Studies of Chelation. Part 6.[†] Reactions of Ditertiary Alkylphosphine Complexes of Group 6 Metal Carbonyls with Nitrosonium Hexafluorophosphate. Preparation and Reactions of Hydrido-complexes of Chromium(II), Molybdenum(II), and Tungsten(II) [‡]

By **Joseph A. Connor,* Paul I. Riley,** and **Colin J. Rix,** Department of Chemistry, University of Manchester, Manchester M13 9PL

Substitution of *cis*-[M(CO)$_4$(L–L)] [M = Cr, Mo, or W; L–L = R$_2$P(CH$_2$)$_2$PR$_2$ (dcpe, R = C$_6$H$_{11}$; dmpe, R = Me)] by [NO][PF$_6$] in methyl cyanide produces [M(CO)$_3$(NO)(L–L)][PF$_6$] which probably has the *fac* configuration. Where M = Cr, the final product of reaction is paramagnetic *fac*-[Cr(NCMe)$_3$(NO)(L–L)][PF$_6$]$_2$ which undergoes exchange of MeCN for Me$_2$CO in acetone solution. The processes leading to these products have been examined. Where M = W, addition of further [NO][PF$_6$] produces an isomeric complex which is probably dimeric. With *cis*-[Mo(CO)$_2$(dmpe)$_2$], [NO][PF$_6$] produces [MoH(CO)$_2$(dmpe)$_2$][PF$_6$] in hydrogen-containing solvents, but in liquid SO$_2$ the product is [Mo(CO)$_2$(SO$_2$)(dmpe)$_2$][PF$_6$]$_2$. Oxidation of *cis*-[Cr(CO)$_2$(dmpe)$_2$] with [NO]-[PF$_6$] gives both *trans*-[Cr(CO)$_2$(dmpe)$_2$][PF$_6$] and [CrH(CO)$_2$(dmpe)$_2$][PF$_6$] in methanol, but in methyl cyanide *cis*-[Cr(NCMe)(CO)$_2$(dmpe)$_2$][PF$_6$]$_2$ is formed. The preparation of [WH(CO)$_2$(dmpe)$_2$]$^+$ is reported. The hydride [MoH(CO)$_2$(dmpe)$_2$][PF$_6$] is reduced by 1,8-bis(dimethylamino)naphthalene to *cis*-[Mo(CO)$_2$(dmpe)$_2$], but [MoH(CO)$_2$(dmpe)$_2$]I is converted into [MoI(CO)$_2$(dmpe)$_2$]I by the same reagent. Reaction with alkyl halide RX (R = prop-2-enyl or benzyl) and with iodine produces [MoX(CO)$_2$(dmpe)$_2$]$^+$. The new complexes are characterised by i.r., n.m.r. (^{1}H and ^{31}P), e.s.r., and visible spectra, and by conductivity and microanalysis. Comparisons are made with reactions of analogous complexes of Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dppe) and Ph$_2$PCH$_2$PPh$_2$ (dppm), from which it is apparent that the precise nature of the ditertiary phosphine exercises an important influence on the course of both oxidation and substitution reactions in this system.

CHANGES in the type of substituent at phosphorus in a ditertiary phosphine ligand can have a profound influence on the ease with which transition-metal complexes containing these ligands undergo oxidation, reduction, and substitution reactions.[1] By choosing a simple reagent which is capable of effecting both oxidation and substitution, [NO][PF$_6$], we were interested to know how the reactions of complexes of the type *cis*-[M(CO)$_{6-2n}$(L–L)$_n$] (M = Cr, Mo, or W; n = 1 or 2; L–L = ditertiary phosphine) might be affected by such changes in the ligand, L–L. By using ligands which have cone angles,[1] θ, less than [Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe), θ 107°], and greater than [(C$_6$H$_{11}$)$_2$PCH$_2$CH$_2$P(C$_6$H$_{11}$)$_2$ (dcpe), θ 142°] that of Ph$_2$PCH$_2$CH$_2$PPh$_2$ [dppe, θ 125°], we have tried to take account of steric influences on reactivity. Also, although many mononuclear Group 6 metal nitrosyl complexes have been prepared which also contain carbonyl ligands,[2] the majority of these, which do not also contain η-arene ligands, are complexes of molybdenum and tungsten;[3] thus we have attempted to compare the reactions of all the three metals in Group 6 where possible.

RESULTS AND DISCUSSION

Tetracarbonyl Complexes.—Molybdenum and tungsten. The product of the reaction between equimolar quantities of [NO][PF$_6$] and *cis*-[M(CO)$_4$(dmpe)] (M = Mo or W) in methyl cyanide was the yellow crystalline diamagnetic complex [M(CO)$_3$(NO)(dmpe)][PF$_6$], a 1 : 1 electrolyte in solution, analogous to [M(CO)$_3$(NO)(dppe)][PF$_6$] formed[4] in a similar reaction from *cis*-[M(CO)$_4$(dppe)] (M = Mo or W). The i.r. spectra of the dmpe complexes show three ν(CO) bands ($2A' + A''$ under C_s symmetry) and one ν(NO) band (Table 1) at wavenumbers which are slightly (5—15 cm^{-1}) lower than their dppe analogues for which, however, only two ν(CO) frequencies were reported.[4,5] The frequency assignment is based on the presumption that the nitrosyl ligand is a better π acceptor than the ditertiary phosphine so that[6] the A'' mode will be of lowest frequency. The ^{1}H n.m.r. spectra of the readily soluble dmpe complexes show the methyl hydrogens as a pair of doublets [$^2J(PCH)$ 9.5 (Mo) and 10.0 (W) Hz] centred at τ 8.60, 8.82 (Mo) and 8.26, 8.49 (W) p.p.m. ([^{2}H$_6$]acetone solution). An unambiguous assignment of *fac* or *mer* stereochemistry to the [MC$_3$NP$_2$] skeleton was not possible on the basis of this spectroscopic evidence, but a *fac* structure appears most likely on the basis of comparison with the paramagnetic chromium complexes discussed below. A similar reaction between *cis*-[W(CO)$_4$(dcpe)] and [NO][PF$_6$] in methyl cyanide gave [W(CO)$_3$(NO)(dcpe)][PF$_6$] as expected, together with a very small quantity of a complex which may perhaps be [W(CO)(NO)(NCMe)$_2$(dcpe)][PF$_6$] [ν(CO) at 1 932 cm^{-1} in CH$_2$Cl$_2$]. Whereas [Mo(CO)$_3$(NO)(dppe)][PF$_6$] reacts[5] with dppe in acetone to form [Mo(CO)(NO)(dppe)$_2$]-

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[†] Part 5, J. A. Connor and P. I. Riley, *Inorg. Chim. Acta*, 1975, **15**, 191.

