



DIAZADIENE AND ISOCYANIDE CHLOROCOMPLEXES OF TUNGSTEN IN VARIOUS FORMAL OXIDATION STATES

A variety of tungsten chlorocomplexes with the diazabutadiene $\widehat{N}N=RN=CHCH=NR$ (where $R=4-C_6H_4OMe$) or the diamine $\widehat{N}N=Me_2NCH_2CH_2NMe_2$ as chelating or bridging ligands were prepared in a wide range of the metal oxidation state (from +5 to +2), from reactions of WCl_6 or $[WCl_4(PPh_3)_2]$.

Reaction of WCl_6 with $\widehat{N}N$, in the presence of zinc amalgam, yielded the $W(V)$ species $[WCl_4(\mu-\widehat{N}N)]$ and the $W(IV)$ complex $[WCl_4(\widehat{N}N)]$. Other $W(IV)$ complexes, $[WCl_4(\widehat{N}N)_2]Cl_2$ and $[WCl_3(\widehat{N}N)(\mu-\widehat{N}N)]Cl_2$, were derived from substitution reactions of $[WCl_4(PPh_3)_2]$; a related molybdenum(III) species, $[MoCl_3(\widehat{N}N)(\mu-\widehat{N}N)]$, was formed from a similar reaction of $[MoCl_3(thf)_3]$ with $\widehat{N}N$.

Species in which the tungsten metal appears to be in a formal oxidation state of +3 were prepared from reduction of WCl_6 by zinc amalgam in the presence of an excess of $\widehat{N}N$: $[WCl_4(\widehat{N}N)(\mu-Cl)_2]$ and $[W(\widehat{N}N)_3]Cl_3$.

Further reduction to $W(II)$ was also achieved in the following complexes: $[WCl_2(\widehat{N}N)(\mu-\widehat{N}N)_2]$ prepared from reduction of WCl_6 by zinc amalgam in the presence of $\widehat{N}N$; $[WCl_2(\widehat{N}N)_2]$ from reduction of $[WCl_4(PPh_3)_2]$ by magnesium metal in the presence of $\widehat{N}N$ (the analogous $Mo(II)$ complex $[MoCl_2(\widehat{N}N)_2]$ was also prepared from reduction of $[MoCl_3(thf)_3]$ by sodium in the presence of $\widehat{N}N$).

Methylisocyanide may also bind these metal sites and the $W(IV)$ complex $[WCl_4(CNMe)(\mu-\widehat{N}N)]$ was prepared from reaction of the above mentioned species $[WCl_4(\mu-\widehat{N}N)]$ with an excess of $CNMe$. An isocyanide complex with the tungsten atom in a formal oxidation state of +2, $[WCl_2(CNMe)(\widehat{N}N)]$ was also prepared from the reaction of $[WCl_4(PPh_3)_2]$ with $\widehat{N}N$ in the presence of $CNMe$ and sodium sand.

1 — INTRODUCTION

Diazadienes, unsaturated compounds formulated as $RN=C(R')C(R')=NR$, when ligating a metal atom, may exhibit various formal charges and different binding modes. This potential behaviour may provide the metal site with a high flexibility to adapt itself to the electronic and stereochemical requirements of other co-ligands to participate in a versatile chemistry.

When ligating a transition metal atom, diazadienes may behave as predominant σ donors but the bonding may also have a strong π component namely when the metal site is electron rich and an electronic acceptance of unfilled C-N π antibonding ligand orbitals occurs [1] from metal d filled orbitals.

The electron release and withdrawing abilities of the diazadienes may also be accounted for by VB representations such as those shown in fig. 1 which refer to a chelating ligand. Resonance forms (a) and (b) are the higher weighted ones when the diazadienes behave mainly as σ donors, whereas forms (c) and (d) account for the electron withdrawing ability of those ligands

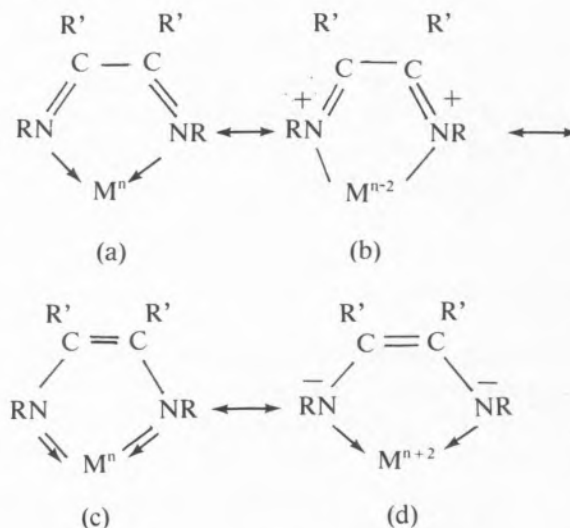


Fig. 1

VB representation of a chelating diazadiene ligand

The binding versatility of the diazadienes has already been ascertained in various compounds.

Hence, they may behave as σ monodentate ligands, through coordination via σ donation of the electron

pair located at one of the nitrogen atoms, as in the complexes $[\text{PdCl}_2(\text{DAB})_2]$ [2] and $[\text{M}(\text{CO})_5(\text{DAB})]$, [3] where DAB is a diazobutadiene (diazadiene with $\text{R}' = \text{H}$) and $\text{M} = \text{Cr}, \text{Mo}$ or W .

Diazabutadienes acting as σ, σ donors bridging two metal atoms are also known as in the complexes $[\{\text{PtCl}_2(\text{PBU}_3)\}_2(\mu\text{-DAB})]$ [4], and $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2(\mu\text{-DAB})]$, [2] whereas a σ, σ chelating binding is common, being present, *e.g.*, in the complexes $[\text{M}(\text{CO})_4(\text{DAB})]$ [1,5] ($\text{M} = \text{Cr}, \text{Mo}$ or W).

Although a diazadiene is expected to be able to electronic π acceptance from an electron rich metal site, it may also be regarded, in some cases, as a π donor through the filled C-N π bonding orbital, as authenticated by the X-ray structure determination of $[\text{Fe}_2(\text{CO})_6(\text{DAB})]$ where the DAB species behaves as a six-electron σ, π donor ligand [6].

