Reaction of *cis*-Bis[1,2-bis(dimethylphosphino)ethane]dicarbonyl-chromium and -molybdenum Complexes with Silver(I) Salts. Reduction of Nitrite Ion to Dinitrogen Oxide †

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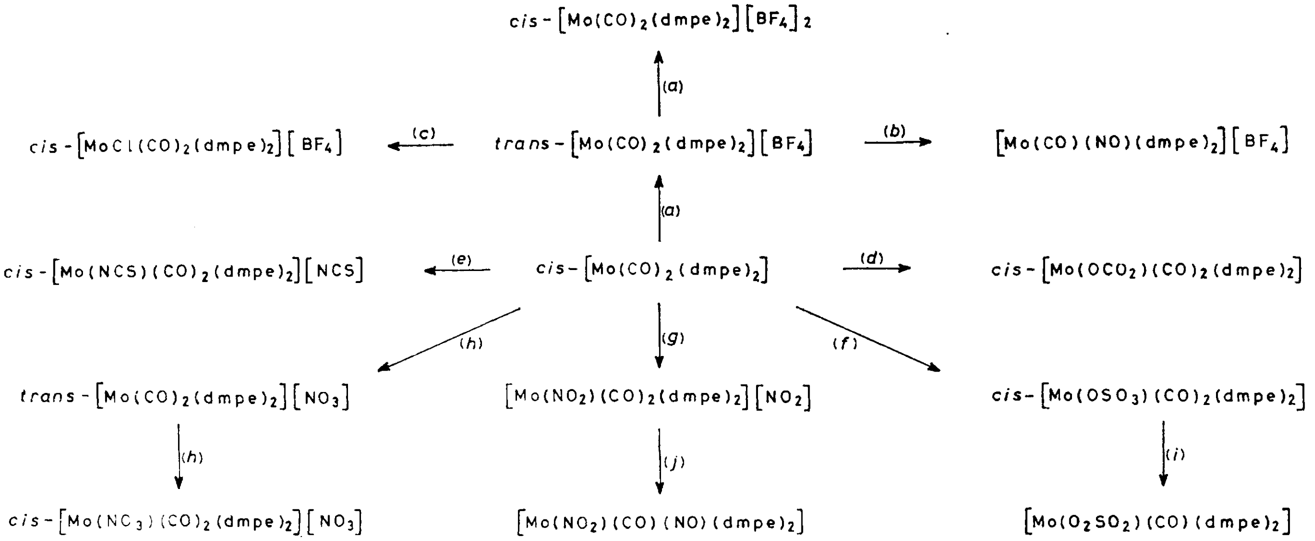
The complexes *cis*-$[M(CO)_2(dmpe)_2]$ (M = Cr or Mo; dmpe is $Me_2PCH_2CH_2PMe_2$) undergo one-electron oxidation by $Ag[BF_4]$ in solution to give paramagnetic complexes *trans*-$[M(CO)_2(dmpe)_2][BF_4]$. Oxidation of *cis*-$[Mo(CO)_2(dmpe)_2]$ with silver(I) salts of co-ordinating anions Ag_nX (n = 1, X = $[NCS]^-$, $[NO_3]^-$, or $[NO_2]^-$; n = 2, X = $[CO_3]^{2-}$ or $[SO_4]^{2-}$) produces the seven-co-ordinate molybdenum(II) complexes *cis*-$[MoX(CO)_2(dmpe)_2]X$ (X = NCS or NO_3), $[MoX(CO)(NO)(dmpe)_2]$ (X = NO_2), and zwitterions *cis*-$[Mo(OZO_m)(CO)_2(dmpe)_2]$ (Z = C, m = 2; Z = S, m = 3). Photolysis of *cis*-$[Mo(OSO_3)(CO)_2(dmpe)_2]$ gives $[Mo(O_2SO_2)(CO)(dmpe)_2]$. The mechanisms of the elimination reactions are discussed and comparisons are made with the reactions of some isoelectronic systems. Disproportionation of molybdenum(I) in *trans*-$[Mo(CO)_2(dmpe)_2]^+$ ion is recognised as an important feature of certain oxidations.

SILVER(I) salts have been used as one-electron oxidising agents in transition-metal chemistry for some time. For example, reaction of $[ReCl(N_2)(dppe)_2]$ (dppe is $Ph_2PCH_2CH_2PPh_2$) with silver(I) salts in ethanol produced [1] the rhenium(II) cation $[ReCl(N_2)(dppe)_2]^+$. More recently, this procedure has been applied successfully to the oxidation of organometallic compounds. Examples include cationic isocyanide complexes [2] of chromium(0), $[Cr(NO)(CNR)_5]^+$, carbonyl complexes of metals of Group 6 {*e.g.* *cis*-$[M(CO)_2(dppm)_2]$ (M = Cr or Mo; dppm is $Ph_2PCH_2PPh_2$)},[3] Group 7 {*e.g.* $[Mn(\eta\text{-}C_5H_5)(CO)(dppe)]$},[4] and Group 8 {*e.g.* $[Fe(CO)_3(dppe)]$},[5] carbene complexes, $[Fe(CO)_3L(PR_3)]$ (L = *NN'*-diethylimidazolidinylidene),[6] and arene complexes such as $[Fe(\eta\text{-}C_5H_5)(dppe)X]$ (X = H, Me, Cl, or $SnMe_3$).[7] The one-electron oxidation product of these reactions is usually isolated as the salt of a non-co-ordinating anion such as tetrafluoroborate or hexafluorophosphate and is characterised by e.s.r. spectroscopy.



