	10.2
-3.602	-6.480	6.928	8.5
-3.398	-6.220	6.984	9.6
-3.125	-5.939	6.992	9.8



C. ELECTROCHEMICAL STUDIES

(1) INSTRUMENTATION

Electrochemical measurements were made using E.E. and G. Princeton Applied Research Model 157 and Model 174A electrochemical analysers, an E.E. and G. Princeton Applied Research Model 363 potentiostat, an E.E. and G. Princeton Applied Research 303 suspended/dropping mercury electrode system and a Farnell X-Y recorder.

Cyclic voltammetry with a suspended mercury drop electrode and controlled potential electrolysis with a mercury pool cathode were carried out in single compartment cells. The counter electrode was a platinum wire. All potentials are referred to the silver/silver chloride reference electrode.

The organic products were identified by gas-liquid chromatography using a Perkin Elmer F33 instrument with a Hewlett Packard 3390A integrator. The column used was a 2m x 3mm diameter stainless steel, 2½% O.V. 17 on Chromosorb G., D.M.C.S. 80-100 mesh at an oven temperature of 295°C. Gas flow rates were for N_2 : 25 cm^3 min^{-1}, for H_2 : 25 cm^3 min^{-1} and for Air : 28 cm^3 min^{-1}. Confirmation of the identity of the organic product from the controlled potential electrolysis of $[WF(N_2HCH{:}C(CN)_2)(dppe)_2]^+BF_4^-$ in thf under dinitrogen was also obtained by i.r. and mass spectrometry of the isolated material.

(2) SOLVENT AND REAGENT PRETREATMENTS

Thf and methanol were dried and distilled as described in section A.2.

The supporting electrolyte used in all electrochemical measurements was tetrabutylammonium tetrafluoroborate, prepared from tetrabutylammonium bromide and recrystallised from ethyl acetate-pentane by the method of House et. al. (116). This was used in concentrations of 0.1-0.2 mol dm^{-3}. All measurements were made on degassed solutions under a dinitrogen or carbon monoxide atmosphere, as indicated.

The concentration of the HBF_4 used in the protonation reactions was determined by titration with standard sodium hydroxide solutions. Solutions of the dicyanovinylhydrazido(2-) tungsten complexes were prepared by adding either a stoichiometric or slight molar excess quantity of acid to a solution of the appropriate dicyanovinyldiazenido tungsten complex in either thf or methanol.

A cyclic voltammogram was recorded using a solution of the supporting electrolyte only, prior to any other measurements, to ensure that the supporting electrolyte was electrochemically pure.

(3) CYCLIC VOLTAMMETRY

The current-potential characteristics of tungsten dicyanovinyl diazenido/hydrazido(2-) complexes are presented in table 9 (solvent : thf) and table 10 (solvent : methanol). All potentials are referred to the silver/silver chloride reference electrode, at which trans[$W(N_2)_2(dppe)_2$] undergoes a reversible one electron oxidation at -0.11V (-0.15V versus the saturated calomel electrode (36)), in thf under dinitrogen (figure 27). The Ep from the cyclic voltammogram of aminocyanopyrazole is included for comparison.

A typical cyclic voltammogram for the dicyanovinyldiazenido-

Table 9

Current-potential characteristics for the reduction of tungsten diazenido/hydrazido(2-)-diazoalkene complexes in thf under dinitrogen

Complex	Ep^1/V	$\Delta Ep^1/mV$[a]	ip^{red}/ip^{ox}	n[b]	Ep^2/V[c]
$[WF(N_2CH{:}C(CN)_2)(dppe)_2]$	-0.41	170	0.9±0.1		n.o.
$[WF(N_2HCH{:}C(CN)_2(dppe)_2]^+BF_4^-$	-0.32	110	0.2	4	-0.75
$[WF(N_2CCl{:}C(CN)_2)(dppe)_2]$	-0.40	180	0.9		n.o.
$[WF(N_2HCCl{:}C(CN)_2)(dppe)_2]^+BF_4^-$	-0.33	100	0.2		-0.75
$[WBr(N_2CH{:}C(CN)_2)(dppe)_2]$	-0.42	160	1.0		n.o.
$[WBr(N_2HCH{:}C(CN)_2)(dppe)_2]^+BF_4^-$	-0.32	120	0.3	4	-0.73
$[WBr(N_2CCl{:}C(CN)_2)(dppe)_2]$	-0.41	170	0.9		n.o.
$[WBr(N_2HCCl{:}C(CN)_2(dppe)_2]^+BF_4^-$	-0.33	130	0.4		-0.76
$[WBr(N_2CH_3CH{:}C(CN)_2(dppe)_2]^+PF_6^-$	-0.38	200	1.0	4	-0.80, -0.98
Aminocyanopyrazole	Ep = -0.77V, irreversible				

[a] $\Delta Ep^1 = |Ep^1red - Ep^1ox|$, [b] obtained from controlled potential electrolysis, [c] n.o. = not observed

Table 10

Current-potential characteristics for the reduction of tungsten diazenido/hydrazido(2-)-dicyanoalkene complexes in methanol under dinitrogen

Complex	Ep^1/V	ΔEp^1/mV	ip^{red}/ip^{ox}	n
$[WF(N_2CH:C(CN)_2)(dppe)_2]$	-0.58	irreversible	-	-
$[WF(N_2HCH:C(CN)_2)(dppe)_2]^+BF_4^-$	-0.16	150	1.0	2

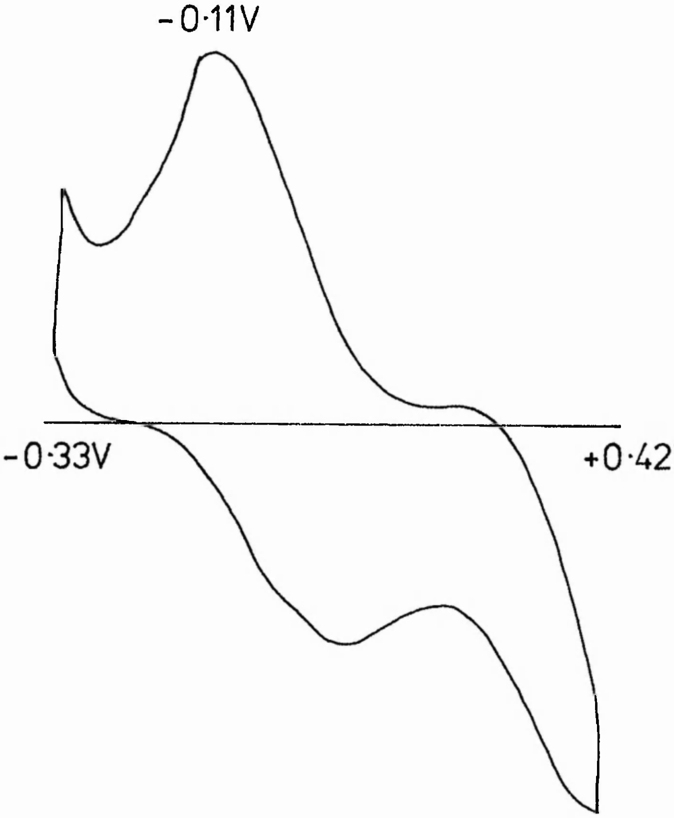
tungsten complex is given in figure 29 and for the hydrazido(2-) analogue in figure 30. The cyclic voltammograms for other dicyanovinyl tungsten complexes are analogous.

(4) CONTROLLED POTENTIAL ELECTROLYSIS

Solutions of $[WF(N_2HCH:C(CN)_2(dppe)_2]^+BF_4^-$ were reduced at a mercury pool cathode under dinitrogen or carbon monoxide atmospheres. Solvents used were thf or methanol as indicated.

Electrolyses were carried out at a potential 100 mV more negative than Ep^{red} (Ep^{red} = peak reduction potential) for the complex. The decrease in cell current with time was monitored, and plots of cell current, i/mA, against charge passed, $q/Fmol^{-1}$, were thus obtained. The plots for the controlled potential electrolysis of $[WF(N_2HCH:C(CN)_2$-$(dppe)_2]^+BF_4^-$ in thf (number of moles of complex used : 3.5×10^{-4}) and methanol (number of moles of complex used = 1.7×10^{-4}) under dinitrogen are given in figures 35 and 37 respectively. The electrolysis was also carried out in thf under carbon monoxide. The cyclic voltammogram for the oxidation of the catholyte is given in figure 28, and the cyclic voltammogram for the oxidation of cis$[W(CO)_2(dppe)_2]$ is given in figure 36. The plot for the controlled potential electrolysis of $[WBr(N_2CH_3CH$:$C(CN)_2)(dppe)_2]^+PF_6^-$ in thf under dinitrogen (number of moles of complex used : 1.5×10^{-4} is given in figure 36.

trans[$W(N_2)_2(dppe)_2$]

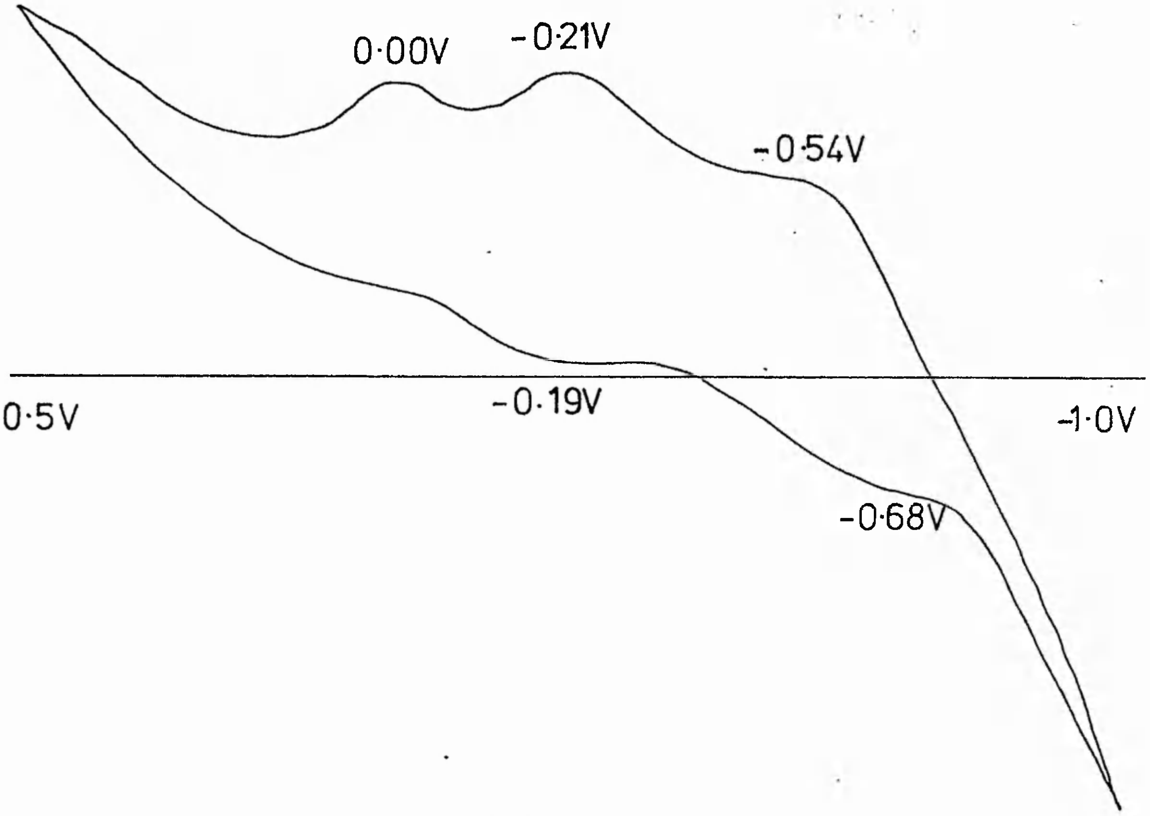


Scan rate = 200 mVsec^{-1}

Solvent = thf, N_2

Figure 27

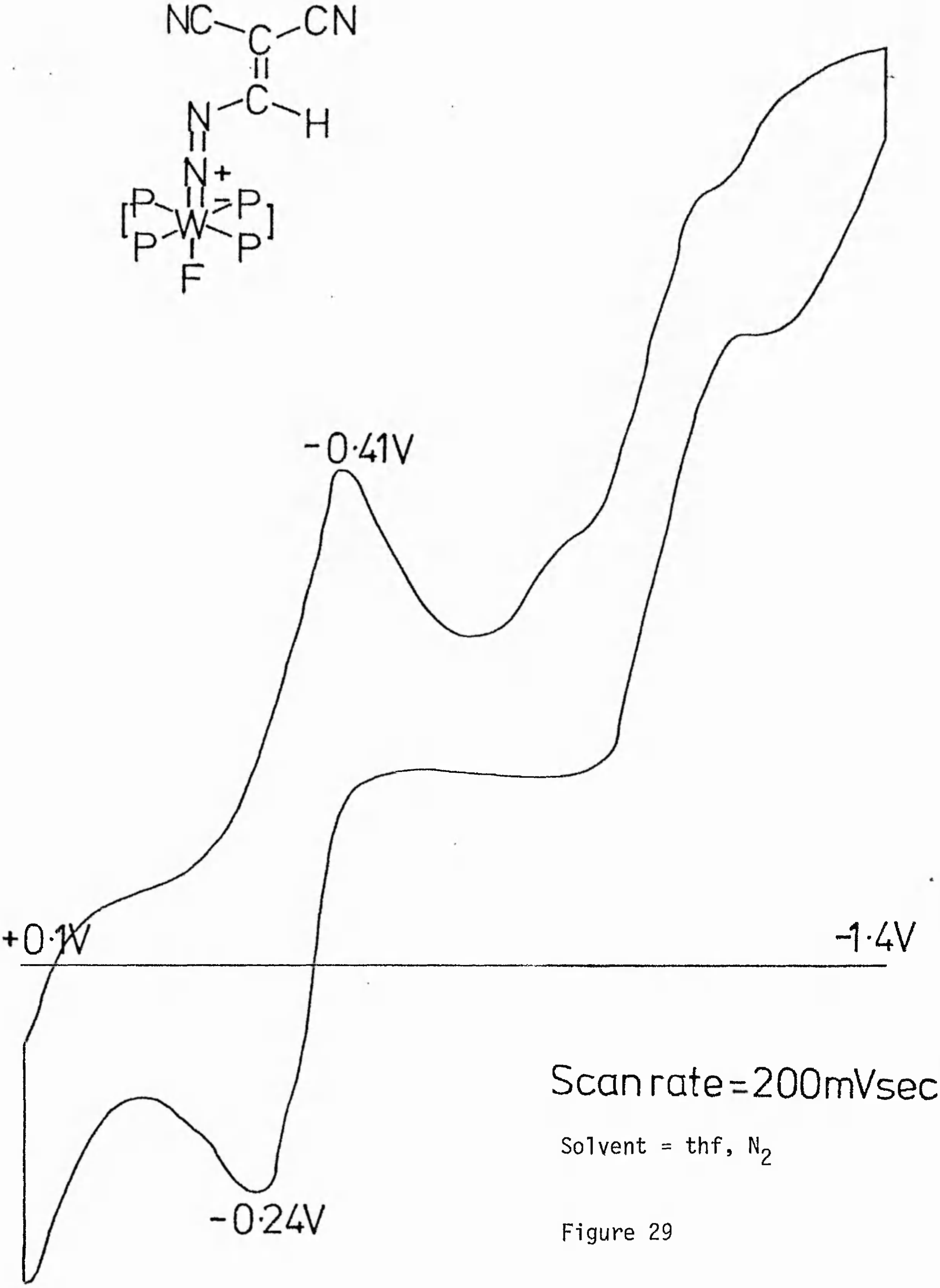
cis[W(CO)$_2$(dppe)$_2$]



