Cationic Carbonylnitrosyl Complexes of Molybdenum and Tungsten

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The complexes $[M(CO)_4(diphos)]$ [M = Mo and W; diphos = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$] and $NOPF_6$ react in methanol–toluene to afford $[M(CO)_3(NO)(diphos)]PF_6$ which, in turn, react with halides, X^-, and dithiocarbamate salts, $Na[S_2CNR_2]$ (R = Me and Et), to give $[M(CO)_2(NO)(diphos)X]$ and $[M(CO)(NO)(diphos)(S_2CNR_2)]$ respectively. With phosphine ligands, L, $[Mo(CO)_3(NO)(diphos)]PF_6$ reacts in chloroform to yield $[M(CO)(NO)(diphos)(L)Cl]$ [L = PPh_3, $P(OPh)_3$, $P(OMe)_3$, and diphos] and in acetone to give $[Mo(CO)_2(NO)(diphos)(PPh_3)]_2(PF_6)_2$,2acetone and $[Mo(CO)(NO)(diphos)_2]PF_6$. When heated under reflux in chloroform the complex $[Mo(CO)_3(NO)(diphos)]PF_6$ is decarbonylated to yield $[Mo(NO)(diphos)Cl_2]_n$ and other polynuclear nitrosyl species.

ALTHOUGH many nitrogen monoxide complexes of the Group VI metals are known,[1,2] few have been reported which also contain carbon monoxide. Apart from a recent report [3] of mononuclear complexes of the type $[M(CO)_2(NO)(L)Cl]$ [L = diphos $Ph_2PCH_2CH_2PPh_2$, 2,2′-bipyridine (bipy), *etc.*], the majority of Group VI carbonylnitrosyl complexes are polynuclear, such as $[Mo(CO)_2(NO)(bipy)]_2$ [4] or $[Mo(CO)_2(NO)(OH)]_4,4OPPh_3$,[5] or contain π-cyclopentadienyl (cp) or similar ligands, such as $[(cp)Mo(CO)_2(NO)]$ [6] or $[RB(pz)_3Mo(CO)_2(NO)]$ [7] (pz = pyrazolyl; R = alkyl group).

Interest in cationic nitrosyl complexes [8,9] † and their reactivity towards nucleophilic reagents has led to an investigation of the reactions of the nitrosyl cation, NO^+, with Group VI metal carbonyl derivatives, such as $[M(CO)_4(diphos)]$, and to a preliminary report of the preparations of the complexes $[M(CO)_3(NO)(diphos)]PF_6$ (M = Mo and W).[10] Details of a study of these species, which are useful precursors to a wide range of cationic and neutral, mono- and poly-nuclear metal nitrosyl complexes, are now presented.

RESULTS AND DISCUSSION

In mixtures of methanol and toluene, or in acetonitrile, the complexes $[M(CO)_4(diphos)]$ (M = Mo and W) react with $NOPF_6$ to give good yields of the yellow, cationic carbonylnitrosyl complexes $[M(CO)_3(NO)(diphos)]PF_6$. These species, as well as the other new complexes described here, were characterised by elemental analysis and i.r. spectroscopy (Table). In contrast to the molybdenum and tungsten complexes, $[Cr(CO)_4(diphos)]$ is oxidised by $NOPF_6$ in methanol–toluene to afford $[Cr(CO)_4(diphos)]PF_6$. The deep purple cation is decomposed in polar solvents, but may be purified by rapid recrystallisation from dichloromethane–diethyl ether. In acetonitrile, formation of the complex $[Cr(NO)_2(MeCN)_4](PF_6)_2$ [11] from $[Cr(CO)_4(diphos)]$ and $NOPF_6$ again contrasts with the behaviour of the molybdenum and tungsten analogues.

The complexes $[M(CO)_3(NO)(diphos)]PF_6$ (M = Mo and W) react with a variety of anionic and neutral ligands yielding a range of neutral and cationic carbonylnitrosyl complexes. In general the tungsten complex reacts much more slowly than the molybdenum analogue and its chemistry is rather limited. With halide ions in acetone or CH_2Cl_2, the cationic complexes react to give $[M(CO)_2(NO)(diphos)X]$ (X = Cl, Br, and I) as air-stable, yellow to orange crystalline solids. The chloro-complexes have been prepared previously from $[M(CO)_3(MeCN)_3]$, nitrosyl chloride, and diphos.[3] The reactions of Me_4NI with $[M(CO)_3(NO)(diphos)]PF_6$ illustrate the lesser reactivity of the tungsten complex. The complex $[Mo(CO)_2(NO)(diphos)I]$ is formed readily at room temperature whereas $[W(CO)_2(NO)(diphos)I]$ is formed only when heated under reflux in acetone.