SCHEME 1 (*a*) $Ag[BF_4]$,MeCN, 293 K, 5 min; (*b*) $Ag[NO_2]$ or $[NEt_4][NO_2]$, CH_2Cl_2, 293 K, 0.5—3 h; (*c*) RCl, pyridine, 293 K; (*d*) $Ag_2[CO_3]$, CH_2Cl_2, 293 K; (*e*) Ag[NCS], CH_2Cl_2, 293 K; (*f*) $Ag_2[SO_4]$, CH_2Cl_2, 293 K; (*g*) $Ag[NO_2]$, CH_2Cl_2, 293 K; (*h*) $Ag[NO_3]$, CH_2Cl_2, 293 K; (*i*) **$h\nu$**, solid state, 293 K, 48 h; (*j*) 2—3 min

Chemical and electrochemical studies [3,8-12] on a series of $[M(CO)_2(P\text{–}P)_2]^{Z+}$ (M = Cr, Mo, or W; P–P is a bidentate phosphorus ligand; and Z = 0—2) complexes have shown that either *cis*- or *trans*-octahedral configurations can be adopted, depending on the formal oxidation state, Z. Products having a *cis* configuration are usually obtained in the synthesis of the neutral 18-electron compounds ($Z = 0$), although the formation of some *trans*-$[Cr(CO)_2(dppe)_2]$ has been reported.[8] In contrast, only *trans* isomers are isolated in the case of 17-electron complexes ($Z = 1$).[3,9,12] The 16-electron $[M(CO)_2(P\text{–}P)_2]^{2+}$ complexes have not been isolated hitherto, but only observed at low temperatures in electrochemical experiments.[3,12] The formation of *cis* and *trans* isomers in both the 17- and 18-electron systems has been studied by double-potential-step chronoamperometry. Measurements of the rate of isomerisation have indicated that isomerisation occurs *via* a twist mechanism.[13]

We report on the oxidation of ditertiary phosphine complexes of Group 6 metal carbonyls, *cis*-$[M(CO)_2$-

† No reprints available.

(dmpe)$_2$] (dmpe is $Me_2PCH_2CH_2PMe_2$) by various silver(I) salts, AgX, in which the anion X can be either non-co-ordinating (X = $[BF_4]^-$) or potentially co-ordinating (X = $[NCS]^-$, $[NO_2]^-$, $[NO_3]^-$, $[CO_3]^{2-}$, or $[SO_4]^{2-}$). We shall show some unexpected consequences of the use of co-ordinating anions in the oxidation. These reactions have provided the paramagnetic 17-electron cation *trans*-[M(CO)$_2$(dmpe)$_2$] and, subsequently, either a six- or seven-co-ordinate molybdenum species as shown in Scheme 1. A few of these results were reported in preliminary form elsewhere.[14,15]

TABLE 1

Analytical [a] and other physical properties

Compound	Analysis (%) C	H	N	P	Mo	Colour	Λ [b]
trans-[Mo(CO)$_2$(dmpe)$_2$][BF$_4$]·MeCN	33.4 (33.2)	5.8 (6.1)	2.0 (2.4)	21.0 (21.4)	17.3 (16.6)	Orange-red powder [c]	75 [d]
cis-[MoCl(CO)$_2$(dmpe)$_2$][BF$_4$]	29.1 (29.2)	5.4 (5.6)		21.5 (21.6)		Yellow crystals	100
cis-[Mo(NCS)(CO)$_2$(dmpe)$_2$][NCS]	33.2 (33.8)	5.1 (5.6)	4.9 (4.9)			Yellow crystals	
cis-[Mo(NO$_3$)(CO)$_2$(dmpe)$_2$][NO$_3$]	28.0 (28.8)	5.6 (5.6)	4.3 (4.9)	21.4 (21.6)		Yellow crystals	109
cis-[Mo(OSO$_3$)(CO)$_2$(dmpe)$_2$] [e]	30.2 (30.6)	5.9 (5.8)		21.9 (22.6)	17.8 (17.5)	Yellow crystals [c,f]	<17
[Mo(O$_2$SO$_2$)(CO)(dmpe)$_2$]	29.7 (30.0)	6.3 (6.2)		23.6 (23.9)	18.5 (17.9)	Violet powder [g]	<20
cis-[W(NO$_3$)(CO)$_2$(dmpe)$_2$][NO$_3$]	24.8 (25.3)	4.6 (4.8)	4.3 (4.2)	18.7 (18.7)		Yellow crystals	

[a] Calculated values are given in parentheses. [b] Conductivity (S cm^2 mol^{-1}) for 10^{-3} mol dm^{-3} solutions in MeNO$_2$. [c] Photosensitive; handle in dark. [d] In MeCN solution. [e] S, 6.2 (5.8)%. [f] Decomp. >373 K. [g] Decomp. >433 K.

TABLE 2

Spectroscopic measurements

Compound	$\tilde{\nu}$(CO)/cm^{-1}	$\tilde{\nu}$(NO)/cm^{-1}	$\tilde{\nu}$(SO$_4$)/cm^{-1}	$\lambda_{max.}$/nm
trans-[Mo(CO)$_2$(dmpe)$_2$][BF$_4$]	1 858vs [a]			477 [a]
cis-[Mo(CO)$_2$(dmpe)$_2$][BF$_4$]$_2$ [b]	1 944vs, 1 886s [c]			
cis-[MoCl(CO)$_2$(dmpe)$_2$][BF$_4$]	1 946vs, 1 886s [c]			
cis-[Mo(NCS)(CO)$_2$(dmpe)$_2$][NCS]	1 950vs, 1 886s [c]			
cis-[Mo(NO$_3$)(CO)$_2$(dmpe)$_2$][NO$_3$] [d]	1 953vs, 1 892s [c]			
[Mo(CO)(NO)(NO$_2$)(dmpe)$_2$]	1 938vs [c]	1 606s [c]		
[Mo(CO)(NO)(dmpe)$_2$][BF$_4$]	1 945vs [c]	1 650s [c]		
cis-[Mo(OSO$_3$)(CO)$_2$(dmpe)$_2$]	1 930vs, 1 870s		1 167, 1 030 (ν_3), 977 (ν_1), 665 (ν_4) [e]	305, 350 [c]
[Mo(O$_2$SO$_2$)(CO)(dmpe)$_2$]	1 802vs [c]		1 220, 1 130, 1 090 (ν_3), 950 (ν_1), 640 (ν_4) [f]	340, 490 [c]
cis-[Mo(OCO$_2$)(CO)$_2$(dmpe)$_2$] [g]	1 938vs, 1 874s [c]			
trans-[Cr(CO)$_2$(dmpe)$_2$][BF$_4$]	1 840vs [a]			
cis-[W(NO$_3$)(CO)$_2$(dmpe)$_2$][NO$_3$]	1 942vs, 1 862s [c]			

[a] In MeCN solution. [b] The possibility that this species could be seven-co-ordinate, *cis*-[Mo(CO)$_2$(dmpe)$_2$(NCMe)][BF$_4$]$_2$, cannot be discounted. [c] In CH$_2$Cl$_2$ solution. [d] ν(NO$_3$) at 1 482, 1 387, 1 346, and 1 287 cm^{-1}. [e] Nujol mull. [f] KBr disc. [g] ν(CO$_3$) at 1 625 cm^{-1}.

