Preparation, Properties, and Stereochemistry of Nitrosyl Derivatives of Tetracarbonyl[*o*-phenylenebis(dimethylarsine)]-molybdenum and -tungsten

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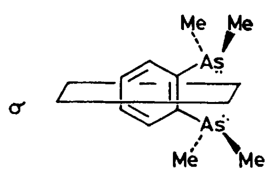
In methanol–toluene [NO][PF_6] and [M(pdma)$(CO)_4$] [pdma = *o*-phenylenebis(dimethylarsine)] give *mer*-[M(pdma)$(CO)_3$(NO)][PF_6] (1; M = Mo or W) which reacts with halide ion, [S_2CNMe_2]$^-$, and Group 5 donor ligands to yield [M(pdma)$(CO)_2$X(NO)] (2; X = Cl, Br, or I), [M(pdma)$(CO)_{2-n}$(NO)(S_2CNMe_2)] (3; M = Mo, n = 1), (4; M = W, n = 0), and [M(pdma)$(CO)_2$L(NO)][PF_6] (5; L = phosphine or phosphite) respectively. In the absence of other ligands (1) yields [M(pdma)$(CO)_2$(NO)(O_2PF_2)] (6) in refluxing acetone, but with excess of pdma a mixture of [Mo$(pdma)_2$(NO)(O_2PF_2)] (7) and [Mo$(pdma)_2$(CO)(NO)][PF_6] (8) is formed. The latter reacts with [NO][PF_6] in CH_2Cl_2 to give *cis*-[Mo$(pdma)_2(NO)_2$][PF_6]$_2$ (9). In refluxing $CHCl_3$, (1; M = Mo) gives polymeric [{Mo(pdma)Cl_2(NO)}$_n$] (10). The determination of stereochemistry by i.r. and n.m.r. spectroscopy, and the detection or isolation of reaction intermediates, has allowed comments to be made on the mechanisms of the formation and substitution reactions of (1).

We have previously described the synthesis and reactions of the cationic carbonylnitrosyl complexes [M(L–L)$(CO)_3$(NO)]$^+$ (L–L ‡ = dppe,[1] phen, or bipy [2]) and, in the absence of more definitive data, assigned structures to these species on the basis of their carbonyl i.r. spectra. Our assignments, however, differ from those of Connor *et al.*[3] for the dmpe and dcpe analogues.

N.m.r. studies on similar complexes containing the pdma ligand would assist structural assignment in two ways. First, the four methyl groups in the free ligand and in the octahedral precursor [M(pdma)$(CO)_4$] (M = Mo or W) are magnetically equivalent. Thus only one methyl resonance is observed in the ^{1}H or ^{13}C n.m.r. spectrum. However, replacement of one or more of the carbonyl ligands of the complex will destroy this equivalence giving either two or four methyl signals. Secondly, the *o*-phenylene ring protons in both the free ligand and [M(pdma)$(CO)_4$] give rise to an $[AB]_2$ pattern in the ^{1}H n.m.r. spectrum due to the presence of the mirror plane. This pattern will remain in the spectrum provided that the plane, σ, is present; in the absence of σ a complex multiplet will be observed. Similar arguments apply to the ^{13}C n.m.r. spectra. For those complexes with the mirror plane σ, three ring-carbon resonances are to be expected whereas for those without σ six such signals will arise.



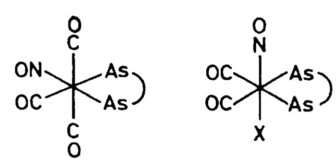
We have therefore prepared [M(pdma)$(CO)_3$(NO)]$^+$ and its derivatives and determined their stereochemistry by a combination of i.r. and n.m.r. spectroscopy. The isolation, or detection, of intermediates in the reactions, together with the structural results obtained, have allowed us to comment further [2] on the mechanism of the formation of the cation [M(L–L)$(CO)_3$(NO)]$^+$ and of its substitution reactions.

‡ Abbreviations used are: dppe, 1,2-bis(diphenylphosphino)-ethane; dmpe, 1,2-bis(dimethylphosphino)ethane; dcpe, 1,2-bis-(dicyclohexylphosphino)ethane; pdma, *o*-phenylenebis-(dimethylarsine); phen, 1,10-phenanthroline; bipy, 2,2′-bipyridyl.

Results and Discussion

The complex [M(pdma)$(CO)_4$], prepared by the method of Metzger and Feltham (M = W) [4] or by an improvement thereof (M = Mo, see Experimental section), reacts with [NO][PF_6] in methanol–toluene to give [M(pdma)$(CO)_3$(NO)][PF_6] (1; M = Mo or W) in near quantitative yields. The yellow crystalline complexes, and their derivatives described below, have been fully characterised by elemental analysis, conductance measurements, i.r. spectroscopy (Table 1), mass spectrometry where appropriate, and ^{1}H (Table 2) and ^{13}C n.m.r. spectroscopy.

Some disagreement exists concerning the structures of the cations [M(L–L)$(CO)_3$(NO)]$^+$. A comparison of the positions and relative intensities of the carbonyl absorptions of the dppe, phen, and bipy complexes led us to assign the *mer* structure to [W(phen)$(CO)_3$(NO)]$^+$ and [M(dppe)$(CO)_3$(NO)]$^+$ (M = Mo or W) and the *fac* structure to [Mo(L–L)$(CO)_3$(NO)]$^+$ (L–L = phen or bipy).[2] By contrast, Connor *et al.*[3] have assigned the *fac* geometry to [M(L–L)$(CO)_3$(NO)]$^+$ (M = Mo or W, L–L = dmpe or dcpe) even though the i.r. carbonyl spectrum is much more similar to that of *mer*-[M(dppe)$(CO)_3$(NO)]$^+$ than to that of *fac*-[Mo(L–L)$(CO)_3$(NO)]$^+$. The ^{1}H n.m.r. spectrum of (1; M = Mo or W) (Table 2) and the proton-decoupled ^{13}C n.m.r. spectrum of (1; M = W) [in CH_2Cl_2: 13.5, 15.0 (CH_3); 131.1, 131.3,



(a) (b)