The overall molecular geometry of the $[M(CO)_2(NO)(diphos)X]$ complexes cannot be inferred from their i.r. spectra, although the presence of two carbonyl absorptions of similar intensity implies that the carbonyl groups are *cis*-arranged. Somewhat surprisingly the positions of the carbonyl and nitrosyl absorptions show no marked dependence on the halide ligand.

The reactions of the complexes $[M(CO)_3(NO)(diphos)]PF_6$ with the dithiocarbamate salts $Na[S_2CNR_2]$ (R = Me and Et) underline the difference in reactivity between the molybdenum and tungsten complexes. Although the complexes $[M(CO)(NO)(diphos)(S_2CNR_2)]$ (M = Mo and W; R = Me and Et) have all been isolated as dark red, crystalline solids, the tungsten species are formed much more slowly than are the molybdenum complexes.

Monitoring, by i.r. spectroscopy, the course of the reaction between the complex $[W(CO)_3(NO)(diphos)]PF_6$ and the salt $Na[S_2CNMe_2]$, enabled an intermediate in the formation of $[W(CO)(NO)(diphos)(S_2CNMe_2)]$ to be identified. In acetone solution the complex $[W(CO)_3(NO)(diphos)]PF_6$ exhibits carbonyl stretching absorptions at 2 097 and 2 017 cm^{-1}. On addition of

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† *Note added in proof:* See also M. Green and S. H. Taylor, *J.C.S. Dalton*, 1972, 2629.

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[4] E. Lindner, H. Behrens, and G. Lehnert, *Z. Naturforsch.*, 1970, **25***b*, 104.

[5] V. Albano, P. Bellon, G. Ciani, and M. Manassero, *Chem. Comm.*, 1969, 1242.

[6] R. B. King, *Inorg. Chem.*, 1967, **6**, 30.

[7] S. Trofimenko, *Inorg. Chem.*, 1969, **8**, 2675.

[8] B. F. G. Johnson and J. A. Segal, *J. Organometallic Chem.*, 1971, **31**, C79.

[9] N. G. Connelly and J. D. Davies, *J. Organometallic Chem.*, 1972, **38**, 385.

[10] B. F. G. Johnson, S. Bhaduri, and N. G. Connelly, *J. Organometallic Chem.*, 1972, **40**, C36.

[11] N. G. Connelly and L. F. Dahl, *Chem. Comm.*, 1970, 880.