Scan rate = 200 mVsec^{-1}

Solvent = thf, N$_2$

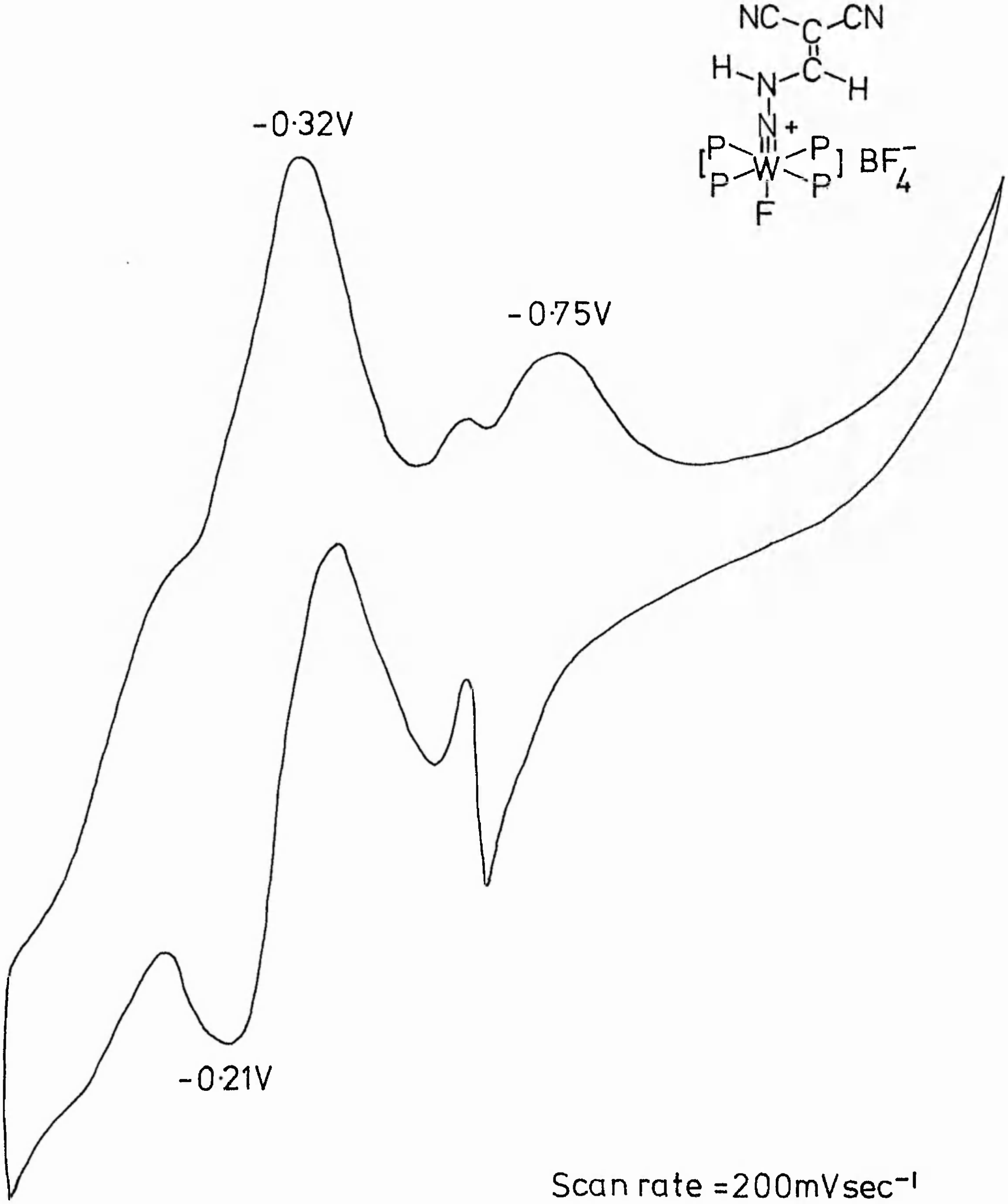
Figure 28



Scan rate = 200mVsec^{-1}

Solvent = thf, N_2

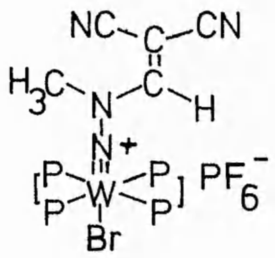
Figure 29

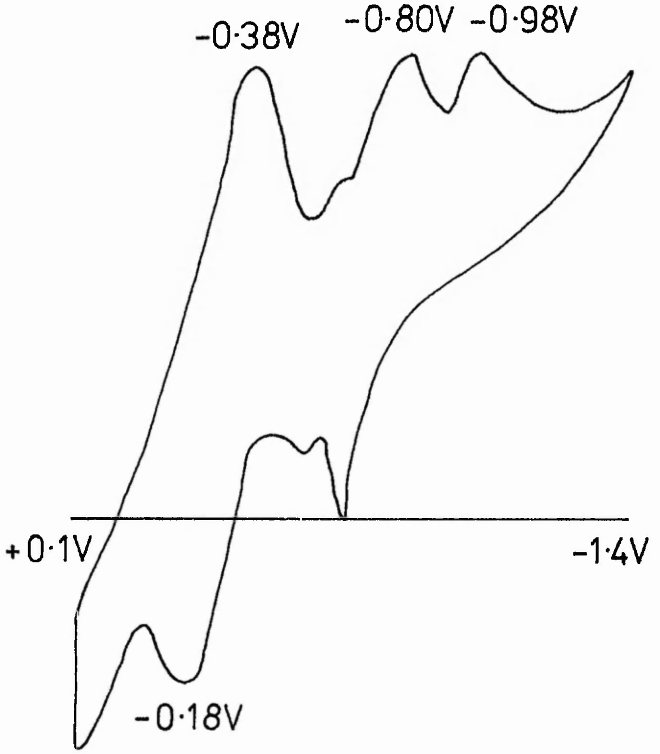


Scan rate =200mVsec^{-1}

Solvent = thf, N$_2$

Figure 30

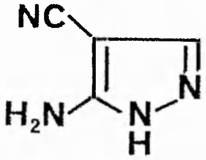


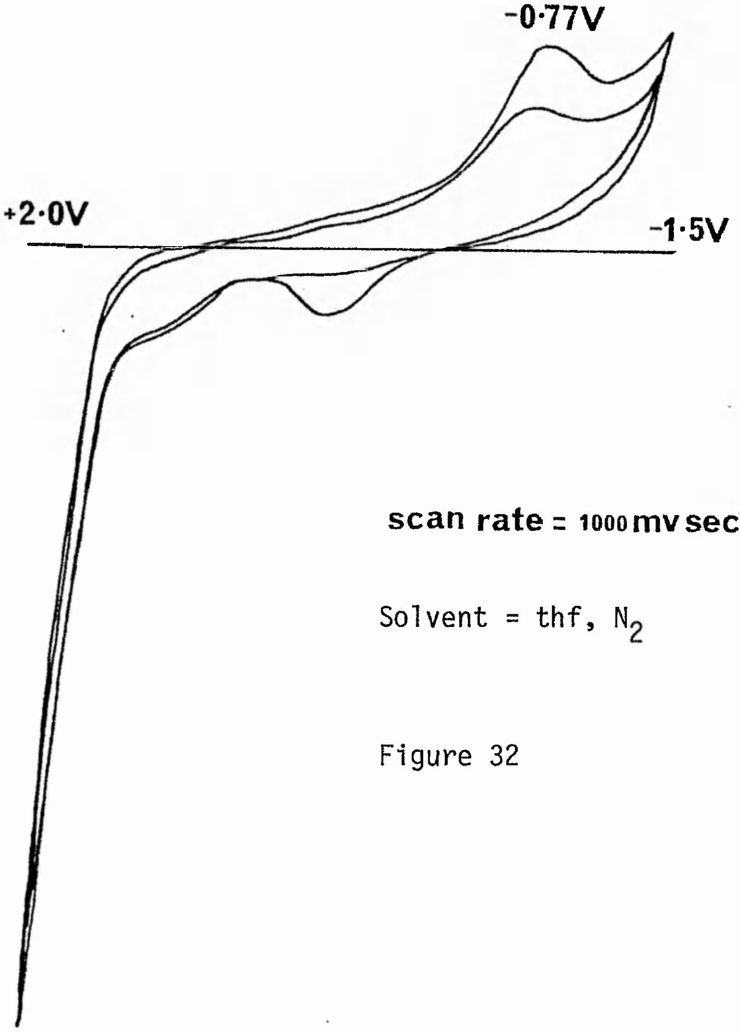


Scan rate = 200 mV sec^{-1}

Solvent = thf, N_2

Figure 31

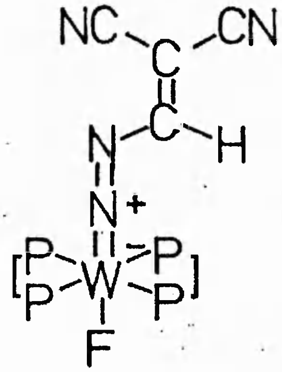


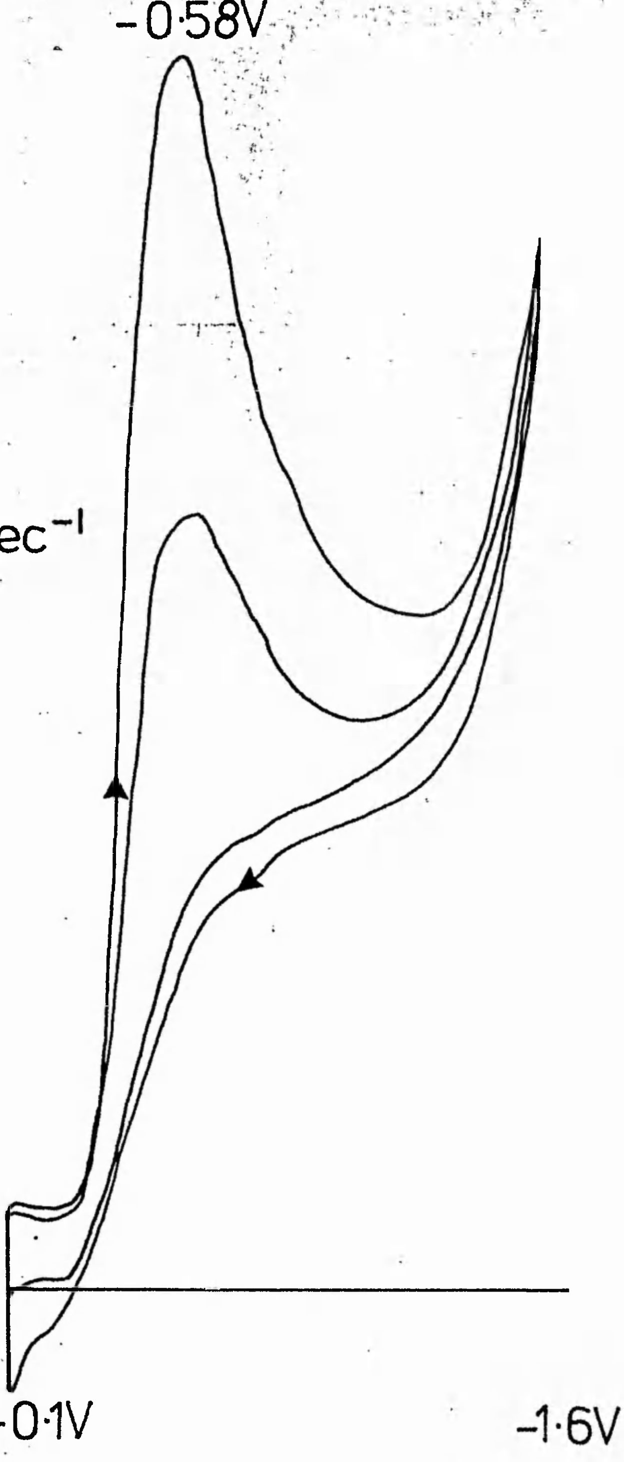


scan rate = 1000 mv sec^{-1}

Solvent = thf, N_2

Figure 32

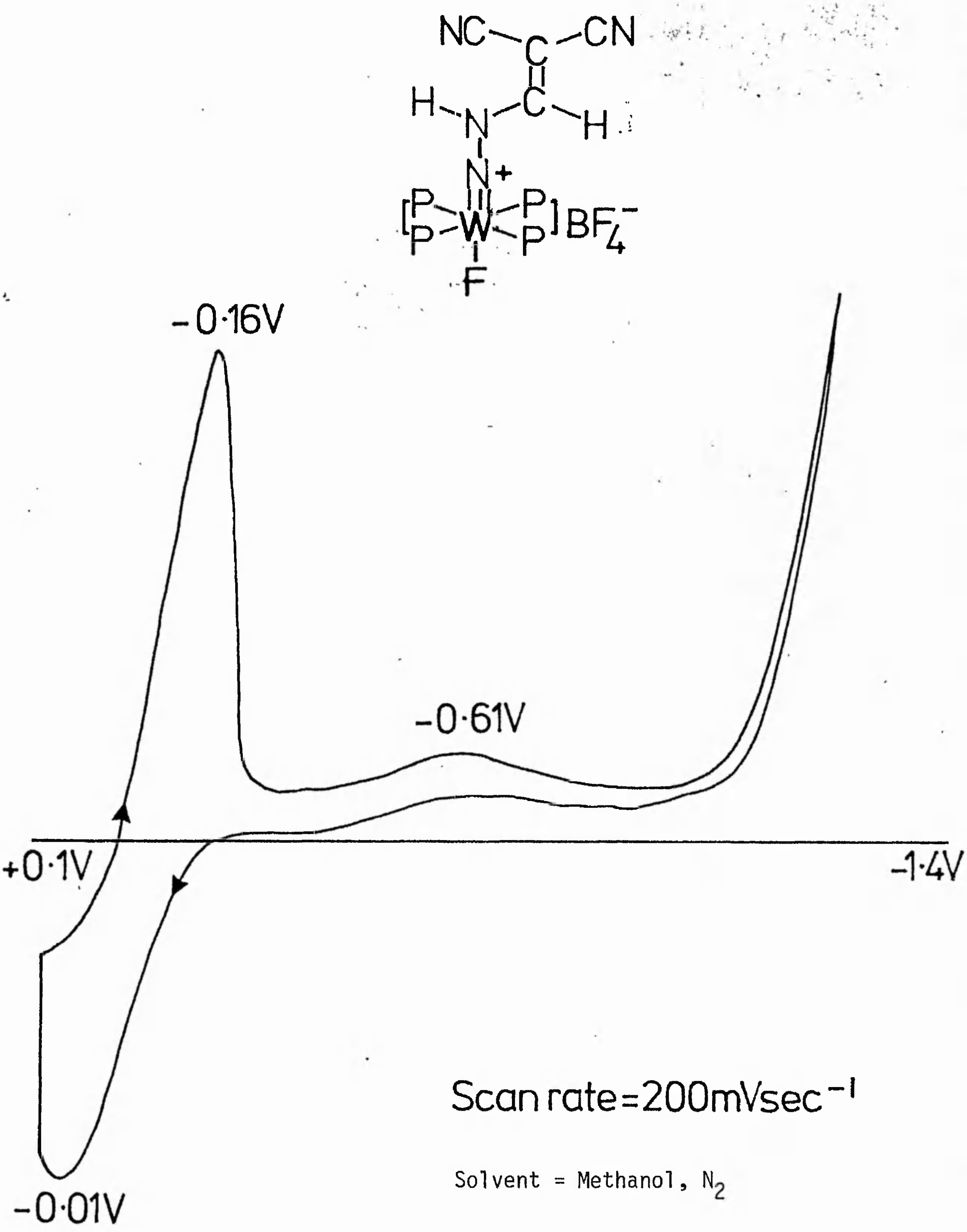




Scan rate = 200mVsec^{-1}

Solvent = Methanol, N_2

Figure 33

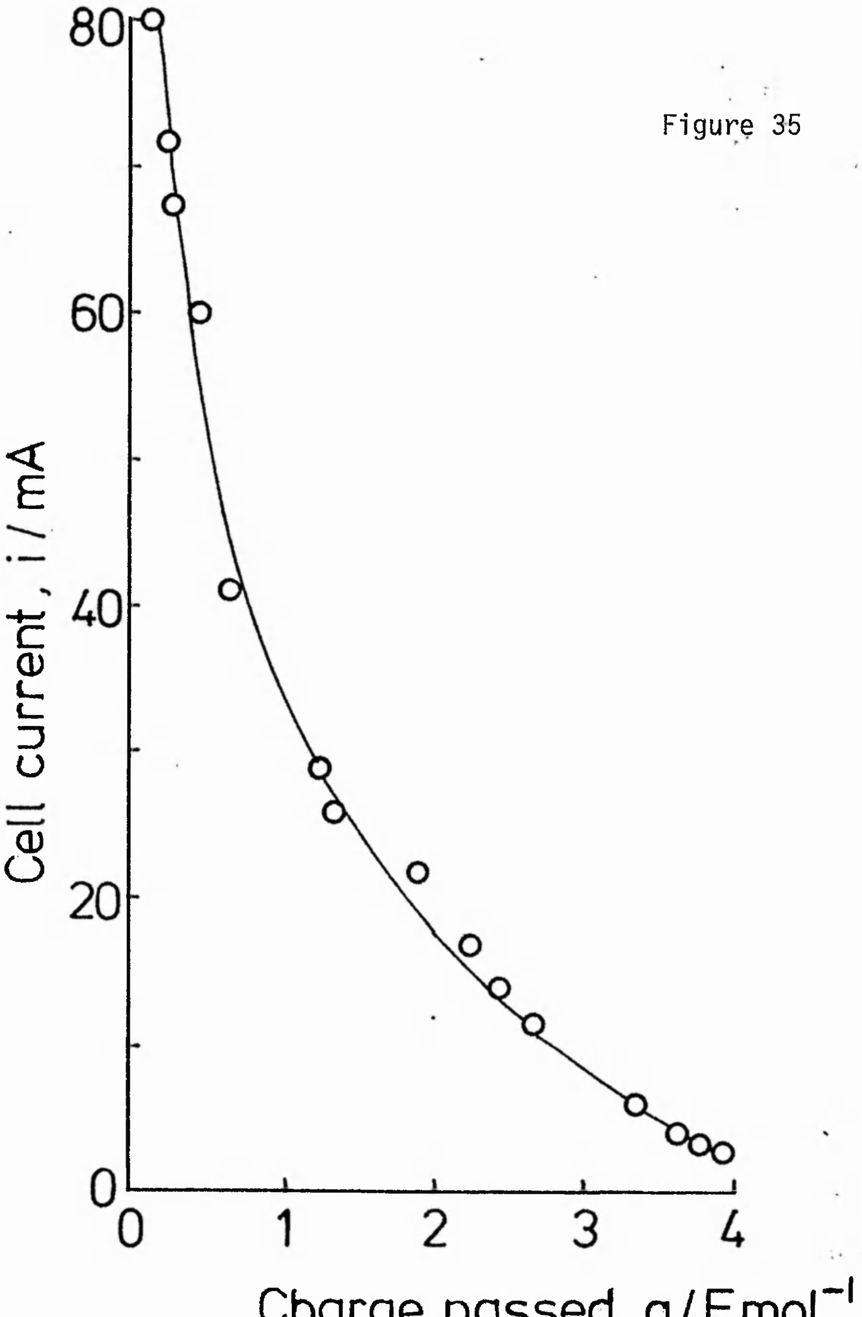


Solvent = Methanol, N_2

Figure 34

Controlled Potential Electrolysis of $[WF(N_2HCH:C(CN)_2(dppe)_2]^+BF_4^-$ in thf under dinitrogen

Figure 35



Controlled Potential Electrolysis of $[WBr(N_2CH_3CH{:}C(CN)_2(dppe)_2]^+PF_6^-$ in thf under dinitrogen

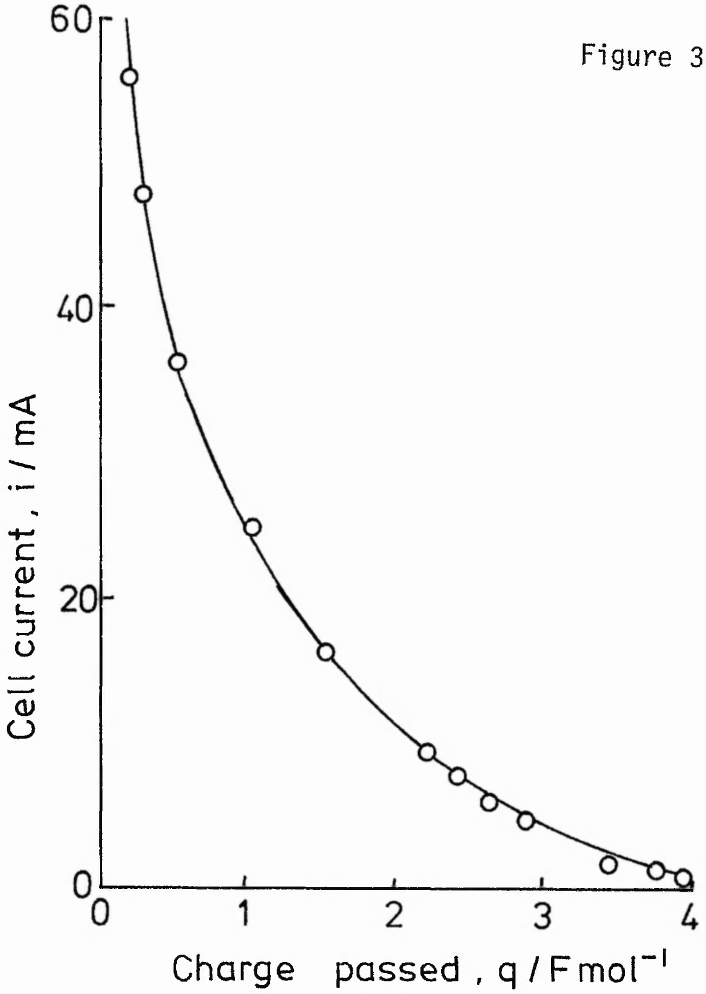


Figure 36

Controlled Potential Electrolysis of $[WF(N_2HCH:C(CN)_2)(dppe)_2]^+BF_4^-$ in methanol under dinitrogen

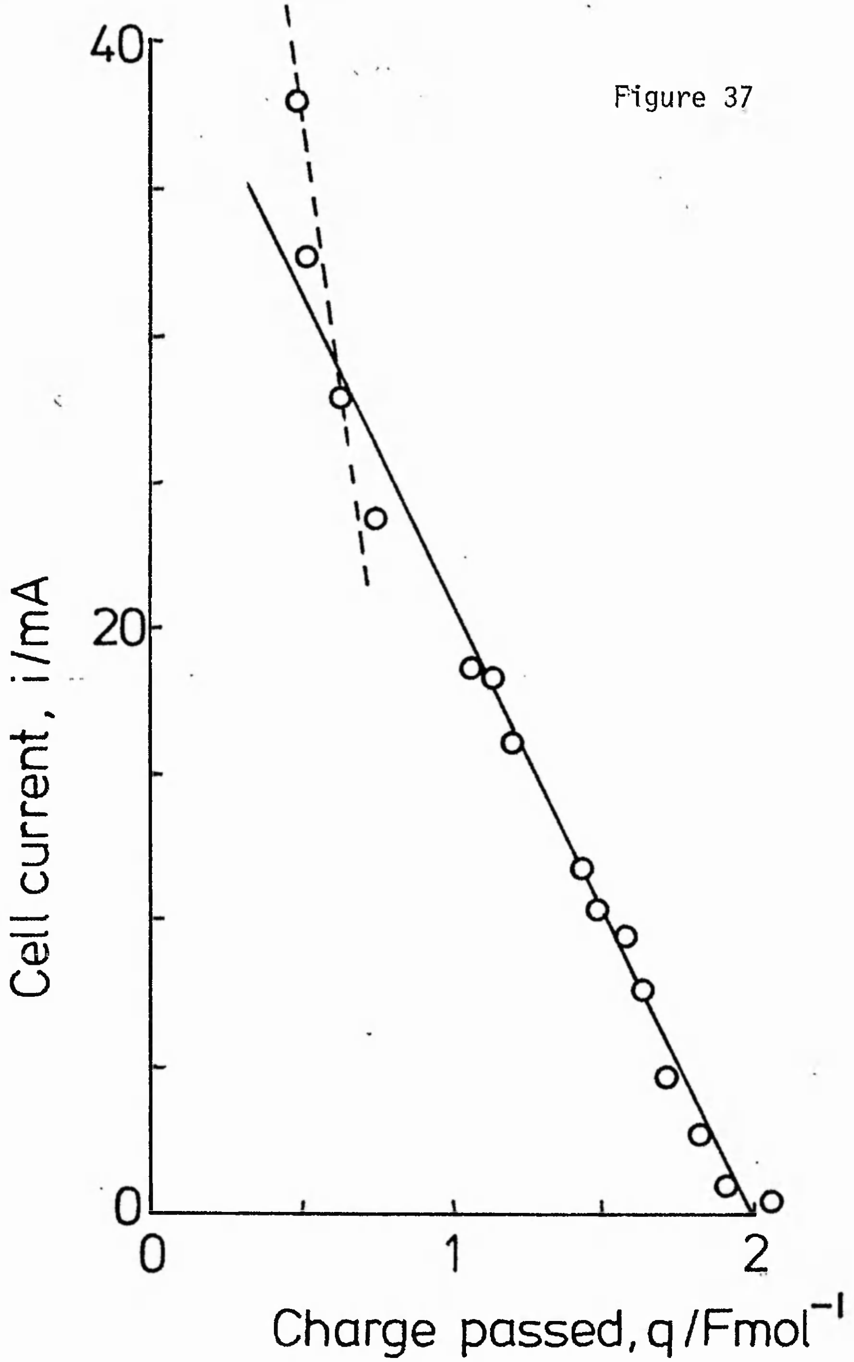
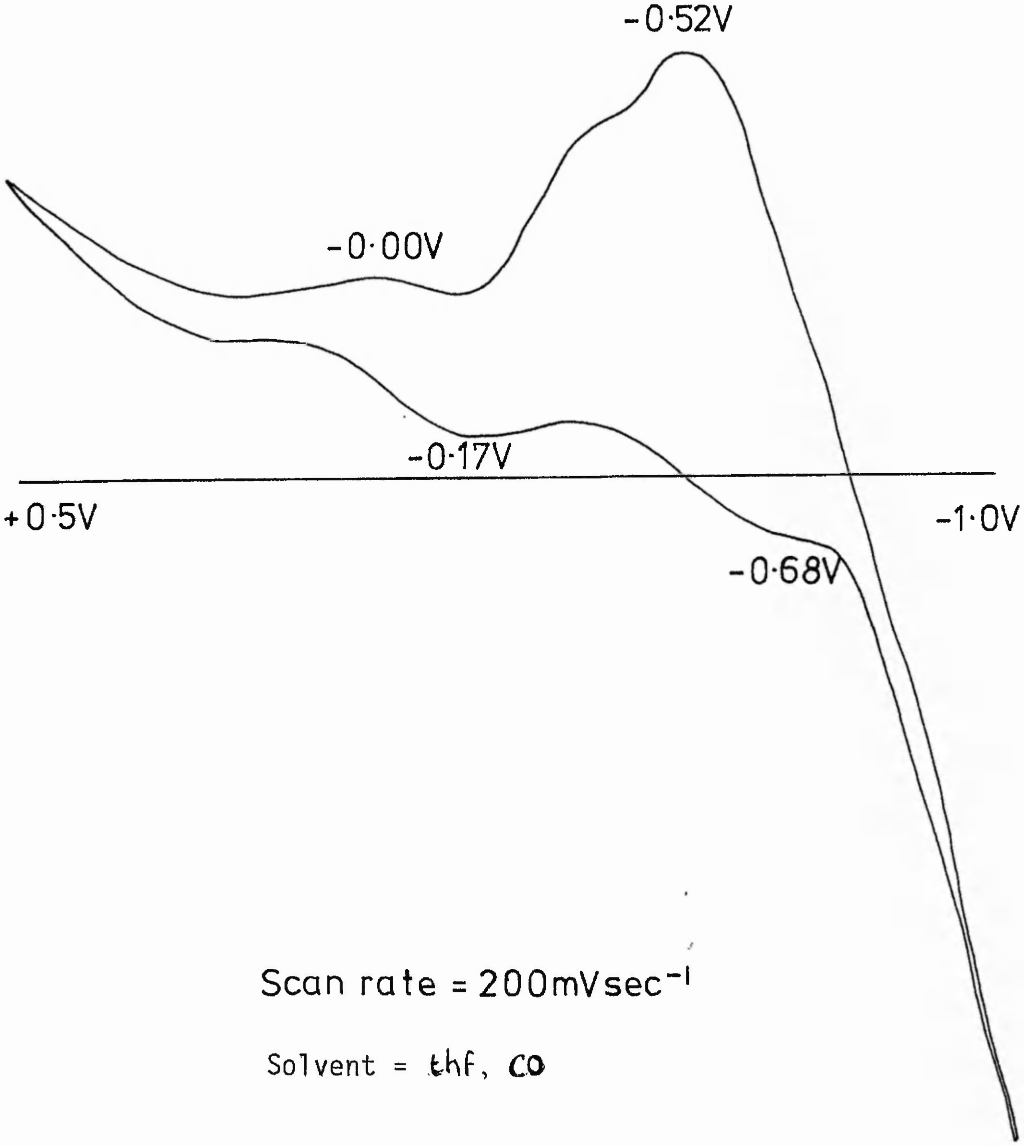


Figure 37

Cyclic voltammetry on catholyte from controlled potential electrolysis of $[WF(N_2HCH:C(CN)_2)(dppe)_2]^+BF_4^-$ under carbon monoxide in thf



Scan rate = 200mVsec^{-1}

Solvent = thf, CO

Figure 38

(5) GAS CHROMATOGRAPHIC IDENTIFICATION OF PRODUCTS FROM ELECTROCHEMICAL CLEAVAGE REACTIONS

Preparation of Aminocyanopyrazole

To hydrazine hydrochloride (0.69g, 10 mmol) dissolved in ethanol (50 cm^3) was added 1,1-dicyano-2-ethoxyethene (1.06g 10 mmol) with rapid stirring. The solution was refluxed for five hours, filtered and cooled. The solvent was removed *in vacuo*, and the residue dissolved in the minimum of hot water. This was quickly filtered and the product precipitated out as the solution cooled. Further cooling to 0°C and filtering gave the product as an orange-brown powder, which was washed with a little CH_2Cl_2 and dried *in vacuo*. Yield = 0.76g, 70%; m.p. = 174-175°C; i.r. spectrum (nujol mull) ν(N-H) 3420, 3340, 3150 cm^{-1} (s), ν(C≡N) 2140 cm^{-1} (s), ν(N-H) 1645 cm^{-1} (s), ν(C=C) 1570 cm^{-1} (s).

Under the chromatographic conditions described earlier, a sample of aminocyanopyrazole had a mean retention time of 34(±1) seconds (ten determinations).

Preparation of 5-amino-4-cyano-1-methylpyrazole

Prepared by the method of R. K. Robins et. al. (117). Yield = 80%; m.p. = 220-222°C. Under the chromatographic conditions described earlier, a sample of 5-amino-4-cyano-1-methylpyrazole had a mean retention time of 47(±2) seconds (ten determinations)

Examples of the chromatograms obtained for these two compounds, and from the catholytes of $[WF(N_2HCH{:}C(CN)_2)(dppe)_2]^+BF_4^-$ and $WBr(N_2CH_3CH{:}C(CN)_2)(dppe)_2]^+PF_6^-$ are given in figure 39.

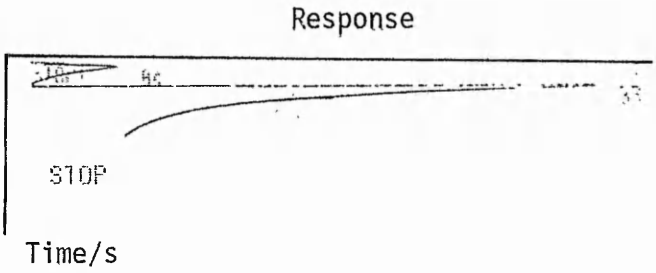
Analysis of the catholyte during controlled potential electrolysis

5µl samples of the catholyte were withdrawn during the electrochemical reduction and injected directly onto the chromatography column. Only peaks with retention times corresponding to aminocyanopyrazole and/or the supporting electrolyte were observed. The formation of aminocyanopyrazole was monitored by comparison of peak areas for the samples with a calibration graph of peak area plotted against solutions of authentic aminocyanopyrazole at known concentrations. The reduction of $WF(N_2HCH{:}C(CN)_2(dppe)_2]^+BF_4^-$ in thf under dinitrogen or carbon monoxide was complete after approximately two hours. No organic products were detected during the electrolysis of this complex in methanol under dinitrogen.

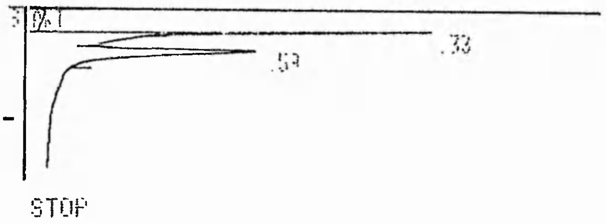
Analysis of catholyte after controlled potential electrolysis

After the complete reduction of $[WF(N_2HCH{:}C(CN)_2)(dppe)_2]^+BF_4^-$ in thf under dinitrogen (cell current fell to less than 5% original value, which corresponded to background current), the catholyte (50 cm³) was taken to dryness *in vacuo*, extracted into CH_2Cl_2 (10 cm³) and water (10 cm³). After vigorous shaking, the water layer was separated and the CH_2Cl_2 layer washed with further portions of water (3 x 10 cm³). The water washings were combined and diluted to 50 cm³ in a volumetric flask and analysed by chromatography as indicated.

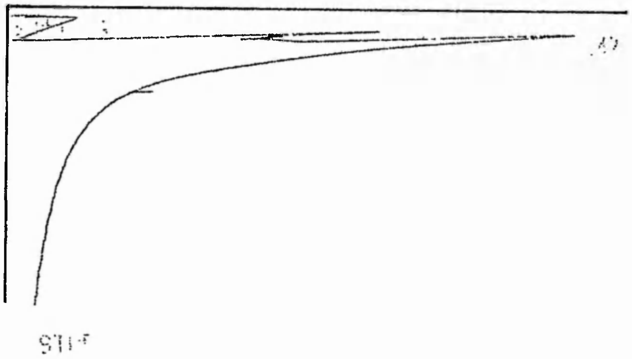
Aminocyanopyrazole



Catholyte from reduction of $[WF(N_2HCH:C(CN)_2)(dppe)_2]^+BF_4^-$



5-amino-4-cyanol-1-methyl pyrazole



Catholyte from reduction of $[WBr(N_2(CH_3)CH:C(CN)_2)(dppe)_2]^+PF_6^-$

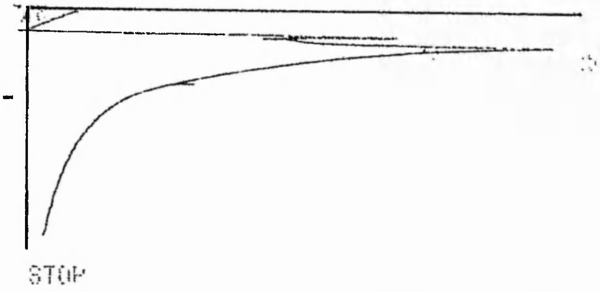


Figure 39

By this method, yields of 40-46% of aminocyanopyrazole were detected, based upon five electrochemical reductions.

A quantity of aminocyanopyrazole was isolated from the catholytes to enable characterisation of this material by i.r. spectroscopy and mass spectrometry. The i.r. spectrum compared favourably with the i.r. spectrum for an authentic sample of aminocyanopyrazole, and no bands assignable to a tetrabutylammonium salt impurity were found. The mass spectrum of the material had a molecular ion peak at 108, corresponding to the molecular weight of aminocyanopyrazole, and the major fragmentation process appeared to be loss of HCN. The sample again appeared to be quite pure and free from impurities, compared with a mass spectrum of an authentic sample. The spectra are given in figures 40 (sample from electrochemical reduction) and 41 (authentic sample).

The reduction of this complex in thf under CO produced aminocyanopyrazole in 29% and 33% yield, based upon two electrochemical reductions. Cyclic voltammetry of the catholyte indicated that cis-$[W(CO)_2(dppe)_2]$ was the metal containing product.

The reduction of $[WF(N_2HCH{:}C(CN)_2(dppe)_2]^+BF_4^-$ in methanol under dinitrogen gave no organic products, but a new dicyanovinylhydrazido(2-) complex was indicated by cyclic voltammetry.

The reduction of $[WBr(N_2CH_3CH{:}C(CN)_2(dppe)_2]^+PF_6^-$ in thf under dinitrogen gave an organic product, identified by gas-liquid chromatography, with a mean retention time of 45 seconds. This corresponds to the retention time for an authentic sample of 5-amino-4-cyano-1-methylpyrazole under identical conditions.