RESULTS AND DISCUSSION

(a) *Non-co-ordinating Anions.—Silver*(I) *tetrafluoroborate*. Reaction between equimolar amounts of *cis*-[Mo(CO)$_2$(dmpe)$_2$] and Ag[BF$_4$] in acetonitrile solution proceeds rapidly at ambient temperature. A photosensitive orange-red solid can be isolated from the solution at *ca.* 230 K with some difficulty. Analysis shows that this solid salt contains one molecule of solvent per formula unit and has the constitution [Mo(CO)$_2$(dmpe)$_2$][BF$_4$]·MeCN (Table 1). The paramagnetic [$\mu_{eff.}$ 1.6$_6$ B.M.* at 295 K (Evans' method)] [16] 17-electron complex cation is characterised as *trans*-[Mo(CO)$_2$(dppe)$_2$]$^+$ by its i.r. spectrum which shows a single intense carbonyl-ligand stretching absorption, ν(CO) at 1 858 cm^{-1} (MeCN). The i.r. spectrum (KBr disc) of the solid showed a weak broad absorption centred at 2 280 cm^{-1} which may be assigned to acetonitrile of crystallisation. The analogous chromium salt, *trans*-[Cr(CO)$_2$(dmpe)$_2$][BF$_4$] is obtained by oxidation of *cis*-[Cr(CO)$_2$(dmpe)$_2$] with Ag[BF$_4$] in acetonitrile solution and also shows one intense i.r. ν(CO) absorption at 1 840 cm^{-1} (MeCN).

Whereas the e.s.r. spectrum of the chromium(I) cation in solution at ambient temperature shows a well defined, symmetric, five-line pattern, the e.s.r. spectrum of the molybdenum(I) analogue is rather more complex. A similar distinction between analogous chromium and molybdenum species has been reported [3] in the case of *trans*-[M(CO)$_2$(dppe)$_2$]$^+$ (M = Cr or Mo) ions. The average *g* values together with the large coupling constants a_P (M = Cr, $g = 2.003$, $a_P = 30.0$ G; M = Mo, $g = 2.053$, $a_P = 25.0$ G) confirm the *trans* geometry of the M(CO)$_2$P$_4$ unit and suggest that the electronic ground state of the ion is $^2B_{2g}$ with the unpaired electron in the metal d_{xy} orbital in each case.

The reaction between equimolar amounts of *trans*-[Mo(CO)$_2$(dmpe)$_2$][BF$_4$] and Ag[BF$_4$] in acetonitrile produces a species which is tentatively identified as *cis*-[Mo(CO)$_2$(dmpe)$_2$]$^{2+}$ on the basis of its i.r. spectrum in solution (Table 2). The possibility that the cation should be formulated as seven-co-ordinate *cis*-[Mo(NCMe)(CO)$_2$(dmpe)$_2$]$^{2+}$ cannot be excluded as we were unable to isolate the solid complex. The same product is obtained directly from *cis*-[Mo(CO)$_2$(dpme)$_2$] (1 mol) on reaction with 2 mol of Ag[BF$_4$] in acetonitrile solution,

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2; 1 G = 10^{-4} T; 1 eV ≈ 1.60 × 10^{-19} J.

as indicated by the i.r. spectrum of the mixture. The dication, which is photosensitive, decomposes rapidly at room temperature in solution. Studies of the electrochemical oxidation of *cis*-[$M(CO)_2(P\text{–}P)_2$] (M = Cr or Mo; P–P = dppm or dppe) have also shown [3] that the dicationic species have little inherent stability at room temperature. This may indicate that the dications are six-co-ordinate and that the decomposition is due to the fact that the molybdenum requires a more strongly co-ordinating ligand than the acetonitrile solvent to achieve co-ordinative saturation. An indication of the specific nature of this requirement is provided by the observation that the addition of Ag[BF_4] (2 mol) to a solution containing *cis*-[$Mo(CO)_2(dmpe)_2$] (1 mol) and pyridine (1 mol) in dichloromethane produced *cis*-[$MoCl(CO)_2(dmpe)_2$][BF_4] * as a result of chloride-ion abstraction from the solvent. This suggests that an anionic ligand is preferred to a neutral ligand in achieving seven-co-ordination. Separate experiments showed that *trans*-[$Mo(CO)_2(dmpe)_2$][BF_4] reacts with alkyl halides, RX (CCl_4 or $PhCH_2I$), in acetonitrile to produce *cis*-[$MoX(CO)_2(dmpe)_2$][BF_4]. Just as the pyridine complex [$Mo(CO)_2(py)(dmpe)_2$][BF_4]$_2$ is not formed when *cis*-[$Mo(CO)_2(dmpe)_2$] is oxidised with Ag[BF_4] in the presence of pyridine in halocarbon solution, there was no evidence for the formation of the tricarbonyl complex [$Mo(CO)_3(dmpe)_2$][BF_4]$_2$ on oxidation of *cis*-[$Mo(CO)_2(dmpe)_2$] with Ag[BF_4] in acetonitrile solution saturated with carbon monoxide. Addition of excess (4 mol) of Ag[BF_4] to *cis*-[$Cr(CO)_2(dmpe)_2$] in acetonitrile did not result in oxidation beyond the chromium(I) stage.

