REACTIONS OF NITRIC OXIDE WITH TRANSITION METAL ALKYL COMPLEXES.

A thesis submitted

by

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ABSTRACT

The reaction of nitric oxide with a variety of metal alkyl complexes has been studied.

Reaction with diamagnetic alkyls gives complexes with N-alkyl-N-nitroso hydroxylaminato groups, bound to the metal. These ligands may be unidentate, chelating or bridging between two metals.

Reaction with paramagnetic alkyls takes a different course and forms nitrosoalkane derivatives. These complexes may react further in the presence of nitric oxide to give complexes with either terminal or bridging oxo groups. Metal alkyl complexes containing metal-metal bonds react with initial cleavage of the metal-metal bonds.

The resulting complexes have been characterised spectroscopically, (ir, ^{1}H, ^{31}P nmr), and reaction mechanisms and pathways to their formation are discussed.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professor Sir Geoffrey Wilkinson, F.R.S., for his guidance and continuous encouragement throughout the supervision of this work, and to the Science Research Council for support.

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TO

PATRICIA,

MUM, DAD AND JANE

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LIST OF ABBREVIATIONS

R	Alkyl
Me	Methyl
Et	Ethyl
Ph	C_6H_5
Cp	η^5-cyclopentadienyl
THF	Tetrahydrofuran
M	Molecular weight
b.p.	Boiling Point
m.p.	Melting Point
h	Hours
μ_{eff}	Effective magnetic moment
B.M.	Bohr Magnetons
ir	Infrared
F.T.	Fourier transform
DMSO	Dimethylsulphoxide
d	ppm down field of TMS
ν	Stretching vibration
δ	Deformation vibration
s	Strong
m	Medium
w	Weak
v	Very
sh	Shoulder
br	Broad
epr	Electron paramagnetic resonance
G	Gauß (10^{-4} Tesla)
nmr	Nuclear magnetic resonance
s	Singlet
m	Multiplet
ppm	Parts per million
TMS	Tetramethylsilane

INTRODUCTION

Nitric oxide is one of the few simple odd electron species. Like carbon monoxide, nitric oxide has a long and distinguished coordination chemistry and although it forms few binary metal complexes $M(NO)_x$ it is found in transition metal complexes with ligands ranging from 'harder' or 'type A' ligands such as ammonia or chloride to softer 'π-acceptor' types such as phosphines or carbon monoxide.[1,2] Nitrosyls are also well known in organometallic systems in which alkyls, olefins and π-complexed carbocycles occur.[3]

A number of reviews on nitrosyl complexes, their structures, bonding and reaction chemistry have appeared.[1-10]

The main impetus for research into the reactions of coordinated NO is derived from the occurrence of nitrogen oxides as an environmental hazard produced in combustion processes.[11,12] Due to its electronic difference, a comparison of the reactivity of nitric oxide to its carbon analogue CO[13,14] is interesting from the academic point of view and furthermore the use of metal nitrosyl complexes for the purpose of forming carbon-nitrogen bonds represents an alternative approach in organic synthesis, as well as being of potential industrial significance.

The reactions of coordinated nitric oxide can be split into two distinct types.[1-10] Electrophilic attack at the nitrosyl nitrogen which is particularly favourable for 'bent' nitrosyl groups. Electrophiles reacting in this way include 'O_2' to give nitro and nitrato species, 'H^+' to give complexes containing HNO, NHOH and NH_2OH entities, and with a further molecule of NO to give hyponitrite species, (ONNO).

Probably the most important reaction of coordinated nitric oxide is that of nucleophilic attack at nitrogen which is particularly favoured in linear nitrosyl species. Nucleophiles which have been found to attack linear nitrosyls include OH^-, NH_2OH, N_2H_4, ROH to give coordinated NO_2, N_2O, ($N_2O + N_3$), RONO groups respectively.

The most important reaction of this type is that of carbon nucleophiles to form carbon-nitrogen bonds. However in recent years, although many reactions have been reported, only in a few instances have the products been characterised. In a recent review by R. Eisenberg and P.E. Hendrickson[15] the progress in this area was summed up:-

> " One aspect of nitrosyl chemistry that poses an interesting and significant problem in this regard is the apparent reluctance of nitrosyls to undergo migratory insertion reactions <u>via</u> I. "

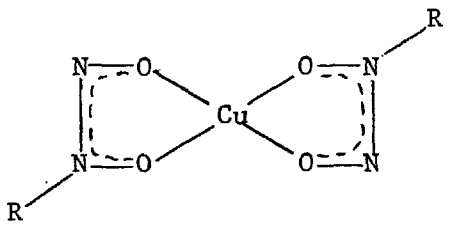
I

The formation of nitrogen-carbon bonds has, in fact, been observed in several instances. One example is the reaction of N,N-dialkylanilines with ruthenium nitrosyls (II), in which the electron rich π-system attacks a coordinated nitrosyl in the para position to the $-NR_2$ group.[16]

$$[RuCl(bipy)_2NO]^{2+} + C_6H_5NR_2 \longrightarrow [RuCl(bipy)_2N(O)C_6H_4NR_2]^{+} + H^{+}$$

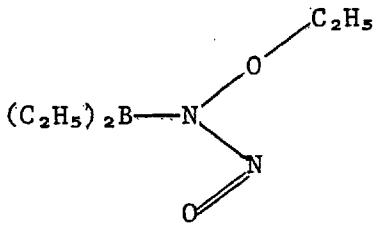
Other examples include the reaction of $Fe(NO)(CN)_5^{2-}$ with ketones[17] which gives rise to oximes, and a similar reaction of $Ru(NO)_2(PPh_3)_2$ with benzyl halide,[18] which in the presence of CO gives $Ru(CO)_2X_2(PPh_3)_2$ plus PhCH=NOH which partially dehydrates to give some PhCN.

Probably, the first report of nitric oxide reacting with a metal alkyl species was that by Frankland in 1856, who reported the reaction of NO with dimethyl and diethyl zinc.[19] This in fact gives polymeric products of the types $[Zn(ONRNO)_2]$ (Chapter 1.2A) rather than $[C_4H_5ZnNO_2]$ which he assigned to the ethyl derivative. In 1903 Sand and Singer[20] isolated N-alkyl-N-nitrosohydroxylamines, [RN(NO)OH] from the reaction of NO with Grignard reagents. The initial crystalline products having been hydrolysed to give the organic product. A similar reaction with methyl Grignard followed by treatment with Cu^{2+} led to a copper complex to which they assigned the structure III.

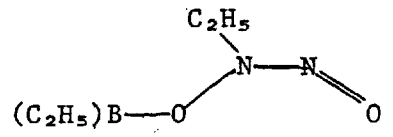


III

More recently, Brois[21] and Inatome and Kuhn[22] treated alkyl borons with NO. At -30°C the product was said to be the N-bonded complex $(C_2H_5)_2BN(NO)OC_2H_5$, IV. However, the nmr data and decomposition studies are equally valid for an O-bonded complex, V.

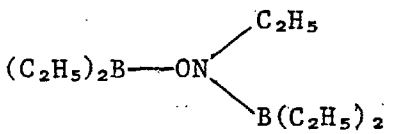


IV

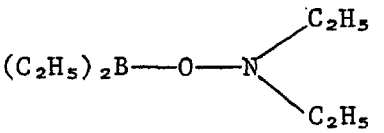


V

When the reaction was carried out at 70°C, however, a reversal of the mode of insertion was found and the compounds isolated were VI and VII

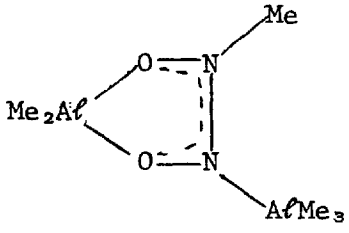


VI

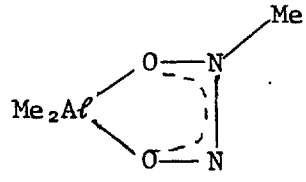


VII

More recently, trimethyl aluminium has been shown to react with NO[23] to give two complexes of stoichiometry $Al Me_3(NO)$ and $Al Me_3(NO)_2$ which were shown to contain N-methyl-N-nitroso-hydroxylaminato groups, VIII, IX.

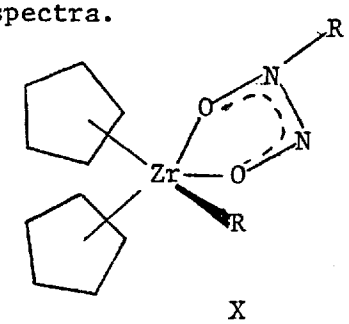


VIII

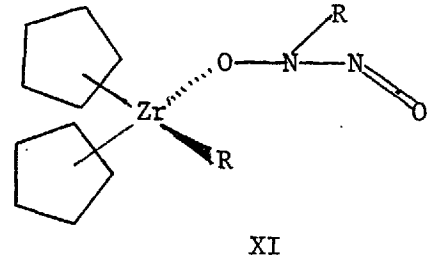


IX

The first reaction of NO with a transition metal alkyl complex to be studied in recent times is that of NO with Cp_2ZrMe_2 and Cp_2TiMe_2 by Wailes, Weigold and Bell in 1972.[24] Both Cp_2ZrMe_2 and $Cp_2Zr(Cl)Me$ reacted with two moles of NO to give N-methyl-N-nitroso-hydroxylaminato groups, X. Although they were said to be unidentate XI, they were almost certainly chelating due to the absence of a band due to $\nu(N=O)$ in the infrared spectra.



X

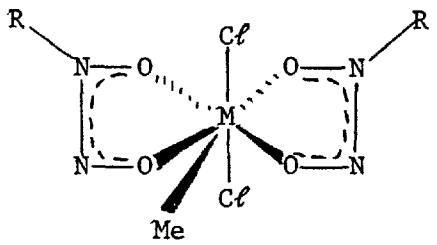


XI

The titanium analogue $Cp_2TiMe(ONMeNO)$ was also prepared but this was shown to be tetrameric presumably involving bridging N-methyl-N-nitrosohydroxylaminato groups. Attempts to insert more NO into the remaining metal alkyl bonds failed and $Cp_2TiCl(Me)$ failed to react.

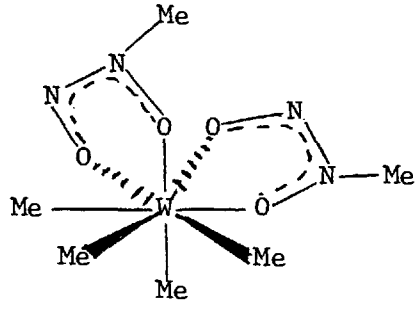
Similarly the monocyclopentadiene complex $CpTiMe_3$ also reacts with NO[25] to give the complex $CpTiMe(ONMeNO)_2$ where the ligands derived from the insertion reaction are both chelating.

The reactions of methyl niobium(V) and tantalum(V) chlorides MMe_3Cl_2 and MMe_2Cl_3 have also been studied.[26] An X-ray diffraction study of the complex $MeTaCl_2(ONMeNO)_2$ confirmed the structure to be seven coordinate, XII, where the third methyl group appears to be inert due to coordinative saturation of the metal.



XII

Similarly the reaction of hexamethyltungsten[27,28] gives a complex, XIII, $WMe_4(ONMeNO)_2$ where the tungsten is eight coordinate and has four unreacted methyl groups.

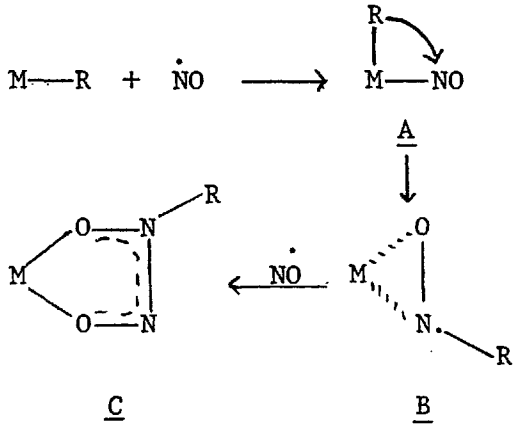


XIII

In each case the products of these reactions contain chelating N-methyl-N-nitroso hydroxylaminato groups.

The formation of these N-alkyl-N-nitroso hydroxylaminato groups probably involves three rapid steps, XIV.

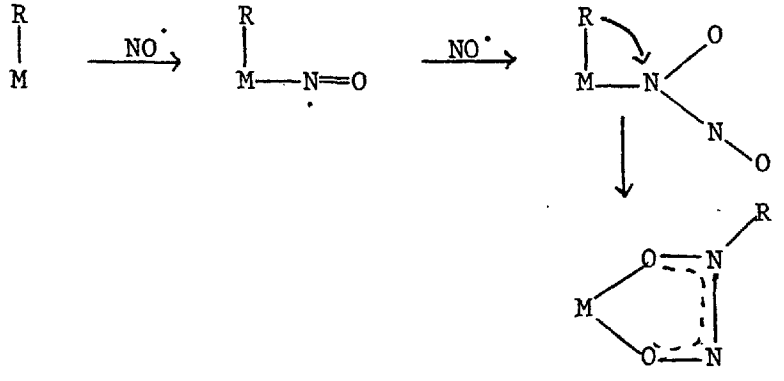
Initial reaction of nitric oxide almost certainly involves binding to the metal centre <u>via</u> nitrogen. Although metal-oxygen bonding is conceivable, there is as yet, no evidence for this type of interaction.



XIV

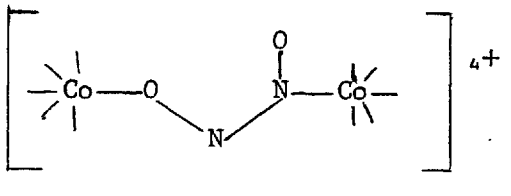
Methyl transfer to this radical species would also generate a radical, B and further reaction with NO can then rapidly occur to generate the (ONRNO) group, C.

As no intermediates in this reaction have been detected, a further mechanism may be proposed involving the electrophilic attack of NO on the coordinated nitric oxide before alkyl migration. The alkyl group could then migrate to a coordinated hyponitrite group, XV.

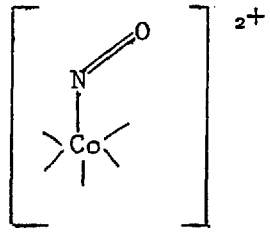


XV

Evidence for this type of electrophilic attack by NO on a coordinated nitrosyl group is the reaction of $Co(II)(NH_3)_6$ with NO to give red and black isomers of $[CoNO(NH_3)_5]^{2+}$,[29,30] the red isomer of which has been shown to contain a hyponitrite bridge, XVI. The black isomer being the mononuclear precursor, XVII.

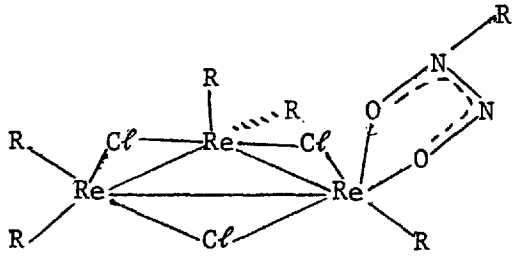


XVI



XVII

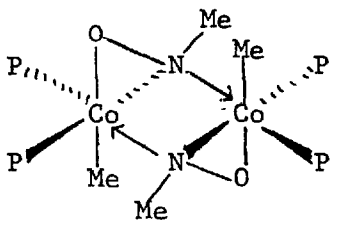
Also, the reaction of NO with $Pt(PPh_3)_4$[31] gives the hyponitrite complex $(PPh_3)_2Pt(ONNO)$. Although no intermediates within the formation of these N-alkyl-N-nitrosohydroxylaminato groups have been detected, the stepwise nature of these reactions has been shown for the hexamethyltungsten derivative;[27,28] The complex $WMe_5(ONMeNO)$ being observed by nmr although it was not isolated. In each case it has been observed that the reaction has continued until coordinative saturation has occurred. One complex, $Re_3Cl_3(CH_2SiMe_3)_6$, however, does not follow this general rule. Only one alkyl group migrates to NO to form the complex $Re_3Cl_3(CH_2SiMe_3)_5(ONCH_2SiMe_3NO)$, XVIII.[32]



XVIII

Further reaction with NO does not lead to insertion products but to a complex in which terminal nitrosyl groups are present on the other two rhenium atoms. This difference was explained by the electronic properties within the cluster being altered due to the formation of the N-alkyl-N-nitrosohydroxylaminato ligand.

Although the reactions of NO with diamagnetic alkyls have proved to be reasonably consistent, there are few reports of reactions with paramagnetic alkyl complexes. The reaction of NO with the alkyl $Co^{II}Me_2(PMe_3)_4$[33] gives a dimeric product, XIX, where the resulting nitrosomethane groups bridge via the lone pair on nitrogen.

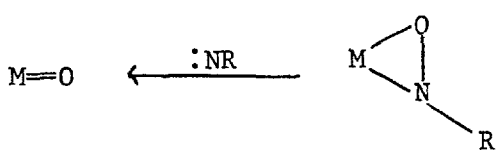


XIX

However, the reaction of the paramagnetic d^1-alkyls, $ReOMe_4$ and $ReO(CH_2SiMe_3)_4$ leads to $Re(O)_2Me_3$[34] and $Re_2O_3(CH_2SiMe_3)_6$ respectively. The formation of oxo groups was explained[34] by a nitroso methane intermediate.

Initial reaction of NO with a paramagnetic alkyl complex, XX, would involve spin pairing of the unpaired electron on the metal with the unpaired electron on NO to give a diamagnetic species containing a 'bent' nitrosyl group and an oxidised metal centre, A.

A



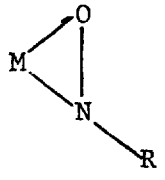
C B

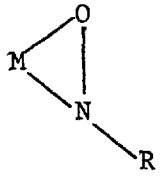
XX

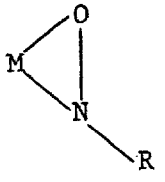
Alkyl migration would then result in a nitroso methane complex, B, which could then react further to give an oxo group, C. The loss of nitrenes in the reaction of $ReOMe_4$ was confirmed by the observation of azomethane.[34]

The nitrosoalkane complexes formed by alkyl transfer to a coordinated nitrosyl group could be expected to behave as other such complexes formed by more conventional methods.

Nitrosoalkane complexes can be prepared by a variety of routes (a - c), and can be considered to be either neutral or

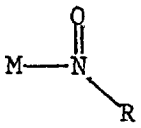
a. Nitrosoalkane (RNO) + ML_2 ⟶  + L_2

b. Nitroalkane (RNO_2) + M—(CO) or M—PR'_3 ⟶  + CO_2 or OPR'_3

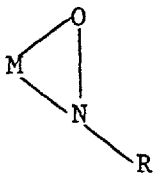
c. Hydroxylamine (RNHOH) + M=O ⟶  + H_2O

dianionic. The complexes $(PR_3)_2NiONR$[36] prepared from $Ni(PR_3)_4$ and RNO_2 are considered to contain neutral nitrosoalkane ligands bound via both oxygen and nitrogen but the palladium complex, $PdCl_2(ONPh)_2$[37] has a neutral nitrosoalkane ligand bound through nitrogen only. Furthermore, reactions with cluster

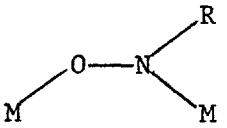
carbonyls have shown that the nitrosoalkane group may bridge between two metals.[40] Thus, three structures are possible, (d - f), with the possibility of e and f being either neutral or dianionic



d



e



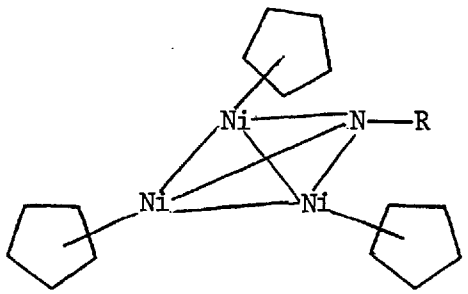
f

Differentiation between the type of nitrosoalkane groups present in any complex can be made by reference to the infrared spectra. Complexes of type d give a band at ca. 1490-1520 cm^{-1}, whilst e and f give a band at ca. 950-1050 cm^{-1} .

Coordinated nitrosoalkane groups take part in two types of reaction. The simplest is the substitution of a neutral nitrosoalkane group for another donor ligand such as carbon monoxide or tertiary phosphines.[36] The other involves cleavage of the N-O bond to give an oxo group and a nitrene, either of which may be retained by the metal centre.

Examples of complexes where the nitrene is retained have been reported in cluster carbonyls, and also in complexes containing reducing agents such as tertiary phosphines (PR_3) or cyclohexyl isocyanide.[40-43] The oxo group is transferred to the reducing agent to form CO_2 or OPR_3, whilst the nitrene fragment remains bound to

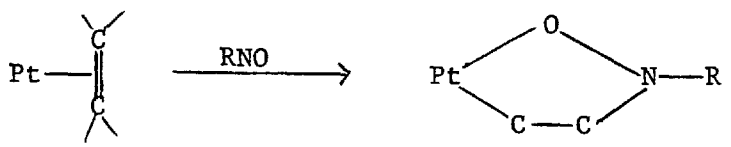
the metal, as an imido group. One example where this occurs in the absence of a reducing agent is a reaction involving direct nucleophilic attack of PhLi on CpNiNO to form a trimer,[44] XXII. One nitrene entity is retained and bridges three NiCp units.



XXII

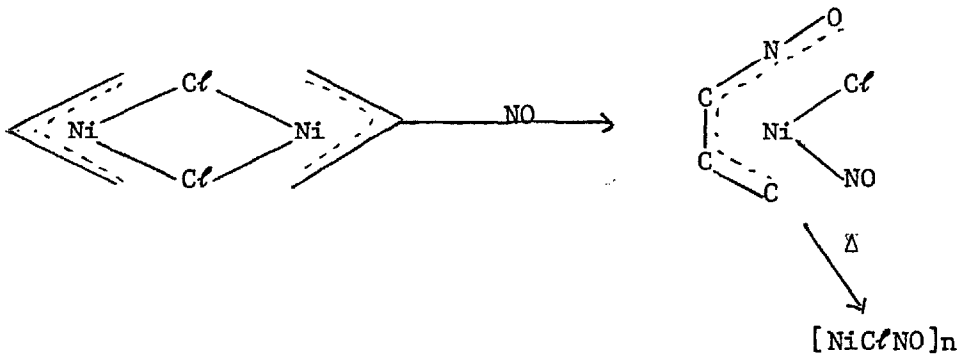
The thermal reaction of $L_2X_2MoO(ONR)$[38,39] in the presence of an olefin, however, gives the dioxo compound $L_2X_2Mo(O)_2$. The liberated nitrene was trapped by the olefin to give an azindine which under the reaction conditions, converted to a more stable allylic amine.

Although the liberation of free nitrenes can be postulated, the recent preparation of a platinum complex, XXIII,[45] in which a nitrosoalkane reacted with an olefin complex to give an insertion product illustrates the possibility of a concerted reaction involving the metal centre.



