Phosphorus–Phosphorus Coupling Constants in Trifluoromethylphosphine Group VIA Metal Complexes

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Phosphorus–phosphorus coupling constants, $^2J(PP')$, have been evaluated from ^{19}F (and in certain cases ^1H and ^{31}P) n.m.r. spectra of *cis*-$L_2M(CO)_4$ complexes [L = $(CF_3)_2PR$ or CF_3PQ_2; M = Cr, Q = H; M = Mo, Q = Cl, Br, H; R = Cl, Br, I, H]. The data, together with published values for the $(CF_3)_2PF$ and CF_3PF_2 complexes, indicate that the magnitude of $^2J(PP')$ for the molybdenum series decreases in the order R = F > Cl > Br > I > H and Q = F > Cl $\sim$ Br $\gg$ H. The values for the CF_3PH_2 complexes are unusually small. The complexes *cis*-$[(CF_3)_2PNMe_2]_2Mo(CO)_4$ and *cis*-$[(CF_3)_2PNCS]_2Mo(CO)_4$ are described and solution n.m.r. data suggest that intermolecular phosphine exchange is occurring.

THERE is current interest [1,2] in the factors affecting the magnitude and signs of geminal phosphorus–phosphorus coupling constants, $^2J(PP')$, of transition-metal phosphine complexes. As an extension of our previous n.m.r. studies on fluorophosphine transition-metal complexes,[3-7] we have prepared a related series of trifluoromethylphosphine Group VIA metal carbonyl derivatives of the type *cis*-$L_2M(CO)_4$ [$L = (CF_3)_2PR$, M = Mo, R = Cl, Br, I, H, NCS, NMe_2; $L = CF_3PQ_2$, M = Cr, Q = H; M = Mo, Q = Cl, Br, H], which are examples of $[X_6A]_2$ and $[X_3A]_2$ nuclear spin systems (here X = fluorine, A = phosphorus). The effect of any other magnetic nuclei in the R or Q groups is discussed later.

The general appearance of the X part of n.m.r. spectra of the $[X_nA]_2$ type has been discussed in detail elsewhere [1,8,9] and is critically dependent on the relative magnitudes of $[J(AX) - J(AX')]$ and $J(AA')$. For strongly coupled systems $J(AA') \gg [J(AX) - J(AX')]$ and 'deceptively simple' patterns are often observed and make accurate evaluation of the coupling constants extremely difficult.[1] When, however, $J(AA') \ll [J(AX) - J(AX')]$ as is the case in fluorophosphine complexes [here $J(AX) = {}^1J(PF)$ which lies in the 1000—1400 Hz range and $J(AX') = {}^3J(PF')$ is small], the X part of the spectrum is well resolved and all the coupling constants can usually be accurately evaluated.

Transition-metal complexes of the trifluoromethylphosphines $(CF_3)_2PR$ and CF_3PQ_2 seemed particularly attractive for n.m.r. investigation because $^2J(PF)$ values for the free ligands lie in the 60—100 Hz range [10,11] and only change slightly when the phosphine is coordinated. Previous work [3] on molybdenum complexes of $(CF_3)_2PF$ and CF_3PF_2 suggested $^2J(PP')$ would always be smaller than $^2J(PF) - {}^4J(PF')$ for similar trifluoromethylphosphine complexes, thus fulfilling the requirement for accurate spectral analysis. Many of the trifluoromethylphosphines employed had not been used previously as ligands in transition-metal complexes.

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[1] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345 and references therein.

[2] E. G. Finer, R. K. Harris, and J. R. Woplin, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 61 and references therein.

[3] C. G. Barlow, J. F. Nixon, and J. R. Swain, *J. Chem. Soc.* (*A*), 1969, 1082.

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[5] J. F. Nixon and T. R. Johnson, *J. Chem. Soc.* (*A*), 1969, 2518.

[6] T. R. Johnson, R. M. Lynden-Bell, and J. F. Nixon, *J. Organometallic Chem.*, 1970, **21**, P15.

[7] R. M. Lynden-Bell, J. F. Nixon, J. Roberts, J. R. Swain, and W. McFarlane, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1187.

[8] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[9] R. K. Harris, *Inorg. Chem.*, 1966, **5**, 701.

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[11] J. F. Nixon, *J. Chem. Soc.*, 1965, 777.

Synthesis and Characterisation of the Complexes.—The trifluoromethylphosphine complexes listed in Table 1 were obtained by displacement of norbornadiene from the appropriate tetracarbonyl norbornadiene metal complex, $C_7H_8M(CO)_4$ (M = Cr or Mo), by treatment with excess ligand (equations 1 and 2).

$$2(CF_3)_2PR + C_7H_8Mo(CO)_4 \longrightarrow cis\text{-}[(CF_3)_2PR]_2Mo(CO)_4 + C_7H_8 \quad (1)$$

(C_7H_8 = norbornadiene, R = Cl, Br, I, NMe_2, NCS, H)

$$2CF_3PQ_2 + C_7H_8M(CO)_4 \longrightarrow cis\text{-}[CF_3PQ_2]_2M(CO)_4 + C_7H_8 \quad (2)$$

(M = Mo, Q = Cl, Br, H; M = Cr, Q = H)

The molybdenum complexes were readily formed at room temperature, but the chromium complex was best prepared by heating the reactants to 60°. Hexane was used as solvent when the very volatile phosphines $(CF_3)_2PH$ and CF_3PH_2 were involved.