Catalysis constitutes another recent aspect in the studies of diazadiene complexes, and, *e.g.*, $[\text{Ni}(\text{RN}=\text{CHCH}=\text{NR})_2]$ ($\text{R} = \text{CHPr}^t$) is a catalyst for the tetramerization of $\text{HC}\equiv\text{CX}$ (where $\text{X} = \text{CH}_2\text{OH}, \text{CMe}_2\text{OH}, \text{CH}_2\text{OMe}, \text{CMe}_2\text{NH}_2$), $[\text{Fe}(\text{RN}=\text{CHCH}=\text{NR})_2]$ activated by AlEt_3 catalyses the dimerization of dienes, and the coordinatively unsaturated complex $[\text{Cr}(\text{RN}=\text{CHCH}=\text{NR})_2]$ or $[\text{V}(\text{RN}=\text{CHCH}=\text{NR})_3]$ with trialkylaluminium catalyses the tail-to-tail dimerization of isoprene [7]. Apart from the abovementioned importance of the diazadiene complexes, we are also interested on the fixation of isocyanides to transition metals and on the study of the reactivity of the derived species, in attempting to establish the experimental conditions which may be suitable for binding and activation of dinitrogen once the analogy of behaviour between these two species has been previously demonstrated [8].

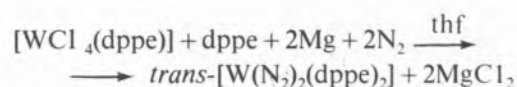
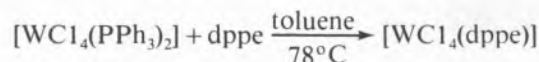
In a previous paper [9], we have reported the products from the reactions of $[\text{MoCl}_3(\text{thf})_3]$ (which is a parent of *trans*- $[\text{Mo}(\text{N})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$) with diazadienes and isocyanides, and we wish now to present the results from the reactions of another dinitrogen complex precursor, $[\text{WCl}_4(\text{PPh}_3)_2]$ (and of the parent WCl_6), with the diazabutadiene $\text{RN}=\text{CHCH}=\text{NR}$ (where $\text{R} = 4\text{-C}_6\text{H}_4\text{OMe}$), the diamine $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ and the methylisocyanide.

2 — RESULTS

2.1 — REACTIONS OF $[\text{WCl}_4(\text{PPh}_3)_2]$ WITH DIAZADIENE ($\text{N}\equiv\text{N}$) OR DIAMINE ($\text{N}\equiv\text{N}$)

2.1.1 COMPLEXES WITHOUT ISOCYANIDE

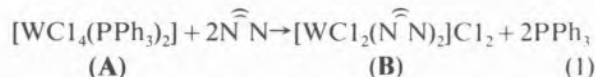
Once the dinitrogen complex *trans*- $[\text{W}(\text{N})_2(\text{dppe})_2]$ (where $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) is conveniently prepared [10] from $[\text{WCl}_4(\text{PPh}_3)_2]$ according to scheme 1, we have started by attempting similar reactions using the diazabutadiene $\text{RN}=\text{CHCH}=\text{NR}$ ($\text{N}\equiv\text{N}$ where $\text{R} = 4\text{-C}_6\text{H}_4\text{OMe}$) instead of the dppe species.



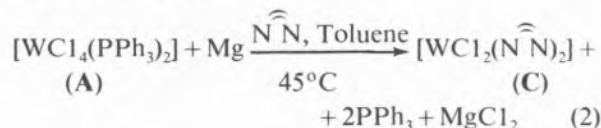
Scheme 1

Preparation of *trans*- $[\text{W}(\text{N})_2(\text{dppe})_2]$

Hence, from reaction of $[\text{WCl}_4(\text{PPh}_3)_2]$ (**A**) with $\text{N}\equiv\text{N}$, first in toluene and then in thf, under N_2 , a species formulated as $[\text{WCl}_2(\text{N}\equiv\text{N})_2]\text{Cl}_2$ (**B**) was formed upon replacement (reaction 1) of the phosphine and chloride ligands by the diazabutadiene (used in a total amount corresponding to a molar ratio of 2.5:1 relative to the W metal).



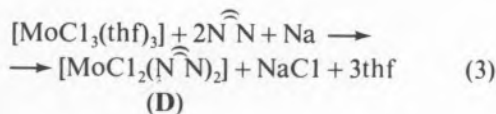
Moreover, in the presence of Mg, reduction also occurs and by using a smaller amount of diazabutadiene [2.0 excess relative to the starting species (**A**)], the complex $[\text{WCl}_2(\text{N}\equiv\text{N})_2]$ (**C**) was obtained according to reaction (2).



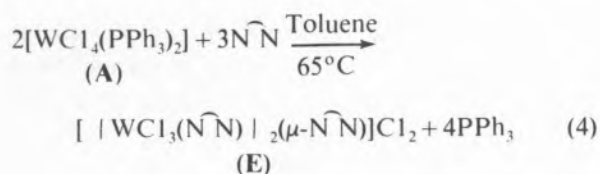
Complexes (**B**) and (**C**) have been formulated on the basis of microanalytical and infrared data and magnetic susceptibility measurements.

They display broad bands in the infrared spectrum at $240\text{--}300\text{ cm}^{-1}$ which are ascribed to $\nu(\text{W-C1})$, and two strong bands at *ca.* 1600 and 1500 cm^{-1} due to $\nu(\text{C}=\text{N})$ of the ligating diazabutadiene, as it has been observed [9] in other diazabutadiene species such as $[\text{MoCl}_3(\text{CNMe})(\text{N}\equiv\text{N})]$ and

[MoCl₂(CNMe)₂($\widehat{\text{N}}\widehat{\text{N}}$)]. Complex (**C**) is analogous to [MoCl₂($\widehat{\text{N}}\widehat{\text{N}}$)₂] (**D**), which was also prepared in the present work, upon reduction of [MoCl₃(thf)₃] by sodium in the presence of $\widehat{\text{N}}\widehat{\text{N}}$ (equation 3). Species (**D**) has $\nu(\text{Mo}-\text{Cl})$ at 330 cm⁻¹, $\nu(\text{C}=\text{N})$ at 1595 and 1493 cm⁻¹, and (**B**), (**C**) and (**D**) are paramagnetic with values of μ_{eff} which agree with two unpaired electrons as it may be expected for octahedral d² (in complex **B**) or d⁴ (in complexes **C** and **D**) metal atoms.

