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Phosphorus-Fluorine Chemistry. Part XXVIII.¹ Fluorophosphines with **Bulky Substituents as Ligands in Transition Metal Carbonyl Complexes**

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Bis(t-butyl)fluorophosphine, the first stable dialkylfluorophosphine, and the corresponding difluorophosphine, were evaluated with regard to their ligand properties. A series of transition-metal carbonyl derivatives of types (CO)₃NiL. $(CO)_{4}ML, cis-(CO)_{4}MoL_{2}, cis-(CO)_{3}MoL_{3}$ (L = Bu^tPF₂ and Bu^t₂PF; M = Cr, Mo, W) was prepared. Using i.r. and n.m.r. data (1H, ¹⁹F, ³¹P) the relative π -acceptor character of the phosphines in the series PF_{3-n}Bu^t_n (n = 0-3) was assessed. It is proposed to use the quantity $\Delta J/J_{\rm L}$ ($\Delta J = J_{\rm C} - J_{\rm L}$; $J_{\rm C} = P-F$ or P-H coupling constant of the co-ordinated ligand; $J_{\rm L}$ = P-F or P-H coupling constant of the free ligand) as a measure of the π -donor strength of the metal carbonyl fragments, $M(CO)_x$ (M = Ni, x = 3; M = Cr, W, x = 5; or M = Mo, x = 3-5).

³¹P Chemical-shift values of the free phosphines, $Bu_n^t PF_{3-n}$ (n = 1-3) were calculated for a range of bond angles, on the assumption of a bond skeleton of C_{3v} symmetry. Evidence for an increase in bond angle from Bu^tPF₂ to Bu^t₃P was found.

As against numerous studies involving perfluoroalkylfluorophosphine ligands,² the co-ordination chemistry of fluorophosphines, $R_n PF_{3-n}$ (R = alkyl or aryl; n = 1, 2), has been little investigated.²⁻⁴ The main reason for this seems to be the ease with which these compounds, especially the alkylfluorophosphines, undergo spontaneous redox disproportionation,^{5,6}

$$3R_2PF \longrightarrow R_2P-PR_2 + R_2PF_3$$
 and
 $2RPF_2 \longrightarrow RPF_4 + \frac{1}{n}(RP)_n$

In the course of an investigation of the redox disproportionation of R₂PF and RPF₂ we have found that bis-(t-butyl)fluorophosphine, But, PF, does not undergo this reaction, while t-butyldifluorophosphine, Bu^tPF₂, disproportionates very slowly.7 Dimethylfluorophosphine⁸ and methyldifluorophosphine,⁵ by contrast, undergo very rapid disproportionation with formation of dimethyltrifluorophosphorane and tetramethyldiphosphine or methyltetrafluorophosphorane and methylcyclopentaphosphine, respectively. It appears reasonable to assume that the unusual properties of the t-butyl compounds are a consequence of the steric effect of the bulky t-butyl groups.

We have undertaken spectroscopic investigations of the unco-ordinated phosphines, and of some of their transition-metal carbonyl derivatives. In order to assess the significance of steric effects in the fluorophosphines, But₂PF and ButPF₂, a comparison of n.m.r. parameters within the series R₃P, R₂PF, RPF₂, and PF₃ was made for R = Me, Bu^t , Ph, and CF_3 .

RESULTS AND DISCUSSION

Free Phosphines.-N.m.r. parameters of these compounds are listed in Table 1. Particularly striking are the strongly negative (*i.e.* shifted to low field) values of

- ⁴ R. Schmutzler, Chem. Ber., 1965, 98, 552.
 ⁵ V. N. Kulakova, Yu. M. Zinovev, and L. Z. Soborovskij, Zhur. obshchei Khim., 1959, 29, 3957.
 ⁶ F. Seel, K. Rudolph, and R. Budenz, Z. anorg. Chem., 1965, 2011, 106
- **341**, 196.
- M. Fild and R. Schmutzler, J. Chem. Soc. (A), 1970, 2359. ⁸ F. Seel and K. H. Rudolph, Z. anorg. Chem., 1968, 359, 233.

¹ Part XXVII, S. C. Peake, M. Fild, M. J. C. Hewson, and

<sup>R. Schmutzler, Inorg. Chem., in the press.
² J. F. Nixon, Adv. Inorg. and Radiochem., eds. H. J. Emeléus and A. G. Sharpe, Academic Press, 1970, vol. 13, p. 363.
³ F. Seel, K. Ballreich, and R. Schmutzler, Chem. Ber., 1961,</sup>

^{94, 1173.}

 $\delta_{\rm P}$ for all phosphines of the types R₂PF and RPF₂, as compared to the $\delta_{\rm P}$ values of the corresponding types R₃P, and of PF₃. The deviations from additivity (E_1 and E_2) of the $\delta_{\rm P}$ values of R₂PF and RPF₂ are negative $(\zeta_1 = \text{shift contribution of the } p \text{ electrons; } B(v), f(v) = \text{constants; } v = \text{co-ordination number of phosphorus;} n_{\pi} = \text{number of electrons in } d\text{-orbitals, in such cases}$ where no d-orbitals are involved in the σ -bonds). The

TABLE 1

Chemical shifts, $\delta_{\rm P}$ and $\delta_{\rm F}$; deviations of ³¹P chemical shifts from additivity (E_1 and E_2), and coupling constants for some fluorophosphines