Carbonylnitrosyl complexes of molybdenum and tungsten

Complex	Colour	M.p. (t/°C)	Yield (%)	Analysis (%)										I.r.		
				C		H		N		P		Others				
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	ν(CO)	ν(NO)	Medium
$\mathrm{[Cr(CO)_4(diphos)]PF_6}$	Purple	decomp. > 200	45	50·95	50·15	3·4	3·3	0·0	0·0					2 090s, 2 015ms, 1 978s		$\mathrm{CH_2Cl_2}$
$\mathrm{[Mo(CO)_3(NO)(diphos)]PF_6}$	Yellow	decomp. >155	80	46·3	46·25	3·2	3·35	1·85	1·7	12·3	12·15			2 111m, 2 040vs	1 735vs	$\mathrm{CH_2Cl_2}$
$\mathrm{[W(CO)_3(NO)(diphos)]PF_6}$	Yellow	decomp. >160	53	41·4	41·25	2·9	2·9	1·65	1·6					2 102m, 2 025vs	1 725vs	$\mathrm{CH_2Cl_2}$
$\mathrm{[Mo(CO)_2(NO)(diphos)Cl]}$	Pale yellow	decomp. >160	55	54·6	54·15	3·95	4·1	2·25	2·05					2 045vs, 1 982vs 2 038vs, 1 974vs	1 639vs 1 624vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[Mo(CO)_2(NO)(diphos)Br]}$	Yellow	decomp. >150	28	51·05	50·45	3·65	3·7	2·1	2·0					2 045vs, 1 982vs 2 034vs, 1 970vs	1 639vs 1 624vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[Mo(CO)_2(NO)(diphos)I]}$	Yellow-orange	decomp. >150	35	47·55	47·15	3·4	3·45	2·0	1·9					2 039vs, 1 979vs 2 027vs, 1 964vs	1 642vs 1 641vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[W(CO)_2(NO)(diphos)Cl]}$	Pale yellow	decomp. >180	57	47·8	47·9	3·45	3·55	2·0	1·85					2 031vs, 1 959vs 2 023vs, 1 953vs	1 621vs 1 607vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[W(CO)_2(NO)(diphos)Br]}$	Yellow	decomp. >175	43	44·95	45·3	3·25	3·4	1·85	1·9					2 031vs, 1 961vs 2 018vs, 1 948vs	1 621vs 1 613vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[W(CO)_2(NO)(diphos)I]}$	Yellow	decomp. >190	45	42·3	42·55	3·05	3·15	1·75	1·7					2 029vs, 1 959vs 2 015vs, 1 947vs	1 625vs 1 629vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[Mo(CO)(NO)(diphos)\text{-}(S_2CNMe_2)]}$	Red	decomp. then melts 215	56	53·55	53·8	4·5	4·7	4·15	4·2					1 923vs	1 597vs	$\mathrm{CHCl_3}$
$\mathrm{[Mo(CO)(NO)(diphos)\text{-}(S_2CNEt_2)]}$	Red	decomp. 140	30	54·85	54·7	4·9	4·75	4·0	4·1					1 909vs	1 597vs	$\mathrm{CHCl_3}$
$\mathrm{[W(CO)(NO)(diphos)\text{-}(S_2CNMe_2)]}$	Red	decomp. then melts 218—220	53	47·4	47·2	4·0	3·85	3·7	3·55					1 899vs	1 571vs	$\mathrm{CHCl_3}$
$\mathrm{[W(CO)(NO)(diphos)\text{-}(S_2CNEt_2)]}$	Red	204—205	41	48·75	48·35	4·35	4·1	3·55	3·55					1 901vs	1 569vs	$\mathrm{CHCl_3}$
$\mathrm{[Mo(CO)(NO)(diphos)\text{-}(PPh_3)Cl]}$	Pale yellow	decomp. >165	42	63·55	63·3	4·6	4·65	1·65	2·05			4·15 (Cl)	4·5	1 949vs 1 930vs	1 597vs 1 600vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[Mo(CO)(NO)(diphos)\text{-}\{P(OPh)_3\}Cl]}$	Pale yellow	decomp. >170	7	60·2	59·9	4·4	4·1	1·55	1·7	10·35	10·7	3·95 (Cl)	4·35	1 979vs 1 965vs	1 621vs 1 620vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[Mo(CO)(NO)(diphos)\text{-}\{P(OMe_3)\}Cl]}$	Pale yellow	decomp. 155	13	50·6	51·15	4·65	4·8	1·95	1·8					1 957vs 1 935vs	1 613vs 1 610vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[Mo(CO)(NO)diphos)_2Cl]}$	Pale yellow	decomp. 180	38	64·55	64·95	4·9	5·2	1·4	1·45			3·6 (Cl)	4·2	1 953vs 1 935vs	1 601vs 1 601vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[Mo(CO)_2(NO)(diphos)(PPh_3)]\text{-}PF_6}$, acetone	Orange-yellow	decomp. 125	22	56·25	56·25	4·35	4·45	1·35	1·3	11·85	12·05	10·9 (F)	11·05	1 935vs 1 710wk (acetone) 1 943vs, 1709 wk (acetone)	1 620vs 1 658m 1 629vs 1 657m	Nujol $\mathrm{CH_2Cl_2}$
$\mathrm{[Mo(CO)(NO)(diphos)_2]PF_6}$	Tangerine	decomp. 185	21	58·1	58·1	4·4	4·7	1·3	1·25					1 945vs 1 940vs	1 645vs 1 640vs	$\mathrm{CHCl_3}$ Nujol
$\mathrm{[Mo(NO)(diphos)_2]_2,CH_2Cl_2}$	Yellow	decomp. 210	31	65·35	65·2	5·1	5·4	1·45	1·45						1 510s	Nujol
$\mathrm{[Mo(NO)(diphos)Cl_2]}_n$	Lilac	decomp. 250	4	52·45	51·9	4·05	4·25	2·35	2·3	10·4	10·3	11·9 (Cl)	11·85		1 625vs	Nujol
(C)	Orange	decomp. > 200			47·1		3·85		2·95						1 627vs 1 650vs 1 662vs	$\mathrm{CH_2Cl_2}$ Nujol $\mathrm{CHCl_3}$
(D)	Orange	decomp. > 200			47·2		3·8		2·85						1 655vs 1 665vs	Nujol $\mathrm{CHCl_3}$

$Na[S_2CNMe_2]$ to the solution, the i.r. spectrum rapidly changed so that, after 30 min, the original absorptions had been replaced by bands at 2 004 and 1 909 cm^{-1}. Continuation of the reaction then caused a band at 1 891 cm^{-1} to develop which, after 6½ h, was the only absorption observable in the carbonyl region. As the band at 1 891 cm^{-1} is due to the complex [W(CO)(NO)(diphos)(S_2CNMe_2)], it is possible to suggest that the bands at 2 004 and 1 909 cm^{-1} are due to intermediate formation of [$W(CO)_2$(NO)(diphos)(S_2CNMe_2)] in which the sulphur ligand is probably monodentate. Attempts to isolate this intermediate met with limited success. Termination of the reaction between the complex [$W(CO)_3$(NO)(diphos)]PF_6 and the salt $Na[S_2CNMe_2]$, after 15 min and evaporation of the mixture to dryness, afforded an orange-red solid. On treatment of the solid with CH_2Cl_2, and removal of $NaPF_6$ by filtration, an orange solution was obtained which showed i.r. absorptions at 2 013, 1 913, and 1 625 cm^{-1}. However, chromatography of the solution on silica gel afforded only one band which, on elution, exhibited absorptions at 1 900 and 1 575 cm^{-1} due to the complex [W(CO)(NO)(diphos)(S_2CNMe_2)].