XXIII

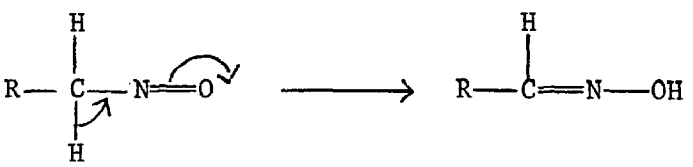
The reaction of metal allyl complexes with NO has also been studied by Parshall and coworkers.[46] In particular, the reaction of the chloro-bridged dimer $(NiCl C_3H_5)_4$ with NO gives a polymeric product, $[NiCl NO]_n$, XXIV, plus acrylonoxime *via* a complex in which the oxime was said to be bound to the metal.



XXIV

A reaction of CO with $L_2Ir(C_3H_5)NOCl$[47] also gives acrylonoxime plus the metal complex, $L_2IrCl(CO)_3$. The presence of carbon monoxide promotes the insertion reaction and resultant reductive elimination.

In both reactions the observed organic product is acrylonoxime. Oximes were also observed as organic byproducts of the reaction of $Ru(NO)_2(PPh_3)_2$ with benzyl halides[18] to give $Ru(CO)_2X_2(PPh_3)_2$ and the reaction of $FeNO(CN)_5^{2-}$ with ketones.[17] This is quite consistent with an alkyl migratory insertion reaction to form a nitrosoalkane complex as any liberated nitrosoalkane with tautomerisable hydrogen atoms may rearrange to give the appropriate oxime.[48]



In conclusion, it can be seen that although a simple migratory insertion reaction may take place to form a nitroso-alkane complex, this group can then react further in a variety of ways. Clearly, many possibilities exist, particularly in poly-alkyl complexes where different reactions may take place on successive reactions with nitric oxide. The order in which these reactions occur will determine the final product and clearly the reaction types will be influenced markedly by the metal involved as well as the presence of other ligands.

This thesis is primarily concerned with the expansion of knowledge in this area, so that it may be possible to predict the products formed from the reaction of any metal alkyl complex with nitric oxide.

CHAPTER ONE

DIAMAGNETIC ALKYL COMPLEXES

Although several examples have been reported,[24-32] the reactions of nitric oxide with diamagnetic alkyls have been limited. In each case the alkyl group has been a methyl group and the metal has had a d^0 configuration. The reaction of only one compound, $Re_3Cl_3(CH_2SiMe_3)_6$[32] has been studied where this does not apply and its subsequent reactions were shown to be different. Clearly, there could be several reasons for this. In this chapter the reactions of diamagnetic alkyls with nitric oxide are studied while varying the alkyl groups, metals, and electronic configuration.

1. d^0 Alkyls.

A. Titanium, Zirconium

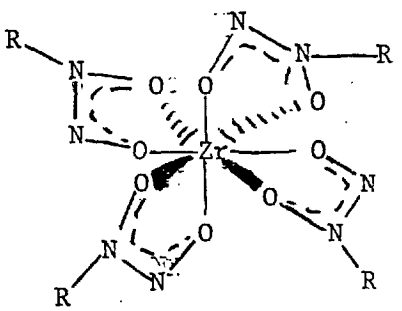
(i) Binary Zirconium Alkyl Complexes.

Interaction of nitric oxide with the zirconium alkyls ZrR_4 ($R = CH_2SiMe_3$, CH_2CMe_3) leads to the uptake of eight molecules of nitric oxide per zirconium to give the N-alkyl-N-Nitroso hydroxylaminato derivatives $Zr(ONRNO)_4$. The large colourless crystals are air stable but absorb moisture slowly. They are quite soluble in organic solvents such as acetone, THF, dichloromethane and toluene but are insoluble in petroleum and ether. The complexes are both diamagnetic and are monomeric in solution. The mass spectrum of the trimethylsilylmethyl complex shows a peak with the correct isotopic pattern for the molecular ion $ZrC_{16}H_{44}N_8C_8Si_4^+$ and both

complexes give a fragmentation pattern, due to the successive loss of methyl groups as well as loss of fragments such as RNO and $R(NO)_2$.

The ir spectra of these complexes (Table 1) have no bands in the terminal nitrosyl region, $\nu_{(N\equiv O)}$, and allowing for bands due to the alkyl groups, the spectra closely resemble that of the known complex $Cu(ONMeNO)_2$.[20] Bands at ca. 1280, 1200, 1140, 960 cm^{-1} are indicative of N-alkyl-N-nitrosohydroxylaminato ligands. The ^1H nmr spectra (Table 2) contain only two peaks in each case due to methyl and methylene protons of equivalent alkyl groups. The resonances due to the methylene protons are downfield compared to the initial alkyl complexes. This is consistent with alkyl groups which have been transferred from the metal to nitrogen.

These complexes, XXV, are clearly the eight coordinate tetrakis N-alkyl-N-nitroso hydroxylaminates where the chelating ligands are bound through both oxygen atoms. Eight coordination of this type is not unusual for zirconium and other complexes of this type include the carboxylates $Zr(RCOO)_4$[49] and the dithiocarbamates $Zr(S_2CNR_2)_4$[50,51] which may also be formed in a similar insertion reaction involving zirconium tetramide $[Zr(NR_2)_4]$ and CS_2.



XXV

Interaction of the π-allyl complex $Zr(\eta^3\text{-}C_3H_5)_4$ with nitric oxide in petroleum at room temperature also results in the uptake of eight molecules of nitric oxide to give a complex, $Zr(ONC_3H_5NO)_4$. This yellow complex is clearly similar to those prepared above and is the first allyl complex observed to react in this way. The complex $Zr(ONC_3H_5NO)_4$ is air-stable but is less soluble than the neopentyl analogues. It is however, soluble in acetone from which it can be obtained as large crystals. It is diamagnetic in the solid state and monomeric in solution.

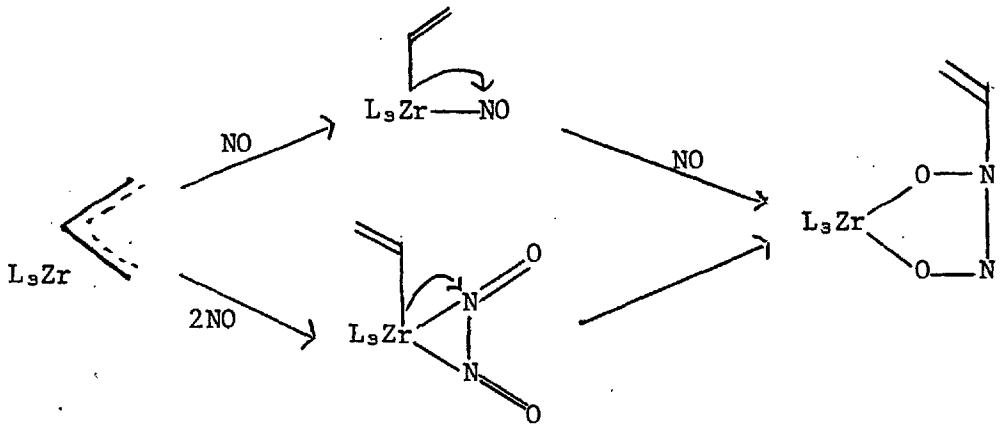
The principal bands in the ir spectrum (Table 1) are at 1280, 1225, 1160, 980 cm^{-1} and clearly indicate the presence of N-alkyl-N-nitrosohydroxylaminato groups . A further weak band is present at 1635 cm^{-1} and can be assigned to $\nu_{(C=C)}$ of the allyl group.

Unlike the neopentyl analogues, the ^1H nmr spectrum is complicated. The resonances occur as three groups in the ratio 1:2:2.

The methylene protons next to nitrogen occur as a doublet (δ 4.52), whilst the methylene proton occurs as a multiplet at (δ 5.9). The olefinic methylene protons are clearly inequivalent and occur as a doublet at δ 5.35 and a broadened singlet of equal intensity at δ 5.20.

The formation of N-allyl-N-nitrosohydroxylaminato groups from a π-allyl system clearly must involve a $\sigma(\eta^1)$ allyl which can then migrate to nitrogen. Nmr studies of allyl complexes of this type have illustrated their fluxional nature in solution via η^1-intermediates.[52,53]

In the presence of NO an η^3-allyl could revert to an η^1-allyl in order to accommodate a terminal nitrosyl or hyponitrite group on the metal, XXVI. In the presence of excess nitric oxide the η^1-allyl group could migrate to nitrogen to give an N-allyl-N-nitrosohydroxylaminato group.



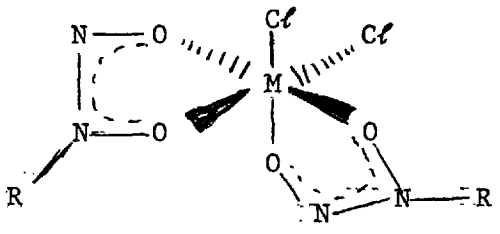
XXVI

(ii) Mixed Alkyl Chloro Complexes, MR_2Cl_2.

Solutions containing the mixed alkyl chloro complexes, MR_2Cl_2 (R = CH_2SiMe_3, CH_2CMe_3, M = Ti, Zr) can easily be made in situ by mixing the appropriate quantities of tetralkyl and tetrachloride in ether or petroleum.

Interaction of these solutions with nitric oxide leads to white precipitates of $MCl_2(ONRNO)_2$. These air-stable complexes are exceedingly hygroscopic, which with their insoluble nature in aromatic solvents precluded a molecular weight determination. These diamagnetic complexes are however, soluble in dichloromethane and THF. The mass spectra did not contain molecular ions but only fragments.

The ir spectra (Table 1) are virtually identical to the zirconium tetrakis(N-alkyl-N-nitrosohydroylaminato) complexes above. The $\nu_{(M-C\ell)}$ region of these spectra contain bands due to the trimethylsilylmethyl ligands but two weak bands can be assigned to $\nu_{(M-C\ell)}$. This is indicative of cis-chlorines rather than trans which would result in a single $\nu_{(M-C\ell)}$ band. The ^1H nmr spectra (Table 2) are also similar to the zirconium complexes, of the methylene protons are shifted downfield confirming the migration of the alkyl groups to nitrogen. The structure of these complexes, XXVII, evidently contains two chelating N-alkyl-N-nitrosohydroxylaminato groups and two chlorines that are cis



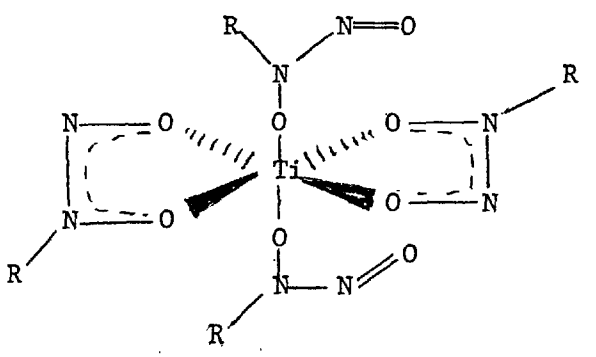
XXVII

(iii) Titanium Alkyl Complexes.

The titanium alkyl complex $Ti(CH_2SiMe_3)_4$ would be expected to react with nitric oxide in the same way as its zirconium analogue $Zr(CH_2SiMe_3)_4$. The reaction takes place rapidly at room temperature to give an orange complex of stoichiometry $Ti(CH_2SiMe_3)_4(NO)_8$. The complex is air stable and is quite soluble in organic solvents

with the exception of petroleum. It is diamagnetic in the solid state and is monomeric in solution. The mass spectrum does not contain a molecular ion but a fragmentation pattern similar to the zirconium complex with successive loss of methyl groups as well as RNO and $R(NO)_2$.

The ir spectrum is similar to that of $Zr(ONCH_2SiMe_3NO)_4$ with the most intense bands at 1280, 1200, 1125 and 965 cm^{-1}, indicative of N-alkyl-N-nitroso hdyroxylaminato groups. However, a further band is present in the titanium complex at 1550 cm^{-1}, which can be assigned to $\nu_{(N=O)}$. Although this could conceivably be due to a terminal nitrosyl group, this is unlikely, as the ^1H nmr spectrum (Table 2), clearly indicates that each trimethylsilylmethyl group has been transferred from the metal to nitrogen. Unlike the zirconium complex, there are four resonances, [δ 0.06(9), 0.14(9), 3.47(2), 2.76(2)], which indicates two different environments for the alkyl groups. The only plausable explanation is that there are both chelating and unidentate N-alkyl-N-nitrosohydroxylaminato ligands present, XXVIII and the band at 1550 cm^{-1} is due to $\nu_{(N=O)}$ of the unidentate ligands. Whether the complex is *cis* or *trans* cannot be deduced from the available data.

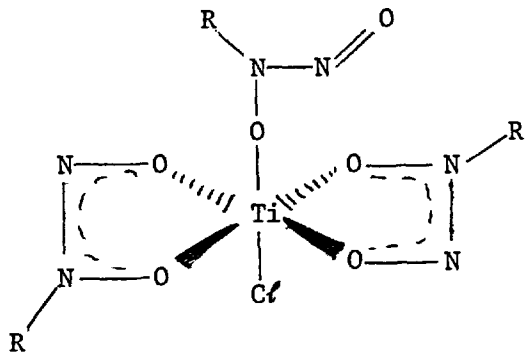


XXVIII

A unidentate group was proposed for the complex $(\eta^5\text{-}C_5H_5)_2\text{-}ZrCH_3(ONCH_3NO)$[24] but this complex did not have a comparable band at 1550 cm^{-1} so the N-methyl-N-nitrosohydroxylaminato group is probably chelating as suggested earlier.

The mixed titanium alkyl chloro complex $TiCl(CH_2CMe_3)_3$ also reacts in petroleum with NO to give a yellow complex, $TiCl(ONCH_2CMe_3NO)_3$ in which two N-neopentyl N-nitrosohydroxylaminato groups are chelating and the third is unidentate, XXIX. This complex has similar properties to the titanium trimethylsilylmethyl complex. It is an air stable, diamagnetic, very soluble, crystalline solid. It has a low melting point and is considerably stronger in colour than the zirconium complexes of the titanium complexes containing two chlorine atoms. This complex has been shown to be monomeric in solution and this is confirmed by the mass spectrum which had a mass peak with the correct isotopic pattern for the molecular ion $TiC_{12}H_{33}N_6O_6Cl^+$ as well as a corresponding fragmentation pattern. The ir spectrum confirmed the structure. Bands at 1285, 1200, 1135 and 962 cm^{-1} are due to the N-alkyl-N-nitrosohydroxylaminato groups and a unidentate ligand is confirmed by the presence of a band at 1550 cm^{-1} $\nu_{(N=O)}$. A band at 345 cm^{-1} can be assigned to $\nu_{(Ti-Cl)}$.

The ^1H nmr spectrum indicates the presence of two types of alkyl group in the ratio 2:1, both of which have been transferred to nitrogen. The structure of this complex, XXIX may be cis or trans as it is not possible to distinguish between these isomers with the available data.



XXIX

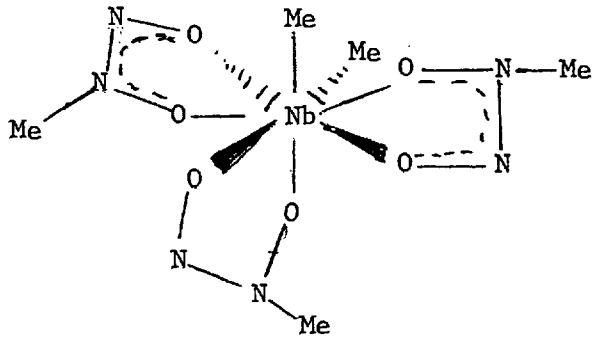
The difference in structure between the zirconium and titanium analogues is almost certainly due to the preference of titanium for six-coordination. However, the reasons for the reaction of all four alkyl groups in the titanium case to give unidentate ligands and with only a limited number of alkyl groups in other complexes such as hexamethyl tungsten,[27,28] remains unclear. One possible explanation is that the titanium atom might expand its coordination sphere above six to enable nitric oxide to approach the metal, but having reacted the product reverts to the more favoured six-coordination.

B. Vanadium, Niobium, Tantalum.

The reactions of mixed chloroalkyls MCl_2Me_3, MCl_3Me_2 (M = Nb, Ta) with NO[26] have been shown to give seven coordinate species containing two N-methyl N-nitrosohydroxylaminato groups and three remaining groups terminally bound to the metal. Interaction of nitric oxide with the penta-methyl complexes, however, gives complexes with different stoichiometry.

Interaction of pentamethylniobium with nitric oxide gives a yellow crystalline complex, $NbMe_2(ONMeNO)_3$. This complex is air sensitive and turns white after a short period in air. It is soluble in most organic solvents including ether, THF and toluene but is insoluble in petroleum. It was shown to be monomeric in solution and diamagnetic both in solution and the solid state. The ir spectrum(Table 1) has bands at 1270, 1165, 1115, 970 cm^{-1} which indicates the presence of N-methyl-N-nitrosohydroxylaminato groups.

The ^1H nmr spectrum (Table 2) confirms the presence of three equivalent alkyl groups bound to nitrogen (δ 3.20) and two equivalent methyl groups remaining bound to niobium (δ 0.63). The structure of this complex, XXX, is eight coordinate but the relative stereochemistry is impossible to determine from the spectroscopic data.

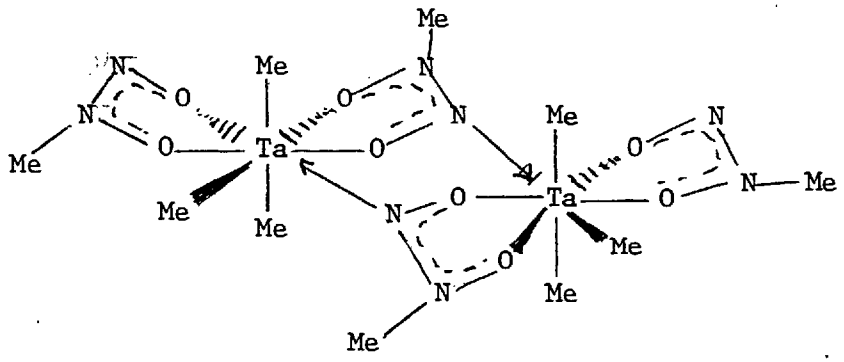


XXX

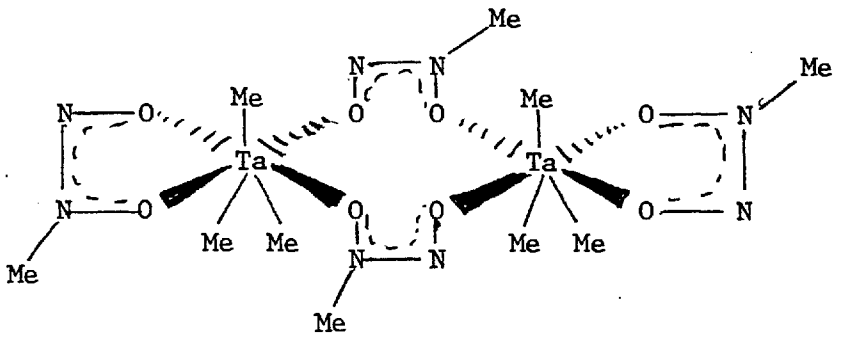
It is interesting to note that this complex is eight coordinate whilst the mixed chloroalkyl complexes are only seven coordinate[26] even if a further methyl group is present. The reasons for this may be stereochemical, due to the relative sizes of the chlorine and methyl groups, however, it is more likely to be the lack of reactivity of the third methyl group in $NbMe_3Cl_2$. This lack of reactivity of a lone methyl group has also been observed in $Cp_2TiClMe$[24] which does not react with NO, whilst Cp_2TiMe_2 reacts readily to give $Cp_2TiMe(ONMeNO)$.

The tantalum complex $TaMe_5$ also reacts with NO at -70^oC to give a colourless crystalline complex of stoichiometry $[TaMe_5(NO)_4]_2$. This complex is air sensitive and quite soluble in organic solvents such as ether, THF and toluene but is only sparingly soluble in petroleum. It is diamagnetic in the solid state and was shown to be dimeric in solution. The ir spectrum does not contain any bands due to terminal nitrosyl groups but contains bands at 1275, 1170, 1115, 1070 and 945 cm^{-1}, indicating the presence of N-methyl-N-nitrosohydroxylaminato groups. The ^1H nmr spectrum (Table 2) has one resonance due to the three equivalent methyl groups which remain attached to the metal. The other two methyl groups are inequivalent, although their position confirmed that they are both bound to nitrogen (δ 3.42, 4.18). Together with the fact that this complex is dimeric there are two possible structures containing both chelating and bridging N-methyl-N-nitrosohydroxylaminato groups, XXXIA or B.

Structure XXXI A is probably the most likely as the tantalum atoms are eight coordinate as in the niobium complex.



XXXI A



XXXI B

Other diamagnetic d^0 alkyls such as $VO(CH_2SiMe_3)_3$ and the carbene bridged species $M_2(CH_2SiMe_3)_4(CSiMe_3)_2$ (M = Nb, Ta)[54] failed to react with nitric oxide at ambient temperatures. No efforts were made to repeat these reactions above room temperature. The reasons for this non-reactivity probably involve coordinative saturation of the metal,

II d^{10} Complexes.

a. Zinc Alkyls

The reaction of nitric oxide with zinc alkyls studied by Frankland in 1856[19] was probably the first report of such a reaction with nifric oxide. However, due to the lack of spectroscopic and crystallographic data, he was unable to determine the precise nature of the products.

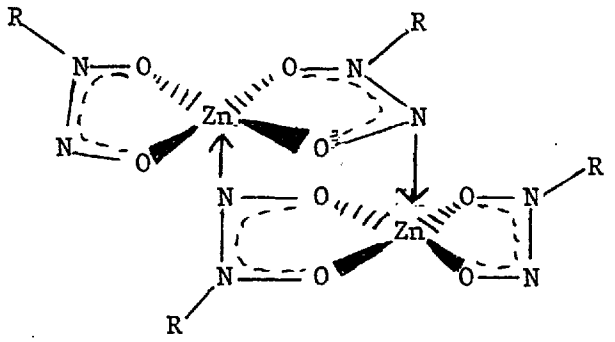
Interaction of petroleum solutions of zinc alkyls ZnR_2 (methyl, neopentyl) with nitric oxide gives white crystalline complexes of stoichiometry $ZnR_2(NO)_4$.

Both complexes are air stable but hygroscopic. The methyl complex is poorly soluble in organic solvents such as petroleum, THF toluene and dichloromethane, but the neopentyl complex is quite soluble in THF and dichlormethane. Both complexes are diamagnetic in the solid state and although the methyl complex was too insoluble to obtain a satisfactory molecular weight determination, the neopentyl complex was shown to be tetrameric in solution. The mass spectra of these complexes did not contain molecular ions, but the polymeric nature of these complexes was confirmed,as the highest mass peaks were due to dimeric species minus one and two methyl groups for the neopentyl and methyl complexes respectively.