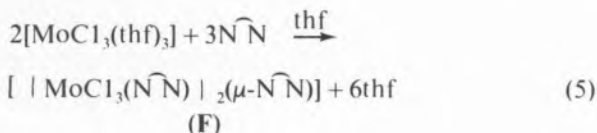


Reactions of $[\text{WC1}_4(\text{PPh}_3)_2]$ (**A**) with diamine $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ($\widehat{\text{N}}\widehat{\text{N}}$) have also been tried, and from a mixture of (**A**) with $\widehat{\text{N}}\widehat{\text{N}}$ (1:3) in toluene at 65°C , a species formulated as $[\{\text{WC1}_3(\widehat{\text{N}}\widehat{\text{N}})\}_2(\mu\text{-}\widehat{\text{N}}\widehat{\text{N}})]\text{Cl}_2$, (**E**), was obtained (reaction 4). In its infrared spectrum, $\nu(\text{W-C1})$ appears at 310 s, br and 345 w , and strong and broad bands may also be seen at 2560 and 2450 cm^{-1} ; similar bands have also been observed in other diamine complexes (see below) and they are suggested to be due to $\nu(\text{C-H})$ where the hydrogen atom is involved in hydrogen bond probably with a chlorine atom.



Complex (E) is paramagnetic and the value of μ_{eff} (2.5) agrees with an octahedral d^2 metal.

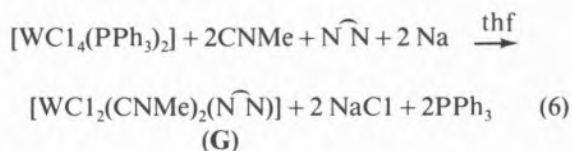
A molybdenum(III) species which is related to complex (E) was also prepared in the present study from reaction of $[\text{MoCl}_3(\text{thf})_3]$ with the diamine $\text{N}\widehat{\text{N}}$ (1:3.5) in thf (reaction 5); its formulation as $[\text{MoCl}_3(\text{N}\widehat{\text{N}})]_2(\mu\text{-N}\widehat{\text{N}})$, (F), was also based on the elemental microanalytical and infrared data and on the value of μ_{eff} (3.6 B.M.).



In the infrared spectrum of complex (**F**), $\nu(\text{Mo}-\text{Cl})$ is observed at 300 and 275 cm^{-1} , whereas strong and broad bands at 2550 and 2440 cm^{-1} are also present as in the related species (**E**).

2.1.2 — ISOCYANIDE COMPLEXES

From reaction in thf of $[\text{WCl}_4(\text{PPh}_3)_2]$ with CNMe and the diamine NN (in molar ratios of 1:4:2.2), in the presence of sodium metal, the tungsten(II) complex $[\text{WCl}_2(\text{CNMe})_2(\text{N}\text{N})]$, (**G**), was obtained according to reaction 6, *via* metal reduction and phosphine displacement.



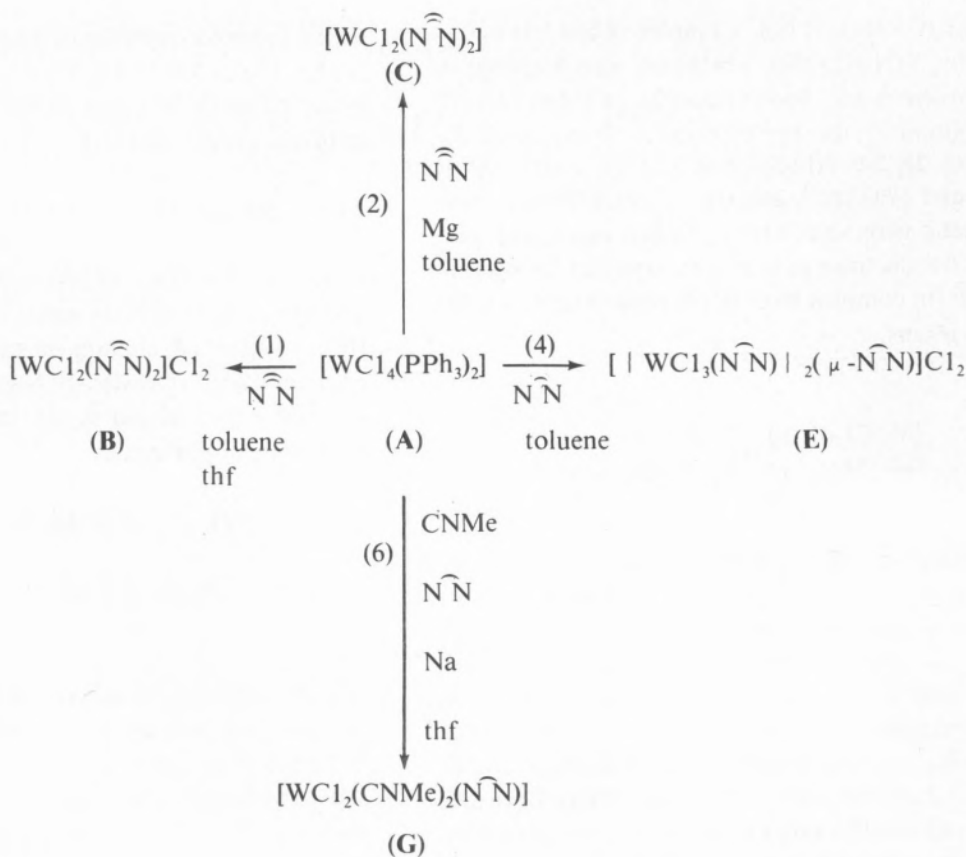
The characterization of complex (**G**) was based on the same techniques used for the previous species. Its infrared spectrum shows $\nu(\text{W}-\text{Cl})$ and $\nu(\text{C}\equiv\text{N})$ of the coordinated isocyanide as broad and strong bands at 305 and 2150 cm^{-1} , respectively. The value of μ_{eff} , 2.7 B.M., agrees with a high spin d^4 metal site. This complex is analogous to the previously reported [9] $[\text{MoCl}_2(\text{CNMe})_2(\text{N}\widehat{\text{N}})]$, which exhibits $\nu(\text{C}\equiv\text{N})$ at 2145 and 2130 cm^{-1} and $\nu(\text{Mo}-\text{Cl})$ at 305 cm^{-1} .

The two expected bands for $\nu(\text{C}\equiv\text{N})$ are not observed probably due to their broadness and overlap. All the abovementioned reactions of $[\text{WCl}_4(\text{PPh}_3)_2]$ are summarized in the scheme 2.