$\delta_{\mathbf{P}}$ (p.p.m.)					$\delta_{\mathbf{F}}$ (p.p.m.))	${}^{1}J_{P-F}$ (${}^{19}F$ n.m.r.) (Hz)				
R	$\Delta x \ ^{a}$	$\widetilde{\mathrm{PF}_{3}}$	PF,R	E_1	PFR,	E_2	PR3	$\widetilde{PF_3}$	PF2R	PFR,	PF ₃	PF2R	PFR,
But	1.38	-97.0 %	-231·2 g	-145.7	-210.4 9	-136.3	-62.7	+35 %	+111.5	+215.4	1441 0	1219 0	-873.6 9
CH,	1.33		-250.7 °	-206.7	-187 °	-196	+62.0 °		+92 °	+195.5 °		1167·0 °	ء 823،0
C.H.	1.23		-208·3 b	-146	168 d	-140.1	+6.6 .		+92.3 b	+202.0 d		1173.0 0	905·0 d
C₽₃°	$<\!1.23$		-158.3 0	-96	-123·9 b	-93	+2.6 °		+106.9 %	+219.0 %		1250·0 b	996·0 s
							-						

^a $\Delta x =$ difference in electronegativity between F and group R, *i.e.*, $\Delta x = x_F - x_R$. ^b R. Schmutzler, 'Advances in Fluorine Chemistry,' vol. 5, p. 254 (1965). ^e Cf. ref. 7. ^d C. Brown, M. Murray, and R. Schmutzler, J. Chem. Soc. (C), 1970, 878. ^e See ref. 10. ^f See ref. 25. ^g See ref. 8 and 11.

throughout (Table 1 and Figure 1); E_1 roughly equals E_2 . This also has been found in other series, $R_{3-n}PX_n$ (X = H, Cl, Br, R').⁹ The absolute values of E_1 and E_2 , however, were much smaller.



FIGURE 1 Deviations from additivity, E_1 and E_2 , in the ³¹P n.m.r. chemical shifts of the intermediate compounds in the substitution series $R_{3-n}PF_n$ (n = 0-3)

According to Van Wazer and Letcher 10a the deviation E_2 may be expressed as follows,

$$E_2 = \delta_{\mathrm{PR}_2\mathrm{F}} - \frac{2}{3}\delta_{\mathrm{PR}_3} - \frac{1}{3}\delta_{\mathrm{PF}_3} \tag{1}$$

Assuming $\delta = \delta_{\pi} + \delta_{\sigma} + \delta_{0}$ ($\delta_{0} = \text{constant}$) the following equation may be formulated for the deviations,

$$E = {}^{\sigma}E_i + {}^{\pi}E_i \tag{2}$$

 $(i = 1, 2; {}^{\sigma}E_i = \sigma$ -bond contribution, ${}^{\pi}E_i = \pi$ -bond contribution). The quantum mechanical treatment of the ³¹P chemical shift of symmetrical phosphines PR₃ or PX₃ (R = H, alkyl, aryl; X = halogen, OR, etc.) gives ¹⁰⁶

$$\delta - \delta_0 = B(\mathbf{v})\zeta_1 + 2 \cdot 8[B(\mathbf{v})f(\mathbf{v})]n_{\pi}$$
(3)

* V. Mark and J. R. Van Wazer, unpublished work, quoted in ref. 10, p. 204.

expression for the calculation of δ_P in compounds of trivalent phosphorus is as follows, 10e

$$\delta = 11,828 \cdot 5 - 7940 k_1 \zeta_1 - 149 k_2 n_{\pi}$$

δ and ζ_1 are functions of the angles η and η' (Figure 2); $k_1 = 0.972$ and $k_2 = 2.80$.

Using a Fortran-IV computer program provided by Van Wazer and Letcher ^{10c} we have calculated δ_P values for the phosphines, Bu^tPF₂, Bu^t₂PF, and Bu^t₃P, for a number of combinations of angles (η and η'). Group electronegativities of 2.55 for the t-butyl group and of 3.93 for fluorine were employed.^{10f} According to our calculations there are a number of angular combinations (η , η') for which the δ_P values calculated for Bu^tPF₂ and Bu^t₂PF are in agreement with the experimental values. If, however, all cases with $\eta \neq \eta'$ (*i.e.* $\phi = 120^{\circ}$) are excluded, this being arbitrary, as long as the geometry of phosphines PX₂Y is unknown, the values listed in Table 2 are obtained. The value for the bond angle in

TABLE 2

Calculated angles, η , η' , and bond angles θ for the homologous substitution series. But PF_n, (n = 1-3)

sgoue susse	toution sorrow	$n^{-1} = 3^{-n} (n^{-1})^{-1} = 3^{-n} (n^{$	~ ~,	
	η°	$\eta^{\prime \circ}$	θ°	
PF_3			96 a	
Bu ^t PF ₂	115	115	103	
Bu ^t ₂ PF	112	112	107	
$\operatorname{But}_{3}^{-}P$	110	110	109	

^a E. Hirota and Y. Morino, J. Mol. Spectroscopy, 1970, 33, 460.

PF₃ was added for comparison. For the three compounds, But₃P, But₂PF, and But_{PF₂}, n_{π} was set equal to zero. The very high values of $\delta_{\rm F}$ seem to provide an argument against substantial $(p \rightarrow d)\pi$ interaction in the P-F bond. The bond angle F-P-F of PF₃ is noticeably increased upon introduction of one t-butyl group, while the effect of a further t-butyl group is less. In But₃P, finally, the tetrahedral angle is achieved (see Table 2).

¹⁰ M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, 'Topics in Phosphorus Chemistry,' Wiley, 1967, vol. 5; (a) p. 208; (b) p. 179; (c) p. 217; (d) p. 88; (e) p. 216; (f) p. 190; (g) p. 206-207; (h) p. 190.

The strongly negative values of $\delta_{\rm P}$ (and of E_1 and E_2) for the remaining fluorophosphines listed in Table 1 may be rationalized similarly (with $\phi = 120^{\circ}$, $\eta = \eta'$) with plausible bond angles assumed to lie between those of the extreme members of the series, PF₃ and PR₃. If, in the case of the unsymmetrical phosphines, PZ₂T and PZT₂, T or Z are held constant while Z or T are changed, it seems to be the difference in electronegativity x of Z and T, $\Delta x = x_Z - x_T$, which controls $\delta_{\rm P}$ and, consequently, E_1 and E_2 (see Table 3). The strikingly negative $\delta_{\rm P}$ values of the unsymmetrical fluorophosphines, R₂PF and RPF₂, are probably caused also through the strong diamagnetic anisotropy.