132.7, 132.9, 138.3, 138.7 (C_6H_4); 196.9, 200.2 (CO) p.p.m. (downfield from $SiMe_4$)] are clearly only compatible with the *mer* structure (a) for (1), and similarities in the i.r. spectra of (1) and $[M(L-L)(CO)_3(NO)]^+$ (M = Mo or W, L–L = dppe,[1] dmpe or dcpe;[3] M = W, L–L = phen[2]) show them to be isostructural. As further confirmation of the structure of the dppe complexes the proton-decoupled ^{31}P n.m.r. spectrum (in $CDCl_3$) of $[Mo(dppe)(CO)_3(NO)][PF_6]$ shows, apart from

TABLE 1

Conductance, analytical, and i.r. data for nitrosyl complexes of *o*-phenylenebis(dimethylarsine) substituted Group 6 metal carbonyls

Complex	Λ [a] / S cm^2 mol^{-1}	Yield (%)	Analysis [b] (%) C	H	N	I.r. data (cm^{-1}) [c] $\tilde{\nu}$(CO) [d]	$\tilde{\nu}$(NO) [d]
fac-$[Mo(pdma)(CO)_3(PPh_3)]$		27	51.1 (51.1)	4.4 (4.3)		1 938, 1 836	
mer-$[Mo(pdma)(CO)_3(NO)][PF_6]$	127	85	24.4 (24.4)	2.6 (2.5)	2.2 (2.2)	2 102m, 2 029vs	1 741
mer-$[W(pdma)(CO)_3(NO)][PF_6]$	153	84	21.4 (21.4)	2.4 (2.2)	1.8 (1.9)	2 097m, 2 014vs	1 731
$[Mo(pdma)(CO)_2Cl(NO)]$		29	28.3 (28.6)	3.2 (3.2)	2.6 (2.8)	2 042, 1 972	1 642
$[Mo(pdma)(CO)_2Br(NO)]$		36	26.4 (26.3)	3.1 (2.9)	2.5 (2.6)	2 049, 1 971	1 646
$[Mo(pdma)(CO)_2I(NO)]$		44	24.4 (24.2)	2.8 (2.7)	2.4 (2.4)	2 037, 1 971	1 649
$[W(pdma)(CO)_2Cl(NO)]$		56	24.7 (24.4)	2.8 (2.7)	2.3 (2.4)	2 026, 1 950	1 628
$[W(pdma)(CO)_2Br(NO)]$		52	22.5 (22.7)	2.6 (2.5)	2.0 (2.2)	2 026, 1 950	1 628
$[W(pdma)(CO)_2I(NO)]$		57	21.2 (21.1)	2.5 (2.3)	2.0 (2.0)	2 023, 1 951	1 630
$[W(pdma)(CO)_3I(NO)]$		31	22.3 (22.0)	2.4 (2.4)	2.0 (2.0)	2 099w, 1 011s, 2 001s [e]	1 674m
$[Mo(pdma)(CO)_2(NO)(O_2PF_2)]$		41	25.4 (25.3)	2.9 (2.8)	2.3 (2.5)	2 048, 1 980	1 658
$[W(pdma)(CO)_2(NO)(O_2PF_2)]$		56	22.4 (21.9)	2.8 (2.5)	1.9 (2.1)	2 032, 1 952	1 642
$[Mo(pdma)(CO)(NO)(S_2CNMe_2)]$		40 [f]	30.0 (30.0)	4.2 (4.0)	5.0 (5.0)	1 898	1 589
$[W(pdma)(CO)_2(NO)(S_2CNMe_2)]$		27	26.6 (26.6)	3.4 (3.3)	4.2 (4.1)	2 004, 1 908	1 630
$[Mo(pdma)(CO)_2(PMe_2Ph)(NO)][PF_6]$		7	32.0 (32.0)	3.7 (3.6)	1.9 (1.9)	2 039, 1 974	1 703
$[Mo(pdma)(CO)_2\{P(OMe)_3\}(NO)][PF_6]$ [g]	140 [f]	74 [f]	24.0 (24.4) [f]	3.5 (3.4)	2.1 (1.9)	2 048, 1 981	1 671
$[Mo(pdma)(CO)_2\{P(OMe)_3\}(NO)][PF_6]$ [h]						2 046, 1 981	1 708
$[Mo(pdma)_2(CO)(NO)][PF_6]$	121	52	28.8 (29.0)	3.8 (3.7)	1.7 (1.6)	1 949	1 659
$[Mo(pdma)_2(CO)Cl(NO)]$	48	3	33.7 (33.1)	4.3 (4.2)	2.4 (2.2)	1 949	1 605
$[Mo(pdma)_2(NO)(O_2PF_2)]$		6	30.1 (30.1)	4.3 (4.0)	1.4 (1.7)		1 547 [i]
$[Mo(pdma)_2Cl(NO)_2][PF_6]$ [j]		8	34.8 (34.7)	4.2 (4.2)	3.7 (4.0)		1 773, 1 667
$[Mo(pdma)_2(NO)_2][PF_6]_2$	234	41	23.7 (23.6)	3.2 (3.2)	2.5 (2.7)		1 816, 1 733 [i]
$[\{Mo(pdma)Cl_2(NO)\}_n]$		16	24.5 (24.9)	3.4 (3.3)	2.8 (2.9)		1 613 [i]

[a] 10^{-4} mol dm^{-3} in acetone. [b] Calculated values are given in parentheses. [c] In CH_2Cl_2 unless otherwise stated. [d] All the absorptions are strong unless otherwise stated (w = weak, s = strong, v = very, and m = medium). [e] In hexane. [f] For a mixture of isomers. [g] Isomer (A). [h] Isomer (B). [i] In Nujol. [j] Isolated as a CH_2Cl_2 solvate.