Figure 40

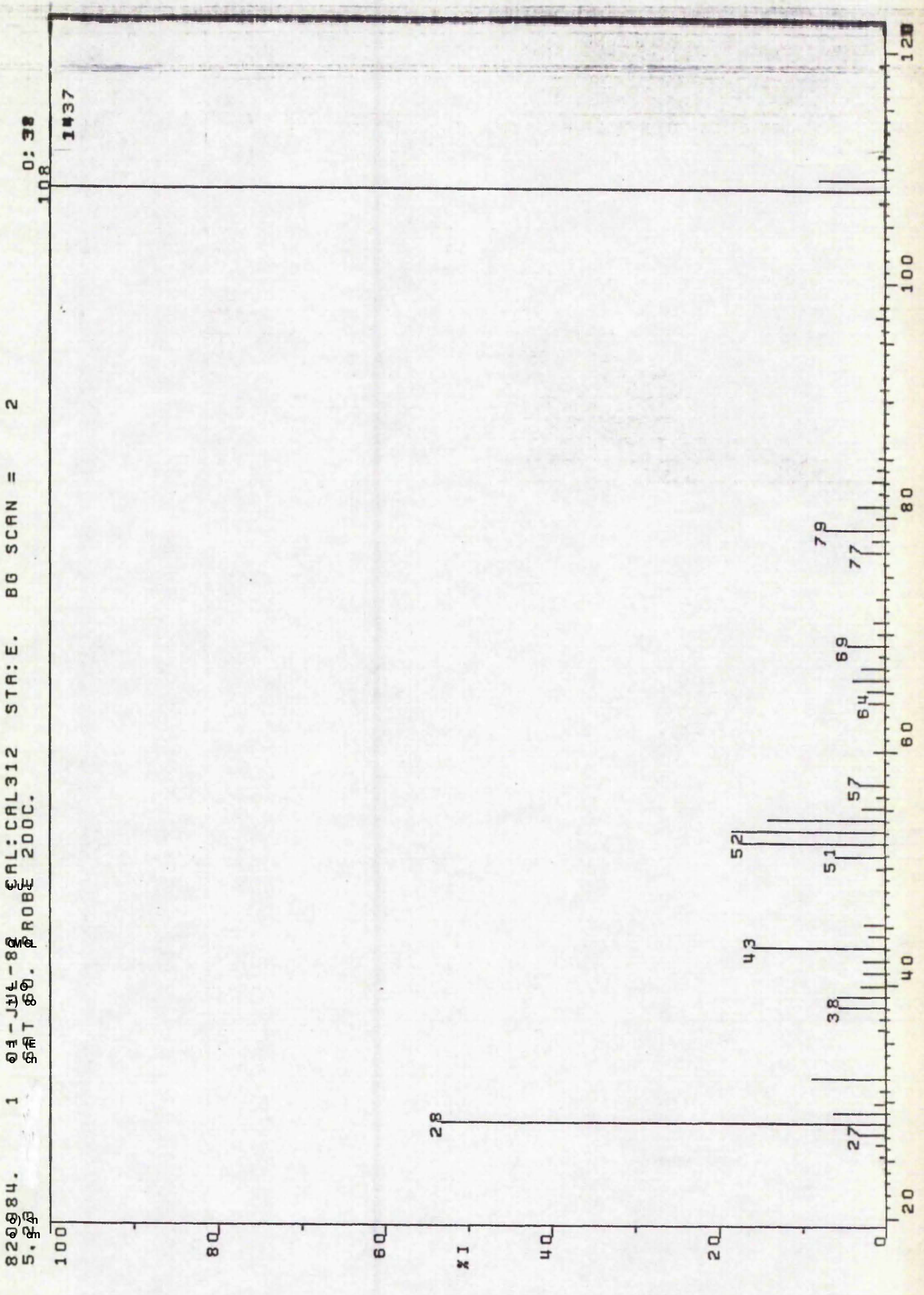
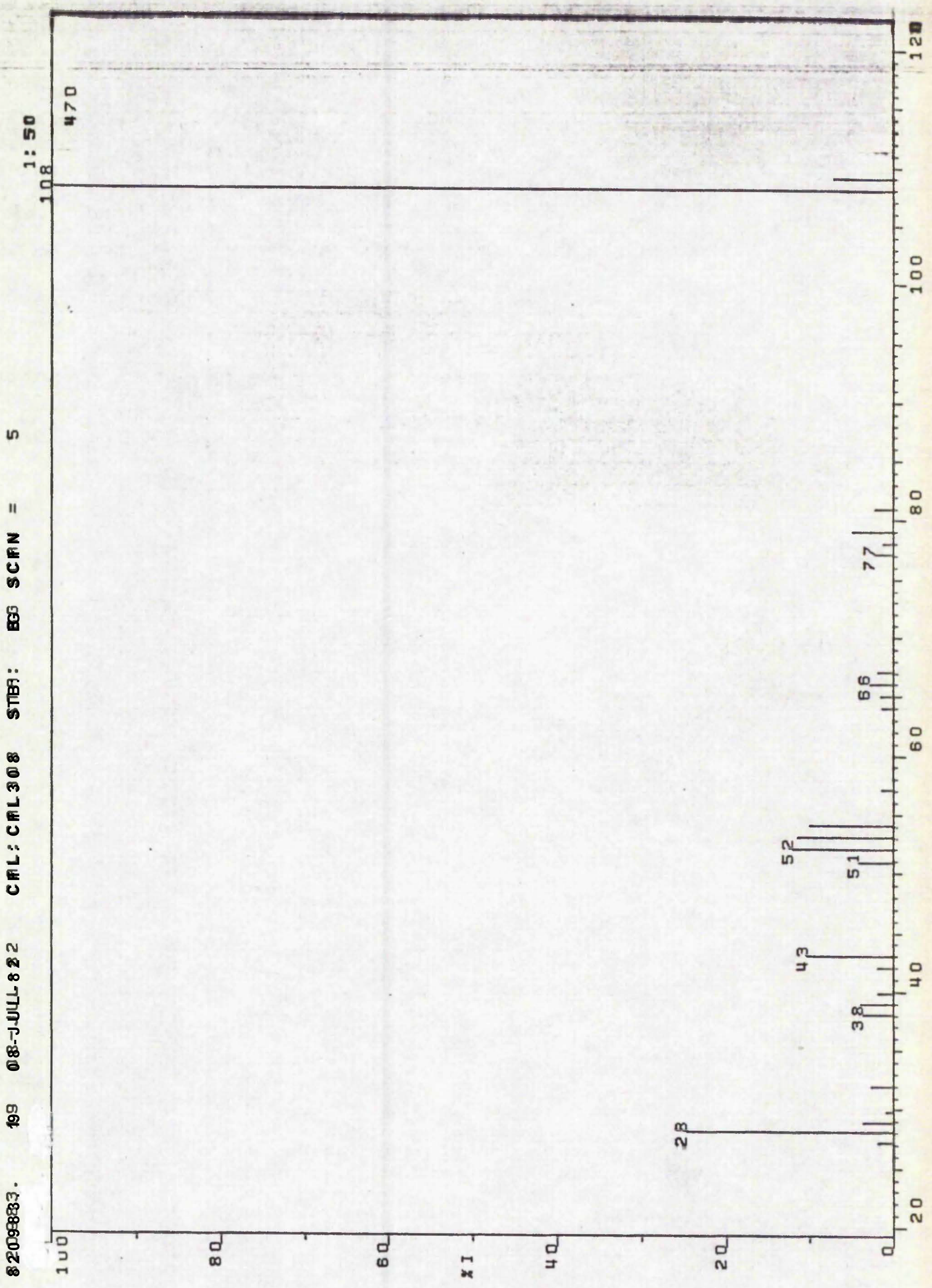

820384. 1 01-JUL-82 CAL:CAL312 STA:E. BG SCAN = 2 0:38
5.23 SAT 60. PROBE 200C. 1437
108
100
80
60
% I
40
20
0
28
27
38
43
51
52
57
64
69
77
79
20
40
60
80
100
120

Figure 41



820983. 199 08-JUL-82 CAL:CAL308 STB: BG SCAN = 5
1:50
470
108
77
66
52
51
43
38
28
20
40
60
80
100
120
0
20
40
60
80
100
%I

Attempts to isolate the metal products from these reactions were unsuccessful, owing to the presence of a large excess of tetrabutylammonium tetrafluoroborate and the similarity in solubilities of these two species. Cyclic voltammetry of the catholytes demonstrated the absence of trans[$W(N_2)_2$(dppe)]. However, the i.r. spectrum of the crude solid obtained from the CH_2Cl_2 solution of the catholyte from the reduction of [$WF(N_2HCH{:}C(CN)_2)$(dppe)$_2$]$^+BF_4^-$ (i.e. after the removal of aminocyanopyrazole) had weak bands at 3380 cm^{-1} and 3280 cm^{-1} assignable to the hydrazido(2-) complex [$WF(N_2H_2)$(dppe)$_2$]$^+BF_4^-$. Additional bands assignable to the phosphine ligands were also observed. It is possible that column chromatography could be used to separate the supporting electrolyte from the metal complex, although this was not investigated.

Attempts to produce a cyclic process based upon [$WF(N_2HCH{:}C(CN)_2)$(dppe)$_2$]$^+$ BF_4^-

A thf solution of the complex was reduced under dinitrogen as described. A 5µl sample of the catholyte was withdrawn and analysed by gas chromatography. To the remaining catholyte was added, with stirring, a molar equivalent quantity of Et_3N, and then a molar equivalent quantity of 1-chloro-2,2-dicyanoethene. The cell current rose immediately and the solution was again electrolysed as described. A sample of the catholyte was again withdrawn and analysed, and molar equivalent quantities of HBF_4, Et_3N and alkene were added sequentially, allowing a few minutes between addition of each component to ensure each stage of the reaction was complete. No current was passing through the catholyte during these addition processes. The reduction process was then repeated and the catholyte analysed. This sequence was repeated a further two times, so that the "cycle" should have turned four times. The yields of aminocyanopyrazole at the end of each cycle are given in table 11.

Table 11

Run 1

Cycle	% Yield of aminocyanopyrazole (± 1%)
1	41
2	49
3	51
4	53

Run 2

Cycle	% Yield of aminocyanopyrazole (± 1%)
1	46
2	53
3	55
4	55

No increase in cell current was observed until the alkene had been added to the catholyte, and in the absence of further addition of alkene, no further increase in the quantity of aminocyanopyrazole in solution was observed. During each reduction sequence, the catholyte was electrolysed until the cell current fell to a background level.

CHAPTER THREE

RESULTS AND DISCUSSION

A. PREPARATIVE STUDIES

(i) Synthesis of trans$[W(N_2)_2(dppe)_2]$ and $[Mo(N_2)_2(PPh_3)(triphos)]$

The current literature method for the preparation of trans$[W(N_2)_2(dppe)_2]$ (118) involves the following reaction sequence:

$$\begin{array}{l} [WCl_6] \\ \quad\downarrow \ \text{Zn, } CH_2Cl_2 \\ [WCl_4(PPh_3)_2] \\ \quad\downarrow \ \text{dppe, toluene, 70°C} \\ [WCl_4(dppe)] \\ \quad\downarrow \ \text{Mg, } N_2\text{, thf, dppe} \\ [W(N_2)_2(dppe)_2] \end{array}$$

Figure 42

with the isolation of each intermediate. This preparation may be carried out more conveniently in a "one-pot" synthesis, without the need for isolation of intermediates by the zinc-magnesium metal reduction of WCl_6 in the presence of dppe in thf under dinitrogen at room temperature. The reaction is complete within 36 hours and gives a high (ca. 70%) yield of product. The complex is a bright red crystalline material after recrystallisation from CH_2Cl_2/acetone, and appears to be very stable in air (no decomposition observed after several months) but it is sensitive to oxidation in solution. The ease of handling, were the major reasons for the use of this complex in the work described here. However, the advantages of stability, presumably arising from the presence of two five membered chelate rings on the complex, are counterbalanced by the disadvantage of the steric bulk of the phenyl groups on the phosphine ligands. This will be discussed in more detail, but during the work, it became obvious that an alternative, less sterically crowded dinitrogen complex would be of value. The recently-synthesised complex $[Mo(N_2)_2(PPh_3)(triphos)]$ (53) was investigated briefly, though initial attempts to prepare the tungsten analogue of this using WCl_6 or $[WCl_4\ (PPh)_2]$ with magnesium/zinc metal or sodium amalgam as reducing agents in the presence of stoichiometric quantities of triphenylphosphine and triphos in thf under dinitrogen did not produce the bis(dinitrogen) complex. A material, present in solution and identified by i.r. spectroscopy, had bands assignable to

$\nu(N{\equiv}N)$ at 2020 and 1955 cm^{-1}, but this could not be isolated in pure form. The molybdenum complex $[Mo(N_2)_2(PPh_3)(triphos)]$ was however prepared in low yield via the sodium amalgam reduction of $[MoCl_3(thf)_3]$ in the presence of triphenylphosphine and triphos in thf under dinitrogen. This material is moderately stable in thf solution under dinitrogen, but rapidly loses dinitrogen in the solid state. Both $[W(N_2)_2(dppe)_2]$ and $[Mo(N_2)_2(PPh_3)(triphos)]$ may be characterised by the $\nu(N{\equiv}N)$ bands in their infra red spectra, the former at 1956 cm^{-1} (s) and the latter at 1970 cm^{-1} (s). The remainder of the infra red spectrum in the range 1500-625 cm^{-1} is characteristic of the phosphine coligands in each case.

(ii) Reactions between trans$[W(N_2)_2(dppe)_2]$ and alkenes

As indicated in the Introduction, the reactivity of the bis-(dinitrogen) complexes is relatively limited. The only type of reaction previously observed between $[W(N_2)_2(dppe)_2]$ and alkenes was with alkenes capable of forming stable radical anions. Thus, the reaction between $[W(N_2)_2(dppe)_2]$ and TCNE produces the tungsten (I) complex $[W(N_2)_2(dppe)_2]^+[TCNE]^{\overline{\cdot}}$ (29). In this work it was found that another cyanoalkene capable of radical anion formation, TCNQ, produced a complex which analysed as $[W(N_2)_2(dppe)_2]^+[TCNQ]^{\overline{\cdot}}[TCNQ]_2$ (toluene). The infra red spectrum shows a shift in the band assigned to $\nu(N{\equiv}N)$ from 1956 cm^{-1} (s) for the tungsten (0) complex to 2005 cm^{-1} for the tungsten (I) complex. This is consistent with a reduction in the extent of electron donation from the metal d orbitals to the π^* orbital of the dinitrogen ligand, as would be expected from the increased positive charge on the metal. The bands assigned to $\nu(C{\equiv}N)$ at 2175 and 2140 cm^{-1} show a shift to lower frequencies, compared with free TCNQ consistent with a negative charge on the TCNQ molecule. The u.v. spectrum has peaks assignable to both neutral (398 nm) and anionic (398, 845 nm) TCNQ, the 398 nm band being a composite of both neutral and anionic TCNQ (119). The optimum yields of the product were obtained when 1 mole of $[W(N_2)_2(dppe)_2]$ were reacted with 3 moles of TCNQ. The material is moderately stable in air, but unstable in solution. This complex apparently represents the first example of a 1 : 1 : 2 (i.e. cation : anion : neutral ligand) TCNQ complex. Other types, e.g. 1 : 1, 1 : 2, 1 : 1 : 1 are fairly common (119). Attempts to grow single crystals of the material for X-ray analysis failed due to the instability of the material in solution. The organic electron acceptor TCQ, was found to react analogously to produce the complex $[W(N_2)_2(dppe)_2]^+TCQ^{\cdot}$ (toluene), identified by i.r. spectroscopy and elemental analysis. However, other organic electron acceptor molecules, benzoquinone and DDQ for example, did not react analogously. A comparison of the half-wave reduction potentials for these organic electron acceptor molecules indicate that the reduction potentials of those molecules which produce the tungsten (I) cation lie within a narrow range;

Organic Electron Acceptor	$E_{\frac{1}{2}}^{red}$
Benzoquinone	-0.52
TCQ	+0.02
TCNQ	+0.13
TCNE	+0.15
DDQ	+0.41

Benzoquinone, with a negative value for $E_{\frac{1}{2}}^{red}$ would be expected to be the weakest electron acceptor and is unreactive in this system. Conversely, DDQ has a comparitively high reduction potential, and produces an oxidation of the bis(dinitrogen) complex with complete loss of dinitrogen.

It was clear that in such systems it was the central metal atom which was undergoing a reaction and not the terminal nitrogen, the reaction between bis(dinitrogen) complexes and alkenes was not pursued further.

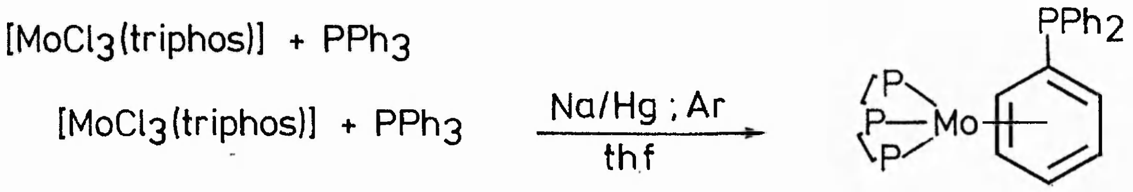
Furthermore, the reaction between the cyanoalkenes TCNE and TCNQ and $[Mo(N_2)_2(PPh_3)(triphos)]$ was not investigated, since oxidation of molybdenum bis(dinitrogen) complexes from molybdenum (0) to molybdenum (I) almost invariably produces loss of dinitrogen (28, 120).

(iii) Synthesis of hydrazido(2-) complexes of molybdenum and tungsten

An alternative source of coordinated dinitrogen is the hydrazido(2-) ligand, readily prepared from the parent bis(dinitrogen) complex. The hydrazido(2-) complexes used in this work were $[WBr(N_2H_2)(dppe)_2]^+Br^-$,

$[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and $[MoF(N_2H_2)(PPh_3)(triphos)]$. The tungsten hydrazido(2-) complexes were prepared by the addition of excess aqueous HBr or HBF_4 respectively to a CH_2Cl_2 solution of $[W(N_2)_2(dppe)_2]$. The complexes are obtained in quantitative yield and may be recrystallised from CH_2Cl_2/diethyl ether mixtures. Both are remarkably stable complexes, apparently indefinitely stable in the solid state, and very stable in solution. The use of vacuum lines and anhydrous reagents was found to be unnecessary (16) and the preparations may be carried out in reagent-grade CH_2Cl_2 without any precautions to exclude air The hydrazido(2-) complexes may be characterised by infra red spectroscopy. Both complexes possess νN-H bands, which are generally weak in intensity, $[WBr(N_2H_2)(dppe)_2]^+Br^-$ has νN-H at 3300 cm^{-1} and $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ has νN-H at 3335 and 3255 cm^{-1}. The remainder of each spectrum is characteristic of the dppe ligands. The rate of formation of the hydrazido(2-) complex from $[W(N_2)_2(dppe)_2]$ is high. For example, protonation of $[W(N_2)_2(dppe)_2]$ with HBr in thf has a rate constant of 5.7×10^4 dm^3 mol^{-1} s^{-1} with a second order dependence on acid concentration (106).

In contrast protonation of $[Mo(N_2)_2(PPh_3)(triphos)]$ with HX (X = Br, BF_4) produces the very air sensitive cation $[MoX(N_2H_2)(PPh_3)(triphos)]^+$ (X = Br, F) in low yield. The quantity of acid and the solvent used appear to be critical in this reaction, since the use of excess HBr produces $[MoBr_3(triphos)]$ and free NH_3, and the use of CH_2Cl_2 appears to produce a complete loss of free dinitrogen. Thus, the protonation of $[Mo(N_2)_2(PPh_3)(triphos)]$ with a stoichiometric quantity of HBF_4 in thf produces the hydrazido(2-) complex $[MoF(N_2H_2)(PPh_3)(triphos)]^+BF_4^-$ The preparation must be carried out in the absence of air. The analogous $[MoBr(N_2H_2)(PPh_3)(triphos)]^+Br^-$ has been isolated by George et. al. (121). A possible side reaction occurring during the protonation reaction is the production of an η^6-arene complex, observed in the reduction of $[MoCl_3(triphos)]$ in thf under argon (122);


$[MoCl_3(triphos)] + PPh_3$

$[MoCl_3(triphos)] + PPh_3 \xrightarrow[thf]{Na/Hg\,;\,Ar}$

Figure 43

The hydrazido(2-) complex is very unstable in air, the band assigned to $\nu(N\text{-}H)$ in its infra red spectrum (3260 cm^{-1} (w)) disappearing rapidly on contact of the solution with air.

The ^{31}P nmr of $[WF(N_2H_2)(PPh_3)(triphos)]^+$ is very complex, and the positions of the resonances are given in the experimental section. The AB_2X system of phosphine ligands where the triphos ligand is meridional, would be expected to produce a doublet of triplets ($-PPh_3$) and two doublets (P_A and P_B, figure 73). However, ^{19}F - ^{31}P coupling would be expected to complicate the spectrum considerably, and the spectrum obtained cannot be interpreted straight forwardly.

(iv) Reactions of hydrazido(2-) complexes with activated alkenes

As with $[W(N_2)_2(dppe)_2]$, only certain alkenes will react with the hydrazido(2-) complex. Since the terminal nitrogen of the hydrazido(2-) complex has some nucleophilic character, the type of alkene which will react with this species must be susceptible to nucleophilic attack i.e. the alkene double bond must be electron defficient. This may be achieved by having highly electron withdrawing substituents σ bonded to the double bond, as described in the Project Outline (Chapter 1, Section D). One of the most highly activated alkenes towards nucleophilic attack is TCNE. Indeed equimolar quantities of $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and TCNE reacted under dinitrogen in thf, forming a red solution. On filtering this solution, approximately half the starting hydrazido(2-) complex was recovered, indicating that the overall stoichiometry of the reaction was one mole of hydrazido(2-) complex to two moles of TCNE. Thus, using this 1:2 stoichiometry and the work-up procedure described in the Experimental section, a black-green crystalline complex was obtained in high yield. The complex may be obtained pure by recrystallisation from CH_2Cl_2/acetonitrile or by column chromatography using cellulose with acetone as the eluant (the complex decomposes to a mixture of products on an alumina column).

The structure of the complex (figure 44) was determined by a single crystal X-ray study, and the mechanism proposed for its formation is as follows; initially the hydrazido(2-) complex is oxidised by one mole of TCNE (known to be a powerful oxidising agent (123)) which is thereby reduced to 1,1,2,2,tetracyanoethane, the latter

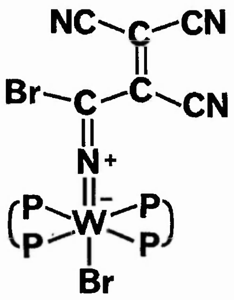


Figure 44

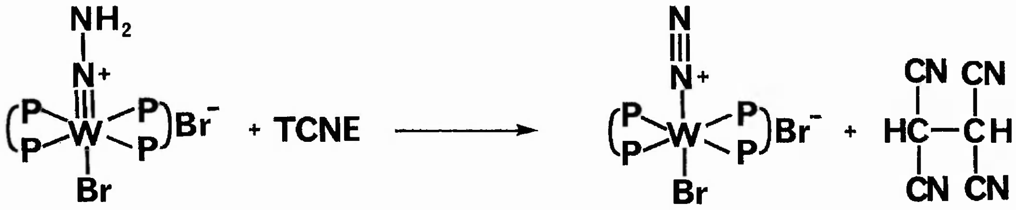


Figure 45

has in intense red colour (124), in solution and may well be responsible for the red colour of the crude solid before recrystallisation. The tungsten (II) dinitrogen complex formed in this oxidation must be extremely unstable and readily loses dinitrogen. Thus, in this system, dinitrogen is evolved and replaced by a second mole of TCNE, bonded to the metal via a nitrile nitrogen;

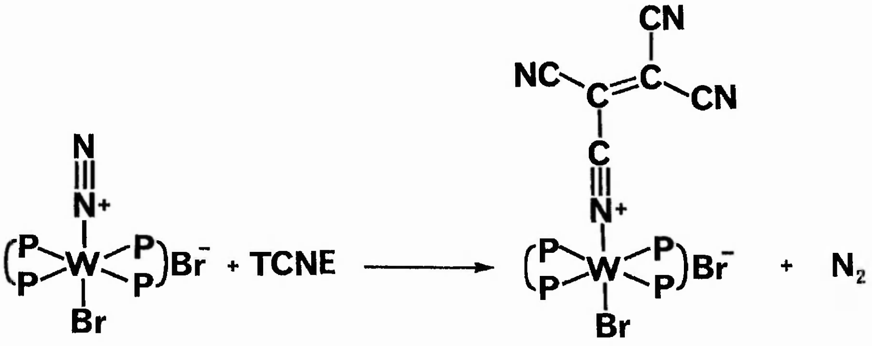


Figure 46

The coordination of a nitrile group of TCNE to a metal centre in this manner has been observed previously (figure 47, (124));

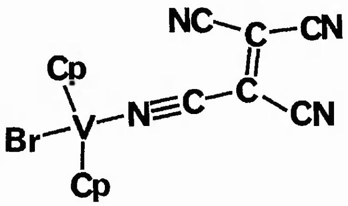


Figure 47

In the 16-electron tungsten complex however, two electrophilic positions on the molecule are available for attack by the bromide ions present in solution (figure 48);

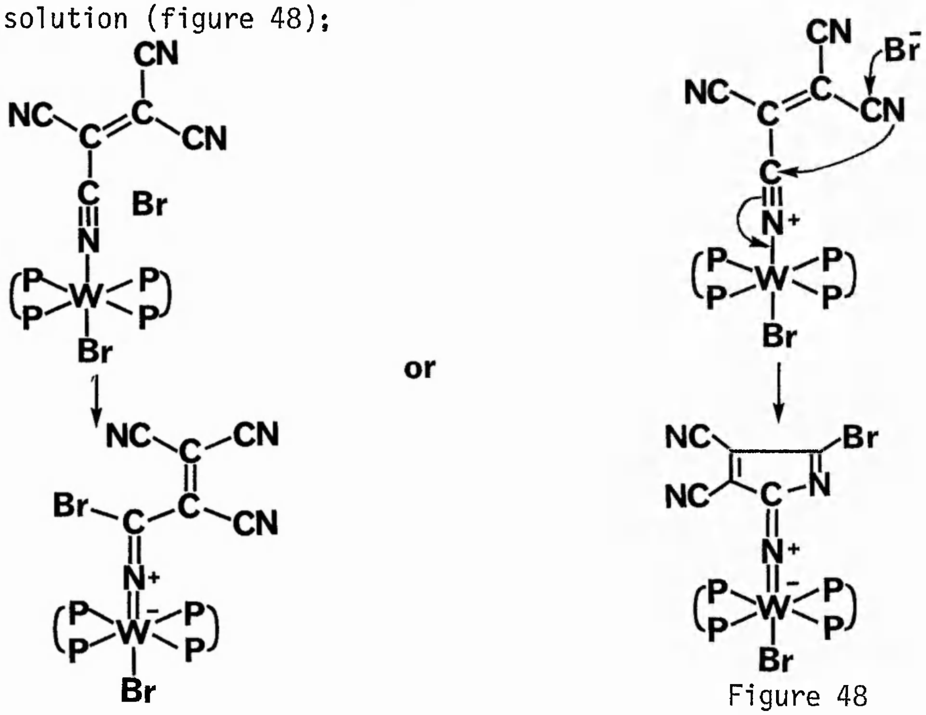


Figure 48

Since the postulated products are structural isomers, the elemental analysis is consistent with both formulations.