TABLE 3

Relationship between the deviation from additivity of δ_P (E_1, E_2) and the electronegativity differences in compounds PZ₂T and PZT₂

				$\Delta x ==$
Z	Т	$E_1 (PZ_2T)^a$	$E_2 (PZT_2)^a$	$x_{\rm Z} - x_{\rm T}$
Cl	Br	- 6	-3	+0.21
Cl	I	-6	-16	+0.62
Cl	CH ₃	-40	-30	+0.55
Cl	OCH ₃	+12	-2	-0.40
Cl	SCH ₃	-18	-32	+0.55
Me	Н	-22	-18	+0.20
Me	$N(CH_3)_2$	- 39	-25	-0.20
F	$N(CH_3)_2$	-38	-36	+0.83
\mathbf{F}	OC,H5	-3		+0.38
Br	I		-14	+0.44
Ph	Н	-43	-40	+0.60
	^a See r	ef. 10g. b Se	e ref. 10h.	

It is further evident from Table 1 that the t-butyl compounds do not follow the trend for E_1 and E_2 , derived from Δx values,

$$\operatorname{But}_2\operatorname{PF} > \operatorname{Me}_2\operatorname{PF} > \operatorname{Ph}_2\operatorname{PF} > (\operatorname{CF}_3)_2\operatorname{PF}$$

 $\operatorname{But}_\operatorname{PF}_2 > \operatorname{Me}\operatorname{PF}_2 > \operatorname{Ph}\operatorname{PF}_2 > \operatorname{CF}_3\operatorname{PF}_2$

We suggest this to be due to the stronger increase in bond angle, caused through the t-butyl group, as compared to other groups R in fluorophosphines. This gives rise to a down-field shift of $\delta_{\rm P}$ in the t-butylphosphine series, Bu^tPF₂, Bu^t₂PF, and Bu^t₃P, E_1 and E_2 becoming smaller (see Figure 2). The widening of the bond angles is also borne out in the increase in s character of the P hybrid orbitals, as reflected in the higher values of ${}^{1}J_{\rm P-F}$ for the t-butyl compounds, compared to those for the analogous methyl compounds.

The shielding of the ¹⁹F nuclei increases very substantially in the order $PF_3 < Bu^t PF_2 < Bu^t_2 PF$. It is suggested that the inductive effect of the Bu^t-group causes an increasing polarization in the sense $P^{\delta+}-F^{\delta-}$, and thus gives rise to an increase of electron density at fluorine.

The P–F coupling constants shown in Table 1 are absolute values. In the case of But_2PF a negative sign

was found for ${}^{1}J_{P-F}$ by the INDOR technique.¹¹ This seems to be true, too, for the other fluorophosphines.^{10,12,13} The coupling constants, ${}^{3}J_{P-H}$ and ${}^{4}J_{F-H}$, were observed in both t-butylfluorophosphines. They decrease from



FIGURE 2 Definition of the bond angles η , η' , and ϕ of the EPZ₂T molecule (E = lone pair). Drawn after J. H. Letcher and J. R. Van Wazer, 'Topics in Phosphorus Chemistry,' Wiley 1967, vol. 5, p. 131

Bu^tPF₂ via Bu^t₂PF to Bu^t₃P (${}^{3}J_{P-H}$) and from Bu^tPF₂ to Bu^t₂PF (${}^{4}J_{F-H}$) (see Table 4).

TABLE 4

P-H and F-H coupling constants in the t-butylfluorophosphine series $Bu^{t} PF = (n = 1 - 3)$

phosphin	o solution, Du_n	- 3 - n (n	-	0,
	$\operatorname{But}\operatorname{PF}_2$	$\operatorname{But}_{2}\operatorname{PF}$		${\operatorname{But}}_{3}{\operatorname{P}}$
${}^{3}I_{P-H}$ (Hz)	12.3	11.3		9.7
${}^{4}J_{\rm F-H}$ (Hz)	1.8	1.7		

Metal Complexes of t-Butyl Fluorophosphines of the Types $LM(CO)_5$ and $L(CO)_3Ni$ (L = But_nPF_{3-n} ; n = 1, 2; M = Cr, Mo, W).—Like tris-(t-butyl)phosphine,¹⁴ both t-butylfluorophosphines readily form complexes with transition-metal carbonyls. A suitable method of preparation of mono-substituted derivatives of Group VI metal carbonyls involves photochemical replacement of CO by the ligand in tetrahydrofuran as a solvent,¹⁵

$$M(CO)_{6} + Bu^{t}{}_{n}PF_{3-n} \xrightarrow{0-20^{\circ}} CO + (CO)_{5}M-PBu^{t}{}_{n}F_{3-n}$$
$$(n = 1, 2)$$

If pentane is employed as a solvent the *cis*-disubstituted derivatives, $L_2M(CO)_4$, are obtained as by-products. The tricarbonylnickel derivatives are readily obtained at room temperature in pentane as a solvent,

 $Ni(CO)_4 + L \longrightarrow CO + LNi(CO)_3$

All the derivatives $Ni(CO)_3L$ are liquid at room temperature; the complexes involving Cr(0), Mo(0), or W(0) are either solids which are readily sublimable or

¹¹ C. Schumann, H. Dreeskamp, and O. Stelzer, *Chem. Comm.*, 1970, 619.

¹² R. R. Dean and W. McFarlane, Chem. Comm., 1967, 840.

¹³ S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, J. Amer. Chem. Soc., 1967, **89**, 4544.

¹⁴ H. Schumann, O. Stelzer, and U. Niederreuther, J. Organometallic Chem., 1969, **16**, P64.

¹⁵ W. Strohmeier, Z. Naturforsch., 1960, **15**b, 675; Angew. Chem., 1964, **76**, 873.

liquids distillable without decomposition. The complexes are reasonably stable to moisture. They are decomposed with formation of dark products only on prolonged exposure to the atmosphere.