TABLE 2

Hydrogen-1 n.m.r. data for nitrosyl complexes of *o*-phenylenebis(dimethylarsine) substituted Group 6 metal carbonyls

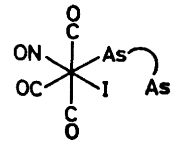
Complex	pdma Resonances (τ) [a] Ring protons [b]	Methyl protons	Other protons
$[Mo(pdma)(CO)_4]$	2.21 (4, $[AB]_2$)	8.27 (12, s)	
$[W(pdma)(CO)_4]$	2.20 (4, $[AB]_2$)	8.17 (12, s)	
fac-$[Mo(pdma)(CO)_3(PPh_3)]$ [c]	2.23 (4, $[AB]_2$)	8.41 (6, s), 9.04 (6, s)	2.80 (15, m, PPh_3)
mer-$[Mo(pdma)(CO)_3(NO)][PF_6]$	2.12 (4, m)	7.90 (6, s), 8.10 (6, s)	
mer-$[W(pdma)(CO)_3(NO)][PF_6]$	2.10 (4, m)	7.79 (6, s), 8.01 (6, s)	
$[Mo(pdma)(CO)_2Cl(NO)]$	2.16 (4, $[AB]_2$)	8.18 (6, s), 8.25 (6, s)	
$[Mo(pdma)(CO)_2Br(NO)]$	2.20 (4, $[AB]_2$)	8.14 (6, s), 8.30 (6, s)	
$[Mo(pdma)(CO)_2I(NO)]$	2.20 (4, $[AB]_2$)	8.01 (6, s), 8.30 (6, s)	
$[W(pdma)(CO)_2Cl(NO)]$	2.14 (4, $[AB]_2$)	8.13 (6, s), 8.20 (6, s)	
$[W(pdma)(CO)_2Br(NO)]$	2.12 (4, $[AB]_2$)	8.02 (6, s), 8.18 (6, s)	
$[W(pdma)(CO)_2I(NO)]$	2.11 (4, $[AB]_2$)	7.88 (6, s), 8.19 (6, s)	
$[W(pdma)(CO)_3I(NO)]$	2.22 (4, m)	7.84 (6, s), 8.69 (6, s)	
$[Mo(pdma)(CO)_2(NO)(O_2PF_2)]$	2.14 (4, $[AB]_2$)	8.16 (6, s), 8.21 (6, s)	
$[W(pdma)(CO)_2(NO)(O_2PF_2)]$	2.11 (4, $[AB]_2$)	8.08 (6, s), 8.16 (6, s)	
$[Mo(pdma)(CO)(NO)(S_2CNMe_2)]$ [d]	2.27 (4, m)	8.23 (3, s), 8.35 (3, s), 8.45 (3, s), 8.71 (3, s)	6.59 (3, s, S_2CNMe_2), 6.69 (3, s, S_2CNMe_2)
$[Mo(pdma)(CO)(NO)(S_2CNMe_2)]$ [e]	2.27 (4, m)	8.26 (3, s), 8.35 (6, s), 8.55 (3, s)	6.61 (3, s, S_2CNMe_2), 6.81 (3, s, S_2CNMe_2)
$[Mo(pdma)(CO)_2\{P(OMe)_3\}(NO)][PF_6]$ [d]	2.14 (4, m)	7.99 (6, s), 8.18 (6, s)	6.30 [9, d, ^3J(PH) 9 Hz, $P(OMe)_3$]
$[Mo(pdma)(CO)_2\{P(OMe)_3\}(NO)][PF_6]$ [e]	2.22 (4, m)	7.99 (3, s), 8.07 (3, s), 8.21 (3, s), 8.28 (3, s)	6.21 [9, d, ^3J(PH) 12 Hz, $P(OMe)_3$]
$[Mo(pdma)_2(CO)(NO)][PF_6]$	2.24 (8, m)	7.96 (6, s), 8.01 (3, s), 8.07 (3, s), 8.29 (3, s), 8.43 (3, s), 8.61 (3, s), 8.92 (3, s)	
$[Mo(pdma)_2(NO)(O_2PF_2)]$ [f]	2.19 (8, $[AB]_2$)	7.93 (12, s), 8.00 (12, s)	
$[Mo(pdma)_2(NO)_2][PF_6]_2$	2.22 (8, m)	8.54 (6, s), 8.14 (6, s), 7.76 (6, s), 7.59 (6, s)	

[a] In CD_3NO_2 unless otherwise stated. Intensity and multiplicity in parentheses (s = singlet, d = doublet, m = multiplet). [b] The ring-proton resonance appears either as a multiplet or as an $[AB]_2$ pattern, see introduction. [c] A small amount of the *mer* isomer is also present (see text). [d] Isomer (A). [e] Isomer (B). [f] In CD_2Cl_2.

a septet at −144.3 p.p.m. (relative to H_3PO_4) due to the $[PF_6]^-$ anion [^1J(PF) 711.2 Hz], two doublets at 45.4 and 32.6 p.p.m. [J(PP) 8.5 Hz], as expected for the *mer* isomer; the *fac* isomer would exhibit only one singlet.

The substitution reactions of (1) are generally similar to those of $[M(L{-}L)(CO)_3(NO)]^+$ (L–L = dppe,[1] phen, or bipy[2]) although significant differences occur. Addition of halide ion to (1) in $CHCl_3$ affords yellow solutions from which $[M(pdma)(CO)_2X(NO)]$ (2; M = Mo or W; X = Cl, Br, or I) may be isolated as yellow crystals (Table 1). For each complex the mass spectrum shows a parent ion followed by the sequential loss of two carbonyls and four methyl groups. The observation of two carbonyl bands of equal intensity in the i.r. spectrum, of the ^1H n.m.r. spectrum (Table 2), and of the proton-decoupled ^{13}C n.m.r. spectrum of (2; M = Mo, X = I) [in $(CD_3)_2CO$: 12.1, 12.7 (CH_3); 131.7, 132.0, 140.8 (C_6H_4) p.p.m. downfield from $SiMe_4$] establishes structure (b) for (2). It is likely that this structure is adopted by all of the analogous complexes $[M(L{-}L)(CO)_2X(NO)]$.[1,2] Inspection of the i.r. spectra of these species shows that the position of $\tilde{\nu}$(NO) is almost invariant, as might be expected if the nitrosyl group is *trans* to X, whereas $\tilde{\nu}$(CO) changes markedly with the donor–acceptor properties of L–L [$\tilde{\nu}$(CO) decreases in the order dppe > pdma > phen > bipy]. In addition, the proton-decoupled ^{31}P n.m.r. spectrum of $[W(dppe)(CO)_2Cl(NO)]$ [in $(CD_3)_2CO$: 33.0 p.p.m. (relative to H_3PO_4), ^{183}W satellites at 30.0 and 36.0 p.p.m., $^1J(^{183}W{-}P)$ 246.1 Hz] is as expected for a complex isostructural with (2).

