Instant Ligands. Part 1. Preparation of Some Bidentate Fluorophosphine Ligands derived from Straight Chain Organic Substrates, and their Reactions to form Molybdenum Complexes

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The compounds $(F_2P)S(CH_2)_nS(PF_2)$ (n = 2—6) and $(F_2P)O(CH_2)_nO(PF_2)$ (n = 3—6) have been prepared by reactions of $S(PF_2)_2$ with the appropriate dithiols and diols, and have been characterised by n.m.r. and i.r. spectroscopy. N.m.r. parameters for oxygen compounds with n = 7—10 and 12 have also been obtained. The compounds react with *N*-methylpyridinium pentacarbonyliodomolybdate to give compounds with two $Mo(CO)_5$ units linked by the ligands. With tetracarbonyl(norbornadiene)molybdenum two types of products can be formed, depending on ligand chain length. The predominant products for n = 3—6 have two bidentate ligands bridging between two *cis*-$Mo(CO)_4$ units. For n = 2, 3, or 4 monomeric species with a single chelating ligand on a *cis*-$Mo(CO)_4$ unit are also generated, and their abundance depends on the concentrations of reactants. The metal complexes have been characterised by n.m.r., i.r., and mass spectroscopy.

Many compounds containing $-OPF_2$ groups have been reported[1-4] and their chemistry has been studied in some detail. The majority of these compounds are simple organic derivatives, $ROPF_2$, but species in which the oxygen is bound to other elements, such as silicon and phosphorus, are also known. In contrast very little work has been reported for the $-SPF_2$ analogues, and CH_3SPF_2 is the only organic derivative described so far.[3,5,6]

These fluorophosphines, whether bound to sulphur or oxygen, are all potential ligands, and we have therefore prepared a series of compounds containing two $-OPF_2$ or $-SPF_2$ groups, to be used as bidentate ligands. Most work with bidentate fluorophosphine ligands reported to date has concentrated on compounds of the type $RN(PF_2)_2$,[1,7] in which the two phosphorus atoms are close together, such that they either chelate to a single metal atom or bridge between two adjacent metal atoms. The compounds we have prepared are $(F_2P)Y(CH_2)_nY(PF_2)$, with Y = oxygen or sulphur and n being between 2 and 12. These bidentate ligands therefore have relatively large distances between the donor sites, and their chemistry depends on the number of intervening chain atoms.

These new ligands can be prepared in a pure form or in solution in a few minutes by a one-step process, which is why we refer to them as 'instant ligands.' Samples of many different ligands can therefore be prepared when they are required, and it is only necessary to maintain a stock of $S(PF_2)_2$. The compounds are thus particularly attractive for studies involving bidentate ligands with different distances or geometrical relationships between the co-ordinating groups. In this paper we describe compounds in which the chain linking the two phosphine groups is long and flexible.

Results and Discussion

The ligands $(F_2P)S(CH_2)_nS(PF_2)$ and $(F_2P)O(CH_2)_nO(PF_2)$ were prepared by reaction of $S(PF_2)_2$ with the appropriate dithiol or diol [equations (1) and (2)]. The major advantage of this synthetic route is that it is very simple to purify the products, which are liquids of low volatility. Standard vacuum-line techniques were used to remove the volatile by-products, and any solvent that might be used. All the ligands were obtained in effectively 100% yield. As fluorophosphines are very sensitive to air and moisture, it was not possible to obtain microanalytical data. The absence of additional resonances in ^1H, ^{19}F, ^{31}P, and ^{13}C n.m.r. spectra was therefore taken as evidence of purity.