TABLE 1

Trifluoromethylphosphine Group VIA metal carbonyl complexes

Complex	M.p. or b.p.	I.r. C≡O stretching frequencies (in CCl_4 solution)
cis-$[(CF_3)_2PCl]_2Mo(CO)_4$	b.p. 40°, 10^{-3} mmHg	2084s, 2019s,sh, 2000vs
cis-$[(CF_3)_2PBr]_2Mo(CO)_4$	b.p. 50°, 10^{-3} mmHg	2080s, 2014s,sh, 1995vs
cis-$[(CF_3)_2PI]_2Mo(CO)_4$	m.p. *ca.* 25°	2072s, 2005s,sh, 1988vs †
cis-$[(CF_3)_2PH]_2Mo(CO)_4$	m.p. 52·5—54° (sublimes at 20°, 10^{-3} mmHg)	2074s, 2000s, 1978vs
cis-$[(CF_3)_2PNMe_2]_2Mo(CO)_4$	m.p. 73—74 (dec.)	2065s, 1989s, 1966vs,br
cis-$[(CF_3)_2PNCS]_2Mo(CO)_4$	b.p. 40°, 10^{-4} mmHg	2084s, 1980vs,br
cis-$(CF_3PCl_2)_2Mo(CO)_4$	b.p. 50°, 10^{-3} mmHg	2071s, 2006s,sh, 1985vs,br
cis-$(CF_3PBr_2)_2Mo(CO)_4$	b.p. 60°, 10^{-4} mmHg	2070s, 2005sh,s, 1990vs,br
cis-$(CF_3PH_2)_2Mo(CO)_4$	m.p. 53·5—54° (sublimes at 50°, 10^{-4} mmHg)	2051s, 1973s, 1955vs,br
cis-$(CF_3PH_2)_2Cr(CO)_4$	m.p. 53—55° (sublimes at 50°, 10^{-4} mmHg)	2043s, 1965s, 1945vs,br

† In hexane solution.

Apart from *cis*-$[(CF_3)_2PI]_2Mo(CO)_4$, all the compounds prepared (many of which are liquids at room temperature), are volatile and their mass spectra show parent-ion peaks. In contrast to the spontaneous inflammability of the free trifluoromethylphosphines, their metal complexes are not noticeably air-sensitive. Difficulty was experienced in obtaining an analytically pure sample of *cis*-$[(CF_3)_2PI]_2Mo(CO)_4$ and characterisation depended on its distinctive i.r. and n.m.r. spectra. An attempted synthesis of *cis*-$[CF_3PI_2]_2Mo(CO)_4$ under analogous mild conditions led to carbon monoxide evolution and extensive decomposition.

Infrared Spectra.—The i.r. spectra of the trifluoromethylphosphine metal complexes in the C≡O stretching frequency region show patterns typical of *cis*-$L_2M(CO)_4$ systems (Table 1). Comparison with published data[12] on the complexes *cis*-$[(CF_3)_2PF]_2Mo(CO)_4$ and *cis*-$(CF_3PF_2)_2Mo(CO)_4$ indicates that the highest frequency C≡O stretching mode decreases in the order R = F > Cl ~ NCS > Br > I ~ H > NMe_2 for *cis*-$[(CF_3)_2PR]_2$-$Mo(CO)_4$ complexes and in the order Q = F > Cl > Br > H for *cis*-$(CF_3PQ_2)_2Mo(CO)_4$ compounds.

N.m.r. Spectra.—The ^{19}F nuclear magnetic resonance spectra of all the halogenotrifluoromethylphosphine complexes are, as expected, clearly resolved and accurate values for $^2J(PP')$ can be readily obtained by inspection. Typical ^{19}F n.m.r. spectra are shown in Figures 1 and 2. For complexes of the ligands $(CF_3)_2PH$ and CF_3PH_2, $^1J(PH)$ is greater than 300 Hz and therefore in principle $^2J(PP')$ can be obtained from both the ^{19}F and the ^1H n.m.r. spectra. In practice, however, the accuracy of $^2J(PP')$ evaluated from either spectrum was limited by overlapping of lines arising from coupling between hydrogen and fluorine nuclei. A reasonable estimate of $^2J(PP')$ for *cis*-$[(CF_3)_2PH]_2Mo(CO)_4$ was made from the ^{19}F n.m.r. spectrum and values of $^2J(PP')$ for the complexes *cis*-$[CF_3PH_2]_2M(CO)_4$ (M = Cr, Mo) were obtained from the ^1H n.m.r. spectra (Figures 3 and 4). The ^{19}F n.m.r. spectra of the latter complexes were fully consistent with the values of $^2J(PP)$ determined from the ^1H n.m.r. spectra.