[‡] No reprints available.

[1] C. A. Tolman, *Chem. Rev.*, 1977, **77**, in the press.

[2] N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, **6**, 47.

[3] C. G. Barraclough, J. A. Bowden, and C. J. Commons, *Austral. J. Chem.*, 1973, **26**, 241; R. B. King, M. S. Saran, and S. P. Anand, *Inorg. Chem.*, 1974, **13**, 3038; R. Colton and C. J. Commons, *Austral. J. Chem.*, 1973, **26**, 1487; W. R. Robinson and M. E. Swanson, *J. Organometallic Chem.*, 1972, **35**, 315; R. Colton and C. J. Commons, *Austral. J. Chem.*, 1973, **26**, 1493.

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

[5] N. G. Connelly, *J.C.S. Dalton*, 1973, 2183.

[6] L. W. Houk and G. R. Dobson, *Inorg. Chem.*, 1966, **5**, 2119.

$[PF_6]$, we found that *fac*-$[W(CO)_3(NO)(dmpe)][PF_6]$ does not react with excess of dmpe in refluxing acetone.

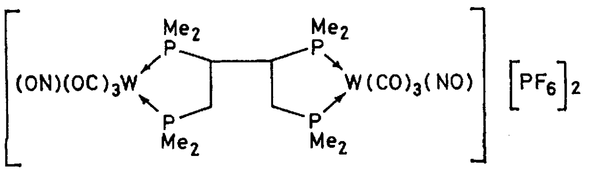
When $[NO][PF_6]$ (2 mol) was added to *cis*-$[W(CO)_4(dmpe)]$ (1 mol) in methyl cyanide solution a green solid complex was obtained which behaved as a 1 : 2 electrolyte in solution ($MeNO_2$) and had a very complicated ^1H n.m.r. spectrum at 300 MHz. The n.m.r. spectrum showed no signal which might be due to a metal hydride. The i.r. spectrum [2 090m, 2 034w, 2 018 (sh), 2 008vs, and 1 722 cm^{-1} in CH_2Cl_2] and elemental analysis of this complex were very similar to that of $[W(CO)_3(NO)(dmpe)][PF_6]$. These results lead to the view that, in the green product, deprotonation of the dmpe ligand may have caused dimerisation through the methylene carbon atoms as indicated by structure (1). The absence of a resonance due to W–H in the n.m.r. strongly suggests that intramolecular oxidative addition of a C–H bond to tungsten as [7] in $[Ru(dmpe)_2]$ has not occurred, although it should be remembered that the hydride complexes $[\{PtH(SiR_3)(PR_3)\}_2]$ show no hydride resonance.[8] Attempts to grow crystals of the green solid suitable for diffraction studies were unsuccessful, as has often been the case for other dmpe complexes we have prepared.[9]

TABLE 1

Infrared spectra of $[M(CO)_3(NO)(L-L)][PF_6]$ and related complexes in the range 1 700—2 200 cm^{-1} in CH_2Cl_2 solution

Complex	ν(CO)			ν(NO)
fac-$[Cr(CO)_3(NO)(dmpe)][PF_6]$	2 086m(*A'*),	2 026 (sh)(*A'*),	2 016vs(*A''*)	1 754
fac-$[Mo(CO)_3(NO)(dmpe)][PF_6]$	2 098m,	2 026 (sh),	2 018vs	1 730
fac-$[W(CO)_3(NO)(dmpe)][PF_6]$	2 092m,	2 020 (sh),	2 018vs	1 722
fac-$[W(CO)_3(NO)(dcpe)][PF_6]$	2 088m,	2 010 (sh),	2 000vs	1 722
$[Mo(CO)_3(NO)(dppe)][PF_6]$ *	2 111, 2 040			1 735
$[W(CO)_3(NO)(dppe)][PF_6]$ *	2 102, 2 025			1 725
cis-$[Cr(CO)_4(dmpe)][PF_6]$	2 086s, 2 026s, 1 957vs			
cis-$[Cr(CO)_4(dcpe)][PF_6]$	2 079s, 2 026s, 1 950vs			
cis-$[Cr(CO)_4(dppe)][PF_6]$ *	2 090s, 2 015m, 1 978s			

* Ref. 5.



(1)

Chromium. In contrast to the foregoing, the addition of $[NO][PF_6]$ (2 mol) to *cis*-$[Cr(CO)_4(L-L)]$ (1 mol) in methyl cyanide produced the orange paramagnetic complexes $[Cr(NCMe)_3(NO)(L-L)][PF_6]_2$ [$\lambda_{max.}$ 393 (ε 1 320) and 460 (423), L–L = dmpe; 412 (1 000) and 470 nm (200), L–L = dcpe]. The complexes are 1 : 2 electrolytes in solution ($MeNO_2$). The i.r. spectra show one ν(NO) band (1 722 cm^{-1} in MeCN) and two ν(CN) bands [2 315 nm, 2 290s (dmpe); 2 310m, 2 282s cm^{-1} (dcpe) in Nujol]. The e.s.r. spectra of the complexes in solution (MeCN) consist of a well resolved 1 : 2 : 1 triplet on which no ^{14}N-superhyperfine structure is observed. The equivalence of the phosphorus atoms requires that these $[Cr(NCMe)_3(NO)(L-L)]^{2+}$ cations have a *fac* stereochemistry. When these methyl cyanide complexes are dissolved in acetone, a red solution ($\lambda_{max.}$ 354 and 534 nm) is produced. The e.s.r. spectrum of the red solution consists of a 1 : 2 : 1 triplet as before, but the *g* value (1.987, L–L = dmpe) is lower than formerly (*g* 1.993), consistent with the substitution of methyl cyanide by a weaker donor ligand (acetone). The *g* values measured for other low-spin d^5 chromium(I) nitrosyl complexes, with which these $[Cr(NO)Q_3(L-L)]^{2+}$ (Q = MeCN or Me_2CO) salts may be compared, show a similar variation (Table 2).

When only 1 mol of $[NO][PF_6]$ was added to *cis*-$[Cr(CO)_4(dmpe)]$ (1 mol) in methyl cyanide solution a red solution was produced. When excess of diethyl ether was added rapidly to this red solution a pink solid was precipitated. The i.r. spectrum of this pink solid in dichloromethane shows that it consists of a mixture of unchanged *cis*-$[Cr(CO)_4(dmpe)]$ together with *cis*-$[Cr(CO)_4(dmpe)][PF_6]$ and *fac*-$[Cr(CO)_3(NO)(dmpe)][PF_6]$. The e.s.r. spectrum of the pink solid shows a broad band with *g ca.* 2.0 which is attributed to *cis*-$[Cr(CO)_4(dmpe)][PF_6]$.

