Further Studies on the Interaction of Nitric Oxide with Transition-metal Alkyls

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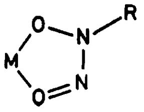
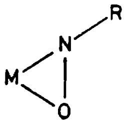
The interaction of nitric oxide with peralkyl compounds of Zn, Cu, Re, Cr, Mo, W, and Zr and with the phosphine complexes Ni(η-C_5H_5)Me(PPh_3), $CoMe_3(PMe_3)_3$, and $RhMe(PPh_3)_3$ has been studied. In addition to *N*-alkyl-*N*-nitrosohydroxylaminate, ON(R)NO, complexes normally formed from diamagnetic alkyls, and η^2 or bridged nitrosoalkane, ONR, compounds usually obtained from paramagnetic alkyls, complexes with M=O or M–O–M groups may be formed from the latter or from the interaction of NO with certain diamagnetic complexes that may give paramagnetic intermediates, *e.g.* by dissociation. Among new compounds characterised by i.r. and n.m.r. spectra are the tetrameric $\{Cu[ON(CH_2SiMe_3)NO]\}_4$, the nitric oxide adduct of hexamethylrhenium, $ReMe_6(NO)$, the complex $Re_2O_3Me_4(ONMe)_2$, and the oxo-compounds of molybdenum and tungsten of stoicheiometry $M_2O_3(NO)_2(ONR)_2$, R = CH_2SiMe_3 or CH_2CMe_3. The interaction of molybdenum and tungsten hexacarbonyls with nitrobenzene and nitromethane gives oxo-species with ONR groups.

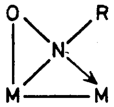
THE nature of the reaction[1] between nitric oxide and a transition-metal alkyl depends upon whether the latter is diamagnetic or paramagnetic. For diamagnetic d^0 alkyls the product is a chelate complex with *N*-alkyl-*N*-nitrosohydroxylaminato-groups (1), whereas paramagnetic alkyls with one unpaired electron can give η^2, or bridged, nitrosoalkane complexes (2a, 2b) which may readily decompose with loss of RN=NR (identified in certain cases) to produce compounds with M=O or M–O–M bonds.[2]



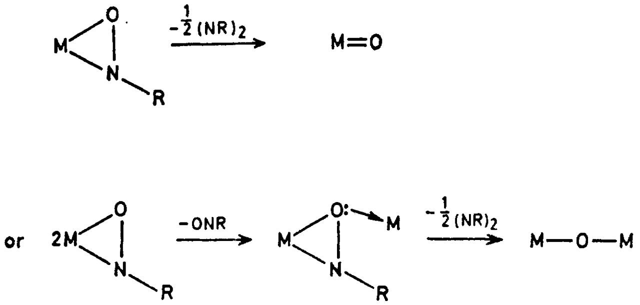
(1)



(2a)



(2b)



We have extended our previous studies to a further range of transition-metal alkyls.

RESULTS AND DISCUSSION

Zinc.—The reaction of NO with zinc alkyls was first studied by Frankland.[3] Dimethyl- and dineopentylzinc give air-stable white solids whose i.r. and n.m.r. spectra confirm the presence of *N*-alkyl-*N*-nitrosohydroxylaminato-groups. The complexes are polymeric, the methyl compound being sparingly soluble in hydrocarbon solvents while the neopentyl is a tetramer in benzene. Both compounds give a mass spectrum in which the highest peaks correspond to dimers minus some methyl fragments. The most likely structures of the compounds involve bridging *via* the lone pair of the non-alkylated nitrogen as shown in (3) for a dimer. Bridging of this type is quite common for other ligands in five-co-ordinate zinc complexes.[4]

The compounds are more soluble in solvents that may cleave the bridges, *e.g.* dimethyl sulphoxide, and they are soluble in hot water. We have been unable to obtain suitable crystals for *X*-ray study.

Copper.—The tetrameric alkyl $[Cu(CH_2SiMe_3)]_4$ and NO produce the diamagnetic pale yellow complex $\{Cu[ON(CH_2SiMe_3)NO]\}_4$. The mass spectrum shows a peak with the correct isotopic pattern for the molecular ion $C_{16}H_{44}Cu_4N_8O_8Si_4^+$ as well as stronger peaks where methyl groups have been lost. The i.r. spectrum has bands at 1 270, 1 138, and 972 cm^{-1} characteristic of ON(R)NO groups, while the ^1H n.m.r. spectrum has the expected two peaks due to CH_3, δ 0.11(9), and CH_2, δ 3.57(2), of the alkyl bound to nitrogen. Considering the types of structure known for copper(I) bridged complexes (ref. 4, p. 803) a structure of type (4) seems most likely.

Prolonged interaction of $[Cu(CH_2SiMe_3)]_4$ with NO gives a blue solution from which can be isolated the monomeric copper(II) complex $Cu[ON(CH_2SiMe_3)NO]_2$. This is paramagnetic ($\mu_{eff.}$ 2.0 B.M.) * and in frozen toluene has an e.s.r. spectrum with $g_{\parallel} = 2.5956$ and $g_{\perp} = 1.5854$ which would give $g_{iso.} = 2.2589$.

Similarly, the interaction of a slurry of $(CuMe)_n$ produces only the known $Cu[ON(Me)NO]_2$ [5] and copper metal; any intermediate copper(I) species evidently disproportionate rapidly in this case. The mass spectrum shows the molecular ion and the e.s.r. spectrum in frozen toluene solutions ($g_{\parallel} = 2.6371$, $g_{\perp} = 1.58$) agrees with data for the solid (for powdered sample $g_{iso.} = 2.384$ [5]).

The reaction of NO with silver alkyls (made *in situ* at low temperature) led only to decomposition to metal.

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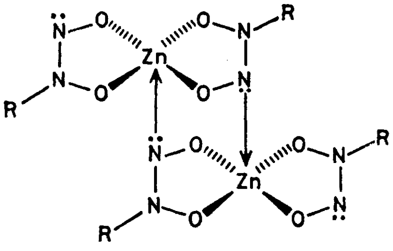
* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2; 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

Nickel.—The diamagnetic Ni(η-C_5H_5)Me(PPh_3) gives a non-crystalline blue complex of apparent stoicheiometry $Ni_6(C_5H_5)_3O(NO)_2(PPh_3)$. From the i.r. spectrum the complex contains terminal NO, η-C_5H_5, and PPh_3 groups. It seems that the reaction must initially lead to a neutral nitrosomethane ligand as in the cobalt system, noted later.