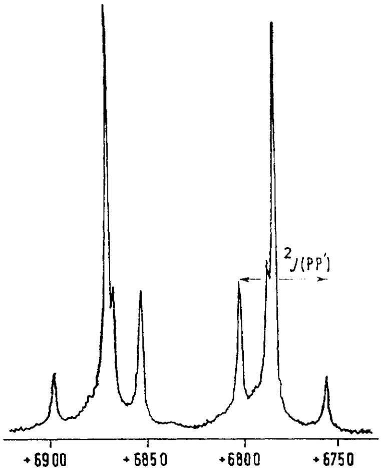

FIGURE 1 Fluorine n.m.r. spectrum (at 94·1 MHz) of *cis*-$(CF_3PBr_2)_2Mo(CO)_4$; scale in Hz relative to CCl_3F

Analysis of the ^1H n.m.r. spectra of both *cis*-$[CF_3PH_2]_2$-$M(CO)_4$ complexes, (M = Cr, Mo), established that

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[12] C. G. Barlow, J. F. Nixon, and M. Webster, *J. Chem. Soc.* (*A*), 1968, 2216.

^1J(PH) and ^3J(PH′) have the same sign, (most likely positive since ^1J(PH) is positive in unco-ordinated CF_3PH_2),[13] while ^1J(PH) and ^3J(PH′) are both larger in magnitude for the chromium complex than for the molybdenum compound in agreement with previous observations made on the analogous phosphine complexes *cis*-$(PH_3)_2M(CO)_4$.[14]

The coupling constants ^2J(PF) and ^4J(PF′) were found to have the same sign in all the trifluoromethylphosphine complexes and are considered positive since ^2J(PF) is known to be positive in the free phosphines[15,16] and only changes slightly in magnitude on co-ordination. Recently double resonance experiments established a positive sign for ^2J(PF) in *cis*-$(CF_3PH_2)_2Mo(CO)_4$.[17] Both ^2J(PF) and ^4J(PF′) in *trans*-$[CF_3PPh_2]_2PdCl_2$ are also believed to have the same sign.[18]

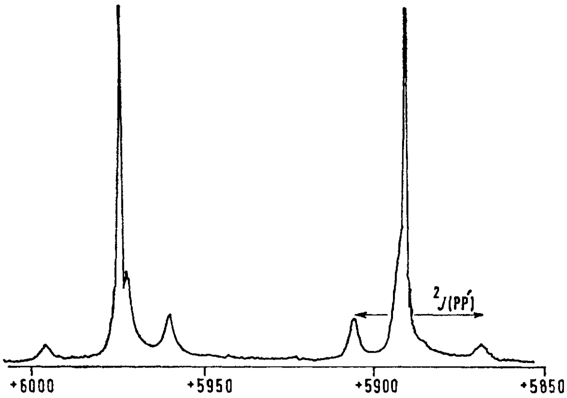

FIGURE 2 Fluorine n.m.r. spectrum (at 94·1 MHz) of *cis*-$[(CF_3)_2PBr]_2Mo(CO)_4$; scale in Hz relative to CCl_3F

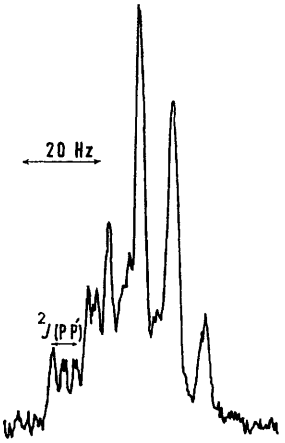

FIGURE 3 High field half of the ^1H n.m.r. spectrum (at 60 MHz) of *cis*-$(CF_3PH_2)_2Cr(CO)_4$

Grobe[19,20] has obtained values for ^4J(PF′) for complexes of the type $[Fe(CO)_3P(CF_3)_2X]_2$ and $[Co(CO)_3$-$P(CF_3)_2]_2$ containing $(CF_3)_2P$-bridging groups, which are considerably larger in magnitude than those found in the present work, and in one case ^4J(PF′) was found to be of opposite sign to ^2J(PF).[19] However, in these complexes ^2J(PP′) is large compared with [^2J(PF) − ^4J(PF′)] making accurate analysis of the spectra more difficult.