When the pink solid was redissolved in methyl cyanide, further reaction, which can be monitored by i.r. spectroscopy, took place at room temperature, while the solution changed colour from red to orange. After 30 min the i.r. spectrum in the 1 800—2 200 cm^{-1} region showed the presence of *cis*-$[Cr(CO)_4(dmpe)]$ only. The e.s.r. spectrum of the orange solution consists of a 1 : 2 : 1 triplet, centered at *g* 1.993, characteristic of *fac*-$[Cr(NCMe)_3(NO)(dmpe)][PF_6]_2$, which was confirmed by a band at 1 722 cm^{-1} [ν(NO)] in the i.r. spectrum. The pattern of observations is the same if the pink solid is redissolved in acetone, leading to $[Cr(OCMe_2)_3(NO)(L-L)]^{2+}$, and if the complex used initially is *cis*-$[Cr(CO)_4(dcpe)]$. These reactions can be described by equations (1)—(3) (Q = MeCN or Me_2CO). As the stereochemistry of the final nitrosyl-containing product has been established as *fac*, it is reasonable to imply the same stereochemistry for the precursors of this complex and for the appropriate molybdenum and tungsten analogues. The decrease in ν(NO) from *fac*-$[Cr(CO)_3(NO)(dmpe)]^+$ (1 754 cm^{-1}) to

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[7] F. A. Cotton, B. A. Frenz, and D. L. Hunter, *J.C.S. Chem. Comm.*, 1974, 755.

[8] M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Chem. Comm.*, 1976, 671.

[9] P. I. Riley, Ph.D. Thesis, Manchester University, 1976.

fac-$[Cr(NCMe)_3(NO)(dmpe)]^{2+}$ (1 722 cm^{-1}) suggests that the effect of replacement of three good π-acceptor ligands (CO) by three inferior π-acceptor ligands (MeCN), which would tend to decrease ν(NO), outweighs the effect of

$$2\,cis\text{-}[Cr(CO)_4(L\text{-}L)] + 2[NO][PF_6] \longrightarrow cis\text{-}[Cr(CO)_4(L\text{-}L)][PF_6] + NO + fac\text{-}[Cr(CO)_3(NO)(L\text{-}L)][PF_6] \quad (1)$$

$$cis\text{-}[Cr(CO)_4(L\text{-}L)][PF_6] + fac\text{-}[Cr(CO)_3(NO)(L\text{-}L)][PF_6] \longrightarrow cis\text{-}[Cr(CO)_4(L\text{-}L)] + fac\text{-}[Cr(CO)_3(NO)(L\text{-}L)][PF_6]_2 \quad (2)$$

$$fac\text{-}[Cr(CO)_3(NO)(L\text{-}L)][PF_6]_2 \xrightarrow{Q} fac\text{-}[CrQ_3(NO)(L\text{-}L)][PF_6]_2 \quad (3)$$

oxidation of Cr^0 to Cr^I which would tend [10] to increase ν(NO) by *ca.* 100 cm^{-1}.

These observations are in marked contrast to those reported [5] for the reaction of *cis*-$[Cr(CO)_4(dppe)]$ with $[NO][PF_6]$. In methanol–toluene solution the dppe complex is oxidised to the cation *cis*-$[Cr(CO)_4(dppe)]^+$, but in methyl cyanide solution the product is *trans*-$[Cr(NCMe)_4(NO)_2][PF_6]_2$.

TABLE 2

E.s.r. spectra of chromium(I) nitrosyl complexes in solution

Complex	Solvent	$g_{av.}$	a_P/G	Ref.
fac-$[Cr(NO)(NCMe)_3(dmpe)][PF_6]_2$	*a*	1.993 [b]	32	*c*
fac-$[Cr(NO)(NCMe)_3(dcpe)][PF_6]_2$	*a*	1.991	34	*c*
fac-$[Cr(NO)(OCMe_2)_3(dmpe)][PF_6]_2$	*d*	1.987	32	*c*
fac-$[Cr(NO)(OCMe_2)_3(dcpe)][PF_6]_2$	*d*	1.984	35	*c*
$[Cr(NO)(CNMe)_5][PF_6]_2$	*e*	1.996 8		10
$[Cr(NO)(CN)_5]^{3-}$	*f*	1.994 9		*g*
$[Cr(NO)(OH_2)(CN)_2]$	*f*	1.983 2		*h*
$[Cr(NO)(NH_3)_5]^{2+}$	*f*	1.979		*g*
$[Cr(NO)(OH_2)_5]^{2+}$	*f*	1.967 1		*g*

[a] Methyl cyanide. [b] Powder (35 GHz): $g_1 = 1.999$; $g_2 = 1.992$. [c] This work. [d] Acetone. [e] Dichloromethane. [f] Water. [g] B. A. Goodman, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 1973. [h] J. Burgess, B. A. Goodman, and J. B. Raynor, *J. Chem. Soc.* (*A*), 1968, 501.

Dicarbonyl Complexes.—The complex $[Mo(CO)(NO)(dppe)_2][PF_6]$ has been prepared [5] from the reaction between $[Mo(CO)_3(NO)(dppe)][PF_6]$ and dppe in refluxing acetone. A similar reaction does not occur in the case of dmpe analogues as mentioned above. The reaction of $[NO][PF_6]$ with *cis*-$[Mo(CO)_2(dppe)_2]$ does not produce $[Mo(CO)(NO)(dppe)_2][PF_6]$ but instead, without displacing CO from the metal, successive one-electron oxidations will take place.[11,*]

We found that when $[NO][PF_6]$ (2 mol) is mixed with *cis*-$[Mo(CO)_2(dmpe)_2]$ (1 mol) in either dichloromethane or methyl cyanide which had been carefully purified, dried, and distilled prior to use, the only product was the molybdenum(II) hydride, *trans*-$[MoH(CO)_2(dmpe)_2][PF_6]$,† characterised as a 1 : 1 electrolyte with ν(CO) at 1 872 cm^{-1} in the i.r. spectrum and a triplet of triplets centred at τ 16.8 p.p.m. (Mo–*H*) in the ^1H n.m.r. spectrum. We have to conclude either that significant quantities of water were present in these reactions despite our best efforts to exclude it, or else that hydride-ion abstraction occurs from the solvent (CH_2Cl_2 or MeCN). There are several precedents for the latter alternative.[12] The important role of the nitrosonium ion in this proton abstraction is emphasised by the fact that *cis*-$[Mo(CO)_2(dmpe)_2]$ can be recovered unchanged from its solutions in CH_2Cl_2 and MeCN which have been heated under reflux.