Cobalt.—Interaction of the paramagnetic methyl complex $CoMe_2(PMe_3)_4$ gives a product [CoMe(ONMe)(PMe_3)$_2$]$_2$ for which a structure with η^2-bridging MeNO groups as in (2b) was proposed.[6] The similar $CoMe_3$(PMe_3)$_3$ complex[7] reacts rapidly with NO at room temperature to give a red solution from which two compounds may be isolated. The first, [CoMe(NO)(ONMe)($OPMe_3$)]$_2$, is insoluble in light petroleum and diethyl ether but soluble in tetrahydrofuran (thf), from which it crystallises with 1 mol of solvent. The highest peak in the mass spectrum corresponds to the dimer minus one Me_3PO group. The complex is paramagnetic in the solid state ($\mu_{eff.}$ = 2.1 B.M.) but did not show an e.s.r. spectrum in frozen toluene. The i.r. spectrum has a band at 1 660 cm^{-1}, which can be assigned to a terminal Co(NO) group[1] (see also ref. 4, p. 92). The band at 1 020 cm^{-1} can be assigned to the N–O stretch of a η^2-ONMe group. Strong bands at 1 145 and 950 cm^{-1} are due to P=O and P–Me bands of Me_3PO, while bands at 1 050 and 870 cm^{-1} indicate the presence of thf. A reasonable structure for the complex is (5) with μ^2-ONMe groups; with a bent Co–NO and neutral ONMe the octahedral cobalt is in the II oxidation state.



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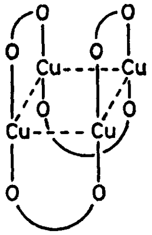
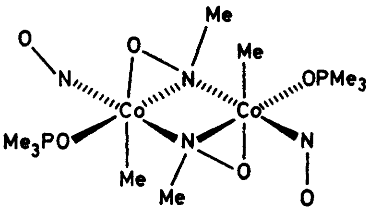


(4) O⌒O = $ON(CH_2SiMe_3)NO$



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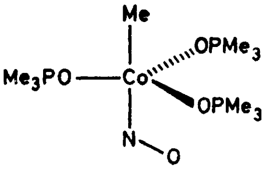

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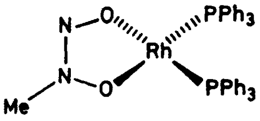


(7)

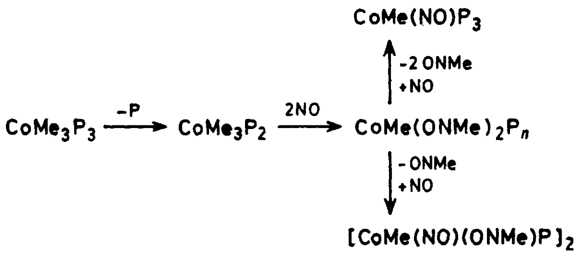
The second complex, CoMe(NO)($OPMe_3$)$_3$, crystallises from diethyl ether as red plates. The mass spectrum shows the molecular ion $C_{10}H_{30}CoNO_4P_3^+$ and a fragmentation pattern due to loss of Me_3PO groups. It is paramagnetic ($\mu_{eff.}$ = 1.8 B.M.) but did not give an e.s.r. spectrum in frozen toluene. The i.r. spectrum has bands at 1 660 [terminal Co(NO)], 1 145, and 950 cm^{-1} (Me_3PO). The complex could be trigonal bipyramidal (6) or square pyramidal and is probably fluxional.

In order to account for the formation of these two complexes, we postulate initial dissociation from the diamagnetic $CoMe_3(PMe_3)_3$ of PMe_3 leading to $CoMe_3$(PMe_3)$_2$ which could be paramagnetic with two unpaired electrons and react to form ONMe groups while the dissociated phosphine is rapidly converted into the oxide by the well known reaction (1).[8] The sequence could be as in Scheme 1.

$$PMe_3 + 2NO \rightleftharpoons PMe_3O + N_2O \qquad (1)$$

Rhodium.—The diamagnetic rhodium(I) complex $RhMe(PPh_3)_3$ gives the expected Rh[ON(Me)NO](PPh_3)$_2$ which crystallises with 2 mol of either thf or CH_2Cl_2. The i.r. has bands at 1 287, 1 180, and 985 cm^{-1} [ON(Me)NO] and the ^{1}H n.m.r. a resonance at δ 2.30 (N–Me) as well as resonances due to PPh_3 and solvent. The structure is doubtless planar as in (7).

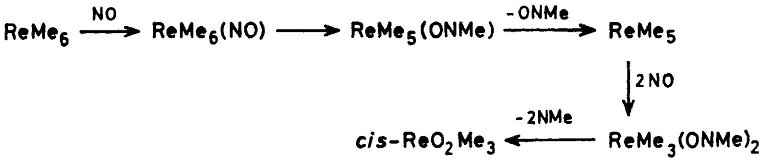
Rhenium.—(*a*) $ReMe_6$. Interaction of NO with a green light petroleum solution of $ReMe_6$ at −78 °C produces orange-red needles of the adduct $ReMe_6(NO)$; any excess of NO must be removed at −78 °C, otherwise further reaction occurs on warming. This air-sensitive complex is stable at room temperature, diamagnetic and monomeric in solution. Although the parent ion was not detected in the mass spectrum, peaks from $ReMe_5(NO)^+$ to $Re(NO)^+$ formed by successive loss of methyl groups and having the correct isotopic patterns were observed.



SCHEME 1 P can be PMe_3 and/or $POMe_3$

The i.r. spectrum has CH_3 stretches and a band at 1 710 cm^{-1} that can be assigned as a terminal Re–NO. The ^1H n.m.r. shows a single methyl resonance from 30 to −78 °C suggesting a non-rigid seven-co-ordinate structure (8); the peak is markedly solvent dependent, δ 1.21 ($CDCl_3$), 0.69 (C_6D_6).

When the reaction is carried out in diethyl ether the $ReMe_6(NO)$ remains in solution at −78 °C and on warming to room temperature under NO the orange solution pales and on work-up only the volatile *cis*-ReO_2Me_3, originally made [9] by interaction of $ReOMe_4$ and NO, is obtained.



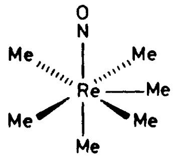
SCHEME 2

The reaction with $ReMe_6$ presumably does not involve a co-ordinatively unsaturated diamagnetic intermediate otherwise a complex with an ON(Me)NO group would have been formed. A reaction sequence of the type shown in Scheme 2 is probably involved.

(*b*) $Li_2[ReMe_8]$. The lithium salt, $Li_2[ReMe_8]$, also reacts with NO at −78 °C to give a diamagnetic yellow rhenium complex of stoicheiometry $Re_2O_3Me_4(ONMe)_2$; the lithium salt Li[ON(Me)NO] is probably also formed but was not isolated.

The rhenium complex is only sparingly soluble in benzene, but in Me_2SO the molecular weight corresponds to the dimeric formulation above. The mass spectrum showed the molecular ion $C_6H_{18}N_2O_5Re_2^+$ with the correct isotopic pattern together with peaks resulting from loss of CH_3 and CH_3NO down to $Re_2O_3^+$.

Methyl resonances occur in the ^1H n.m.r. spectrum at δ 1.21 (Re–*Me*) and δ 2.18 (N–*Me*) p.p.m. In the i.r. spectrum, a band at 970 cm^{-1} can be assigned as the N–O stretch of η^2-ONMe; bands at 935 and 712 cm^{-1} are consistent with the presence of a linear O=Re–O–Re=O group.[10] The complex thus appears to have the structure (9).