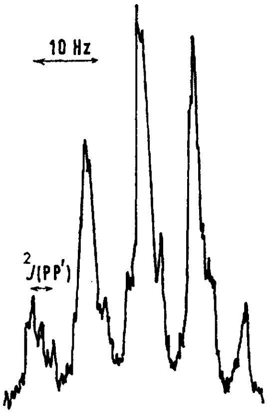

FIGURE 4 High field half of the ^1H n.m.r. spectrum (at 60 MHz) of *cis*-$(CF_3PH_2)_2Mo(CO)_4$

The 40·5 MHz ^{31}P n.m.r. spectrum of *cis*-$[CF_3PCl_2]_2$-$Mo(CO)_4$ is reproduced in Figure 5, together with the spectrum calculated for the A part of an $[X_3A]_2$ spin system[21] using parameters derived from the ^{19}F n.m.r. spectrum. The ^{31}P chemical shift of *cis*-$[(CF_3)_2PCl]_2$-$Mo(CO)_4$ (recorded at 24·29 MHz, stationary tube) is found to be 63 p.p.m. downfield from the free ligand value. A downfield ^{31}P chemical shift was also observed for *cis*-$[CF_3PH_2]_2Mo(CO)_4$ using the INDOR technique (Table 3).

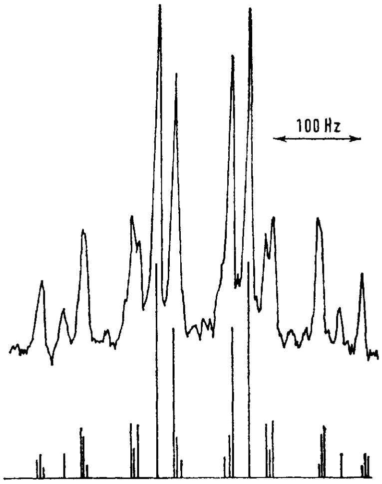

FIGURE 5 Observed and calculated 40·5 MHz ^{31}P n.m.r. spectra of *cis*-$(CF_3PCl_2)_2Mo(CO)_4$

[13] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1148.

[14] E. Moser and E. O. Fischer, *J. Organometallic Chem.*, 1968, **15**, 157.

[15] A. V. Cunliffe, E. G. Finer, R. K. Harris, and W. McFarlane, *Mol. Phys.*, 1967, **12**, 497.

[16] S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Amer. Chem. Soc.*, 1967, **89**, 4544.

[17] W. McFarlane, J. F. Nixon, and J. R. Swain, *Mol. Phys.*, 1970, **19**, 141.

[18] A. J. Rest, *J. Chem. Soc.* (*A*), 1968, 2212.

[19] J. Grobe, *Z. anorg. Chem.*, 1968, **361**, 32, 47.

[20] J. Grobe and H. Stierand, *Z. anorg. Chem.*, 1969, **371**, 99.

[21] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 747.

The ^{19}F n.m.r. spectra of *cis*-$[(CF_3)_2PNMe_2]_2Mo(CO)_4$ and *cis*-$[(CF_3)_2PNCS]_2Mo(CO)_4$, unlike the systems discussed so far, show only a basic 1 : 1 doublet from coupling to phosphorus. Such a pattern would only be exhibited by $[X_6A]_2$ spin systems (X = fluorine, A = phosphorus) if $J(AX')$ and $J(AA')$ were both zero. This is rather unlikely since values for $J(AA')$ [$= {}^2J(PP')$] are usually greater than 30 Hz for the other $(CF_3)_2PR$ complexes studied. It also seems that these phosphines are not likely to be bonded to the metal *via* the nitrogen of the Me_2N-group or the sulphur of the NCS group.

TABLE 2

^{19}F N.m.r. data for trifluoromethylphosphine complexes *cis*-$L_2M(CO)_4$

M	L	$^2J(PP')$	$^2J(PF)$	$^4J(PF')$ [a]	$\Phi(F)$ [b]	Solvent	$\Delta^2J(PF)$ [c]	$\Delta\Phi Z(F)$ [d]
Mo	$(CF_3)_2PCl$	37.5 ± 0.5	88·4	0·7	65·0	hexane	+3·3	+3·6
Mo	$(CF_3)_2PBr$	36.5 ± 0.5	83·4	0·5	63·05	hexane	+2·8	+3·55
Mo	$(CF_3)_2PI$	34.4 ± 0.4	74·9	0·6	60·1	hexane	+1·7	+4·7
Mo	$(CF_3)_2PNCS$	*e*	91·4 [f]		65·7	40—60° petrol	+4·1	+3·8
Mo	$(CF_3)_2PNMe_2$	*e*	72·5 [f]		59·6	benzene	−13·1	−0·4
Mo	$(CF_3)_2PH$ [g]	23 ± 2	73·6	0·4	53·9	benzene	+5·0	+6·4
Mo	CF_3PCl_2	45.4 ± 0.3	97·6	0·8	75·0	neat	+17·7	+2·9
Mo	CF_3PBr_2	45.8 ± 0.3	87·9	0·9	72·5	neat	+18·3	+4·7
Mo	CF_3PH_2 [h]	*i*	59·7 [j]		51·1	benzene	+11·2	+8·7
Cr	CF_3PH_2 [k]	*i*	57·6 [j]		51·0	benzene	+9·1	+8·6

[a] $^2J(PF)$ and $^4J(PF')$ have the same sign (probably both positive). [b] Relative to CCl_3F internal standard. [c] $\Delta^2J(PF) = {}^2J(PF)$ complex $- {}^2J(PF)$ ligand. [d] $\Delta\Phi(F) = \Phi(F)$ complex $-\Phi(F)$ ligand. [e] Not observed. [f] Observed doublet splitting. [g] $^3J(FH) = 7.1$. [h] $^3J(FH) = 9.0$. [i] Not resolved. [j] $^2J(PF) + {}^4J(PF')$. [k] $^3J(FH) = 8.8$. N.m.r. parameters for the unco-ordinated ligands are given in refs. 10 and 11, and in J. Dyer and J. Lee, *J. Chem. Soc.* (*B*), 1970, 409. All coupling constants are in Hz and all chemical shifts in p.p.m.