In order to avoid hydride formation the reaction between *cis*-$[Mo(CO)_2(dmpe)_2]$ (1 mol) and $[NO][PF_6]$ (2 mol) was carried out in liquid sulphur dioxide. The resulting green solid product was shown to be *cis*-$[Mo(SO_2)(CO)_2(dmpe)_2][PF_6]_2$ by microanalysis, i.r. spectroscopy [1 925vs and 1 889s cm^{-1} (KBr disc)], and conductivity. Solutions of this salt in methyl cyanide, dimethyl sulphoxide, and acetone decompose, releasing SO_2. These observations show that, when hydride formation is not possible, oxidation gives *cis*-$[Mo(CO)_2(dmpe)_2]^{2+}$ which will react with a donor such as SO_2 which is present in large excess, but substitution of a carbonyl ligand does not occur.

A yellow crystalline solid can be isolated from the reaction between equimolar quantities of $[NO][PF_6]$ and *cis*-$[Cr(CO)_2(dmpe)_2]$ in dry methanol. The i.r. spectrum of the solid shows *two* ν(CO) frequencies (1 862vs and 1 850s cm^{-1}) and conductivity measurements indicate that the solid is a 1 : 1 electrolyte. E.s.r. spectra show that the solid is paramagnetic with a five-line spectrum (*g* 2.003; a_P 30 G) ‡ due to coupling of an unpaired

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* *Note added in proof*: M. R. Snow and F. L. Wimmer (*Austral. J. Chem.*, 1976, **29**, 2349) have re-examined the reaction between $[NO][PF_6]$ and *cis*-$[Mo(CO)_2(dppe)_2]$ since this manuscript was submitted. In CH_2Cl_2, the product which was previously reported [11] as *cis*-$[Mo(CO)_2(dppe)_2][PF_6]$ is shown to be *cis*-$[MoF(CO)_2(dppe)_2][PF_6]$. In nitroalkane solvents, the oxidation products include $[\{Mo(CO)_2(dppe)_2\}_2F][PF_6]_3$ and *cis*-$[MoF(CO)_2(dppe)_2][PF_6]$, rather than *cis*-$[Mo(CO)_2(dppe)_2][PF_6]$ as reported [11] earlier. In acetonitrile or benzonitrile solution the product is shown to be $[Mo(NCR)(CO)_2(dppe)_2][PF_6]_2$ (R = Me or Ph) rather than *cis*-$[Mo(CO)_2(dppe)_2][PF_6]$ as reported by others.[4]

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

‡ Throughout this paper: 1 G = 10^{-4} T; 1 Torr = (101 325/760) Pa.

[10] M. K. Lloyd and J. A. McCleverty, *J. Organometallic Chem.*, 1973, **61**, 261.

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

[12] N. G. Connelly and R. L. Davis, *J. Organometallic Chem.*, 1976, **120**, C16.

electron with four equivalent phosphorus atoms. On this evidence and comparison with the analogous molybdenum system, the solid consists of a mixture of *trans*-$[Cr(CO)_2(dmpe)_2][PF_6]$ [ν(CO) at 1 850 cm^{-1}] and *trans*-$[CrH(CO)_2(dmpe)_2][PF_6]$ [ν(CO) at 1 862 cm^{-1}]. The mixture could not be separated by fractional crystallisation. The addition of perchloric acid in methanol solution failed to convert all the chromium(I) salt into the chromium(II) hydride salt, so that it was not possible for us to detect the expected high-field resonance in the n.m.r. spectrum of the latter.

TABLE 3

Infrared and n.m.r. spectra of $[MH(CO)_2(L{-}L)_2]Y$ complexes and related molecules

Complex	$\tilde{\nu}$(CO)/cm^{-1}	τ(M–H)	^2J/Hz HMP$_A$	HMP$_B$	Ref.
(*a*) ^{1}H n.m.r.					
$[CrH(CO)_2(dmpe)_2][PF_6]$	1 862				*a*
$[CrH(CO)_2(dppm)_2][ClO_4]$	1 881 ^{b}	17.1 ^{c}	109	27	16
$[MoH(CO)_2(dmpe)_2]I$	1 872 ^{b}	17.4 ^{d}	69	8	9
$[MoH(CO)_2(dmpe)_2][SFO_3]$	1 872 ^{b}	17.1 ^{e}	70	8	*a*
$[MoH(CO)_2(dmpe)_2][PF_6]$	1 872 ^{b}	16.8 ^{d}	73	8	*a*
$[MoH(CO)_2(dmpe)_2][BF_4]$	1 874 ^{b}	16.7 ^{d}	72	8	*a*
$[MoH(CO)_2(dmpe)_2][HCl_2]$	1 872 ^{b}	16.6 ^{d}	70	8	*a*
$[MoH(CO)_2(dppe)_2][H(OCOCF_3)_2]$	1 880 ^{b}	15.4 ^{d}	72	12	*m*
$[MoH(CO)_2(dppm)_2][ClO_4]$	1 894 ^{b}	11.99 ^{c}	66	14	16
$[WH(CO)_2(dmpe)_2][HCl_2]$	1 857 ^{b}	16.5 ^{c}	73	9	*a*
$[WH(CO)_2(dmpe)_2][BF_4]$	1 855 ^{b}	16.5 ^{d}	72	9	*a*
$[WH(CO)_2(dppe)_2][SO_2(OCF_3)]$	1 862 ^{b,f}	14.91 ^{d}	74	13	22
$[WH(CO)_2(dppm)_2][ClO_4]$	1 878 ^{b}	11.54 ^{c}	66	14	16
$[NbH(CO)_2(dmpe)_2]$ ^{g}	1 700—1 750 ^{h}	14.46 ^{h}	92	14	*i*
$[TaH(CO)_2(dmpe)_2]$ ^{g}	1 737 ^{h}	14.2 ^{h,d}	89	14	14, *j*
$[WH(CO)(CS)(dppe)_2][SO_2(OCF_3)]$	1 958 ^{b}	12.79 ^{d}	72	13	22
$[WH(C_2H_4)_2(dppe)_2][SO_2(OCF_3)]$		18.23	92	17	*k*
$[WH(N_2)_2(dppe)_2][HCl_2]$		13.50 ^{c}	7	0.5	15