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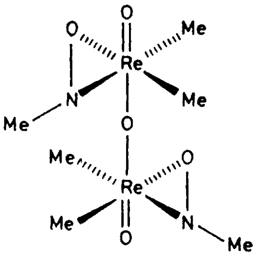
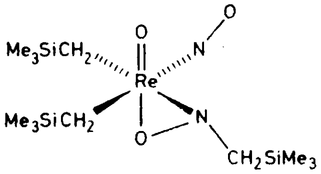


(9)



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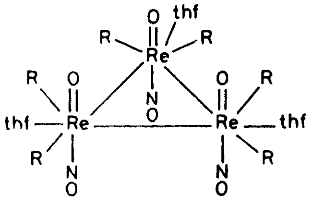


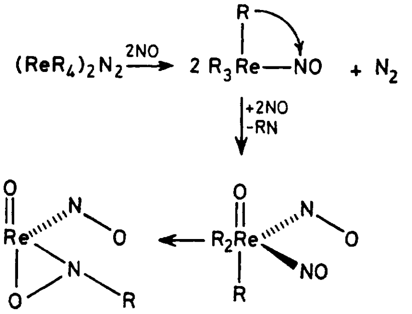
(11)

(*c*) $[Re(CH_2SiMe_3)_4]_2N_2$. In solution at −60 °C this complex does not react with NO but on warming the colour changes from purple to green and then brown: work-up leads to large orange crystals of $ReO(CH_2SiMe_3)_2(NO)(ONCH_2SiMe_3)$.

The ^1H n.m.r. spectrum indicates that one alkyl group is bound to nitrogen [δ 0.28(9), 2.42(2)] and two are bound to rhenium [δ 0.22(18), 0.34(4)] while the i.r. spectrum shows a terminal nitrosyl (1 690 cm^{-1}), a Re=O group (972 cm^{-1}), and a η^2-nitrosoalkane group (1 020 cm^{-1}). The structure proposed is thus of the type (10) although the exact stereochemistry cannot be specified; it contains rhenium(V). A possible formation sequence is shown in Scheme 3.

The reaction of $ReO(CH_2SiMe_3)_2(NO)(ONCH_2SiMe_3)$ with tetrahydrofuran {or reaction of $[Re(CH_2SiMe_3)_4]_2N_2$ and NO in thf} leads to displacement of the nitrosoalkane (see below) and formation of a yellow powder, $ReO(CH_2SiMe_3)_2(NO)\cdot thf$. This complex is quite soluble in tetrahydrofuran and CH_2Cl_2, but only sparingly soluble in hydrocarbons.

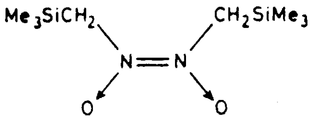
The ^1H n.m.r. spectrum has bands showing thf [δ 1.85(4), 3.74(4)] and $Re(CH_2SiMe_3)_2$ [δ 0.21(18), 1.28(4)] while the i.r. spectrum has bands confirming the presence of thf (1 025, 850 cm^{-1}), a Re=O group (975 cm^{-1}), and a terminal Re–NO (1 730 cm^{-1}). The molecular weight corresponds to that required for a trimer so that a structure of the type (11) is suggested; it is possible that there are bridging as well as terminal alkyl groups.



SCHEME 3 R = CH_2SiMe_3

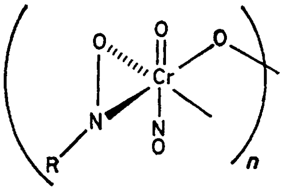
The neutral nitrosoalkane formed in the reaction has been isolated as colourless crystals. The mass spectrum shows the parent ion of the dimer $C_8H_{22}N_2O_2Si_2^+$ while the i.r. spectrum has bands at 1 412, 1 387, 1 345, 1 085, and 1 025 cm^{-1}, that correspond to those observed in other *cis*-nitrosoalkane dimers (12).[11]

When triphenylphosphine is present in the tetrahydrofuran reaction of $ReO(CH_2SiMe_3)_2(NO)(ONCH_2SiMe_3)$ the neutral nitrosoalkane is again displaced, but a complex of stoicheiometry $[ReO(CH_2SiMe_3)_2(NO)]_3(PPh_3)$ is now isolated. The ^1H n.m.r. spectrum (in CD_2Cl_2) showed resonances due to CH_2SiMe_3 and PPh_3 in the ratio 6 : 1 confirming the ratio according to analytical figures. The NO stretch was again in the terminal Re(NO) region at 1 720 cm^{-1}. The complex is probably triangular like the thf complex, but with only one rhenium having a phosphine ligand; *triangulo*-trirhenium species with bulky alkyls like trimethylsilylmethyl have been found to form adducts with different numbers of phosphines.[12]



(12)

Chromium.—Although the first stable paramagnetic peralkyls were found to react with NO the products were not characterised.[13] Interaction of NO with $Cr(CH_2SiMe_3)_4$ gives a green-brown powder of apparent stoicheiometry $CrO_2(NO)(ONCH_2SiMe_3)$, the molecular weight for which, in CH_2Cl_2, corresponds to a hexamer. The complex is soluble in CH_2Cl_2, thf, and toluene, but all attempts to obtain crystals suitable for *X*-ray study have failed. The compound is paramagnetic in the solid state ($\mu_{eff.}$ = 2.9 B.M.) and the e.s.r. spectrum in frozen toluene gave a broad band with g = 1.996 and nitrogen-hyperfine splitting, 0.45 mT, which is consistent with Cr^{III}. The i.r. spectrum had a strong band at 1 840 cm^{-1} indicative of a linear nitrosyl group and bands at 1 010 and 940 cm^{-1} are assignable respectively as due to N–O and Cr=O, while a broad band at 560 cm^{-1} is assigned to oxo-bridges.



(13)

With oxo-bridges, Cr=O groups, and a neutral nitrosoalkane in a polymeric structure of the type (13) we have octahedral Cr^{III}.

Interaction of NO with the neopentyl $Cr(CH_2CMe_3)_4$ gave a green complex with similar spectroscopic properties.

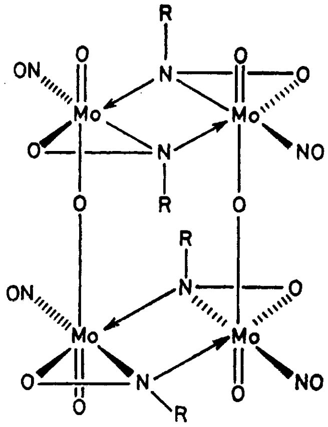
Molybdenum and Tungsten.—(*a*) M_2R_6. The diamagnetic triply metal–metal bonded alkyls[13] M_2R_6 (R = CH_2SiMe_3 or CH_2CMe_3; M = Mo or W) react with NO at room temperature to give yellow diamagnetic complexes of stoicheiometry $M_2O_3(NO)_2(ONR)_2$. The neopentyl complexes crystallise from CH_2Cl_2 or thf with 1 mol of solvent but from toluene without.