2.2 — REACTIONS OF WCl_6 WITH DIAZADIENE OR DIAMINE

Tungsten hexachloride is the precursor for $[\text{WCl}_4(\text{PPh}_3)_2]$ (**A**) which is derived from the former upon reduction by zinc amalgam in CH_2Cl_2 in the presence of PPh_3 [10].

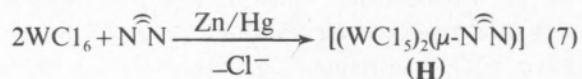
Once we are interested in the preparation of complexes of diazadienes which may be precursors for new dinitrogen complexes with these co-ligands, we have also investigated the reactivity of $WC1_6$ towards the diazabutadiene $\widehat{N}N$ and a related diamine $\widehat{N}N$ mentioned above, under reduction conditions which are similar to those used in the preparation of $[WC1_4(PPh_3)_2]$.



Scheme 2

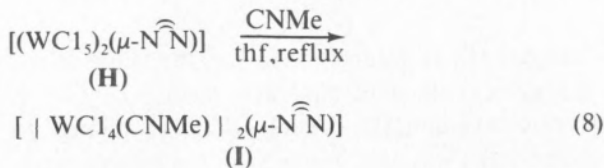
Reactions of $[\text{WC1}_4(\text{PPh}_3)_2]$ with diazabutadiene ($\widehat{\text{N}}\widehat{\text{N}}$) or diamine ($\widehat{\text{N}}\widehat{\text{N}}$) and methylisocyanide

Hence, from reaction in CH_2Cl_2 of WC1_6 with $\widehat{\text{N}}\widehat{\text{N}}$ in a molar ratio of 1:1.1 and in the presence of Zn/Hg, reduction of the metal occurs and the tungsten(V) complex, with bridging diazabutadiene, $[(\text{WC1}_3)_2(\mu\text{-}\widehat{\text{N}}\widehat{\text{N}})]$, (**H**), was isolated after ca. 10h reaction (equation 7). This species was characterized on the basis of microanalytical and infrared data and of the magnetic properties. Bands in the infrared spectrum due to $\nu(\text{C}=\text{N})$ of the diazabutadiene ligand are present at 1605, 1575 and 1500 cm^{-1} , whereas bands at 345 and 332 cm^{-1} are ascribed to $\nu(\text{W}-\text{Cl})$. The value of μ_{eff} (1.4 B.M.) agrees with a d¹ metal centre.



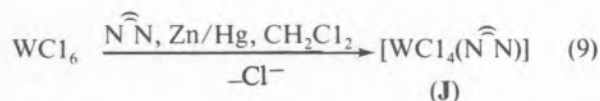
Complex (**H**) reacts with methylisocyanide (1:6) in thf at reflux, yielding the methylisocyanide tungsten(IV) species $[|\text{WC1}_4(\text{CNMe})|_2(\mu\text{-}\widehat{\text{N}}\widehat{\text{N}})]$,

(**I**), which retains the bridging diazabutadiene ligand (reaction 8). In the infrared spectrum of this complex, $\nu(\text{C}\equiv\text{N})$ of the coordinated isocyanide appears at 2220 cm^{-1} , well above the value encountered for free CNMe (ca. 2160 cm^{-1}) in



agreement with the expected predominance of the σ electronic donation (from the ligating isocyanide to the electron poor metal) over the π acceptance of that ligand. Bands at 1695 and 1630 cm^{-1} are also present and they are assigned to $\nu(\text{C}=\text{N})$ of the ligating diazabutadiene; $\nu(\text{W}-\text{Cl})$ appears at 305 and 290 cm^{-1} . Complex(**I**) is also paramagnetic and the value of μ_{eff} , 2.6 B.M., is in agreement with a high-spin d² metal centre.

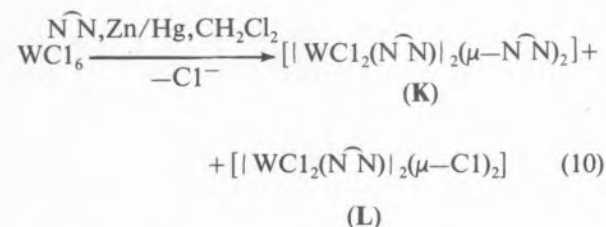
Another species, tentatively formulated as $[\text{WC}_4(\text{N}\widehat{\text{N}})]$ or $[(\text{WC}_4)_2(\mu\text{-N}\widehat{\text{N}})_2]$, (**J**), was isolated after 24 h reaction of WC_6 with an excess (1.5:1) of the diazabutadiene, also in CH_2Cl_2 and in the presence of Zn/Hg (reaction 9). In the infrared spectrum $\nu(\text{C}=\text{N})$ appears at 1600 and 1505 cm^{-1} , whereas $\nu(\text{W}-\text{Cl})$ is observed at *ca.* 303 and 275 cm^{-1}



Species (**J**) is diamagnetic but the low solubility in the usual solvents precluded N.M.R. studies and molecular weight measurements, thus preventing the distinction between the two formulations.

Reactions of WC_6 with the diamine $\text{N}\widehat{\text{N}}$ were also tried, and various reduced species with chelating or bridging diamine appear to be formed in the presence of zinc amalgam as a reducing agent.

Hence, two species formulated as $[\text{WC}_4(\text{N}\widehat{\text{N}})]_2$ ($\mu\text{-N}\widehat{\text{N}}_2$), (**K**), and $[\text{WC}_4(\text{N}\widehat{\text{N}})]_2(\mu\text{-Cl})_2$, (**L**), have been isolated from the reaction mixture of WC_6 with an excess of $\text{N}\widehat{\text{N}}$ (1:7.2) and Zn/Hg in CH_2Cl_2 (reaction 10).

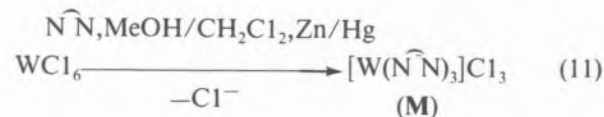


The infrared spectra of these complexes exhibit $\nu(\text{W}-\text{Cl})$ as broad bands at 290 (**K**) and 280 cm^{-1} (**L**). Strong and broad bands at *ca.* 2720 (**K**), 2705 (**L**), 2560 (**K,L**) and 2440 cm^{-1} (**K,L**) are also observed, as it has been mentioned above for the diamine complexes (**E**) and (**F**) and they are also assigned to $\nu(\text{C}-\text{H}\dots\text{Cl})$ (see below).