(*b*) ^{31}P N.m.r. of $[MH(CO)_2(dmpe)_2][HCl_2]$

M	δ(^{31}P) ^{l}/p.p.m.	J/Hz ^2J(HMP$_i$)	^1J(WP)	*i*
Mo	−31.1	8		X
	−53.6	70		A
W	−9.5	9	193	X
	−31.9	72	162	A

^2J(PP) in AA′XX′

M	J(AX)	J(AX′)	|J(AA′)|	|J(XX′)|
Mo	±43.0	∓27.6	40.7	10.6
W	±32.2	∓22.7	32.7	13.5

[a] This work. [b] In CH_2Cl_2. [c] In CD_2Cl_2. [d] In $CDCl_3$. [e] In $(CD_3)_2CO$. [f] Also at 1 968w cm^{-1}. [g] Stereochemically non-rigid. [h] In C_6D_6. [i] R. R. Schrock, *J. Organometallic Chem.*, 1976, **121**, 373. [j] F. N. Tebbe, *J. Amer. Chem. Soc.*, 1973, **95**, 5823. [k] J. W. Byrne, H. U. Blaser, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1975, **97**, 3872. [l] Relative to 85% H_3PO_4. [m] M. R. Snow and F. L. Wimmer, personal communication.

When $[NO][PF_6]$ (2 mol) was added to *cis*-$[Cr(CO)_2(dmpe)_2]$ (1 mol) in methyl cyanide solution an orange colour developed. The salt *cis*-$[Cr(CO)_2(NCMe)(dmpe)_2][PF_6]$ [ν(CO) at 1 952vs and 1 883s cm^{-1} in MeCN solution; ν(CN) at 2 290w cm^{-1} in Nujol] is formed. The formation of *trans*-$[Cr(CO)_2(dmpe)_2]^+$ as an intermediate in this reaction was indicated by the e.s.r. spectrum of the reaction mixture.

Hydrido-complexes.—Reaction between *cis*-$[Mo(CO)_2(dmpe)_2]$ and $[NO][PF_6]$ in methanol, or $[OEt_3][BF_4]$ in CH_2Cl_2, or $BF_3{\cdot}Me_2O$, or $SFO_2(OMe)$ in CH_2Cl_2, led either directly or eventually to the formation of the *trans*-$[MoH(CO)_2(dmpe)_2]^+$ cation in the form of its hexafluorophosphate, tetrafluoroborate, or fluorosulphate salt. The formation of a tetrahalogenoborate anion $[BX_4]^-$ from BX_3 has previously been observed [13] in the reaction of BX_3 with *trans*-$[Cr(CO)_4(PMe_3)\{C(OMe)Me\}]$. In addition, we have prepared *trans*-$[WH(CO)_2(dmpe)_2][HCl_2]$ by the reaction of HCl with *cis*-$[W(CO)_2(dmpe)_2]$. The hydrogendichloride salt was converted into the tetrafluoroborate by treatment with cyclopentadienylthallium and silver(I) tetrafluoroborate. Some i.r. and n.m.r. spectroscopic measurements relating to these hydride complexes are shown in Table 3. The ^{1}H n.m.r. spectra are invariant in the temperature range 220—320 (Mo) and 220—350 K(W). The magnitudes of ^2J(PMH) suggest that the [P–M–H] unit is not linear in both the molybdenum and tungsten cations, so that with the carbonyl groups essentially *trans* to one another the hydrogen atom could occupy one face of the $[MC_2P_4]$ octahedron in the sense of a monocapped octahedral structure. The complex $[TaH(CO)_2(dmpe)_2]$, which is isoelectronic with the tungsten cation, has a capped-octahedral structure;[14] however, the comparable cation $[WH(N_2)_2(dppe)_2]^+$ has been shown to have a pentagonal-bipris-

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[13] E. O. Fischer and K. Richter, *Chem. Ber.*, 1976, **109**, 3079.

[14] P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1025.

matic structure.[15] The preparation of these hydrides is similar to that of *trans*-$[MH(CO)_2(dppm)_2][ClO_4]$ (M = Cr, Mo, or W; dppm = $Ph_2PCH_2PPh_2$) from *cis*-$[M(CO)_2(dppm)_2]$ by oxidation with oxygenated $HClO_4$ in dichloromethane.[16]

The addition of excess (>10 molar) of 1,8-bis(dimethylamino)naphthalene (bdn) to *trans*-$[MoH(CO)_2(dmpe)_2][PF_6]$ in refluxing methyl cyanide caused reduction of the molybdenum as a result of proton abstraction to form *cis*-$[Mo(CO)_2(dmpe)_2]$. This is in contrast to the addition of only 1 mol of the same ditertiary amine, bdn, to *trans*-$[MoH(CO)_2(dmpe)]I$ in refluxing methyl cyanide. Over a period of 24 h reduction of the cationic hydride to *cis*-$[Mo(CO)_2(dmpe)_2]$ and, presumably, [bdn]I is followed by re-oxidation to form *cis*-$[MoI(CO)_2(dmpe)_2]I$ as a result of equilibria such as $[bdn]I \rightleftharpoons bdn + HI$ and $2HI \longrightarrow H_2 + I_2$ which generate iodine. The reaction between *cis*-$[Mo(CO)_2(dmpe)_2]$ and iodine is known[17] to produce *cis*-$[MoI(CO)_2(dmpe)_2]I$ quantitatively.

The addition of a 2—3 molar excess of an alkyl bromide RBr (R = prop-2-enyl or benzyl) to *trans*-$[MoH(CO)_2(dmpe)_2]Y$ (Y = I or PF_6) in refluxing methyl cyanide resulted in the substitution of hydride by bromide and the formation of *cis*-$[MoBr(CO)_2(dmpe)_2]Y$. The formation of $[Mo(\eta\text{-}C_3H_5)(CO)(dmpe)_2]Y$ was not observed. Addition of iodine to *trans*-$[MoH(CO)_2(dmpe)_2]Y$ under the same conditions produced *cis*-$[MoI(CO)_2(dmpe)_2]Y$. The addition of bromine or iodine to *trans*-$[MoH(CO)_2(dppm)_2]^+$ in dichloromethane is known[16] to produce *cis*-$[MoX(CO)_2(dppm)_2]X$ (X = I or Br).