TABLE 3

^1H N.m.r. data for trifluoromethylphosphine complexes *cis*-$L_2M(CO)_4$

M	L	$^1J(PH)$	$^3J(PH')$ [a]	$\tau(H)$	$^2J(PP')$	$^3J(HF)$	Solvent
Mo	CF_3PH_2	329	3	6·0	3.5 ± 0.3	8·5	C_6D_6
Mo	$(CF_3)_2PH$	*ca.* 356 [b]		5·0 [c]	*d*	*ca.* 7	C_6D_6
Mo	$(CF_3)_2PNMe_2$	*e*		8·1 [c]	*f*	*e*	C_6H_6
Cr	CF_3PH_2	338·5	11·5	6·0	6.0 ± 0.5	8·5	C_6D_6

[a] $^3J(PH')$ has the same sign as $^1J(PH)$ (both positive). [b] $^1J(PH) + {}^3J(PH')$. [c] Relative to external tetramethylsilane. [d] Not resolved. [e] $^5J(HF)$ not resolved, $^3J(PH) = 10$. [f] Not observed.

^{31}P N.m.r. data for trifluoromethylphosphine complexes

cis-$[(CF_3)_2PCl]_2Mo(CO)_4$	$\delta(P)$ [a] $= -112.6$ [free ligand $\delta(P) = -50.0$ [c]]
cis-$(CF_3PH_2)_2Mo(CO)_4$	$\delta(P)$ [b] $= +47$ [free ligand $\delta(P) = +129$ [d]]

[a] Shifts are relative to 85% H_3PO_4. [b] Determined by Dr. W. McFarlane by use of the INDOR technique. [c] Ref. 10. [d] J. Dyer and J. Lee, *J. Chem. Soc.* (*B*), 1970, 409. All coupling constants are in Hz and all chemical shifts in p.p.m.

The observation of a C–H stretching mode at 2806 cm^{-1} in the i.r. spectrum of *cis*-$[(CF_3)_2PNMe_2]_2Mo(CO)_4$ suggests that the ligand is bonding through phosphorus rather than *via* the nitrogen atom.[22] Chemical[23] and spectroscopic data,[3,24] on the related *cis*-$[F_2PNMe_2]_nMo(CO)_{6-n}$ ($n = 2$ or 3) complexes also strongly favour co-ordination *via* the phosphorus atom.

Changes in Φ_F and $^2J(PF)$ on co-ordination of the phosphine might be expected to be rather small if the ligands were not bonded *via* phosphorus, and although Φ_F for *cis*-$[(CF_3)_2PNMe_2]_2Mo(CO)_4$ differs only slightly from the free ligand value, $^2J(PF)$ is lowered by 13 Hz. The $(CF_3)_2PNCS$ complex shows changes in both Φ_F and $^2J(PF)$ similar to those observed for the other $(CF_3)_2PR$ complexes (R = Cl, Br, I, H) where phosphorus must be the donor atom. Since solutions of *cis*-$[(CF_3)_2PNMe_2]_2Mo(CO)_4$ undergo fairly rapid decomposition to unidentified brown solids it seems likely that the 1 : 1 doublets in the ^{19}F n.m.r. spectra are the result of chemical exchange between the complex and small amounts of free phosphine. Intermolecular exchange is known to cause relaxation of AX coupling in AA′X spin systems if A and A′ are strongly coupled, and the resulting spectrum may appear as a doublet.[25]

DISCUSSION

The magnitude and signs of phosphorus–phosphorus coupling constants, $^2J(PP')$, in transition-metal phosphine complexes have been discussed previously in terms of a simplified Pople–Santry molecular orbital model.[1,2,26] Previous results on fluorophosphine complexes of the type *cis*-$L_2M(CO)_4$ (M = Cr, Mo, or W; L = RPF_2; R = F, CF_3, CCl_3, CCl_2H, CH_2Cl, CH_3, H, *etc.*)[1,3,7,27] led us to suggest[3] that the magnitude of $^2J(PP')$ within a series of phosphine complexes of similar stereochemistry was related to the electronegativity of the substituents bonded to phosphorus.

The coupling constant, $^2J(PP')$, was found to decrease

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[22] J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 1958, 2780.

[23] C. G. Barlow, R. Jefferson, and J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2692.

[24] R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 415.

[25] J. P. Fackler, jun., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 1969, **91**, 1941.