The mass spectrum of the trimethylsilylmethyl tungsten complex had a peak with the correct isotopic pattern for the molecular ion, $C_8H_{22}N_4O_7Si_2W_2^+$, together with peaks corresponding to loss of RNO and NO groups; the other complexes showed similar mass spectral behaviour. For these complexes, the i.r. spectra had a band *ca.* 1 760 cm^{-1} due to terminal M–NO, while bands characteristic of O=M–O–M=O units were also present at *ca.* 940 (M=O) and 705 cm^{-1} (M–O–M). The band at *ca.* 970 cm^{-1} is assignable to the N–O stretch of a nitrosoalkane group. In solution, the molecular weights correspond to twice that of the above stoicheiometry, *i.e.* to M_4 species, so that in solution and in the solid state the structure of the compounds is probably that in (14). The ^1H n.m.r. spectra show somewhat broadened resonances for the alkyl groups which may result from some dissociation.

The molybdenum complex $[Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2]_2$ in toluene reacts very rapidly with PMe_2Ph to give a very sparingly soluble diamagnetic product of stoicheiometry $Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2(PMe_2Ph)_2$ whose i.r. spectrum is virtually identical with that of the starting material except for the additional bands due to PMe_2Ph. This suggests cleavage of the Mo_4 species to give a substituted complex (15).

(*b*) $Mo_2Me_4(PMe_3)_4$. The reaction with NO gives a yellow complex of stoicheiometry $Mo_2O(NO)_2(ONMe)_2(OPMe_3)_2$ which is only sparingly soluble in tetrahydrofuran or CH_2Cl_2, but readily soluble in Me_2SO in which it is monomeric. The ^1H n.m.r. spectrum confirms the presence of Me_3PO [δ 1.40, 1.54 p.p.m., J(P–H) = 12.6

Hz] and an N–Me group (δ 2.11 p.p.m.). The i.r. spectrum confirms Me_3PO [ν(P–O) 1 145 cm^{-1}; ν(P–Me) 948 cm^{-1}] and Mo–NO (1 735 cm^{-1}), while a band at 1 060 cm^{-1} is probably the N–O stretch of the ONMe ligand. A strong band at 860 cm^{-1} is lower than expected for Mo=O and we assign it to a Mo–O–Mo unit. The low solubility suggests a structure such as (16) where there are bridging ONMe groups and which could be readily cleaved by Me_2SO. The Me_3PO evidently results from oxidation of dissociated PMe_3 as in the case of $CoMe_3(PMe_3)_3$.



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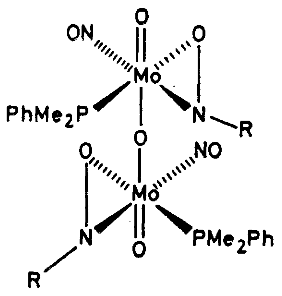

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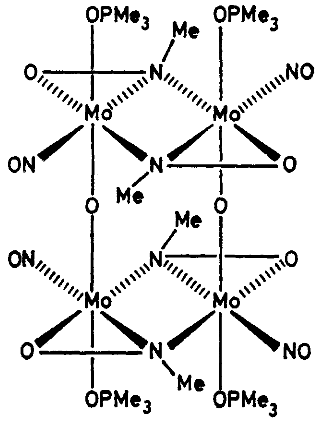


(16)

The formation of ONR and oxo-bridges from the multiply bonded metal–metal alkyls can be accounted for by initial cleavage of the M–M bond by NO. Cleavages by isocyanides under mild conditions are well established,[14] while the alkoxides[15] $M_2(OR)_6$ and $Mo_2Cl_4(PMe_3)_4$[16] have been shown to be cleaved by NO to give nitric oxide complexes, such as $W(OBu^t)_3(NO)$ and $MoCl_2(NO)_2(PMe_3)_2$.

The fact that *N*-alkyl-*N*-nitrosohydroxylaminato-complexes are not formed suggests that the initially formed reactive intermediates are paramagnetic.

(*c*) *Interaction of* $Mo(CO)_6$ *and nitroalkanes.* Nitrosoalkane derivatives may be obtained in other ways,[1] *e.g.* by interaction of nitroalkanes with metal carbonyls, equation (2).[17]

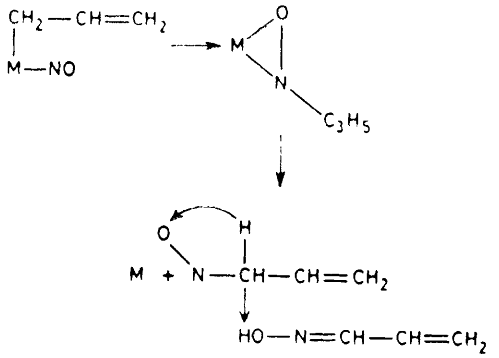
$$ML_n(CO)_2 + RNO_2 \longrightarrow ML_n(ONR) + CO_2 + CO \quad (2)$$

The reaction of $Mo(CO)_6$, however, is clearly complicated. From nitrobenzene and nitromethane, blue and green products respectively, have stoicheiometry $MoO_2(ONR)$. They are sparingly soluble in most organic solvents and probably polymeric but they dissolve in Me_2SO in which they are monomeric. The i.r. spectra show no M–CO bands; two bands in the 800—910 cm^{-1} region suggest *cis*-dioxo-groups, while a band at 950 cm^{-1} can be assigned to RNO. Both compounds are paramagnetic with $\mu_{eff.} = 2.0$ B.M. in the solid state.

The reaction of $Mo(CO)_6$ with *o*-nitrotoluene also produces CO_2, but the red solid formed has stoicheiometry $Mo(ONR)_3$. This paramagnetic ($\mu_{eff.} = 2.1$ B.M.) complex is also sparingly soluble except in Me_2SO in which it is monomeric. The i.r. spectrum has a band at 952 cm^{-1} (RNO) but no Mo–O bands.

We have been unable to obtain crystals of these complexes.

Zirconium.—We have previously[1] isolated *N*-alkyl-*N*-nitrosohydroxylaminato-compounds from reaction of NO with the tetra-alkyls. We now find that zirconium tetra-allyl reacts similarly to give $Zr[ON(C_3H_5)NO]_4$; in some other cases[18] complex allyls of Ni, Rh, Ir, and Ru give the oxime.



The orange crystalline complex, $Zr[ON(C_3H_5)NO]_4$, is air stable. The i.r. spectrum has bands at 1 280, 1 225, 1 160, and 980 cm^{-1} [ON(R)NO] and 1 635 cm^{-1} (C=C). The reaction with NO presumably involves initial conversion of a η^3 into a σ allyl, followed by the usual insertion reaction.

EXPERIMENTAL

Microanalyses were by Pascher (Bonn) and Imperial College Laboratories. The spectrometers used were the Perkin-Elmer R12B, R32 (^1H), Bruker WM-250 (^1H, ^{13}C, ^{31}P), Perkin-Elmer PE 457, 257 (i.r.), and the VG Micromass (mass). Molecular weights in solution 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' n.m.r. technique.

All operations were performed under oxygen-free nitrogen or argon or *in vacuo* 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. The light petroleum used had b.p. 40—60 °C. Nitric oxide (British Oxygen Co.) was purified by trap-to-trap distillation, *in vacuo*. Melting points were determined in sealed capillaries under nitrogen and are uncorrected.

Infrared spectra were taken in Nujol mulls unless otherwise stated. Hydrogen-1 n.m.r. spectral data are in p.p.m. *vs.* $SiMe_4$.