$$S(PF_2)_2 + HY(CH_2)_nYH \longrightarrow \underset{\textbf{(1)}}{(F_2P)Y(CH_2)_nYH} + PF_2HS \quad (1)$$

$$S(PF_2)_2 + (F_2P)Y(CH_2)_nYH \longrightarrow \underset{\textbf{(2)}}{(F_2P)Y(CH_2)_nY(PF_2)} + PF_2HS \quad (2)$$

$$(Y = S, n = 2\text{—}6;\ Y = O, n = 3\text{—}6)$$

Table 1. N.m.r. parameters for $(F_2P)S(CH_2)_nSH$

n	2	3	4	6
$\delta(^{31}P)$/p.p.m.	233.9	234.4	n.s.	235.7
$\delta(^{19}F)$/p.p.m.	−67.8	−68.4	−68.4	n.s.
$^1J(^{31}P^{19}F)$/Hz	1 265	1 264	1 263	1 260
$^3J(^{31}P^1H)$/Hz	9.0	8.5	n.s.	8.5

n.s. = Not studied. Chemical shifts are positive to high frequency of the external standards 85% H_3PO_4 (^{31}P) and CCl_3F (^{19}F). Spectra recorded for CCl_3D solutions at 300 K.

For Y = S it was possible to observe the intermediate species (**1**) by using n.m.r. spectroscopy (Table 1). For Y = O the reaction using 2 mol of $S(PF_2)_2$ was too rapid for the intermediate (**1**) to be observed, and reactions using smaller amounts were not studied. Attempts to prepare and isolate $(F_2P)S(CH_2)_nSH$ (n = 3—6) were not successful, but they may be sufficiently stable for reactions with transition-metal complexes to be attempted.

Most of the bis(difluorophosphine) ligands (**2**) were stable in solution at room temperature for several hours. However, the compounds $(F_2P)Y(CH_2)_2Y(PF_2)$ decompose by elimination of PF_3 to yield ring-closed fluorophospholane products [equation (3)]. The reaction of the oxygen compound was rapid,

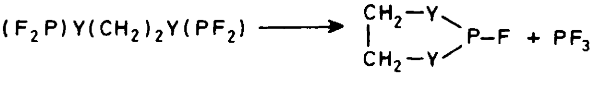

(3)

Table 2. N.m.r. parameters for $(F_2P)Y(CH_2)_nY(PF_2)$[a]

Y	S	S	S	S	S	O	O	O	O	O[b]	O[b]	O[b]	O[b]	O[b]
n	2	3	4	5	6	3	4	5	6[a]	7	8	9	10	12
$\delta(^{31}P)$	233.1	233.2	233.9	234.2	235.5	111.6	111.7	111.8	111.8	112.3	112.2	112.2	112.3	112.2
$\delta(^{19}F)$	−69.9	−68.4	−68.5	−68.6	−68.6	−48.7	−48.6	−48.6	−49.5	−48.6	−48.5	−48.6	−48.5	−48.6
$\delta[^{1}H(1)]$	3.18[c]	3.05	2.95[c]	2.93	2.92	4.18	4.10[c]	4.07	3.66	n.s.	n.s.	n.s.	n.s.	n.s.
$\delta[^{1}H(2)]$		2.07	1.82[c]	1.72[c]	1.70[c]	1.99	1.76[c]	1.69[c]	1.26[c]	n.s.	n.s.	n.s.	n.s.	n.s.
$\delta[^{1}H(3)]$				1.52[c]	1.43[c]			1.50[c]	1.03[c]	n.s.	n.s.	n.s.	n.s.	n.s.
$\delta[^{13}C(1)]$	28.3	24.5	27.7	25.4	26.4	58.7	62.3	62.8	62.9	63.1	63.2	63.3	63.3	63.3
$\delta[^{13}C(2)]$		33.6	30.3	31.2	31.7	30.9	26.4	29.7	30.0	30.2	30.2	30.3	30.3	30.3
$\delta[^{13}C(3)]$				26.8	27.5			21.6	24.9	25.3	25.3	25.4	25.4	25.4
$\delta[^{13}C(4)]$											28.8	28.9	28.9	29.0
$\delta[^{13}C(5)]$												29.3	29.3	29.4
$\delta[^{13}C(6)]$														29.4
$^{1}J(^{31}P^{19}F)$	1 270	1 267	1 264	1 262	1 261	1 291	1 290	1 289	1 288	1 289	1 289	1 290	1 289	1 289
$^{3}J[^{31}PH(1)]$	9[c]	8.2	8.4	8.7	8.8	6.2	6.6[c]	6.5	6.6	7.0	7	7	7	7
$^{4}J[^{19}F^{1}H(1)]$	n.s.	1.5	1.6	1.6	1.6	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
$^{3}J[^{1}H(1)^{1}H(2)]$		6.9	7.0[c]	7.2	7.3	6.0	n.s.	6.4	6.6	n.s.	n.s.	n.s.	n.s.	n.s.
$^{2}J[^{31}P^{13}C(1)]$	24.2	24.9	24.4	24.5	24.3	4	4	4	4	4	4	4	4	4
$^{3}J[^{31}P^{13}C(2)]$		2.2	2.3	2.5	2.6	3.0	3.0	2.9	3.0	3	3	3	3	3
$^{3}J[^{19}F^{13}C(1)]$	6.0	6.4	6.5	6.2	6.0	9.9	9.8	9.5	9.4	9.6	9.3	9.4	9.3	9.3
$^{4}J[^{19}F^{13}C(2)]$		1.1	n.o.[d]	1.2	0.9	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.