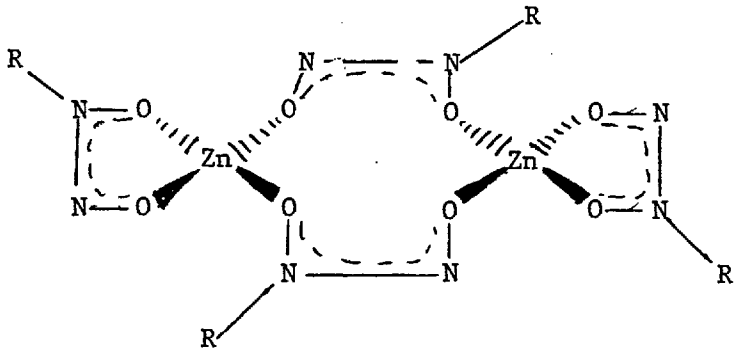
The ir spectra of both complexes (Table 1) contain strong bands at 1290, 1150, 960 cm^{-1}, confirming the presence of N-alkyl-N-nitroso-hydroxylaminato groups whilst the absence of bands above 1500 cm^{-1}

confirms that they are chelating and/or bridging but not unidentate. The nmr spectra are in accord with this, the alkyl groups in each case are equivalent and are shifted downfield compared to the parent alkyl, confirming the transfer from zinc to nitrogen.

Due to their polymeric nature, the structure of these complexes must contain bridging N-alkyl-N-nitrosohydroxylaminato groups. Two types of bridging may occur, XXXIIA and XXXIIB, both types could be consistent with the observed data.



XXXIIA



XXXIIB

Both types of structure have precedents in the chemistry of zinc dithiocarbonates where it has been shown that $Zn(S_2CNMe_2)_2$ and $Zn(S_2CNEt_2)$ have two different types of bridging ligands.[55,56] Thus it is possible that within a series of N-alkyl-N-nitroso hydroxylaminates the types of bridging may vary and indeed, a complex may contain both types.

It is interesting to note that in both complexes the highest mass peak observed is close to that of a dimeric species whilst the molecular weight determination indicates that the neopentyl derivative is in fact tetrameric in solution. This could be indicative of a weaker bridging between what are basically dimeric units.

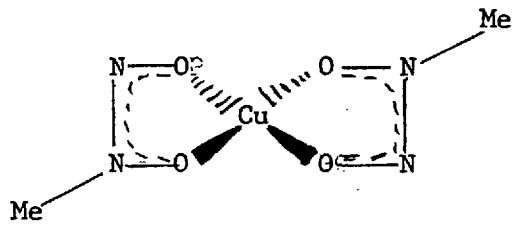
Although these complexes are not particularly soluble in organic solvents, they can be dissolved in hot water.

Frankland,[19] reacted these hot solutions with a variety of metal salts to obtain complexes of the following stoichiometries, based on his elemental analyses. $NaR(NO)_2$, $MgR_2(NO)_4$, $CaR_2(NO)_4$, $BaR_2(NO)_4$, $AgR(NO)_2$, $CuR_2(NO)_4$. These complexes almost certainly contained N-alkyl-N-nitrosohydroxylaminato groups but no attempts were made to repeat these observations.

B. Copper Alkyls.

Interaction of nitric oxide with a slurrry of the copper alkyl [CuMe]n in THF eventually gives a blue solution and a dark precipitate of copper metal. The blue solution gives crystals of the complex $Cu(ONMeNO)_2$, which is non-solvated when recrystallised from toluene,

but has solvent of crystallisation present from polar solvents such as ether or THF. This air stable complex is quite soluble in organic solvents such as THF and dichloromethane but insoluble in petroleum. It was shown to be monomeric in solution and the mass spectrum had a mass peak with the correct isotopic pattern for the molecular ion $CuC_2H_6N_4O_4^+$, as well as a fragmentation pattern due to loss of methyl groups. The ir spectrum (Table 1) has bands at 1280, 1165, 948 cm^{-1} due to N-methyl-N-nitrosohydroxylaminato groups and is in fact identical to the known complex XXXIV, where the copper is present as Cu(II). The presence of Cu(II) was confirmed by the magnetic moment (μ_{eff} = 1.89 BM) measured at room temperature and the esr spectrum which, in frozen toluene has $g_{\|}$ = 2.6371 and $g_{\perp}$ = 1.5854 which was in close agreement with g_{iso} = 2.284 measured in the solidestate by P.C. Wailes, et al.;[24]

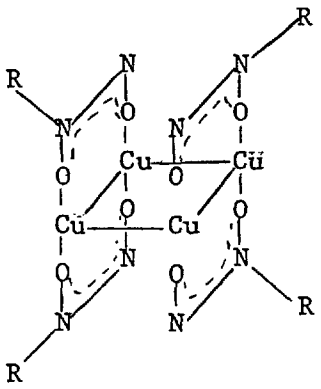


XXXIV

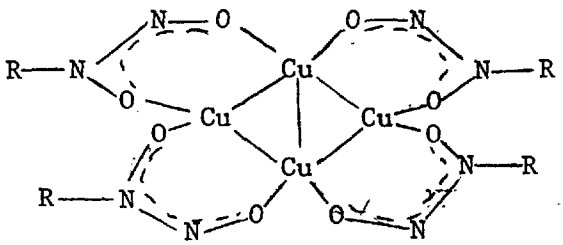
A similar reaction of the trimethylsilylmethyl complex, $[CuCH_2SiMe_3]_4$ with nitric oxide in petroleum initially gives a pale yellow crystalline complex, $[Cu(ONCH_2SiMe_3NO)]_4$. It is quite soluble in polar organic solvents such as THF and dichloromethane but is only sparingly soluble in toluene, ether or petroleum. It has been shown

to be diamagnetic in the solid state and is tetrameric in solution. The tetrameric structure is confirmed by the mass spectrum in which the highest mass peak had the correct isotopic pattern for the molecular ion $Cu_4C_{16}H_{44}N_8O_8Si_4^+$ and stronger mass peaks dùe to the successive loss of several methyl groups. The spectroscopic data for this complex is also consistent with the formulation. The ir spectrum, Table 1, has bands at 1270, 1138, 972 cm^{-1} due to N-trimethylsilylmethyl-N-nitrosohydroxylaminato groups and the nmr spectrum (Table 2) confirmed that each alkyl group is equivalent but has been transferred from copper to nitrogen (δ 0.11(9), 3.57(2).

The structure of Cu(I) species of this type may contain a variety of polynuclear structures.[57] The structures XXXVA-B illustrate two of several types which could be consistent with the observed spectroscopic data, but without an X-ray crystallographic study, differentation cannot be made.



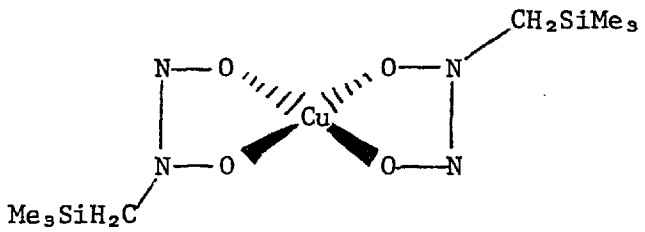
XXXVIA



XXXVIB

From the reaction of the copper alkyl $[CuCH_2SiMe_3]_4$ with nitric oxide, a further complex was also isolated. The blue complex $Cu(ONCH_2SiMe_3NO)_2$, XXXVII, was apparently isostructural with the methyl analogue above. As in the methyl complex recrystallisation from ether results in the presence of solvent of crystalisation but from toluene no solvent was present. This complex is air stable and is very soluble in organic solvents. Separation from the Cu(I) complex $[Cu(ONCH_2SiMe_3NO)]_4$ can easily be made by extraction into ether. The Cu(II) complex is paramagnetic in the solid state (μ_{eff} = 2.0 BM), and the esr spectrum in frozen toluene gives $g_{\parallel}$ = 2.5956, and $g_{\perp}$ = 1.5854 which would give g_{iso} = 2.2589. The complex is monomeric in solution and a monomeric formulation was supported by the mass spectrum which had a mass peak with the correct isotopic pattern for the molecular ion, $CuC_8H_{22}N_4O_4Si_2^+$ as well as a fragmentation pattern involving loss of methyl groups.

The ir spectrum has bands at 1278, 1192, 950 cm^{-1}, which confirm the presence of N-alkyl-N-nitrosohydroxylaminato groups.



XXXVII

The formation of Cu(II) complexes from Cu(I) alkyls clearly involves oxidation of the metal centre. Although oxidation involving nitric oxide is a possibility, the presence of copper metal suggests a disproportionation reaction.

$$2Cu^{+} \rightleftharpoons Cu^{2+} + Cu^{\circ} \qquad E^{\circ} = 0.37V \qquad k = \frac{[Cu^{2+}]}{[Cu^{+}]^2} \approx 10^6$$

This equilibrium can easily be displaced in either direction and it is not entirely surprising that both Cu(I) and Cu(II) complexes may be isolated from one reaction.

From the reactions of zinc and copper alkyls it appears that the reaction of nitric oxide with d^{10} dimeric alkyls follows the same course as for d° alkyls and that the formation of N-alkyl-N-nitrosohydroxylaminato groups appears to be quite consistent. Attempts were made to react silver alkyls, [AgR] with nitric oxide at low temperatures, however, no compounds were isolated and on warming to room temperature the majority of silver was recovered as the metal.

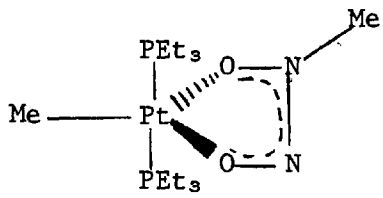
III Other Diamagnetic Complexes.

The diamagnetic alkyls studied so far have been of d^0 and d^{10} electronic configuration. In both cases there is no possibility of nitric oxide reacting with unpaired electrons, even if the geometry of the complex is significantly altered by interaction with nitric oxide. In these complexes it is clear that the incoming unpaired electron has remained on the nitric oxide molecule and further reaction has taken place to give N-alkyl-N-nitrosohydroxylaminato groups.

In this section further diamagnetic alkyls are studied, where there is an uncompleted d shell, but diamagnetism is achieved due to the relative geometries of the ligands.

A. Platinum Alkyls.

Interaction of nitric oxide with a THF solution containing cis$[PtMe_2(PEt_3)_2]$, gives colourless crystals of the complex $PtMe(ONMeNO)(PEt_3)_2$. This complex is air stable and is quite soluble in THF, dichloromethane and aromatic solvents. It is diamagnetic in the solid state and was shown to be monomeric in dichloromethane. The structure of this complex, XXXVIII, is probably trigonal bypyramidal with the phosphines in the apical or equatorial positions.



XXXVIII

The presence of an N-alkyl-N-nitroso hydroxylaminato group is confirmed by the ir spectrum. Bands at 1260, 1165, 1030 and 960 cm^{-1} are consistent with a chelating group, as no bands occur in the terminal nitrosyl region, $\nu_{(N=O)}$. Bands are also present due to the triethylphosphine groups and the absence of a band due to $\nu_{(P=O)}$ confirms that these have not been converted to phosphine oxide. The ^{31}P nmr spectrum indicates the equivalence of the phosphine groups (triplet at 0.755 ppm, relative to 85% aqueous H_3PO_4, J_{P-Pt} = 1969 Hz), which may be due to the complex being fluxional in solution.

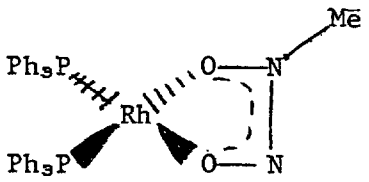
The ^1H nmr spectrum has resonances due to PEt_3 which occur as multiplets at δ 1.0m (18) and δ 2.05 (12). These are of greater multiplicity than that expected due to coupling of protons only. A singlet resonance occurred between these at δ 1.50 (3) which can be assigned to ($N-CH_3$). Part of a muliplet is also present at δ 0.62 that is probably due to ($Pt-CH_3$) but due to its close proximity to the larger resonance may be associated with the phosphine methyl multiplet.

A five coordinate formulation for this complex is consistent with the diamagnetic nature of this complex. Five coordinate compounds are resonably well known for Pd and Pt, particularly with chelating ligands such as tris-[o-diphenylarsino)-phenyl]arsine, and dithiocarbamates.[58] Complexes of this type also exist with monodentate ligands such as $SnCl_3$, e.g., $[Pt(SnCl_3)_5]^{3-}$.[59]

The formation of this complexes from $Pt(PEt_3)_2Me_2$ is clearly analogous to the reactions of d^0 and d^{10} alkyls observed in parts I and II. The incoming unpaired electron on nitric oxide is clearly retained on nitrogen and is not transferred to the metal.

B. Rhodium Alkyls.

Interaction of the rhodium alkyl complex, $Rh(PPh_3)_3Me$ with nitric oxide at room temperature gives a yellow complex, $Rh(PPh_3)_2(ONMeNO)$. It was difficult, to obtain a consistent analyses for this complex as it contained solvent of crystallisation. However, the spectroscopic data indicates a structure, XXXIX, which is probably square planar with a chelating N-methyl-N-nitroso-hydroxylaminato group. Bands in the ir spectrum at 1287, 1180, 985 cm^{-1} are consistent with this, and the presence of triphenylphosphine is also evident. The ^1H nmr spectra contain a singlet at δ 2.30 which can be assigned to the ($N-CH_3$) group and in each spectrum there are resonances due to triphenylphosphine and the relevant solvent.



XXXIX

This complex is quite soluble in dichloromethane and THF but insoluble in petroleum and ether. It is diamagnetic as expected for a square planar d^8 system, but a molecular weight determination of 902 must be held with suspicion due to the solvent of crystallisation. The observed figure however, is close to that expected from the analysis if two solvent molecules are associated with the complex in solution.

The formation of this complex is again similar to the reactions of d^0 and d^{10} alkyls. Initial reaction probably involves dissociation oftriphenylphosphine to give a three coordinate species $Rh(PPh_3)_2Me$. This would also be planar and diamagnetic and could react with nitric oxideto give an N-methyl-N-nitroso hdyroxylaminato group.

C. Cobalt Alkyls.

Interaction of theparamagnetic cobalt(II) complex $CoMe_2(PMe_3)_4$ has been shown to give the complex $[CoMe(ONMe)(PMe_3)_2]_2$ where the η^2-nitrosomethane groups form bridges between two cobalt atoms.[33]

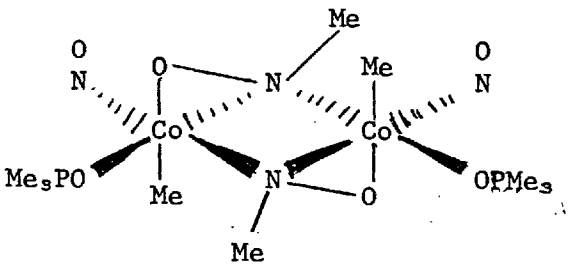
Interaction of the similar diamagnetic Co(III) complex, $CoMe_3(PMe_3)_3$ was expected to behave as other diamagnetic alkyls to give N-methyl-N-nitroso hydroxylaminato groups. This does not occur, but a rapid reaction takes place at room temperature which is clearly exothermic. From the reaction mixture two compounds can be isolated. The first red-brown compound is insoluble in petroleum and ether, but soluble in THF and dichloromethane. From analytical and spectroscopic data it is $CoMe(NO)(ONMe)(OPMe_3)$, and it crystallised from THF with one molecule of solvent. This complex is air-sensitive and particularly hygroscopic, and due to its insolubility in benzene no molecular-weight determinations were possible.

The mass spectrum had a highest mass peak at $Co_2C_7H_{21}N_4O_5P^+$ which is equivalent to a dimeric formulation minus one trimethylphosphine oxide group. Trimethylphosphine oxide was also found in the mass spectrum. This complex is paramagnetic in the solid state and in solution (μ_{eff} = 2.1 BM) and hence the nmr spectrum was poor, only broad, ill-defined

peaks being observed. Also, it did not exhibit an esr spectrum in frozen toluene above 10°K (-164°C).

The ir spectrum of this complex, however is more informative. A band at 1660 cm^{-1} is due to a bent terminal nitrosyl group, and a band at 1020 cm^{-1} can be assigned to $\nu_{(N-O)}$ of a η^2-nitrosomethane group. The strongest bands in the spectrum occur at 1145 and 950 cm^{-1} and are due to $\nu_{(P=O)}$ and $\nu_{(P-CH_3)}$ bands of the trimethylphosphine oxide ligand. The presence of THF is also confirmed by bands at 1050 cm^{-1} and 870 cm^{-1}.

Due to the dimeric nature of this complex, in the mass spectrum this compound is almost certainly XL, with the η^2-nitrosomethane groups bridging between two octahedral cobalt atoms.



XL

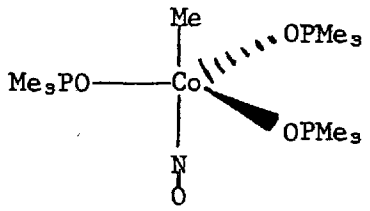
Clearly, several isomers of this complex may exist, but the precise isomer cannot be deduced from the available data.

As the terminal nitrosyl band occurs at 1660 cm^{-1}, this can be assumed to be 'bent' and therefore, uninegative. Thus, depending on the formulation of the η^2-nitrosoalkane group as neutral or dianionic the cobalt atoms can be considered to be low spin Co(II) or Co(IV). Both of these formulations are consistent with the observed magnetic moment (μ_{eff} = 2.1 BM) but due to cobalt's preference for low oxidation states, the η^2-nitrosomethane group is almost certainly neutral.

Further evidence for the neutrality of the nitrosomethane group in this complex comes from the second complex isolated from the reaction. This complex is similar in colour to the nitroso methane complex, but is far more soluble in ether and petroleum.

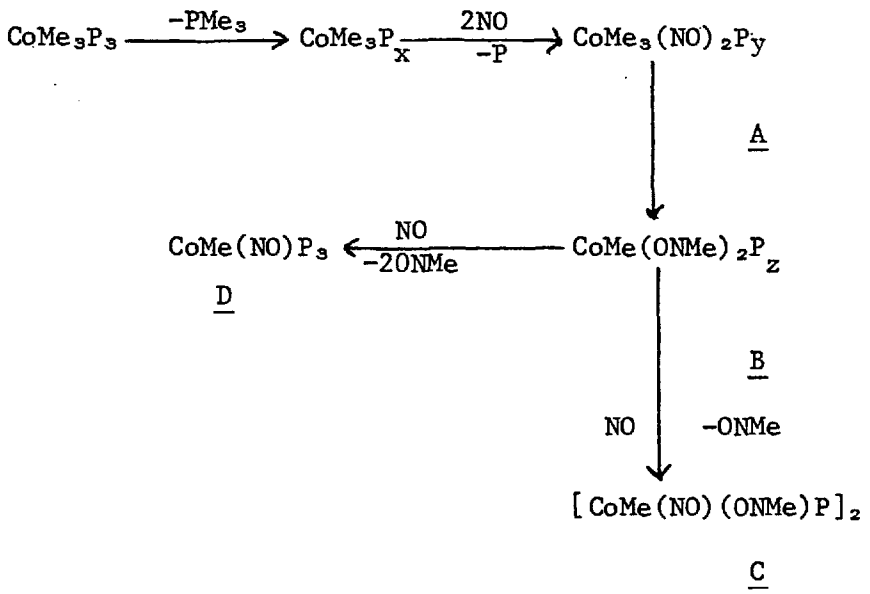
The complex $CoMe(NO)(OPMe_3)_3$ crystallises as red plates. It is air-sensitive and very hygroscopic. The mass spectrum had a mass peak due to the molecular ion, $CoC_{10}H_{30}NO_4P_3^+$, and a fragmentation pattern due to the loss of trimethylphosphine oxide groups. This complex has similar properties to the nitrosomethane complex. It is paramagnetic (μ_{eff} = 1.8 BM), the nmr spectrum was poor, and it did not give an epr spectrum in frozen toluene above 109°K (-164°C). The band in the ir spectrum at 1020 cm^{-1} was not present indicating the absence of any nitroso methane groups and the bands due to THF were not present. However, the remainder of the spectrum was virtually identical to the nitroso methane complex. Thus, bands at 1660 cm^{-1} and 1145, 950 cm^{-1} were due to a 'bent' terminal nitrosyl group and trimethylphosphine oxide respectively. This complex is almost certainly XLI, where the cobalt is five coordinate, however, the precise isomer cannot be established from the available data.

The formation of these two complexes from $CoMe_3(PMe_3)_3$ can be explained if one considers that an octahedral Co(III) system (d^6) is diamagnetic because of the geometry of ligands around the metal. Dissociation of a phosphine into solution would give a five coordinate species $CoMe_3(PMe_3)_2$ which would necessarily have a different electronic configuration and possibly two unpaired electrons. This could then



XLI

react rapidly with nitric oxide in the way expected of paramagnetic alkyls (Chapter 2). Alkyl migration to the coordinated nitrosyl groups would give nitrosomethane groups, XLII, which due to cobalts preference for low oxidation states would be neutrally bound to the metal. This would result in an intermediate B, with two nitrosomethane



XLII

groups. These neutral ligands can easily be displaced by nitric oxide, trimethylphosphine or trimethylphosphine oxide and hence, loss of one group gives complex C, which dimerises rather than associating with further trimethylphosphine oxide, and loss of both nitrosomethane groups gives compound D. The presence of trimethylphosphine oxide in these complexes is not surprising as any trimethylphosphine dissociated from the metal will react rapidly with nitric oxide, XLII.[33,36]

$$PR_3 + 2NO \longrightarrow OPR_3 + N_2O$$

XLII

The presence of Co(II) in the final products is surprising as it is paramagnetic and could react with further nitric oxide to give a diamagnetic complex. However, the non-reactivity of a lone methyl group has been observed previously (Section 1) and this, with cobalts preference for low oxidation states may account for the stability of these complexes.

D. Nickel Alkyls.

Interaction of nitric oxide with the diamagnetic alkyl complex, $CpNiMe(PPh_3)$, gives a blue soluble complex of stoichiometry $Ni_6Cp_3(NO)_2O(PPh_3)$. No suitable crystals have yet been obtained from a crystallographic study, but small needles can be obtained for dichloromethane/methanol (1:1). The ir spectrum of this complex is dominated by bands due to triphenylphosphine and cyclopentadiene ligands, but a strong band at 1745 cm^{-1} is due to a terminal nitrosyl

group. The absence of a band due to $\nu_{(P=O)}$ confirms the presence of triphenylphosphine. The ^1H nmr spectrum consists of a broad resonance in the region expected for aromatic protons and can be assigned to both triphenylphosphine and cyclopentadienyl groups. The broad nature of this resonance may be due to the weak paramagnetism shown by this compound.

The structure of this complex clearly contains a metal cluster,[60] but the precise structure cannot be deduce without a crystallographic study.

The formation of this complex is clearly similar to the reaction of the cobalt alkyls. Loss of triphenylphosphine into solution would give a complex, CpNiMe, which is almost certainly paramagnetic. This can react with nitric oxide with the liberation of neutral nitrosomethane groups (Section 2). The resultant reduced nickel species could quite conceivably interact to give a cluster complex.

This section has shown that the reaction of metal alkyls with incomplete d shells with nitric oxide are very dependent on the electronic configuration and in particular that of any intermediate species generated in solution prior to the initial interaction with nitric oxide.

