Instant Ligands. Part 2.[1] Preparation of Some Bidentate Ligands containing PF_2O Groups from Aromatic Hydroxy Compounds, and their Reactions to form Molybdenum and Tungsten Complexes

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Three isomers of $C_6H_4(OPF_2)_2$, two of $(C_6H_4OPF_2)_2$, and seven of $C_{10}H_6(OPF_2)_2$ have been prepared by reactions of $S(PF_2)_2$ and the appropriate dihydroxy derivatives of benzene, biphenyl, and naphthalene, respectively. From these bidentate ligands, complexes have been prepared containing two $Mo(CO)_5$ units or one $Mo(CO)_5$ and one $W(CO)_5$ unit linked by the ligands. With tetracarbonyl(norbornadiene)molybdenum, cyclic products with ligands bridging between *cis*-$Mo(CO)_4$ units are formed. The relative stabilities of the various cyclic oligomers depend on the distance between the phosphorus donor sites, which varies widely in this set of ligands.

We have described[2] a general reaction (1) for the preparation of

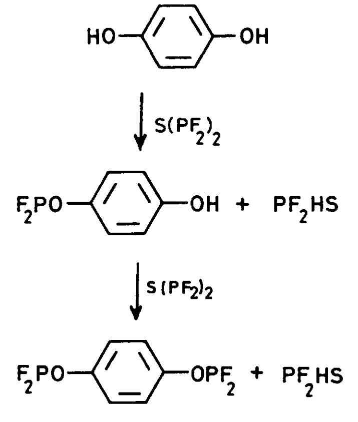
$$RYH + S(PF_2)_2 \longrightarrow RYPF_2 + PF_2HS \qquad (1)$$

compounds containing $-OPF_2$, $-SPF_2$, or $=NPF_2$ groups from the corresponding $-OH$, $-SH$, or $=NH$ compounds. The reaction is useful with a wide range of substrates, including inorganic hydroxides such as phosphoric acid,[3,4] but has particular potential for the preparation of multidentate fluorophosphines from polyhydroxy organic compounds. These fluorophosphines, which we call 'instant ligands' because they can be prepared very quickly by a one-step process, can be made with almost any desired separation between the donor sites, by choosing an organic starting material having an appropriate structure. We have published an account[1] of the preparation and spectroscopic and chemical properties of compounds of the type $(F_2P)Y(CH_2)_nY(PF_2)$ ($Y = O$ or S, $n = 3$—12), and shown that their behaviour as ligands depends on the chain length. All these compounds have a very flexible chain structure, and so by changing their conformation the phosphine groups can attach themselves to metal centres which are close together.

In the present paper we report the preparation and properties of bidentate ligands derived from benzene, biphenyl, and naphthalene. These compounds were chosen to give a wider range of separations between the potential donor sites and to restrict the freedom of movement of the fluorophosphine groups relative to each other. The products should therefore be useful bidentate ligands in situations where the binding sites are separated by a fixed distance.

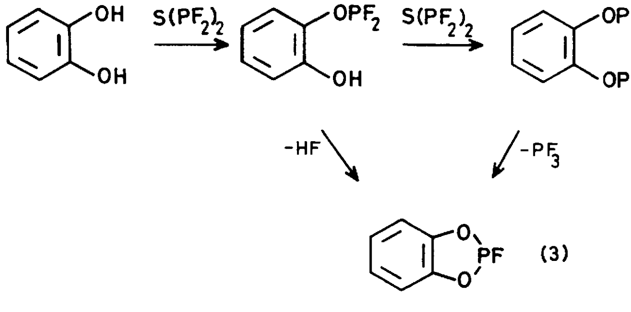
Results and Discussion

Preparation and Identification of the Ligands.—The compounds $1,3\text{-}C_6H_4(OPF_2)_2$ and $1,4\text{-}C_6H_4(OPF_2)_2$ were prepared by the reaction of a two-fold excess of $S(PF_2)_2$ with the appropriate diol (resorcinol or hydroquinone) in diethyl ether or chloroform solution [equation (2)]. The products, which had vapour pressures of a few mmHg at room temperature, were purified by fractional condensation in a vacuum line, and were obtained in essentially 100% yield. When the diol and $S(PF_2)_2$ were taken in equimolar amounts, compounds containing one $-OPF_2$ group were obtained in *ca.* 60% yield, with equal amounts of the unchanged diol and the bis-OPF_2 compounds as impurities. The intermediate compounds were not purified, but were used in the preparation of mixed molybdenum–tungsten carbonyl complexes.