When *trans*-$[MoH(CO)_2(dmpe)_2]I$ was heated in refluxing methyl cyanide solution or irradiated in methyl cyanide solution with light from a medium-pressure mercury discharge lamp there was no evidence for the formation of $[MoHI(CO)(dmpe)_2]$, in contrast to *cis*-$[MoI(CO)_4(dmpe)]I$ which readily forms $[MoI_2(CO)_3(dmpe)]$ under the same conditions.[17] Irradiation with light from a medium-pressure mercury discharge lamp of a dilute methyl cyanide solution containing equimolar quantities of *trans*-$[MoH(CO)_2(dmpe)_2][PF_6]$ and $[Mo(\eta\text{-}C_5H_5)(CO)_3Me]$ gave no evidence for the formation of a metal–metal-bonded species such as $[(\eta\text{-}C_5H_5)(CO)_3Mo\text{-}Mo(CO)_2(dmpe)_2][PF_6]$. The hydride was recovered, but the metal alkyl decomposed, so that $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ was formed.

Conclusions.—The deduction of a *fac* stereochemistry for complexes of the type $[M(CO)_3(NO)(L\text{-}L)][PF_6]$ (L–L = dcpe or dmpe) indicates that the reaction between *cis*-$[M(CO)_4(L\text{-}L)]$ and $[NO][PF_6]$ results in substitution of a carbonyl ligand *cis* to the chelating ditertiary phosphine. This is consistent with many other results which show that carbonyl groups *cis* to phosphorus are labile to substitution.[18] The fact that the stereochemistry is maintained even for the more sterically demanding dcpe ligand (θ 142°) may suggest that the approach of the $[NO]^+$ electrophile is governed by the greater electron density at the metal in complexes of alkyl- compared to aryl-phosphines. If it is assumed that the reaction involves a bimolecular transition state, then these facts imply that the preferred direction of approach of $[NO]^+$ to the $[MC_4P_2]$ octahedron is at one or other of the two trigonal $M(CO)_3$ faces.

There are no significant differences between the products of the reactions between $[NO][PF_6]$ and the molybdenum and tungsten complexes *cis*-$[M(CO)_4(L\text{-}L)]$ in methyl cyanide solution which result from changing the ligand L–L. For chromium this is not the case; with ditertiary alkylphosphines we find that L–L is retained and the metal is oxidised to form *fac*-$[Cr(NCMe)_3(NO)(L\text{-}L)]^{2+}$, but when L–L is less basic (dppe) no oxidation occurs, L–L is displaced,[5] and the product is $[Cr(NCMe)_4(NO)_2][PF_6]_2$. This difference is consistent with the greater ease of oxidation[19] of dmpe complexes compared to their dppe analogues, and emphasises the harder acid character of Cr^{II} compared to Mo^{II}.

It has not,[20] so far, been possible to prepare complexes of the type $[M(CO)_2(dcpe)_2]$ so that our comparison of reactivity is restricted. Notwithstanding this limitation, we notice that whereas oxidation of *cis*-$[Mo(CO)_2(dppe)_2]$ by $[NO][PF_6]$ produces a six-co-ordinate complex of Mo^I initially and, with excess of $[NO][PF_6]$, a seven-co-ordinate complex[20b] of Mo^{II}, similar reaction of *cis*-$[Mo(CO)_2(dmpe)_2]$ produces uniquely a seven-co-ordinate molybdenum(II) complex the nature of which is dependent on the solvent. This behaviour is very similar to that[16] of *cis*-$[Mo(CO)_2(dppm)_2]$. It is particularly noteworthy that the dmpe complex does not undergo substitution of CO by $[NO]^+$ because it has been shown[21] that the cation which would result, $[Mo(CO)(NO)(dmpe)_2]^+$, can be prepared simply by reaction of *cis*-$[Mo(CO)_2(dmpe)_2]$ with $Ag[NO_2]$. In this latter reaction both CO_2 and N_2O are produced; it would seem that the formation of these gaseous products provides a driving force for the reaction with nitrite ion which is not available in the case of nitrosonium ion.

The reaction between *cis*-$[Cr(CO)_2(dmpe)_2]$ and $[NO][PF_6]$ is different again. In methanol solution oxidation produces both Cr^I and a chromium(II) hydrido-complex; in methyl cyanide solution oxidation proceeds *via* a chromium(I) intermediate to give a chromium(II) solvato-complex cation. Both $[NO][PF_6]$ and $Ag[ClO_4]$ are reported[16] to oxidise *cis*-$[Cr(CO)_2(dppm)_2]$ to paramagnetic *trans*-$[Cr(CO)_2(dppm)_2]^+$ [ν(CO) at 1 869 cm^{-1}; *g* 2.00; a_P 27.4 G] in dichloromethane; reaction with $HClO_4$ causes oxidation to the chromium(II) cation *trans*-

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[15] G. A. Heath, J. Chatt, and R. L. Richards, *J.C.S. Dalton*, 1974, 2074.

[16] A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, 1975, **14**, 2526.

[17] J. A. Connor, G. K. McEwen, and C. J. Rix, *J.C.S. Dalton*, 1974, 589.

[18] R. J. Angelici, *Organometallic Chem. Rev.*, 1968, **3**, 173.

[19] M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, and G. K. McEwen, *J.C.S. Dalton*, 1973, 1743.

[20] (*a*) J. A. Connor and P. I. Riley, *J. Organometallic Chem.*, 1975, **94**, 55; (*b*) F. L. Wimmer, M. R. Snow, and A. M. Bond, *Inorg. Chem.*, 1974, **13**, 1617.

[21] J. A. Connor and P. I. Riley, *J.C.S. Chem. Comm.*, 1976, 149.

$[CrH(CO)_2(dppm)_2]^+$ [ν(CO) at 1 881 cm^{-1}] which on standing in either acetone or dichloromethane is reduced to *trans*-$[Cr(CO)_2(dppm)_2]^+$. In contrast to *cis*-$[Cr(CO)_4(dmpe)]$, which on oxidation with $[NO]^+$ in methyl cyanide undergoes substitution of CO by MeCN, the oxidation product of *cis*-$[Cr(CO)_2(dmpe)_2]$ does *not* undergo substitution of either CO or dmpe.

A number of interesting conclusions can be drawn from the spectroscopic properties of the series of cationic hydrides of the general type $[MH(CO)_2(L\text{–}L)_2]^+$ (M = Cr, Mo, or W; L–L = dmpe, dppe, or dppm) which we and others [14,16,22] have measured (Table 3). We wish to draw particular attention to the following. First, that the value of ν(CO) increases in the order L–L = dmpe < dppe < dppm for each metal. Secondly, that the value of τ(M–H) is not significantly influenced by the anion used and decreases in the order L–L = dmpe > dppe > dppm. These two pieces of information are consistent with there being a decrease in electron density at the metal atom in the cations from dmpe to dppm. It is possible that the rather large high-field shift of the hydride resonance in $[CrH(CO)_2(dppm)_2]^+$ may be the result of perturbations caused by the presence of paramagnetic contaminants, as this cation is reported [16] to decompose to *trans*-$[Cr(CO)_2(dppm)_2]^+$ on standing in solution.