CHAPTER 2

PARAMAGNETIC ALKYL COMPLEXES

I. Complexes with one unpaired electron.

A. i) Bis(cyclopentadienyl)dimethyl niobium (IV)

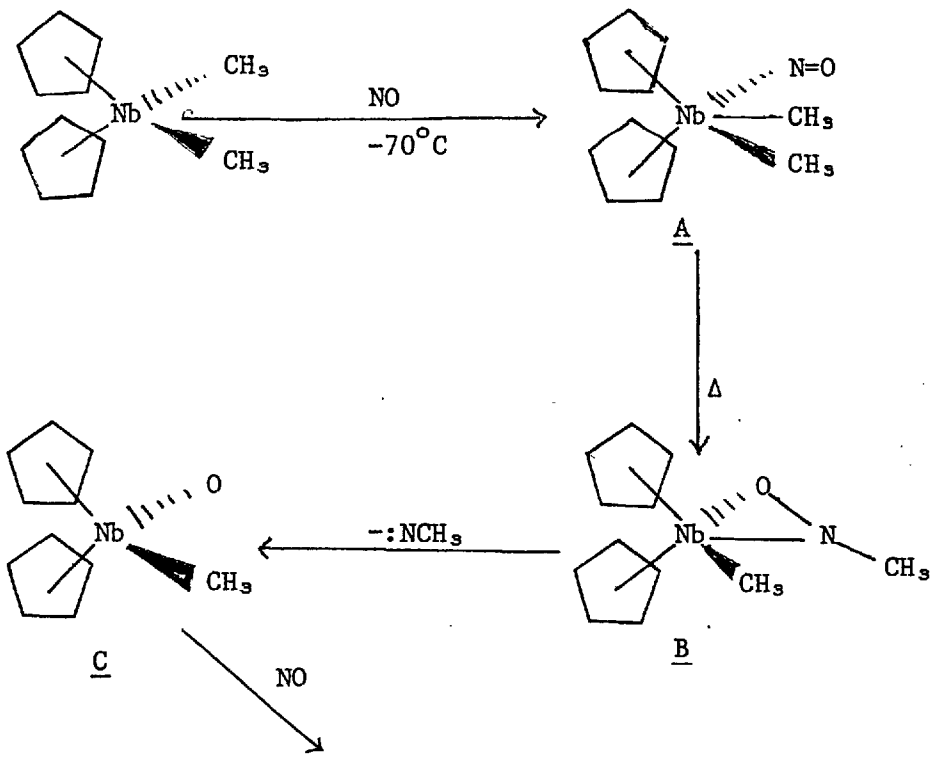
Interaction of the red d^1 complex, $(Cp)_2NbMe_2$ with nitric oxide at room temperature gives an insoluble white precipitate, $Cp_2NbO[ONMeNO]$. This complex is air stable but too insoluble to determine its molecular weight or its nmr spectrum. The ir spectrum of this complex has bands due to cyclopentadiene ligands, and a band at 850 cm^{-1} which can be assigned to $\nu_{(Nb=O)}$. Bands at 1310, 1200, 950 cm^{-1} are consistent with an N-methyl-N-nitrosohydroxylaminato group, which must be chelating or bridging. Various types of bridges have been discussed earlier (Chapter 1) but little information can be obtained due to this compound's insolubility. However, this compound is undoubtedly polymeric similar to the complex $Cp_2TiMe(ONMeNO)$.[24]

If this reaction is carried out at -70°C, a different product is formed. The yellow, toluene soluble complex is stable only for short periods at room temperature as it decomposes (below). However, it can be handled for short periods under nitrogen in order to obtain the relevant spectroscopic data. No satisfactory analysis could be obtained, although it was evident that this complex contained nitrogen. It is diamagnetic in solution (nmr) and the ir spectrum has a band at 1670 cm^{-1} which can be assigned to a terminal nitrosyl group, $\nu_{(N=O)}$.

The nmr spectrum has two singlets at δ 0.12 and δ 0.94, indicating the presence of inequivalent methyl groups as well as a singlet at δ 5.92, due to cyclopentadiene ligands. The spectroscopic data is consistent with A in the scheme, XLIV.

On monitoring the nmr spectrum at room temperature the peak at δ 0.12 ppm (Nb-CH_3) diminishes and is replaced by a peak at δ 2.83 ppm (N-CH_3), consistent with methyl migration to form an unstable η^2-nitroso methane complex, B. This complex cannot be isolated as it decomposes with loss of azomethane to give $Cp_2Nb(O)Me$. The intermediate B was not observed alone in the nmr spectrum, but only in the presence of the other complexes involved in the reaction sequence. The liberation of azomethane as a product of this reaction can be detected by trapping of the gaseous products. The mass spectrum of the gas had a mass peak due to the molecular ion $C_2H_6N_2^+$ and a characteristic fragmentation pattern.[51] Under the experimental conditions, the most abundant fragments were $CH_3N_2^+$, $CH_2N_2^+$, CH_3N^+, N_2^+, $C_2H_4^+$ and CH_3^+.

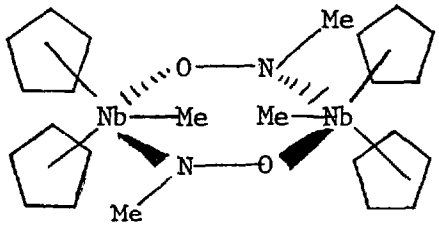
The final colourless product formed in this reaction sequence is $Cp_2Nb(O)Me$, C. This complex is apparently air stable and soluble in organic solvents such as toluene, THF and dichloromethane, but is insoluble in petroleum and ether. It is diamagnetic in the solid state and was shown to be monomeric in solution. The nmr spectrum indicates that the remaining methyl group is bound to the metal, and the ir spectrum (Table 4) has a band at 835 cm^{-1} which is in the region expected for a $\nu_{(Nb=O)}$, although this region does contain a further strong band due to the cyclopentadienyl ligands. Further reaction of this complex with nitric oxide at room temperature gives the complex $Cp_2NbO(ONMeNO)_2$.



$[Cp_2Nb(O)(ONMeNO)]_n$

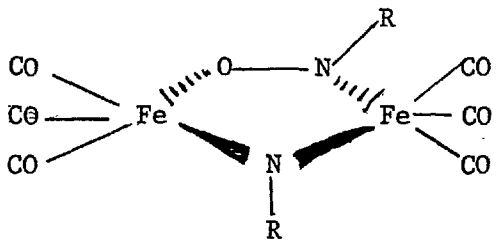
LXIV

It is not possible to be certain whether the nitrosomethane intermediate B has a 3-membered η^2-nitrosomethane group or bridging nitrosomethane groups, XLV, as both structures are consistent with the observed spectroscopic data.



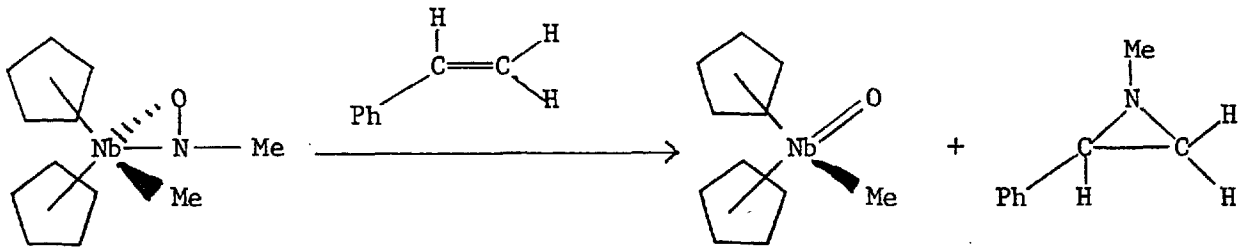
XLV

The mechanism of decomposition of nitrosomethane intermediates is equally unclear, but the liberation of free nitrenes can be postulated. Evidence for this mechanism comes from the formation of nitrene complexes such as $Fe(CO)_6(ONR)(NR)$[40] XLVI and $(CpNi)_3NR$, XXII.[42]



XLVI

Further evidence for free nitrene liberation in this case is the reaction of interemediate B made in situ, with styrene to give 1-methyl-2-phenyl aziridine and $Cp_2Nb(O)Me$, XLVII.



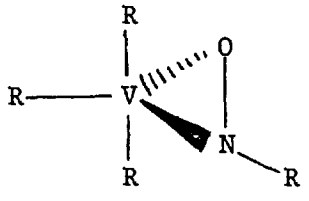
XLVII

The azridine can be isolated by chromatography and was characterised by its mass spectrum in which a molecular ion $C_9H_{11}N^+$ was observed and its ^1H nmr spectrum which is quite chracteristic due to the non-equivalence of the three protons. This results in three quartets at δ 1.5, 1.7, 2.1, whilst the ($N-CH_3$) protons occur as a singlet, δ 2.38.[62,63]

The transfer of a nitrene to olefins has also been observed in molybdenum η^2-PhNO complexes,[38,39] except in this case the azindines were not isolated and during the work up they rearranged to give more stable allylic amines. If the products from the reaction of styrene or 1-methylcyclohexene with the niobium complex are worked up in acidic conditions, polymeric amines are obtained. The mass spectra of these organic compounds had highest mass peaks equivalent to dimeric species which can be formed via nucleophilic attack by nitrogen on a protonated azridine.[64] The ^1H nmr spectra of these compounds were complex and contained olefinic protons as well as saturated hydrocarbons.

ii) Tetrakis(trimethylsilylmethyl)vanadium(IV).

Reaction of the green d^1 alkyl $V(CH_2SiMe_3)_4$ with nitric oxide at -70^oC gives a red solution and on reduction of the solution red crystals of the complex $V(CH_2SiMe_3)_3ONCH_2SiMe_3$, XLVIII. This complex is temperature sensitive and decomposes at ambient temperatures. Elemental analysis proved unsuccessful, although the presence of nitrogen was confirmed. This complex is diamagnetic in solution, and the ^1H nmr spectrum indicates that one trimethylsilylmethyl group has been transferred to nitrogen to give a coordinated nitrosoalkane group [δ 0.3 (CH_3), 3.45 (CH_2)] as well as three equivalent alkyls bound to vanadium (δ 0.2 (CH_3) 0.32 (CH_2)]. The ir spectrum is consistent with this, no bands occur in the terminal nitrosyl region $\nu_{(N=O)}$ and although the spectrum is dominated by bands due to the trimethylsilylmethyl groups, a band at 960 cm^{-1} can be assigned to $\nu_{(N-O)}$ of an η^2-nitrosoalkane group. The equivalence of the alkyl groups is almost certainly due to this complex being fluxional in solution. However, no detailed nmr studies were carried out.



XLVIII

On warming to room temperature, although the red solid is stable for short periods under nitrogen, the complex eventually pales, and upon recrystallisation, lemon needles of stoichiometry $VO(CH_2SiMe_3)_3$ can be obtained. Spectroscopic and analytical data (Tables 4-6) confirm that this complex is identical to the known compound,[65] prepared from $VOCl_3$ and a deficiency of trimethylsilylmethyl Grignard reagent. The decomposition of $V(CH_2SiMe_3)_3ONCH_2SiMe_3$ to give $VO(CH_2SiMe_3)_3$ almost certainly involves loss of trimethylsilylmethyl nitrene, but no organic product was isolated from this reaction.

The diamagnetic alkyl $VO(CH_2SiMe_3)_3$ does not react further with nitric oxide, presumably due to coordinative saturation of vanadium.

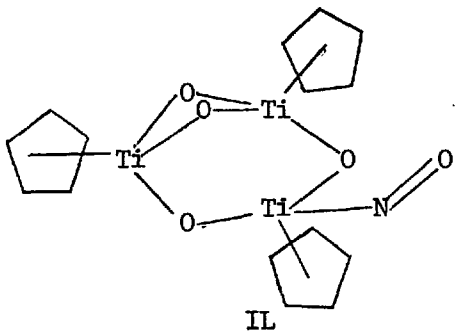
iii) Bis(cyclopentadienyl)phenyl (and benzyl) titanium(III).

The paramagnetic d^1 titanium(III) complexes Cp_2TiR (R = C_6H_5, $CH_2C_6H_5$) react with nitric oxide in both cases to give the same product. The orange complex has a stoichiometry $Cp_3Ti_3O_4(NO)$, where not only has the phenyl or benzyl group been lost but also one cyclopentadiene group per titanium.

This complex is air stable but is only sparingly soluble in organic solvents such as dichloromethane or THF. It is totally insoluble in ether, petroleum or toluene. The complex was shown to be trimeric in dichloromethane and the mass spectrum had a peak with the correct isotopic pattern for the molecular ion, $Ti_3C_{15}H_{15}NO_5^+$, together with a fragmentation pattern involving loss of cyclopentadiene groups.

The difference from the vanadium and niobium compounds can be ascribed to the known preference of titanium to form Ti-O-Ti bonds rather than multiple 'Ti=O' bonds. The initial transfer of Ph or $PhCH_2$ groups to nitric oxide can be expected after nitrene elimination to result in an unstable '$Cp_2Ti=O$' intermediate which can then react further in the presence of nitric oxide.

This type of path has been proposed for the formation of the complex $Cp_6Ti_6O_8$[66] in the reaction of $Cp_2Ti(CO)_2$ with carbon monoxide and hydrogen and in which a (η^2-OCH) intermediate was invoked. In the nitric oxide reaction, one can consider a $Cp_3Ti_3O_4$ unit with one unpaired electron as an intermediate which could then be trapped by reaction with nitric oxide to give $Cp_3Ti_3O_4(NO)$ rather than proceding to give $Cp_6Ti_6O_8$. The structure of the nitric oxide complex by analogy with that of the Ti_6 species characterised by an X-ray structural determination is probably IL, where the CpTi units are linked by oxo bridges.. Binding of nitric oxide in the 'bent' form then accounts for the diamagnetism.



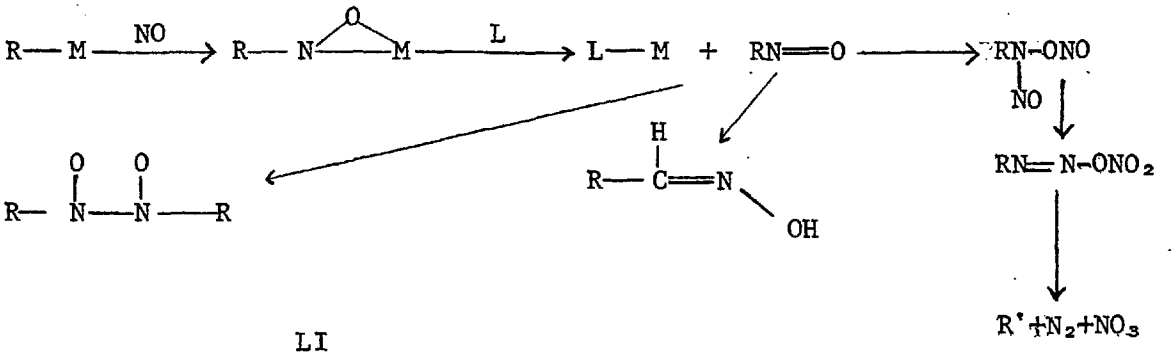
IL

The spectroscopic data is consistent with this structure. The ^1H nmr spectrum has two peaks (δ 6.30, 6.37 ppm) in the ratio 2:1 due to the two environments of the Cp rings, whilst the ir spectrum has a band at 1550 cm^{-1} which can be assigned to a 'bent' terminal nitrosyl group. The ir spectrum also has a broad band at 580 cm^{-1} which is probably due to the oxo bridges, $\nu_{(Ti-O-Ti)}$.

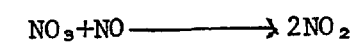
It is interesting to note that although six alkyl groups have been lost, only four oxygen atoms remain. This could be due to alkyl groups being lost as alkanes, L,

L

but more likely as neutral nitrosoalkanes, LI, which may dimerise, rearrange to give oximes,[17,18,49] or most likely react further with



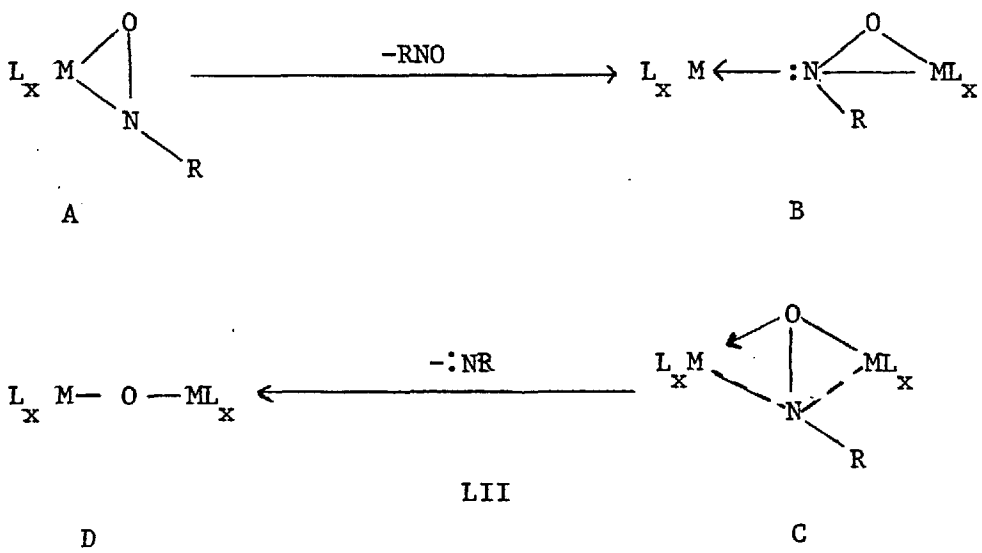
LI



two molecules of nitric oxide to give an ON disubstituted hydroxylamine which may decompose via rearrangement to a diazonium nitrate [77,99]

The displacement of neutral nitrosoalkanes by other ligands has been well documented (Introduction) and the apparent loss of alkyl groups in nitric oxide reactions has also been observed in the reaction of $ReO(CH_2SiMe_3)_4$ to give $Re_2O_3(CH_2SiMe_3)_6$. In this case a bridging oxo group is also present within the product. This observation could be consistent with a mechanism, LII. Following an insertion reaction to form an η^2-nitrosomethane intermediate, A, one neutral nitrosoalkane group can dissociate from the metal centre, to be replaced by the lone pair of another bound nitrosoalkane group, B.

This group can decompose with liberation of a nitrene to give a bridging oxo group, D.



A B

LII

D C

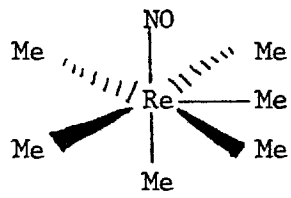
The formation of a μ-oxo group from a nitrosoalkane complex has recently been observed by G. LaMonica and S. Cennini.[43] The complex $ReCl_3(ONR)OPPh_3$ reacted with cyclohexylisocyanide to give the complex $[Re_2OCl_6(NR)_2(CNC_6H_{12})_2]$ where not only was an oxo group retained, but also the nitrene fragments as imido groups.

II. Rhenium Alkyls.

A. Hexamethylrhenium.

Careful interaction of nitric oxide with a green solution of $ReMe_6$ at -80°C gives orange-red needles of the complex $ReMe_6NO$. This complex is air sensitive and well soluble in organic solvents including ether, THF and toluene, but it is only sparingly soluble in petroleum, particularly at low temperatures. This complex is surprisingly stable and no further reaction takes place on warming to room temperature, provided excess nitric oxide has been removed at -80°C. It is diamagnetic and has been shown to be monomeric in solution. The mass spectrum does not have a mass peak corresponding to the molecular ion but peaks with the corrct isotopic pattern due to the successive loss of methyl groups from $ReMe_5NO^+$ to $ReNO^+$.

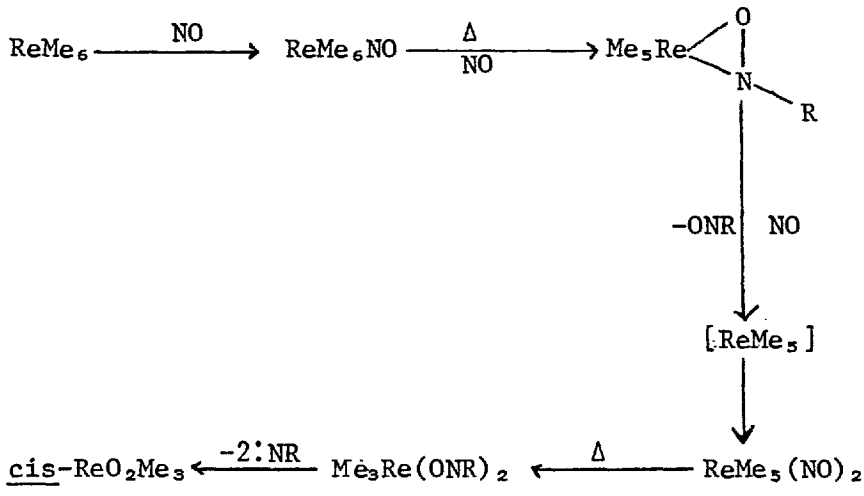
The ir spectrum of this complex confirms the presence of a terminal nitrosyl group $\nu_{(N=O)}$ 1710 cm^{-1}, and the complex is clearly seven coordinate, LIII, with six terminal methyl groups as well as the nitrosyl group.



LIII

Seven coordinate species may have several structural configurations and are generally fluxional (non-rigid)[67] resulting in the equivalence of the ligands in the nmr spectrum. Not surprisingly, this occurs in the complex $ReMe_6NO$. The ^1H nmr spectrum contains only one resonance which is markedly solvent dependent, [δ 1.21 ($CDCl_3$), 0.69 (C_6D_6)]. On cooling, the sample to -70°C, the single peak in the spectrum does not resolve, indicating the low energy barrier to exchange in this complex.

Whilst the complex $ReMe_6NO$ is produced from the reaction of $ReMe_6$ and nitric oxide at -80°C, in petroleum, if the reaction is carried out in toluene the initial orange product remains in solution. On warming in the presence of excess nitric oxide, the solution eventually pales to yellow and the volatile complex, ReO_2Me_3 can be obtained. It has been shown by spectroscopic methods to be identical to the known complex,[34] cis-ReO_2Me_3, prepared from the reaction of $ReOMe_4$ and nitric oxide. The reaction of $ReMe_6$ with nitric oxide to give ReO_2Me_3 has been reported earlier,[34] but the product was not produced in sufficient quantities to be fully characterised. The formation of ReO_2Me_3 from $ReMe_6$ and nitric oxide involves the loss of three methyl groups, with the retention of two oxo groups. As any diamagnetic alkyl intermediate would be expected to react with nitric oxide to give N-methyl-N-nitroso hydroxylaminato groups. The first insertion reaction probably results in a neutral nitroso methane group LIV, which can be lost to give a paramagnetic intermediate, $ReMe_5$, rather than $ReOMe_5$ which would be diamagnetic. The resulting paramagnetic alkyl, $ReMe_5$ could react swiftly with nitric oxide to give $ReMe_5(NO)_2$ which with alkyl migration and nitrene elimination would result in the observed alkyl ReO_2Me_3.

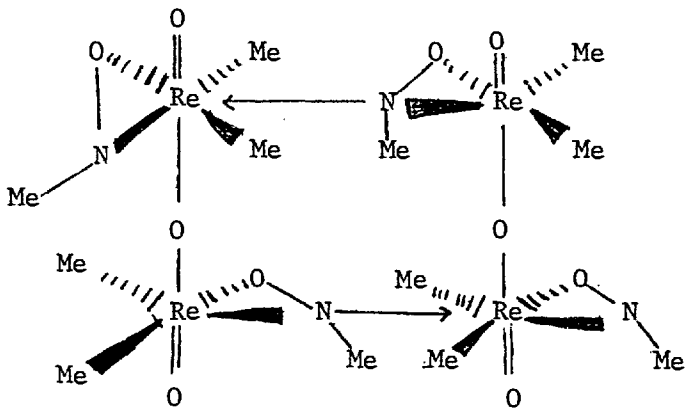


Dilithium Octamethylrhenate(VI).