N.m.r. Spectra of the Complexes, Ni(CO)₃L and M(CO)₅L (M = Cr, Mo, W).—The co-ordination chemical shifts,¹⁶ $\Delta \delta_{\rm P} = \delta_{\rm P}$ (complex) — $\delta_{\rm P}$ (ligand) are negative throughout; they depend upon the nature of the transition metal (Table 6).

bond (and thus from fluorine), or by $(p-d)\pi$ interaction between phosphorus and fluorine.¹⁷ In contrast to ${}^{1}J_{P-F}$ the values of the coupling constants ${}^{3}J_{P-H}$ are found to increase upon complex formation; they reach a maximum value in the case of the tungsten compounds. The F-H coupling constant, ${}^{4}J_{F-H}$, like ${}^{1}J_{P-F}$, is smaller in the complexes than in the free ligands.

Tetra- and Tri-carbonylfluorophosphinemolybdenum Complexes.—The two fluorophosphines, Bu^t₂PF and

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N.m.r. parameters for monosubstituted transition-metal complexes of t-butylfluorophosphines,	M(CO) ₅ L and	d
Ni(CO) ₂ L (M = Cr. Mo. W: L = But _n PF _{2-n} ; $n = 0-2$)		

m

		¹ H n.m.r.			¹⁹ F n.m.	r.	³¹ P n.	.m. r .
Complex	³ <i>J</i> _{Р-н} (Нz)	${}^{4}J_{\mathrm{F-H}}$ (Hz)	$\left \frac{\Delta J}{J}\right ^{a}$	$\delta_{\mathbf{F}}$ (p.p.m.)	¹ <i>J</i> _{Р-F} (Hz)	$\left \frac{\Delta J}{J}\right $. 10 °	$\delta_{\mathbf{P}}$ (p.p.m.)	$^{1}J_{P-F}$ (Hz)
PF_3 - $Cr(CO)_5$ PF_3 - $Mo(CO)_5$ PF- $W(CO)$				$+2.06 \ {}^{b}$ +4.70 b +7.89 b	1315 b 1310 b 1245 b	0.87 ° 0.905 ° 1.36 °		
$PF_{2}Bu^{t}-Cr(CO)_{5}$ $PF_{3}Bu^{t}-Mo(CO)_{5}$	$17.0 \\ 16.9$	$1 \cdot 1 \\ 1 \cdot 3$	$0.38 \\ 0.37$	+67.3 + 66.4	1184 1114	0·29 0·86	-285.5 -262.2	$1195 \\ 1090$
$PF_{2}Bu^{t}-W(CO)_{5}$ $PFBu^{t}-Cr(CO)_{5}$	$17.4 \\ 13.7$	$1\cdot 3$ $1\cdot 2$	0·41 0·21	$^{+66}_{+164\cdot2}$	$\begin{array}{c} 1104 \\ 865 \end{array}$	$\begin{array}{c} 0.94 \\ 0.10 \end{array}$	$-235 \cdot 1 \\ -269 \cdot 8$	$\begin{array}{r} 1089 \\ 857 \end{array}$
$PFBu_{2}^{t}-Mo(CO)_{5}$ $PFBu_{2}^{t}-W(CO)_{5}$	$14.0 \\ 14.5$	$1 \cdot 2 \\ 1 \cdot 4$	$0.27 \\ 0.28$	$^{+169\cdot2}_{+182\cdot3}$	853 848	0·24 0·29	-250.5 -232.5	$\begin{array}{c} 862 \\ 878 \end{array}$
$PBu_{3}^{t}-Cr(CO)_{5}$ $PBu_{3}^{t}-Mo(CO)_{5}$	11.6 d 11.7 d		$0.20 \\ 0.21 \\ 0.22$				-105.4 -103.0 08.7	
$PF_{2}Bu^{t}-Ni(CO)_{3}$ $PFBu^{t}-Ni(CO)_{3}$	16·3 13·7	1·3 1·4	0.23 0.33 0.21	$^{+71\cdot 2}_{+179\cdot 8}$	$\begin{array}{c} 1135\\ 870 \end{array}$	$0.69 \\ 0.05$	-247.0 -238.0	$\begin{array}{r}1173\\868\end{array}$
PBu ^t ₃ -Ni(CO) ₃	11.8 •		$0.\overline{22}$, 2.5 0	- • •		-91.0	

^a Maximum error ±0.02. ^b F. Ogilvie, R. J. Clark, and J. G. Verkade, *Inorg. Chem.*, 1969, **8**, 1904. ^c The value of $J_{P-F} = 1441$ Hz was used to calculate these ratios; see E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084. ^d Cf. ref. 14. ^e H. Schumann, O. Stelzer, U. Niederreuther, and L. Rösch, *Chem. Ber.*, 1970, **103**, 1383.

This finding may be rationalized in terms of the different extent of π -interaction between transition metal and phosphorus, or phosphorus and fluorine. This will give rise to a series of low-lying energy states, leading to a decrease of the mean excitation energy $\overline{\Delta E}$ in the complexes.^{10d} Interestingly, the decrease in $|{}^{1}J_{P-F}|$ is

Table 6	
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Co-ordination chemical shifts, $\Delta \delta_P = \delta_P(\text{complex}) - \delta_P$ (free ligand)

	× ×	0 ,		
		L =	L =	L =
Compound	$L = PF_3$	ButPF_2	$\operatorname{But}_2\operatorname{PF}$	But₃P
$L-Cr(CO)_5$	a	-54.3	-59.4	-42.7
L-Mo(CO) ₅	a	-32.0	-40.1	-40.3
$L-W(CO)_5$	a	3.9	$-22 \cdot 1$	-36.0
L_2 -Mo(CO) ₄	-51.5	$-32 \cdot 2$	-37.3	
L ₃ -Mo(CO) ₃	-53.5	$-32 \cdot 2$	-49.1	
L–Ni(CO) ₃	39·5 ^b	-15.8	-27.6	-28.0