n.s. = Not studied, n.o. = not observed; for coupling constants this implies a magnitude of < 1.0 Hz. Chemical shifts are positive to high frequency of the external standards 85% H_3PO_3 (^{31}P), CCl_3F (^{19}F), and $SiMe_4$ (^{13}C and ^{1}H).

[a] Chemical shifts in p.p.m., coupling constants in Hz: recorded for solutions in CCl_3D at 300 K, except Y = O, *n* = 6, for which the solvent used was diethyl ether with $(CD_3)_2CO$ as capillary lock. [b] M. Whittaker, unpublished work. [c] Approximate value: the spectrum is second order. [d] Resolution <2.0 Hz.

Table 3. N.m.r. parameters for metal complexes[a]

Complex	Y	*n*	δP	δF	δC_a	δC_b	$^{1}J(PF)$	$^{2}J(PP')$	$^{3}J(PF')$[b]	$^{2}J(PC_a)$		$^{2}J(PC_b)$	
										c	*d*	*d*	*c*
$[\{Mo(CO)_4[(F_2P)Y(CH_2)_nY(PF_2)\}_2]$	S	2	222.7	−29.3	n.s.	n.s.	1 196	55	2.5	n.s.		n.s.	n.s.
	S	3	224.5	−29.3	202.3	206.2	1 194	45	3.2	15		n.s.	n.s.
	S	4	225.6	−29.8	202.5	206.6	1 193	45	3.2	13		63	18[e]
	S	5	226.2	−30.1	202.6	206.6	1 193	46	3.2	13		56	21[e]
	S	6	226.5	−30.3	202.6	206.7	1 193	46	3.2	13		55	21[e]
	O	3	152.9	−20.0	n.s.	n.s.	1 234	53	3	n.s.		n.s.	n.s.
	O	4	152.8	−19.9	n.s.	n.s.	1 235	55	4	n.s.		n.s.	n.s.
	O	5	152.8	−19.9	203.1	206	1 234	54	4	15		n.s.	n.s.
	O	6	152.7	−20.0	203.2	206	1 232	54	3	15		n.s.	n.s.
$[Mo(CO)_4\{(F_2P)Y(CH_2)_nY(PF_2)\}]$	S	2	242.1	−19.7	n.s.	n.s.	1 176	25	2	n.s.		n.s.	n.s.
	S	3	245.9	−14.7	n.s.	n.s.	1 151	30	3	n.s.		n.s.	n.s.
	O	3	171.9	−8.7	n.s.	n.s.	1 128	39	3	n.s.		n.s.	n.s.
	O	4	155.8	−16.4	n.s.	n.s.	1 256	52	2	n.s.		n.s.	n.s.
	O	5	152.7	−17.2	n.s.	n.s.	1 243	51	4	n.s.		n.s.	n.s.
$[(OC)_5Mo\{(F_2P)Y(CH_2)_nY(PF_2)\}Mo(CO)_5]$	S	3	226	−30.9	205.9	202.2	1 197				52		12
	S	4	226	−31.5	206.1	202.3	1 197				50		13
	S	5	226	−31.6	205.8	201.5	1 196				50		12
	S	6	227	−31.8	206.3	202.4	1 196				50		13
	O	3	151.0	−21.1	205.7	202.4	1 238				46		15
	O	4	151.0	−20.9	205.6	202.5	1 238				47		14
	O	5	150.9	−20.9	205.7	202.6	1 238				45		15
	O	6	150.9	−21.0	205.8	202.6	1 238				46		15