The complex Li_2ReMe_8 also reacts with nitric oxide at low temperature. This reaction is exothermic and produces a yellow complex $Re_2O_3Me_4(ONMe)_2$, where five methyl groups have been lost per rhenium. This complex is air stable but hygroscopic. It is surprisingly insoluble in THF and dichloromethane. It is diamagnetic and the mass spectrum has a highest mass peak with the correct isotopic pattern for the molecular ion, $Re_2C_6H_{18}N_2O_5^+$ as well as peaks due to successive loss of methyl groups and nitrosomethane fragments to $Re_2O_3^+$. The complex is too insoluble in dichloromethane or benzene to obtain a satisfactory molecular weight determination, but it is soluble in DMSO, in which it was shown to be monomeric (Re_2). The observed ^1H nmr spectrum of this complex was poor due to solubility problems, but resonances were present due to both terminal methyl groups (δ 1.21) and methyl groups bound to nitrogen (δ 2.18).

The ir spectrum contains no bands that can be assigned to a terminal nitrosyl group $\nu_{(N=O)}$, but a band at 970 cm^{-1} can be assigned to $\nu_{(N-O)}$ of an η^2-nitrosomethane group.

The oxygen core of this complex could consist of any one of three configurations: a linear O=Re-O-Re=O system or with cis- or trans- oxo groups. A structure for this complex containing a bent Re-O-Re bridge can be excluded as this would require an absorption band in the 400-550 cm^{-1} region.[68,69] The cis- or trans- isomers can usually be differentiated by the frequencies of the M-O-M vibration which is in the range 730-950 cm^{-1} as compared with 650-700 cm^{-1}, in the linear case,[69-71] In this case the absorbtion band occurs at 712 cm^{-1} which, although nearer to the range expected for a linear isomer is intermediate in frequency. In cis- complexes of (M_2O_3) there are two strong bands assigned as terminal $\nu_{(M=O)}$ stretches whereas in trans- and linearcomplexes there is only one.[72] Furthermore, in linear complexes, the Re=O frequencies are in the range 910-950 cm^{-1} whereas they are higher at 950-1050 cm^{-1} in non-linear isomers. Since $Re_2O_3Me_4(ONMe)_2$ has one band at 935 cm^{-1}, this confirms the presence of a linear isomer. The structure of this complex, LV, therefore contains a linear Re_2O_3 configuration with two terminal methyl groups and one η^2-nitrosomethane group per rhenium. The insoluble nature of this complex is almost certainly due to the presence of polymerisation, via the lone pair on the nitrogen of the η^2-nitrosomethane group.



LV

These weak interactions may be broken down in strongly coordinating solvents such as DMSO which can explain its monomeric nature.in this solvent.

In this complex the η^2-nitrósomethane ligand can be considered as dianionic or neutral and the rhenium atom can be Re(V) or Re(VII).

Other complexes with Re_2O_3 systems have been studied and in each case the linear system appears to be the preferred configuration for even electron species, e.g., Re(V) $[Re_2O_3(CN)_8]^{4-}$,[78] $[Re_2O_3(dtc)_4]$,[70] $[Re_2O_3(sal_2en)_2]$,[74] whilst systems with odd numbers of electrons prefer the <u>cis</u>- configuration, e.g., Re(VI) $[Re_2O_3(CH_2SiMe_3)_6]$,[35] $[Re_2O_3(OR)_6]$.[75]

The formation of this complex from Li_2ReMe_8 and nitric oxide clearly involves several stages of alkyl migration to coordinated nitric oxide resulting in both nitrene elimination and nitrosomethane dissociation. Clearly this reaction must invovle a similar concerted reaction step to the reaction of $ReO(CH_2SiMe_3)_4$ to give $Re_2O_3(CH_2SiMe_3)_6$, but why the μ-oxo bridge should be formed in the reaction of Li_2ReMe_8 and not $ReMe_6$ in unclear.

C. μ-dinitrogen bis[tetrakis(trimethylsilylmethyl)rhenium(IV)].

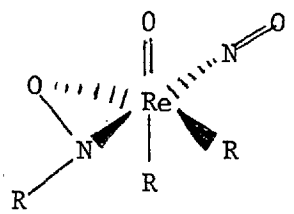
Interaction of a purple solution of $[Re(CH_2SiMe_3)_4]_2N_2$ with nitric oxide at -60°C does not give an instant colour change but on warming to room temperature, in the presence of nitric oxide, the colour gradually changes through a green intermediate to brown.

From this brown solution can be obtained large orange crystals of $ReO(NO)(CH_2SiMe_3)_2ONCH_2SiMe_3$.

This complex is air sensitive over moderate periods in air and is quite soluble in organic solvents such as toluene, benzene, THF, and dichloromethane. It is diamagnetic in the solid state and was shown to be monomeric in solution.

The ^1H nmr spectrum of this complex (Table 5) indicates that one of the three remaining alkyl groups has been transferred to nitrogen [δ 0.38(9), 2.42(2) whilst the other two alkyl groups remain bound to rhenium (δ 0.22(18), 0.34(4)]. The ir spectrum (Table 4) is in accord with this. One nitrosyl group is terminally bound to the metal $\nu_{(N=O)}$ 1690 cm^{-1} and two bands occur at 972 cm^{-1} and 1020 cm^{-1} which can be assigned to a terminal oxo group $\nu_{(Re=O)}$ and an η^2-nitrosoalkane group $\nu_{(N-O)}$ respectively.

The structure of this complex LVI, is clearly six coordinate, but the relative stereochemistry is not possible to determine from the data available.

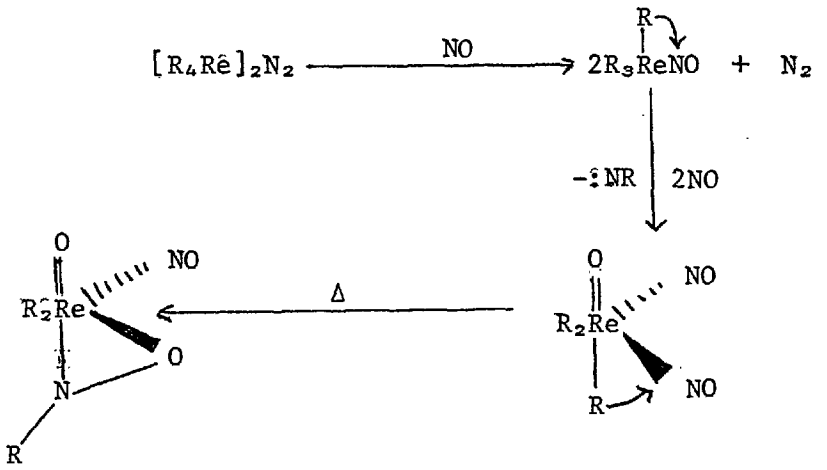


LVI

The position of the nitrosyl $\nu_{(N=O)}$ band in the ir spectrum suggests that it is 'bent' acting as a one-electron donor. This is consistent with the complex being diamagnetic. The rhenium can be ascribed as Re(V) or Re(VII), depending on the assignment of the η^2-nitrosoalkane group as neutral or dianionic.

The formation of this complex from $[Re(CH_2SiMe_3)_4]_2N_2$ can easily be explained. Initial reaction of nitric oxide would break the dinitrogen bridge to give two ostensibly Re(IV) alkyls with the liberation of dinitrogen LVII. Rapid reaction with nitric oxide would follow to give ReR_4NO, which has two remaining electrons. If these were unpaired they could be expected to react swiftly with nitric oxide. Loss of one nitrene and a further alkyl migration would give the complex LVI, as the product of this reaction.

It is interesting to note that as in the proposed reaction sequence for $ReMe_6$ with nitric oxide, nitric oxide reacts with each of the electrons available on the metal.



LVII

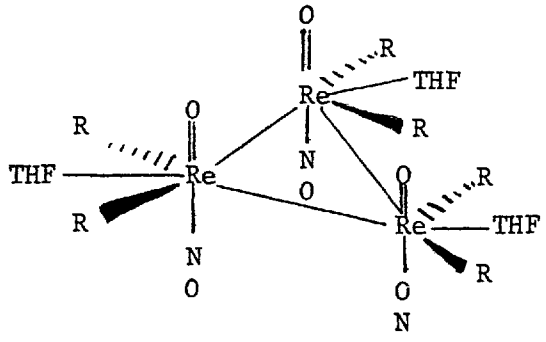
The η^2-nitrosoalkane ligand in this complex may be considered as neutral or dianionic, as this complex has properties consistent with both Re(V) and Re(VII). However, if this complex is treated with other donor ligands, the reactivity of the nitrosoalkane ligand follows that expected of a neutral ligand.

Reaction with THF.

If the complex LVI is stirred in THF, or the initial reaction is carried out in THF, a further product may be isolated. This yellow crystalline complex has a stoichiometry $[ReO(NO)(CH_2SiMe_3)_2.THF]_3$ and can be obtained from THF as large yellow crystals. Further molecules of solvent are present on initial crystallisation but these are removed by pumping (10^{-3} mmHg). These crystals are air stable, but crumble on the removal of the excess solvent of crystallisation.

This complex is only sparingly soluble in hydrocarbon solvents such as petroleum, benzene and toluene but is quite soluble in THF and dichloromethane. The ^1H nmr spectrum of this complex indicates the presence of two equivalent trimethylsilylmethyl groups bound to the metal [δ 0.21(18), 1.28(4)] and the presence of THF [δ 1.85(4), 3.74(4)]. The ir spectrum also confirms the presence of THF due to bands at 1025 and 850 cm^{-1}. Terminal nitrosyl groups are present in this complex and give a band at 1730 cm^{-1} $\nu_{(N=O)}$, and a band at 975 cm^{-1} can be assigned to the terminal oxo groups $\nu_{(Re=O)}$.

Although an X-ray crystallographic study would be desirable, this complex appears to be trimeric containing three rhenium(V) atoms. The structure LVII probably contains a triangle of rhenium atoms with five terminal groups on each metal.

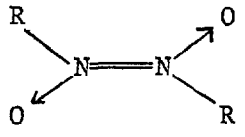


LVII

The THF molecules also appear to be coordinated and not present as solvent of crystallisation. Although further solvent is present initially, this was easily removed by pumping in vacuum. The three remaining THF molecules, however, are not easily removed. Trimeric rhenium clusters are well known for the Re(III)[32] and Re(IV)[76] oxidation states, and they appear to form quite readily in the absence of donor ligands. In this case, the loss of a neutral nitrosoalkane group into solution would result in $ReO(NO)R_2$ fragments which are coordinatively unsaturated. These can then react to give trimeric species.

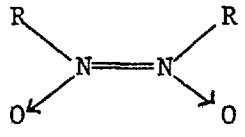
The formation of a trimeric species is surprising due to the presence of THF and nitrosoalkane, however, the similar Re(IV) clusters (Re_3R_{12})[76] were also formed in the presence of THF and any nitrosoalkane liberated into solution will dimerise or react further. The liberation of a neutral nitroso alkane group from the rhenium complex is confirmed by its isolation from the reaction mixture. Nitrosoalkanes generally form dimers[77] and nitrosotrimethylsilylmethyl is no exception. The ^1H

nmr spectrum of this organic compound is simple; resonances at δ 0.01(9) and 1.20(2) indicate the equivalence of the trimethylsilylmethyl groups. Nitrosoalkane dimers can exist in two isomeric forms, LIX which can be reacily distinguished by ir spectroscopy.



trans

or



cis

LIX

The trans isomers give a very strong band at 1200-1300 cm^{-1}.[77] A band at 1262 cm^{-1} does occur in this range but can be assigned to the trimethylsilylmethyl groups. The cis isomerson the other hand have several bands of medium intensity and bands in the spectrum of $(CH_3SiCH_2NO)_2$ at 1412, 1387, 1345, 1085, and 1025 cm^{-1} correspond closely to those observed in other cis-nitrosoalkane dimers.[77]

The ready dissociation of a neutral nitrosoalkane in this case is a clear example of how this dissociative step may take place in the reaction of nitric oxide with other metal alkyls.

Reaction with Triphenylphosphine.

Interaction of the orange nitrosoalkane complex $ReO(NO)(CH_2SiMe_3)_2(ONCH_2SiMe_3)$, LVI, with triphenylphosphine in THF was expected to give a simple substitution product, or an imido complex with the

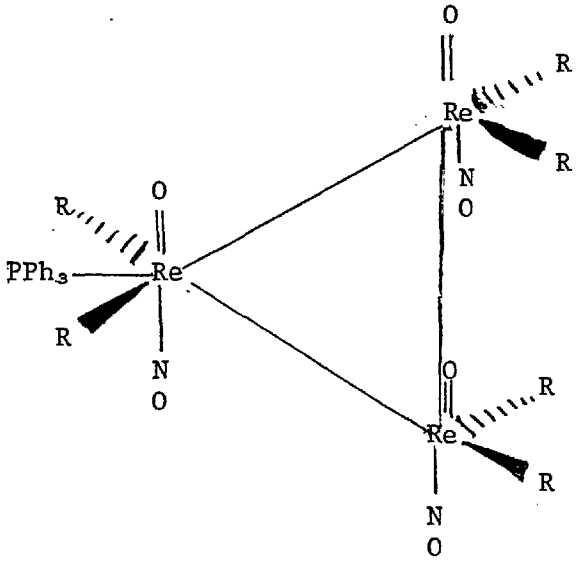
production of $OPPh_3$. However, rather than the expected monomeric complex a more complex trimeric compound is formed. The nitrosoalkane group has clearly been lost but only one triphenylphosphine is present per three rhenium atoms $[ReO(NO)R_2]_3PPh_3$. This white complex is air sensitive and gives black decomposition products if exposed to air particularly in solution. It is quite soluble in polar solvents such as THF and dichloromethane but is insoluble in toluene, petroleum and ether. The mass spectrum had a mass peak with the correct isotopic pattern for $ReO(NO)(CH_2SiMe_3)_2^+$ as well as fragments of lower mass, but no higher mass peaks. Unfortunately, due to this compound's lack of solubility in benzene and air sensitive nature in dichloromethane, a satisfactory molecular weight determination was not possible.

The ^1H nmr spectrum of this complex indicates the presence of trimethylsilylmethyl groups [δ 0.15(4) 2.12(12) and triphenylphosphine (δ 7.43br (15)] in the ratio 6:1 which confirms the stoichiometry of one phosphine per rhenium triangle. The ir spectrum is dominated by bands due to triphenylphosphine and trimethylsilylmethyl groups but has a strong band at 1720 cm^{-1} due to terminal nitrosyl groups $\nu_{(N=O)}$.

The terminal oxo $\nu_{(Re=O)}$ region of the ir spectrum has a band at 970 cm^{-1} as in the THF and nitrosoalkane complexes but this is quite weak. However, a strong new band at 910 cm^{-1} is present and this could be due to $\nu_{(Re=O)}$.

The structure of this complex is probably trimeric as the THF complex is, but with only one seven coordinate rhenium atom being bound to triphenylphosphine, LX. This type of complex with odd stoichiometric quantities of phosphine has been observed in Re(III) clusters.[78]

An X-ray crystallographic determination of the complex $Re_3Me_9(PEt_2Ph)_2$[32] has illustrated that such a cluster takes up an isosceles triangle configuration with the rhenium bound to phosphine, having the smallest angle. The resulting change of angles and bond lengths within the cluster caused by phosphine association would clearly make further associations more difficult due to the steric constraints applied to the other two rhenium atoms. Triphenylphosphine, being a bulky phosphine,[79] is likely to produce this type of complex.



LX

III. Complexes with more than one unpaired electron.

i) Chromium.

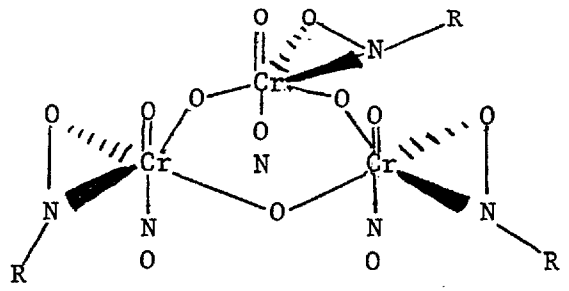
Chromium tetralkyls are paramagnetic and contain two unpaired electrons. Their reactions with nitric oxide have been studied previously [80] but the products were not isolated. Interaction of a purple solution of tetrakis(trimethylsilylmethyl)chromium(IV) with nitric oxide at room temperature gives a green-brown complex of stoichiometry $Cr(CH_2SiMe_3)O_2(NO)_2$. This complex is air stable and quite soluble in dichloromethane, THF and toluene, but insoluble in petroleum or ether.

The complex is paramagnetic (μ_{eff} = 2.9 BM) in the solid state and was shown to be hexameric in solution. The mass spectrum did not show a molecular ion but the highest mass peak had the correct isotopic pattern for $[CrO_2(NO)_2]_3^+$.

The ^1H nmr spectrum gives only broad ill-defined peaks and the esr spectrum gives a broad line g = 1.996, in frozen toluene with a nitrogen hyperfine splitting α_N = 0.45 mI. The spectrum also contains a much weaker line at g = 4.0834 with no hyperfine structure; this may be due to impurity, or to two different Cr(III) environments within this complex.

The ir spectrum has a strong band at 1840 cm^{-1} which is indicative of a linear nitrosyl group. Bands occur in the spectrum at 1010 cm^{-1} and 940 cm^{-1} and can be assigned to $\nu_{(N-O)}$ and $\nu_{(Cr=O)}$ respectively. A broad band at 560 cm^{-1} can be assigned to a $\nu_{(Cr-O-Cr)}$ chromium bridge.

This complex was non-crystalline, thus precluding an X-ray crystallographic determination, and any assignment of the structure of this complex must be tentative. However, from the observed spectroscopic data, the most likely structure is trimeric, LXI, with one bridging and one terminal oxo groups per chromium. A η^2-nitrosoalkane group and a linear nitrosyl group gives each chromium atom an octahedral configuration.



LXI

Further bridging by nitrosoalkane groups between trimeric units can give a hexameric molecular weight reading in solution.

The linear nitrosyl group in this complex is clearly bound as a three electron donor, and if the nitrosoalkane group is considered as neutral the chromium atoms have an oxidation state equal to three. This is consistent with both the magnetic moment and the epr spectrum. The magnetic moment of this complex (μ_{eff} = 2.9 BM), is lower than that expected for the spin only value (3.88 BM), which can be explained by any $d\pi$-$p\pi$ bonding that may be involved in the oxo bridges.

The formation of this complex can be rationalised as each alkyl group can be accounted for if one neutral nitrosoalkane group is lost in the formation of an oxygen bridge. The formation of a trimeric species is clearly complicated and prediction of a reaction path is difficult. However, chromium's preference for chromium(III) is evident in the final reaction step with the terminal nitrosyl groups being bound in its linear mode.

ii) Manganese.

Interaction of nitric oxide with pale solutions containing the paramagnetic alkyls MnR_2 ($R = CH_2SiMe_3$, CH_2CMe_3) at -60^oC gave an immediate colour change to brown. These brown solutions did not give crystalline products but only brown powders of variable stoichiometry. The ir spectra contained many bands due to $\nu_{(N=O)}$ which suggested that these powders contained a mixture of compounds.

iii) Vanadium.

Interaction of Cp_2VMe with nitric oxide at -60^oC gave a yellow, sparingly soluble precipitate. This complex gave a reasonably consistent analysis, but the carbon content was very low. Again, no crystalline compound or complex of a reasonable stoichiometry could be obtained.

iv) Tungsten.

Interaction of $W(CH_2C_6H_5)_4$ with nitric oxide at -60^oC gave an orange precipitate. This was only sparingly soluble and although the analyses appeared to be consistent it did not represent a complex of simple stoichiometry.

CHAPTER 3

ALKYL COMPLEXES WITH METAL-METAL BONDS

1. Binary Alkyls of Molybdenum and Tungsten M_2R_6.

Interaction of nitric oxide with dark yellow solutions of the complexes M_2R_6(M=Mo, W, R = CH_2SiMe_3, CH_2CMe_3) at room temperature gives yellow complexes of stoichiometry $[M_2O_3R_2(NO)_4]$.

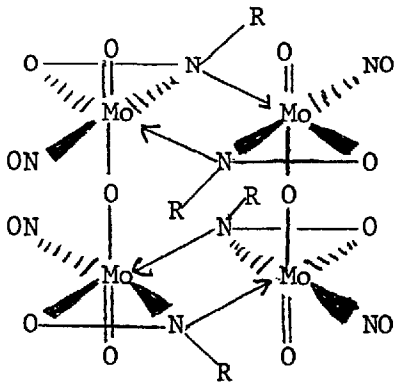
The neopentyl complexes crystallise from dichloromethane or THF with one molecule of solvent per metal but, initially, from toluene without.

All of these complexes are air stable, but quite hygroscopic. They are soluble in organic solvents such as dichloromethane, THF and toluene, but are insoluble in petroleum and ether.

These complexes are diamagnetic in the solid state and were shown to be dimeric (Re_4) in solution. The mass spectrum of the tungsten trimethylsilylmethyl derivative had a mass peak with the correct isotopic pattern for $W_2O_3(CH_2SiMe_3)_2(NO)_4^+$, together with peaks corresponding to loss of RNO groups and nitrosyl groups. The other complexes however, only showed equivalent fragmentation patterns.

The ir spectra of these complexes, Table 7, are quite similar. They each contain one band due to a terminal nitrosyl group at ca. 1760 cm^{-1}, whilst bands typical of a linear O=M-O-M=O group were also present at ca. 940 cm^{-1}, $\nu_{(M=O)}$ and 705 cm^{-1} $\nu_{(M-O-M)}$[74] (see chapter 2.IVB). The other nitrosyl moiety is bound to the remaining alkyl group as a nitrosoalkane group. and a band in each spectrum at ca. 970 cm^{-1}, $\nu_{(N-O)}$ indicates that this is an η^2-nitrosoalkane group.

The structure of these complexes, LXII, contains a linear Mo_2O_3 group with terminal nitrosyl groups on each molybdenum. The molecular weight data in dichloromethane indicates a dimeric structure in solution which is almost certainly due to bridging via the lone pair on each nitroso alkane group. This is not surprising as without this bridging each molybdenum atom would be only five coordinate.