^a δ_P Values are not available. ^b R. Mathieu, M. Lenzi, and R. Poilblanc, Compt. rend., 1968, 266, 806

greater the smaller $|\Delta \delta_{\rm P}|$ is for the same complex. The corresponding $\delta_{\rm F}$ values, however, will change only slightly in going from chromium *via* molybdenum to tungsten and nickel (see Table 5). The decrease of $\delta_{\rm F}$ upon complex formation may be interpreted either by assuming a withdrawal of σ -electrons from the P-F

¹⁶ G. S. Reddy and R. Schmutzler, *Inorg. Chem.*, 1967, 6, 823.
 ¹⁷ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution of the second sec

tion Nuclear Magnetic Resonance Spectroscopy,' Pergamon, 1968, vol. 2, p. 874.

 $\operatorname{But}\operatorname{PF}_2$, both react readily with bicycloheptadienetetracarbonylmolybdenum, with displacement of the olefinic ligand.¹⁹

$$C_7H_8Mo(CO)_4 + 2L \longrightarrow cis-L_2Mo(CO)_4 + C_7H_8$$

($C_7H_8 = bicycloheptadiene$)

The corresponding tricarbonyl derivatives are obtained in an analogous manner from cycloheptatrienetricarbonylmolybdenum,¹⁸

$$C_7H_8Mo(CO)_3 + 3L \longrightarrow cis-L_3Mo(CO)_3 + C_7H_8$$

($C_7H_8 = cycloheptatriene$)

In both cases the *cis*-substituted products are exclusively obtained.

It may be noted that the reactions of the diffuorophosphine, Bu^tPF_2 , with both olefin complexes occur readily while the monofluorophosphine, Bu^t_2PF , does not react completely with cycloheptatrienetricarbonylmolybdenum, even over a period of two weeks at room temperature.

The complexes are stable to air and moisture. The solid compounds are usually colourless, (XVI) is yellow. The complex (XIV) is a colourless liquid which may be distilled without decomposition.

¹⁸ R. B. King, Inorg. Chem., 1963, 2, 936.

¹⁹ E. W. Abel, M. A. Bennett, and G. Wilkinson, J. Chem. Soc., 1959, 2323.

Inorg. Phys. Theor.

N.m.r. Spectra of Tetra- and Tri-carbonyl t-Butylfluorophosphine Molybdenum Complexes.-The parameters, $\delta_{\rm F}$, $\delta_{\rm P}$, ${}^{3}J_{\rm P-H}$, and ${}^{4}J_{\rm F-H}$, for the multiply substituted products (Table 7) are comparable to those of the monosubstituted carbonyl complexes. The spectra represent spin systems of the type $[AX]_2$ or $[AX_2]_2$. We intend to carry out complete spectral analyses, in order to obtain J_{AX} , $J_{AX'}$, $J_{AA'}$, and $J_{XX'}$. The sum of ${}^{1}J_{P-F}$ + ${}^{3}J_{P-F}$ may be taken direct from the spectra; this quantity, however, is of limited value in understanding the bonding situation in the complexes.

W; $L = Bu^t PF_2$, $Bu^t_2 PF$, and $Bu^t_3 P$). In the CO region they exhibit the frequencies listed in Table 8. The values for the corresponding PF₃ complexes have been included for comparison.

Assuming that the stretching frequency $v(CO)-A_1$ provides a measure of the π -acceptor character ²⁰ of the ligand L, the following series may be written, $PF_3 >$ $Bu^{t}PF_{2} > Bu^{t}_{2}PF > Bu^{t}_{3}P$. This order which is derived from i.r. data is also reflected in the change of the n.m.r. parameters accompanying the complex formation for the ligands L. The coupling constant J_{P-F} is a

TABLE 7

N.m.r. parameters of multiply substituted derivatives of Group VI carbonyls, cis-Mo(CO)₄L₂ and cis-Mo(CO)₄L₂ $(L = Bu_n^t PF_{3-n}; n = 1-3)$

			$^{1}I_{P-F}$ and		
	δρ	$\delta_{\mathbf{F}}$	${}^{3}J_{P-F}$ (sum)	³∫р-н	4Јғ.н
Complex	(p.p.m.)	(p.p.m.)	(Hz)	(Hz)	(Hz)
PF ₃) ₂ Mo(CO) ₄ ^a	-148.5	+2.9	1305		
PF ₂ Bu ^t) ₂ Mo(CO) ₄	$-263 \cdot 4$	$+65 \cdot 4$	1104	16.6	$1 \cdot 2$
$PFBu_{2}^{t}Mo(CO)_{4}$	-247.7	$+172 \cdot 1$	855	$13 \cdot 1$	1.3
$PF_{a}_{a}Mo(CO)_{a}^{b}$	-150.6	+2.1	1306		
PF ₂ Bu ^t) ₃ Mo(CO) ₃	$-263 \cdot 4$	+63.4	1087	15.9	0.8
$PFBu_{2}^{t}Mo(CO)_{3}$	-259.5	+170.0		13.6	0.7

^a J. F. Nixon and A. Pidcock, Ann. Rev. N.M.R. Spectroscopy, 1969, p. 414. ^b See ref. 16.