[26] R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1908.

[27] C. G. Barlow, T. R. Johnson, J. F. Nixon, and J. R. Swain, unpublished results.

in magnitude in the order $F > CF_3 > CCl_3 > CCl_2H > CH_2Cl > CH_3 \sim H$ for *cis*-disubstituted tetracarbonyl molybdenum complexes. These results were supported by later data of Harris *et al.*[28] on derivatives of the type *cis*-$L_3Mo(CO)_3$ [$L = PF_3$, $PhOPF_2$, $C_6H_4O_2PF$, $PhPF_2$], and by Verkade *et al.*[29] on a wider range of compounds.

The expression for the phosphorus–phosphorus coupling constant, $^2J(PP')$, of metal phosphine complexes involves a term for every possible electron excitation from occupied to empty orbitals. An excitation between orbitals of the same symmetry contributes a term of negative sign to $^2J(PP')$ while a transition involving orbitals of different symmetry makes a positive contribution.[1,26] For all *cis*-$L_2M(CO)_4$ complexes containing monodentate phosphines so far studied, $^2J(PP')$ has been found to be negative,[7,26,29] whereas positive signs are known in *trans*-complexes.[2,26] Varying the substituents on phosphorus affects $^2J(PP')$ by (*i*) changing the energies of the molecular orbitals and (*ii*) altering the *s*-character of the phosphorus hybrid orbital forming the σ-bond to the metal, and the amplitude of the *s*-orbital evaluated at the nucleus $\Psi_s(0)^2$.

TABLE 4

$^2J(PP')$ (Hz) for *cis*-$L_2Mo(CO)_4$ complexes

L	$^2J(PP')$	L	$^2J(PP')$
$(CF_3)_2PF$	41 ± 1 [a]	CF_3PF_2	48·5 ± 1 [a]
$(CF_3)_2PCl$	37·5 ± 0·5	CF_3PCl_2	45·4 ± 0·3
$(CF_3)_2PBr$	36·5 ± 0·5	CF_3PBr_2	45·8 ± 0·3
$(CF_3)_2PI$	34·4 ± 0·4	CF_3PH_2	3·5 ± 0·3
$(CF_3)_2PH$	23 ± 2		

[a] Data from ref. 3.

Changes in (*ii*) affect the magnitude rather than the sign of $^2J(PP')$, and available data for most *cis*-$L_2M(CO)_4$ and *cis*-$L_3M(CO)_3$ complexes (L = phosphine) are consistent with the expected increase in the phosphorus *s*-orbital coefficients and the valence *s*-orbital density at the nucleus as more electron withdrawing substituents are attached to phosphorus.

The $^2J(PP')$ values for the new trifluoromethylphosphine complexes listed in Table 4 also show the expected decrease in magnitude as less electronegative groups are bonded to phosphorus. The values found for the CF_3PH_2 chromium and molybdenum complexes are, however, much smaller than those of the corresponding complexes of phosphine, *cis*-$(PH_3)_2M(CO)_4$, (M = Cr, Mo)[14] in spite of the presence of the electron-withdrawing trifluoromethyl group. The value for the CF_3PH_2 compounds presumably reflects a rather delicate balance between factors (*i*) and (*ii*). The general success in correlating the magnitude of $^2J(PMP')$ with the nature of the substituents at phosphorus supports the view[26] that any orbital contribution, shown recently to be important for $^2J(FCF')$ coupling constants,[30] probably acts in the same sense as the contact term in these metal phosphine systems.

EXPERIMENTAL

General Procedure.—Since the trifluoromethylphosphines are volatile and spontaneously inflammable in air all manipulations were carried out using a standard high vacuum system. All reactions were performed in sealed, evacuated pyrex glass tubes and volatile products separated by trap to trap fractionation.

CF_3PI_2 and $(CF_3)_2PI$ were prepared using the procedure of Bennett *et al.*[31] and the iodophosphines were converted to CF_3PX_2 and $(CF_3)_2PX$ (X = Cl, Br) by reaction with a large excess of HgX_2 at room temperature. $(CF_3)_2PNMe_2$,[32] $(CF_3)_2PNCS$,[10] $(CF_3)_2PH$,[32] and CF_2PH_2 [33] were prepared by literature methods. The phosphines were fractionated by trap to trap distillation in the high-vacuum manifold and their purity checked by vapour-pressure, molecular-weight, and i.r. measurements. Solvents were rigorously dried before use.

^1H N.m.r. spectra were recorded on either a Varian A60 spectrometer operating at 60 MHz or a Varian HA 100 operating at 100 MHz using internal or external tetramethylsilane as standard. ^{19}F N.m.r. spectra were recorded on the Varian HA 100 instrument operating at 94·1 MHz using CCl_3F as internal standard. The ^{31}P n.m.r. spectrum of *cis*-$[(CF_3)_2PCl]_2Mo(CO)_4$ was recorded on a Perkin-Elmer R10 spectrometer operating at 24·29 MHz using a stationary 8 mm tube with 85% H_3PO_4 as external standard. The high resolution ^{31}P n.m.r. spectrum was obtained (by Dr. D. Shaw, Varian Associates Ltd.) on a Varian HA 100 operating at 40·5 MHz using a spinning 5 mm tube. I.r. spectra were recorded on a Perkin-Elmer PE 337 spectrometer.