There is prior evidence for the cyclisation of TCNE in a somewhat similar situation (figure 49); step A would be equivalent to coordination of TCNE to the metal centre, step B would correspond to attack by the bromide anion and subsequent cyclisation, step C is not observed in the reaction with the hydrazido(2-) complex. This, coupled with the observation of only two resonances assignable to the nitrile groups initially lead to the assignment of the structure of the complex as the cyclised isomer. However, a single-crystal-X-ray study demonstrated that the complex is, in fact, the linear isomer.

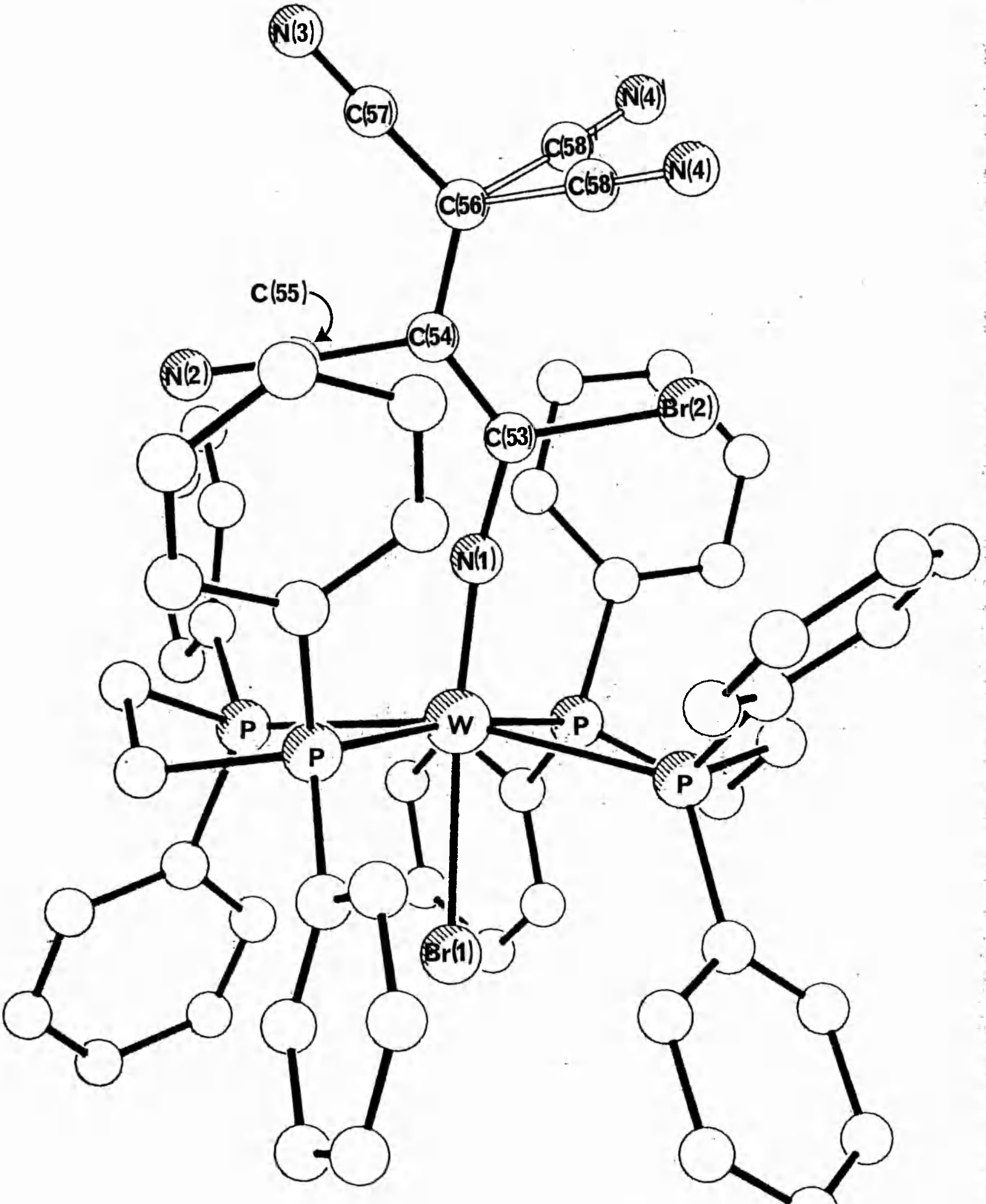


Figure 50

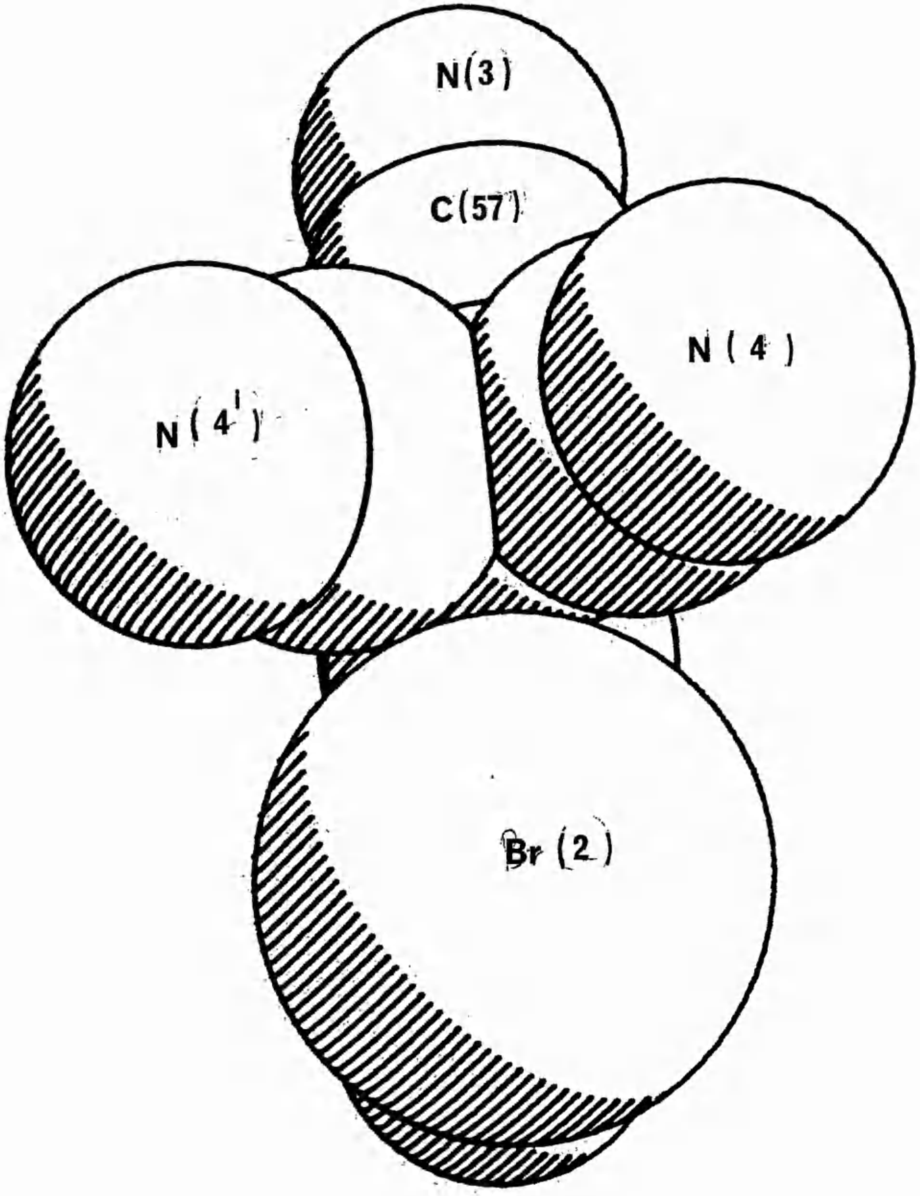


Figure 51

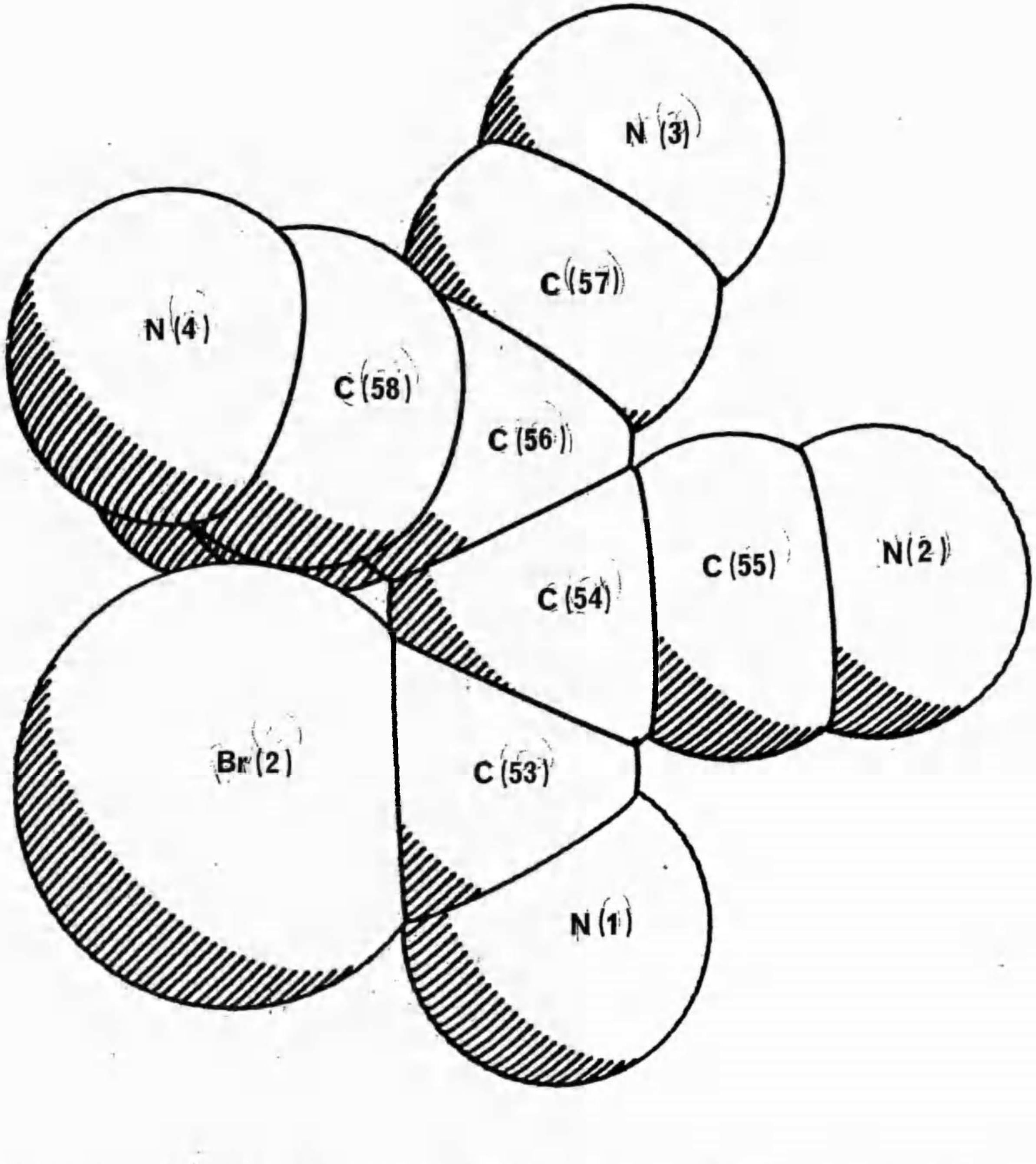


Figure 52

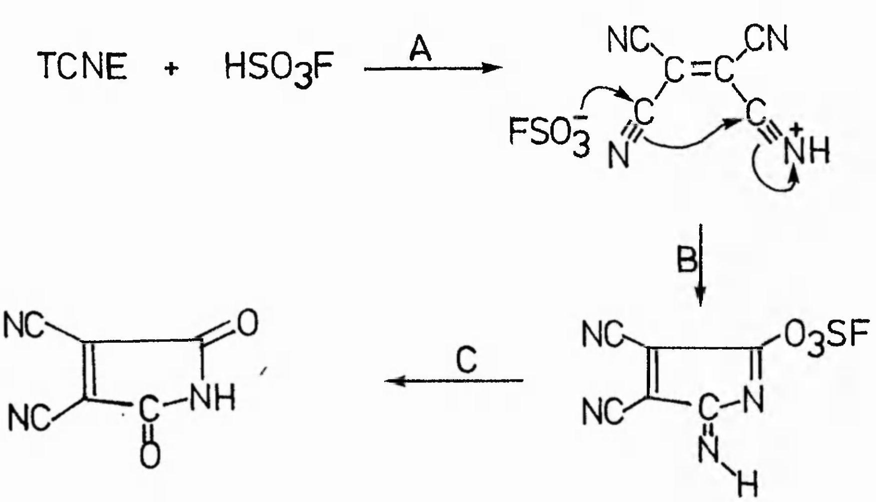


Figure 49

The molecular structure of this complex is illustrated in figure 50 and selected bond lengths and angles are as follows; W-P 2.523(2)-2.561(2), W-Br(1) 2.558(1), W-N(1) 1.777(6), N(1)-C(53) 1.34(1), C(53)-Br(2) 1.902(8), C(53)-C(54) 1.37(1), C(54)-C(56) 1.43(2), C(56)-C(57) 1.37(2) Å; ∠W-N(1)-C(53) 171.4(5)°, ∠Br(1)-W-N(1) 174.8(2)°.

The structure shows disorder in the terminal $C(CN)_2$ group, the group undergoing a tetrahedral distortion with the nitrile carbon C(58), C(58^1) displaced approximately 1Å ether above or below the mean place of the alkene. This results from a steric interaction between the nitrile group [C(58)-N(4)] and the adjacent bromine atom which prevents the alkene achieving coplanarity of all its substituents. This can be seen in figures 51 and 52 which give space-filling representations of this region of the structure. A resonance strucuture which is consistent with the observed pyramidal distortion at C(56) is shown in figure 53

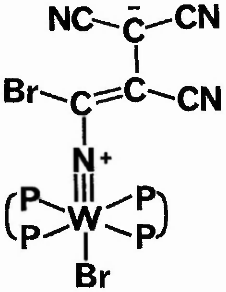


Figure 53

Figure 52 gives the space-filling perspective of the bromotricyanoprop-2-enylideneamino ligand, showing the steric interaction between bromo- and cyano- substituents. Figure 51 shows the same model viewed end-on, revealing the sterically-enforced pyramidalisation of C(56), and showing the two alternative positions of the disordered cyano-group.

It is thought that the third nitrile resonance is absent from the ^{13}C n.m.r. of this complex because of overlapping resonances from the phenyl groups on the phosphines.

The following resonance structures may be drawn from the complex;

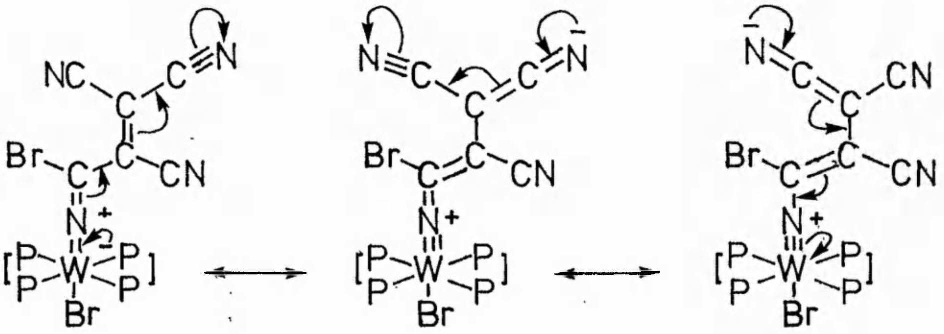


Figure 53A

implying that there is high electron density directly adjacent to the cyano groups, accounting for the very low nitrile stretching frequencies observed in the infra-red spectrum of the complex. The intense colour of the complex may also be related to the delocalisation implied by the above resonance strucutres, since both cyano groups on the terminal carbon atom of the alkene double bond can take part in conjugation with the metal. The steric crowding of the terminal cyano group by the bromine atom, the concequent reduction of conjugation and the tack of planarity of the bromotricyanoprop-2-enylideneamino tungsten system is reflected in the high value for λ_{max}, the distortion producing a red shift in the λ_{max}, compared with the uncrowded analogues; see page 30) and is consistent with the destabilization of the ground state of the molecule producing an increase in the ground state energy and thus a decrease in $\Delta E = E_{excited} - E_{ground}$, which is observed as a red shift.

There is no previous evidence for TCNE reacting with transition metal complexes in this way, although somewhat analogous methyleneamino complexes of rhenium are known; (146)

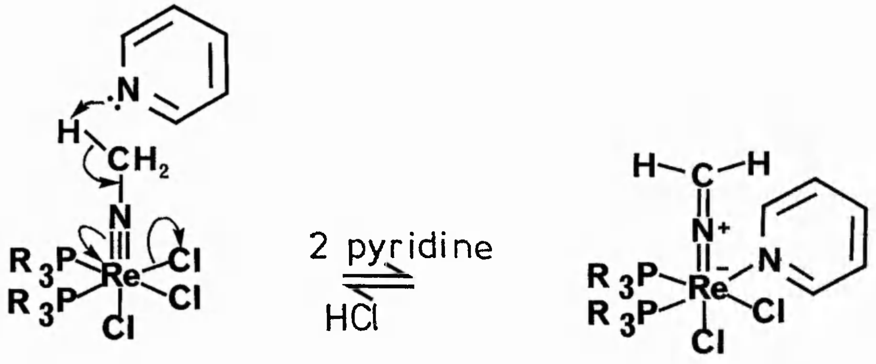


Figure 54

and TCNE reacts with certain transition metal alkyls to give N-bonded complexes, though the mode of addition is substantially different;

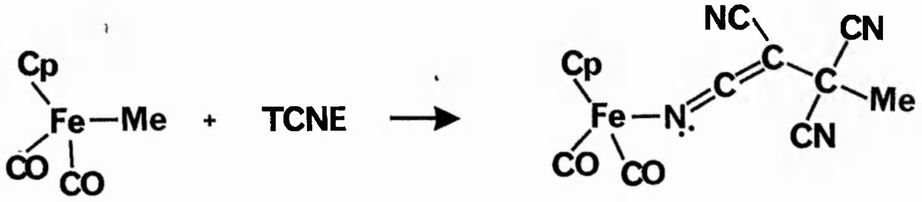


Figure 55

Here, the resulting ligand is only a one electron donor whereas in both the tungsten and rhenium complexes, the methyleneamino group is a three electron donor.

Treatment of $[WBr(NC(Br)C(CN):C(CN)_2)(dppe)_2]$ in CH_2Cl_2 with trifluoroacetic acid produces a yellow solution, the infra red spectrum of which indicates the absence of any nitrile groups. The reaction is reversible and addition of Et_3N leads to the reappearance of the nitrile absorption bands. Obviously all three nitrile groups are involved in the reaction with acid, but are not irreversibly destroyed. Attempts to isolate this complex yielded only starting materials, and the nature of the protonated complex in solution remains somewhat obscure.

The reaction between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and TCNE was also investigated. The expected product would be:

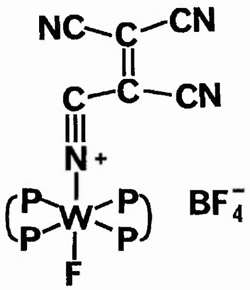


Figure 56

the BF_4^- anion being insufficently nucleophilic to attack the electrophilic centre adjecent to the metal. This is a 16-electron complex, therefore it would be expected to be very unstable, and in fact, a pure product could not be isolated.

The reaction between $[WBr(N_2H_2(dppe)_2]^+Br^-$ and certain other cyanoalkenes gives products directly analogous to that from $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and TCNE. The identity of the alkenes and the products are tabulated below:

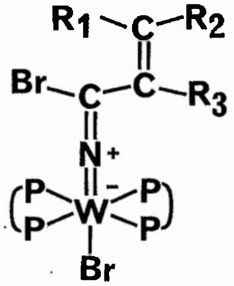
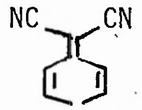


Figure 57

Alkene	R_1	R_2	R_3
TCNE	-CN	-CN	-CN
trans,1,2-dicyanoethene	-H	-CN	-H
chlorotricyanoethene	-CN	-CN	-Cl
TCNQ			-CN

The reactions with trans-1,2-dicyanoethene and chlorotricyanoethene required the initial addition of Et_3N to the reaction mixtures, since these alkenes do not oxidise the hydrazido(2-) complex in the initial step, and the loss of dinitrogen presumably occurs by oxidation of the diazenido ligand and subsequent generation of the five-coordinate intermediate $[WBr(dppe)_2]^+$, to which the nitrile group will rapidly coordinate.

The u.v. spectra of the complexes indicate that their is little steric crowding in the ligands and the λ_{max} for these complexes occurs at lower wavenumbers compared with that for the TCNE product. The product from the reaction with TCNQ has an additional band at long wavenumbers, presumably due to additional electron delocalisation within the cyclic ligand. The product from the reaction with chlorotricyanoethene was obtained in very low yield, perhaps reflecting the general instability of this alkene in the presence of base (112).

The hydrazido(2-) complex did not react with less oxidising nitriles eg. acetonitrile, benzonitrile under similar reaction conditions.

(v) Synthesis and characterisation of vinyldiazenido(1-) tungsten complexes

As indicated in the Introduction, addition of a weak base to a solution of a hydrazido(2-) complex produces deprotonation of the terminal nitrogen and the generation of a diazenido (N_2H) complex. This ligand has somewhat greater nucleophilicity compared with the hydrazido(2-) ligand, and, coupled with the fact that the diazenido complex is a neutral complex, is therefore more likely to undergo reaction with an electrophilic centre, and a greater degree of reactivity with alkenes activated towards nucleophilic attack would be expected. The diazenido complex may be generated in situ by addition of base to a reaction mixture consisting of a hydrazido(2-) complex and a suitable reactant, thereby rendering the isolation of the diazenido complex unnecessary. This type of reaction system has two major drawbacks; decomposition of a base sensitive reactant, and, if the reaction between the diazenido complex and reactant is slow, some decomposition of the complex may occur due to the base sensitivity of the diazenido ligand in solution. For these cases, the use of the isolated diazenido complex may be preferable.

Thus, a generalised reaction for the interaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and alkenes activated towards nucleophilic attack in the presence of Et_3N may be envisaged as;

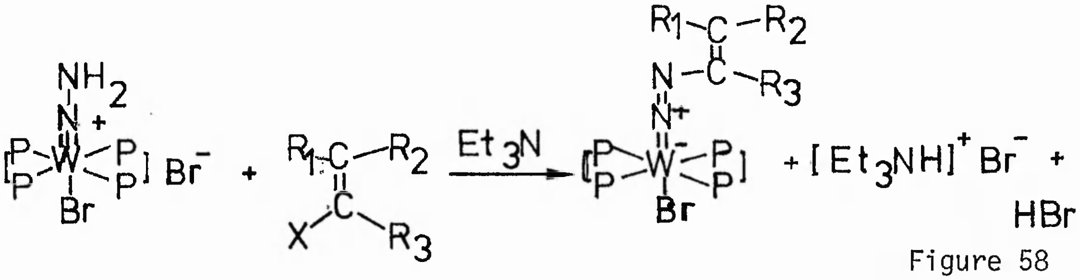


Figure 58

Systematic variation of the substituents on the alkene should indicate; (i) the degree of activation necessary for reaction to occur ie. the ability of R_1 and R_2 to attract electrons to themselves; (ii) the most suitable leaving group, X; (iii) the size of R_3 which will allow reaction to occur. This group will fit into the "sandwich" position between the phenyl groups on the phosphine ligands, discussed later (59).

The alkenes which in fact reacted according to this equation are given below:

R_1	R_2	R_3	X
-CN	-CN	-H	-Cl
-CN	-CN	-Cl	-Cl
-CN	$-CO_2Et$	-H	-Cl
-CN	-CN	-H	-OEt

Briefly, the products were obtained by mixing equimolar quantities of $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and the alkene in CH_2Cl_2 under dinitrogen at room temperature, and then adding NEt_3, the solutions darkening immediately. Addition of methanol, and reduction in volume of the solution in vacuo precipitated the products. They may be recrystallised from CH_2Cl_2/methanol mixtures. The fluorine analogues may be prepared similarly, where X = -OEt, the solvent was methanol and the product precipitated out of solution after 20 minutes stirring.

The complexes are either brown-green (bromine complexes) or orange-red (fluorine complexes) in colour and form intensely coloured solutions in acetone or CH_2Cl_2, in which they are quite soluble. The ultra-violet spectra of these complexes in CH_2Cl_2 solutions have λ_{max} around 400 nm, the position of which appears markedly affected by the nature of the trans halide ligand on the tungsten centre, and indicates that this ligand must affect the electron distribution within the dicyano- or cyano-ethoxycarbonylvinyldiazenido-tungsten-halide system. The position of λ_{max} for the diazenido-fluoro complexes occurs at slightly shorter wavelengths, compared with the diazenido-bromo analogues. This is consistent with a degree of polarisation of electron density away from the vinyldiazenidotungsten system when the trans halide ligand is the more electronegative fluorine atom, hence raising the energy of the system, and producing the observed absorption band at shorter wavelengths than the analogues containing the less electronegative bromine atom. The nature of the R_2 or R_3 groups does not affect the position of the absorption bands.