These results may be compared with those obtained in studies of the reaction between [NO][PF_6] and *cis*-[$M(CO)_2(dmpe)_2$] (M = Cr or Mo) in acetonitrile solution. When M is Cr the acetonitrile complex *cis*-[$Cr(NCMe)(CO)_2(dmpe)_2$][PF_6]$_2$ is formed, but when M is Mo the hydride *trans*-[$MoH(CO)_2(dmpe)_2$][PF_6] is produced.[17] That other factors such as solvent, the phosphine ligand, and the counter anion have a profound influence on these oxidation reactions is shown by the reactions of *cis*-[$Mo(CO)_2(dppe)_2$] with [NO][PF_6]. In dichloromethane solution the product is *cis*-[$MoF(CO)_2(dppe)_2$][PF_6], but in acetonitrile solution the product is shown [18] to be *cis*-[$Mo(NCMe)(CO)_2(dppe)_2$][PF_6]$_2$.

(b) *Co-ordinating Anions*.—(*i*) *Silver*(I) *thiocyanate*. Reaction of *cis*-[$Mo(CO)_2(dmpe)_2$] with 2 mol of Ag[NCS] proceeds smoothly at ambient temperature in dichloromethane solution. A pale yellow solid can be isolated from the reaction which is shown to involve the formation of *trans*-[$Mo(CO)_2(dmpe)_2$]$^+$ ion as an intermediate. Analytical (Table 1) and spectroscopic (Table 2) measurements [ν(CN) at 2 082s(sh) (co-ordinated) and 2 070vs (ionic) cm^{-1}] show that the product is the seven-co-ordinate molybdenum(II) complex *cis*-[$Mo(NCS)(CO)_2(dmpe)_2$][NCS]. The related complexes *cis*-[$M(NCS)_2(CO)_2(dppm)_2$] (M = Mo or W) were prepared from the reaction between [$MCl_2(CO)_4$], dppm, and [NH_4][NCS] in ethanol solution.[19] Those complexes were shown to be seven-co-ordinate with one dppm ligand unidentate, and to contain *N*-bonded thiocyanate groups. In the present instance there is no evidence from n.m.r. spectroscopy for a unidentate dmpe ligand. The i.r. criterion for bonding of the thiocyanate group cannot operate unambiguously because the parent compound, *cis*-[$Mo(CO)_2(dmpe)_2$], and related molybdenum(II) complexes [20] such as *cis*-[$MoX(CO)_2(dmpe)_2$]X (X = Cl, Br, or I) have absorptions of medium intensity in the region 700—830 cm^{-1}. Analogy would suggest [21] that the thiocyanate is bound through nitrogen to molybdenum in *cis*-[$Mo(NCS)(CO)_2(dmpe)_2$][NCS].

(*ii*) *Silver*(I) *nitrate*. Whereas *cis*-[$M(CO)_2(dmpe)_2$] (M = Mo or W) will react [14] with Ag[NO_3] to give *trans*-[$M(CO)_2(dmpe)_2$][NO_3] and, with another mol of Ag[NO_3] to give *cis*-[$M(NO_3)(CO)_2(dmpe)_2$][NO_3], the analogous *cis*-[$Cr(CO)_2(dmpe)_2$] is oxidised only to *trans*-[$Cr(CO)_2(dmpe)_2$][NO_3] in acetonitrile solution; further oxidation to chromium(II) is not observed when an excess (more than 2 mol) of Ag[NO_3] is added to the reaction.

(*iii*) *Silver*(I) *nitrite*. Addition of Ag[NO_2] (2 mol) to *cis*-[$Mo(CO)_2(dmpe)_2$] in dichloromethane results in the rapid deposition of metallic silver, leaving a clear golden-yellow solution. After *ca*. 1—3 min, rapid gas evolution occurs in the solution. The gas was shown by i.r. and g.c. to be a mixture of carbon dioxide and dinitrogen oxide, together with some carbon monoxide. An i.r. spectrum of the slowly decomposing solution recorded when the gas evolution had subsided but *not* ceased showed two strong absorptions, one ν(CO) band (1 938 cm^{-1}) and one ν(NO) band (1 606 cm^{-1}). Conductimetric measurements showed the species in solution to be a non-electrolyte. Addition of triphenylphosphane to the solution prior to the addition of Ag[NO_2] resulted in the formation of oxotriphenylphosphorane in addition to carbon dioxide and dinitrogen oxide. Care was taken to ensure that the reagents and solvents were anhydrous, but we are unable to exclude the possibility that trace amounts of water may have been present in the reaction.[22] In another experiment we could show that, with only 1 mol of Ag[NO_2] per mol of *cis*-[$Mo(CO)_2(dmpe)_2$], half of the molybdenum(0) complex remained unchanged after gas evolution (both CO_2 and N_2O) had ceased.

The requirements of 2 equivalents of nitrite ion per molybdenum atom for the formation of dinitrogen oxide is emphasised by the observation that addition of Ag[NO_2] to a solution containing *trans*-[$Mo(CO)_2(dmpe)_2$]X (X = BF_4 or NO_3) in dichloromethane results in the evolution of carbon dioxide (and some carbon monoxide) *only*. The i.r. spectrum of the very air-sensitive solution remaining after gas evolution had ceased showed two strong absorptions as before, one ν(CO) band (1 942 cm^{-1}) and one ν(NO) band which had shifted to higher frequency (1 650 cm^{-1}) compared to the product of the Ag[NO_2] : Mo^0 = 2 : 1 reaction just described. Comparison with the data recorded [23] for

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* The designation *cis* and *trans* in seven-co-ordinate dicarbonyl complexes refers to the relative stereochemistry of the carbonyl groups.