Interpretation of I.r. and N.m.r. Spectra of t-Butylphosphine Metal Carbonyl Complexes.-I.r. spectra were

TABLE 8

CO Stretching frequencies for t-butylphosphine metal carbonyl complexes

• • • •	o j .	•••P				
PF_3 -Cr(CO) ₅ ^a	2083		1963	1955		
PF3-Mo(CO)5 b	2104	2012	1990			
PF ₃ -W(CO) ₅ ^a	2101	2004	1979			
PF, But-Cr(ČO)	2081	1988	1969	1962		
PF.But-Mo(CÓ),	2088	1988	1974	1967		
PF _a Bu ^t -W(CO) ₅	2088	1985	1966	1960		
PFButCr(CO)	2068	1989	1959	1947		
PFBu ^t ₅-Mo(CÓ)₅	2076	1991	1961	1953		
PFButW(CO)	2075	1986	1955	1945		
PBut,-Čr(CO),	2055	1931				
PBut -Mo(CO)	2067	1944	1936			
PBut -W(CO)	2066	1933				
PFNi(CO),	2111	2048	5			
PF.But-Ni(CO)	2093	2031	2023			
PFBut_Ni(CO)	2076	2008	1999			
PBut -Ni(CO), d	2060	1971				
cis-(PFa) - Mo(CO), e	2091	2072	2022	2003	1983	1972
cis-(PF, But),-Mo(CO),	2054	1967	1959	1951	1980	
cis-(PFButa) -Mo(CO)	2074	2022	1956	1932	1914	
cis-(PF.)Mo(CO).	2065	2012				
cis-(PF, But),-Mo(CO),	2001	1934				
cis-(PFBut,),-Mo(CO),	1968	1916				

^a W. Strohmeier and F. J. Müller, Chem. Ber., 1967, 100, 9. ^b R. J. Clark and P. J. Hobermann, *Inorg. Chem.*, 1965, 4, 1771.
 ^e M. Bigorgne, *J. Inorg. Nuclear Chem.*, 1964, 26, 107.
 ^e H. Schumann, O. Stelzer, U. Niederreuther, and L. Rösch, *Chem. Ber.*, 1970, 103, 1383.
 ^e C. G. Barlow, J. F. Nixon, and Wichstein L. Chem. Soc. (A) 1068, 29216. and M. Webster, J. Chem. Soc. (A), 1968, 2216.

recorded for the complexes of the types (CO)₃Ni(L), $(CO)_{5}M(L)$, $(CO)_{4}MoL_{2}$, and $(CO)_{3}MoL_{3}$ (M = Cr, Mo,

20 W. D. W. Horrocks and R. C. Taylor, Inorg. Chem., 1963, 2, 723. ²¹ W. McFarlane, *Quart. Rev.*, 1969, **2**, 187.

function of three molecular parameters: (i) the product of the gyromagnetic ratios $\gamma_{\rm P}\gamma_{\rm F}$, (ii) the product of the magnitudes of the valence s-orbitals of P and F, (iii) the mutual polarizability, π_{PF} , of the valence s-orbitals of P and F. γ_P and γ_F are constants.²¹

For a first approximation we assume that the values of $\pi_{\rm PF}$ remain constant on complex formation. The quantity $\left|\frac{\Delta J}{J_{\rm L}}\right|$ (where $J_{\rm L}$ is the P-F coupling constant in the free ligand and ΔI is the change of this coupling constant on complex formation) may be taken as a rough measure of the relative change in s-character of the $\label{eq:p-F-bond} P-F \text{ bond.} \quad It \text{ decreases from } PF_3 \textit{ via } Bu^t PF_2 \text{ to } Bu^t_2 PF.$ The corresponding values, $\left|\frac{\Delta J}{J_{\rm L}}\right|$, taken from the ¹H n.m.r. spectra ($J_{\rm L}$ are the coupling constants ${}^{3}J_{\rm P-H}$ in the free ligand, ΔI the change of these values on complex formation) should reflect the relative change of the s-character in the P-C-C-H bond system. They decrease within the series, $Bu^{t}PF_{2} > Bu^{t}PF > Bu^{t}PF_{3}P$. Taking into account the widening of the bond angles from PF₃ to Bu^t₃P, as derived from δ_P values, it seems reasonable to ascribe the decreasing effect of the complex formation in the above series to the increase of the bond angles at phosphorus. The ligands become more rigid in the series PF_3 to Bu_3^tP (cf. Table 5).

The absolute values $\left|\frac{\Delta J}{J_{\rm L}}\right|$ for a given phosphine ligand L decrease in the order $W(CO)_5 L > Mo(CO)_5 L >$ $Cr(CO)_5L > Ni(CO)_3L$. The chromium and nickel compounds may change their positions within this series.

We propose to replace the terms ' π -donor capability ' of the metal carbonyl fragments, as well as ' π -acceptor strength ' of the phosphine ligand L, as obtained from i.r. spectral data,²² by the quantity $\left|\frac{\Delta J}{J_{\rm L}}\right|$. The above classification of the metal carbonyl fragments according to their ' π -donor capability ' is slightly different from that reported by Müller ²³ and Strohmeier,²² Ni(CO)₃ < W(CO)₅ < Mo(CO)₅ < Cr(CO)₅. However, since the quantities $\left|\frac{\Delta J}{J_{\rm L}}\right|$ are related to changes within the ligand L they provide immediate information about the complexing properties of L and the effect of the transition metal on the ligand L.

EXPERIMENTAL

All experiments were conducted in a dry, oxygen-free atmosphere of nitrogen, purified over a BASF BTS catalyst. Sulpholane was purified by repeated distillation *in vacuo* through a 30-cm Vigreux column. Tetrahydrofuran and pentane were dried over lithium aluminium hydride, measured relative to a P_4O_6 standard and were converted into the H_3PO_4 standard, using the relation $\delta_P(H_3PO_4) = \delta(P_4O_6) - 113$. ¹⁹F Shifts are given relative to an internal CCl₃F standard.

The estimated error in the n.m.r. parameters is as follows: $\delta_P \pm 1$ p.p.m., $\delta_F \pm 0.5$ p.p.m., $J_{P-F} \pm 1.0$ Hz, $J_{P-H} \pm 0.2$ Hz, and $J_{F-H} \pm 0.2$ Hz.

I.r. spectra were recorded on dilute solutions of the compounds in carbon tetrachloride in 1-mm NaCl cells, using a Beckman IR 20 A instrument. The accuracy is believed to be ± 3 cm⁻¹.