^1H N.m.r. spectra of the complexes [M(CO)(NO)(diphos)(S_2CNR_2)] confirm the formulation of the complexes and also allow a *cis*-carbonylnitrosyl arrangement to be deduced. The diethyldithiocarbamato-species have complex spectra but the dimethyldithiocarbamates each show, in $CDCl_3$, two singlets of equal intensity ($M = Mo$, resonances at τ 7·40 and 7·10; $M = W$, resonances at τ 7·50 and 7·25) which may be assigned to two inequivalent methyl substituents on the sulphur ligand. Since the methyl groups in the complexes *trans*-[M(CO)(NO)(diphos)(S_2CNMe_2)] are geometrically equivalent, whereas those in the *cis*-isomer are inequivalent (due to the lack of free rotation about the $C\overset{...}{-}N$ bond of the co-ordinated dithiocarbamate ligand), *cis*-arrangement of the carbonyl and nitrosyl groups must occur. However, no distinction may be made between the two possible *cis*-complexes, in which the nitrosyl ligand is either *trans* to phosphorus or *trans* to sulphur. The variable-temperature ^1H n.m.r. spectrum of the complex [W(CO)(NO)(diphos)(S_2CNMe_2)] in chlorobenzene shows that at *ca.* 90 °C the two methyl resonances collapse to a broad singlet. The methyl groups probably become equivalent *via* a mechanism involving the formation of a monodentate dithiocarbamato-linkage, such a mechanism having been suggested to account for the temperature dependence of the ^1H n.m.r. spectra of the complexes [$Mo(NO)_2(S_2CNMe_2)_2$] and [$Mo(NO)(S_2CNMe_2)_3$].[12] A more detailed study of the ^1H n.m.r. spectra of the complexes [M(CO)(NO)(diphos)(S_2CNR_2)] will be reported at a later date.

The reactions of the complexes [$M(CO)_3$(NO)(diphos)]PF_6 with neutral phosphine ligands lead to a variety of products, the identities of which largely depend on the solvent. When heated under reflux in chloroform the complex [$Mo(CO)_3$(NO)(diphos)]PF_6 reacts with ligands [$L = PPh_3$, $P(OPh)_3$, $P(OMe)_3$, and diphos] to give reaction mixtures from which [Mo(CO)(NO)(diphos)(L)Cl] may be isolated by chromatography on alumina. Yields of the phosphine derivatives, particularly those in which L is $P(OPh)_3$ or $P(OMe)_3$, are fairly low since considerable amounts of the polynuclear species formed by decarbonylation of the complex [$Mo(CO)_3$(NO)(diphos)]PF_6 also occur.

The physical appearance of the complex [Mo(CO)(NO)$(diphos)_2$Cl] and its i.r. spectrum in the carbonyl and nitrosyl regions are very similar to those of [Mo(CO)(NO)(diphos)(PPh_3)Cl]. It therefore seems probable that [Mo(CO)(NO)$(diphos)_2$Cl] is six-co-ordinate, containing a monodentate diphos ligand. It should be noted that this complex is probably identical to the second species isolated by Robinson *et al.*,[3] from [$Mo(CO)_3(MeCN)_3$], nitrosyl chloride, and diphos, which they formulated, on the basis of i.r. absorptions at 1 947 and 1 610 cm^{-1}, as *trans*-[$Mo(CO)_2$(NO)(diphos)Cl]. The chloride ligands in [Mo(CO)(NO)(diphos)(L)Cl] are obviously abstracted from the chloroform solvent and it is probable that this abstraction occurs before substitution of the second carbonyl ligand by L. Monitoring of the reactions between the salt [$Mo(CO)_3$(NO)(diphos)]PF_6 and L by i.r. spectroscopy showed that an intermediate was formed which exhibited carbonyl and nitrosyl absorptions at wavenumbers identical to those of [$Mo(CO)_2$(NO)(diphos)Cl]. In support of this, [$W(CO)_3$(NO)(diphos)]PF_6 reacts with PPh_3 in boiling chloroform to yield only [$W(CO)_2$(NO)(diphos)Cl]. No evidence for substitution by PPh_3 could be found even after prolonged heating under reflux.