Analytical data are collected in the Table. In all cases, except where specified, nitric oxide was passed through solutions of the reactant at 1 atm pressure.

Analytical data for new compounds

Compound	Colour	M.p. (θ_c/°C)	Found (%) C	H	N	Other	M [a] found	Required (%) C	H	N	Other	M [a] calc.
$[Zn(ONMeNO)_2]_n$	White	155	10.1	2.6	26.5			11.1	2.8	26.0		
$\{Zn[ON(CH_2CMe_3)NO]_2\}_4$	White	90	36.0	6.1	16.8		1 220	36.6	6.7	17.1		1 308
$\{Cu[ON(CH_2SiMe_3)NO]\}_4$	Yellow	180	24.1	5.5	13.2		765	22.8	5.2	13.3		840
$Cu[ON(CH_2SiMe_3)NO]_2{\cdot}0.5(C_2H_5)_2O$	Blue	115	29.1	6.8	13.2		365	30.4	6.8	14.2		358
$Ni_6(\eta\text{-}C_5H_5)_3O(NO)_2(PPh_3)$	Blue	140	45.0	3.5	2.7	5.6 (O) 3.5 (P)	1 030	44.7	3.4	3.2	5.4 3.5	885
$CoMe(NO)(ONMe)(OPMe_3){\cdot}C_5H_8O$	Dark red	55	34.4	8.4	8.6	22.0 (O) 11.4 (P)		34.5	6.7	8.9	20.4 9.9	
$CoMe(NO)(OPMe_3)_3$	Red	45	31.5	7.2	3.7			31.6	7.9	3.7		
$Rh(ONMeNO)(PPh_3)_2{\cdot}2CH_2Cl_2$	Yellow	180	52.0	3.9	3.5	15.5 (Cl)	900	53.7	4.2	3.2	16.3	844
$ReMe_6(NO)$	Red	70 [d]	22.5	5.5	4.8		298 [b]	23.5	5.9	4.6		306
$Re_2O_3Me_4(ONMe)_2$	Orange	110	12.4	3.0	6.0	14.0 (O)	510 [c]	12.6	3.2	4.9	13.9	570
$ReO(CH_2SiMe_3)_2(NO)[ON(CH_2SiMe_3)]$	Orange	60	25.7	6.7	5.0	9.7 (O)	580 [b]	27.5	6.3	5.3	9.2	523
$[ReO(CH_2SiMe_3)_2(NO)(C_5H_8O)]_3$	Yellow	130	30.8	6.4	1.7		1 590	30.1	6.3	2.9		1 434
$[ReO(CH_2SiMe_3)_2(NO)]_3(PPh_3)$	White	95	33.0	4.1	2.9	4.4 (P)		34.0	5.5	2.8	2.1	
$[CrO_2(NO)(ONCH_2SiMe_3)]_6$	Green	180	21.1	4.9	11.7	25.4 (O)	1 490	20.8	4.8	12.1	27.7	1 386
$Mo_2O_3(NO)_2[ON(CH_2SiMe_3)]_2$	Yellow	110	17.0	3.8	10.9		1 090	18.0	4.1	10.5		1 068
$Mo_2O_3(NO)_2[ON(CH_2CMe_3)]_2{\cdot}2CH_2Cl_2$	Yellow	200	20.8	3.5	7.6	18.5 (O)	1 060	21.4	3.9	8.3	16.1	1 004
$W_2O_3(NO)_2[ON(CH_2SiMe_3)]_2$	Yellow	190	13.5	3.0	8.3	16.4 (O)	1 520	13.5	3.1	7.9	15.8	1 420
$W_2O_3(NO)_2[ON(CH_2CMe_3)]_2$	Yellow	210	24.3	5.3	5.9		1 390	26.3	4.6	6.8		1 356
$Mo_2O_3(NO)_2[ON(CH_2SiMe_3)]_2(PMe_2Ph)_2$	Yellow	140	32.1	4.5	6.2			35.6	5.4	6.9		542
$Mo_2O(NO)_2(ONMe)_2(OPMe_3)_2$	Yellow	160	18.7	4.6	8.9	23.2 (O) 11.5 (P)	265 [c]	17.7	4.4	10.3	20.7 11.4	542
$MoO_2(ONPh)$	Blue	>250	29.8	1.9	5.9	22.2 (O)	219 [c]	30.6	2.1	6.0	21.3	225
$MoO_2(ONMe)$	Green	>250	6.6	2.2	8.9	24.7 (O)	160 [c]	6.9	1.7	8.1	27.7	173
$Mo(ONC_6H_4Me)_3$	Red	>250	55.2	3.7	9.1	10.4 (O)	420 [c]	54.9	4.6	9.1	10.5	459
$Zr[ON(C_3H_5)NO]_4$	Yellow	130	28.0	4.0	22.5		560	29.1	4.0	22.6		495

[a] Osmometrically in dichloromethane unless otherwise stated. [b] Cryoscopically in benzene. [c] Cryoscopically in dimethyl sulphoxide. [d] Decomposition.

Bis(N-*methyl*-N-*nitrosohydroxylaminato*)*zinc*(II).—Dimethylzinc[19] (1 g) in light petroleum (30 cm^3) at −30 °C instantaneously gave a white precipitate which was collected, washed with light petroleum and diethyl ether, and dried *in vacuo*. The compound may be recrystallised from CH_2Cl_2. Yield 2.2 g, 93%. I.r. bands at 1 290s, 1 140s, 1 060w, 953s, 700s, 660m, 575m, 540m, and 260w cm^{-1}. Proton n.m.r.: 3.70 p.p.m. (N–Me).

Bis(N-*neopentyl*-N-*nitrosohydroxylaminato*)*zinc*(II).—As for $ZnMe_2$, but using $Zn(CH_2CMe_3)_2$[20] to give colourless microcrystals from CH_2Cl_2. Yield 1.5 g, *ca.* 95%. I.r. bands at 1 290s, 1 185m, 1 115m, 975s, 900m, 762m, 575m, 482w, 345m, and 300w cm^{-1}. Proton n.m.r. 0.95 (9, C–Me) and 3.82 p.p.m. (2, NCH_2).

Tetrakis[N-*nitroso*-N-(*trimethylsilylmethyl*)*hydroxylaminatocopper*(I)]; *Bis*[N-*nitroso*-N-(*trimethylsilylmethyl*)-*hydroxylaminato*]*copper*(II).—At room temperature $[Cu(CH_2SiMe_3)]_4$[21] (2 g) in light petroleum (50 cm^3) rapidly gave a pale yellow precipitate; excess of NO was removed by N_2, the solid was collected and recrystallised from thf as pale yellow crystals. Yield 1.68 g, 60%.