$[Mo(CO)(NO)(dppe)_2][PF_6]$ [ν(CO) at 1 945, ν(NO) at 1 645 cm^{-1}] suggests that the product of the reaction between $Ag[NO_2]$ and *trans*-$[Mo(CO)_2(dmpe)_2]X$ is $[Mo(CO)(NO)(dmpe)_2]X$. Dinitrogen oxide is not formed in this reaction, as indicated by i.r. and g.c.

$$\begin{tikzcd}
cis\text{-}[Mo(CO)_2(dmpe)_2] \arrow[r, "2Ag{[NO_2]}"] & cis\text{-}[Mo(ONO)(CO)_2(dmpe)_2][NO_2]\ \text{(A)} \arrow[d, "\text{slow}"] \\
{[Mo(CO)(NO)(dmpe)_2][NO_2]} & cis\text{-}[Mo(NO_2)(CO)_2(dmpe)_2][NO_2]\ \text{(B)} \arrow[l, "CO_2"']
\end{tikzcd}$$

Scheme 2

The role of the silver(I) ion in the reaction between nitrite ion and $[Mo(CO)_2(dmpe)_2]^{Z+}$ ($Z = 0$ or 1) is shown by experiments using $[NEt_4][NO_2]$, in which the cation is not an oxidising agent. There is no reaction between $[NEt_4][NO_2]$ and *cis*-$[Mo(CO)_2(dmpe)_2]$ in dichloromethane solution. The addition of $[NEt_4][NO_2]$ to a solution containing *trans*-$[Mo(CO)_2(dmpe)_2][BF_4]$ in dichloromethane results in the evolution of carbon dioxide (and some carbon monoxide) *only*, together with both *cis*-$[Mo(CO)_2(dmpe)_2]$ and $[Mo(CO)(NO)(dmpe)_2][BF_4]$[ν(CO) at 1 942, ν(NO) at 1 650 cm^{-1}]. Dinitrogen oxide is not formed in this reaction.

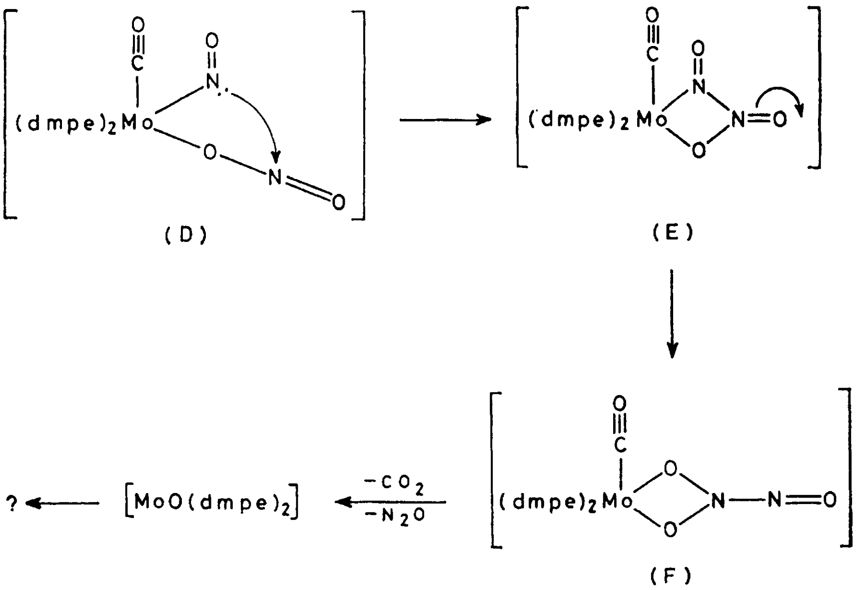
Although we have not been able to isolate a pure molybdenum-containing product from these reactions, we consider that the observations we have made are consistent with the reactions set out in Scheme 2, as regards the formation of carbon dioxide. The *O*-bonded nitrito-complex, (A), is formed initially. The slow isomerisation of (A) to the *N*-bonded nitro-complex, (B), could account for the induction period which is observed prior to gas evolution. Oxygen transfer from the nitro-group to a co-ordinated CO ligand produces carbon dioxide and the nitrosyl complex, (C). A similar reaction scheme has been proposed [24] for the reaction between *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ and $Na[NO_2]$ in dimethylformamide, in which *cis*-$[Ru(NO)_2(PPh_3)_2]$ is formed together with carbon dioxide and carbon monoxide. Triphenylphosphane is oxidised to oxotriphenylphosphorane in the same system. In the present instance, it was not possible to observe either the *O*-bonded nitrito- or the *N*-bonded nitro-ligands in the i.r. spectra because their characteristic vibrations [25] [*ca.* 1 460 and 1 065 cm^{-1} (ONO), 1 420 and 1 310 cm^{-1} (NO_2)] coincide with absorptions of the dmpe ligand.

From our own experiments it is clear that unless both nitrogen-containing groups, whether as nitro (NO_2), nitrito (ONO), or nitrosyl (NO), can become co-ordinated to molybdenum the formation of dinitrogen oxide will not occur. When this is prevented by a non-co-ordinating anion, carbon dioxide and carbon monoxide are the only gaseous products. It is therefore necessary to propose that the nitrate ion in (C) enters the co-ordination sphere of the metal to generate the seven-co-ordinate neutral compound (D), and that it is (D) which

$$\underset{\text{(C)}}{[Mo(CO)(NO)(dmpe)_2][NO_2]} \longrightarrow \underset{\text{(D)}}{[Mo(ONO)(CO)(NO)(dmpe)_2]}$$

is observed in the i.r. spectrum with ν(CO) at 1 938 and ν(NO) at 1 606 cm^{-1}. The exchange of oxygen atoms in systems of this kind is now well documented.[26] Alternatively, the neutral compound (D) could contain an *N*-bonded nitro-ligand.