In acetone the complex [$Mo(CO)_3$(NO)(diphos)]PF_6 reacts with L to give cationic substitution products. With PPh_3 an orange-yellow complex, purified by chromatography on silica gel in acetone, and analysing for [$Mo(CO)_2$(NO)(diphos)(PPh_3)]PF_6,acetone, is formed. The i.r. spectrum of this complex in CH_2Cl_2 in the region 2 000—1 600 cm^{-1} (Figure) cannot easily be explained on the basis of a monomeric structure. Apart from the band at 1 709 cm^{-1}, due to the ketonic carbonyl group of acetone (and also present in a spectrum of the solid complex in Nujol), bands at 1 943vs, 1 657m, and 1 629vs cm^{-1} were also observed. The bands at 1 943 and 1 629 cm^{-1} may be assigned to terminal carbonyl and nitrosyl absorptions respectively and, in the absence of the band at 1 657 cm^{-1}, this data would allow a monomeric structure for the complex to be postulated in which the two carbonyl groups occur in a *trans*-arrangement. However, in the presence of the band at 1 657 cm^{-1}, this formulation is thought to be improbable. The low wavenumber of this band probably rules out the possibility that it is due to a bridging carbonyl vibration and it is more probable that it is, together with the absorption at 1 629 cm^{-1}, due to terminal nitrosyl stretching vibrations. A possible dimeric structure for the complex, in which the diphosphine ligands bridge two six-co-ordinate metal atoms, is shown below. The complex

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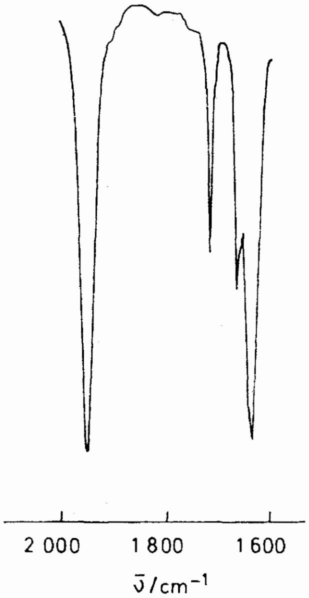
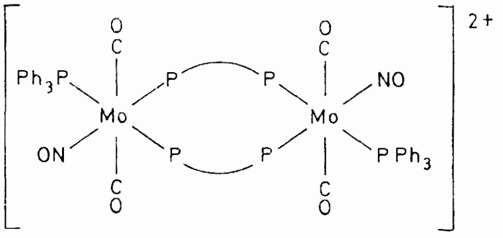
[12] R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 994.

$[Mo(CO)_2(NO)(diphos)(PPh_3)]_2(PF_6)_2$,2acetone reacts with Ph_4AsCl in chloroform at room temperature to give [*Mo(CO)(NO)(diphos)*$(PPh_3)Cl$].



I.r. spectrum of the complex $[Mo(CO)_2(NO)(diphos)(PPh_3)]_2(PF_6)_2$,2acetone in CH_2Cl_2

With an excess of diphos in acetone, the complex $[Mo(CO)_3(NO)(diphos)]PF_6$ reacts to form a mixture from which two complexes may be isolated. Diethyl ether extraction of the reaction mixture, followed by evaporation to dryness of the extracts, chromatography and recrystallisation from dichloromethane–hexane, yielded a yellow complex which elemental analysis suggested to be $[Mo(NO)(diphos)_2],\frac{1}{2}CH_2Cl_2$. The i.r. spectrum of the complex confirms the absence of carbonyl ligands and the PF_6^- anion and the presence of diphos and the nitrosyl ligand. The absorption assigned to ν(NO), at 1 510 cm^{-1} in Nujol, is rather low but not incompatible with the presence of a terminal nitrosyl ligand bonded to a highly phosphine-substituted metal atom. If the molybdenum atom in this species is to obey the 18-electron rule, the complex should be formulated as a dimer, $[Mo(NO)(diphos)_2]_2,CH_2Cl_2$, with a metal–metal bond. A similar structure has been assigned to the complex $[Mo(NO)(CO)_2(bipy)]_2$ [4] which may be considered to be another derivative of the unknown $[Mo(NO)(CO)_4]_2$, a molecule electronically equivalent to $[Mn_2(CO)_{10}]$.