Tris-(t-butyl)phosphine (I),²⁴ bis-(t-butyl)fluorophosphine (II), and t-butyldifluorophosphine⁷ (III) were prepared according to literature methods.

Tris-(t-butyl)phosphine Pentacarbonyl Complexes, Bu^t₃PM(CO)₅ (M = Cr, Mo, W) (IV), (V), (VI).^{14,25}—Tris-(t-butyl)phosphine (2.02 g, 0.01 mol) was added dropwise with vigorous stirring and u.v. irradiation to suspensions of 0.01 mol each of hexacarbonyl chromium (2.20 g), hexacarbonylmolybdenum (2.64 g), and hexacarbonyltungsten (3.52 g) in tetrahydrofuran (100 ml). The end of the

		Moleculer (
Complex	c	Н	~Р	F	weight	
$PBu_{a}-Cr(CO)_{e}$ (IV)	52.5	7.0			400	
	(51.8)	(6.9)			(394.4)	
$PBu_{a}^{t}-Mo(CO)_{r}$ (V)	46.3	6.6	7.4		450	
	(46.6)	(6.2)	(7.1)		(438.3)	
$PBu_{\bullet}^{t}-W(CO)_{\pi}$ (VI)	38.6	5.3	6.1		538	
	(38.8)	(5.1)	(5.9)		(526.2)	
$PFBu_{\circ}-Cr(CO)_{\varepsilon}$ (VII)	44 ·0	5.1	8.5	4.9	366	
2 ()3 ()	(43.9)	(5.1)	(8.7)	(5.3)	(356.2)	
PFBut _o -Mo(CO) _c (VIII)	41.1	5.0	7.4	4.0	420	
2 ()5 ()	(39.0)	(4.5)	(7.7)	(4.7)	(400.2)	
PFBu ^t ₉ -W(CO) ₅ (IX)	`32 ∙4	`3 ∙8′	6.6	` 3·7 [′]	515	
2 ()5 ()	(32.0)	(3.7)	(6 · 4)	(3.9)	(488.1)	
$PF_{2}Bu^{t}-Cr(CO)_{5}(X)$	`34 ·2	`2 ·9́	`9 ∙8́	ì1·9́	`320	
2 ()0()	(34.0)	(2.9)	(9.7)	(11.9)	(318.1)	
PF ₂ Bu ^t -Mo(CO) ₅ (XI)	`30·4	2.7'	(/	· · ·	· · ·	
2 () 0 ()	(29.9)	(2.5)			$(362 \cdot 1)$	
$PF_{2}Bu^{t}-W(CO)_{5}$ (XII)	24.4	$2 \cdot 3^{\prime}$	$7 \cdot 1$	8.6	450	
2 () 5 ()	(24.0)	(2.0)	(6.9)	(8.4)	(450.0)	
cis-(PFBu ^t ₂) ₂ -Mo(CO) ₄ (XIII)	44.5	` 6 ∙8́	11.5	`7.1	· · · ·	
	(44.8)	(6.8)	(11.5)	(7.1)	$(536 \cdot 4)$	
cis-(PF,But),-Mo(CO), (XIV)	31.5	`4 ·0	13.4	16.5	()	
	(31.3)	$(3 \cdot 9)$	(13.5)	(16.2)	(460.2)	
$cis-(PF_2Bu^t)_3-Mo(CO)_3$ (XV)	31.7	`4 ·7 [´]	16.1	18.3	538	
	(32.3)	$(4 \cdot 9)$	(16.6)	(20.2)	(558.2)	
cis-(PFBu ^t ₂) ₃ -Mo(CO) ₃ (XVI) ^b	46 ⋅8	` 6 ∙8́	12.0	8.2	. ,	
	(48.2)	(8.1)	(13.8)	(8.5)	$(672 \cdot 6)$	
PFBu ^t ₂ -Ni(CO) ₃ (XVII)	43.2	5.8	10.0	6.3	315	
	(43.0)	(5.9)	(10.1)	(6.2)	(306.9)	
PF ₂ Bu ^t -Ni(CO) ₃ (XVIII)	31.6	3.7	11.7	14-4	281	
	(31.3)	(3.3)	(11.5)	(14·1)	$(258 \cdot 9)$	

TABLE 9

^a Calculated values in parentheses. ^b It was impossible to obtain this compound in a better state of purity, and erratic analytical values were obtained on several attempts.

acetone over sodium sulphate. Molecular weights were determined cryoscopically on $10^{-2}\mathcharmonumber{----}10^{-1}\mbox{M}$ solutions in benzene.

N.m.r. spectra were recorded on a Varian HA 60 A instrument at 60, 56.4, and 24.3 MHz for ¹H, ¹⁹F, and ³¹P, respectively. Calibration of spectra was made by the sideband technique. In all n.m.r. measurements benzene, distilled over lithium aluminium hydride and saturated with argon, was employed as a solvent. ³¹P Shifts were

reaction was determined by measuring the amount of carbon monoxide split off. The reaction mixtures were filtered through a layer of 2—3 cm of cellulose powder, and were partially evaporated *in vacuo*. The crude crystalline products were precipitated from tetrahydrofuran-pentane, and were obtained in high purity through sublimation at 10^{-4} — 10^{-5} mmHg and 100 °C. The yields were close to quantitative. Analytical data are listed in Table 9.

²² W. Strohmeier, F. Guttenberger, and F. J. Müller, Z. Naturforsch., 1967, 22b, 1091.

Bis-(t-butyl)fluorophosphine Pentacarbonyl Complexes, ²⁴ H. Hoffmann and P. Schellenbeck, Chem. Ber., 1967, 100, 692.

²³ F. J. Müller, Dissertation, Würzburg, 1968, p. 168.

²⁵ O. Stelzer, Dissertation, Würzburg, 1969, p. 187.