Elemental analyses were determined by Mr. A. G. Olney of this laboratory (C, H, and N) and other elements by A. Bernhardt, Microanalytical Laboratory, Elbach über Engelskirchen, W. Germany.

cis-*Tetracarbonylbis[chlorobis(trifluoromethyl)phosphine]-molybdenum.*—Chlorobis(trifluoromethyl)phosphine (4·588 g, 22·43 mmol) and tetracarbonyl(norbornadiene)molybdenum (2·790 g, 9·30 mmol) were shaken at room temperature in a sealed glass tube for 1 h. The tube was attached to the vacuum line and opened and volatile products, 1·535 g (expected 1·633 g), were recovered. Distillation of the residue at 40°, 10^{-3} mmHg yielded *the product* as a colourless liquid. (Found: C, 15·6; H, 0·1. $C_8Cl_2F_{12}MoO_4P_2$ requires C, 15·6; H, 0·0%). I.r. spectrum: 2084s, 2019s,sh, 2000vs,br, 1197vs, 1169vs, 1160sh, 1135vs cm^{-1} (hexane solution).

cis-*Tetracarbonylbis[bromobis(trifluoromethyl)phosphine]-molybdenum.*—Similarly bromobis(trifluoromethyl)phosphine (0·737 g, 2·96 mmol) and tetracarbonyl(norbornadiene)molybdenum (0·327 g, 1·09 mmol) after 18 h at room temperature afforded 0·269 g (expected 0·295 g) of volatile products. Distillation of the brown liquid residue at 50°, 10^{-3} mmHg gave the pale yellow *liquid complex* (Found: C, 14·5; H, 0·3. $C_8Br_2F_{12}MoO_4P_2$ requires C, 13·6; H, 0·0%). I.r. spectrum: 2080s, 2014s,sh,

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1995vs,br, 1196vs, 1169s, 1152s, 1135vs, 1121sh cm^{-1} (CCl_4 solution).

cis-*Tetracarbonylbis[iodobis(trifluoromethyl)phosphine]-molybdenum.*—Iodobis(trifluoromethyl)phosphine (4·245 g, 14·34 mmol) and tetracarbonyl(norbornadiene)molybdenum (1·554 g, 5·15 mmol) formed a red solution on warming from −196° to room temperature. Volatile products weighed 1·12 g (expected 1·67 g), and the product was a purple solid, m.p. *ca.* 25°. No evidence of free iodine was obtained but the compound was not volatile and satisfactory analysis was not obtained. The complex was identified by its characteristic i.r. and n.m.r. spectra (see text). I.r. spectrum: 2072s, 2005s,sh, 1988vs,br, 1190vs, 1162s, 1145s, 1130s, 1113m cm^{-1} (CCl_4 solution).

cis-*Tetracarbonylbis[thiocyanatobis(trifluoromethyl)phosphine]molybdenum.*— Thiocyanatobis(trifluoromethyl)phosphine (0·505 g, 2·22 mmol) and tetracarbonyl(norbornadiene)molybdenum (0·251 g, 0·84 mmol) afforded 0·182 g (expected 0·202 g) of volatile products after 2 h at room temperature. Distillation of the residue at 40°, 10^{-4} mmHg gave the *product* as a yellow-brown liquid (Found: C, 19·0; H, 0·0; N, 4·6. $C_{10}F_{12}MoN_2O_4P_2S_2$ requires C, 18·1; H, 0·0; N, 4·2%). I.r. spectrum: 2650w, 2084s, 1980vs,br, 1194vs, 1174vs, 1139vs, 1043m cm^{-1} (CCl_4 solution).

cis-*Tetracarbonylbis[dimethylaminobis(trifluoromethyl)-phosphine]molybdenum.*— Dimethylaminobis(trifluoromethyl)phosphine (0·480 g, 2·25 mmol) and tetracarbonyl-(norbornadiene)molybdenum (0·213 g, 0·71 mmol) afforded 0·434 g (expected 0·449 g) of volatile products. The crude solid residue was extracted with dry hexane and the solution cooled to −78° when *white crystals of the complex* separated out, were filtered off and dried, m.p. 73—74° (dec.) (Found: C, 22·9; H, 1·6; N, 4·6. $C_{12}H_{12}F_{12}MoN_2O_4P_2$ requires C, 22·7; H, 1·9; N, 4·4%). I.r. spectrum 2933m, 2903m, 2860m, 2827w, 2806w, 2065s, 1987s, 1966vs,br, 1452m, 1277m, 1184vs, 1146vs, 1105s, 1057m, 980s, 697s cm^{-1} (CCl_4 solution).