Complex (**K**) is diamagnetic, whereas (**L**) is paramagnetic with $\mu_{\text{eff}} = 4.0$ B.M. in agreement with a high-spin d^3 metal centre, (the spin only value is 3.87 B.M.). The low solubility of complex (**K**) in the usual solvents precluded N.M.R. measurements.

If an excess of diamine is added to solid WC_6 , a vigorous reaction occurs and addition of a mixture

of $\text{MeOH}/\text{CH}_2\text{Cl}_2$ followed by Zn/Hg , leads to the formation of a species which may be formulated as the tungsten(III) complex $[\text{W}(\text{N}\widehat{\text{N}})_3]\text{Cl}_3$, (**M**) (reaction 11).



This species is paramagnetic with $\mu_{\text{eff}} = 3.5$ B.M., its infrared spectrum does not exhibit any band which could be assigned to $\nu(\text{W}-\text{Cl})$, whereas broad bands are observed at 2620 s, 2570 s, 2450 s and 2410 sh. These bands are only partially replaced by others (also broad, at 2000, 1920 and 1845 cm^{-1}) by stirring for two days in a mixture of $\text{thf}/\text{D}_2\text{O}$. Hence they are not ascribed to $\nu(\text{N}-\text{H})$ once in this case the H/D exchange would be very facile; we suggest they refer to $\nu(\text{C}-\text{H})$ where the H atom is involved in hydrogen bonding [11] with a chlorine atom. Similar bonds were also observed in other diamine complexes (**E,F,K** and **L**) as reported above.

The abovementioned reactions of WC_6 are summarized in scheme 3.

3 — FINAL REMARKS

The preparation of the complexes described in the present study is strongly dependent and very sensitive to the experimental conditions employed. Diazabutadiene or diamine appear to chelate or bridge tungsten atoms in a wide range of oxidation states [including the very unusual W(III) oxidation state] and methylisocyanide ligating W(IV) or W(II) metal sites exhibits in the infrared spectra $\nu(\text{C}\equiv\text{N})$ at higher or only slightly lower values than in the free molecule. Hence, these centres are not able to bind dinitrogen, and lower metal oxidation states are undoubtedly required for such [8,12].

However, the potential lability of these complexes which may be susceptible to variations in the metal oxidation state and to replacement and rearrangement of versatile ligands to different binding types, constitutes an interesting feature which may be worthwhile to exploit namely in catalysis.

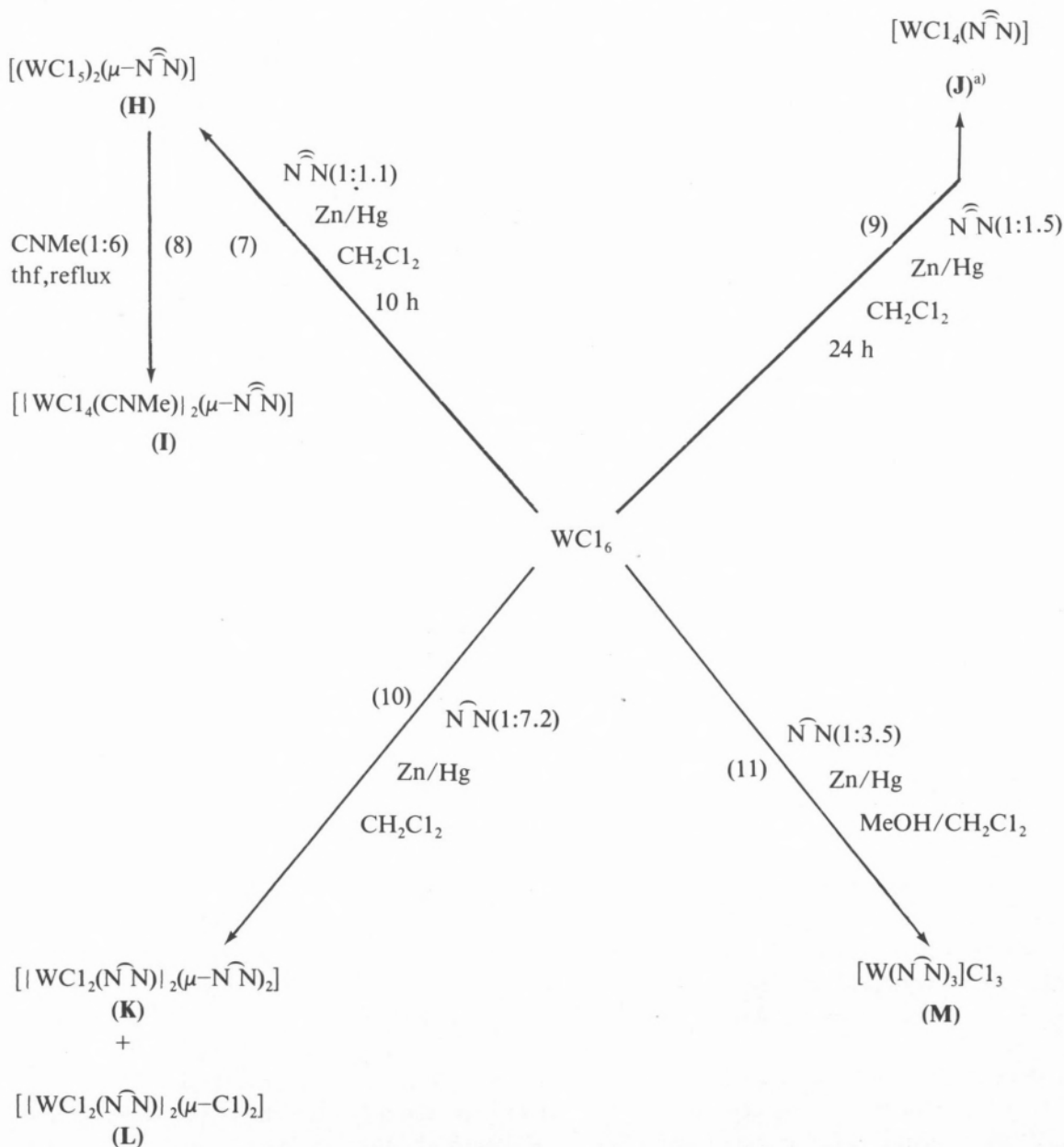
4 — EXPERIMENTAL

All the reactions were carried out under dinitrogen using dried and purified solvents by standard methods, unless otherwise stated.

Infrared spectra were recorded on a 577 or 457 Perkin Elmer Grating Infrared Spectrophotometer using Nujol mulls between caesium iodide plates.