Bu^t₂PFM(CO)₅ (M = Cr, Mo, W) (VII), (VIII), (IX).— Mixtures of 0·01 mol (1·64 g) of bis-(t-butyl)fluorophosphine and 0·01 mol each of hexacarbonylchromium (2·20 g), hexacarbonylmolybdenum (2·64 g), and hexacarbonyltungsten (3·52 g) in tetrahydrofuran (60 ml) were irradiated, using a Heraeus u.v. immersion lamp TQ 81, until 0·01 mol of carbon monoxide (220 ml) was split off. The residues remaining after removal of the solvent (at 10 mmHg) were dissolved in pentane (100 ml), and chromatographed on a 15-cm silica gel column. The clear solutions thus resulting were partially evaporated and cooled to -70 °C. The compounds were precipitated as colourless to light yellow crystals. The yields were close to quantitative. The products were obtained in high purity upon sublimation at 90 °C/10⁻³ mmHg.

t-Butyldifluorophosphine Pentacarbonyl Complexes. $(Bu^{t}PF_{2})M(CO)_{5}$ (M = Cr, Mo, W) (X), (XI), (XII).-Suspensions of 0.02 mol each of hexacarbonylchromium (4.40 g), hexacarbonylmolybdenum (5.28 g), and hexacarbonyltungsten (7.04 g) in tetrahydrofuran (60 ml) were irradiated and stirred vigorously until 448 ml of carbon monoxide were split off. The solutions were then cooled to -30 °C, and were stirred for 5–7 h at that temperature, after 2.52 g (0.02 mol) of (III) had been added. The solvent was removed at reduced pressure (ca. 30 mmHg). Some unchanged carbonyl compound was always suspended in the resultant oily liquids. It was separated by centrifuging, and the liquid products were purified by short-path distillation at 10⁻³-10⁻⁴ mmHg, 90-100 °C. The yields were (crude products): (X) 6.05 g (ca. 100%), (XI) 8.9 g (ca. 100%), and (XII) 2.0 g (28%). Analyses of the products are listed in Table 9.

cis-(t-Butylfluorophosphine)tetracarbonylmolybdenum(0) Complexes, $cis-L_2Mo(CO)_4$; (XIII; $L = But_2PF$) (XIV; $L = Bu^t PF_2$).— Bicycloheptadienetetracarbonylmolybdenum ²⁶ (1.5 g, 0.005 mol) was mixed with bis-(t-butyl)fluorophosphine (1.64 g, 0.01 mol) and t-butyldifluorophosphine (1.26 g, 0.01 mol),18 respectively. Reaction took place readily with discharge of colour. After a 5 h stirring period the bicycloheptadiene displaced by the fluorophosphine ligand was condensed in vacuo (ca. 0.1 mm) into a trap cooled with liquid nitrogen, and was identified by its i.r. and ¹H n.m.r. spectrum. The colourless solid product formed from bis-(t-butyl)fluorophosphine and bicycloheptadienetetracarbonylmolybdenum was dissolved in the minimum amount of pentane. The solution was filtered through a 5-cm layer of silica gel. On cooling the filtrate, 2.5 g (93%) of light cream coloured crystals were obtained.

²⁷ F. A. Cotton, J. A. McCleverty, and J. E. White, *Inorg.* Synth., 1967, 9, 121. The diffuorophosphine complex (XIV) was obtained as a yellow oil which became colourless upon short-path distillation at 10^{-4} mmHg, 100 °C. The yield was $2 \cdot 2 g$ (96%). For the elemental analyses of the complexes see Table 9.

cis-Tris-(t-butyldifluorophosphine)tricarbonylmolybdenum-(0) (XV).—A mixture of cycloheptatrienetricarbonylmolybdenum (1.36 g, 0.005 mol)²⁷ and (III) (1.89 g, 0.015 mol) was allowed to stand for 24 h, during which period the colour was discharged. The cycloheptatriene formed was condensed at 0.01 mmHg into a trap cooled with liquid nitrogen, and was identified by i.r. and ¹H n.m.r. spectroscopy. The light brown product remaining was chromatographed on a 10 cm silica gel column using pentane as a solvent. Upon cooling the clear solution to -80 °C the colourless complex was precipitated in the form of fine crystals (2.6 g, 93%). The complex was identified as the *cis*-isomer by its i.r. spectrum in the carbonyl region (in CCl₄ solution), ν (C=O)1996 cm⁻¹ (A₁), 1942 cm⁻¹ (E).

cis-Tris(di-t-butyl)fluorophosphinetricarbonylmolybdenum-(0), (XVI).—A mixture of cycloheptatriene tricarbonylmolybdenum (1.36 g, 0.005 mol) and (II) (2.4 g, 0.014 mol) was sealed in a heavy wall glass tube. After 14 d at room temperature the tube was opened, and cycloheptatriene as well as the excess of fluorophosphine and cycloheptatrienetricarbonylmolybdenum were condensed *in vacuo* into a trap, cooled to -78 °C. The residue was dissolved in tetrahydrofuran, and chromatographed on a 15-cm silica gel column. The yield was 2.0 g (60%). The *cis*-structure of the complex was established from its i.r. spectrum (solution in CCl₄, 1 mm cell), v(C=O) 1968 cm⁻¹ (A₁) and 1916 cm⁻¹ (E).

Complexes (CO)₃Ni(L) [L = $Bu_{2}^{t}PF$ (XVII) and $Bu^{t}PF_{2}$ (XVIII)].—Tetracarbonylnickel (1.70 g, 0.01 mol) was added dropwise with stirring to a solution of (II) (1.64 g, 0.01 mol) and (III) (1.26 g, 0.01 mol), respectively, in pentane (5 ml). Reaction with evolution of carbon monoxide readily commenced. After the calculated amount of carbon monoxide (224 ml, 0.01 mol) had been split off, the remaining oily residue was distilled in a high vacuum at 50 °C and 10⁻⁴ mmHg. The yield of (XVII) was 3.05 g (100%) and of (XVIII) 2.5 g (93%).

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²⁶ R. Pettit, J. Amer. Chem. Soc., 1959, 81, 1266.