The formation of (2) from (1) results in nitrosyl group migration from a *trans* to a *cis* position relative to arsenic. The isolation and full characterisation of an intermediate in the reaction between (1; M = W) and $[PMePh_3]I$ has allowed a mechanism to be deduced for this migration. Although no apparent change in the carbonyl i.r. spectrum occurs during the room-temperature reaction between (1) and $[PMePh_3]I$, the nitrosyl absorption of (1), at 1 731 cm^{-1}, is almost immediately replaced by another at 1 661 cm^{-1}. If the reaction is terminated after the band at 1 731 cm^{-1} has disappeared from the spectrum (*ca.* 15 min) the tricarbonyl $[W(pdma)(CO)_3I(NO)]$ may be isolated and fully characterised; its carbonyl spectrum in CH_2Cl_2 is almost identical to that of (1) suggesting that the *mer* configuration is retained. The ^1H n.m.r. spectrum (Table 2) shows one of the two methyl resonances to be at unusually high field clearly indicating that one $AsMe_2$ group of the ligand is unco-ordinated; a seven-co-ordinate structure containing a bent nitrosyl is therefore not adopted. In that the nitrosyl group, as a three-electron donor, is a better π acceptor than CO one would expect the arsenic atom *trans* to NO to be preferentially labilised and therefore that $[W(pdma)(CO)_3I(NO)]$ has structure (c). Decarbonylation and co-ordination of the free arsenic atom would result in (2). It is apparent, therefore, that the geometry of the product of the substitution reaction of (1) with halide ion is determined by the *trans*-labilising effect of the nitrosyl ligand. It should be noted here that this product is kinetically, but not necessarily thermodynamically, favoured (see below). Previous studies[1] of the reaction between $[W(dppe)(CO)_3(NO)]^+$ and iodide ion did not reveal the presence of a tricarbonyl

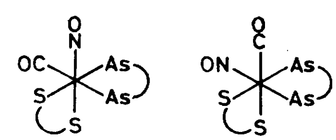


(c)

intermediate. A reinvestigation has shown, however, that $[W(dppe)(CO)_3I(NO)]$ is formed [$\tilde{\nu}$(CO) = 2 102m and 2 025vs cm^{-1}; $\tilde{\nu}$(NO) = 1 665s cm^{-1} (in $CHCl_3$)] {*cf.* $\tilde{\nu}$(NO) = 1 725 cm^{-1} for $[W(dppe)(CO)_3(NO)][PF_6]$} but cannot be isolated.

As in the case of $[W(phen)(CO)_3(NO)][PF_6]$,[2] refluxing (1) in acetone gave the difluorophosphato-complex $[M(pdma)(CO)_2(NO)(O_2PF_2)]$ (6) [M = Mo: $\tilde{\nu}_{sym}$(PO) = 1 322 cm^{-1}, $\tilde{\nu}_{asym}$(PO) = 1 156 cm^{-1}, $\tilde{\nu}$(PF) = 883 and 856 cm^{-1}. M = W: $\tilde{\nu}_{sym}$(PO) = 1 323 cm^{-1}, $\tilde{\nu}_{asym}$(PO) = 1 155 cm^{-1}, $\tilde{\nu}$(PF) = 887 and 863 cm^{-1} (Nujol)], *via* hydrolysis of the $[PF_6]^-$ anion. Although the acetone used was distilled, and dried over $Mg[SO_4]$, sufficient water is presumably present for hydrolysis. The ^1H n.m.r. spectrum of (6) (Table 2) shows it to be isostructural with (2).

The reaction of (1; M = Mo) with $Na[S_2CNMe_2]\cdot 2H_2O$ in acetone rapidly affords $[Mo(pdma)(CO)_2(NO)(S_2CNMe_2)]$ [$\tilde{\nu}$(CO) = 2 001 and 1 911 cm^{-1}] which could not be isolated due to slow decarbonylation and formation of orange-red $[Mo(pdma)(CO)(NO)(S_2CNMe_2)]$ (3). The i.r. spectrum of (3) shows only one carbonyl band and one nitrosyl band. The ^1H n.m.r. spectrum, however, shows the presence of two isomers, in *ca.* 5 : 2 ratio, with structures (d) and (e). (The *trans*-carbonyl-



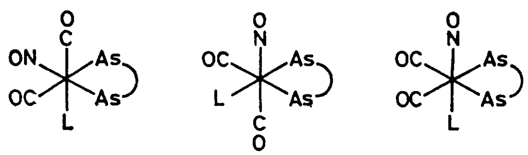
(d) (e)

nitrosyl isomer would give rise to only one sulphur-ligand methyl absorption and to two for the arsenic ligand.)

Although the dicarbonyl intermediate could not be isolated for molybdenum, (1; M = W) and $[S_2CNMe_2]^-$ gave $[W(pdma)(CO)_2(NO)(S_2CNMe_2)]$ (4) which did not decarbonylate further. Unfortunately the structure of this species could not be deduced from the poorly resolved ^1H n.m.r. spectrum.

Complex (1) reacts with phosphines or phosphites in acetone to give solutions containing the monosubstituted cations *cis*-$[M(pdma)(CO)_2L(NO)]^+$ [5; M = Mo or W, L = $PMePh_2$, PPh_3, or $P(OMe)_3$]. Although i.r. and microanalytical data for (5; M = Mo, L = $PMePh_2$)

were obtained (Table 1), quantities sufficient for ^{1}H n.m.r. studies were isolated only in the case of [5; M = Mo, L = $P(OMe)_3$]. The i.r. spectrum of [Mo(pdma)$(CO)_2\{P(OMe)_3\}(NO)$][PF_6] showed the presence of two *cis*-dicarbonyl isomers and the ^{1}H n.m.r. spectrum showed a total of six pdma methyl resonances. After storing the n.m.r. sample under nitrogen for several days two of the pdma methyl signals had disappeared and the remaining four had intensified; at this point the i.r. spectrum showed the presence of only one dicarbonyl complex. The spectral changes suggest that isomerisation occurs and that the thermodynamically more-stable isomer (B), containing four magnetically inequivalent pdma methyl groups, has either structure (f) or (g). Clearly the less-stable isomer (A), showing only two pdma methyl resonances in the ^{1}H n.m.r. spectrum, has structure (h), analogous to that of (2). Since (A) and (B) have very similar carbonyl spectra (Table 1) it is likely that the carbonyls are *trans* to similar ligands in each isomer; structure (f) is therefore the more likely for (B). In addition, if (f) is the adopted geometry, the necessity for the *trans* disposition of CO