The reduction of nitrogen monoxide to dinitrogen



Scheme 3

oxide with concurrent oxidation of carbon monoxide to carbon dioxide has been studied intensively recently [27] and a variety of metal catalysts has been used. These studies suggest that the intermediates in the catalytic reactions are either of the $[M(CO)(NO)_2L_n]$ or $[M(CO)(NO)(NO_2)L_n]$ types. The structure of *cis*-$[Pt(O_2N_2)(PPh_3)_2]$, formed in the reaction between nitrogen monoxide and $Pt(PPh_3)_3$, contains a *cis*-hyponitrite ion, bonded to platinum through the oxygen atoms.[28] This platinum complex reacts with CO to form N_2O and CO_2. We suggest that in the molybdenum system considered here a *cis*-hyponitrite is an unlikely intermediate for the production of N_2O. Instead, we propose that a trioxodinitrate [29] ligand is constructed from (D), and that this could be involved as an intermediate in the production of both dinitrogen oxide and carbon dioxide from (D). We envisage the reaction (Scheme 3) proceeding by intramolecular nucleophilic attack of the co-ordinated nitrosyl ligand on the *O*-bonded nitrito-group to give (E), which rearranges to the trioxodinitrate complex (F), before decomposing to give CO_2 and N_2O. This possibility has not been considered hitherto.[27] There are no reports of transition-metal complexes of trioxodinitrates to our knowledge.[30]

The observation that disproportionation occurs when $[NEt_4][NO_2]$ reacts with *trans*-$[Mo(CO)_2(dmpe)_2][BF_4]$ indicates the following explanation (Scheme 4) in the light of the foregoing:

$$\textit{trans}\text{-}[Mo(CO)_2(dmpe)_2][BF_4] + [NEt_4][NO_2] \rightleftharpoons [NEt_4][BF_4] + \textit{trans}\text{-}[Mo(CO)_2(dmpe)_2][NO_2]$$

$$\textit{trans}\text{-}[Mo(CO)_2(dmpe)_2][BF_4] + \textit{trans}\text{-}[Mo(CO)_2(dmpe)_2][NO_2] \longrightarrow \textit{cis}\text{-}[Mo(CO)_2(dmpe)_2] + \textit{cis}\text{-}[Mo(NO_2)(CO)_2(dmpe)_2][BF_4]$$

$$\textit{cis}\text{-}[Mo(NO_2)(CO)_2(dmpe)_2][BF_4] \xrightarrow{-CO_2} [Mo(CO)(NO)(dmpe)_2][BF_4]$$

SCHEME 4

Support for this proposal is provided by the reaction between equimolar quantities of *cis*-$[Mo(CO)_2(dmpe)_2]$ and $Ag[NO_2]$ for which the following steps (Scheme 5) can be written:

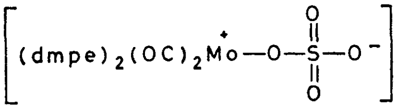
$$\textit{cis}\text{-}[Mo(CO)_2(dmpe)_2] + Ag[NO_2] \longrightarrow Ag + \textit{trans}\text{-}[Mo(CO)_2(dmpe)_2][NO_2]$$

$$2\,\textit{trans}\text{-}[Mo(CO)_2(dmpe)_2][NO_2] \longrightarrow \textit{cis}\text{-}[Mo(CO)_2(dmpe)_2] + \textit{cis}\text{-}[Mo(NO_2)(CO)_2(dmpe)_2][NO_2]$$

SCHEME 5

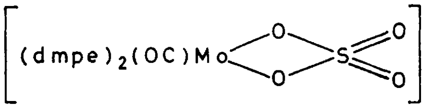
We have recently reported a similar disproportionation of the chromium(I) complex *cis*-$[Cr(CO)_4(dmpe)][PF_6]$ in solution.[17]

(*iv*) *Silver*(I) *sulphate*. Photosensitive pale yellow crystals can be isolated in good yield from the reaction between equimolar amounts of $Ag_2[SO_4]$ and *cis*-$[Mo(CO)_2(dmpe)_2]$ in dichloromethane in the dark at ambient temperature. The yellow solid is a non-electrolyte. Analytical (Table 1) and spectroscopic measurements (Table 2) are consistent with the characterisation of the yellow solid as *cis*-$[Mo(SO_4)(CO)_2(dmpe)_2]$. The compound gives a weak parent ion in the mass spectrum (*m*/*e*, *I*%: 548, 4, M^+; 520, 7, $[M - CO]^+$; 492, 4, $[M - 2CO]^+$; 452, 83, $[M - SO_4]^+$; 424, 100, $[M - CO - SO_4]^+$ based on ^{96}Mo). The values of ν(CO) for this dicarbonyl complex are consistent with those of other molybdenum(II) compounds, but are both *ca*. 20 cm^{-1} lower in wavenumber. The i.r. spectrum also shows that the sulphate ligand is unidentate,[31] so that the compound should be formulated as a zwitterion:



$$\left[(\text{dmpe})_2(\text{OC})_2\overset{+}{\text{Mo}}-\text{O}-\underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{O}}{\|}}{\text{S}}}-\text{O}^-\right]$$

When the yellow solid complex is exposed to direct sunlight, carbon monoxide is released (identified by i.r. spectroscopy) and a violet solid complex is formed. The violet solid is a non-electrolyte. Quantitative analysis (Table 1) and spectroscopic measurements (Table 2) are consistent with the characterisation of the violet solid as $[Mo(SO_4)(CO)(dmpe)_2]$. The compound gives a parent ion in the mass spectrum (*m*/*e*, *I*%: 520, 14, M^+; 492, 1, $[M - CO]^+$; 424, 100, $[M - SO_4]^+$ based on ^{96}Mo), and the molecular weight measured in solution (600) is consistent with a monomer (520). The i.r. spectrum indicates that the sulphate ligand is bidentate [31] so that the violet molybdenum(II) complex has the seven-co-ordinate structure:



(*v*) *Silver*(I) *carbonate*.—A precipitate of silver is rapidly formed when $Ag_2[CO_3]$ is added to *cis*-$[Mo(CO)_2(dmpe)_2]$ in dichloromethane. The i.r. spectrum of the pale yellow solution showed two carbonyl stretching frequencies which were consistent with those of a molybdenum(II) compound having *cis* stereochemistry, but, as with the sulphate system just described, *ca*. 20 cm^{-1} lower (1 938vs and 1 870s cm^{-1}) than those of complexes such as *cis*-$[MoCl(CO)_2(dmpe)_2]Cl$ (1 952vs and 1 890s cm^{-1}). In addition, the i.r. spectrum showed an intense broad absorption centred at 1 625 cm^{-1} which is assigned [32] to the ν_1 mode of co-ordinated carbonate which is forbidden in the free ion. All attempts to isolate the pure compound were unsuccessful; the carbonate is lost very easily and the complex decomposes. On the evidence available, especially comparison with the yellow sulphate complex described in the previous section, we believe that the compound formed is the zwitterionic seven-co-ordinate, neutral molybdenum(II) complex *cis*-$[Mo(OCO_2)(CO)_2(dmpe)_2]$. The only comparable compound is formed when the labile product of the reaction between *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ and carbon dioxide in toluene is dissolved in tetrahydrofuran. An *X*-ray determination of the crystal structure of this compound showed [33] it to be a carbonate-*OO′O″*-bridged dimer $[L_3(OC)Mo(\mu_3\text{-}CO_3)_2Mo(CO)L_3]$ ($L = PMe_2Ph$).