P⌒P = diphos

The diethyl ethyl-insoluble residue from the reaction of the complex $[Mo(CO)_3(NO)(diphos)]PF_6$ with diphos in acetone may be chromatographed to yield tangerine crystals of $[Mo(CO)(NO)(diphos)_2]PF_6$. It is interesting to note that this complex cannot be made directly from $[Mo(CO)_2(diphos)_2]$ and $NOPF_6$. In dichloromethane,[13] methanol–toluene, or acetonitrile,[10] oxidation of the dicarbonyl complex takes place to give *cis*- and/or *trans*-$[Mo(CO)_2(diphos)_2]^+$, and in nitromethane, further oxidation occurs to yield *cis*-$[Mo(CO)_2(diphos)_2]^{2+}$.[13]

The reaction between the complex $[Mo(CO)_3(NO)(diphos)]PF_6$ and boiling chloroform yields a mixture of at least three polynuclear molybdenum nitrosyl complexes. The use of chromatography on alumina allowed the isolation of three species which have only partly been characterised. The first complex to be eluted from the chromatography column was isolated as a lilac solid which showed one nitrosyl absorption in its i.r. spectrum at 1 625 cm^{-1}, but no bands due to co-ordinated carbonyl ligands or to the PF_6^- anion. Elemental analysis (for C, H, N, P, and Cl) allows the empirical formula $[Mo(NO)(diphos)Cl_2]$ to be deduced for the complex. Assuming that each metal atom obeys the 18-electron rule, and that the nitrosyl ligand is a three-electron donor, structures containing molybdenum–molybdenum bonds and chlorine bridges may be postulated.

The two other species which have been isolated as crystalline complexes [(C) and (D), see Experimental section] are both orange-brown with essentially identical i.r. spectra in Nujol in the region 3 000—625 cm^{-1}. Each spectrum shows one terminal nitrosyl absorption, at *ca.* 1 650 cm^{-1}, and the presence in the complexes of the PF_6^- anion and the diphos ligand. Elemental analyses (C, H, and N) of the two species (Table) are also virtually identical suggesting, with the spectral evidence, that the two complexes may be isomers. Although meaningful formulae have not been deduced, the analyses do suggest that the two complexes are polynuclear. It is probable that *X*-ray structural studies are the only means by which these species can be fully identified.

EXPERIMENTAL

The preparation and purification of the complexes described below were carried out under nitrogen atmospheres, unless otherwise stated. Although air was not excluded in the running of chromatography columns, eluted solutions were collected under an atmosphere of nitrogen. The complexes $[Mo(CO)_4(diphos)]$ and $[W(CO)_4(diphos)]$ were prepared by published methods.[14] $NOPF_6$ was purchased from Ozark Mahoning Co. Ltd., Tulsa, Oklahoma.

I.r. spectra were recorded on a Perkin-Elmer PE 257 spectrophotometer. N.m.r. spectra were recorded on a Varian Associates HA 100 instrument. Microanalyses were determined by Alfred Bernhardt Microanalytical Laboratories, Elbach über Engelskirchen, West Germany, F. and A. Pascher, Microanalytical Laboratories, Bonn, West

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[13] R. H. Riemann and E. Singleton, *J. Organometallic Chem.*, 1971, **32**, C44.

[14] F. Zingales and F. Canziani, *Gazzetta*, 1962, **92**, 343.

Germany, or by the Microanalytical Department of the School of Chemistry, University of Bristol. M.p.s are uncorrected.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*tricarbonylnitrosylmolybdenum Hexafluorophosphate*.—To a vigorously stirred solution of the complex [Mo(CO)$_4$(diphos)] (1·2 g) in toluene (50 cm^3)–methanol (7 cm^3) was added an excess of solid NOPF$_6$ (*ca.* 0·8 g). Carbon monoxide was evolved and the yellow complex was precipitated. Addition of diethyl ether (50 cm^3) ensured complete precipitation. The *product* was collected by filtration and recrystallised from dichloromethane–hexane to give [Mo(CO)$_3$(NO)(diphos)]PF$_6$ (1·2 g) {80% yield based on [Mo(CO)$_4$(diphos)]}. The complex is soluble in polar solvents such as acetone, CH$_2$Cl$_2$, and to a lesser extent CHCl$_3$ to give yellow solutions which are very slowly decomposed in air. [1,2-*Bis*(*diphenylphosphino*)-*ethane*]*tricarbonylnitrosyltungsten hexafluorophosphate* was prepared in the same manner, as yellow crystals {63% yield based on [W(CO)$_4$(diphos)]}.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*dicarbonylchloronitrosylmolybdenum*.—To the complex [Mo(CO)$_3$(NO)(diphos)]-PF$_6$ (0·25 g) in CH$_2$Cl$_2$ (30 cm^3) was added Ph$_4$AsCl (0·28 g). On stirring at 30—35 °C the yellow solution darkened to orange and carbon monoxide was evolved. After 1 h the mixture was reduced in volume by evaporation at the water pump, and then placed on a chromatography column of silica gel in CH$_2$Cl$_2$. Elution with CH$_2$Cl$_2$ afforded a pale yellow band which was collected as a yellow solution. After addition of hexane partial evaporation of the mixture afforded the *product* (0·11 g) as pale yellow needles. (55% yield based on [Mo(CO)$_3$(NO)(diphos)]PF$_6$.)