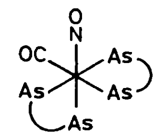


(f) (g) (h)

and NO, both good π acceptors, is avoided. The reaction of [Mo(pdma)$(CO)_4$] with molten PPh_3 [5] gave predominantly *fac*-[Mo(pdma)$(CO)_3(PPh_3)$] although the ^{1}H n.m.r. spectrum revealed the presence of small amounts of the *mer* isomer. Reaction of the isomeric mixture with [NO][PF_6] in CH_2Cl_2 gave, on work-up, a yellow oil which ^{1}H n.m.r. spectroscopy suggested to contain only isomer (A) of (5; M = Mo, L = PPh_3). The product could not, however, be fully purified for characterisation. The reaction of (2; M = Mo, X = I) and Ag[BF_4] in CH_2Cl_2 in the presence of $P(OMe)_3$ gave a mixture of approximately equal amounts of [5; M = Mo, L = $P(OMe)_3$] as isomers (A) and (B).

The formation of isomers of [M(L–L)$(CO)_2$L(NO)]$^+$ has been observed in the reaction between *fac*-[Mo(L–L)$(CO)_3$(NO)]$^+$ (L–L = phen or bipy) [2] and PPh_3 but lack of structural information has prevented a complete study of the isomerisation process. The ^{13}C n.m.r. spectrum of [W(phen)$(CO)_2(PPh_3)$(NO)][PF_6], prepared from *mer*-[W(phen)$(CO)_3$(NO)][PF_6] and PPh_3,[2] is complex and does not allow unequivocal assignment of structure. Its complexity, however, rules out a structure similar to (h).

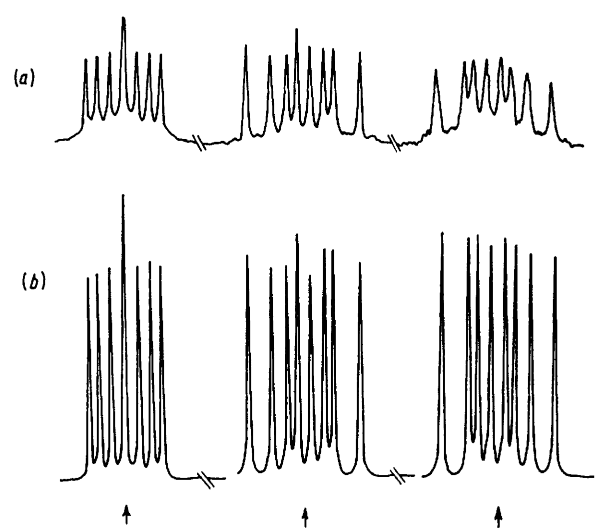
The reaction of (1; M = Mo) with pdma in refluxing acetone initially affords a *cis*-dicarbonyl the i.r. spectrum of which [$\tilde{\nu}$(CO) = 2 039 and 1 970 cm^{-1}] is similar to those of (5) and suggests formation of [Mo$(pdma)_2(CO)_2$(NO)][PF_6] with one unidentate pdma ligand. Further reaction yields small amounts of a yellow precipitate of [Mo$(pdma)_2$(NO)(O_2PF_2)] (7), and a red solution from which [Mo$(pdma)_2$(CO)(NO)][PF_6] (8) can be isolated as an orange-red solid. The ^{1}H n.m.r. spectrum of (7) clearly reveals the *trans* arrangement of the NO and O_2PF_2 ligands; the latter again originates from the [PF_6]$^-$ anion. By contrast the two pdma ligands of (8) are not mutually *trans*. The ^{1}H n.m.r. spectrum in this case shows seven methyl resonances (one twice the intensity of the remaining six) and, therefore, that the structure of (8) is (i).



(i)

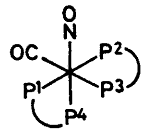
The formation of (7) does not involve (8) as an intermediate; heating the latter in refluxing acetone for 7 d does not give the former. Similarly (7) does not arise by the reaction between pdma and (6). It is likely, therefore, that (7) and (8) are formed *via* [Mo$(pdma)_2(CO)_2$(NO)]$^+$ by competing reactions.

The reaction between *mer*-[Mo(dppe)$(CO)_3$(NO)][PF_6] and dppe differs from that between (1; M = Mo) and pdma in that [{Mo$(dppe)_2$(NO)}$_2$] is formed as the second product; [Mo$(dppe)_2$(CO)(NO)][PF_6], however, is isostructural with (8). For a *trans*-carbonylnitrosyl structure only one singlet would be expected in the proton-decoupled ^{31}P n.m.r. spectrum of the dppe complex (apart from the septet due to the [PF_6]$^-$ anion). The observed and computer-simulated spectra of [Mo$(dppe)_2$(CO)(NO)][PF_6] are shown in the Figure, and the spectral data are given in Table 3. The numbering of the phosphorus atoms is shown in (j). It is noticeable that the peaks due to P^4, *trans* to NO, are broadened, corroborating the assignment for that particular atom.