Conclusion.—There is a marked difference in the reactivity of analogous chromium and molybdenum compounds of the type *cis*-$[M(CO)_2(dmpe)_2]$ (M = Cr or Mo) towards silver(I) ion. Whereas the chromium(0) complex is not oxidised beyond the chromium(I) stage as in *trans*-$[Cr(CO)_2(dmpe)_2][BF_4]$, the molybdenum(0) analogue typically undergoes further oxidation to give a molybdenum(II) product. We have shown that the choice of counter anion in silver(I)-promoted oxidation of the molybdenum(0) complex may have a profound influence upon the nature of the product formed. The common substrate in these reactions *cis*-$[Mo(CO)_2(dmpe)_2]$ is characterised by a low first ionisation potential [6.00 eV (vertical), compared with those for Ca (6.11 eV) and $C_2(NMe_2)_4$ (5.95 eV)], and a low reduction potential in solution[34] (−0.23, + 0.82 V *versus* standard calomel electrode). With a non-co-ordinating anion it has been possible to characterise two one-electron oxidation products in solution. The first of these, *trans*-$[Mo(CO)_2(dmpe)_2]^+$, is found as a component in other systems described here and in oxidative-addition reactions of alkyl halides with *cis*-$[Mo(CO)_2(dmpe)_2]$ which we have investigated.[35] With silver(I) salts of co-ordinating anions, AgX, oxidation proceeds *via* the molybdenum(I) salt, *trans*-$[Mo(CO)_2(dmpe)_2]X$, to form the seven-co-ordinate molybdenum(II) complex *cis*-$[MoX(CO)_2(dmpe)_2]X$ (X = NCS or NO_3). In the case where X = NO_2, further reaction within the co-ordination sphere of the molybdenum is possible and both CO_2 and N_2O are formed. Dinitrogen oxide is not formed unless two nitrite ions per molybdenum atom are present, but carbon dioxide is produced even when only one nitrite ion is present per molybdenum atom. It appears that the formation of CO_2, which is accompanied by conversion of a nitro- into a nitrosyl ligand, precedes the formation of dinitrogen oxide. The intervention of a trioxodinitrate, $[O_2NNO]^{2-}$, ligand in the synthesis of dinitrogen oxide is suggested. Disproportionation of the molybdenum(I) intermediate, *trans*-$[Mo(CO)_2(dmpe)_2][NO_2]$, is involved in these reactions; we have no evidence that a process of the following general type is

$$2\ trans\text{-}[Mo(CO)_2(dmpe)_2]X \longrightarrow cis\text{-}[Mo(CO)_2(dmpe)_2] + cis\text{-}[MoX(CO)_2(dmpe)_2]X$$

involved in the synthesis of the other molybdenum(II) complexes (X = CNS, NO_3, Cl, Br, or I) which we have prepared.

Oxidation of *cis*-$[Mo(CO)_2(dmpe)_2]$ with silver(I) salts of dianions of general type Ag_2Y produces a zwitterionic molybdenum(II) complex *cis*-$[MoY(CO)_2(dmpe)_2]$. No evidence of a molybdenum(I) intermediate, presumed to be $\{trans\text{-}[Mo(CO)_2(dmpe)_2]\}_2Y$, was obtained, but this may simply indicate that the disproportionation reaction analogous to that given above is rapid. The zwitterionic complex *cis*-$[Mo(OSO_3)(CO)_2(dmpe)_2]$ undergoes a photoinduced chelation reaction in which carbon monoxide is eliminated.

These reactions which result in the elimination of a carbonyl ligand, whether as a result of reaction within the co-ordination sphere (to form CO_2 in the case of $Ag[NO_2]$) or by chelate-ring formation (in the case of $Ag_2[SO_4]$), would appear to be driven, in part at least, by the need to avoid an eight-co-ordinate, 20-electron, molybdenum(II) centre.

These oxidation reactions are also interesting in comparison with reactions of other $[ML_2(R_2PCH_2CH_2PR_2)_2]$ (L = N_2 or CS) complexes. Oxidation of *trans*-$[Mo(N_2)_2(dppe)_2]$ by silver(I) results in the loss of co-ordinated dinitrogen;[36] the reaction between $Ag[BF_4]$ and $[W(CO)(CS)(dppe)_2]$ produces[37] the silver(I)-bridged complex $[Ag\{SCW(CO)(dppe)_2\}_2][BF_4]$. In general, the dinitrogen ligands of *trans*-$[Mo(N_2)_2(dppe)_2]$ are either more readily displaced or are more reactive (*e.g.* towards acids and alkyl halides[38]) than the carbonyl ligands in the isoelectronic *cis*-$[Mo(CO)_2(dmpe)_2]$, or its dppe analogue. The reactions of the bis(dinitrogen) complex and the dicarbonyl complex which are known at the present time suggest that if the Mo–N_2 and Mo–CO units are regarded as 1,3-dipoles M–A–B having canonical forms (I) and (II) then the dinitrogen complexes are

$$\text{(I)}\ \overset{+}{M}{=}A{=}\overset{-}{B} \qquad \text{(II)}\ \overset{-}{M}{=}A{=}\overset{+}{B}$$

best represented by (I), that is $\overset{+}{Mo}{=}N{=}\overset{-}{N}$, whereas the carbonyl complexes are better represented by (II), that is $\overset{-}{Mo}{=}C{=}\overset{+}{O}$. Our attempts to observe nucleophilic attack at oxygen by a variety of bases have been unsuccessful.