The complexes have a high degree of stability towards air and moisture in both the solid state and in solution at room temperature. This stability and the intense colour of the complexes in solution may be attributed to the following resonance structures with consequent electron delocalisation;

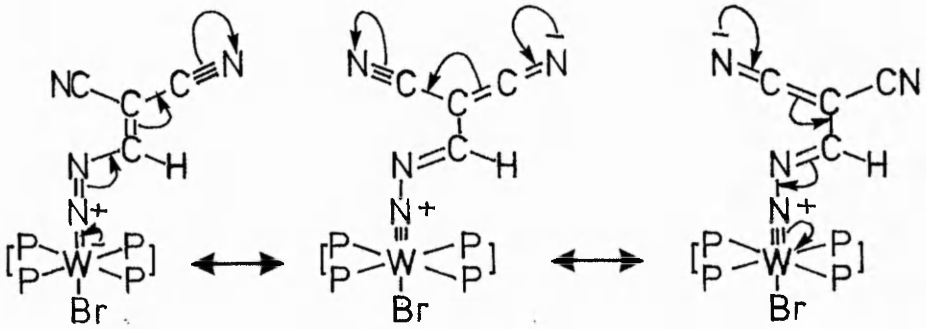
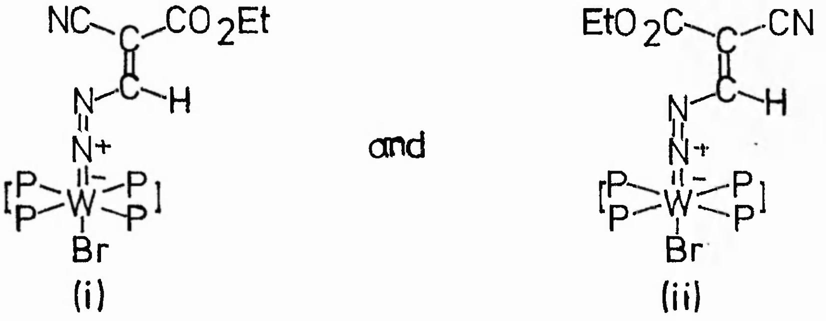


Figure 59

The infra-red spectra of these complexes show a decrease in the stretching frequencies of the -CN and the C=C groups by an average of 40 cm^{-1} and 70 cm^{-1} respectively. This shift is consistent with coordination of the alkene to a transition metal complex, since the tungsten metal centre with a high electron density will readily release electrons to a suitable conjugated system. The increasing negative charge on the nitrile and alkene multiple bonds, in turn reduces the stretching frequency of thse bonds in the infra red spectrum. The C=C stretching frequency appears to be sensitive to the nature of the R_3 group. Thus νC=C, where R_3 = Cl, occurs at lower frequencies, compared with R_3 = H. This is probably the result of an inductive effect where -I values are in the order -Cl > -H, and hence greater electron attracting properties of the halide from the alkene bond lowering the stretching frequency. Confirmation of this by comparison with other R_3 groups was precluded due to the limitations in size imposed on the R_3 group by the phosphine ligands.

The ^{13}C n.m.r. of the complexes showed resonances arising from each nitrile group present, between 114-119 ppm (tms = 0). Resonances assignable to the alkene could not be identified with any certainty, but are tentatively assigned to two resonances at approximately 135 ppm. Resonances due to the dppe ligands are observed between 127-132 ppm (therefore coincidental with the resonances assinged to C=C). For the complex where $-R_1$ = -CN and $-R_2$ = $-CO_2Et$, resonances assignable to -CN, C=O, $-CH_2$-O- and CH_3 are found. The presence of only one nitrile resonance indicates that a possible mixture of geometrical isomers;



(i) (ii)

Figure 60

is not found since in a transition state, rotation about a carbon-carbon single bond is possible, the complex may take up the most sterically favourable configuration. However, space filling molecular models indicate that there will be no steric preference for one particular isomer, the ethoxycarbonyl group being too far removed from the phosphine ligands for any interaction to occur. The largest substituents at either end of the carbon-carbon double bond would be expected to take up a trans configuration (ie. in the starting alkene, the -Cl and $-CO_2Et$ group will be trans) and since the -Cl group will be replaced by the bulkier diazenido complex, isomer (i) (figure 61) will be expected.

In each case, a very large number of scans (typically 20,000) using Fourier transform techniques were necessary to obtain a spectrum, due to the insolubility and high molecular weight of the complexes. Consequently the quality of the spectra was not always high.

A ^1H n.m.r. of the complex where $R_1 = -CN$, $R_2 = -CO_2Et$ showed the expected triplet-quartet pattern for the methyl and methylene groups in the ethoxycarbonyl group. In addition, all complexes showed resonances assignable to P-Ph and $-P(CH_2)_2P-$ from the phosphine ligands. The former generally occured as a poorly defined multiplet and the latter occurred as a very broad singlet or doublet.

The pathway proposed for the formation of these complexes involves an "addition-elimination" mechanism. This mechanism has been investigated by several workers (125, and references therein) and three possible routes may be envisaged (figure 61).

Route C is unlikely since the base present in the reaction mixture will remove the excess protons. Both routes A and B are conceivable. Route A represents an S_N2 mechanism with simultaneous addition of the nucleophile and elimination of the leaving group. Route B represents an "addition-elimination" mechanism (Ad_NE). The latter is the most likely mechanism, since the kinetics of the reaction are consistent with the existence of an addition-elimination intermediate (see next section), and delocalisation of the negative charge on the R_1 and R_2 groups clearly stabilises the intermediate carbanion. A simple S_N2 mechanism has never been demonstrated for vinylic substrates (126, 127).

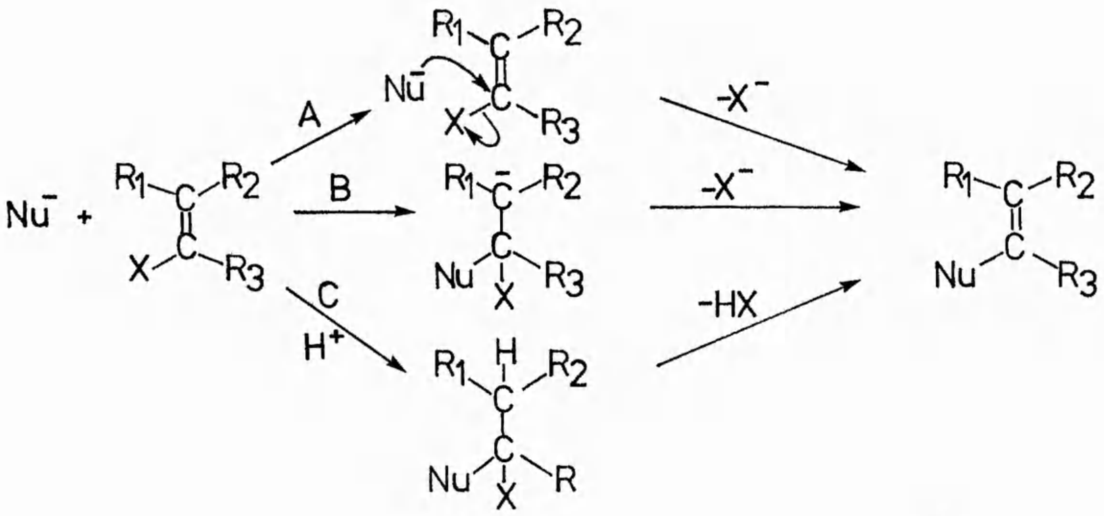


Figure 61

Routes A and B for the formation of the vinyldiazenido complexes are given in figure 62.

The intermediacy of the diazenido complex was demonstrated by the following results:- (1) the hydrazido(2-) complex and the alkenes do not react in the absence of base, and (2) reaction occurred between equimolar quantities of the diazenido complex and the alkenes, without the addition of base, to produce the substituted diazenido complexes. Hence it is the diazenido ligand and not the hydrazido(2-) ligand which is acting as the nucleophile.

A similar, though not directly analogous, series of reactions have been investigated by King and Saran (128). They demonstrated attack on dicyano- activated alkenes ($(CN)_2C{=}C(Cl)R_3$; where R_3 = H, Cl, CN) by the moderately nucleophilic anions $[(C_5H_5)M(CO)_3]^-$ (M = Mo, W) and $[Mn(CO)_5]^-$ resulting in displacement of Cl^- and coordination of the alkene to the metal centre. Where R_3 = H or Cl, this type of behaviour is found in the reaction with the terminal nitrogen of $[WX(N_2H)(dppe)_2]$ (X = F or Br). However, where R_3 = CN the analogy breaks down and a different type of reaction is observed, as described earlier.

The dicyanovinyl ligand has been compared in its behaviour to the

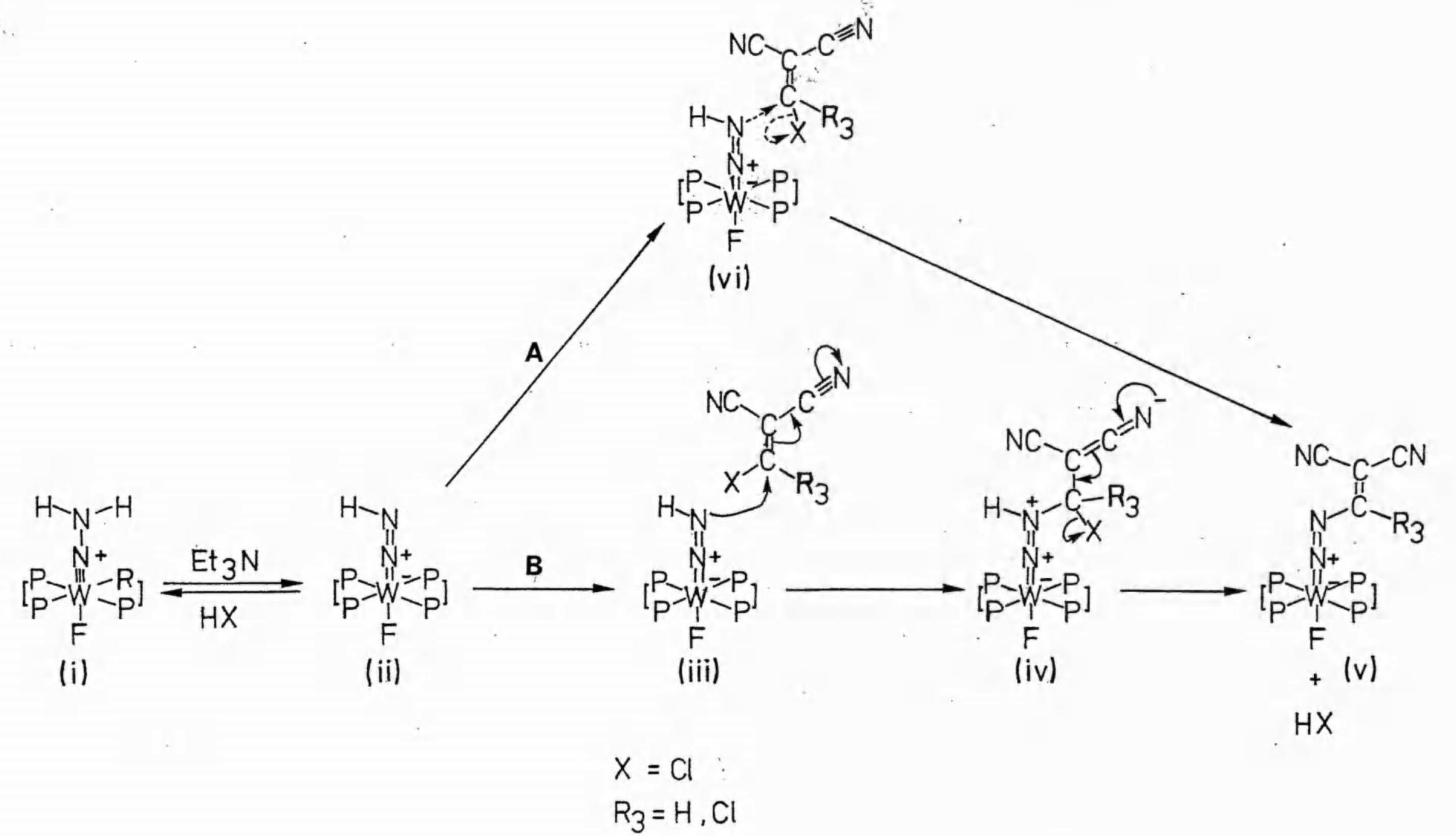


Figure 62

carbonyl ligand (144);

Figure 63

hence the 1,1-dicyanovinyldiazenido group may be considered analogous to the formyldiazenido group;

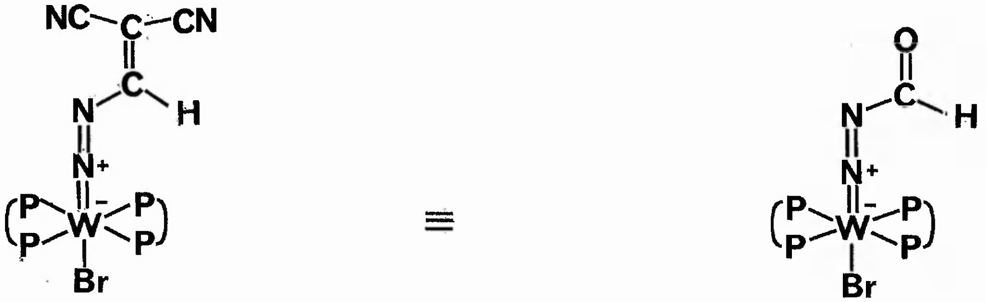


Figure 64

The 1,1-dicyano-2-chlorovinyldiazenido tungsten complex has been prepared previously by Colquhoun (77) via a different synthetic route to that described here;

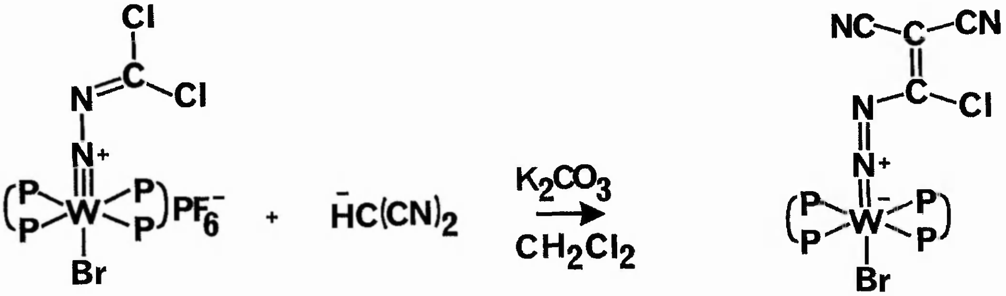


Figure 65

A single crystal X-ray structure has been obtained for this complex and hence further supports the structure of the complexes described here.

The complexes may be protonated with trifluoroacetic acid in CH_2Cl_2 as solvent; eg.

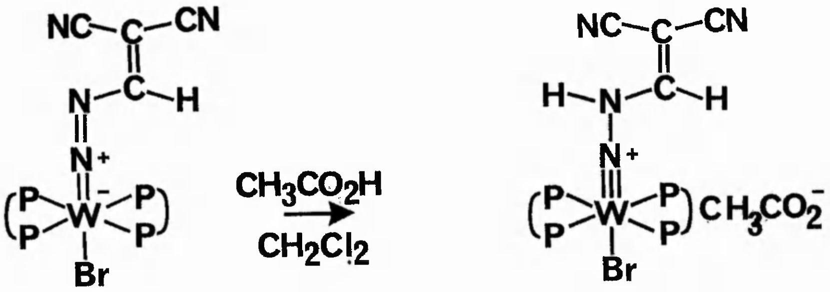


Figure 66

The substituted hydrazido(2-) complexes cannot be isolated since the terminal nitrogen is only very weakly basic and the proton is readily lost on contact with weak bases (for example, water) regenerating the starting diazenido complex. The ultra violet spectra of solutions of the hydrazido(2-) complex in CH_2Cl_2 show λ_{max} at 350 nm, irrespective of the trans halide ligand on the tungsten metal centre. This is consistent with a considerable reduction in the electron delocalisation within the system upon protonation and concomitant reduction in the energy of the excited state of the complex compared with the ground state, producing the marked blue shift in the λ_{max} (compared with the highly conjugated diazenido analogues). The trans halide ligand cannot take part in conjugation with the trans ligand system and therefore does not affect the position of λ_{max}.

The protonation reaction is reversible on addition of excess Et_3N, and ultra violet spectra of these solutions show the presence of the starting diazenido complexes.

When thf/HBF_4 is used as the medium to protonate the diazenido complex, an analogous reaction occurs where R_1 = CN and R_2 = CO_2Et. However, where R_1 = R_2 = CN a different reaction is observed. The λ_{max} at 350 nm is produced initially, but disappears after a few seconds with the slow formation of a new absorption band at slightly higher wavenumbers compared with the starting diazenido complex. The only difference between the two systems is the nature of the group on the alkene double bond which is trans to the transition-metal complex ie. -CN or -CO_2Et. Thus, where the trans group is -CN, the initial protonation would lead to a hydrazido(2-) complex which may isomerise, via a proton shift and give a diazoalkane type complex;

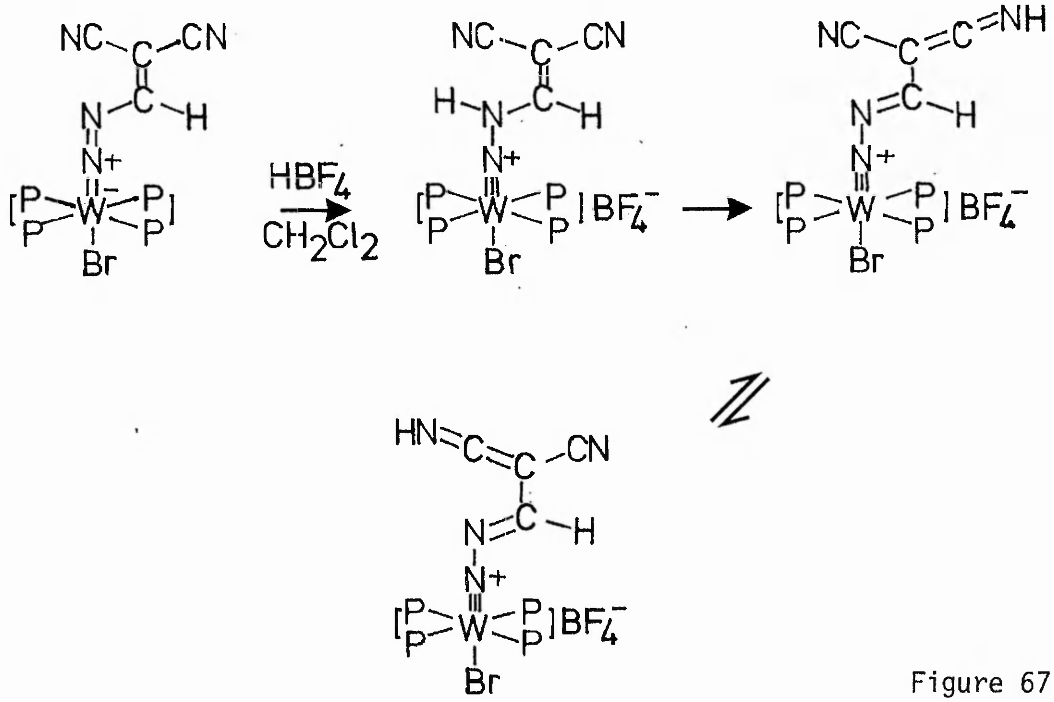


Figure 67

The reaction between the methyl-substituted hydrazido(2-) complex $[WBr(N_2HCH_3)(dppe)_2]^+BF_4^-$ and 1,1-dicyano-2-chloroethene was investigated briefly. In the presence of base in CH_2Cl_2 these reactants produced the complex;

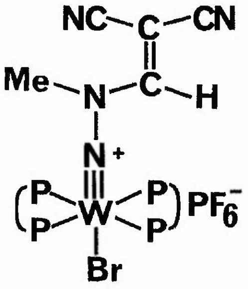


Figure 68

which, in contrast to the protonated hydrazido(2-) complexes described above, is isolable and has the expected spectroscopic and analytical properties. It is a green air stable solid in keeping with the existence of an analogous protonated hydrazido(2-) complex in solution, since these solutions are also green in colour. $[WBr(N_2(CH_3)CH:C(CN)_2-(dppe)_2]^+PF_6^-$ has an absorption band at 366 nm, again consistent with its formulation as a dicyanovinylhydrazido(2-) complex.

(vi) Unreactive alkenes

In addition to the above, cyanoalkenes which did react with the hydrazido(2-) complex or diazenido(1-) complex, a number of apparently similar alkenes were found which failed to react. These are listed in table 1. The failure of these alkenes to react may be rationalised on the basis of:

(1) Steric factors, and
(2) Electronic effects.

(1) Steric factors

The best leaving group on the alkene was found to be -Cl, illustrated by the unreactivity of R_3 = H, X = OEt compared with R_3 = H, X = Cl when R_1 = CN, R_2 = CO_2Et. It is observed that R_3 can be no larger than a chlorine atom.

A methyl group will occupy a greater volume of space and consequently, even if it is able to approach close enough to the diazenido(1-) complex to react, the transition state will be considerably destabilised. This is also consistent with the non-occurrence of addition reactions, eg. the addition of 1,1-dicyano-2,2-dimethylethene would be predicted to produce the complex;

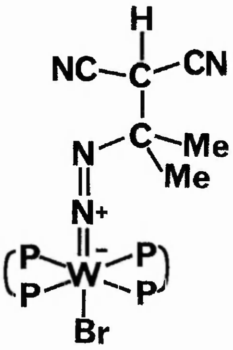


Figure 69

and although the complex

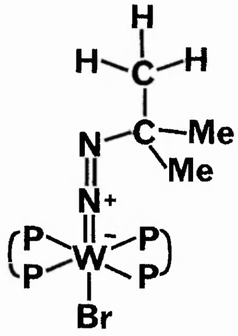


Figure 70

is known and is quite stable, any further increase in the size of the ligand is predicted to be sterically unfavourable.

The restrictions imposed on the reactivity of $[WX(N_2H_2)(dppe)_2]^+$ (X = F, Br) by the bulky phosphine ligands have been observed previously. Chatt et. al. reported that in the condensation of aldehydes and ketones ($O{=}C.R_1R_2$) with $[WBr(N_2H_2)(dppe)_2]^+Br^-$, the smallest group always takes up the position nearest the phosphine ligands (59). The largest group that would fit into the "sandwich" or endo position between the two sets of phenyl groups was found to be $-CH_3$. This group is pointing *away* from the phosphines and therefore fits into the limited space available. In a dicyanovinyl substituted complex where $R_3 = -CH_3$, the methyl group would be pointing *towards* the phosphines and therefore no reaction is observed. The failure of $R_1 = R_2 = -CO_2Et$, $R_3 = H$, X = Cl to react may be due to the presence of two bulky ethoxycarbonyl activating groups preventing a sufficiently close approach of the alkene and the diazenido complex for reaction to occur. It is more probable however, that the unreactivity is attributable to electronic effects (ethoxycarbonyl is less electron-withdrawing than cyano).

The formation of a tricyanovinyldiazenido(1-) complex from $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and chlorotricyanoethene, where X = -Cl and R_3 = CN (figure 58), was not observed. It is possible that the X tricyanovinyldiazenido(1-) group is somewhat more sterically demanding compared with the already bulky tricyanovinyl(bromo)methyleneamino grouping.

(2) Electronic effects

The electron attracting ability of the cyano, chloro and ethoxycarbonyl groups decreases in the order

$$-CN > -CO_2Et > -Cl$$

therefore the most reactive alkenes contained the $R_1 = R_2 = CN$ grouping. When $R_1 = R_2 = -CO_2Et$ no reaction occurred indicating that at least one cyano group plus one other electron withdrawing group is required for a reaction to occur. In general, -OR groups (R = Me or Et) will act as π electron donors when attached to an electron demanding centre (129). Thus the poorer activating ability of the ethoxycarbonyl group is probably due to the carbonyl oxygen atom attracting electrons to produce the following resonance structures;

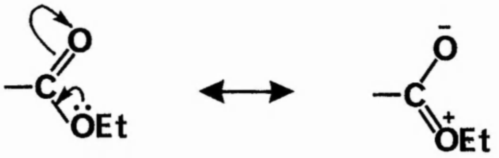


Figure 71

thus rendering the withdrawal of electrons from the rest of the system less effective. This type of effect is also observed in the reactivities of the leaving groups, X, (where X = Cl) is more versatile in this system than X = OEt, the former activating and the latter deactivating the alkene), and also in the unreactivity of 1-amino-1-chloro- 2,2-dicyanoethene, where the lone pair on the nitrogen of $R_3 = NH_2$ renders the alkene double bond less susceptable to nucleophilic attack.

(vii) Attempted cyanoethylation reactions

Cyanoethylation of the diazenido complex using acrylonitrile was attempted in an effort to produce a complex of the type in figure 72. Ammonia and amines readily undergo cyanoethylation either in the absence of a catalyst, or using acid or base catalysis (130). However, no cyanoethylation of the diazenido (or hydrazido(2-) complex was observed.

(viii) The reaction between $[MoF(N_2H_2)(PPh_3)(triphos)]^+BF_4^-$ and dicyanoalkenes

Because of the severe steric restrictions placed upon the type of alkenes used in the reactions with the 1,2-bis(diphenylphosphino) ethane complexes, an alternative source of coordinated dinitrogen was sought, where the metal environment would be similar, but the phosphine ligands would be less bulky. It was originally thought that protonation of the complex $[Mo(N_2)_2(PPh_3)(triphos)]$ with HBF_4 would produce the neutral hydrazido(2-) complex,

$[MoF_2(N_2H_2)(triphos)]$ by analogy with the protonation of cis$[Mo(N_2)_2(PMe_2Ph)_4$ to give the complex $[MoX_2(N_2H_2)(PMe_2Ph)_3]$ (82) (X = Cl-Br, I). This would give a less sterically crowded complex, with the possibility that the tridentate phosphine ligand would impart some stability to the complex, compared with the relatively less stable hydrazido(2-) complexes containing monodentate phosphine ligands. However, the protonated complex retained the triphenylphosphine group and the cationic hydrazido(2-) complex $[MoF(N_2H_2)(PPh_3)_2(triphos)]^+BF_4^-$ was formed, (the bromine analogue, $[MoBr(N_2H_2)(PPh_3)(triphos)]^+Br^-$, has been reported briefly (121)).

The reaction between this complex and 1,1-dichloro-2,2-dicyanoethene in CH_2Cl_2 in the presence of base under dinitrogen was found to produce $[MoF(N_2C(Cl){:}C(CN)_2)(PPh_3)_2(triphos)]$, directly analogous to the 1,2-bis(diphenylphosphino)ethane complexes. This complex is moderately stable in air, and markedly more stable than the parent bis(dinitrogen) and hydrazido(2-) complexes. Indeed the complex was sufficiently stable to allow an elemental analysis to be carried out, which gave good agreement with the theoretical values. The ultra-violet and infra-red spectroscopic properties are consistent with the formulation of the complex as a chloro-dicyanovinyldiazenidomolybdenum complex. The complex is protonated by trifluoroacetic acid in CH_2Cl_2 solution, producing a characteristic colour change from brown to green in the solution, although the solution of the hydrazido(2-) is unstable under dinitrogen and decomposition of the complex was observed.