Observed (*a*) and computer-simulated (*b*) proton-decoupled ^{31}P n.m.r. spectrum of [Mo$(dppe)_2$(CO)(NO)]$^+$

The reaction of (8) with chloride ion did not result in carbonyl displacement but gave the yellow complex



(j)

$[Mo(pdma)_2(CO)Cl(NO)]$. In solution it exhibits two nitrosyl bands, one corresponding to that of (8), suggesting that ionisation occurs as in (1), and in acetone

$$[Mo(pdma)_2(CO)Cl(NO)] \rightleftharpoons [Mo(pdma)_2(CO)(NO)]^+ + Cl^- \quad (1)$$

$[Mo(pdma)_2(CO)Cl(NO)]$ is partially conducting (Table 1). If the complex is chromatographed on CH_2Cl_2–alumina

TABLE 3

Proton-decoupled ^{31}P n.m.r. spectrum [a] of $[Mo(dppe)_2(CO)(NO)]^+$

Chemical shift [b]		Coupling constant (Hz)	
		$J(P^1P^2)$	+96.9
P^1	14.9	$J(P^1P^3)$	−22.3
		$J(P^1P^4)$	−4.2
P^2	15.7	$J(P^2P^3)$	−4.2
		$J(P^2P^4)$	−22.6
P^3	2.1	$J(P^3P^4)$	−20.7
P^4	−13.2		

[a] In $(CD_3)_2CO$. [b] In p.p.m. downfield from H_3PO_4. Numbering scheme as in (j).

only an orange band is eluted which has an i.r. nitrosyl spectrum identical to that of (8). On standing the eluate slowly becomes yellow and the nitrosyl band of $[Mo(pdma)_2(CO)Cl(NO)]$ reappears. The complex $[Mo(dppe)_2(CO)Cl(NO)]$ shows no similar tendency to ionise in solution.

Substitution of the carbonyl group of (8) can be effected by reaction with $[NO]^+$ in CH_2Cl_2. The unusual, deep green, dicationic complex *cis*-$[Mo(pdma)_2(NO)_2][PF_6]_2$ which results shows two nitrosyl-stretching absorptions in the i.r. spectrum, and four methyl resonances in the ^1H n.m.r. spectrum. It reacts with chloride ion to give $[Mo(pdma)_2Cl(NO)_2][PF_6]$, which may be isolated as a CH_2Cl_2 solvate and which probably contains one unidentate pdma ligand.

Whereas (6) results from the reaction of (1) in boiling acetone, (1; M = Mo) gives the pink polymer $[\{Mo(pdma)Cl_2(NO)\}_n]$ (10) in boiling $CHCl_3$. Although its structure could not be determined by n.m.r. spectroscopy it is analogous to the previously described dppe complex.

Conclusion.—The study of the substitution reactions of (1) and its analogues has revealed no evidence for isolable intermediates containing 'bent' nitrosyl ligands. In general the geometries of the substitution products are governed by the relative *trans*-directing abilities of the ligands present. Thus, initial substitution occurs *trans* to NO as the strongest π acceptor. In certain cases the initially formed, kinetically stable isomer may be converted into thermodynamically more favourable isomers.

Although nitrosyl bending and straightening may not be implicated in the substitution reactions studied, the formation of (1) may involve this phenomenon. Substitution of $[M(L-L)(CO)_4]$ by a Lewis base L′ to give $[M(L-L)L'(CO)_3]$ is normally [6] slow and results in formation of the *fac* isomer. The rapidity of the reaction between $[NO]^+$ and $[M(L-L)(CO)_4]$ and the formation of *mer*-$[M(L-L)(CO)_3(NO)]^+$ may depend on the initial production of a seven-co-ordinate Lewis acid-base adduct $[M(L-L)(CO)_4(NO)]^+$ in which the 'bent' formally $[NO]^-$ group acts as a one-electron donor. Subsequent straightening of the M–N–O linkage and decarbonylation to give (1) occurs. The approach of $[NO]^+$ to the least-hindered side of the tetracarbonyl might be expected to favour final formation of the *mer* isomer.

EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated the solid complexes are moderately stable in air and dissolve in polar solvents such as CH_2Cl_2 or acetone to give solutions which slowly decompose in air. *o*-Phenylenebis(dimethylarsine) [7] and $[W(pdma)(CO)_4]$ [4] were prepared by published procedures, and $[NO][PF_6]$ was purchased from Ozark Mahoning Co., Tulsa, Oklahoma. All the solvents were dried by standard methods and deoxygenated before use.

Infrared spectra were recorded on Perkin-Elmer PE 257 or PE 457 spectrophotometers and calibrated against the absorption of polystyrene at 1 601 cm^{-1}. Hydrogen-1 n.m.r. spectra were recorded on Varian Associates HA 100 or T 60, or JEOL PS 100 or PFT 100 instruments, and ^{13}C and ^{31}P n.m.r. spectra on a JEOL PFT 100 spectrometer; ^1H and ^{13}C n.m.r. spectra were calibrated using $SiMe_4$ as an internal reference, ^{31}P n.m.r. spectra against the resonance of H_3PO_4. Mass spectra were obtained on an A.E.I. MS9 instrument. Microanalyses were by the Microanalytical Service of the School of Chemistry, University of Bristol. Conductivity measurements were made using a Cambridge Instruments Co. Ltd. conductivity bridge.

Tetracarbonyl[o-*phenylenebis*(*dimethylarsine*)]*molybdenum*, $[Mo(pdma)(CO)_4]$.—Hexacarbonylmolybdenum (4.6 g, 17.4 mmol) and pdma (4.0 cm^3, 19.6 mmol) were heated under reflux in n-heptane (100 cm^3) until the carbonyl absorptions of $[Mo(CO)_6]$ were absent from the i.r. spectrum (*ca*. 24 h). The yellow solution was then evaporated to dryness. Column chromatography of the residue on alumina–CH_2Cl_2 afforded a yellow band which on elution with CH_2Cl_2 gave a yellow solution. Addition of n-hexane followed by partial evaporation gave pale yellow crystals of $[Mo(pdma)(CO)_4]$, yield 6.2 g {72% based on $[Mo(CO)_6]$}.

Tricarbonyl[o-*phenylenebis*(*dimethylarsine*)](*triphenylphosphine*)*molybdenum*, $[Mo(pdma)(CO)_3(PPh_3)]$.—The complex $[Mo(pdma)(CO)_4]$ (0.30 g, 0.61 mmol) and PPh_3 (0.20 g, 0.76 mmol) were allowed to react in the molten state (*ca*. 160—210 °C) for 320 min. On cooling, the resulting solid was chromatographed on an alumina–hexane (90%)–CH_2Cl_2 (10%) column. The yellow band was eluted with a hexane–CH_2Cl_2 (9 : 1) to give a yellow solution which on cooling to 0 °C gave pale yellow $[Mo(pdma)(CO)_3(PPh_3)]$ as an inseparable mixture of isomers, yield 0.12 g {27% based on $[Mo(pdma)(CO)_4]$}.