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*bromodicarbonylnitrosylmolybdenum*.—The complex [Mo(CO)$_3$(NO)(diphos)]PF$_6$ (0·25 g) and LiBr (0·1 g) were stirred together in dry acetone (30 cm^3) for 90 min. The solution was then evaporated to *ca.* 10 cm^3 and chromatographed on alumina–acetone. The pale yellow band was eluted with acetone and then partially evaporated, in the presence of hexane, until cloudy. After 12 h at 0 °C, the *complex* (0·06 g) was collected as orange-yellow crystals {28% yield based on [Mo(CO)$_3$(NO)(diphos)]-PF$_6$}.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*dicarbonyliodonitrosylmolybdenum* {from [Mo(CO)$_3$(NO)(diphos)]PF$_6$ and Me$_4$NI, stirred for 3 h}, [1,2-*bis*(*diphenylphosphino*)*ethane*]*dicarbonylchloronitrosyltungsten* {from [W(CO)$_3$(NO)(diphos)]PF$_6$ and Ph$_4$AsCl; stirred for 3 h at 40 °C}, [1,2-*bis*(*diphenylphosphino*)*ethane*]*bromodicarbonylnitrosyltungsten* {from [W(CO)$_3$-(NO)(diphos)]PF$_6$ and LiBr; stirred for 6¼ h at 40 °C}, and [1,2-*bis*(*diphenylphosphino*)*ethane*]*dicarbonyliodonitrosyltungsten* {from [W(CO)$_3$(NO)(diphos)]PF$_6$ and Me$_4$NI, heated under reflux for 30 min} were prepared similarly in 35—60% yields. All the complexes dissolved in solvents such as acetone, CH$_2$Cl$_2$, and CHCl$_3$ to give yellow or pale orange solutions which are only slowly decomposed by air.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*carbonyl*(*dimethyldithiocarbamato*)*nitrosylmolybdenum*.—The complex [Mo(CO)$_3$-(NO)(diphos)]PF$_6$ (0·25 g) and NaS$_2$CNMe$_2$,2H$_2$O (0·09 g) were stirred in acetone (30 cm^3) for 1½ h. The resulting orange-red solution was then evaporated to dryness and the residue dissolved in the minimum volume of CH$_2$Cl$_2$. Chromatography on alumina–dichloromethane afforded a red band which was eluted with CH$_2$Cl$_2$ and evaporated to *ca.* 15 cm^3. Addition of ethanol (40 cm^3) and storage at 0 °C overnight gave the *product* (0·13 g) as red crystals {yield 56% based on [Mo(CO)$_3$(NO)(diphos)]PF$_6$}. The complex is soluble in solvents such as acetone, CH$_2$Cl$_2$, and CHCl$_3$ to give red-orange solutions which are only very slowly decomposed in air. The corresponding *diethyldithiocarbamato-complex* and the *tungsten analogues* were prepared as red crystalline solids by similar methods. The preparation of the tungsten complexes, however, required reaction times of *ca.* 6 h. Yields of the complexes were in the range 40—60%.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*carbonylchloronitrosyl*(*triphenylphosphine*)*molybdenum*.—The complex [Mo(CO)$_3$-(NO)(diphos)]PF$_6$ (0·5 g) and PPh$_3$ (0·5 g) were heated under reflux in CHCl$_3$ (60 cm^3) for 3½ h. The resulting orange-brown solution was then evaporated to dryness and the residue dissolved in the minimum volume of CHCl$_3$. Chromatography on alumina–chloroform then afforded a yellow band which, on elution with CHCl$_3$, gave a yellow solution. Addition of hexane to the solution followed by partial evaporation afforded yellow [Mo(CO)(NO)(diphos)-(PPh$_3$)Cl] {0·2 g, yield 42% based on [Mo(CO)$_3$(NO)-(diphos)]PF$_6$}. The complex is soluble in acetone, CH$_2$Cl$_2$, and CHCl$_3$ and sparingly soluble in diethyl ether to give yellow solutions which slowly decompose in air. The *triphenyl phosphito-* (7%), *trimethyl phosphito-* (13%, after heating under reflux for 6½ h), and the *bis*(*diphos*) *complexes* (38%) were prepared by similar methods.

Bis{[1,2-*bis*(*diphenylphosphino*)*ethane*]*dicarbonylnitrosyl*(*triphenylphosphine*)*molybdenum*} *Bis*(*hexafluorophosphate*)–*Acetone* (1 : 2).—The complex [Mo(CO)$_3$(NO)(diphos)]PF$_6$ (0·25 g) and PPh$_3$ (0·27 g) were heated under reflux in dry acetone (30 cm^3) for 4½ h. The orange solution was then evaporated to *ca.* 15 cm^3 and hexane (50 cm^3) added. After 12 h at 0 °C an impure yellow solid was collected. Chromatography of the solid on alumina–acetone afforded a yellow-orange band which, on elution with acetone, gave a yellow-orange solution. Addition of hexane followed by partial evaporation until the mixture was cloudy and subsequent storage at 0 °C yielded the *complex* (0·08 g) as yellow-orange needles {yield 22% based on [Mo(CO)$_3$(NO)(diphos)]PF$_6$}. The complex is soluble in acetone, CH$_2$Cl$_2$, and CHCl$_3$ giving yellow-orange solutions which are moderately stable in air.