Magnetic susceptibilities were measured using a Faraday balance.

$WC1_6$, $[WC1_4(PPH_3)_2]$ [10] and $RN=CHCH=NR$ [13] (for $R=4-C_6H_4OMe$) and $CNMe$ [14] were prepared by published methods. The diamine $Me_2NCH_2CH_2NMe_2$ was purchased from BDH and used after purification by refluxing over KOH for 3h followed by distillation.



Scheme 3
Reactions of $WC1_6$ with diazabutadiene ($N\hat{N}$) or diamine ($N\hat{N}$) in the presence of a reducing agent (Zn/Hg)

^{a)} $[(WC1_4)_2(\mu-N\hat{N})_2]$ constitutes another possible formulation.

4.1 — REACTIONS OF $[WCl_4(PPh_3)_2]$, (A).

4.1.1 — PREPARATION OF COMPLEXES WITHOUT THE ISOCYANIDE LIGAND.

Bis[1,4-bis(4-methoxyphenyl)-1,4-diazabutadiene] dichloro tungsten(II) dichloride, $[WCl_2(RNCHCHNR)_2]$ ($R = 4-MeOPh$), (B)

Diazabutadiene (0.20 g, 0.75 mmol) was added to a suspension of $[WCl_4(PPh_3)_2]$ (0.50 g, 0.59 mmol) in toluene (8 ml) and the mixture was heated to ca. 60°C for 3 h. The solid was filtered off the solution, washed by toluene and dissolved in thf (ca. 10 ml). The thf solution was filtered to solid diazabutadiene (0.20 g, 0.75 mmol) and left overnight at ca. 65°C with a reflux condenser. The solution was then filtered and complex (B) precipitated out as a dark brown solid by addition of diethylether and cooling (50 mg, ca. 10% yield).

Bis[1,4-bis(4-methoxyphenyl)-1,4-diazabutadiene] dichloro tungsten(II) $[WCl_2(RNCHCHNR)_2]$ ($R = 4-MeOPh$), (C)

Diazabutadiene ($\widehat{N}\widehat{N}$) (0.128 g, 0.478 mmol) was added to a suspension of $[WCl_4(PPh_3)_2]$ (0.203 g, 0.239 mmol) with an excess of magnesium in toluene (5 ml) and the mixture was heated to ca. 45°C and left stirring overnight.

The solution was then filtered and the very dark solid was washed by toluene. It was recrystallised from thf/ether affording the dark brown solid (C) (0.040 g, 0.050 mmol, 21% yield).

$\mu-(N,N,N',N'-tetramethyl-1,2-diaminoethane)$ bis(trichloro($N,N,N',N'-tetramethyl-1,2-diaminoethane$)tungsten(IV))dichloride, $[WCl_2(Me_2NCH_2CH_2NMe_2)_2]$ ($\mu-Me_2NCH_2CH_2NMe_2$)Cl₂, (E)

The diamine $\widehat{N}\widehat{N}$ (0.104 ml, 0.690 mmol) was added to a suspension of $[WCl_4(PPh_3)_2]$ (0.196 g, 0.231 mmol) in toluene (ca. 25 ml) and the mixture was left stirred overnight at 65°C. The solution was filtered and the brown solid, (E), was washed by toluene (0.030 g, 0.060 mmol, 26% yield).

4.1.2 — PREPARATION OF COMPLEXES WITH THE ISOCYANIDE LIGAND

Dichlorobis(methylisocyanide)($N,N,N',N'-tetramethyl-1,2-diaminoethane$) tungsten(II), $[WCl_2(CNMe)_2(Me_2NCH_2CH_2NMe_2)]$, (G)

To a suspension of $[WCl_4(PPh_3)_2]$ (0.214 g, 0.252 mmol) in thf (10 ml), sodium metal, methyl isocyanide (0.0474 ml, 1.0 mmol) and the diamine $\widehat{N}\widehat{N}$ (0.0836 ml, 0.554 mmol) were added in this order. The solution was filtered after 1 h, concentrated and crude complex (G) was obtained as a light green solid which was recrystallised from CH_2Cl_2/Et_2O (0.040 g, 0.074 mmol, 30% yield).

4.2 — REACTIONS OF WCl_6

Preparation of $\mu-[1,4-bis(4-methoxyphenyl)-1,4-diazabutadiene]$ bis[pentachlorotungsten(V)], $[(WCl_5)_2(\mu-RNCHCHNR)]$ ($R = 4-MeOPh$), (H)

A solution of $\widehat{N}\widehat{N}$ (0.37 g, 1.4 mmol) in CH_2Cl_2 (10 ml) and zinc amalgam (1.0 g) were added to a solution of WCl_6 (0.50 g, 1.3 mmol) in CH_2Cl_2 (15 ml). A dark brown suspension was formed which was left stirring overnight. The solution was filtered, concentrated under vacuo, and complex (H) precipitated as a dark brown solid (ca. 0.20 g, 32% yield) upon addition of ether and cooling at ca. -5°C. Decomposition occurred on attempted recrystallisation from CH_2Cl_2 .

Preparation of $\mu-[1,4-bis(4-methoxyphenyl)-1,4-diazabutadiene]$ bis[tetrachloro(methylisocyanide) tungsten(IV)], $[WCl_4(CNMe)_2(\mu-RNCHCHNR)]$ ($R = 4-MeOPh$), (I)

CNMe (0.090 ml, 1.9 mmol) was added to a suspension of complex (H) (0.30 g, 0.30 mmol) in thf (20 ml) and the mixture was refluxed for 2 h. The resulting brown solid was then filtered off, recrystallised from CH_2Cl_2/Et_2O and dried under vacuum (I; 0.15 g, 60% yield).

Preparation of [1,4-bis(4-methoxyphenyl)-1,4-diazabutadiene] tetrachlorotungsten(IV), $[WCl_4(RNCHCHNR)]$ ($R = 4-MeOPh$), (J)

An excess of Zn/Hg (2.5 g) was added to a solution of WCl_6 (0.50 g, 1.3 mmol) and $\widehat{N}\widehat{N}$ (0.50 g, 1.9 mmol) in CH_2Cl_2 (20 ml), and the mixture was stirred for 24 h. The resulting dark green solid with Zn/Hg was filtered off and the former was dissolved in thf; the resulting solution was filtered and a dark green solid (J, ca. 0.20 g, 37% yield) was obtained on concentration under vacuum, addition of diethylether and cooling to ca. -5°C.