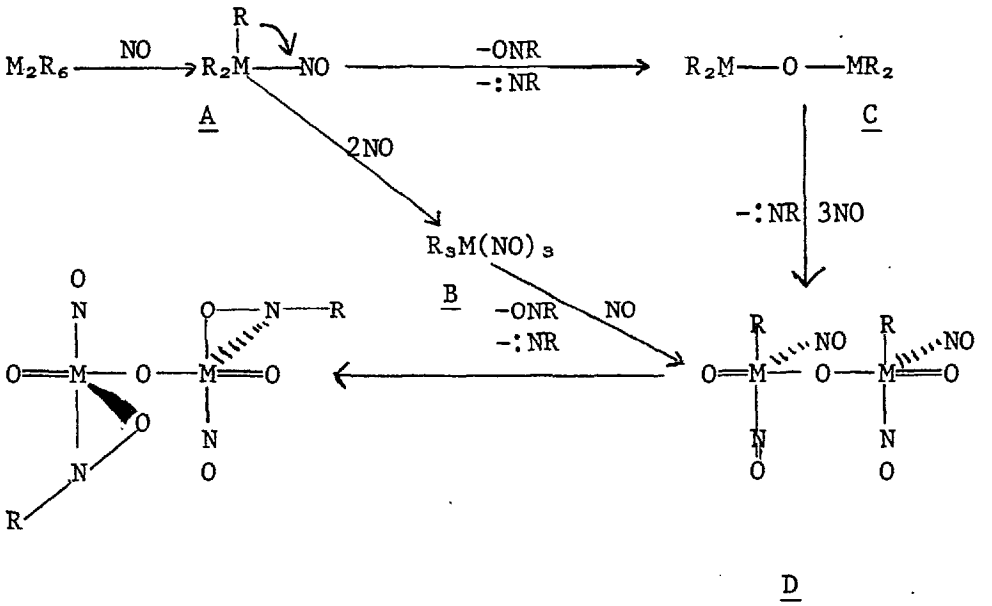


LXIII

The ^{1}Hnmr spectra of these complexes (Table 8) are consistent with the presence of both bridging and non-bridging nitroso alkane groups in solution. In all four cases the spectra showed inequivalence of the alkyl groups either giving rise to broad resonances and in one case, two distinct types of alkyl group.

The formation of these complexes from M_2R_6 can be explained by successive reactions of nitric oxide. Initial reaction of nitric oxide with a metal-metal bonded species of this type would be expected to break the metal-metal bond. This reaction has been observed in other complexes of this type such as $Mo_2C\ell_4(PMe_3)_4$[81] and $M_2(OR)_6$[82] (M = Mo, W)

to give complexes $MoCl_2(NO)_2(PMe_3)_2$ and $M(OR)_3NO$ respectively. By analogy with the alkoxide reaction, one might expect the alkyls M_2R_6 to give an intermediate complex, MR_3NO, A LXIV.



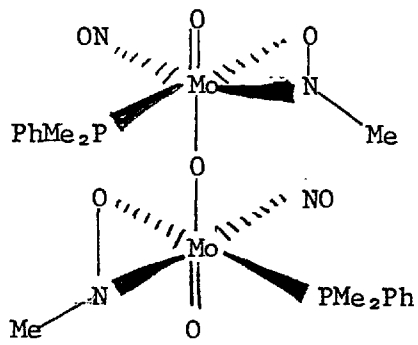
LXIV

This intermediate contains Mo(IV) which has two electrons. As those are most likely to be unpaired, there will be a tendancy to react with two further molecules of nitric oxide to give $R_3M(NO)_3$, however, as this did not take place in the corresponding alkoxide complexes, an insertion reaction may take place beforehand to give either a bridging or terminal oxo group.

This intermediate will be paramagnetic and will react with further molecules of nitric oxide. Clearly, it is not possible to predict with absolute certainty the order in which these reactions take place, however, the formation of the final product must have involved the reaction steps indicated in the scheme.

Reaction of $Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2$ with PMe_2Ph.

Interaction of the molybdenum trimethylsilylmethyl derivative, $Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2$ with PMe_2Ph in toluene gives an immediate precipitate of the phosphine adduct $[Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2(PMe_2Ph)_2]n$. This complex is diamagnetic and virtually insoluble in most organic solvents. The ir spectrum was virtually identical to $Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2$ with bands at 1760 cm^{-1}, $\nu_{(N=O)}$, 965 cm^{-1} $\nu_{(N-O)}$; 940 cm^{-1} $\nu_{(Re=O)}$ and 705 cm^{-1} $\nu_{(Re-O-Re)}$ except for the addition of these bands expected for dimethylphenylphosphine. The complex was too insoluble to obtain a molecular weight determination or nmr spectra but the most likely structure of this complex, LXV, has PMe_2Ph groups in place of the nitrosoalkane bridges.



LXV

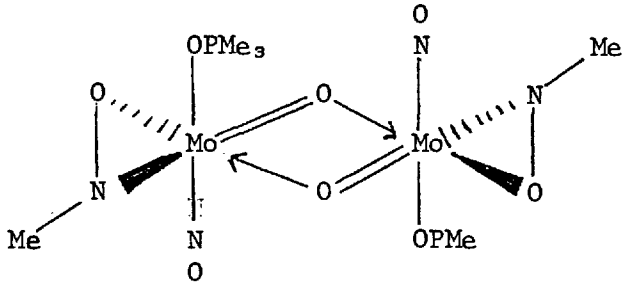
$Mo_2Me_4(PMe_3)_4$.

The reaction of a blue solution of $Mo_2Me_4(PMe_3)_4$ with nitric oxide at room temperature gives a yellow complex, $[MoO(NO)ONMe(OPMe_3)]n$. This complex is air stable and only sparingly soluble in organic solvents such as THF and dichloromethane. It is, however, soluble in DMSO. This compound is almost certainly polymeric in the solid state, but was shown to be monomeric in DMSO. The structure of this complex cannot

be absolutely identified from the spectroscopic data and many possibilities may be proposed. The ^1H nmr spectrum indicates that the remaining methyl group has been transferred to nitrogen (δ 2.11), and also confirms the presence of trimethylphosphine oxide (doublet, δ 1.40, 1.54, J_{P-H} 12.6 Hz).

The ir spectrum confirms the presence of trimethylphosphine oxide rather than trimethylphosphine $\nu_{(P=O)}$ 1145 cm^{-1}, $\nu_{(P-CH_3)}$ 948 cm^{-1}, and the presence of a terminal nitrosyl group; $\nu_{(N=O)}$, 1735 cm^{-1}. A band at 1060 cm^{-1} may be due to $\nu_{(N-O)}$ of the η^2-nitrosomethane group, but this is rather high and $\nu_{(N-O)}$ is probably obscured by the strong band at 948 cm^{-1}. The strongest band in the ir spectrum occurs at 860 cm^{-1} and is the only band that can be assigned to $\nu_{(Mo=O)}$. This is significantly lower than that expected for a simple terminal oxo stretch and is more consistent with an assymetrical bridge. Assymetrical bridges have been known[83,84] to reduce the stretching frequency in the ir spectra and the presence of a bridge could be consistent with the diamagnetic nature of this complex.

The most likely structure of this complex, LXVI, has a double assymetric bridge, with the possibility of a $d\pi$-$p\pi$ interaction of Mo-Mo interaction accounting for the diamagnetism. Further polymerisation may also occur via the nitrosomethane groups.



LXVI

The assymetric oxo bridges in this compound may be broken down in strongly coordinating solvents such as DMSO.[84] This, or the replacement of trimethylphosphine oxide groups by DMSO could explain the monomeric molecular weight determination in this solvent.

The formation of this complex from $Mo_2Me_4(PMe_3)_4$ can be explained by successive reactions with nitric oxide. As in the similar complex $Mo_2Cl_4(PMe_3)_4$, initial reaction with nitric oxide will give a monomeric complex, $MoMe_2(PMe_3)_2(NO)_2$. Two insertion reactions can take place, one with liberation of methyl nitrene to give a terminal oxo group, and the other remains as a nitrosomethane group bound to molybdenum. This complex can then react further with nitric oxide to give a terminal nitrosyl group. The presence of trimethylphosphine oxide is expected as any trimethylphosphine liberated into solution will rapidly react with nitric oxide.

EXPERIMENTAL SECTION

Microanalyses were by Pascher (Bonn) and Imperial College Laboratories. Spectrometers: Perkin-Elmer R12B, R32 (^{1}H nmr), Varian XL-100 (^{1}H, ^{13}C, ^{31}P, F.T.); Perkin-Elmer PE457, 257 (ir). Molecular weights were determined cryoscopically or osmometrically using a Perkin-Elmer-Hitachi osmometer. Magnetic moments were measured in the solid state using an Evans' balance or in solution using Evans' nmr technique.

All operations were performed under oxygen-free nitrogen or argon or in vacuum and all solvents (except CH_2Cl_2) were dried over sodium and distilled under nitrogen before use. Dichloromethane was dried over calcium hydride and distilled under nitrogen. Petroleum used had b.p., 40-60°C. Nitric oxide was from British Oxygen Company and was purified by trap to trap distillation, the head fractions being discarded. Melting points were determined in sealed capillaries under nitrogen and are uncorrected.

EXPERIMENTAL CHAPTER I

Tetrakis(trimethylsilylmethyl)zirconium(IV)

Nitric oxide was bubbled through a petroleum solution containing 1 g of $Zr(CH_2SiMe_3)_4$[85] at room temperature. The resulting white precipitate was collected, washed with petroleum and recrystallised from toluene to give the product $Zr(ONCH_2SiMe_3NO)_4$ as colourless microcrystals.

Excellent large crystals may be obtained from acetone, however, the yield is considerably reduced. Yield from toluene, 1.5 g, 97% based on $Zr(CH_2SiMe_3)_4$.

Tetrakis(neopentyl)Zirconium(IV)

Nitric oxide was bubbled through a petroleum solution containing 1 g of $Zr(CH_2CMe_3)_4$[85] at room temperature. The resulting white precipitate was collected, washed with petroleum and recrystallised from toluene to give the product $Zr(ONCH_2CMe_3NO)_4$ as a colourless microcrystalline solid.

Excellent colourless crystals can be obtained from acetone. However, the yield is considerably reduced. Yield from toluene 1.6 g, 98% based on $Zr(CH_2CMe_3)_4$.

Tetrakis(allyl)zirconium(IV).

Nitric oxide was bubbled through a red petroleum solution containing $Zr(C_3H_5)_4$[86], 1 g, at room temperature. The resulting pale

yellow precipitate was collected, washed with petroleum and recrystallised from toluene to give the product $Zr(ONC_5H_5NO)_4$ as a pale yellow crystalline solid. Large crystals may be obtained from acetone. Yield from toluene 1.65 g, 85% based on $Zr(C_5H_5)_4$.

Dichlorobis(trimethylsilylmethyl)zirconium(IV).

An etherial solution of $ZrCl_2(CH_2SiMe_3)_2$ was obtained by mixing equimolar quantities of $Zr(CH_2SiMe_3)_4$ and $ZrCl_4$ in ether. This mixture was stirred for 1 h. Nitric oxide was passed through this solution at room temperature to give a white precipitate. This was collected, washed with petroleum and recrystallised from THF/toluene (1:1) to give the product $ZrCl_2(ONCH_2SiMe_3NO)_2$ as colourless microcrystals. Yield 75% based on zirconium from both $Zr(CH_2SiMe_3)_4$ and $ZrCl_4$.

Dichlorobis(trimethylsilylmethyl)titanium(IV).

A petroleum solution of $TiCl_2(CH_2SiMe_3)_2$ was obtained by mixing equimolar solutions of $Ti(CH_2SiMe_3)_4$ and $TiCl_4$ in petroleum. The petroleum solution was stirred for 1 h. Nitric oxide was bubbled through this solution at room temperature to give a white precipitate. This was collected, washed with petroleum and recrystallised from a mixture of THF and toluene (1:1), to give the product $TiCl_2(ONCH_2SiMe_3NO)_2$ as colourless microcrystals. Yield, 85% based on titanium from both $Ti(CH_2SiMe_3)_4$ and $TiCl_4$.

Dichlorobis(neopenyl)titanium(IV).

A petroleum solution of $TiCl_2(CH_2CMe_3)_2$ was obtained by mixing equimolar solutions of $Ti(CH_2CMe_3)_4$ and $TiCl_4$ in petroleum. The petroleum solution was stirred for 1 h. Nitric oxide was bubbled through this solution at room temperature to give a white precipitate. This was collected, washed with petroleum and recrystallised from a mixture of THF and toluene (1:1) to give the product $TiCl_2(ONCH_2CMe_3NO)_2$ as colourless microcrystals. Yield 80% based on titanium from both $Ti(CH_2SiMe_3)_4$ and $TiCl_4$.

Tetrakis(trimethylsilylmethyl)titanium(IV).

Nitric oxide was bubbled through a petroleum solution containing 1 g of $Ti(CH_2SiMe_3)_4$[85] at room temperature. The resulting yellow-orange solution was reduced to small volume until an orange gum remained. This was recrystallised from ether to give the product $Ti(ONCH_2SiMe_3NO)_4$ as orange crystals. Yield, 1.5 g, 94% based on $Ti(CH_2SiMe_3)_4$.

Chlorotris(neopentyl)titanium(IV).

A petroleum solution of $TiCl(CH_2CMe_3)_3$ was prepared by mixing equimolar solutions of $Ti(CH_2CMe_3)_4$ and $TiCl_4$ in the ratio (3:1). The resulting solution was stirred for 1 h. Nitric oxide was passed through this solution at room temperature. The resulting yellow solution was reduced to small volume to give a yellow gum. This was recrystallised from ether to give the product $TiCl(ONCH_2CMe_3NO)_3$ as yellow crystals. Yield 95% based on titanium from $Ti(CH_2CMe_3)_4$ and $TiCl_4$.

Pentamethyl niobium(V)

Nitric oxide was bubbled through a petroleum solution containing ca. 1 g of $NbMe_5$[87] at -70°C. The resulting yellow precipitate was collected, and washed with petroleum at -70°C. The yellow precipitate was warmed to room temperature and extracted into toluene. The solution was reduced to small volume and cooled to -30°C to give the product $NbMe_2(ONMeNO)_3$ as orange crystals. Yield 1.45 g, 70% based on $NbMe_5$.

Pentamethyl tantalum(V)

Nitric oxide was bubbled through a petroleum solution containing ca. 1 g of $TaMe_5$[87] at -70°C. The resulting white precipitate was collected, and washed with petroleum at -70°C. The white precipitate was warmed to room temperature and extracted into toluene. The resulting colourless solution was reduced to small volume and cooled to -30°C to give the product $[TaMe_3(ONMeNO)_2]_2$ as colourless crystals. Yield 1.0 g, ca. 70% based on $TaMe_5$.

Dimethyl zinc(II)

Nitric oxide was bubbled through a petroleum solution containing $ZnMe_2$[88] (1 g) at -30°C. An instantaneous reaction took palce to precipitate a white solid. This was collected, washed with petroleum and ether and dried in vacuo to give the product $[Zn(ONMeNO)_2]$ as a white powder. This analytically pure powder may be recrystallised from dichloromethane. Yield 2.2 g, 93% based on $ZnMe_2$.

Bis(neopentyl)zinc.

Nitric oxide was bubbled through a petroleum solution containing $Zn(CH_2CMe_3)_2$[88] (1 g) at -30°C. This gave a white precipitate which was collected, washed with petroleum and ether. The resulting white powder was recrystallised from dichloromethane to give the product $[Zn(ONCH_2CMe_3NO)_2]_4$ as colourless microcrystals. Yield 1.5 g, 95% based on $Zn(CH_2CMe_3)_2$

[Methyl Copper(I)]$_n$

Nitric oxide was bubbled through a slurry of yellow [CuMe]$_n$[89] (1 g) in THF (50 ml) at room temperature, with vigorous stirring. The mixture gradually darkened to give a blue solution and a dark precipitate of copper metal. When the reaction appeared to be complete (10-15 mins), nitric oxide was replaced by nitrogen and the solution filtered from the precipitate. The blue solution was reduced to dryness, and the resulting crude solid was recrystallised from dichloromethane to give the product $Cu(ONMeNO)_2$ as blue crystals. Yield 1.1 g, 40% based on [CuMe].

[Trimethylsilylmethyl Copper(I)]$_4$

Nitric oxide was bubbled through a colourless petroleum solution containing $[Cu(CH_2SiMe_3)]_4$[90] (2 g) at room temperature. Initially, a pale yellow precipitate was formed, which was followed by a darkening of the solution. The reaction was stopped immediately the yellow precipitate was produced and the solid collected. This was recrystallised from THF to give the product $[Cu(ONCH_2SiMe_3NO)]_4$ as large pale yellow crystals. Yield 1.68 g, 60% based on $[CuCH_2SiMe_3]$.

If the reaction mixture is allowed to stand overnight, the resultant mixture darkened appreciably. The mixture was taken to dryness and extracted with ether (3 x 20 ml) to give a blue solution which, on cooling to -30°C, gave $Cu(ONCH_2SiMe_3NO)_2$ as blue microcrystals. Yield 1.2 g, 25% based on $CuCH_2SiMe_3$.

Following the ether extraction, there remained an amount of yellow $[CuONCH_2SiMe_3NO]_4$ which can be recrystallised from THF. Yield 0.84 g, 30% based on $CuCH_2SiMe_3$.

Dimethylbis(triethylphosphine)platinum(II)

Nitric oxide was bubbled through a colourless petroluem solution containing 2 g $PtMe_2(PEt_3)_2$[91] at room temperature for ten minutes. The solution appeared to change colour only slightly. The pale yellow solution was filtered, reduced to small volume and cooled to -30°C. The product $PtMe(ONMeNO)(PEt_3)_2$ forms pale yellow crystals which can be collected and washed with ether. Yield 2.1 g, 93% based on $PtMe_2(PEt_3)_2$.

Methyltris(triphenylphosphine)rhodium(I)

Nitric oxide was bubbled through a THF solution containing $Rh(PPh_3)_3Me$[92] (1 g) at room temperature for ten minutes. The red solution darkened slightly. The resulting solution was filtered then reduced to small volume. On cooling to -30° a yellow precipitate was formed. This was collected, washed with ether and dried *in vacuo* to give the product $Rh(PPh_3)_2(ONMeNO).2THF$ as a pale yellow powder. Recrystallisation from dichloromethane give the dichloromethane solvate. Yield 0.85 g, 91% based on $Rh(PPh_3)_3Me$.

Trimethyltris(trimethylphosphine)cobalt(III)

Nitric oxide was bubbled through a petroleum solution containing 2 g of $CoMe_3(PMe_3)_3$[93] at room temperature. The solution turned red immediately and precipitated an orange-red solid. The solid was collected, and extracted into ether until all the complex appeared to have dissolved. The red etherial solution was reduced to small volume and cooled to -30°C to give the product $CoMe(NO)(OPMe_3)_3$ as red plates. Yield 0.65 g, 28% based on $CoMe_3(PMe_3)_3$.

The remaining solid following the etherial extraction was extracted into THF until there remained only what appeared to be a dark intractable solid. The red brown THF solution was filtered, reduced to small volume and cooled to -30°C. The complex $[CoMe(NO)(ONMe)OPMe_3]_2$, was isolated as a red-brown THF adduct. Crystals of this complex could be obtained on slow cooling. Yield 0.8 g, 55% based on $CoMe_3(PMe_3)_3$.

η^5-cyclopentadienyl,(methyl)triphenylphosphine Nickel(II)

Nitric oxide was bubbled through a green toluene solution containing 1 g of $CpNiMe(PPh_3)$[94] at room temperature. The solution rapidly turned blue and a yellow solid was produced. The blue solution was filtered and reduced to small volume. On cooling to -30°C, the product, $Ni_6Cp_3(NO)_2O(PPh_3)$, precipitates as a blue solid. Recrystallisation from many different solvents gave powders although recrystallisation from methanol/dichloromethane (1:1) gave the product as small blue needles. Yield from toluene, 0.15 g, 42% based on $CpNiMe(PPh_3)$.

TABLE 1

Infrared Spectral Data of Complexes Derived from Diamagnetic Alkyl Complexes.[a]

Compound	i.r./cm^{-1}
$Zr(ONCH_2SiMe_3NO)_4$	1280s, 1250s, 1200s, 1140s, 965s, 850s, 740m, 705w, 655s, 535m, 370m, 330m.
$ZrCl_2(ONCH_2SiMe_3NO)_2$	1280m, 1250s, 1200m, 1130s, 970s, 860s, 745m, 705m, 660m, 535m, 370m, 330m, 300w, 265w.
$Zr(ONCH_2CMe_3NO)_4$	1275s, 1200s, 1145s, 960s, 895s, 750s, 532s, 475s, 360w, 320w, 280w.
$Zr(ONC_5H_5NO)_4$	1635w, 1280s, 1225s, 1160s, 1128m, 980s, 940s, 930s, 840m, 762s, 720s, 520br, 400m.
$Ti(ONCH_2SiMe_3NO)_4$	1548s, 1280s, 1250s, 1200s, 1125s, 965s, 850s, 710s, 665m, 618s, 540s 420w, 380w, 280w, 250w.
$TiCl_2(ONCH_2SiMe_3NO)_2$	1290s, 1250s, 1200s, 1130s, 960s, 850s, 710s, 655m, 618s, 540s, 420w, 380w, 345w, 320w, 298m, 270w.

/..... continued.

TABLE 1 (cont.)

Compound	i.r./cm^{-1}
$TiCl(ONCH_2CMe_3NO)_3$	1545s, 1285s, 1230s, 1200s, 1135s, 1020m, 962s, 900m, 860m, 800s, 750s, 700m, 560s, 492s, 430w, 345w.
$TiCl_2(ONCH_2CMe_3NO)_2$	1285s, 1230s, 1200s, 1150s, 975s, 900m, 770s, 700s, 550w, 490m, 320w, 280w.
$NbMe_2(ONMeNO)_3$	1270s, 1165s, 1115s, 1060m, 1030w, 970m, 850m, 800m, 710m, 690m, 662w, 555s, 480s, 380s, 280s
$[TaMe_3(ONMeNO)_2]_2$	1275s, 1170s, 1115s, 1070m, 1030w, 945s, 795m, 715s, 575m, 500m, 325m.
$[Zn(ONMeNO)_2]_n$	1290s, 1140s, 1060w, 953s, 700s, 660m, 575m, 540m, 260w.
$[Zn(ONCH_2CMe_3)_2]_4$	1290s, 1185m, 1115m, 975s, 900m, 762m, 575m, 482w, 345m, 300w.
$Cu(ONMeNO)_2$	1280s, 1165s, 1060w, 948s, 800w, 705s, 592m, 492m, 374m, 345w.
$[Cu(ONCH_2SiMe_3NO)]_4$	1270s, 1253s, 1230m, 1215m, 1200s, 1138s, 1065w, 1030w, 972s, 860s, 800w, 775w, 757m, 710w, 700w, 663w, 622w, 538w, 432m, 392m, 340w, 328w, 250w.

/..... continued.

TABLE 1 (cont.)

Compound	i.r./cm^{-1}
$Cu(ONCH_2SiMe_3NO)_2$	1278s, 1250s, 1228w, 1192s, 1138m, 1118s, 950s, 855s, 774w, 748m, 710m, 663m, 619m, 592s, 492m, 468w, 395s, 352s, 321w, 250w.
$PtMe(ONMeNO)(PEt_3)_2$	1312s, 1260s, 1165w, 1100w, 1030s, 990sh, 960sh, 935m, 815m, 768m, 748s, 725s, 708m, 618w, 548w, 502m, 428w, 383w, 260w, 235w.
$Rh(ONMeNO)(PPh_3)_2.2CH_2Cl_2$	1290s, 1180s, 1115s, 1025w, 985w, 925w 842m, 810m, 742m, 720s, 690s, 610w, 538s, 420w, 365m.
$[CoMe(NO)(ONMe)(OPMe_3)_2.THF$	1660m, 1310w, 1300m, 1260m, 1145s, 1120m, 1020w, 950s, 868m, 800m, 750m, 700w, 365w, 250m, 235m.
$CoMe(NO)(OPMe_3)_3$	1660m, 1310w, 1300m, 1262w, 1145s, 953s, 867m, 835w, 752m, 368m, 260m.
$Ni_6(\eta^5-C_5H_5)_3(NO)_2O(PPh_3)$	1745s, 1305w, 1260w, 1180w, 1158w, 1090m, 1025w, 1000w, 970w, 920w, 842w, 800m, 738m, 685s, 570w, 520s, 505s, 495s, 450w, 305w.