Chemical shifts are positive to high frequency of the external standards 85% H_3PO_4 (^{31}P), CCl_3F (^{19}F), and $SiMe_4$ (^{13}C).

[a] Chemical shifts in p.p.m., coupling constants in Hz: recorded for CCl_3D solutions at 300 K; CCl_2D_2 solutions for $[(OC)_5Mo\{(F_2P)Y(CH_2)_nY(PF_2)\}Mo(CO)_5]$. [b] The sign of this coupling is opposite to that for $^{1}J(PF)$. [c] Coupling between *cis* ligands. [d] Coupling between *trans* ligands. [e] The sign of the coupling is opposite to that for $^{1}J(PC_b)$.

and the bis(difluorophosphine) species $(F_2P)O(CH_2)_2O(PF_2)$ was not observed at all, but the sulphur compound $(F_2P)S(CH_2)_2S(PF_2)$ was stable enough to be characterised in solution, and then to undergo subsequent reaction. However, the rate of ring closure increased as the solution was concentrated, and it was not possible to isolate the pure compound. Why the rings should form is not clear, as it has been reported that $(F_2P)O(CH_2)_2O(PF_2)$ can be isolated, as a stable, volatile liquid.[8] It may be, of course, that in the oxygen case, our reaction leads to the phospholane directly, and $(F_2P)O(CH_2)_2O(PF_2)$ may not even be an intermediate.

The bis(difluorophosphine) compounds (**2**) were characterised by n.m.r. spectroscopy (Table 2) and additional data were obtained by i.r. spectroscopy (see Experimental section).

The ^{13}P, ^{19}F, and ^{13}C n.m.r. spectra are all effectively first order for most of the compounds, but under high resolution the ^{31}P and ^{19}F spectra of $(F_2P)S(CH_2)_2S(PF_2)$ showed second-order features. For the sulphur compounds the phosphorus and fluorine shifts are *ca.* 234 and −68 p.p.m. respectively and the coupling constants between these nuclei are *ca.* 1 265 Hz: the equivalent parameters for the oxygen compounds are 111 and −48 p.p.m. and 1 290 Hz, and there is very little variation in these parameters from compound to compound.

The ^{1}H n.m.r. spectra of the compounds $(F_2P)Y(CH_2)_nY(PF_2)$ were studied. For $n = 3$ the resonances were effectively first order, while for $n = 5$ and 6 the resonances associated with the CH_2 group closest to the $Y(PF_2)$ group were treated as if they were first order, but the remaining resonances were second order under the conditions used. For $n = 2$ and 4 all proton resonances were second order.

All n.m.r. parameters are listed in Table 2. It should be noted that $^{4}J(^{19}F^{1}H)$ was unresolvable (<0.1 Hz) for all the oxygen compounds, whereas it was *ca.* 1.5 Hz for the sulphur compounds. It seems to be generally true that couplings across oxygen are anomalously small.