The reaction between more bulky alkenes and the molybdenum-hydrazido(2-) complex was investigated to determine the largest X and

R_3 groups which would allow a reaction to occur. The use of 1-amino-1-chloro-2,2-dicyanoethene with base produced a loss of the hydrazido(2-) ligand. A complex was isolated for which an infra red and a ^{31}P n.m.r. spectrum were obtained. The former was dominated by a very strong band at 2160 cm^{-1} indicating the presence of $\nu(C{\equiv}N)$, shifted to lower wavenumbers by 45 cm^{-1}, compared with the free alkene. The ^{31}P n.m.r. spectrum indicates loss of both the fluorine and triphenylphosphine ligands, and that a system containing the Mo(triphos) system exists, ie.

Figure 73

P_A occurs as a doublet at 64.2 ppm and P_B as a triplet at 105.6 ppm, and is similar to the ^{31}P spectrum found for fac$[Mo(CO)_3(triphos)]$ (131). However, we were unable to reconcile the elemental analysis with the above spectral interpretation, and the exact identity of the complex remains uncertain.

In contrast, the reaction between $[MoF(N_2H_2)(PPh_3)(triphos)]^+BF_4^-$ and 1,1-dicyano-2-ethoxy-2-methylethene in methanol with base, produced a very low yield of the complex whose structure from its i.r. and u.v.

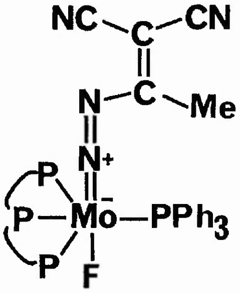


Figure 74

spectra is consistent with that shown in figure 74, although obviously further identification is required. It thus appears that the triphos-triphenylphosphine system is slightly less bulky than the 1,2 bis(diphenylphosphino) ethane system. Indeed, no reaction was observed between the hydrazido(2-) complex and 1,1-dicyano-2-ethoxy-2-ethylethene, a complete loss of dinitrogen occurring.

It is likely that in all of these reactions, by-products of the type [(triphos)Mo(η^6-C_6H_5)P$(C_6H_5)_2$] were produced (122). Owing to the instability of both the transition metal reactants and products from these reactions, work on this system was discontinued in favour of the more stable and more readily characterisable dppe complexes.

(ix) The reaction between tungsten hydrazido(2-) complexes and palladium-alkene complexes

An alternative source of an alkene activated towards nucleophilic attack is a transition-metal alkene complex. Mechanisms for the palladium or platinum-promoted nucleophilic addition of amines to alkenes are well documented (see Introduction), the electrophilic behaviour of the alkene resulting from the transfer of electron density from the alkene to the metal. It was envisaged that the hydrazido(2-) complex [WX(N_2H_2)(dppe)$_2$]$^+$ (X = F, Br) or the diazenido complex [WX(N_2H)(dppe)$_2$] (X = F, Br) could behave analogously to primary or secondary amines respectively in this type of reaction, and that the products from the reaction with alkenes would be directly analogous to those from the reaction between alkenes and simple amines. The proposed pathway for this reaction is given in figure 75, the mechanism being similar to that proposed for the palladium promoted addition of secondary amines to simple alkenes (97).

Palladium-alkene and palladium-allyl complexes were prepared by literature methods, as indicated in the Experimental Section. All reactions were carried out using thf as the solvent under dinitrogen. No reaction was observed between [WBr(N_2H_2)(dppe)$_2$]$^+$Br$^-$ or [WBr(N_2H)(dppe)$_2$] and the palladium-alkene complexes at -78°C. (The low temperature is necessary to prevent the formation of bis(amine)palladium(II)chloride complexes, which is the favoured reaction at higher temperatures (97)). When the reaction between [WBr(N_2H_2)(dppe)$_2$]$^+$Br$^-$ and [PdCl$_2$(1-hexene)]$_2$ was carried out at room temperature, approximately 24 hrs were required for completion (the reaction was considered complete when the ν(N-H) bands in the infra red spectrum of the starting hydrazido(2-) complex had disappeared). The crude product required several recrystallisations from CH_2Cl_2/diethyl ether mixtures to obtain a pure

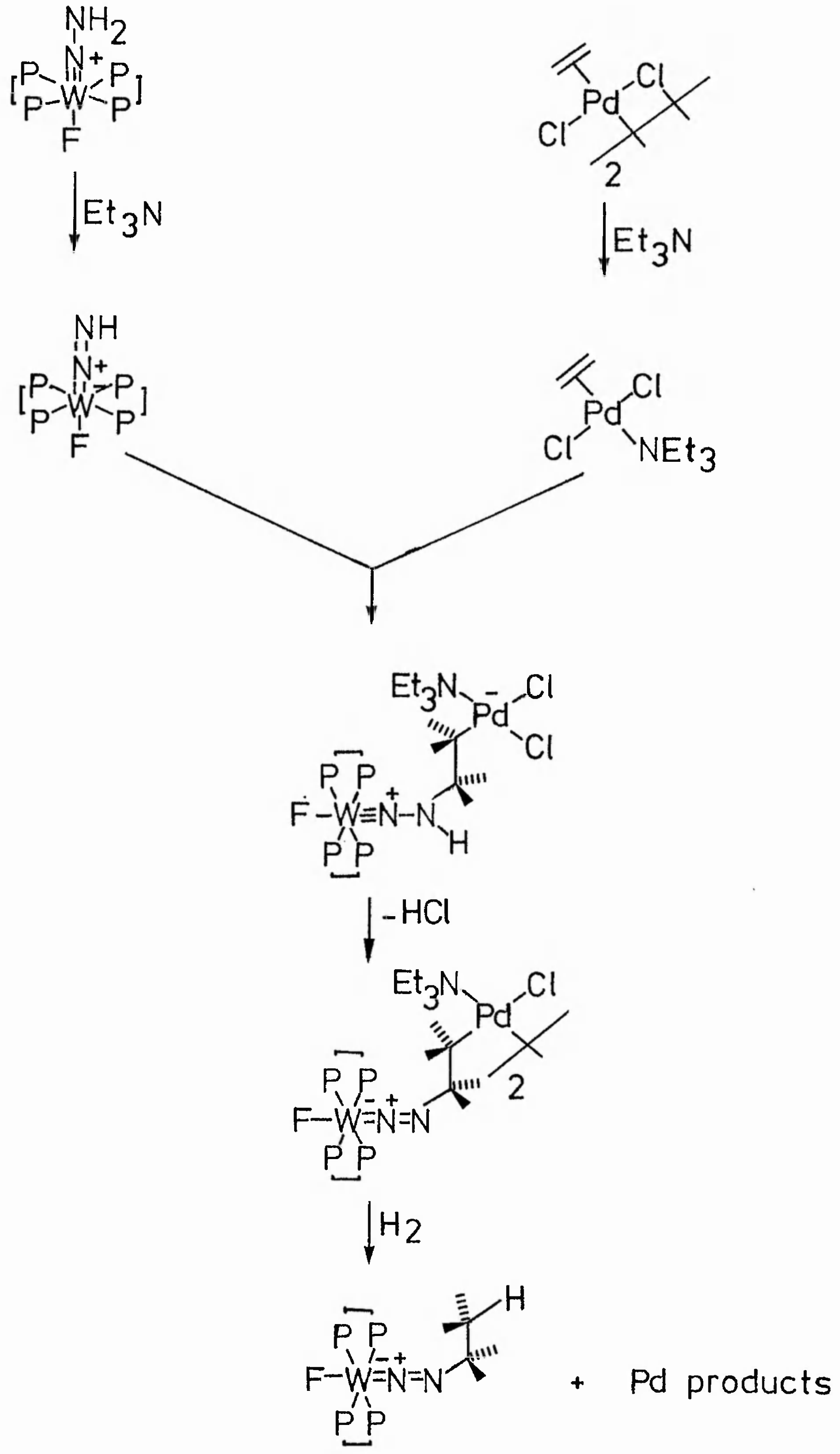

NH2
N+
P
W
F
Et3N
Pd
Cl
2
NH
NEt3
Et3N
Pd
Cl
P
W
N
N
H
-HCl
H2
H
+ Pd products

Figure 75

material.

The dark red crystalline product is somewhat unstable in air as a solid and in solution under dinitrogen. As indicated in the Experimental Section, this reaction also occurs with $[PdCl_2(PhCN)_2]$ (the precursor to the palladium - alkene complexes) and implies that the alkene does not take part in the reaction. Thus, no evidence for the coordination of an alkene to the terminal nitrogen of the hydrazido(2-) ligand was found. The infra red spectrum of the isolated complex indicated that a new hydrazido(2-) complex had been formed (a shift in the band assigned to ν(N-H) in the infra red spectrum was observed, moving to lower wavenumbers), and elemental analysis indicated that the nitrogen ligand was intact. The ^{31}P n.m.r. spectrum of this complex had a single resonance at 30.4 ppm, consistent with the $[W(dppe)_2]$ unit remaining intact. Treatment of this complex with HBF_4 produced a hydrazido(2-) complex as a BF_4^- salt (accompanied by free palladium metal). The position of the ν(N-H) band in the infra-red spectrum of this complex corresponded to that for an authentic sample of $[WBr(N_2H_2)(dppe)_2]^+BF_4^-$ (prepared from $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and $NH_4^+BF_4^-$ in methanol). This indicated that the original tungsten hydrazido(2-)-palladium complex still contained a $[WBr(N_2H_2)(dppe)_2]^+$ unit. On the basis of a detailed elemental analysis (all elements except phosphorus), the structure is assigned as $([WBr(N_2H_2)(dppe)_2]^+)_2[PdCl_2Br_2]^{2-}$. The anion is formed by displacement of the two benzonitrile molecules (or alkene molecules) from the palladium metal centre by the nucleophilic bromide anions of the starting hydrazido(2-) complex.

This mixed chloro-bromo-palladium anion has been described only once previously (132), being prepared by the reaction between phosphonium bromide salts and palladium chloride to form complexes of the type $P_2[PdCl_2Br_2]$ (where P = phosphonium cation, for example $[(C_6H_5CO)_2CH-(CH_2)_2P(C_6H_5)_3]^+$ or $[(CH_3CO)(C_6H_5CO)CH(CH_2)_2P(C_6H_5)_3]^+$). These complexes contain a relatively large cation, analogous to the hydrazido(2-) cation. Both the hydrazido(2-) and the phosphonium salts are red in colour.

Reaction between the diazenido complex $[WBr(N_2H)_2(dppe)_2]$ and $[PdCl_2(1\text{-hexene})]_2$ produces complete decompsition of the diazenido complex with loss of dintrogen. An analogous reaction occurs using $[PdCl_2(PhCN)_2]$ as the palladium species. Addition of Et_3N to a suspension of $[WBr(N_2H_2)(dppe)_2]_2{}^+[PdCl_2Br_2]^{2-}$ again produces decomposition, with no evidence for the formation of a diazenido ligand. This further supports the formulation of the complex as a hydrazido(2-)-palladium species.

Attempts to grow crystals of the complex failed owing to: (1) the instability of the complex in solution, precipitating either Pd(0) or $PdCl_2$ and, perhaps more significantly, (2) after prolonged dissolution in CH_2Cl_2, a light green crystalline material precipitated out of solution. The elemental analysis of this complex demonstrated that it was a palladium complex containing a dppe ligand, the dppe arising presumably from the decomposition of the tungsten hydrazido(2-) complex. The complex was not conclusively identified owing to the presence of a small quantity of palladium metal, but seems likely to be $[PdCl_2(dppe)]$ or a closely related complex.

An analogous reaction between $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ and $[PdCl_2(PhCN)_2]$ occurred. (Again, no reaction between the hydrazido(2-) complex and a palladium-alkene complex was observed). A new hydrazido(2-) complex was produced, on the evidence of the shift in the position of the ν(N-H) band and the absence of a band assignable to ν(B-F) in the infra-red spectrum. Addition of the BF_4^- anion to the palladium metal centre would not be expected. The elemental analysis of this complex indicated a 1:1 ratio of tungsten to palladium. A detailed elemental analysis (all elements except phosphorus and fluorine) supports the structure $[WF(N_2H_2)(dppe)_2]^+[PdCl_3]^-$ and a band at 335 cm^{-1} (m) is assigned to ν(Pd-Cl). The ^{19}F n.m.r. spectrum of this complex exhibits a quartet of resonances at 137.7 ppm ($J\ ^{185}W-^{19}F = 44Hz$) which is shifted to lower field by 34.5 ppm compared with the W-F resonance of the starting hydrazido(2-) complex ($[WF(N_2H_2)(dppe)_2]^+BF_4^-$ 172.2 ppm ($J\ ^{185}W-^{19}F = 41Hz$) (133)). This is consistent with the presence of the coordinatively unsaturated palladium in close proximity to the fluorine ligand, and the proposed structure for the complex is as in figure 76 overleaf.

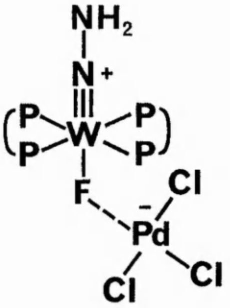


Figure 76

third chlorine ligand may arise from decomposition of the $[PdCl_2(PhCN)_2]$ complex, with formation of Pd(0). The complex exhibits a single resonance at 30.4 ppm in its ^{31}P n.m.r. spectrum, indicating that the $[W(dppe)_2]$ unit is intact. Again, on prolonged recrystallisation attempts, a light-green crystalline solid was isolated which contained no tungsten and appeared to be an impure palladium-dppe complex, formed from the decompsition of the tungsten-dppe complex.

Because of the apparent non-reactivity between alkenes activated towards nucleophilic attack by palladium and the terminal nitrogen atom of $[WX(N_2H_2)(dppe)_2]^+$ (X = Br, F) and the apparent affinity of palladium for the dppe ligand, a different metal was used in the activation of the alkene.

(x) The reaction between tungsten hydrazido(2-) complexes and mercury-alkene complexes

The use of mercury salts in the aminomercuration of alkenes using primary and secondary amines and simple alkenes is a well documented reaction (134-140). It was thought that an analagous reaction between the hydrazido(2-) complex or the diazenido(1-) complex and a suitable mercury alkene complex may occur. In no case was a reaction between the alkene and the terminal nitrogen of the hydrazido(2-) or diazenido(1-) complex observed. Instead a reaction between the hydrazido(2-) complex and the mercury salts occurred, in the presence or absence of alkene (indicating that the alkene plays no part in the reaction), and was dependent upon the identity of the mercury salt. Thus, the use of $Hg(OAc)_2$ produced an immediate decomposition of the hydrazido(2-) complex, with almost complete disappearence of colour in the CH_2Cl_2 solution and the formation of a white powder, presumably free dppe ligand. The use of $Hg(NO_3)_2$ produced, initially a lilac solution of the oxo-complex $[WF(O)(dppe)_2]^+$ which is presumably formed *via* an intermediate of the type;

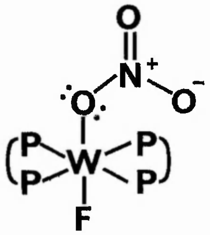


Figure 77

after initial loss of the hydrazido(2-) ligand (bubbles of gas were observed on the surface of the mercury salt). The oxo-complex may be isolated and characterised, in the initial stages of the reaction. However, on prolonged contact the mercury salt produces complete docomposition of the complex and a white powder is obtained. (A similar type of reaction was observed during attempts to protonate $[W(N_2)_2(dppe)_2]$ with HNO_3, a lilac solution of the oxo-complex being formed and then decomposition occurring). Finally, the use of $HgCl_2$ produces, a green solution which, upon workup, gave long yellow needles of product (accompanied by some unreacted starting hydrazido(2-) complex). The infra-red spectrum of this showed that the ν(N-H) band had moved to lower wavenumbers no band assignable to ν(B-F) was present and a band assignable to ν(Hg-Cl) at 435 cm^{-1} was present. On the basis of an elemental analysis (C, H, N, Hg) the structure is assigned as

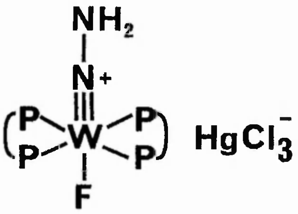


Figure 78

The $[HgCl_3]^-$ anion is well known, and the complex is analogous to that formed by reaction of $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and $[PdCl_2(PhCN)_2]$ as described earlier. An analogous reaction occurs between phosphonium salts and $HgCl_2$ (132) to give free $[HgCl_3]^-$.

Thus, it was concluded that reaction of the hydrazido(2-) and diazenido complexes with a metal-activated alkene is unlikely to lead to C-N bond formation. The unreactivity of the metal-alkene complex may be attributed to the comparatively large size of the complex (compared with the cyano-activated alkenes described earlier) and its consequent inability to approach the hydrazido(2-) sufficiently closely for reactions to occur. Loss of the alkene from the metal enables a reaction between the hydrazido(2-) complex and metal salt to occur. This is particularly true for the palladium system, where the alkene ligand is readily displaced at temperatures above 0°C (97).

(xi) The reaction between $[WX(N_2H)(dppe)_2]$ (X = F, Br) and palladium-allyl complexes

The reaction between $[WX(N_2H)(dppe)_2]$ and palladium-allyl complexes was examined briefly. The latter complexes have the considerable advantage that they are both isolable and stable, hence rendering their handling easier. Two different reactions were observed, depending upon whether the palladium-allyl complex was neutral (eg. $[PdCl_2(\eta^3\text{-1-methylallyl})_2]$ or cationic (eg. $[Pd(PPh_3)_2(\eta^3\text{-1-methylallyl})]^+Cl^-$). In the former case, a black material (presumably palladium metal) is precipitated on addition of aqueous K_2CO_3 to a CH_2Cl_2 solution of the hydrazido(2-) complex and the palladium-allyl complex. However, workup of the solution produces a crystalline complex which appears to contain an allylic ligand (from ^1H n.m.r. spectroscopy), and is presumably an impure sample of the complex (figure 79);

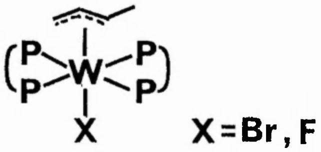


Figure 79

A CH_2Cl_2 solution of this complex slowly produces a lilac colour on exposure to air, which is characteristic of $[WBr(O)(dppe)_2]^+$. Further characterisation of these complexes is necessary. Analogous allylic complexes containing a mixture of dppe and carbonyl ligands are known (141).

In contrast, the use of the cationic palladium-allyl complexes, produces a red tungsten complex and yellow $[PdCl_2(PPh_3)_2]$ (identified by m.p. and i.r. spectroscopy). The tungsten complex could not be isolated in a pure state.

Using either palladium-allyl complex, no coordination of the allyl group to the terminal nitrogen of the diazenido ligand was observed.

(xiii) Attempted intramolecular cyclisation reactions

As an alternative to the intermolecular reactions just described, a situation may be envisaged whereby an intramolecular attack by the terminal nitrogen on an olefinic linkage already bonded to the same nitrogen could occur. This would produce a heterocyclic ligand, and the proposed reaction sequence for the formation of such a complex is given in figure 80.

The alkene could be activated towards nucleophilic attack by the use of a transition metal salt eg. $[PdCl_2(PhCN)_2]$ or K_2PtCl_4.

The advantage in using this type of system is that the alkene may be held in reasonably close proximity to the attacking nitrogen atom, thus increasing the probability that an interaction will occur. The obvious disadvantage is that a suitable ligand must be found to form this type of complex initially. A complex of this type has been described previously (54) from the reaction between trans$[W(N_2)_2(dppe)_2]$ and 4-bromobut-1-ene under free radical conditions. However, a more convenient synthesis of ligands of this type was found to be via acid catalysed condensation of aldehydes or ketones with $[WBr(N_2H_2)(dppe)_2]^+Br^-$, followed by reduction with a hydridic reagent and protonation with aqueous acid.

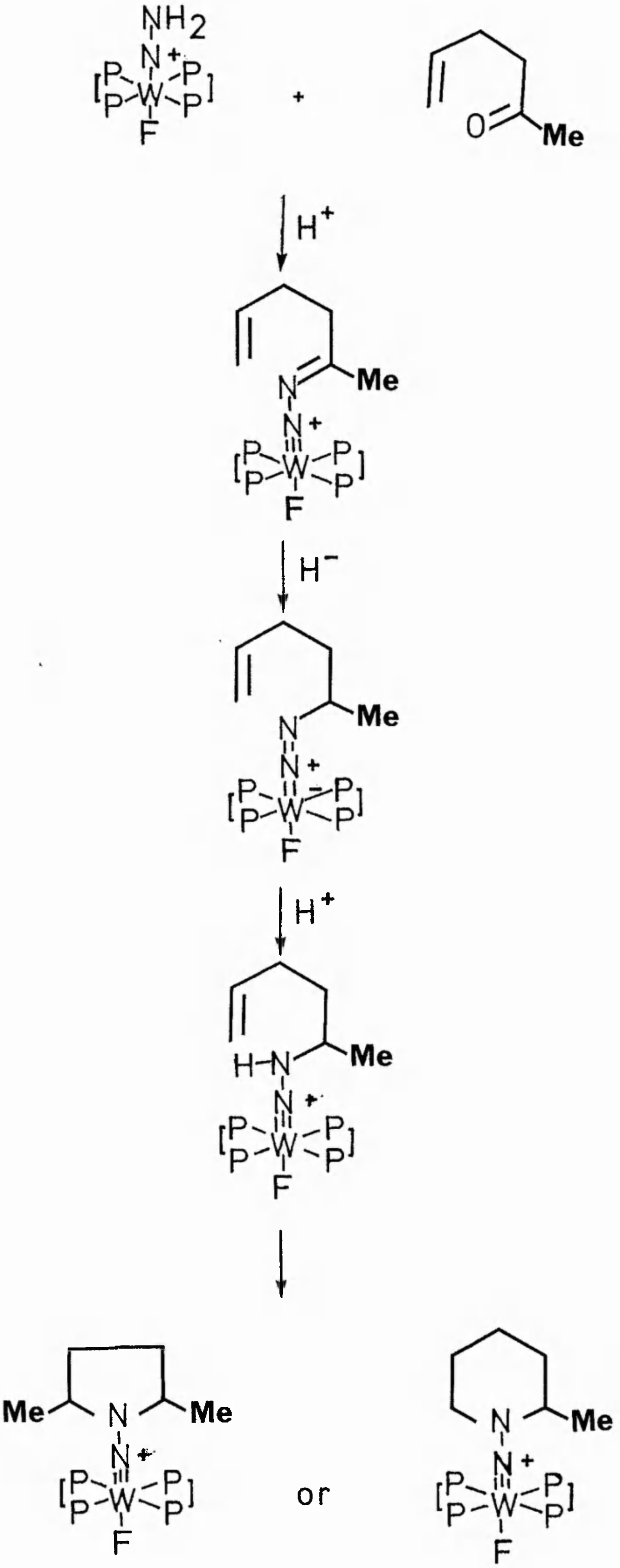


Figure 80

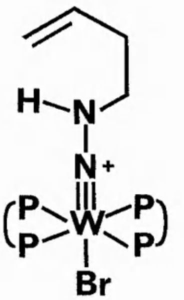
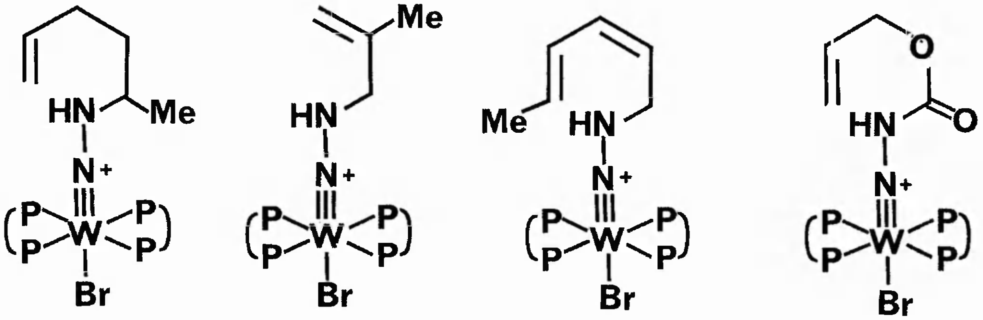


Figure 81

The methods used for the generation of complexes;



XXVI XXXI XXXII XXXIV

Figure 82

are described in the Experimental section.

The initial diazoalkene complexes were prepared using neat trifluroacetic acid as solvent (complexes XXXI and XXXII) in which the starting hydrazido(2-) complex is moderately stable. For the condensation of the ketone hex-5-ene-2-one, more vigorous conditions were required, and the diazoalkane complex was prepared by heating the hydrazido(2-) complex in hex-5-ene-2-one at approximately 60°C under dinitrogen for several hours, in the presence of a relatively large quantity of concentrated HCl. The complexes were characterised by infra-red spectroscopy, ^{1}H n.m.r. spectrometry and elemental analysis. The carbon-nitrogen double bond in the diazoalkane complexes was reduced using sodium borohydride in isopropanol or 95% ethanol.

The use of sodium borohydride ensures that the alkene group remains intact. Where the alkene ligand is conjugated, as in complexes XXIX and XXX, the contact time between the double bond and the hydride

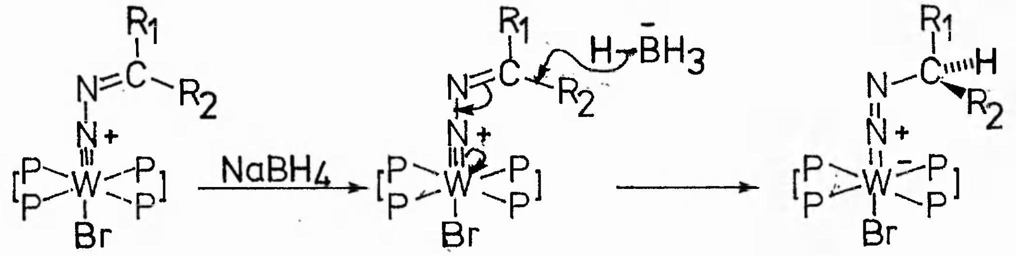


Figure 83

ion should be kept to a minimum, since the double bond may be reduced to the corresponding saturated groups. The diazenido complexes were characterised by infra-red spectroscopy, ^1H n.m.r. spectrometry and elemental analysis. Complex XXXIV was prepared by the nucleophilic attack of the diazenido complex $[WF(N_2H)(dppe)_2]$ on the ligand, allyl chloroformate, eliminating a chloride anion. All the complexes were protonated by HBF_4 in CH_2Cl_2 solution and the hydrazido(2-) complexes were characterised by infra red spectroscopy, ^1H n.m.r. spectrometry and elemental analysis.