[a] Measured in Nujol.

TABLE 2

^{1}H nmr Spectral Data of Complexes Derived from Diamagnetic Alkyl Complexes.

Compound	^{1}H nmr (δ ppm)[a]		Assignment
$Zr(ONCH_2SiMe_3NO)_4$[b]	0.11	(9)	Si-CH_3
	3.52	(2)	N-CH_2-Si
$ZrCl_2(ONCH_2SiMe_3NO)_2$[b]	0.04	(9)	Si-CH_3
	3.42	(2)	N-CH_2-Si
$Zr(ONCH_2CMe_3NO)_4$[b]	0.98	(9)	C-CH_3
	3.55	(2)	N-CH_2-C
$Zr(ONC_5H_5NO)_4$	4.52d	(2)	N-CH_2-CH
	5.20s	(1)	C=CH_2
	5.35d	(1)	
	5.9m	(1)	C-H
$Ti(ONCH_2SiMe_3NO)_4$[b]	0.06	(9)	Si-CH_3 (chelate)
	0.14	(9)	Si-CH_3 (unidentate)
	3.47	(2)	N-CH_2-Si (chelate)
	3.76	(2)	N-CH_2-Si (unidentate)
$TiCl_2(ONCH_2SiMe_3NO)_2$[b]	0.09	(9)	Si-CH_3
	3.27	(2)	N-CH_2-Si
$TiCl(ONCH_2CMe_3NO)_3$[b]	1.02	(18)	C-CH_3 (chelate)
	1.12	(9)	C-CH_3 (unidentate)
	3.58	(4)	N-CH_2-C (chelate)
	3.72	(2)	N-CH_2-C (unidentate)

/..... continued.

TABLE 2 (cont.)

Compound	^{1}H nmr (δ ppm)		Assignment
$TiCl_2(ONCH_2CMe_3NO)_2$ [b]	0.88	(9)	C-CH_3
	3.50	(2)	N-CH_2-C
$NbNe_2(ONMeNO)_3$ [c]	0.63	(2)	Nb-CH_3
	3.20	(3)	N-CH_3
$[TaMe_3(ONMeNO)_2]_2$ [c]	1.78	(3)	Ta-CH_3
	3.24	(1)	N-CH_3 (terminal)
	4.18	(1)	N-CH_3 (bridging)
$[Zn(ONMeNO)_2]_n$ [b]	3.70		N-CH_3
$[Zn(ONCH_2CMeNO)_2]_4$ [b]	0.95	(9)	C-CH_3
	3.82	(2)	N-CH_2-C
$[Cu(ONCH_2SiMe_3NO)]_4$ [b]	0.11	(9)	Si-CH_3
	3.57	(2)	N-CH_2-Si
$PtMe(ONMeNO)(PEt_3)_2$	0.62	(3)	Pt-CH_3
	1.0m	(18)	P-CH_2-CH_3
	1.50s	(3)	N-CH_3
	2.05m	(12)	P-CH_2-CH_3
$Rh(ONMeNO)(PPh_3)_2.2CH_2Cl_2$ [b]	2.30	(3)	N-CH_3
	5.28	(4)	CH_2Cl_2
	7.35 br	(30)	PPh_3

[a] Chemical shift (δ) measured in ppm downfield of TMS

[b] In deutero chloroform

[c] In deutero benzene

TABLE 3

Analytical Data of Complexes Derived from Diamagnetic Alkyl Complexes.

Compound	Colour	M.P.[f] ($\theta^{o}C$)	Found %				M	Required %				M
			C	H	N	Other		C	H	N	Other	
$Zr(ONCH_2SiMe_3NO)_4$	White	120	28.5	6.1	16.1	-	765[a]	28.3	6.5	16.5	-	679
$ZrCl_2(ONCH_2SiMe_3NO)_2$	White	140	20.5	4.6	12.2	13.3[c]	-	21.1	4.8	12.3	15.6[c]	456
$Zr(ONCH_2CMe_3NO)_4$	White	180	39.0	7.2	18.0	-	580[a]	39.0	7.2	18.2	-	615
$Zr(ONC_3H_5NO)_4$	Yellow	130	28.0	4.0	22.5	-	561[a]	29.1	4.0	22.6	-	495
$Ti(ONCH_2SiMe_3NO)_4$	Orange	40	29.7	6.8	17.6	-	605[a]	30.2	6.9	17.6	-	636
$TiCl_2(ONCH_2SiMe_3NO)_2$	White	130	22.3	4.6	12.7	17.1[c]	-	23.2	5.3	13.6	17.2[c]	413
$TiCl(ONCH_2CMe_3NO)_3$	Yellow	60	38.0	6.8	16.8	7.0[c]	455[a]	37.8	6.9	17.6	7.5[c]	476
$TiCl_2(ONCH_2CMe_3NO)_2$	White	130	30.6	6.8	12.8	17.3[c]	-	31.5	5.8	14.7	18.6[c]	381
$NbMe_2(ONMeNO)_3$	Yellow	150	17.1	3.9	22.1	-	380[b]	17.2	4.3	24.1	-	348
$[TaMe_3(ONMeNO)_2]_2$	White	70	15.0	3.3	13.0	-	700[b]	15.9	4.0	15.0	-	750
$[Zn(ONMeNO)_2]_n$	White	155	10.1	2.6	26.5	-	-	11.1	2.8	26.0	-	-
$[Zn(ONCH_2CMe_3NO)_2]_4$	White	90	33.0	6.1	15.3	-	1218[a]	36.6	6.7	17.1	-	1308

/..... continued

TABLE 3 (cont.)

Compound	Colour	M.P.[f] (θ°C)	Found %				M	Required %				M
			C	H	N	Other		C	H	N	Other	
$Cu(ONMeNO)_2$	Blue	195	11.1	2.8	24.2	-	255[a]	11.2	2.8	26.2	-	214
$[Cu(ONCH_2SiMeNO)]_4$	Yellow	180	24.1	5.5	13.2	-	764[a]	22.8	5.2	13.3	-	840
$Cu(ONCH_2SiMe_3NO)_2.0.5ether$	Blue	115	29.1	6.8	13.2	-	365[a]	30.4	6.8	14.2	-	358
$PtMe(ONMeNO)(PEt_3)_2$	Pale Yellow	110	29.5	6.3	5.0	0[c]	555[a]	32.2	6.9	5.4	0[c]	551
$Rh(ONMeNO)(PPh_3)_2.2CH_2Cl_2$	Yellow	180	52.0	3.9	3.5	15.5[c]	902[a]	53.7	4.2	3.2	16.3[c]	844
$CoMe(NO)(ONMe)OPMe_3.THF$	Dark Red	55	34.4	8.4	8.6	22.0[d] 11.4[e]	-	34.5	6.7	8.9	20.4[c] 9.9[e]	-
$CoMe(NO)(OPMe_3)_3$	Red	45	31.5	7.2	3.7	-	-	31.6	7.9	3.7	-	-
$Ni_6(\eta^5\text{-}C_5H_5)_3(NO)_2O(PPh_3)$	Blue	140	45.0	3.5	2.7	5.6[d] 3.5[e]	1029	44.7	3.4	3.2	5.4[d] 3.5[e]	885

[a] Osmometrically in dichloromethane. [b] Cryoscopically in benzene. [c] Chlorine. [d] Oxygen. [e] Phosphorus.

[f] Many compounds decompose over a range of temperatures.

EXPERIMENTAL CHAPTER 2

Bis(η^5-cyclopentadienyl) dimethyl niobium(IV).

Nitric oxide was slowly bubbled into a solution of Cp_2NbMe_2[95] (2 g) in petroleum at -70°C until the red colour of the solution dissappeared. The yellow precipitate of the adduct $Cp_2Nb(Me)_2NO$ was collected at -70°C, washed with cold petroleum and freed from solvent by pumping at -20°C (10^{-3} mmHg). Although this compound was too unstable to analyse properly, it may be handled in nitrogen briefly and spectroscopic data may be collected. If the same reaction is carried out in toluene, the complex remains in solution. When this solution, or a solution of the isolated complex in deuterio toluene is allowed to warm in an nmr tube, the changes in the methyl resonances may be followed readily at room temperature.

The nitric oxide adduct or its solutions were readily converted to $Cp_2Nb(O)Me$ and for direct synthesis of the latter, the precipitate from petroleum was warmed to 25°C, dissolved in warm toluene and the solution cooled to -30°C to give the complex as pale yellow crystals. These were collected, washed with ether and dried. Yield 1.6 g, 80% based on Cp_2NbMe_2.

Interaction of an excess of nitric oxide with Cp_2NbMe_2 (2 g) in toluene at room temperature gave a white precipitate of CpNbO(ONMeNO) which was collected, washed with petroleum, THF and ether and dried in vacuum. Yield, 2.35 g, 95% based on Cp_2NbMe_2.

Interaction of Styrene with bis(η^5-cyclopentadienyl)methyl (η^2-nitrosomethane) Niobium(IV).

A toluene solution of the nitrosyl adduct, Cp_2NbMe_2NO was prepared from ca. 2 g Cp_2NbMe_2 in 40 ml of toluene. An excess (2 ml) of freshly distilled styrene was added at -70°C and the mixture allowed to warm to room temperature. The solution was stirred overnight (16 h). The resulting mixture was reduced to small volume, and the majority of $Cp_2Nb(O)Me$ was collected. The filtered solution (5 ml) was transferred to a silica column and eluted with toluene/petroleum (1:1) which removed initially the excess of styrene. The column was then eluted with dichloromethane. The collected dichloromethane fraction was reduced and 1-methyl-2-phenyl aziridine was distilled at 35°C (0.3 mmHg). Yield of Cp_2NbOMe, 1.7 g, 85% based on Cp_2NbMe_2. Yield of $C_6H_5CHNMeCH_2$, 0.925 g, 88% based on Cp_2NbMe_2.

Tetrakis(trimethylsilylmethyl) Vanadium(IV).

Nitric oxide was bubbled carefully through a green petroleum solution containing 2 g of $V(CH_2SiMe_3)_4$,[65] at -70°C. The solution rapidly turned red. Excess nitric oxide was removed and the solvent slowly removed at -30°C. The product, $V(CH_2SiMe_3)_3(ONCH_2SiMe_3)$ formed red crystals. These were collected and kept at -30°C. They were handled only briefly under nitrogen at ambient temperatures so that the spectroscopic data could be collected. If the reaction was performed in toluene, or ether, the red complex remained in solution, and on warming to room temperature paled through orange to yellow. The solvent was removed in vacuum and the crude precipitate recrystallised from petroleum to give the product $VO(CH_2SiMe_3)_3$ as lemon needles. Yield, 1.2 g, 73% based on $V(CH_2SiMe_3)_4$.

Bis(η^5-cyclopentadienyl)phenyl titanium(III).

Nitric oxide was bubbled through an ether solution containing 1 g of $Cp_2Ti(C_6H_5)$[96] at -70°C. No reaction appeared to take place, so the solution was warmed to room temperature. The dark solution paled and deposited an orange precipitate, which was collected and washed with toluene and ether. The resulting orange powder was recrystallised from dichloromethane to give the product $Cp_3Ti_3O_4(NO)$ as an orange microcrystalline solid. Yield, 0.5 g, 88% based on $Cp_2TiC_6H_5$.

Bis (η^5-cyclopentadienyl)benzyl titanium(III).

Nitric oxide was passed through an ether solution containing 1 g of $Cp_2Ti(CH_2C_6H_5)$[96] at -70°C. No reaction appeared to take place so the solution was warmed to room temperature. The dark solution gradually paled and deposited an orange precipitate which was collected and washed with toluene and ether. The resulting orange powder was recrystallised from dichloromethane to give the product $Cp_3Ti_3O_4(NO)$ as an orange microcrystalline solid. Yield, 0.5 g, 88% based on $Cp_2TiCH_2C_6H_5$.

Hexamethyl rhenium(VI).

Nitric oxide was carefully bubbled through a green petroleum solution containing ca. 1 g of $ReMe_6$[34] at -70°C. The solution immediately turned red, and an orange precipitate was produced. Excess nitric oxide was removed at -70°C, and replaced by nitrogen. The mixture was warmed to room temperature and reduced to dryness. The crude solid was recrystallised from petroleum to give the product $ReMe_6NO$ as red needles. Yield, 0.6 g, 54% based on $ReMe_6$.

Losses occurred mainly on evaporation of solvent as this complex is volatile, and further reaction occurred to form ReO_2Me_3 which is also extremely volatile and was removed on evaporation of solvent.

If the reaction is carried out in ether, the orange complex, $ReMe_6NO$ remains in solution. If the nitric oxide atmosphere is retained and the solution warmed to room temperature, it gradually pales to yellow. The solvent was removed in vacuum at -30^oC and the complex ReO_2Me_3 sublimed to a probe at -70^oC (10^{-3} mmHg). Yield, 0.59 g, 62% based on $ReMe_5$.

Dilithium Octamethylrhenate(VI).

Nitric oxide was bubbled through a red petroleum solution containing ca. 1 g of Li_2ReMe_8[34] at -70^oC. The reaction took place rapidly with the evolution of a great deal of heat. The solution decolourised and a yellow solid was precipitated. This solid was collected, and extracted into THF. The THF extract was filtered, reduced and cooled to -30^oC to give the product $Re_2O_3(CH_3)_4(ONCH_3)_2$ as yellow powder. Yield, 0.3 g, 33% based on Li_2ReMe_8. The yield of $Re_2O_3(CH_3)_4(ONCH_3)_2$ was low, due to the insoluble nature of the complex.

μ-Dinitrogen bis[tetrakis(trimethylsilylmethyl)rhenium(IV)].

Nitric oxide was bubbled through a purple petroleum solution containing 2 g of $[Re(CH_2SiMe_3)_4]_2N_2$,[76] at -70^oC. No reaction appeared to take place, so the solution was gradually warmed to room temperature in the presence of nitric oxide. The solution initially darkened to green, then paled to produce an orange-brown precipitate. The precipitate was collected, and recrystallised from toluene to give the product

$ReO(NO)(CH_2SiMe_3)_2ONCH_2SiMe_3$ as large orange crystals. Yield, 1.58 g, 80% based on $Re_2(CH_2SiMe_3)_8N_2$.

If the reaction was carried out in THF or if $ReO(NO)(CH_2SiMe_3)_2$-$ONCH_2SiMe_3$ was stirred in THF overnight (16 h), the resultant solution was darker in colour. This solution was taken to dryness and the crude mixture was extracted with toluene. The brown toluene solution gave $ReO(NO)(CH_2SiMe_3)_2ONCH_2SiMe_3$ on cooling to -30^oC.

The remaining crude solid was redissolved in THF and cooled to -30^oC to give $[ReO(NO)(CH_2SiMe_3)_2.THF]_3$ as yellow crystals. Yield, 1.1 g, 60% based on $Re_2(CH_2SiMe_3)_8N_2$.

For isolation of the nitrosotrimethylsilylmethyl dimer, the initial crude mixture was extracted with ether and the solution transferred to an alumina column. Elution with ether, followed by reduction of the resulting etherial solution gives $(ONCH_2SiMe_3)_2$ as colourless crystals.

Interaction of [nitrosyl(nitrosotrimethylsilylmethane)oxo]bis(trimethylsilylmethyl)rhenium(V) with triphenylphosphine.

A twofold excess of triphenylphosphine (1 g) was added to a stirred solution of $ReO(NO)(CH_2SiMe_3)_2ONCH_2SiMe_3$ (1 g) in THF. The solution was stirred overnight (16 h) to give a pale solution. This solution was reduced to dryness to give a white solid. This was washed with several portions of ether (20 ml) to remove excess triphenylphosphine. The resulting white solid was recrystallised from THF at -30^oC to give the product $[ReO(NO)(CH_2SiMe_3)_2]_3PPh_3$ as a white powder. Yield, 0.8 g, 85% based on $ReO(NO)(CH_2SiMe_3)_2ONCH_2SiMe_3$.

Tetrakis(trimethylsilylmethyl)chromium(IV).

Nitric oxide was bubbled through a purple petroleum solution containing 2 g of $Cr(CH_2SiMe_3)_4$[97] at -70°C. The solution rapidly decolourised to give a green-brown precipitate. The solid was collected at -70°C and washed with petroleum. The crude solid was warmed to room temperature and repurified from THF to give the product $[CrO(NO)ONCH_2SiMe_3]_3O_3$ as a green-brown powder. Yield, 9.7 g, 92% based on $Cr(CH_2SiMe_3)_4$.

TABLE 4

Infrared Spectral Data of Compounds Derived from Paramagnetic Alkyl Complexes.[a]

Compound	$\nu_{(N-O)}$	$\nu_{(M-O)}$	Other Bands
$(\eta^5\text{-}C_5H_5)_2Nb(CH_3)_2NO$	1670m[b]		3040w, 1100w, 1055m, 1000s, 790sbr, 695m, 600w, 475m, 355s, 278w
$(\eta^5\text{-}C_5H_5)_2Nb(O)CH_3$		835s[d]	3040w, 1255w, 1148w, 1055w, 1000s, 920w, 805s, 720w, 605w, 472m, 353s, 275w
$(\eta^5\text{-}C_5H_5)_2NbO(ONCH_3NO)$		865s[d]	3040w, 1260w, 1220s, 1185s, 1130w, 1060m, 1010m, 950w, 850s, 800m, 715m, 600w, 570w, 525m, 472w, 430w, 382w, 360w, 330w, 290w.
$V(CH_2SiMe_3)_3(ONCH_2SiMe_3)$	960s[c]		1330m, 1250s, 1210w, 1190m, 1110m, 1090m, 1050w, 990w, 960s, 848vs, 745m, 700m, 655m, 610w, 568m, 470w 400w, 300w, 232w

/..... continued.

TABLE 4 (continued)

Compound	$\nu_{(N-O)}$	$\nu_{(M-O)}$	Other Bands
$V(O)(CH_2SiMe_3)_3$		985m[d]	1300m, 1250s, 1100br, 1015m, 930m, 870w, 840s, 750w, 695w, 610w, 530w, 472w, 400br, 305m, 230m.
$(\eta^5\text{-}C_5H_5)_3Ti_3O_4(NO)$	1550m[b]	580br[e]	3100w, 3020w, 1278m, 1060w, 1010s, 920w, 800s, 670br, 400m, 320w, 255w
$Re(CH_3)_6NO$	1715s[b]		1260m, 1175w, 1090m, 1015m, 955w, 915m, 800s, 758w, 705m, 562m, 380br, 280w
$Re(O)_2(CH_3)_3$		922s,[d] 951s[d]	1390m, 1360m, 1150m, 752m, 512w, 350w, 275w
$Re_2O_3(CH_3)_4(ONCH_3)_2$	970m,[c]	935m,[d] 712m[e]	1300m, 1262w, 1170w 1155w, 1060brw, 840w, 800m, 630mbr, 470w, 302w, 250w

/.... continued.

TABLE 4 (continued)

$ReO(NO)(CH_2SiMe_3)_2(ONCH_2SiMe_3)$	1690s,[b] 1020m[c]	972m[d]	1295w, 1246s, 1190w, 1100br, 938w, 855s, 750w, 698w, 678w, 572w, 490w, 450w, 400w, 280w, 250w
$[ReO(NO)(CH_2SiMe_3)_2.THF]_3$	1742s[b]	980m[d]	1292m, 1250s, 1190m, 1115m, 1065w 1028m, 910m, 850s, 800w, 720m, 650br, 600s, 500m, 400w, 300w, 250w
$[ONCH_2SiMe_3]_2$			1412m, 1387m, 1345m, 1260s, 1200w, 1085s, 1065m, 1025s, 900w, 850m, 800s, 705m, 600m, 400br, 320w, 290w, 270w, 235w, 220w
$[ReO(NO)(CH_2SiMe_3)_2]_3PPh_3$	1720m[b]	970w[d] or 910m[d]	1310w, 1260m, 1190m, 1122s, 1075w, 1030w, 1000w, 855m, 800w, 750m, 728s, 695s, 548s, 450br, 328w, 305w, 280w, 250w
$[Cr(O)(NO)(ONCH_2SiMe_3)]_3O_3$	1840s,[b] 1010m[c]	940m,[d] 562br[e]	1250m, 1188m, 1095m, 850s, 800br, 750br, 700w, 658w, 420w, 400w, 350w, 300w

[a] Measured in Nujol. [b] Terminal nitrosyl (M-N=O). [c] η^2-nitrosoalkane (M<O, N, R). [d] terminal oxo (M=O).

[e] Bridging oxo (M-O-M).

TABLE 5

^{1}H nmr Spectral Data of Compounds Derived from Paramagnetic Alkyl Complexes.

Compound	^{1}H nmr (δ ppm)[a]		Assignment
$(\eta^5\text{-}C_5H_5)_2Nb(CH_3)_2NO$[c]	0.12s	(3)	Nb-$\underline{CH_3}$
	0.94s	(3)	Nb-$\underline{CH_3}$
	5.92s	(10)	η^5-$\underline{C_5H_5}$
$(\eta^5\text{-}C_5H_5)_2Nb(O)CH_3$[b,c]	0.88s	(3)	Nb-$\underline{CH_3}$
	5.94s	(10)	η^5-$\underline{C_5H_5}$
$PhCH(NMe)CH_2$[c]	1.5m	(1)	C-$\underline{H}$
	1.7m	(1)	C-$\underline{H}$
	2.1m	(1)	C-$\underline{H}$
	2.38s	(3)	N-$\underline{CH_3}$
	7.2m	(5)	Ph-$\underline{H}$
$V(CH_2SiMe_3)_3ONCH_2SiMe_3$[c]	0.20s	(27)	V-CH_2-Si-$\underline{CH_3}$
	0.32s	(6)	V-$\underline{CH_2}$-Si
	0.38s	(9)	N-CH_2-Si-$\underline{CH_3}$
	3.45s	(2)	N-$\underline{CH_2}$-Si

/..... continued.

TABLE 5 (continued)

Compound	^{1}H nmr (δ ppm)		Assignment
$VO(CH_2SiMe)_3$ [c]	0.10	(9)	Si-$\underline{CH_3}$
	2.50	(2)	V-$\underline{CH_2}$-Si
$(\eta^5\text{-}C_5H_5)_3Ti_3O_4(NO)$ [b]	6.30s	(2)	η^5-$\underline{C_5H_5}$
	6.37s	(1)	η^5-$\underline{C_5H_5}$
$Re(CH_3)_6NO$ [c]	0.69s		Re-$\underline{CH_3}$
$Re(O)_2Me_3$ [c]	2.07	(1)	Re-$\underline{CH_3}$
	2.50	(2)	Re-$\underline{CH_3}$
$Re_2O_3(CH_3)_6(ONMe)_2$ [b]	1.21	(3)	Re-$\underline{CH_3}$
	2.18	(1)	N-$\underline{CH_3}$
$ReO(NO)(CH_2SiMe_3)_2ONCH_2SiMe_3$ [b]	0.22	(18)	Re-CH_2-Si-$\underline{CH_3}$
	0.34	(4)	Re-$\underline{CH_2}$-Si
	0.38	(9)	N-CH_2-Si-$\underline{CH_3}$
	2.42	(2)	N-$\underline{CH_2}$-Si

/..... continued.