Reaction of [Mo(CO)$_2$(NO)(diphos)(PPh$_3$)]$_2$(PF$_6$)$_2$,2acetone *with* Ph$_4$AsCl.—The complex [Mo(CO)$_2$(NO)(diphos)-(PPh$_3$)]$_2$(PF$_6$)$_2$,2acetone (0·06 g) and Ph$_4$AsCl (0·06 g) were stirred together in CHCl$_3$ (10 cm^3). After 90 min Ph$_4$AsPF$_6$ was filtered off from the yellow solution and the filtrate evaporated to dryness. The yellow residue was then chromatographed on alumina–chloroform to afford [Mo-(CO)(NO)(diphos)(PPh$_3$)Cl] {0·02 g, yield 41% based on [Mo(CO)$_2$(NO)(diphos)(PPh$_3$)]$_2$(PF$_6$)$_2$,2acetone}.

Reaction of [Mo(CO)$_3$(NO)(*diphos*)]PF$_6$ *with Diphos in Acetone*.—The complex [Mo(CO)$_3$(NO)(diphos)]PF$_6$ (0·5 g) and diphos (0·56 g) were heated under reflux in dry acetone (60 cm^3) for 5 h. The resulting orange solution was then evaporated to dryness to give a yellow-orange residue. The residue was then extracted with diethyl ether until the extracts were colourless (*ca.* 150 cm^3). Evaporation of the combined extracts to dryness, followed by chromatography of the yellow solid residue on alumina–chloroform, afforded a bright yellow band which was eluted with CHCl$_3$ to give a yellow solution. Precipitation of the yellow *solid* followed by recrystallisation from dichloromethane–hexane gave [Mo(NO)(diphos)$_2$]$_2$,CH$_2$Cl$_2$ (0·15 g). The complex is soluble in acetone, CH$_2$Cl$_2$, CHCl$_3$, and diethyl ether, giving solutions which are fairly stable in air.

The residue from the diethyl ether extraction was then dissolved in $CHCl_3$ and chromatographed on alumina–chloroform. Elution with $CHCl_3$ yielded a yellow band, which was treated as above to give a further 0·05 g of $[Mo(NO)(diphos)_2]_2,CH_2Cl_2$ {total yield 31% based on $[Mo(CO)_3(NO)(diphos)]PF_6$} and an orange band which was eluted to give an orange solution. Treatment of the orange solution with hexane and partial evaporation gave $[Mo(CO)(NO)(diphos)_2]PF_6$ (0·15 g) as tangerine crystals {yield 21% based on $[Mo(CO)_3(NO)(diphos)]PF_6$}. The complex is soluble in polar solvents such as acetone and $CHCl_3$ to give orange solutions which are only slowly decomposed by air.

Reaction of $[Mo(CO)_3(NO)(diphos)]PF_6$ *with* $CHCl_3$.—The complex $[Mo(CO)_3(NO)(diphos)]PF_6$ (1·0 g) was heated under reflux in pure $CHCl_3$ (120 cm^3) until no carbonyl bands could be observed in the i.r. spectrum of the reaction mixture (5½ h). The dark orange-brown solution was then evaporated to dryness to give a brown solid which was dissolved in $CHCl_3$ and chromatographed on alumina–chloroform. Elution with $CHCl_3$ first afforded a pale mauve band, collected as a lilac solution (A), secondly a very weak orange band (B) which was not collected, and thirdly an orange-brown band which was collected as an orange solution (C). Subsequent elution with dichloromethane–acetone (1 : 1) afforded another orange-brown band which was collected as an orange solution (D). Another orange band (E) was left on the column even after elution with acetone. Treatment of solution (A) with hexane and partial evaporation gave $[Mo(CO)(diphos)Cl_2]_n$ (0·03 g) as a mauve solid {yield 4% based on $[Mo(CO)_3(NO)(diphos)]PF_6$}. Similar treatment of solutions (C) and (D) gave 0·16 and 0·03 g of orange solid respectively. The complex $[Mo(NO)(diphos)Cl_2]_n$ is soluble in CH_2Cl_2 and moderately soluble in acetone to give air-stable lilac solutions. Complexes (C) and (D) are soluble in acetone, CH_2Cl_2, and $CHCl_3$ to give air-stable orange solutions.

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