Reactions of bidentate ligands of the form $(F_2P)Y(CH_2)_nY(PF_2)$ with *N*-methylpyridinium pentacarbonyliodomolybdate were monitored by ^{31}P n.m.r. spectroscopy. For the sulphur-containing ligands the phosphorus chemical shift moved to lower frequency on complex formation, from *ca.* 235 to *ca.* 225 p.p.m., and there was an associated reduction of *ca.* 70 Hz in $^{1}J(PF)$ (Tables 2 and 3). For the oxygen-containing ligands the phosphorus chemical shift moved to higher frequency on complex formation, from *ca.* 112 to *ca.* 151 p.p.m., with an associated decrease of 50 Hz in $^{1}J(^{31}P^{19}F)$. In all cases the fluorine resonances shifted to higher frequency on formation of metal complexes. These changes in n.m.r. parameters are consistent with the ligands co-ordinating to molybdenum at one metal site *via* the phosphorus atom [equation (4)].

$$(F_2P)Y(CH_2)_nY(PF_2) + [Mo(CO)_5I]^- \longrightarrow [(OC)_5Mo\{(F_2P)Y(CH_2)_nY(PF_2)\}Mo(CO)_5] + I^- \quad (4)$$
$$(Y = S \text{ or } O, n = 3\text{—}6)$$

For each product the ^{13}C n.m.r. spectra of the carbonyl groups bound to molybdenum show two doublets [$^{2}J(CP)$], with a ratio of intensities of 1:4. The weaker, higher-frequency resonances showed the larger $^{2}J(CP)$ and were therefore assigned to the carbonyl groups *trans* to the fluorophosphine ligands, and the lower-frequency resonances were assigned to the carbonyl groups *cis* to the fluorophosphine ligands. The proposed structure with one bidentate ligand bridging two $Mo(CO)_5$ groups was confirmed by mass spectroscopy. The spectra showed the parent ions $[(OC)_5Mo\{(F_2P)Y(CH_2)_nY(PF_2)\}Mo(CO)_5]^+$ and ions formed by subsequent sequential carbonyl loss.

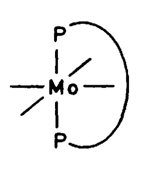
The reactions of $(F_2P)Y(CH_2)_nY(PF_2)$ with tetracarbonyl(norbornadiene)molybdenum $[Mo(nbd)(CO)_4]$ were studied by n.m.r. spectroscopy. For Y = S and $n = 4$—6 one major product with three minor unidentified decomposition PF_2 products were observed. The phosphorus and fluorine n.m.r. spectra of the major product were of the type expected for an $[AX_2]_2$ spin system. The n.m.r. parameters were obtained from the fluorine n.m.r. spectra using the equations of Harris *et al.*[9] However, these spectra were not of high enough resolution to allow the values of $^{4}J(FF')$ to be determined.

The ^{31}P and ^{19}F chemical shifts of the products were to low frequency of those for the free ligands by *ca.* 10 and 28 p.p.m. respectively and $^{1}J(PF)$ was reduced by *ca.* 80 Hz. This is consistent with the ligands co-ordinating to the molybdenum *via* the phosphorus atoms [equation (5)]. It is apparent from the

$$(F_2P)S(CH_2)_nS(PF_2) + [Mo(nbd)(CO)_4] \longrightarrow [\{Mo(CO)_4[(F_2P)S(CH_2)_nS(PF_2)]\}_x] \quad (5)$$
$$(n = 4\text{—}6)$$

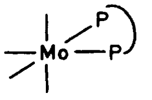
second-order ^{31}P and ^{19}F n.m.r. spectra that two fluorophosphine groups are bound to each molybdenum centre, though it is not possible to assign the co-ordination geometry on the basis of the value of $^{2}J(PP)$.

There are several possible products. The polymer possibility (7) was discounted since most fluorophosphine polymers tend to be insoluble. The ^{13}C n.m.r. spectra of the carbonyl groups bound to molybdenum show two distinct groups of resonances. At lower frequency there was a triplet with a small $^{2}J(CP)$ value, which was assigned to carbons a. The higher-frequency resonances were analysed as arising from the X nuclei of an [ABX] spin system where A and B are ^{31}P and X is ^{13}C. They were assigned to carbons b.