As indicated in the Introduction the formation of a heterocyclic ring structure on the terminal nitrogen of a hydrazido(2-) complex is possible in principle (62, 73). Platinum promoted cyclisation of aminoalkenes in acidic aqueous solution at 60°C has been described (143). The alkenes used were of the type $CH_2{:}CH(CH_2)_nNHR$ where n = 2,3; R = H, Me, $_nC_3H_7$ etc; for example;

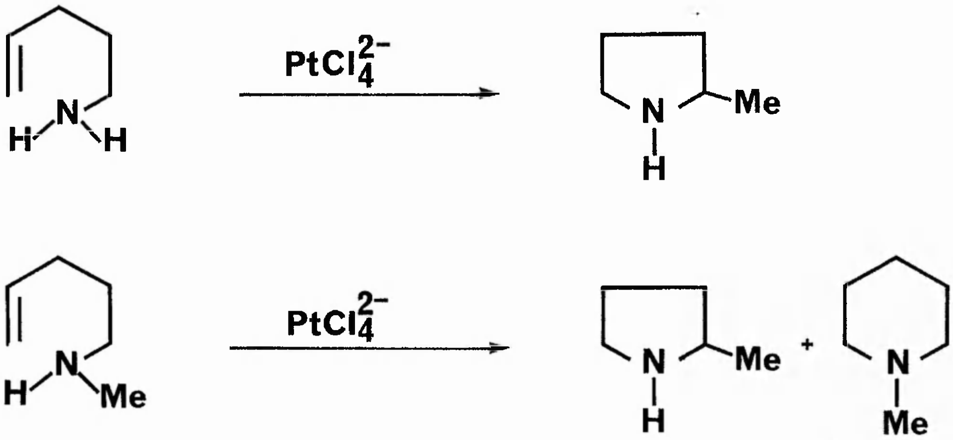


Figure 84

Obvious analogies exist between this reaction and the possible cyclisation of the hydrazido(2-) complexes containing a ligand with a terminal alkene just described. However, products from the reaction with K_2PtCl_4 in methanol under various conditions produced only starting materials or uncharacterised decomposition products. No evidence for the formation of a cyclic ligand was found. It was concluded that an equilibrium of the type;

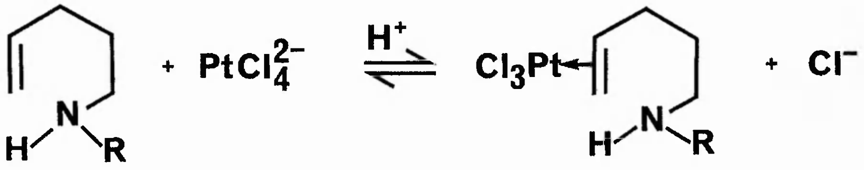


Figure 85

must lie entirely to the left with the hydrazido(2-) ligands.

The use of $[PdCl_2(PhCN)_2]$ was also investigated in the possible cyclisation of complex (XXV). The complex isolated from the reaction mixture was still a hydrazido(2-) complex (ν(N-H) 3280 cm^{-1}) and benzonitrile was still present in the complex (ν(C≡N) 2270 cm^{-1}). A complex of the type;

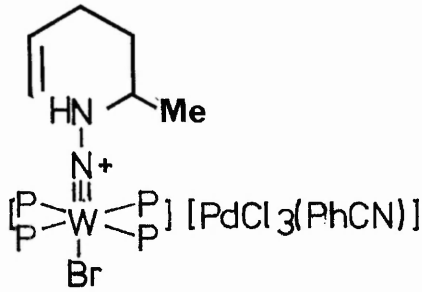


Figure 86

is possible, but since it was obvious that cyclisation had not occurred, the reaction was not pursued further.

In all these reactions involving metal activation of an alkene, the most probable reason for the unreactivity with the hydrazido(2-) complex is that the metal-alkene complex will be comparatively large, and thus preclude any interaction between the alkene and the already crowded terminal nitrogen of the hydrazido(2-) complex.

A further attempt at producing a ring structure using succinic anhydride was successful, producing the complex;

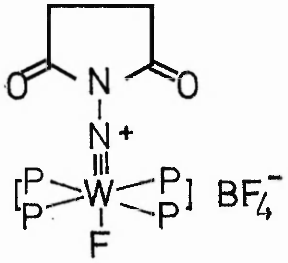


Figure 87

analogous to the complex formed from the hydrazido(2-) complex and succinic dichloride (73) and presumably formed via the following mechanism;

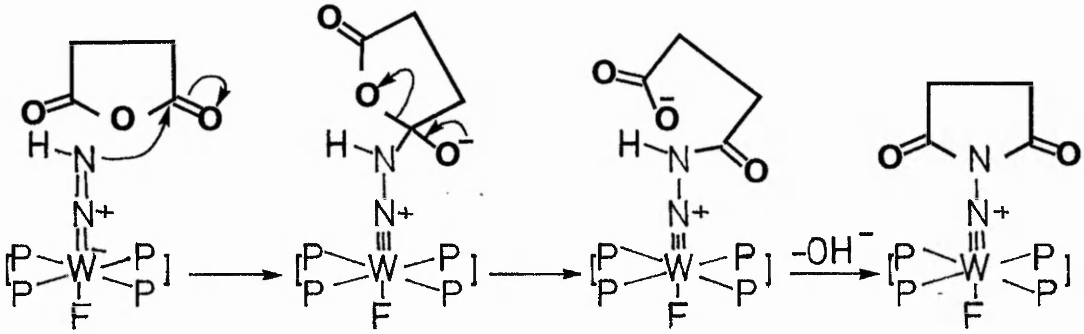


Figure 88

(xiii) The reaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and alkenes in strong acid solutions

Finally, the reaction between the hydrazido(2-) complex and carbonium ions, generated in strong acid solutions from gaseous or liquid alkenes was investigated. An intramolecular reaction of the type (figure 89) was attempted, but no reaction was observed. Intermolecular reactions between the hydrazido(2-) complex and free carbonium ions generated from isobutene, propene, styrene and cyclohexene in either 10% CH_2SO_4/CH_3CO_2H or CF_3SO_2H/CH_2Cl_2 solutions were not observed. However, an increase in the viscosity of the reaction medium suggested that the alkenes were either dimerising via a cationic

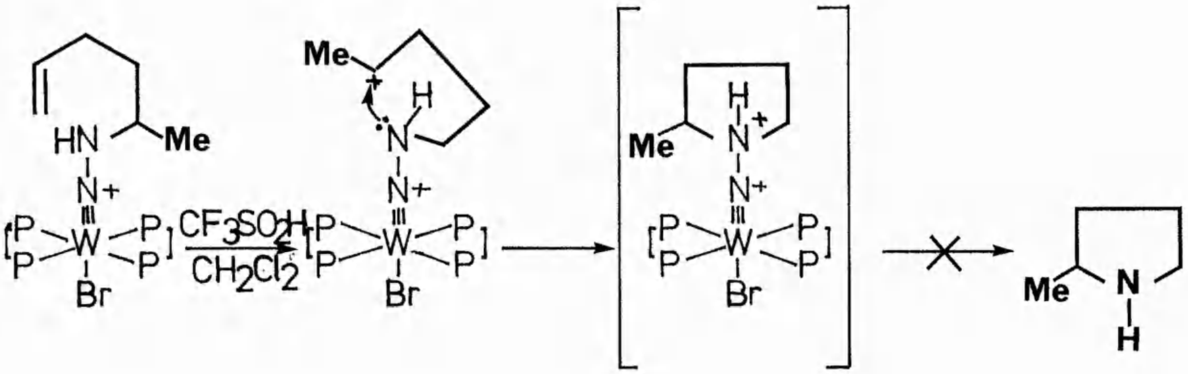


Figure 89

mechanism;

$$Me_2\ C{=}CH_2 \xrightarrow{H_2SO_4} Me_3C^+\ CH_2{=}C(Me)_3 \rightarrow Me_3C.CH_2\overset{+}{C}\ Me_2$$

$$\xrightarrow{-H^+} Me_3CCH{=}CMe_2 \ + \ Me_3CCH_2CMe{=}CH_2$$

or polymerising:

$$Me_2C{=}CH_2 \xrightarrow{H_2SO_4} Me_2C(CH_2C(Me)_2)_n^+$$

Three possible reasons for this lack of reactivity were:

(1) the short lifetime of the carbonium ions in the medium used;

(2) the difficulty of reaction between a large tungsten cation and a positively charged carbonium ion. Obviously two species of like charge will repel each other, hence restricting any interaction which may occur; and

(3) in strong acid solution it is thought that the diazenium cation may exist (23);

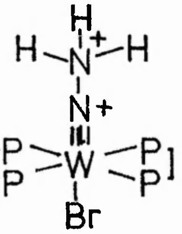


Figure 90

thus the terminal nitrogen is quarternised and unlikely to undergo any further reaction.

It was originally thought that the lack of reactivity may be due to the instability of the product in strong acid;

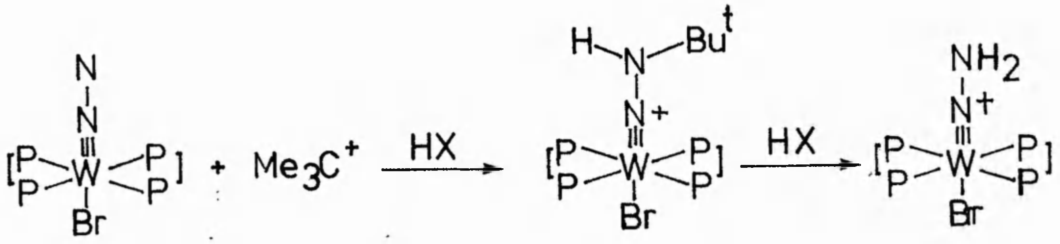


Figure 91

To test this hypothesis the ethyl, isopropyl and tertiary butyl hydrazido(2-) complexes were prepared, dissolved in strong acid solution and the products analysed by infra-red spectroscopy. It was found that whilst the ethyl and isopropyl hydrazido(2-) complexes may be recovered intact from such solutions, the tertiary butyl hydrazido(2-) complex decomposed to give [WBr(N_2H_2)(dppe)$_2$]$^+$. The reason for this instability is unknown, although the tertiary butyl complex is obviously the more sterically crowded of the three complexes and on this basis could be predicted to be the least stable. In addition, the cleavage reaction (figure 92) involves loss of a t-butyl carbonium ion, CMe_3^+ which is much more stable than the corresponding ethyl or isopropyl cations and is therefore more likely to behave as a "leaving group".

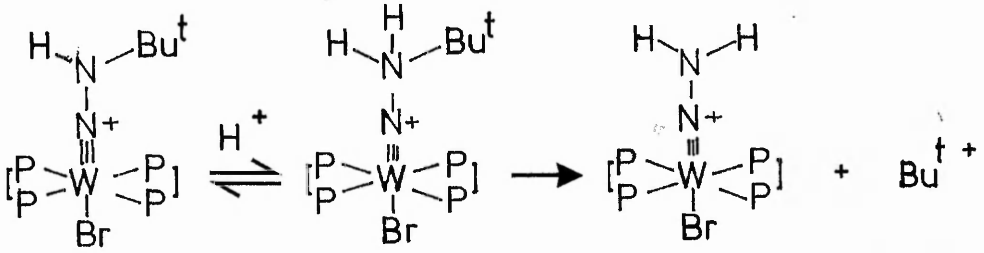


Figure 92

B. KINETIC STUDIES

The kinetics of the reaction between $[WBr(N_2H_2)(dppe)_2]^+Br^-$ and 1,1-dichloro-2,2-dicyanoethene in the presence of base (Et_3N) using CH_2Cl_2 as solvent were investigated as indicated in the Experimental section.

Previous kinetic studies on similar systems have determined the rate of loss of dinitrogen from $[M(N_2)_2(dppe)_2]$ (M = Mo or W) in substitution, free radical alkylation and decomposition reactions (33, 145), and the rate and mechanism for the protonation of $[M(N_2)_2(dppe)_2]$ (M = Mo or W) (106) and cis$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) (87) with halogen acids.

In the work described here, the rates of reaction and order of reaction with respect to each component were obtained by the initial rate method. The rate of a reaction involving three components A, B and D may be expressed in terms of the following equations;

$$\frac{-dC_A}{dt} = K\ C_A^{\,n}\ C_B^{\,n}\ C_D^{\,q}$$

$$\log_{10}\left(\frac{-dC_A}{dt}\right) = \log_{10} K + n\log_{10} C_A + m\log_{10} C_B + q\log_{10} C_D$$

If, for a given series of kinetic runs, the initial concentrations of B and D are held constant and that of A is varied, the initial rate of the reaction $(-dC_A/dt)_\circ$ is related to $(C_A)_\circ$, the initial concentration of A by the equation

$$\log_{10}\left(\frac{-dC_A}{dt}\right)_\circ = \text{constant} + n\log_{10}(C_A)_\circ$$

The order of reaction, n, with respect to component A is obtained from the slope of the graph of $\log_{10}$[Initial Rates] against $\log_{10}$[Initial Concentrations]. In a similar manner the orders of reaction with respect to B and D may also be determined by two further kinetic runs.

The rate constant, K, for the reaction at particular concentrations of A, B and D may then be obtained from the expression;

$$\log_{10} K = \log_{10} \left(\frac{-dC_A}{dt}\right)_o - n \log_{10} C_A - m \log_{10} C_B - q \log_{10} C_D$$

This method has the considerable advantage that it is not dependent upon a knowledge of the orders of reaction with respect to each component. The main disadvantage is the difficulty of drawing accurate tangents to the $C_t{}^P$ against t curves.

This is overcome by monitoring the first 1-2% of the reaction since the curve at this stage of the reaction approximates to a straight line.

Under the conditions of the preparative reaction, the base is always present in a very large excess. To simulate these conditions for stopped flow spectrophotometric analysis, the base was present in one hundred fold excess, over the hydrazido(2-) complex and alkene. As expected, this gave a zero order of reaction with respect to base, since its concentration remains effectively constant. The reaction was found to be first order with respect to metal complex and alkene, ie.

$$\text{Rate} = \frac{d[\text{metal complex}]}{dt} = k^H [\text{metal complex}][\text{alkene}] \qquad \text{(i)}$$

Lowering the base concentration to near stoichiometric (ten fold excess) amount, the orders of reaction obtained with respect to each component were first order in metal complex, alkene and base ie.

$$\text{Rate} = \frac{d[\text{metal complex}]}{dt} = k^L [\text{metal complex}][\text{alkene}][\text{base}] \qquad \text{(ii)}$$

The rate constant had the values $k^H = 1.5 \times 10^5 dm^3 mol^{-1} s^{-1}$ and $k^L = 92 \times 10^5 dm^6 mol^{-2} s^{-1}$, ie. lowering the concentration of base increased the magnitude of the rate constant.

If we assume that the reactive metal species is the diazenido(1-)

complex, formed by a proton transfer reaction which are known to be very rapid (147), then the kinetic scheme may be simplified to;

$$[\mathrm{WBr(N_2H)(dppe)_2}] \quad + \quad \mathrm{Alkene} \quad \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \quad [\mathrm{Intermediate}] \qquad \text{STEP A}$$

$$[\mathrm{Intermediate}] \quad + \quad \mathrm{Et_3N} \quad \xrightarrow{k_3} \quad [\mathrm{Product}] \qquad \text{STEP B}$$

Applying a steady state treatment to the intermediate, we have;

Rate of formation of intermediate = Rate of disappearence of intermediate ie.

$$k_1\left[[\mathrm{WBr(N_2H)(dppe)_2}]\right][\mathrm{Alkene}] = k_2\left[[\mathrm{Intermediate}]\right] + k_3\left[[\mathrm{Intermediate}]\right]\text{-}[\mathrm{Et_3N}]$$

$$\left[[\mathrm{Intermediate}]\right] = \frac{k_1\left[[\mathrm{WBr(N_2H)(dppe)_2}]\right]\ [\mathrm{Alkene}]}{k_2 + k_3[\mathrm{Et_3N}]}$$

$$\therefore \frac{d\left[[\mathrm{Product}]\right]}{dt} = k_3\left[[\mathrm{Intermediate}]\right][\mathrm{Et_3N}]$$

$$= \frac{k_1k_3\left[[\mathrm{WBr(N_2H)(dppe)_2}]\right]\left[\mathrm{Alkene}\right]\left[\mathrm{Et_3N}\right]}{k_2 + k_3\ [\mathrm{Et_3N}]}$$

Thus, at high concentrations of $\mathrm{Et_3N}$

$$k_3[\mathrm{Et_3N}] > k_2$$

$$\text{Rate} = k_1\left[[\mathrm{WBr(N_2H)(dppe)_2}]\right][\mathrm{Alkene}]$$

This is consistent with the observed expression (i), assuming the concentration of the diazenido(1-) complex is equivalent to the concentration of the hydrazido(2-) complex. At low concentration of $\mathrm{Et_3N}$

$$k_2 > k_3[\mathrm{Et_3N}]$$

$$\text{Rate} = \frac{k_1\ k_3}{k_2}\left[[\mathrm{WBr(N_2H)(dppe)_2}]\right][\mathrm{Alkene}][\mathrm{Et_3N}]$$

which is consistent with expression (ii), using the same assumption concerning the concentration of the metal species.

Step B may be envisaged as;

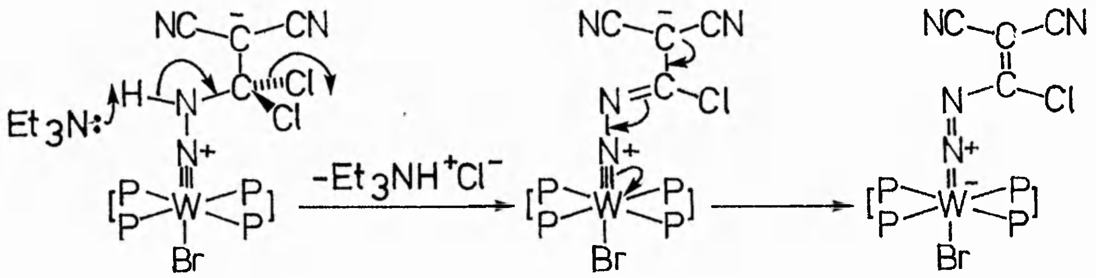


Figure 93

This scheme is entirely consistent with the presence of a multi-step reaction and an "addition-elimination" type intermediate. A similar behaviour in the rate constant for the reaction between acetamide and hydroxylamine is observed (142), where the rate constant decreases with increasing hydroxylamine concentration and the existence of an addition-elimination intermediate is postulated.

C. ELECTROCHEMICAL STUDIES

(i) Introduction

Previous methods used to generate organonitrogen products from substituted hydrazido(2-) complexes have often involved the use of vigorous conditions, eg. concentrated acid, high temperatures, high pressures, concentrated alkalis, as indicated in the Introduction. This generally produced complete destruction of the metal complexes with liberation of free phosphine ligand.

Obviously, if a cyclic process is to be developed, it is necessary to regenerate the transition metal complex containing a new dinitrogen ligand, after cleavage of the organonitrogen product. Recent work at the University of Sussex has demonstrated that it is possible to generate organohydrazines or organoamines from substituted hydrazido(2-) complexes via an electrochemical reduction. The hydrazido(2-) complexes were generated by the free radical reaction between $[M(N_2)_2(dppe)_2]$ (M = Mo, W) and alkyl bromides. The metal complex isolated at the end of the electrochemical reduction was the starting bis(dinitrogen) complexes. The full cycle is given in figure 26.

(ii) The reduction of tungsten-cyanovinylhydrazido(2-) complexes in thf under dinitrogen

It thus appeared possible to reduce complexes of the type $[WX(N_2(R_4)C(R_3):C(CN)R_2)(dppe)_2]^+BF_4^-$ (X = Br, F; R_4 = H, Me; R_3 = H, Cl; R_2 = CN, CO_2Et) electrochemically via a four electron reduction to give organohydrazine compounds of the type

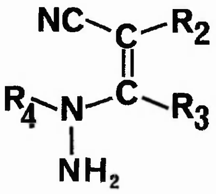


Figure 94

and the starting bis(dinitrogen) complex. It was realised that in the presence of acid the vinylhydrazine shown in figure 94 would immediately cyclise to form an aminocyanopyrazole;

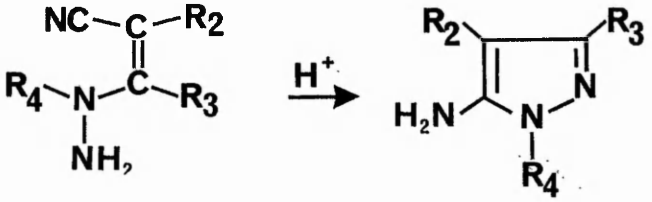


Figure 95

and that in the acidified thf solutions of the tungsten-cyanovinyldiazenido(1-) complexes used to generate the corresponding hydrazido(2-) complexes, the bis(dinitrogen) complex would protonate to give $[WX(N_2H_2)(dppe)_2]^+BF_4^-$.

Cyclic voltammetry on complexes of the type;

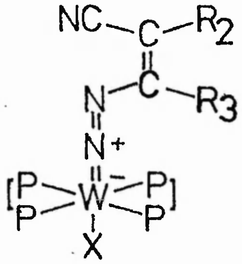


Figure 96

(X = Br, F; R_2 = CN, CO_2Et; R_3 = H, Cl) in thf under dinitrogen underwent a reversible reduction ($ip^{red}/ip^{oxo} \cong 1.0$) at approximately -0.4V, the potential being apparently unaffected by the nature of X, R_2 or R_3. Cyclic voltammetry on the corresponding hydrazido(2-) complexes demonstrated an almost irreversible reduction at a potential at -0.32V, indicating that the hydrazido(2-) complexes were easier to reduce than the diazenido complexes by ≅ 80mV. The ratio of $ip^{red}/ip^{oxo} \cong 0.2$-$0.4$ was obtained at a scan rate of 200 mV s^{-1}. Increasing the scan rate to 500 mV s^{-1} did not increase this ratio, and the electron transfer reaction must be followed by a chemical reaction. Controlled potential electrolysis of these solutions demonstrated that the process was a four electron reduction. A further, completely irreversible, reduction process was observed at more negative potentials (-0.73to-0.76V), and comparison of this value with that obtained from the reduction of an authentic sample of aminocyanopyrazole demonstrated that this reduction process may be associated with the presence of the aminocyanopyrazole nucleus formed by reduction of the hydrazido(2-) complex where X = Br,

R_2 = CN; R_3 = H; R_4 = H (figure 99). Repeated scans at the same mercury drop showed a disappearance of the peak assigned to the metal complex and the appearance of the peak assigned to the organic product.

Controlled potential electrolysis of thf solutions of the hydrazido(2-) complexes under dinitrogen at a potential 100 mV more negative than the peak reduction potential assigned to the metal complex, demonstrated that a four electron reduction process was occurring, and that the reduction was complete after two hours using the amount of complex stated. Analysis of the catholyte by gas-liquid chromatography indicated the presence of aminocyanopyrazole (R_2 = CN; R_3 = H; R_4 = H figure 95) in moderate (≅ 40%) yields.

The proposed mechanism for the formation of aminocyanopyrazole and $[WF(N_2H_2)(dppe)_2]^+BF_4^-$ is given in figure 97 and is analogous to the mechanism for the cycle described earlier (figure 26).

The reduction of the isolable dicyanovinylhydrazido(2-) complex $[WBr(N_2(Me)CH{:}C(CN)_2)(dppe)_2]^+PF_4^-$ under the same conditions, gave 5-amino-4-cyano-1-methylpyrazole, identified by gas-liquid chromatography, providing good evidence for the intermediacy of hydrazido(2-) complexes in the cycle.

The metal-containing product from these reactions was identified as $[WX(N_2H_2)(dppe)_2]^+BF_4^-$ (X = Br, F), although a pure sample of this could not be isolated because of difficulties in separating the hydrazido(2-) complex from the supporting electrolyte. However, the infra-red spectrum of the crude material from the reduction had bands assignable to ν(N-H), compared with an authentic sample. This complex is the precursor to the dicyanovinyldiazenido complexes, which may be readily prepared by sequential addition of Et_3N and alkene. Attempts to generate a true cyclic process are described in the Experimental section. It was observed that, although further organic product is generated on the second cycle, the third and fourth cycles produced little or no further increase in yield. This may be due to decomposition of one or more of the intermediate complexes in solution (especially when the sensitivity of the hydrazido(2-) complex to mercury salts is considered, see Section A, (X)) and it is possible that a different acid, base, solvent or any combination of these three is required to enable the cycle to turn effectvely. Also the use of an alternative

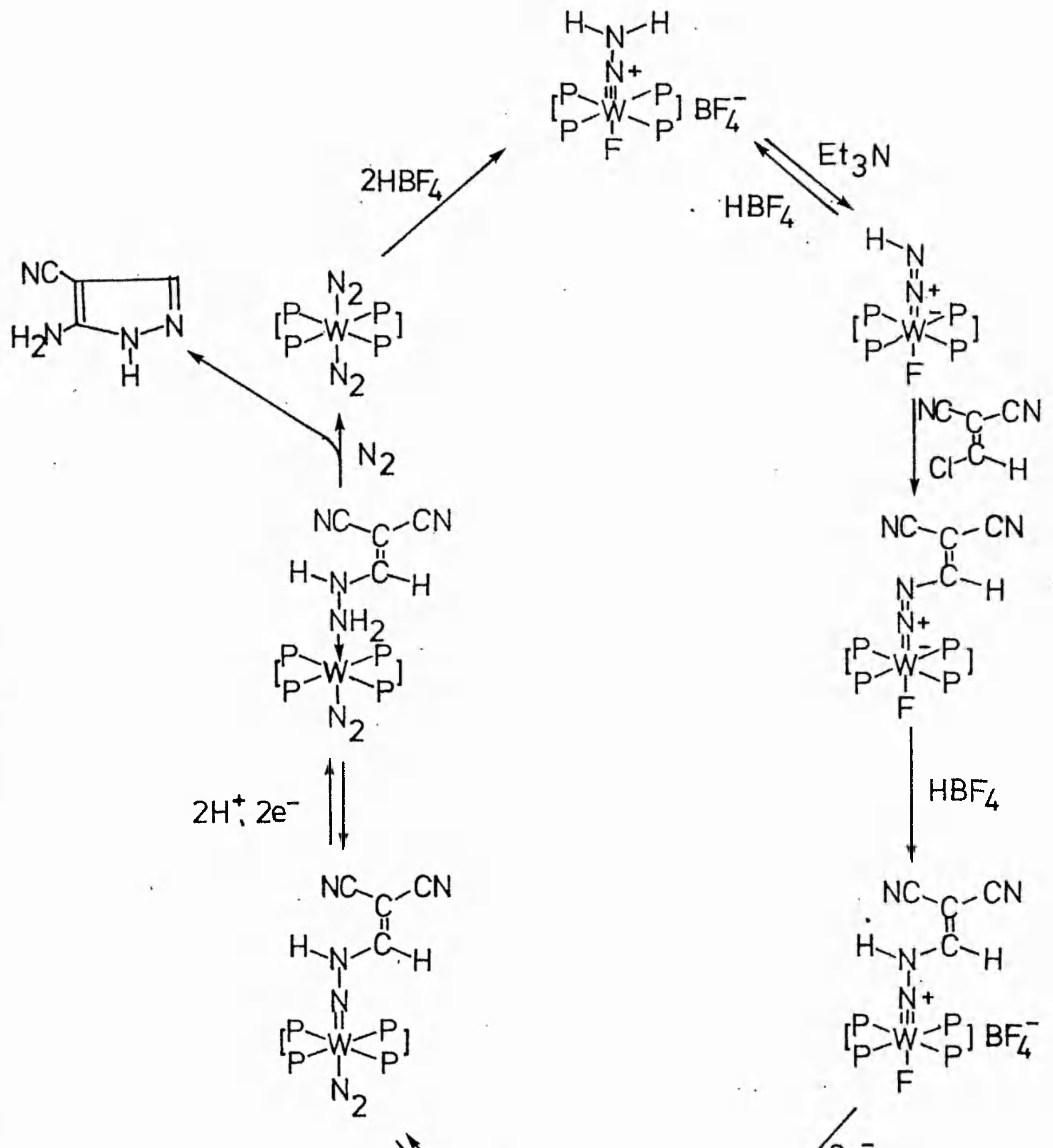


Figure 97

cathode may improve yields, but initial experiments using a platinum electrode were not encouraging.