cis-*Tetracarbonylbis[dichloro(trifluoromethyl)phosphine]-molybdenum.*—Dichloro(trifluoromethyl)phosphine (0·496 g, 2·90 mmol) and tetracarbonyl(norbornadiene)molybdenum (0·303 g, 1·01 mmol) set aside for 3 h at room temperature afforded 0·206 g (expected 0·243 g) of volatile products. Distillation of the residue at 50°, 10^{-3} mmHg gave the colourless *liquid complex* (Found: C, 13·1; H, 0·2; Cl, 25·8; P, 11·1. $C_6Cl_4F_6MoO_4F_2$ requires C, 13·1; H, 0·0; Cl, 25·8; P, 11·3%). I.r. spectrum: 2071s, 2006s,sh, 1985vs,br, 1180vs, 1148vs, cm^{-1} (CCl_4 solution).

cis-*Tetracarbonylbis[dibromo(trifluoromethyl)phosphine]-molybdenum.*—A mixture of dibromo(trifluoromethyl)phosphine (1·624 g, 6·25 mmol) and tetracarbonyl(norbornadiene)molybdenum (0·812 g, 2·71 mmol) shaken for 2 h and left to stand for a further 15 h at room temperature afforded 0·411 g (expected 0·466 g) of volatile products together with a small amount (0·01 mmol) of a non-condensable gas (presumably CO). The brown liquid residue was purified by distillation at 60°, 10^{-4} mmHg to give the yellow *liquid complex* which rapidly turns brown on standing (Found: C, 10·9; H, 0·2. $C_6Br_4F_6MoO_4P_2$ requires C, 9·9; H, 0·0%). I.r. spectrum: 2070s, 2005s,sh, 1990vs,br (CCl_4 solution); 1172vs, 1133vs cm^{-1} (neat liquid).

cis-*Tetracarbonylbis(trifluoromethylphosphine)molybdenum.*—A mixture of trifluoromethylphosphine (0·488 g, 4·78 mmol), tetracarbonyl(norbornadiene)molybdenum (0·629 g, 2·10 mmol) and dry hexane (3 ml) were shaken for 20 h and on cooling a white solid separated out. Fractionation of the volatile products afforded 0·075 g (expected 0·060 g) of unreacted trifluoromethylphosphine. Repeated sublimation of the solid residue at 50°, 10^{-4} mmHg gave the pure, white *solid complex* m.p. 53·5—54° (Found: C, 18·0; H, 1·1. $C_6H_4F_6MoO_4P_2$ requires C, 17·6; H, 1·0%). I.r. spectrum: 2330w, 2051s, 1973s, 1955vs,br, 1180vs, 1146vs, 1070w, 872s cm^{-1} (CCl_4 solution).

cis-*Tetracarbonylbis(trifluoromethylphosphine)chromium.*—A mixture of trifluoromethylphosphine (0·953 g, 9·35 mmol), tetracarbonyl(norbornadiene)chromium (1·098 g, 4·29 mmol) and dry hexane (3 ml) heated at 60° for 6 days afforded 0·109 g unreacted ligand (expected 0·078 g). Repeated sublimation of the residue at 50°, 10^{-4} mmHg yielded the pure *yellow solid complex*, m.p. 53—55° (Found: C, 19·3; H, 1·1. $C_6H_4CrF_6O_4P_2$ requires C, 19·6; H, 1·1%. I.r. spectrum: 2330w, 2043s, 1965s, 1945vs,br, 1182vs, 1145vs, 1070w, 889s, 879s, 663s, 641vs cm^{-1} (CCl_4 solution).

Reaction of Di-iodo(trifluoromethyl)phosphine with Tetra carbonyl(norbornadiene)molybdenum.— Di-iodo(trifluoromethyl)phosphine (5·32 g, 15·0 mmol) and tetracarbonyl-(norbornadiene)molybdenum (1·53 g, 5·10 mmol) reacted immediately on warming the mixture to room temperature. Vigorous bubbling was observed and after standing at room temperature a non-condensable gas (*ca.* 1·5 mmol, presumably CO) was evolved. Removal of volatile products left a liquid residue whose i.r. spectrum in the C≡O stretching region was very complex.

cis-*Tetracarbonylbis[bis(trifluoromethyl)phosphine]molybdenum.*—A solution of bis(trifluoromethyl)phosphine (1·317 g, 7·75 mmol) and tetracarbonyl(norbornadiene)-molybdenum (0·955 g, 3·18 mmol) in dry hexane (2 ml) was shaken at room temperature for 20 h. Excess ligand recovered weighed 0·254 g (expected 0·235 g), and sublimation of the residue at room temperature under high vacuum afforded *the complex* as a white solid, m.p. 52·5—54°. (Found: C, 17·0; H, 0·4. $C_8H_2F_{12}MoO_4P_2$ requires C, 17·5; H, 0·4%). I.r. spectrum: 2330w,br, 2074s, 2000s, 1978vs,br, 1192vs, 1172vs, 1137vs, 870s,br cm^{-1} (CCl_4 solution).

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