Preparation of bis[μ -(*N,N,N',N'*-tetramethyl-1,2-diaminoethane)]bis[dichloro(*N,N,N',N'*-tetramethyl-1,2-diaminoethane)tungsten(II)], [$WCl_2(Me_2NCH_2CH_2NMe_2)_2$] (**K**), and di(μ -chloro)bis[dichloro(*N,N,N',N'*-tetramethyl-1,2-diaminoethane)tungsten(III)], [$WCl_2(Me_2NCH_2CH_2NMe_2)_2(\mu-Cl)_2$] (**L**)

$\widehat{N}\widehat{N}$ (2.0 ml, 13.3 mmol) was added to a solution of WCl_6 (0.74 g, 1.9 mmol) in CH_2Cl_2 (15 ml), the mixture was stirred for 2 h and Zn/Hg (3 g) was then added. After 20 h the resulting greenish-brown solid was filtered off, washed with toluene, and dried under vacuum. Recrystallisation from CH_2Cl_2/Et_2O afforded complex (**K**) as a light brown solid (0.36 g, 40% yield).

The reaction mother liquor (filtered out the greenish-brown solid) was concentrated under vacuum and, upon addition of diethylether, a light brown solid separated out. It was filtered off, washed with toluene and dried under vacuum (**L**; 0.20 g, 26% yield).

Preparation of tris(*N,N,N',N'*-tetramethyl-1,2-diaminoethane) tungsten(III) trichloride, [$W(Me_2NCH_2CH_2NMe_2)_3Cl_3$] (**M**).

$\widehat{N}\widehat{N}$ (2.0 ml, 13.3 mmol), solvent (CH_2Cl_2 and MeOH, 15 ml) and Zn/Hg (3 g) were added in this order to solid WCl_6 (1.5 g, 3.8 mmol) and the mixture was stirred for 2 h. The resulting light brown solid [complex(**M**)] was then filtered off,

washed with CH_2Cl_2 and dried under vacuum (ca. 1.4 g, 60% yield).

4.3 — REACTIONS OF $[MoCl_3(thf)_3]$

Preparation of bis[1,4-bis(4-methoxyphenyl)-1,4-diazabutadiene] dichloromolybdenum(II), [$MoCl_2(RNCHCHNR)_2$] ($R = 4-MeOPh$), (**D**)

Sodium sand (0.10 g, 4.4 mmol) was added to a benzene (19 cm³) solution of $\widehat{N}\widehat{N}$ (0.20 g, 0.74 mmol). The solution colour turned dark reddish-brown upon the addition of $[MoCl_3(thf)_3]$ (0.15 g, 0.37 mmol) and, after a few minutes, a dark greenish suspension began to precipitate. The suspension was left stirring overnight, the dark brown solution was then filtered, concentrated under vacuo, allowed to cool at ca. 5°C and complex (**D**) precipitated as a dark brown solid (0.14 g, 55% yield).

Preparation of μ -(*N,N,N',N'*-tetramethyl-1,2-diaminoethane)bis[trichloro(*N,N,N',N'*-tetramethyl-1,2-diaminoethane)molybdenum(III)], [$MoCl_3(Me_2NCH_2CH_2NMe_2)_2(\mu-Me_2NCH_2CH_2NMe_2)$] (**F**)

Sodium sand (0.10 g, 4.4 mmol) was added to a thf (15 cm³) solution of $[MoCl_3(thf)_3]$ (0.19 g, 0.46 mmol) and $\widehat{N}\widehat{N}$ (0.25 ml, 1.7 mmol). The solution colour turned very dark brown. A very dark suspension started to form and after 2h the solution was filtered, concentrated *in vacuo*, and complex (**F**) precipitated as a brown solid (50 mg, 30% yield) upon addition of ether and cooling at ca. -10°C.

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Table 1
Physical data for diazadiene or diamine complexes derived from $[WCl_4(PPh_3)_2]^{f,g)}$

Complex	Colour	Infrared data ^{b)}				μ_{eff} ^{c)} (B.M.)	Microanalytical data ^{d)}		
		$\nu(C\equiv N)$	$\nu(C=N)$	$\nu(W-Cl)$	others		%C	%H	%N
$[WCl_2(\widehat{N}\widehat{N})_2]Cl_2$, (B)	Dark brown	—	1600 s,br 1500 s	240 w,br		3.0	37.6(37.1)	4.0(3.1)	7.7(7.5)
$[WCl_2(\widehat{N}\widehat{N})_2]$, (C)	Dark brown	—	1590 s,br 1500 s,br	300 s,br		2.8	49.1(48.6)	4.0(4.1)	6.7(7.1)
$[WCl_3(\widehat{N}\widehat{N})_2(\mu-N\widehat{N})]Cl_2$, (E)	Light brown	—	—	345 w,m 310 s,br	2560 m,br ^{e)} 2450 s,br ^{e)}	2.5	20.9(21.6)	4.4(4.8)	7.7(8.4)
$[WCl_2(CNMe)_2(\widehat{N}\widehat{N})]$, (G) ^{h)}	Light green	2145 s	—	305 w,br		2.7	23.9(24.6)	4.5(4.5)	11.0(10.4)

^{a)} $\widehat{N}\widehat{N} = (4-MeOPh)N=CHCH=N(4-MeOPh)$, $\widehat{N}\widehat{N} = Me_2NCH_2CH_2NMe_2$

^{b)} In Nujol mull. $\nu(C\equiv N)$ refers to ligating CNMe, whereas $\nu(C=N)$ refers to coordinated $\widehat{N}\widehat{N}$. ^{c)} Values corrected for the diamagnetic contribution. ^{d)} Calculated values in parenthesis. ^{e)} Assigned to $\nu(C-H\cdots Cl)$. ^{f)} With CH_2Cl_2 of crystallisation.