EXPERIMENTAL

All reactions were performed under an atmosphere of deoxygenated dry nitrogen using conventional vacuum-line and Schlenk-tube techniques. Solvents were thoroughly dried, deaerated, and distilled under an atmosphere of nitrogen prior to use. Melting points were determined on a hot-stage block using capillary tubes sealed under an atmosphere of nitrogen. Infrared spectra were recorded in a variety of solvents using 1.0-mm solution cells or as Nujol or hexachlorobutadiene mulls between NaCl plates on a PE 257 grating spectrometer; KBr-disc i.r. spectra were recorded on a PE 225 spectrometer. Calibration of i.r. spectra was achieved using the peak of polystyrene at 1 602 cm^{-1}. Mass spectra were recorded on an A.E.I. MS 12 instrument with a nominal beam energy of 70 eV. Electronic spectra were obtained on a Unicam SP 800 spectrometer in a variety of solvents. Proton n.m.r. spectra were recorded on a PE R12 (60 MHz), a PE R32 (90 MHz), a Varian HA 100 (100 MHz) or on a Varian SC 300 (300 MHz) spectrometer using a variety of deuteriated solvents with tetramethylsilane as a reference. E.s.r. spectra were obtained on either a Varian V4502 *Q*-band (35 GHz) or on a Varian E4 *X*-band (9.5 GHz) spectrometer using the solids or their solutions in various solvents. Stopped-flow experiments were performed on a Aminco–Morrow stopped-flow spectrometer with DASAR facilities. Gas separations were achieved using a PE 452 gas chromatograph employing a 1-m column of silica gel at 298 K. Analytical services were performed by Mr. M. Hart of this department. Conductivity measurements were made on 10^{-3} mol dm^{-3} nitromethane solutions using a Philips PR 9500 conductivity bridge; under these conditions 1 : 1 and 1 : 2 electrolytes have conductivities in the ranges 75—95 and 160—190 S cm^2 mol^{-1} respectively.[39]

The silver(I) salts, tetrafluoroborate, sulphate, nitrate, and nitrite, were reagent grade chemicals. The compounds *cis*-[M(CO)$_2$(dmpe)$_2$] (M = Cr, Mo, or W),[40] silver(I) thiocyanate,[41] and silver(I) carbonate [41] were prepared by literature methods.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dicarbonylmolybdenum Tetrafluoroborate*.—Silver tetrafluoroborate (0.195 g, 1.0 mmol) in acetonitrile (1 cm^3) was added slowly to a stirred solution of *cis*-[Mo(CO)$_2$(dmpe)$_2$] (0.452 g, 1.0 mmol) in acetonitrile (9 cm^3) at *ca.* 230 K which was well shaded from direct light. Metallic silver was deposited. Filtration of the resulting mixture after 1 h produced a golden-yellow solution. Concentration of this solution by slow evaporation of the solvent in a current of dinitrogen at *ca.* 230 K gave an orange-red solid (0.18 g). This solid is very photosensitive, and its solutions are also photosensitive.

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dicarbonylthiocyanatomolybdenum Thiocyanate*.—Solid Ag[SCN] (0.325 g, 1.96 mmol) was slowly added to a stirred solution of *cis*-[Mo(CO)$_2$(dmpe)$_2$] (0.442 g, 0.98 mmol) in dichloromethane (10 cm^3). The resulting solution was stirred for 0.5 h and filtered to remove the deposit of metallic silver. Addition of hexane and cooling the filtrate produced a yellow powder which was collected and dried under vacuum (0.1 g).

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dicarbonylnitratotungsten Nitrate*.—Silver nitrate (0.17 g, 1 mmol) was added to a stirred solution of [W(CO)$_2$(dmpe)$_2$] (0.260 g, 0.5 mmol) in MeCN (2 cm^3) and CH_2Cl_2 (8 cm^3). A black precipitate of silver metal formed immediately. Filtration provided a pale yellow filtrate from which the pale yellow complex (0.30 g) was precipitated by the addition of hexane.

Reaction of Silver(I) *Nitrite with cis*-[Mo(CO)$_2$(dmpe)$_2$].—Solid Ag[NO$_2$] (0.26 g, 1.72 mmol) was added to a stirred solution of *cis*-[Mo(CO)$_2$(dmpe)$_2$] (0.39 g, 0.86 mmol) in CH_2Cl_2 (15 cm^3). A precipitate of metallic silver appeared immediately and after an induction period (*ca.* 1—3 min) rapid gas evolution occurred from the solution. Once the gas evolution had diminished substantially, the metallic silver was filtered off, leaving a yellow filtrate. Attempts to isolate a solid product from this yellow solution were unsuccessful; only small amounts of very air-sensitive oily dark yellow-brown solids could be obtained.

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dicarbonyl*(*sulphato*-O)*molybdenum*.—Solid Ag$_2$[SO$_4$] (0.174 g, 0.56 mmol) was added to a solution containing *cis*-[Mo(CO)$_2$(dmpe)$_2$] (0.252 g, 0.56 mmol) in dichloromethane (25 cm^3), and the resulting mixture was stirred in the dark for 5 h. The precipitate of metallic silver was filtered off. Addition of hexane to the filtrate caused the deposition of a pale yellow solid which was recrystallised from dichloromethane–hexane (1 : 1) at 273 K. This pale yellow crystalline product is extremely photosensitive.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*carbonyl*(*sulphato*-OO′)*molybdenum*.—A sample of *cis*-[Mo(SO$_4$)(CO)$_2$(dmpe)$_2$] (0.14 g, 0.25 mmol) was sealed in a nitrogen-filled flask and exposed to direct sunlight with regular shaking for a total of 20 h. During this period the pale yellow crystals changed colour to give a violet solid powder and carbon monoxide was evolved.

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