If the reaction mixture is allowed to stand overnight under NO the solution becomes dark. The solvent was removed and the solid first extracted with diethyl ether (3 × 20 cm^3) to give a blue solution which, on cooling to −30 °C, gave $Cu[ON(CH_2SiMe_3)NO]_2{\cdot}0.5(C_2H_5)_2O$ as blue microcrystals. Yield 1.2 g (25%). The residual solid was extracted and recrystallised from thf (20 cm^3) and gave *ca.* 0.85 g of $\{Cu[ON(CH_2SiMe_3)NO]\}_4$. Recrystallisation of the blue complex from toluene gives solvent-free crystals. The mass spectrum of $Cu[ON(CH_2SiMe_3)NO]_2$ shows the molecular ion $C_8H_{22}CuN_4O_4Si_2^+$ and a fragmentation pattern involving loss of methyl groups. I.r. spectra: $\{Cu[ON(CH_2SiMe_3)NO]\}_4$, 1 270s, 1 253s, 1 230m, 1 215m, 1 200s, 1 138s, 1 065w, 1 030w, 972s, 860s, 800w, 775w, 757m, 710w, 700w, 663w, 622w, 538w, 432m, 392m, 340w, 328w, and 250w; $Cu[ON(CH_2SiMe_3)NO]_2$, 1 278s, 1 250s, 1 228w, 1 192s, 1 138m, 1 118s, 950s, 855s, 774w, 748m, 710m, 663m, 619m, 592s, 492m, 468w, 395s, 352s, 321w, and 250w cm^{-1}.

Interaction of NO *with Methylcopper*(I).—A slurry of $(CuMe)_n$[22] (1 g) in thf (50 cm^3) at room temperature with vigorous stirring gave a blue solution and a dark precipitate (Cu). After *ca.* 15 min, the NO was replaced by N_2 and the solution filtered and evaporated. Crystallisation from CH_2Cl_2 gave $Cu[ON(Me)NO]_2$ as blue crystals. Yield 1.1 g, *ca.* 40%. I.r. bands at 1 280s, 1 165s, 1 060w, 948s, 800w, 705s, 592m, 492m, 374m, and 345w cm^{-1}.

Interaction of NO *with* (η-*Cyclopentadienyl*)*methyl*(*triphenylphosphine*)*nickel*(II).—The green solution of $Ni(\eta\text{-}C_5H_5)Me(PPh_3)$[23] (1 g) in toluene (30 cm^3) at room temperature rapidly turned blue and a yellow solid precipitated. The solution was filtered, reduced to *ca.* 5 cm^3, and cooled to −30 °C to give a blue powder which was collected and recrystallised from 1 : 1 $MeOH–CH_2Cl_2$ to give small blue needles. Yield 0.5 g, 42%. I.r. bands at 1 745s, 1 305w, 1 260w, 1 180w, 1 158w, 1 090m, 1 025w, 1 000w, 970w, 920w, 842w, 800m, 738m, 685s, 570w, 520s, 505s, 495s, 450w, and 305w cm^{-1}.

Dimethylbis(μ-nitrosomethane)-dinitrosylbis(trimethylphosphine oxide)dicobalt; Methyl(nitrosyl)tris(trimethylphosphine oxide)cobalt.—At room temperature, $CoMe_3(PMe_3)_3$ [7] (2 g) in light petroleum (50 cm^3) immediately gives a red solution and an orange-red solid. The solid was collected and extracted into diethyl ether (*ca.* 50 cm^3), which was reduced to *ca.* 10 cm^3 and cooled to −30 °C to give red plates of $CoMe(NO)(OPMe_3)_3$. Yield 0.65 g, 28%.

The solid remaining after ether extraction was dissolved in thf (leaving an intractable residue), the solution filtered, concentrated to 10 cm^3, and slowly cooled to −30 °C to give red-brown crystals of $[CoMe(NO)(\mu\text{-}ONMe)(OPMe_3)]_2\cdot$thf. Yield 0.8 g, 55%. I.r. spectra: $[CoMe(NO)(ONMe)(OPMe_3)]_2\cdot$thf, 1 660m, 1 310w, 1 300m, 1 260m, 1 145s, 1 120m, 1 020w, 950s, 868m, 800, 750m, 700w, 365w, 250m, and 235m; $CoMe(NO)(OPMe_3)_3$, 1 660m, 1 310w, 1 300m, 1 262w, 1 145s, 953s, 867m, 835w, 752m, 368m, and 260m cm^{-1}.

N-*Methyl*-N-*nitrosohydroxylaminatobis(triphenylphosphine)rhodium*(I)–*Tetrahydrofuran* (1/2).—At room temperature in 10 min, $RhMe(PPh_3)_3$ [24] (1 g) in thf (20 cm^3) gave a red solution which was filtered, reduced to *ca.* 5 cm^3, and cooled to −30 °C. The yellow precipitate was collected, washed with diethyl ether, and dried *in vacuo*. Yield 0.85 g, 91%. Recrystallisation from CH_2Cl_2 gave the bis solvate. I.r. bands for CH_2Cl_2 solvate at 1 290s, 1 180s, 1 115s, 1 025w, 985w, 925w, 842m, 810m, 742m, 720s, 690s, 610w, 538s, 420w, and 365m cm^{-1}. Proton n.m.r. (C_6D_6): 2.30 (3, N–Me), 5.28 (4, CH_2Cl_2), and 7.35 p.p.m. (30, Ph).

Hexamethyl(nitrosyl)rhenium.—The green solution of $ReMe_6$ [25] (*ca.* 1 g) in light petroleum (20 cm^3) at −78 °C immediately turns red and an orange solid precipitates. After removal of NO by N_2 the solution was warmed to room temperature, filtered, evaporated *in vacuo*, and the residual solid crystallised from light petroleum to give red needles. Yield 0.6 g, 54%. The losses occurred mainly on evaporation of solvent as the complex is volatile and due to further reaction to form the volatile *cis*-ReO_2Me_3.[9]

A similar reaction, but using $ReMe_6$ in diethyl ether, gave an orange solution of $ReMe_6(NO)$ which on warming to room temperature in the presence of NO gradually became yellow. Removal of solvent *in vacuo* at −30 °C and sublimation of the residue to a probe at −78 °C (10^{-3} mmHg) gave *cis*-ReO_2Me_3. Yield 0.59 g, 62%. I.r. bands at 1 715s, 1 260m, 1 175w, 1 090m, 1 015m, 955w, 915m, 800s, 758w, 705m, 562m, 380br, and 280w cm^{-1}.

μ-*Oxo-bis[dimethyl(η²-nitrosomethane)oxorhenium]*.—The complex $Li_2[ReMe_8]$ [25] (1 g) in light petroleum (40 cm^3) reacted exothermally at −70 °C with NO and the red solution became colourless and a yellow solid precipitated. The latter was collected and extracted with thf, the solution filtered, reduced to *ca.* 10 cm^3, and cooled to −30 °C to give a yellow powder. Yield 0.3 g, 33%. I.r. bands at 1 300m, 1 262w, 1 170w, 1 155w, 1 060w, 970m, 935m, 840w, 800w, 712m, 630m, br, 470w, 302w, and 250w cm^{-1}. Proton n.m.r.: 1.21 (6, Re–Me) and 2.18 p.p.m. (N–Me).