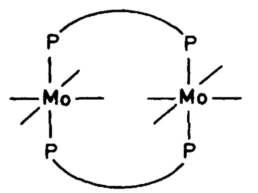
trans chelating

(3)



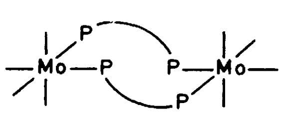
cis chelating

(4)



trans bridging

(5)

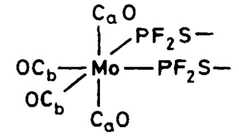


cis bridging

(6)

higher oligomers and polymers

(7)



Mass spectrometry showed that the parent ions corresponded to the dibridged dimolybdenum species $[\{(OC)_4Mo[(F_2P)S(CH_2)_nS(PF_2)]\}_2]^+$. Ions showing sequential loss of carbonyl groups were also observed. The major species formed in the reaction was therefore identified as (6).

The reactions of $(F_2P)S(CH_2)_nS(PF_2)$ ($n = 2$ or 3) with $[Mo(nbd)(CO)_4]$ yielded two sets of products, both of which exhibited $[AX_2]_2$ resonances in the ^{31}P and ^{19}F n.m.r. spectra. For $n = 3$ the lower-frequency resonances were the more intense by a factor of three, but for $n = 2$ the higher-frequency resonances were four times as intense as those at lower frequency. The ^{31}P and ^{19}F n.m.r. parameters for the low-frequency resonances are very similar to those attributed to the dimeric species identified for $n = 4$—6 (δP *ca.* 223 and δF *ca.* −29 p.p.m.), but for the second complex these parameters are distinctly different with δP *ca.* 243 and δF *ca.* −16 p.p.m. The compounds were separated and examined by mass spectroscopy. As expected, in each case one product was found to be the dimeric dibridged species, while the other was identified as the monomeric chelating species (4).

For Y = O several complexes could be formed. With low concentrations of reagents and $n = 3$—5 the monomeric chelate complexes were formed, but with higher concentrations and with $n = 3$—6 bridging dimers and higher oligomers were formed. These products were identified by their n.m.r. parameters and by mass spectroscopy, as described above for the sulphur compounds.

Experimental

All volatile compounds were handled on a conventional Pyrex-glass vacuum line fitted with high-vacuum taps greased with Apiezon N. Bis(difluorophosphino) sulphide was prepared from bromodifluorophosphine and bis(tributyl)stannyl sulphide;[10] its purity was checked spectroscopically. All manipulations of metal complexes were conducted under a purified nitrogen atmosphere using standard techniques.

I.r. spectra were obtained in the range 4 000—400 cm^{-1} using a Perkin-Elmer 598 spectrophotometer and gas or solution cells fitted with KBr windows. N.m.r. spectra were obtained using Bruker WH360 (^{1}H), JEOL FX60 (^{31}P), Bruker WP80 (^{19}F), and Bruker WP200 (^{13}C) spectrometers. Mass spectra were obtained using an AEI MS902 spectrometer, with an ionising potential of 40 eV (6.4×10^{-18} J), at a temperature of 370 K.

Preparation of $(F_2P)S(CH_2)_nS(PF_2)$ ($n = 3$—6).—In a typical reaction, bis(difluorophosphino) sulphide (7.0 mmol) was condensed into a glass ampoule (50 cm^3) fitted with a greaseless tap, containing hexane-1,6-dithiol (3.0 mmol). After 24 h at 298 K the volatile portions, PF_2HS and $S(PF_2)_2$, were removed. The remaining clear colourless liquid was shown spectroscopically to be $(F_2P)S(CH_2)_6S(PF_2)$. Infrared bands characteristic of all the compounds of this type included ν(P–S) 540, 515 cm^{-1}, ν(P–F) 800 cm^{-1}, and S–PF$_2$ def. 410 cm^{-1}.