Tricarbonylnitrosyl[o-*phenylenebis*(*dimethylarsine*)]-*molybdenum Hexafluorophosphate*, [Mo(pdma)$(CO)_3$(NO)]-$[PF_6]$.—To a vigorously stirred solution of [Mo(pdma)-$(CO)_4$] (1.7 g, 3.4 mmol) in a mixture of toluene (20 cm^3) and methanol (4 cm^3) was added an excess of solid [NO]$[PF_6]$ (0.90 g, 5.1 mmol). Carbon monoxide was evolved and a yellow precipitate formed. Addition of diethyl ether (80 cm^3) completed precipitation of the product, yield 1.9 g {85% based on [Mo(pdma)$(CO)_4$]}. The complex may be recrystallised from CH_2Cl_2–n-hexane or acetone–diethyl ether. The yellow complex [W(pdma)$(CO)_3$(NO)]$[PF_6]$ may be similarly prepared in 84% yield.

Dicarbonylchloronitrosyl[o-*phenylenebis*(*dimethylarsine*)]-*molybdenum*, [Mo(pdma)$(CO)_2$Cl(NO)].—To [Mo(pdma)-$(CO)_3$(NO)]$[PF_6]$ (0.40 g, 0.62 mmol) in $CHCl_3$ (75 cm^3) was added $[AsPh_4]$Cl (0.26 g, 0.62 mmol). After stirring until only the carbonyl absorptions of the product were present in the i.r. spectrum (*ca.* 160 min) the solution was evaporated to dryness. Column chromatography of the residue on alumina–CH_2Cl_2 afforded a yellow band which on elution with CH_2Cl_2 gave a yellow solution. Addition of n-hexane followed by partial evaporation of the solvent gave pale yellow crystals of [Mo(pdma)$(CO)_2$Cl(NO)], yield 0.09 g (29%).

The *complexes* [M(pdma)$(CO)_2$X(NO)] (M = Mo, X = Br or I; M = W, X = Cl) may be prepared similarly; [W(pdma)$(CO)_2$X(NO)] (X = Br or I) may be isolated in the same manner after refluxing the reaction mixture for *ca.* 40 min.

Tricarbonyliodonitrosyl[o-*phenylenebis*(*dimethylarsine*)]-*tungsten*, [W(pdma)$(CO)_3$I(NO)].—To a stirred solution of [W(pdma)$(CO)_3$(NO)]$[PF_6]$ (0.40 g, 0.55 mmol) in $CHCl_3$ (50 cm^3) was added $[PMePh_3]$I (0.24 g, 0.59 mmol). After the nitrosyl absorption of $[W(pdma)(CO)_3(NO)]^+$ had disappeared from the i.r. spectrum (*ca.* 15 min) n-hexane was added to the yellow solution. The solvent was then evaporated until precipitation of $[PMePh_3][PF_6]$ was complete. After filtration the solution was evaporated to dryness to give pale yellow [W(pdma)$(CO)_3$I(NO)], yield 0.12 g {31% based on [W(pdma)$(CO)_3$(NO)]$[PF_6]$}. The *complex* is soluble in all common organic solvents to give yellow solutions which very slowly lose CO at room temperature to give [W(pdma)$(CO)_2$I(NO)].

Dicarbonyl(*difluorophosphato*)*nitrosyl*[o-*phenylenebis*-(*dimethylarsine*)]*molybdenum*, [Mo(pdma)$(CO)_2$(NO)(O_2-PF_2)].—The complex [Mo(pdma)$(CO)_3$(NO)]$[PF_6]$ (0.41 g, 0.64 mmol) was heated under reflux in acetone (40 cm^3) until only two carbonyl absorptions were present in the i.r. spectrum (*ca.* 40 min). The yellow solution was then evaporated to dryness and the residue chromatographed on a Florisil–acetone column. Elution of the yellow band with acetone gave a yellow solution which, on addition of n-hexane and partial evaporation, gave pale yellow crystals of [Mo(pdma)$(CO)_2$(NO)(O_2PF_2)], yield 0.15 g (41%). The *complex* [W(pdma)$(CO)_2$(NO)(O_2PF_2)] may be prepared in a similar manner, and purified by recrystallisation from CH_2Cl_2–hexane.

Carbonyl(*dimethyldithiocarbamato*)*nitrosyl*[o-*phenylene*-*bis*(*dimethylarsine*)]*molybdenum*, [Mo(pdma)(CO)(NO)-(S_2CNMe_2)].—The complex [Mo(pdma)$(CO)_3$(NO)]$[PF_6]$ (0.30 g, 0.47 mmol) and $Na[S_2CNMe_2]\cdot 2H_2O$ (84 mg, 0.47 mmol) were stirred in acetone (25 cm^3) until only one carbonyl absorption was present in the i.r. spectrum (*ca.* 150 min). The orange-red solution was then evaporated to dryness and the residue recrystallised from CH_2Cl_2–n-hexane to give orange-red [Mo(pdma)(CO)(NO)(S_2CNMe_2)], yield 0.11 g (40%).

Dicarbonyl(*dimethyldithiocarbamato*)*nitrosyl*[o-*phenylenebis*(*dimethylarsine*)]*tungsten*, [W(pdma)$(CO)_2$(NO)(S_2-$CNMe_2$)].—The complex [Mo(pdma)$(CO)_3$(NO)]$[PF_6]$ (0.40 g, 0.55 mmol) and $Na[S_2CNMe_2]\cdot 2H_2O$ (98 mg, 0.55 mmol) were stirred in acetone (10 cm^3) for 3 min. The orange-red solution was evaporated to dryness and the residue chromatographed on a Florisil–CH_2Cl_2 column. Elution of the orange-red band with CH_2Cl_2 gave an orange-red solution which was partially evaporated, in the presence of n-hexane, to give orange-red [W(pdma)$(CO)_2$(NO)(S_2CNMe_2)], yield 0.10 g (27%).