In terms of chemical behaviour, we have drawn attention to the empirical observations of a similarity between dmpe and dppm as ligands in analogous complexes. This suggests that the electronic effect discussed above is counterbalanced by a steric influence. The cone angle [1] of the dppm ligand (θ 121°) is not greatly different from dppe and is larger than dmpe.

EXPERIMENTAL

The details of general procedures, methods, and materials used in this work have been described before.[17] In addition, e.s.r. spectra were recorded on either a Varian V4502 *Q*-band (35 GHz) or on a Varian E4 *X*-band (9.5 GHz) spectrometer for solids and solutions respectively. Methyl fluorosulphate, 1,8-bis(dimethylamino)naphthalene, and nitrosonium hexafluorophosphate were purchased from Aldrich.

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*dicarbonylchromium*.—The complex $[Cr(CO)_6]$ (0.86 g, 3.9 mmol) and dmpe (1.5 cm^3, 7.8 mmol) were sealed in an evacuated Carius tube (*ca.* 100 cm^3) and heated to 473 K for 72 h. The tube was cooled, opened, and the yellow solid was extracted into dichloromethane. The solvent was removed and *cis*-$[Cr(CO)_4(dmpe)]$ was sublimed from the mixture at 383 K (bath temperature) on to a cooled (acetone–solid CO_2) probe at a pressure of 10^{-2} Torr. The residue was taken up in dichloromethane and pure *cis*-$[Cr(CO)_2(dmpe)_2]$ was isolated by precipitation with hexane. Physical properties of the yellow crystalline solid were in agreement with those measured previously,[17] yield 0.95 g (2.3 mmol, 60%).

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*tricarbonylnitrosyltungsten Hexafluorophosphate*.—Solid $[NO][PF_6]$ (0.39 g, 2.1 mmol) was added to a stirred solution of *cis*-$[W(CO)_4(dmpe)]$ (0.94 g, 2.1 mmol) in methyl cyanide (25 cm^3). When the initial effervescence had subsided the solution was stirred for a further 20 min. The solvent was removed by distillation under reduced pressure and the resulting solid was extracted with dichloromethane. Addition of hexane to the combined extracts produced pale yellow crystals of the complex (0.98 g, 75%) (Found: C, 18.1; H, 2.7; N, 2.5; P, 15.7; W, 30.6. $C_9H_{16}F_6NO_4P_3W$ requires C, 18.2; H, 2.7; N, 2.4; P, 15.7; W, 31.0%). Conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$ at 291 K): 87 S cm^2 mol^{-1}. $\nu(PF_6)$ at 840 cm^{-1} (Nujol). δ in [$^2H_6$]acetone: 2.3 (1 H, m), 1.74 (d, ^2J 10), and 1.51 p.p.m. (3 H, d, ^2J 10 Hz). Similarly, $[Mo(CO)_3(NO)(dmpe)][PF_6]$ was prepared from *cis*-$[Mo(CO)_4(dmpe)]$, and $[W(CO)_3(dcpe)][PF_6]$ from *cis*-$[W(CO)_4(dcpe)]$.

When solid $[NO][PF_6]$ (0.19 g, 1.08 mmol) was added to a stirred solution of *cis*-$[W(CO)_4(dmpe)]$ (0.24 g, 0.54 mmol) in methyl cyanide (25 cm^3) the usual initial effervescence was observed. The gases evolved in this way were shown to consist of a mixture of CO_2, CO, N_2O, and NO_2. The solution was then stirred for 20 min after which the solvent was removed by distillation under reduced pressure. The resulting green solid was extracted with acetone and filtered. Addition of excess of hexane to the filtrate deposited a green oil. The oil was isolated and on drying *in vacuo* (10^{-2} Torr) slowly solidified to a green *solid* (Found: C, 17.7; H, 2.9; N, 2.5; P, 15.6; W, 30.6. $C_{18}H_{30}F_{12}N_2O_8P_6W_2$ requires C, 18.2; H, 2.5; N, 2.4; P, 15.7; W, 31.3%). Conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$ at 291 K): 198 S cm^2 mol^{-1}. $\nu(PF_6)$ at 835 cm^{-1} (Nujol).

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*tris*(*methyl cyanide*)*nitrosylchromium*(I) *Bis*(*hexafluorophosphate*).—Solid $[NO][PF_6]$ (0.145 g, 0.828 mmol) was added to a stirred solution of *cis*-$[Cr(CO)_4(dmpe)]$ (0.13 g, 0.414 mmol) in methyl cyanide (15 cm^3), producing an orange solution. After stirring for 15 min, diethyl ether was added to precipitate an orange solid. The solid was isolated and purified by precipitation with hexane from a dichloromethane solution and finally dried *in vacuo* (0.21 g, 0.33 mmol, 80%) (Found: C, 21.5; H, 3.9; Cr, 7.8; N, 7.7; P, 19.3. $C_{12}H_{25}CrF_{12}N_4OP_4$ requires C, 22.3; H, 3.9; Cr, 8.1; N, 8.7; P, 19.2%). $\nu(PF_6)$ at 835 cm^{-1} (Nujol). Conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$ at 291 K): 163 S cm^2 mol^{-1}.

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*dicarbonylhydridomolybdenum*(II) *Hexafluorophosphate*.—Solid $[NO][PF_6]$ (0.167 g, 0.96 mmol) was added to a stirred solution of *cis*-$[Mo(CO)_2dmpe)_2]$ (0.432 g, 0.96 mmol) in methanol (15 cm^3). A cream solid precipitated from the solution. Precipitation was completed by the addition of diethyl ether (20 cm^3). The precipitate was isolated by filtration and twice recrystallised from dichloromethane–hexane (1 : 3 v/v) to give fawn-yellow crystals of the complex (0.49 g, 0.82 mmol, 85%) (Found: C, 28.1; H, 5.6; Mo, 15.7; P, 26.3. $C_{14}H_{33}F_6MoO_3P_5$ requires C, 28.1; H, 5.5; Mo, 16.0; P, 25.9%). $\nu(PF_6)$ at 830 cm^{-1} (Nujol). Conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$ at 292 K): 84 S cm^2 mol^{-1}. δ in $CDCl_3$: 2.00 (4 H, m), 1.76 (d, ^2J 9.2), and 1.66 p.p.m. (d, 12 H, ^2J 7.4 Hz).