Table 2
Physical data for diazadiene or diamine complexes derived from WCl_6 ^{a)}

Complex	Colour	Infrared data ^{b)}				μ_{eff} ^{c)} (B.M.)	Microanalytical data ^{d)}		
		$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{N})$	$\nu(\text{W}-\text{Cl})$	others		%C	%H	%N
$[(WCl_5)_2(\mu-\widehat{N}\widehat{N})], (\text{H})^{\text{e)}}$	Dark brown		1605 m, br 1575 m, br 1500 s, br	345 sh		1.4	21.0(20.3)	2.0(1.9)	3.0(2.6)
$[WCl_4(CNMe) _2(\mu-\widehat{N}\widehat{N})], (\text{I})^{\text{f)}}$	Brown	2220 m	1695 s 1630 s, br	305 sh 290 s, br		2.6	29.9(29.1)	3.3(3.1)	6.1(6.3)
$[WCl_4(\widehat{N}\widehat{N})], (\text{J})^{\text{g)}}$	Dark green		1600 s, br 1505 s, br	303 s, br 275 sh, br		—	30.0(30.1)	3.5(4.1)	3.3(2.7)
$[(WCl_2(\widehat{N}\widehat{N}))_2(\mu-\widehat{N}\widehat{N})_2], (\text{K})$	Light brown			290 s, br	2720 s ⁱ⁾ 2560 s ⁱ⁾ 2440 s ⁱ⁾	—	30.6(29.9)	7.8(5.8)	10.6(11.6)
$[(WCl_2(\widehat{N}\widehat{N}))_2(\mu-\text{Cl})_2], (\text{L})^{\text{h)}}$	Light brown			280 s, br	2705 s ⁱ⁾ 2560 s ⁱ⁾ 2440 s ⁱ⁾	4.0	25.5(25.3)	5.9(4.5)	5.4(6.2)
$[W(\widehat{N}\widehat{N})_3]Cl_3, (\text{M})$	Light brown				2620 s, br ⁱ⁾ 2570 s, br ⁱ⁾ 2450 s ⁱ⁾ 2410 sh ⁱ⁾	3.5	34.7(34.1)	8.8(7.6)	13.1(13.3)

a), b), c), d) See notes a), b), c), d), for Table 1. ^{e)} With $2CH_2Cl_2$ of crystallisation. ^{f)} With thf of crystallisation. ^{g)} With CH_2Cl_2 of crystallisation. ^{h)} With $\frac{1}{2}C_6H_5CH_3$ of crystallization. ⁱ⁾ Ascribed to $\nu(\text{C-H}\dots\text{Cl})$ (see text).

Table 3
Physical data for diazadiene and diamine complexes derived from $[MoCl_3(thf)_3]^{\text{a)}}$

Complex	Colour	Infrared data ^{b)}			μ_{eff} ^{c)} (B.M.)	Microanalytical data		
		$\nu(\text{C}=\text{N})$	$\nu(\text{Mo}-\text{Cl})$	others		%C	%H	%N
$[MoCl_2(\widehat{N}\widehat{N})_2], (\text{D})$	Dark brown	1595 m 1493 m, s	330 m		2.9	58.8(58.4)	4.7(4.9)	7.6(7.2) ^{d)}
$[MoCl_3(\widehat{N}\widehat{N}) _2(\mu-\widehat{N}\widehat{N})], (\text{F})$	Light brown	—	300 s 275 sh	2550 s, br ^{e)} 2440 s, br ^{e)}	3.6	29.0(28.7)	6.6(6.7)	10.9(11.2)

a), b), c) See notes a), b), c), for Table 1. ^{d)} $\eta_{\text{Cl}} = 9.1(9.1)$. ^{e)} Assigned to $\nu(\text{C-H}\dots\text{Cl})$.

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RESUMO

Clorocomplexos diazadiênicos e isonitrílicos de tungsténio em vários estados formais de oxidação.

Por reacções de WCl_6 ou $[WCl_4(PPh_3)_2]$ com o diazabutadieno $\widehat{N} \widehat{N} = RN = CHCH = NR$ (sendo $R = 4-C_6H_4OMe$) ou a diamina $\widehat{N} \widehat{N} = Me_2NCH_2CH_2NMe_2$ foi possível a preparação de vários clorocomplexos com estes ligandos (sob a forma quelante ou em ponte), apresentando-se o metal com estado formal de oxidação numa vasta gama (de +5 a +2).

As espécies $[(WCl_3)_2(\mu - \widehat{N} \widehat{N})]$, de W(V), e $[WCl_4(\widehat{N} \widehat{N})]$, de W(IV), foram obtidas por reacção de WCl_6 com $\widehat{N} \widehat{N}$ na presença de amálgama de zinco, enquanto que os complexos de W(IV), $[WCl_2(\widehat{N} \widehat{N})_2] Cl_2$ e $[WCl_3(\widehat{N} \widehat{N}) | \frac{1}{2}(\mu - \widehat{N} \widehat{N})] Cl_2$ se formaram por reacções de substituição de $[WCl_4(PPh_3)_2]$; a espécie relacionável de molibdénio(III), $[MoCl_3(\widehat{N} \widehat{N}) | \frac{1}{2}(\mu - \widehat{N} \widehat{N})]$, foi obtida por reacção de $[MoCl_3(thf)_3]$ com $\widehat{N} \widehat{N}$. Os compostos $[WCl_2(\widehat{N} \widehat{N}) | \frac{1}{2}(\mu - Cl)]$ e $[W(\widehat{N} \widehat{N})_3] Cl_3$, de tungsténio(III), foram obtidos na redução de WCl_6 por amálgama de zinco na presença de um excesso de $\widehat{N} \widehat{N}$.

Foi ainda obtida a redução a W(II) nos complexos seguintes: $[WCl_2(\widehat{N} \widehat{N}) | \frac{1}{2}(\mu - \widehat{N} \widehat{N})]$ preparado na redução de WCl_6 por amálgama de zinco na presença de $\widehat{N} \widehat{N}$; $[WCl_2(\widehat{N} \widehat{N})_2]$ obtido na redução de $[WCl_4(PPh_3)_2]$ por magnésio na presença de $\widehat{N} \widehat{N}$ | o complexo análogo de Mo(II), $[MoCl_2(\widehat{N} \widehat{N})_2]$, foi também preparado por redução de $[MoCl_3(thf)_3]$ por sódio na presença de $\widehat{N} \widehat{N}$.

O metilisonitrilo pode também coordenar-se a estes centros metálicos, tendo o complexo de W(IV), $[WCl_4(CNMe)_2] | \frac{1}{2}(\mu - \widehat{N} \widehat{N})]$, sido preparado na reacção de $[(WCl_3)_2(\mu - \widehat{N} \widehat{N})]$ com um excesso de CNMe. Foi também obtido um complexo isonitrílico de W(II), $[WCl_2(CNMe)_2(\widehat{N} \widehat{N})]$, por reacção de $[WCl_4(PPh_3)_2]$ com $\widehat{N} \widehat{N}$ na presença de CNMe e areia de sódio.