Dicarbonylnitrosyl[o-*phenylenebis*(*dimethylarsine*)]-(*trimethyl phosphite*)*molybdenum Hexafluorophosphate*, [Mo-(pdma)$(CO)_2${$P(OMe)_3$}(NO)]$[PF_6]$.—The complex [Mo-(pdma)$(CO)_3$(NO)]$[PF_6]$ (0.37 g, 0.58 mmol) and $P(OMe)_3$ (0.6 cm^3, 5.1 mmol) were stirred in acetone (45 cm^3) until the carbonyl absorptions of the starting material were absent from the i.r. spectrum. The yellow solution was then evaporated to dryness and the residue washed liberally with diethyl ether. The residue was then dissolved in the minimum volume of CH_2Cl_2 (*ca.* 3 cm^3) and added to diethyl ether (80 cm^3). Storage of the mixture at 0 °C gave yellow crystals of [Mo(pdma)$(CO)_2${$P(OMe)_3$}(NO)]$[PF_6]$, yield 0.32 g (74%).

Reaction of [Mo(pdma)$(CO)_3$(NO)]$[PF_6]$ *with pdma*.—The complex [Mo(pdma)$(CO)_3$(NO)]$[PF_6]$ (2.0 g, 3.1 mmol) and pdma (2.4 g, 4.9 mmol) were heated under reflux in acetone (100 cm^3) until the carbonyl bands of the starting material were absent from the i.r. spectrum (*ca.* 7 d). The yellow precipitate which had formed was filtered off and the filtrate was evaporated to dryness to give an orange residue. Soxhlet extraction of the yellow precipitate in acetone for 1 d gave the pale yellow *complex* [Mo$(pdma)_2$(NO)(O_2PF_2)], yield 0.16 g {6% based on [Mo(pdma)$(CO)_3$(NO)]$[PF_6]$}. The complex is rapidly decomposed in air and is only slightly soluble in acetone or CH_2Cl_2.

The orange residue was dissolved in CH_2Cl_2 (5 cm^3) and added to diethyl ether (80 cm^3). Storage at 0 °C gave orange crystals of [Mo$(pdma)_2$(CO)(NO)]$[PF_6]$, yield 1.4 g {52% based on [Mo(pdma)$(CO)_3$(NO)]$[PF_6]$}.

Carbonylchloronitrosylbis[o-*phenylenebis*(*dimethylarsine*)]-*molybdenum*, [Mo$(pdma)_2$(CO)Cl(NO)].—The complex [Mo-$(pdma)_2$(CO)(NO)]$[PF_6]$ (0.34 g, 0.39 mmol) and $[AsPh_4]$Cl (0.50 g, 1.2 mmol) were stirred in $CHCl_3$ (55 cm^3) for 30 min. The resulting solution was evaporated to dryness and the residue dissolved in CH_2Cl_2 (5 cm^3). Addition of n-hexane (70 cm^3), filtration, and evaporation to *ca.* 10 cm^3 afforded pale yellow crystals of [Mo$(pdma)_2$(CO)Cl(NO)], yield 13 mg {3% based on [Mo$(pdma)_2$(CO)(NO)]$[PF_6]$}.

Dinitrosylbis[o-*phenylenebis*(*dimethylarsine*)]*molybdenum Bis*(*hexafluorophosphate*), [Mo$(pdma)_2(NO)_2$]$[PF_6]_2$.—The complex [Mo$(pdma)_2$(CO)(NO)]$[PF_6]$ (0.50 g, 0.49 mmol) and solid [NO]$[PF_6]$ (0.11 g, 0.63 mmol) were stirred in CH_2Cl_2 (50 cm^3) for 80 min. The resulting dark green precipitate was dissolved in acetone and added to diethyl ether (80 cm^3). Storage at 0 °C gave dark green crystals of [Mo$(pdma)_2(NO)_2$]$[PF_6]_2$, yield 0.22 g {41% based on [Mo$(pdma)_2$(CO)(NO)]$[PF_6]$}. The *complex* is moderately stable in air and dissolves in acetone or MeCN to give dark green solutions which slowly decompose in air.

Chlorodinitrosylbis[o-*phenylenebis*(*dimethylarsine*)]-*molybdenum Hexafluorophosphate–Dichloromethane* (1/1), [Mo-$(pdma)_2Cl(NO)_2$]$[PF_6]\cdot CH_2Cl_2$.—The complex [Mo$(pdma)_2$-

$(NO)_2][PF_6]_2$ (0.36 g, 0.35 mmol) and $[AsPh_4]Cl$ (0.17 g, 0.41 mmol) were stirred in acetone (40 cm^3) until the nitrosyl absorptions of the starting material were absent from the i.r. spectrum (*ca.* 40 min). The resulting solution was evaporated to dryness and the residue, dissolved in CH_2Cl_2 (5 cm^3), was added to diethyl ether (50 cm^3). After filtration the mixture was evaporated to dryness and recrystallised twice from CH_2Cl_2–n-pentane at 0 °C to yield green-yellow $[Mo(pdma)_2Cl(NO)_2][PF_6]\cdot CH_2Cl_2$, yield 27 mg {8% based on $[Mo(pdma)_2(NO)_2][PF_6]_2$}. Solutions of the *complex* in polar solvents such as CH_2Cl_2 or acetone rapidly decompose in air.

Dichloronitrosyl[o-*phenylenebis*(*dimethylarsine*)]*molybdenum*, $[\{Mo(pdma)Cl_2(NO)\}_n]$.—The complex $[Mo(pdma)(CO)_3(NO)][PF_6]$ (1.0 g, 1.6 mmol) was heated under reflux in $CHCl_3$ (80 cm^3) until no carbonyl absorptions were present in the i.r. spectrum (*ca.* 7d). The pink precipitate was removed and Soxhlet-extracted with $CHCl_3$ for 5 h to give a red solution. Partial evaporation gave pink $[\{Mo(pdma)Cl_2(NO)\}_n]$, yield 0.12 g (16%). The *complex* is only sparingly soluble in polar solvents such as $CHCl_3$, CH_2Cl_2, or acetone.

We thank Dr. M. Murray for assistance with the interpretation of ^{31}P n.m.r. spectra, and C. G. thanks the S.R.C. for a studentship.

[8/932 *Received*, 18*th May*, 1978]

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