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*dicarbonyl*(*sulphur dioxide*) *molybdenum*(II) *Bis*(*hexafluorophosphate*).—Sulphur dioxide (20 cm^3) was condensed into a Schlenk tube at 195 K and to this was added *cis*-$[Mo(CO)_2(dmpe)_2]$ (0.32 g, 0.71 mmol) which dissolved to form a red solution. Addition of solid $[NO][PF_6]$ (0.248 g, 1.42 mmol) to this solution caused the colour to change to yellow-green. The cooling bath was

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[22] B. D. Dombeck and R. J. Angelici, *Inorg. Chem.*, 1976, **15**, 2397.

removed and the excess of sulphur dioxide was evaporated by a rapid flow of nitrogen. The resulting pale green solid was shaken vigorously for 6 h *in vacuo* (10^{-2} Torr) (Found: C, 21.0; H, 4.3; Mo, 13.0; P, 23.1; S, 3.0. $C_{14}H_{32}F_{12}MoO_4P_6S$ requires C, 20.9; H, 4.0; Mo, 11.9; P, 23.1; S, 4.0%). ν(KBr disc) at 1 313, 1 298, 1 160, 558 (SO_2), and 833 cm^{-1} (PF_6). Conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$ at 293 K): 133 S cm^2 mol^{-1}.

Reactions Leading to the Formation of $[MoH(CO)_3(dmpe)_2]^+$ *Salts.—With* $[OEt_3][BF_4]$. Solid $[OEt_3][BF_4]$ (0.22 g, 1.2 mmol), which had been repeatedly washed with dry diethyl ether and then dried for 6 h *in vacuo* (10^{-2} Torr) prior to use, was added to a stirred solution of *cis*-$[Mo(CO)_2(dmpe)_2]$ (0.536 g, 1.2 mmol) in dichloromethane (20 cm^3). Excess of diethyl ether was immediately added to the solution which on cooling in ice deposited yellow crystals of *trans*-$[MoEt(CO)_2(dmpe)_2][BF_4]$.[21] This crystalline solid and its solution decomposed rapidly at room temperature to give a brown solid from which fawn crystals were obtained by crystallisation (CH_2Cl_2–Et_2O, 1 : 1 v/v) (Found: C, 31.1; H, 6.1; Mo, 17.8; P, 22.9. $C_{14}H_{33}BF_4MoO_2P_4$ requires C, 30.9; H, 6.1; Mo, 18.3; P, 22.5%). ν(BF_4) at 1 050 cm^{-1} (Nujol). Conductivity (10^{-3} mol dm^{-3} solutions in $MeNO_2$): 106 S cm^2 mol^{-1}.

With $SFO_2(OMe)$. Methyl fluorosulphate was first used to rinse the apparatus which was flamed out *in vacuo*; $SFO_2(OMe)$ was then distilled from $SO_2(OMe)_2$ directly into a stirred solution of *cis*-$[Mo(CO)_2(dmpe)_2]$ (0.3 g, 0.66 mmol) in dichloromethane (10 cm^3). The solution changed colour to deep yellow. Hydrogen-1 n.m.r. and i.r. spectra showed that the solution contained *trans*-$[MoMe(CO)_2(dmpe)_2][SFO_3]$.[21] Addition of excess of diethyl ether to the solution after it had stood at room temperature for *ca.* 1 h precipitated a fawn solid which was recrystallised (twice) from CH_2Cl_2–Et_2O (1 : 1 v/v) (Found: C, 30.4; H, 6.1; Mo, 17.0; P, 22.7. $C_{14}H_{33}FMoO_5P_4S$ requires C, 30.4; H, 6.0; Mo, 17.4; P, 22.5%). ν(SFO_3) at 1 285 cm^{-1} (Nujol). Conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$): 82 S cm^2 mol^{-1}.

[1,2-*Bis(dimethylphosphino)ethane*]*dicarbonylhydridotungsten*(II) *Hydrogendichloride.*—Hydrogen chloride gas, dried by passage through concentrated sulphuric acid and molecular sieves, was allowed to mix with a stirred solution of *cis*-$[W(CO)_2(dmpe)_2]$ [17] (0.80 g, 1.48 mmol) in dichloromethane (20 cm^3). The solution became cloudy. Addition of diethyl ether when the gas flow had been stopped caused precipitation of a pale buff solid which was twice recrystallised from CH_2Cl_2–C_6H_{14} (3 : 1 v/v) to give crystals (Found: C, 27.8; H, 5.8; Cl, 11.1; P, 21.0; W, 29.8. $C_{14}H_{34}Cl_2O_2P_4W$ requires C, 27.4, H, 5.5; Cl, 11.6; P, 20.2; W, 30.0%). Conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$): 110 S cm^2 mol^{-1}.

Reaction of cis-$[Cr(CO)_2(dmpe)_2]$ *with* $[NO][PF_6]$.—*In methanol solution.* Solid $[NO][PF_6]$ (0.076 g, 0.44 mmol) was added to a solution of *cis*-$[Cr(CO)_2(dmpe)_2]$ (0.178 g, 0.44 mmol) in methanol (10 cm^3) and the mixture was stirred for 0.5 h at ambient temperature. Methanol was slowly removed by distillation under reduced pressure. Yellow crystals were deposited from the solution and these were collected and dried *in vacuo* (Found: C, 30.0; H, 5.9; Cr, 9.0; P, 27.0. $C_{14}H_{32}CrF_6O_2P_5$ requires C, 30.4; H, 5.8; Cr, 9.4; P, 28.0. $C_{14}H_{33}CrF_6O_2P_5$ requires C, 30.3, H, 5.9; Cr, 9.4; P, 28.0%).

In methyl cyanide. Solid $[NO][PF_6]$ (0.32 g, 1.84 mmol) was added in small portions to a solution of *cis*-$[Cr(CO)_2(dmpe)_2]$ (0.37 g, 0.92 mmol) in methyl cyanide (40 cm^3). An orange colour developed and after stirring for 0.5 h at ambient temperature the addition of dry diethyl ether precipitated a deep yellow-orange solid. The solid was purified by several reprecipitations from methyl cyanide, washed with diethyl ether, and dried *in vacuo* (Found: C, 26.5; H, 4.9; Cr, 7.5; N, 2.0; P, 25.4. $C_{16}H_{35}CrF_{12}NO_2P_6$ requires C, 26.0; H, 4.7; Cr, 7.0; N, 1.9; P, 25.2%). Conductivity (10^{-3} mol dm^{-3} solution in $MeNO_2$): 150 S cm^2 mol^{-1}.

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