Finally a quantity of aminocyanopyrazole was isolated from the reduction of $[WF(N_2HCH:C(CN)_2)(dppe)_2]^+BF_4^-$ and a mass spectrum was obtained, confirming the identity of the organic product. The mass spectrum of the product, and that of an authentic sample of aminocyanopyrazole are given in Chapter 2, section C(V).

(iii) The reduction of tungsten-dicyanovinylhydrazido(2-) complexes in methanol under dinitrogen

A different product is generated from the electrochemical reduction reaction, depending upon the nature of the solvent and the atmosphere present. Thus reduction of $[WF(N_2CH:C(CN)_2)(dppe)_2]$ in methanol at a mercury drop electrode under dinitrogen produces a single reduction peak at -0.58V (no peak assignable to aminocyanopyrazole was observed) which is completely irreversible, even at fast (500 mV s^{-1}) scan rates and disappears very rapidly on repeated scans at the same drop. This indicates that the reduction product is very unstable and decomposes before a reoxidation reaction can occur on the reverse cycle. In contrast, reduction of the corresponding hydrazido(2-) complex, $[WF(N_2HCH:C(CN)_2)(dppe)_2]^+BF_4^-$, in methanol under dinitrogen exhibited a completely reversible ($ip^{red}/ip^{ox} = 1.0$) reduction couple at -0.16V ie. the complex is easier to reduce, compared with the diazenido complex, by 420 mV. Again, the formation of aminocyanopyrazole was not observed. Controlled potential electrolysis of this solution confirmed that no aminocyanopyrazole was produced (gas-liquid chromatography) and that a two electron reduction was occurring. The product from this reduction could be either the five-coordinate intermediate $[W(N_2HCH:C(CN)_2(dppe)_2]$ (analogous to the molybdenum species in figure 26) or $[W(OMe)(N_2HCH:C(CN)_2)(dppe)_2]^+BF_4^-$. The latter appears most likely, considering the affinity of molybdemun and tungsten dinitrogen complexes containing monodentate phosphine ligands, for methoxide anion during protonation reactions in methanol (see Introduction; (87)).

(iv) The reduction of tungsten-dicyanovinylhydrazido(2-) complexes in thf under carbon monoxide

The reduction of $[WF(N_2HCH:C(CN)_2)(dppe)_2]BF_4^-$ was also carried out in thf under carbon monoxide. Unfortunately instrumentation problems prevented accurate plots of cell current against charge being obtained, and therefore the number of electrons involved in the reduction step is not known, but aminocyanopyrazole was detected in the solution after reduction (in lower yield than where the reduction is carried out under dinitrogen) and cyclic voltammetry of the catholyte indicated the presence of cis$[W(CO)_2(dppe)_2]$, indicated by a comparison of the cyclic voltammogram with the cyclic voltammogram obtained for an authentic sample of cis$[W(CO)_2(dppe)_2]$. It therefore seems likely that a four electron reduction is occurring.

The proposed pathways for both the reduction of $[WF(N_2HCH{:}C(CN)_2(dppe)_2]^+BF_4^-$ in methanol under dinitrogen and in thf under carbon monoxide are given in figure 98. In both cases, it is the five coordinate intermediate $[W(N_2HCH{:}C(CN)_2)(dppe)_2]$ generated from the two electron reduction of $[WF(N_2HCH{:}C(CN)_2)(dppe)_2]^+BF_4^-$ which reacts with a suitable ligand to give a six coordinate product.

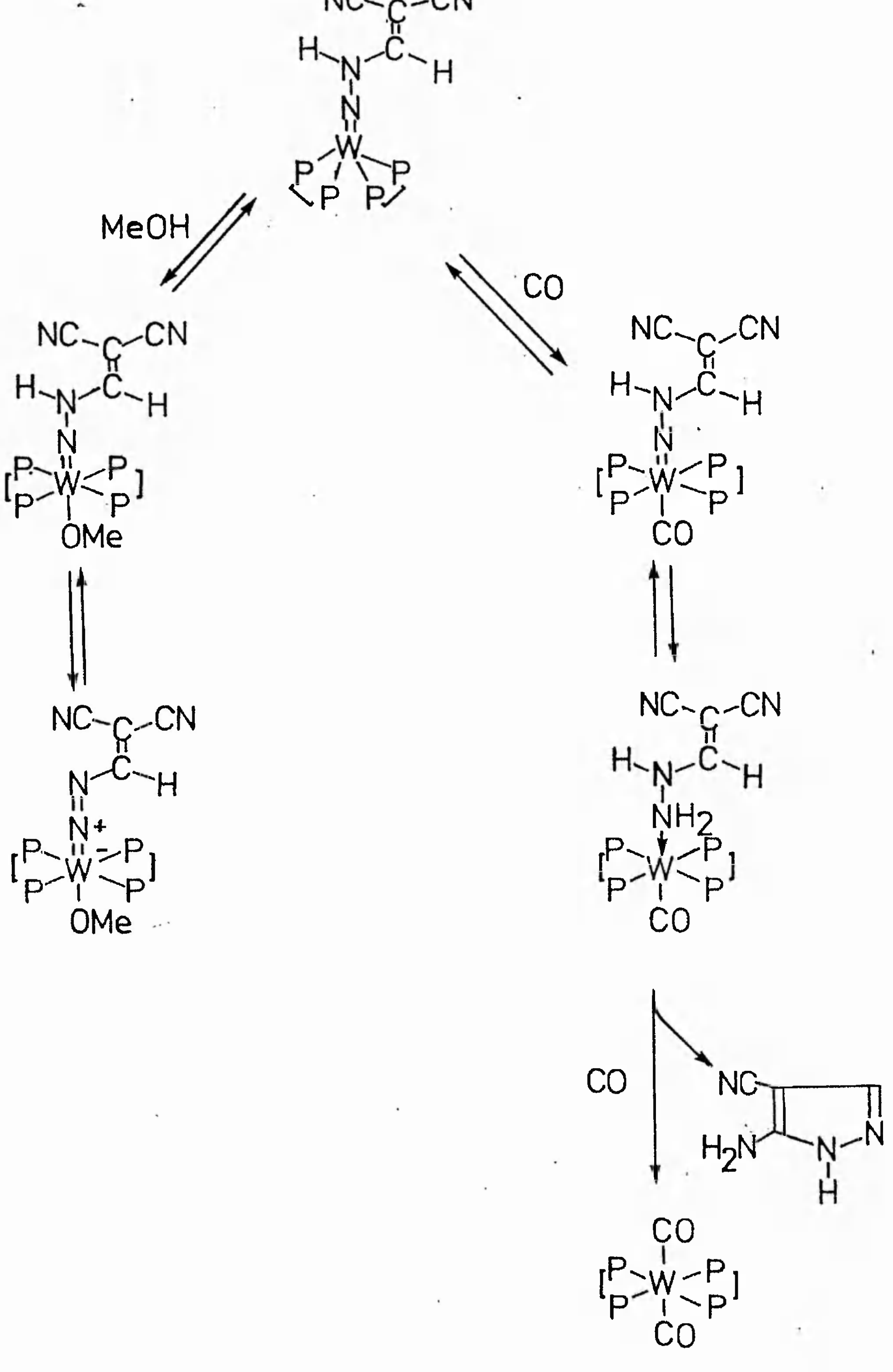


Figure 98

CHAPTER FOUR

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

Several conclusions may be drawn from the work presented in this thesis and they are summarsied below.

1. New, convenient, high yield routes are reported from the synthesis of the bis(dinitrogen) complex trans $[W(N_2)_2(dppe)_2]$ and its hydrazido(2-) derivative $[WX(N_2H_2)(dppe)_2]^+$ (X = Br, F).

2. The hydrazido(2-) complexes will react rapidly with suitable cyanoalkenes in the presence of a weak base to give substituted cyanovinyldiazenido-tungsten complexes in high yield. The complexes are air stable in the solid state.

3. Alkenes which will react with the hydrazido(2-) complexes are either commercially available (1,1-dicyano-2-ethoxyethene; Aldrich Chemical Co. Ltd) or readily synthesised by a one step process as indicated in the Experimental section. More reactive alkenes containing a chloride leaving group (1,1-dicyanovinyl-2-chloroethene, 1,1-dichloro-2,2-dicyanoethene), 2-chloro-1-cyano-1-ethoxycarbonylethene) may be quite readily synthesised as indicated in the Experimental section, and are stable when stored at 0°C.

4. The dicyanovinylhydrazido(2-) complexes, prepared by *in situ* protonation of the diazenido analogues with HBF_4 or from the appropriate alkene and a substituted hydrazido(2-) complex with base, may be reduced electrochemically at a mercury pool cathode to give aminocyanopyrazoles in moderate yields;

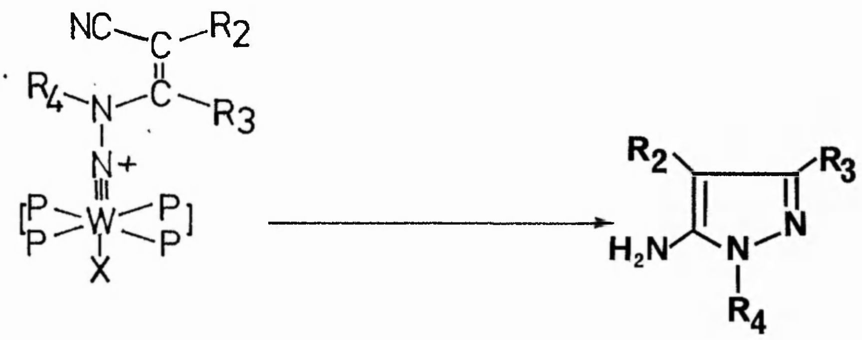


Figure 99

(X = F, Br; R_2 = CN, CO_2Et; R_3 = H, Cl; R_4 = H, CH_3). The range imposed on the substituents R_2, R_3 and R_4 is outlined in the

Results and Discussion section.

5. Comparison of the cycle (figure 97) with the cycle developed at the University of Sussex (figure 26) shows the former has the following features:

   (i) carbon-nitrogen bond formation is very rapid, compared with the free-radical reaction;

   (ii) the organic products obtained at the end of the reduction (aminocyanopyrazoles) are more interesting in terms of industrial importance and synthetic utility, compared with the formation of simple dialkylhydrazines, although the starting reagents are more expensive;

   (iii) it is a true cyclic process (although yields of organic product on the second and subsequent cycles are low, and more work is required in this area).

6. Additionally a series of cyanoalkenes were found which could partake in a substitution reaction with tungsten hydrazido(2-) complexes to produce nitrile derived methyleneamino-complexes.

7. The use of an alternative source of coordinated dinitrogen, $[MoF(N_2H_2)(PPh_3)(triphos)]^+BF_4^-$, in an attempt to overcome the steric difficulties presented by the dppe ligands, was largely unsuccessful. This is attributable to the overall instability of this hydrazido(2-) complex and the readiness with which it will lose the nitrogen ligand in both the solid state and in solution.

8. The use of alkenes activated by metal complexes with $[WX(N_2H_2)(dppe)_2]^+$ (X = F, Br) was unsuccessful, presumably due to the comparatively large size of the metal-alkene π complex. However, a hydrazido(2-) complex was identified, obtained from a reaction between the metal complex used to activate the alkene and the hydrazido(2-) complexes.

9. The kinetics for the formation of the 1,1-dicyano-2-chlorovinyldiazenido(1-) tungsten complex were studied using stopped flow techniques, and were found to be consistent with an addition-elimination mechanism.

10. The bis(dinitrogen) complex, $[W(N_2)_2(dppe)_2]$, was found to react with suitable organic electron acceptors to give radical anion complexes. A novel 1:1:2 complex was isolated when the electron acceptor molecule was TCNQ.

Several areas for further work on the cyanovinyldiazenido(1-) and hydrazido(2-) tungsten complexes are suggested below:

1. Increase the size of R_4 (figure 99) to -Et, Pr^n, Pr^i, Bu^t, for example, in order to investigate how this group affects the coordination of a dicyano- or cyanoethoxycarbonyl-alkene, thereby increasing the versatility of the system.

2. Investigate the use of alternative electrode materials for the electrochemical reduction of the cyanovinylhydrazido(2-) tungsten complexes. The complexes appear to have some reactivity with both mercury and platinum electrodes, and in the former case, possibly accounts for the inability to generate a workable cyclic process. Alternative electrode materials could include gold or carbon.

3. Consider the use of alternative alkenes, preferably cheaper and more readily available than the cyanoalkenes used so far, for example tetrafluoroethene or allene. Also, further investigation into the possibility of a cyanoethylation reaction between the hydrazido(2-) complex and acrylonitrile is recommended.

A more fundamental and perhaps more effective change in the system would be the use of a different source of coordinated dinitrogen. The neutral hydrazido(2-) complexes $[WX_2(N_2H_2)(P)_3]$ (X = Cl, Br, I; P = PMe_2Ph, $PMePh_2$) would be ideal for this system, since the phosphine ligands are less bulky than dppe and the complex is neutral and therefore would be expected to approach the alkene more readily, compared with the cationic $[WX(N_2H_2)(dppe)_2]^+$ (X = F, Br). Unfortunately the advantages are likely to be counterbalanced by the instability of the complex and the lability of the metal-nitrogen bond. The diazenido complex $[WX(N_2H)(P)_3]$, presumably an intermediate in any reaction with an alkene, is unknown. The use of mixed phosphine complexes, for example $[W(N_2)_2(dppe)(PMe_2Ph)_2]$ is possible, but the hydrazido(2-) complex has not been reported. Finally, the use of $[W(N_2)_2(depe)_2]$ may be advantageous, since the ligands are less bulky and more basic than in the corresponding dppe complex and the presence of two chelating diphosphine ligands may lead to exhanced stability in the bis(dinitrogen) complex, compared with the presence of four monodentate phosphine ligands. Unfortunately once again the nydrazido(2-) complex has not been isolated.

CHAPTER FIVE

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Reactions of Cyanoalkenes with a Tungsten Hydrazido(2−) Complex: the *X*-Ray Crystal Structure of [WBr(dppe)$_2${NC(Br)C(CN)C(CN)$_2$}],† a Bromotricyanoprop-2-enylideneamino-complex

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Cyanoalkenes react with the dinitrogen-derived hydrazido(2 −) complex [WBr(dppe)$_2$N$_2$H$_2$]$^+$ Br$^-$ (**1**) to form either vinyldiazenido-complexes or, after loss of the hydrazido(2 −) ligand, to form nitrile-derived methyleneamino-complexes; the product of reaction with tetracyanoethylene is a bromotricyanoprop-2-enylideneamino-complex which has been characterised by single-crystal *X*-ray analysis.

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Dinitrogen-derived hydrazido(2−) complexes of molybdenum and tungsten[1] have been shown to undergo condensations with aldehydes, ketones,[2] and in the presence of base, with 2,4-dinitrofluorobenzene,[3] to give complexes of organodinitrogen ligands. Here we report the results of a study employing the hydrazido(2−) ligand in reactions with alkenes activated by electron-withdrawing substituents. This work not only provides the first examples of carbon–nitrogen bond formation resulting from reactions of alkenes with a dinitrogen-derived ligand, but also shows that the hydrazido(2−) ligand is susceptible to oxidative substitution by certain cyanoalkenes.

In a typical reaction leading to C–N bond formation [equation (1)], the alkene (1 mmol) was added to a solution of (1) (1 mmol) in dichloromethane at room temp. under dinitrogen. Triethylamine (0.5 cm^3) was added dropwise, resulting in an immediate colour change, and the solution was washed with water, dried, evaporated to dryness, and the residue recrystallised from dichloromethane–methanol.‡ Yields were generally

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† dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$.

‡ Satisfactory analytical and spectroscopic data have been obtained for all new complexes.

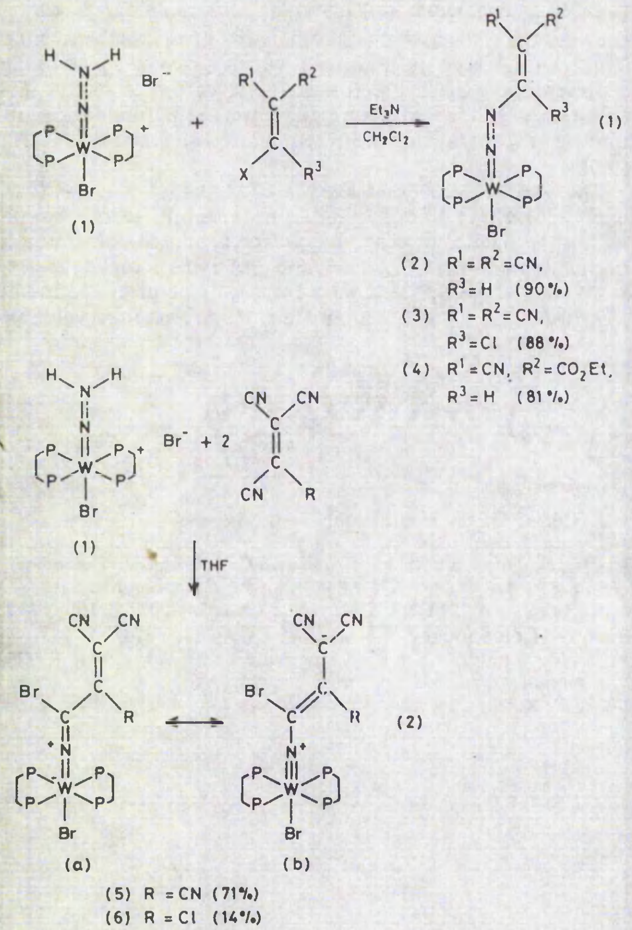

Table 1. Alkenes ($R^1R^2C{:}CR^3X$) which react according to equation (1).

R^1	R^2	R^3	X
CN	CN	H	Cl
CN	CN	Cl	Cl
CN	CO_2Et	H	Cl
CN	CN	H	OEt

>90%. The resulting complexes (**2**), (**3**), and (**4**) showed strong i.r. bands around 2200 (ν C≡N) and 1500 cm^{-1} (ν C=C/N=N), as well as ^{13}C n.m.r. resonances in the range 116—118 p.p.m. (δ Me$_4$Si 0 p.p.m.) assigned to nitrile carbon atoms. Complex (**4**) showed ^{13}C n.m.r. resonances characteristic of the ethoxycarbonyl group at 58.09 (–OCH$_2$–), 14.7 (–CH$_3$), and 160.9 p.p.m. (–CO–), and perhaps most conclusively, the physical and chemical properties of complex (**3**) were identical with those of the compound prepared independently from $[WBr(dppe)_2N_2CCl_2]^+$ and $[CH(CN)_2]^-$, for which an *X*-ray crystal structure is available.[4] We therefore believe complexes (**2**) and (**4**) to have analogous structures.

Table 1 lists those alkenes which react according to equation (1). However, several other apparently similar alkenes failed to react, and there appears to be a dependence on (i), the degree of electron withdrawal provided by R^1 and R^2, (ii), the nature of the potential leaving group X, and (iii), the nature of R^3. Thus, when $R^1 = R^2 =$ CN, reaction occurs readily for X = Cl or OEt, whereas when $R^1 = R^2 = CO_2Et$, no reaction is observed. Alternatively, X = Cl successfully acts as a leaving group when R^1 = CN and $R^2 = CO_2Et$, though X = OEt fails to react when the same substituents are present.

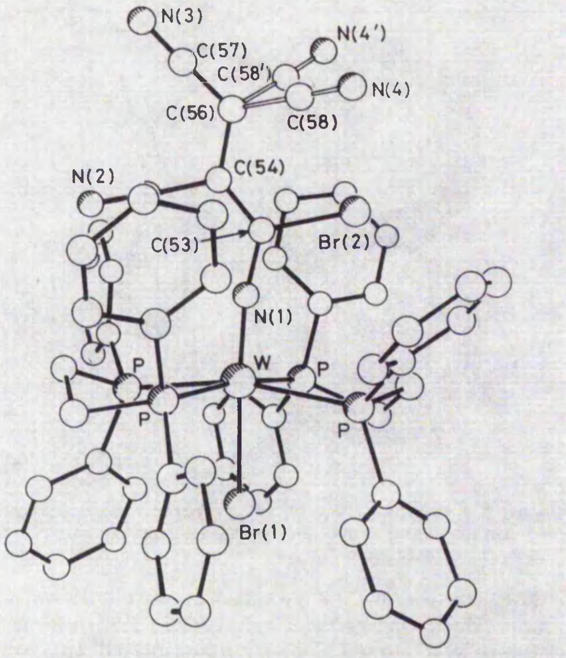

Figure 1. The molecular structure of (**5**). The W atom is displaced 0.25 Å from the mean plane of the four P atoms. Selected bond lengths and angles: W–P 2.523(2)—2.561(2), W–Br(1) 2.558(1), W–N(1) 1.777(6), N(1)–C(53) 1.34(1), C(53)–Br(2) 1.902(8), C(53)–C(54) 1.37(1), C(54)–C(56) 1.43(2), and C(56)–C(57) 1.37(2) Å; W–N(1)–C(53) 171.4(5) and Br(1)–W–N(1) 174.8(2)°.

In a different type of reaction [equation (2)] involving tetracyanoethylene (TCNE) (2 mmol) and complex (**1**) in tetrahydrofuran at room temp. in the *absence* of base, loss of the hydrazido(2−) ligand resulted. The product (**5**) gave strong i.r. bands at 2180, 2150 (ν C≡N), and 1465 cm^{-1} (ν C=C/C=N), the ^{13}C n.m.r. spectrum contained resonances at 119.6 (CN), 114.6 (CN), and 135.3 p.p.m. (C=C), and the visible spectrum had an absorption centred at 510 nm (ε = 51 000).

A single crystal *X*-ray study§ (Figure 1) revealed the structure of this product (**5**), which appears to be formed by addition of a bromide ion to a co-ordinated TCNE molecule.[5] Presumably the first mole of TCNE oxidatively deprotonates the hydrazido(2−) ligand to give an unstable dinitrogen complex $[WBr(dppe)_2N_2]^+$ which loses N$_2$, thereby providing a vacant site for co-ordination of a second mole of TCNE. Addition of bromide to the co-ordinated nitrile results in an 18-electron configuration for the complex. Chlorotricyanoethylene undergoes a similar reaction to give an analogous product (**6**).

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§ *Crystal data:* Crystals of (**5**) are monoclinic, $a = 26.473(5)$, $b = 14.443(4)$, $c = 30.144(4)$ Å, $\beta = 102.51(1)°$, $U = 11\,251$ Å^3, space-group $C2/c$, $Z = 8$. Of the 5770 independent reflections ($\theta \leqslant 50°$), measured on a diffractometer using Cu-K_α radiation, 749 were classified as unobserved. The structure was solved by the heavy-atom method and refined anisotropically using absorption-corrected data to give $R = 0.042$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

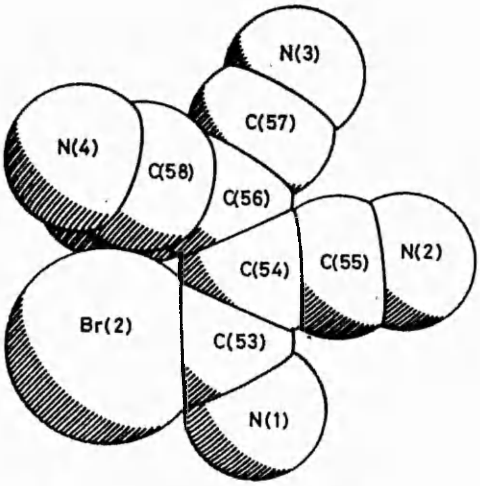

Figure 2. Space-filling model of the bromotricyanoprop-2-enylideneamino-ligand showing the steric interaction between bromo- and cyano-substituents.

The structure of (**5**) shows disorder in the distant $C(CN)_2$ group which undergoes a tetrahedral distortion with the cyano-carbon atom C(58), C(58′) displaced approximately 1 Å either above or below the mean plane of the alkene. This apparently results from a steric interaction between the cyanide [C(58)–N(4)] and the adjacent bromine atom which prevents the alkene achieving coplanarity of all its substituents. This can be seen in Figure 2 which gives a space-filling representation of this region of the structure. A charge-distribution which would permit the observed pyramidal distortion at C(56) is shown in equation (2) [canonical form (**5b**)].

The very similar bond lengths C(53)–C(54), C(54)–C(56), and C(56)–C(57) do in fact indicate substantial delocalisation within the ligand, in keeping with the proposed contribution of the two canonical forms (**5a**) and (**5b**) to the actual structure.

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