TABLE 5 (continued)

Compound	^{1}H nmr (δ ppm)[a]		Assignment
$[ReO(NO)(CH_2SiMe_3)_2.THF]_3$[b]	0.21s	(9)	Si-$\underline{CH_3}$
	1.28s	(2)	Re-$\underline{CH_2}$-Si
	1.85m	(4)	THF
	3.74m	(4)	THF
$[ONCH_2SiMe_3]_2$[c]	0.01s	(9)	Si-$\underline{CH_3}$
	1.20s	(2)	N-$\underline{CH_2}$-Si
$[ReO(NO)(CH_2SiMe_3)_2]_3PPh_3$[b]	0.15s	(54)	Si-$\underline{CH_3}$
	2.12s	(12)	Re-$\underline{CH_2}$-CH_3
	7.4br	(15)	PPh_3

[a] Chemical Shift (δ) measured in ppm downfied of TMS

[b] In deuterochloroform

[c] In deuterotoluene.

TABLE 6

Analytical Data of Complexes Derived from Paramagnetic Alkyl Complexes

Compound	Colour	M.P.[f] (θ°C)	Found %			Other	M	Required %			Other	M
			C	H	N			C	H	N		
$(\eta^5\text{-}C_5H_5)_2Nb(O)CH_3$	White	140	51.0	5.1	0	-	270[b]	52.0	5.1	0	-	254
$(\eta\text{-}^5C_5H_5)_2Nb(O)(ONCH_3NO)$	White	160	41.0	4.3	8.3	-		41.7	4.1	8.9	-	
$V(O)(CH_2SiMe_3)$	Yellow	75	44.1	9.5	0	-		44.3	9.8	0	-	
$(\eta^5\text{-}C_5H_5)_3Ti_3O_4(NO)$	Orange	180	46.0	4.1	4.0	18.9[e]	422[b]	43.6	3.6	3.4	19.4	413
$Re(CH_3)_6NO$	Red	70	22.5	5.5	4.8	-	298[c]	23.5	5.9	4.6	-	306
$Re_2O_3(CH_3)_4(ONCH_3)_2$	Orange	110	12.4	3.0	6.0	14.0[e]	508[d]	12.6	3.2	4.9	13.9	570
$ReO(NO)(CH_2SiMe_3)_2(ONCH_2SiMe_3)$	Orange	60	25.7	6.7	4.1	9.7[e]	582[c]	27.5	6.3	5.3	9.2	523
$[ReO(NO)(CH_2SiMe_3)_2THF]_3$	Yellow	130	30.8	6.4	1.7	-	1590[b]	30.1	6.3	2.9	-	1434
$[ReO(NO)(CH_2SiMe_3)_2]_3PPh_3$	White	95	33.0	4.1	2.9	4.4[f]		34.0	5.5	2.8	2.1	-
$[Cr(O)(NO)(ONCH2SiMe_3)]_3O_3$	Green	180	21.1	4.9	11.7	25.4[e]	1492[b]	20.8	4.8	12.1	27.7	1386

[a]Some Compounds decompose over a range of temperatures. [b]Osmometrically in dichloromethane. [c]Cryoscopically in benzene [d]Cryoscopially in DMSO. [e]Oxygen. [f]Phosphorus

EXPERIMENTAL CHAPTER 3

Hexakis(trimethylsilylmethyl)dimolybdenum(III) (M-M).

Nitric oxide was bubbled through a dark petroleum solution containing 1 g of $Mo_2(CH_2SiMe_3)_6$[65] at -70°C. No reaction took place so the solution was slowly warmed to room temperature. On warming, the solution paled and a yellow precipitate was formed. This was collected and washed with petroleum. The crude solid was repurified from toluene to give the product $[Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2]$ as a yellow powder. Yield, 0.7 g, 91% based on $Mo_2(CH_2SiMe_3)_6$.

Reaction of μ-oxo bis[oxonitrosylnitrosotrimethylsilylmethylmolybdenum(IV)], with dimethyl phenyl phosphine.

An excess of dimethylphenylphosphine (2 ml) was added to a yellow toluene solution containing $[Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2]$ (0.2 g), An immediate reaction took place to precipitate a yellow solid. This solid appeared to be quite insoluble, and was collected, washed with toluene, THF and ether and dried in vacuo, to give the product $[Mo_2O_3(NO)_2(ONCH_2SiMe_3)(PMe_2Ph)_2]$ as a yellow powder. Yield, 0.29 g, 98% based on $[Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2]$.

Hexakis(neopenyl)dimolybdenum(III) (M-M).

Nitric oxide was bubbled through a dark petroleum solution containing 1 g of $Mo_2(CH_2CMe_3)_6$[54] at -70°C. No reaction took place so the solution was warmed to room temperature where it reacted to give a yellow precipitate. This solid was collected and washed with petroleum. The resulting yellow powder was repurified from toluene or dichloromethane which gives the product as a dichloromethane solvate, $[Mo_2O_3(NO)_2(ONCH_2CMe_3)_2.2CH_2Cl_2]$. Yield, 0.8 g, 87% based on $Mo_2(CH_2CMe_3)_6$.

Hexakis(trimethylsilylmethyl)ditungsten(III) (M-M).

Nitric oxide was bubbled through a dark solution containing 1 g of $W_2(CH_2SiMe_3)_6$[65] at room temperature. The resulting yellow precipitate was collected and washed with petroleum. This solid was repurified from toluene to give the product $[W_2O_3(NO)_2(ONCH_2SiMe_3)_2]$ as a yellow powder. Yield, 0.8 g, 98% based on $W_2(CH_2SiMe_3)_6$.

Hexakis(neopentyl)ditungsten(III) (M-M).

Nitric oxide was bubbled through a dark petroleum solution containing 1 g of $W_2(CH_2CMe_3)_6$[65] at room temperature. The resulting yellow precipitate was collected and washed with petroleum. This solid was repurified from toluene, or THF which gives the product as a THF solvate, $[W_2O_3(NO)_2(ONCH_2CMe_3)_2.2THF]$. Yield, 1 g, 93% based on $W_2(CH_2CMe_3)_6$.

Tetra(methyl)tetrakis(trimethylphosphine)dimolybdenum(II) (M-M).

Nitric oxide was bubbled through a blue petroleum solution containing 1 g of $Mo_2Me_4(PMe_3)_4$[98] at room temperature. A yellow-orange precipitate was produced which was collected and washed with petroleum. The crude solid was repurified from a large amount of dichloromethane to give the product $[MoO(NO)ONMe(OPMe_3)]$ as an orange powder. Yield, 0.8 g, 85% based on $Mo_2Me_4(PMe_3)_4$.

TABLE 7

Infrared Spectral Data of Compounds Derived from Alkyl Complexes Containing Metal-Metal Bonds.[a]

Compound	$\nu_{(N-O)}$	$\nu_{(M-O)}$	Other Bands
$Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2$	1790s,[b] 960m[c]	940m,[d] 705,[e]	1252s, 1200w, 1090br, 850s, 760w, 705w, 685w, 660w, 560w, 520w, 422w, 380w, 360w, 260w, 240w
$Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2(PMe_2Ph)_2$	1760s,[b] 965m[c]	940m,[d] 705m[e]	1300s, 1250w, 1200w, 1170br, 1150m, 1120m, 1100br, 1070w, 1000w, 860s, 750s, 610w, 560w, 490m, 440m, 390w, 280w, 250w
$Mo_2O_3(NO)_2(ONCH_2CMe_3)_2, 2CH_2Cl_2$	1770s,[b] 978m[c]	940w,[d] 720m[e]	1290s, 1200s, 1138s, 1070m, 1032m, 900s, 770s, 560w, 485w, 420w, 300m
$W_2O_3(NO)_2(ONCH_2SiMe_3)_2$	1740s,[b] 965m[c]	945m,[d] 705m[e]	1260s, 1200w, 1100s, 1020m, 850s, 800m, 760w, 685w, 620w, 530w, 390m, 284w, 250s

/..... continued

TABLE 7 (continued)

Compound	$\nu_{(N-O)}$	$\nu_{(M-O)}$	Other Bands
$W_2O_3(NO)_2(ONCH_2CMe_3)_2.2THF$	1730s,[b] 975m[c]	940m,[d] 715m[e]	1290m, 1210s, 1130s, 1090w, 1035w, 1010w, 900s, 768w, 560w, 485w, 420w
$[MoO(NO)(ONCH_3)(OPMe_3)]n$	1735s,[b]	860 [d/e]	1305m, 1160m, 1145s, 948s, 860s, 750m, 705w, 610m, 495w, 450w, 362m

[a] Measured in Nujol, [b] Terminal nitrosyl (M-N=O), [c] η^2-nitrosoalkane (M(O)N(R)), [d] Terminal oxo (M=O),

[e] Bridging oxo (M-O-M).

TABLE 8

^{1}H nmr Spectral Data of Complexes Derived from Alkyl Complexes Containing Metal-Metal Bonds.

Compound	^{1}H nmr (δ ppm)[a]		Assignment
$Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2$[b]	0.22s	(9)	Si-CH_3
	0.44s		
	3.80br		N-CH_2-Si
$Mo_2O_3(NO)_2(ONCH_2CMe_3)_2.2CH_2C\ell_2$[b]	0.97s	(9)	C-CH_3
	3.86s	(2)	N-CH_2-C
	5.28s	(2)	CH_2-$C\ell_2$
$W_2O_3(NO)_2(ONCH_2SiMe_3)_2$[b]	0.39br		N-CH_2-Si, Si-CH_3
$W_2O_3(NO)_2(ONCH_2CMe_3)_2.2THF$[b]	0.68s	(9)	C-CH_3
	0.80s	(9)	C-CH_3
	1.85m	(16)	THF
	3.74m	(16)	THF
	4.18br	(4)	N-CH_2-C
$[MoO(NO)(ONCH_3)(OPMe_3)]$[b]	1.40s	(3)	P-CH_3
	1.54s	(3)	P-CH_3
	2.11s	(2)	N-CH_3

[a] Chemical shift (δ) measured in ppm downfield of TMS. [b] In deuterochloroform

TABLE 9

Analytical Data of Complexes derived from Alkyl Complexes containing Metal-Metal Bonds

Compound	Colour	M.P. (θ°C)[a]	Found %			Other	M	Required %			Other	M
			C	H	N			C	H	N		
$Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2$	Yellow	110	17.0	3.8	10.9	-	1091[b]	18.0	4.1	10.5	-	1068
$Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2(PMe_2Ph)_2$	Yellow	140	32.1	4.5	6.2	-	-	35.6	5.4	6.9	-	-
$Mo_2O_3(NO)_2(ONCH_2CMe_3)_2 . 2CH_2Cl_2$	Yellow	200	20.8	3.5	7.6	18.5[d]	1060[b]	21.4	3.9	8.3	16.1[d]	1004
$W_2O_3(NO)_2(ONCH_2SiMe_3)_2$	Yellow	190	13.5	3.0	8.3	16.4[d]	1520[b]	13.5	3.1	7.9	15.8[d]	1420
$W_2O_3(NO)_2(ONCH_2CMe_3) .2THF$	Yellow	210	24.3	5.3	5.9		1394[b]	26.3	4.6	6.8	-	1356
$[MoO(NO)(ONCH_3)(OPMe_3)]$	Yellow	160	18.7	4.6	8.9	23.2[d] 11.5[e]	265[c]	17.2	4.3	10.0	22.9[d] 11.1[e]	279

[a] Some compounds decompose over a range of temperatures [b] Osmometrically in dichloromethane

[c] Cryosopically in DMSO [d] Oxygen [e] Phosphorus

REFERENCES.

1. B.F.G. Johnson, J.A. McCleverty, Prog. Inorg. Chem., 1966, 7, 277.
2. N.G. Connelly, Inorg. Chim. Acta Rev., 1972, 6, 48.
3. W.P. Griffith, Adv. Organomet. Chem., 1968, 7, 211.
4. J.A. Masek, Inorg. Chim. Acta Rev., 1969, 3, 99.
5. B.A. Frenz, J.A. Ibers, M.T.P. Int, Rev. Sci. Phys. Chem. Ser., 1972, 111, 33.
6. J.H. Enemark, R.D. Felthan, Coord. Chem. Rev., 1974, 10, 339.
7. R. Eisenberg, C.D. Meyer, Acc. Chem. Res., 1975, 8, 26.
8. K.G. Caulton, Coord. Chem. Rev., 1975, 14, 317.
9. F. Bottomley, Acc. Chem. Res., 1978, 11, 158.
10. J.A. McCleverty, Chem. Rev., 1979, 79, 53.
11. W. Bortok, A.R. Crawford, A. Skapp, Chem. Eng. Prog., 1971, 67, 64.
12. 'Air Pollution', A.C.S. Rep. Collect. Amer. Chem. Soc., Washington, D.C., 1973.
13. P.E. Cade, W.M. Huo, J.B. Greenshiedls, A.T. Data Nucl. Data Tables, 1975, 15 1.
14. J. Barrett, Atomic and Molecular Structure, Wiley, London, p. 139.
15. R. Eisenberg, D.E. Hendrickson, Advances in Catalysis, 1980, 28, 79.
16. W.H. Bowden, W.F. Little, J.J. Meyer, J. Amer. Chem. Soc., 1974, 96, 5605; 1976, 98, 444.

17a J.H. Swinehart, W.G. Schmidt, Inorg. Chem., 1967, 6, 232.

b S.K. Wolfe, J.H. Swinehart, Inorg. Chem., 1968, 7, 1855.

18. J.A. McCleverty, C.W. Winnes, I. Wolochowitz, Chem. Comm., 1976, 1061.
19. E. Frankland, Justus Liebigs Annalen. Chem., 1856, 99, 342.

20a J. Sand, F. Singer, Justus Liebigs Annalen Chem., 1903, 190, 329.

b E. Muller, H. Metzger, Chem. Ber., 1956, 89, 396.

c M.H. Abraham, J.H.N. Garland, J.A. Hill, L.F. Larkworth, Chem. and Ind., 1962, 1615.

21. S.J. Brois, Tetrahedron Lett., 1964, 345.

22. M. Inatome, L.P. Kuhn, Boron-Nitrogen Chem., A.C.S. Monograph, No. 42, Amer. Chem. Soc., New York, 1964, p. 183.

23. S. Amirkhalily, A.J. Conway, J.D. Smith, J. Organomet. Chem., 1978, 149, 407.

24. P.C. Wailes, H. Weigold, A.P. Bell, J. Organomet. Chem., 1972, 34, 155.

25. R.J.H. Clark, J.A. Stockwell, J.D. Williams, J.C.S. Dalton, 1976, 120.

26. J.D. Williams, M.G.B. Drew, J. Organomet. Chem., 1974, 69, 111.

27. S.F. Fletcher, A.J. Shortland, A.C. Skapski, G. Wilkinson, Chem. Comm., 1972, 922.

28. A.J. Shortland, G. Wilkinson, J.C.S. Dalton, 1973, 872.

29. C.S. Pratt, B.A. Coyle, J.A. Ibers, J.Chem. Soc. (A), 1971, 2146.

30. B.F. Hoskins, F.D. Whillans, D.H. Dale, D.C. Hodgkin, Chem. Comm., 1969, 69.

31. S. Cennini, R. Ugo, G. La Monica, S.D. Robinson, Inorg. Chim. Acta, 1972, 6, 182.

32. P. Edwards, K. Mertis, G. Wilkinson, M.B. Hursthouse, K.M.A. Malik, J.C.S. Dalton, 1980, 334.

33. H.F. Klein, H.H. Karsch, Chem. Berichte, 1976, 109, 1453.

34. K. Mertis, G. Wilkinson, J.C.S. Dalton, 1976, 1488.

35. K. Mertis, D.H. Williamson, G. Wilkinson, J.C.S. Dalton, 1975, 607.

36. R.S. Bereman, J.K. Kochi, Inorg. Chem., 1980, 248.

37. R.G. Little, R.J. Dodens, Inorg. Chem., 1973, 537.

38. L.S. Liebskind, K.B. Sharpless, R.D. Wilson, J.A. Ibers, J.Amer. Chem. Soc., 1976, 7061.

39. D.A. Muccigrosso, S.E. Jacobson, P.A. Agar, F. Mares, J.Amer. Chem. Soc., 1978, 7063.

40. S. Aime, G. Gervasio, L. Milone, R. Rossetti, P.L. Stanghellini, J.C.S. Dalton, 1978, 534.

41. E. Sappa, L. Milone, J. Organomet. Chem., 1973, 61, 383.

42. G.P. Boldrini, A. Umani-Ronchi, M. Panvino, J. Organomet. Chem., 1979, 171, 85.

43. G. La Monica, S. Cennini, J.C.S. Dalton, 1980, 1145.

44. J. Müller, H. Dorner, F.H. Kohler, Chem. Ber., 1973, 106, 1122.

45. D. Mansuy, M. Dreme, J.C. Chottard, J.P. Girault, J. Amer. Chem. Soc., 1980, 844.

46. R.A. Clement, U. Klabunde, G.W. Parshall, J. Mol. Cat., 1978, 4, 87.

47. M.W. Schoonover, E.C. Baker, R. Eisenberg, J. Amer. Chem. Soc., 1979, 101, 1880.

48. A. Touster, Org. React., 1953, 7, 327.

49. J. Ludwig, D. Schwartz, Inorg. Chem., 1970, 9, 607.

50. D. Coucouvanis, Prog. Inorg. Chem., 1970, 11, 234.

51. R. Eisenberg, Prog. Inorg. Chem., 1970, 12, 329.

52. K. Vrieze, H.C. Volger, J. Organomet. Chem., 1967, 9, 537.

53. J.W. Faller, M.E. Thomsen, J. Amer. Chem. Soc., 1969, 91, 6871.

54. W. Mowat, G. Wilkinson, J.C.S. Dalton, 1973, 1120.

55. J.F. Villa, M.M. Bursey, W.E. Hatfield, Chem. Comm., 1971, 307.

56. S.K. Gupta, T.S. Srivastava, J. Inorg. Nucl. Chem., 1970, 32, 1611.

57. 'Advanced Inorganic Chemistry', F.A. Cotton and G. Wilkinson, 3rd Edition, Wiley, p. 907.

58. J.P. Fackler, J.A. Fetchin, W.C. Seidel, J. Amer. Chem. Soc., 1969, 91, 1217

59. A. Terzis, T.C. Strekas, T.G. Spiro, Inorg. Chem., 1971, 10, 2617.

60. G. Langoni, P. Chini, A. Cavalieri, Inorg. Chem., 1976, 15, 3025, 9.

61. Z. Prazil, W. Forst, J. Amer. Chem. Soc., 1968, 90, 3344.

62. J.N. Wells, A.V. Shirodkar, A.M. Knevel, J. Med. Chem., 1966, 9, 195.

63. M. Ohtsuru, K. Tori, J. Mol. Spectrosc., 1968, 27, 296.

64. V. Minoura, M. Takebayashi, C.C. Price, J. Amer. Chem. Soc., 1959,81,4689.

65. W. Mowat, A.J. Shortland, G. Yagupski, N.J. Hill, M. Yaguspki, G. Wilkinson, J.C.S. Dalton, 1972, 533.

66. J.C. Huffman, J.G. Stone, W.C. Krusell, K.G. Caulton, J. Amer. Chem. Soc., 1977, 99, 5829.

67. 'Advanced Inorganic Chemistry', F.A. Cotton and G. Wilkinson, 3rd Edition, Wiley, p. 43.

68. W.P. Griffith, J.Chem. Soc., (A), 1969, 211.

69. B. Jezowska-Trzbialowska, J. Hanuza, M. Baluka, Spectrochim. Acta, 1971, 27A, 1753.

70. J.F. Rowbottom, G. Wilkinson, J.C.S. Dalton, 1972, 826.

71. R.A. Walton, F.A. Cotton, W.R. Robinson, Inorg. Chem., 1967, 6, 223.

72. R.N. Jowitt, P.C.H. Mitchell, J. Chem. Soc. (A), 1970, 1702.

73. R. Shandles, E.O. Schelmper, R.K. Murmann, Inorg. Chem., 1971, 10, 2785.

74. A.R. Middleton, A.F. Masters, G. Wilkinson, J.C.S. Dalton, 1979, 542.

75. P. Edwards, G. Wilkinson, K. Mertis, K.M.A. Malik, M.B. Hursthouse, Chem. Comm., 1979, 1158.

76. A.F. Masters, K. Mertis, J.F. Gibson, G. Wilkinson, Nouveau J. de Chimie, 1978, 1, 389.

77. 'The Chemistry of the Nitro and Nitroso Groups', H. Feur, Wiley, 1969.

78. P. Edwards, Ph.D. Thesis, University of London, 1979.

79. C.A. Tollman, Chem. Rev., 1977, 313.

80. W. Mowat, Ph.D. Thesis, University of London, 1972.

81. T. Nimry, M.A. Urbancic, R.A. Walton, Inorg. Chem., 1979, 691.

82. M.H. Chisholm, F.A. Cotton, M.W. Extine, R.C. Kelly, Inorg. Chem., 1979, 116.

83. L.O. Atovmyan, G.B. Bokii, J. Struct. Chem. USSR, 1963, 4, 524.

84. M. Schroeder, A.J. Nielson, W.P. Griffith, J.C.S. Dalton, 1979, 1607.

85. M.R. Collier, M.F. Lappert, R. Pearse, J.C.S. Dalton, 1973, 445.

86. G. Wilke, et al., Angew. Chem., 1966, 5, 151.

87. R.R. Schrock, J. Organomet. Chem., 1976, 122, 209.

88. G.E. Coates, K. Wade, Organometallic Compounds, Vol. 1, Methuen, 1976

89. Y. Yamomoto, H. Yatagai, A. Sonodo, S. Murahashi, Chem. Comm., 1976, 452.

90. J.A.J. Jarvis, R. Pearce, M.F. Lappert, J.C.S. Dalton, 1977, 999.

91. J. Chatt, B.L. Shaw, J. Chem. Soc., 1959, 705.

92. W. Keim, J. Organomet. Chem., 1968, 14, 179.

93. H.F. Klein, H.H. Karsch, Chem. Ber., 1975, 108, 944, 956.

94. J. Thompson, M.C. Baird, Can. J. Chem., 1970, 48, 3443.

95. I.H. Elson, J.K. Kochi, V. Klabunde, L.E. Manzer,, G.W. Parshall, F.N. Tebbe, J. Amer. Chem. Soc., 1974, 96, 7374.

96. J.H. Teuben, J. Organomet. Chem., 1973, 57, 159.

97. W. Mowat, A.J. Shortland, N.J. Hill, G. Wilkinson, J.C.S. Dalton, 1973,770.

98. R.A. Andersen, R.A. Jones, G. Wilkinson, J.C.S. Dalton, 1979, 446.

99. O.P. Strauz, H.E. Gunning, Can. J. Chem., 1963, 41, 1207