(η²-*Nitrosotrimethylsilylmethane)nitrosyloxobis(trimethylsilylmethyl)rhenium*.—The purple solution of $[Re(CH_2SiMe_3)_4]_2N_2$ [26] (2 g) in light petroleum (30 cm^3) does not react with NO at −70 °C but on warming to room temperature the solution became green then orange-brown and an orange-brown precipitate formed. This was collected and recrystallised from toluene as large orange crystals. Yield 1.58 g, 80%. I.r. bands at 1 690s, 1 295w, 1 246s, 1 190w, 1 100br, 1 020m, 972m, 930w, 855s, 750w, 698w, 678w, 572w, 490w, 450w, 400w, and 280w cm^{-1}. Proton n.m.r.: 0.22 (18, $ReCH_2Si\mathit{CH_3}$), 0.34 (4, $Re\mathit{CH_2}SiMe$), 0.38 (9, $N–CH_2Si\mathit{CH_3}$), and 2.42 (2, $N–\mathit{CH_2}$) p.p.m.

Trinitrosyltrioxotris(tetrahydrofuran)hexakis(trimethylsilylmethyl)-triangulo-*trirhenium*.—If the above reaction is carried out in thf or if $ReO(CH_2SiMe_3)_2(NO)(ONCH_2SiMe_3)$ was stirred overnight (16 h), the resultant solution was darker in colour. This solution was evaporated and the solid extracted first with toluene. The resulting brown solution gave $ReO(CH_2SiMe_3)_2(NO)(ONCH_2SiMe_3)$ on cooling to −30 °C. The remaining crude solid was redissolved in thf and the solution cooled to −30 °C to give $[ReO(CH_2SiMe_3)_2(NO)(thf)]_3$ as yellow crystals. Yield 1.1 g, 60% based on $Re_2(CH_2SiMe_3)_8N_2$. I.r., bands at 1 742s, 1 292m, 1 250s, 1 190m, 1 115m, 1 065w, 1 028m, 980m, 910m, 850s, 800w, 720m, 650br, 600s, 500m, 400w, 300w, and 250w cm^{-1}. Proton n.m.r.: 0.21(9) (Si–CH_3), 1.28(2) (Re–$\mathit{CH_2}$–Si), 1.85(4), and 3.74(4) p.p.m. (thf).

Bis(nitrosotrimethylsilylmethane) could be isolated if the initial solid in this reaction was extracted with diethyl ether. Chromatography on alumina using diethyl ether as eluant gave a solution from which $(ONCH_2SiMe_3)_2$ was obtained as colourless crystals. I.r. bands at 1 412m, 1 387m, 1 345m, 1 260s, 1 200w, 1 085, 1 065m, 1 025s, 900w, 850m, 800s, 705m, 600m, 400br, 320w, 290w, 270w, 235w, and 220w cm^{-1}. Proton n.m.r.: 0.01 (9, $Si\mathit{CH_3}$) and 1.20 (2, N–$\mathit{CH_2}$–Si) p.p.m.

Trinitrosyltrioxohexakis(trimethylsilylmethyl)(triphenylphosphine)-triangulo-*trirhenium*.—To a stirred solution of $ReO(CH_2SiMe_3)_2(NO)(\eta^2\text{-}ONCH_2SiMe_3)$ (1 g) in thf (30 cm^3) was added an excess of triphenylphosphine (1 g) and the solution stirred for 16 h. The solution was then evaporated and the white solid washed with several portions (20 cm^3) of diethyl ether to remove excess of PPh_3. The residual solid was recrystallised from thf at −30 °C as a white powder. Yield 0.8 g, 85%. I.r. bands at 1 720m, 1 310w, 1 260m, 1 190m, 1 122s, 1 075w, 1 030w, 1 000w, 970w, 910m, 855m, 800w, 750m, 728s, 695s, 548s, 450br, 328w, 305w, 280w, and 250w cm^{-1}. Proton n.m.r.: 0.15 (54, Si–Me), 2.12 (12, Re–$\mathit{CH_2}$), and 7.4 p.p.m. (br, 15, Ph).

Interaction of NO with Tetrakis(trimethylsilylmethyl)chromium(IV).—The purple solution in light petroleum (50 cm^3) of $Cr(CH_2SiMe_3)_4$ [13] (2 g) at −70 °C is rapidly decolourised by NO to give a green-brown precipitate which was collected at −70 °C and washed with light petroleum. The compound could only be precipitated from thf solution by light petroleum as a powder and attempts to obtain crystals failed. Yield *ca.* 92%. I.r. bands at 1 840s, 1 250m, 1 188m, 1 095m, 1 010m, 940m, 850s, 800br, 750br, 700w, 658w, 562br, 420w, 400w, 350w, and 300w cm^{-1}.

Interaction of NO with Dimolybdenum and Tungsten Hexa-alkyls.—Nitric oxide was bubbled through light petroleum solutions (*ca.* 30 cm^3) of *ca.* 1 g of the alkyls at −78 °C. The yellow precipitates were collected, washed with light petroleum, and recrystallised.

$Mo_2(CH_2SiMe_3)_6$ [13] gave $Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2$ from toluene. Yield 0.7 g, 91%. I.r. bands at 1 790s, 1 252s, 1 200w, 1 090br, 960m, 940m, 850s, 760w, 705m, 685w, 660w, 560w, 520w, 422w, 380w, 260w, and 240w cm^{-1}. Proton n.m.r.: 0.22 (9, Si–CH_3) and 3.80 p.p.m. (2, N–CH_2).

$Mo_2(CH_2CMe_3)_6$ [27] gave $Mo_2O_3(NO)_2(ONCH_2CMe_3)_2{\cdot}2CH_2Cl_2$ from CH_2Cl_2. Yield 0.8 g, 87%. I.r. bands at 1 770s, 1 290s, 1 200s, 1 138s, 1 070m, 1 032m, 978m, 940w, 770s, 720m, 560w, 485w, 420w, and 300m cm^{-1}. Proton n.m.r. 0.97 (s, 9, CMe), 3.86 (s, 2, N–CH_2), and 5.28 p.p.m. (2, CH_2Cl_2).

$W_2(CH_2SiMe_3)_6$ [13] gave $W_2O_3(NO)_2(ONCH_2SiMe_3)_2$ from toluene. Yield 0.8 g, 98%. I.r. bands at 1 740s, 1 260s, 1 200w, 1 100s, 1 020m, 965m, 945m, 850s, 800m, 760w, 705m, 685w, 620w, 530w, 390m, 284w, and 250s cm^{-1}. Proton n.m.r.: 0.39 p.p.m. (br, $CH_2 + CH_3$).

$W_2(CH_2CMe_3)_6$ [27] gave a yellow powder from toluene and $W_2O_3(NO)_2(ONCH_2CMe_3)_2(thf)_2$ from thf. Yield 1 g, 93%. I.r. bands for thf solvate, 1 730s, 1 290m, 1 210s, 1 130s, 1 090w, 1 035w, 1 010w, 975m, 940m, 900s, 768w, 715m, 560w, 485w, and 420w cm^{-1}. Proton n.m.r. for thf solvate: 0.68 (s, 9, CMe), 1.85 (m, 16, thf), 3.74 (m, 16, thf), and 4.18 p.p.m. (br, 4, N–CH_2).