Preparation of $(F_2P)S(CH_2)_2S(PF_2)$.—Bis(difluorophosphino) sulphide (0.3 mmol) was condensed into a 5-mm n.m.r. tube containing 1,2-ethanedithiol (0.1 mmol) and CCl_3D (0.5 cm^3) as solvent. The tube was sealed and warmed to room temperature and the reaction was then observed by n.m.r. spectroscopy. The product was identified as $(F_2P)S(CH_2)_2S(PF_2)$ and the solution retained for later reaction. An attempt was made to isolate this ligand, as described above, but it decomposed (see main text).

Preparation of $(F_2P)O(CH_2)_nO(PF_2)$ ($n = 3$—5).—In a typical reaction, bis(difluorophosphino) sulphide (5.0 mmol) was condensed into a glass ampoule (50 cm^3) fitted with a greaseless tap, containing propane-1,3-diol (2.0 mmol). After 1 h at 298 K the reaction was complete. Volatile products were passed several times through a bath held at 195 K: the product $(F_2P)O(CH_2)_3O(PF_2)$ was involatile at this temperature. Similar methods were used to prepare the equivalent compounds with $n = 4$ and 5. In the case of $n = 5$ the product was not very volatile and the PF_2HS and unreacted $S(PF_2)_2$ were simply removed by pumping.

Preparation of $(F_2P)O(CH_2)_6O(PF_2)$.—The reaction was essentially the same as those described above, except that prior to the addition of bis(difluorophosphino) sulphide the hexane-1,6-diol was dissolved in diethyl ether (2 cm^3). After the reaction was complete the ether was pumped off, with the PF_2HS and $S(PF_2)_2$. Typical i.r. bands for these compounds included ν(POC) 1 030 and 930 cm^{-1}, ν(P–F) 810, 770 cm^{-1}, and O–PF$_2$ def. 550 cm^{-1}.

Reaction of Ligands of the type $(F_2P)Y(CH_2)_nY(PF_2)$ *with N-Methylpyridinium Pentacarbonyliodomolybdate.*—A solution of the complex (0.2 mmol) in CCl_2D_2 (0.5 cm^3) was mixed with ligand (0.1 mmol) in a 5-mm n.m.r. tube, which was then sealed under vacuum. The reaction was followed by ^{31}P n.m.r. spectroscopy, and was complete after 30 min at 298 K, giving a yellow solution and a white precipitate. The precipitate was identified as *N*-methylpyridinium iodide. The n.m.r. tube was opened and the contents filtered. The filtrate was resealed in a fresh n.m.r. tube, and the product was characterised by n.m.r. spectroscopy. The metal complexes were isolated as yellow, air-sensitive oils, simply by removing the volatile solvents. No solids were obtained even though the oils were triturated with a wide variety of solvents and solvent mixtures. Characteristic CO stretching frequencies are 1 975 cm^{-1} (Y = S) and 1 970, 1 920, and 1 860 cm^{-1} (Y = O).

Preparation of Complexes of the Type $[\{Mo(CO)_4[(F_2P)Y(CH_2)_nY(PF_2)]\}_x]$ ($x = 1$ *or* 2).—A solution of tetracarbonyl-(norbornadiene)molybdenum (0.1 mmol) in CCl_3D (0.5 cm^3) was mixed with ligand (0.1 mmol) in a 5-mm n.m.r. tube, which was then sealed under vacuum. The reaction was followed by ^{31}P n.m.r. spectroscopy and was complete after 2.5 h at 298 K, giving a bright yellow solution. The n.m.r. tube was opened and any monomer ($x = 1$) present was extracted into light petroleum (b.p. 68—80 °C). For Y = oxygen it was not possible to separate the dimer from higher oligomers which were also present. The monomer and dimer were resealed in fresh n.m.r. tubes and identified by n.m.r. spectroscopy. The products were all isolated as yellow, air-sensitive oils, simply by removing the volatile solvents. The oils were triturated with a wide range of solvents, but no solids were obtained, except when diethyl ether was used, in which case a polymeric solid was formed. Characteristic CO stretching frequencies are 1 950 (Y = S) and 1 920 cm^{-1} (Y = O).

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