Interaction of μ-Oxo-bis[(nitrosotrimethylsilylmethane)-nitrosyloxomolybdenum] with Dimethylphenylphosphine.—To the yellow toluene solution (10 cm^3) of $Mo_2O_3(NO)_2(ONCH_2SiMe_3)_2$ (0.2 g) was added PMe_2Ph (2 cm^3). The yellow precipitate was collected, washed with toluene, thf, and diethyl ether, and dried *in vacuo*. Yield 0.29 g, 98%. I.r. bands at 1 760s, 1 300s, 1 250w, 1 200w, 1 170br, 1 150w, 1 120m, 1 100br, 1 070w, 1 000w, 965m, 940m, 860s, 750s, 705m, 610w, 560w, 490m, 440m, 390w, 280w, and 250w cm^{-1}.

Interaction of NO with Tetramethyltetrakis(trimethylphosphine)dimolybdenum(II).—The blue solution in light petroleum (30 cm^3) of $Mo_2Me_4(PMe_3)_4$ [28] (1 g) reacted with NO at room temperature to give a yellow-orange precipitate which was collected, washed with light petroleum, and crystallised from dichloromethane as $Mo_2O(NO)_2(ONMe)_2(OPMe_3)_2$. Yield 0.8 g, 85%. I.r. bands at 1 735s, 1 305m, 1 160m, 1 145s, 948s, 860s, 750m, 705w, 610m, 495w, 450w, and 362m cm^{-1}. Proton n.m.r.: 1.40 (3, P–CH_3), 1.54 (3, P–CH_3), and 2.11 p.p.m. (2, N–CH_3).

Reactions of Molybdenum Hexacarbonyl with Nitro-compounds.—*Nitrobenzene*. The compound $Mo(CO)_6$ (1 g) was refluxed in nitrobenzene (50 cm^3) under nitrogen for 16 h. The resulting blue precipitate was collected, washed with acetone, methanol, thf, and diethyl ether, and dried *in vacuo* to give the product $MoO_2(ONPh)$ as a blue powder. I.r. bands at 1 610m, 1 530m, 1 310m, 1 250w, 1 178w, 1 150w, 1 110w, 1 070w, 1 023m, 960s, 855s, 800s, 710s, 610w, 575m, 445w, and 395m cm^{-1}.

Nitromethane. The compound $Mo(CO)_6$ (1 g) was refluxed in nitromethane (50 cm^3) under nitrogen for 16 h. The resulting green precipitate was collected, washed with acetone, methanol, thf, and diethyl ether, and dried *in vacuo* to give the product $MoO_2(ONMe)$ as a green powder. I.r. bands at 1 550w, 1 300w, 1 262w, 1 160w, 1 100w, 950s, 910s, 845s, 800s, 720s, 660m, 570m, 530w, 410w, and 370m cm^{-1}.

2-*Nitrotoluene*. The compound $Mo(CO)_6$ (1 g) was refluxed in 2-nitrotoluene for 16 h. The resulting red precipitate was collected, washed with acetone, methanol, thf, and diethyl ether, and dried *in vacuo* to give the product $Mo(ONC_6H_4Me)_3$ as a dark red powder. I.r. bands at 1 550w, 1 220m, 1 160m, 1 035w, 953s, 910w, 859m, 790s, 760m, 730s, 665m, 565w, 478w, 440m, and 355w cm^{-1}.

Tetrakis(N-*allyl*-N-*nitrosohydroxylaminato*)*zirconium*(IV).—At room temperature, $Zr(C_3H_5)_4$ [29] (1 g) in light petroleum (30 cm^3) gave a pale yellow precipitate which was washed with light petroleum and recrystallised from toluene or acetone. Yield 1.65 g, 85%. I.r. bands at 1 635w, 1 280s, 1 225s, 1 160s, 1 128m, 980s, 940s, 930s, 840m, 762s, 720s, 520br, and 400m cm^{-1}. Proton n.m.r.: 4.52 (d, 2, N–CH_2), 5.20(s), 5.35 (d, 1, 1, C=CH_2), and 5.9 p.p.m. (m, 1, C–H).

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REFERENCES

[1] J. A. McCleverty, *Chem. Rev.*, 1979, **79**, 53.

[2] A. R. Middleton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 1888; *cf.* also S. Amirkhalli, P. B. Hitchcock, J. D. Smith, and J. G. Stamper, *ibid.*, p. 2493.

[3] E. Frankland, *Justus Liebigs Ann. Chem.*, 1856, **99**, 345.

[4] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley, New York, 1980, p. 600.

[5] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organomet. Chem.*, 1972, **34**, 155.

[6] H-F. Klein and H. H. Karsch, *Chem. Ber.*, 1975, **109**, 1453.

[7] H-F. Klein and H. H. Karsch, *Chem. Ber.*, 1975, **108**, 944, 956.

[8] See, for example, R. S. Bereman and J. K. Kochi, *Inorg. Chem.*, 1980, **19**, 248.

[9] K. Mertis and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 1488.

[10] J. F. Rowbottom and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 826; B. Jesowska-Trebiatowska, J. Hanuza, and M. Baluka, *Spectrochim. Acta, Part A*, 1971, **27**, 1753.

[11] P. A. S. Smith 'The Chemistry of Open-Chain Organic Nitrogen Compounds,' W. A. Benjamin, New York, 1966, vol. 2, ch. 13.

[12] P. Edwards, K. Mertis, G. Wilkinson, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 334.

[13] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 533.

[14] R. A. Andersen and G. S. Girolami, *J. Organomet. Chem.*, 1979, **182**, C43; T. E. Wood, J. C. Deaton, J. Corning, R. E. Wild, and R. A. Walton, *Inorg. Chem.*, 1980, **19**, 2614.

[15] M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. C. Kelly, *Inorg. Chem.*, 1979, **18**, 116.

[16] T. Nimry, M. A. Urbancic, and R. A. Walton, *Inorg. Chem.*, 1979, **18**, 691.

[17] E. A. Matta and R. A. D. Wentworth, *Inorg. Chem.*, 1980, **19**, 2597; see also K. Wieghardt, E. Hofer, W. Holzbach, B. Nuber, and J. Weiss, *ibid.*, 1980, **19**, 2927.

[18] R. A. Clement, U. Klabunde, and G. W. Parshall, *J. Mol. Catal.*, 1978, **4**, 87; M. W. Schoonover, E. C. Baker, and R. Eisenberg, *J. Am. Chem. Soc.*, 1979, **101**, 1880.

[19] A. L. Galyer and G. Wilkinson, *Inorg. Synth.*, 1979, **19**, 253.

[20] G. E. Coates and K. Wade, 'Organometallic Compounds,' Methuen, London, 1976, vol. 1.

[21] J. A. Jarvis, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1977, 999.

[22] Y. Yamamoto, H. Yatagai, A. Sonodo, and S. Murahashi, *J. Chem. Soc., Chem. Commun.*, 1976, 452.

[23] J. Thomson and M. C. Baird, *Can. J. Chem.*, 1970, **48**, 3443.

[24] W. Keim, *J. Organomet. Chem.*, 1968, **14**, 179.

[25] K. Mertis, P. G. Edwards, G. Wilkinson, K. M. A. Malik, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1980, 654.

[26] A. F. Masters, K. Mertis, J. F. Gibson, and G. Wilkinson, *Nouv. J. Chim.*, 1978, **1**, 389.

[27] W. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 1120.

[28] R. A. Andersen, R. A. Jones, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1979, 446.

[29] G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 151.