(2)

The analogous compound $1,2\text{-}C_6H_4(OPF_2)_2$ could be prepared in solution from catechol in a similar way, but as the solution was concentrated, PF_3 was eliminated to give 2-fluoro-1,3,2-benzodioxaphosphole [equation (3)], and in this respect its behaviour is similar to that of $F_2POCH_2CH_2OPF_2$.[1] The intermediate compound, $1,2\text{-}C_6H_4(OH)(OPF_2)$, appears to decompose rapidly by loss of HF to give the same phosphole, and therefore we have not observed it in any n.m.r. spectra. Although $1,2\text{-}C_6H_4(OPF_2)_2$ could not be isolated, it did react with molybdenum complexes in solution.



(3)

The compounds $C_6H_4(OPF_2)_2$ (the 1,4 isomer has been prepared before[5]) are clear liquids, very sensitive to air and moisture, and slightly volatile. Microanalytical data were not therefore obtained, but the identity and purity of each sample was determined by ^{31}P, ^{19}F, ^{13}C, and ^{1}H n.m.r. spectroscopy.

Table 1. N.m.r. parameters for fluorophosphine ligands[a]

Ligand	$\delta(^{31}P)$	$\delta(^{19}F)$	$^1J(PF)$	$\delta(^{13}C)$									
				C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
1,2-$C_6H_4(OPF_2)_2$[b]	112.8	−43,6	1 334	141.1		122.8	126.2						
1,3-$C_6H_4(OH)(OPF_2)$	111.0	−44.2	1 327										
1,3-$C_6H_4(OPF_2)_2$[c]	110.7	−44.3	1 331	149.0	114.5		118.2	130.5					
1,4-$C_6H_4(OH)(OPF_2)$	110.7	−45.5	1 321										
1,4-$C_6H_4(OPF_2)_2$[d]	108.4	−44.4	1 329	144.7	122.1								
2,2′-$(C_6H_4OPF_2)_2$	112.5	−44.0	1 329	130.8	147.4	121.9	132.6	126.2	130.2				
4,4′-$(C_6H_4OPF_2)_2$	110.1	−44.8	1 326	138.6	129.1	122.1	149.2						
1-$C_{10}H_7(OPF_2)$	113.1	−43.6	1 332	145.5[e]	116.7[e]	126.2[e]	125.9	127.5	128.4	127.3	122.1	127.7	135.8
2-$C_{10}H_7(OPF_2)$	110.9	−44.5	1 326	121.3[e]	n.o.	118.1[e]	130.7	128.3?	126.3	127.5?	128.0?	134.7	132.1
1,3-$C_{10}H_6(OH)(OPF_2)$	111.4	−44.5	1 328	n.s.									
1,3-$C_{10}H_6(OPF_2)(OH)$	112.5	−43.7	1 334	n.s.									
1,3-$C_{10}H_6(OPF_2)_2$ (1-)	113.1	−43.7	1 337	146.0[e]	112.1[e]	146.0	115.5[e]	126.8?	128.4?	127.8?	121.9	125.1	134.8
(3-)	111.7	−44.6	1 331										
1,4-$C_{10}H_6(OPF_2)_2$	112.2	−43.7	1 334	143.0[e]	116.2[e]			122.5	128.3			128.7	
1,5-$C_{10}H_6(OPF_2)_2$	112.5	−43.7	1 334	145.5	117.8[e]	126.8	119.9					129.1	
1,7-$C_{10}H_6(OH)(OPF_2)$	111.5	−44.4	1 326	n.s.									
1,7-$C_{10}H_6(OPF_2)(OH)$	114.4	−43.3	1 331	n.s.									
1,7-$C_{10}H_6(OPF_2)_2$ (1-)	113.8	−43.7	1 334	144.7	117.4[e]	125.6	125.6	130.5	122.1[e]	147.5	112.2[e]	127.7	132.9
(7-)	111.7	−44.6	1 330										
2,3-$C_{10}H_6(OPF_2)_2$	111.8	−44.1	1 336	120.6[e]	139.6			127.9?	127.5?			132.0	
2,6-$C_{10}H_6(OPF_2)_2$	110.2	−44.6	1 328	122.6[e]	147.5[e]	118.3[e]	130.3[e]					132.4	
2,7-$C_{10}H_6(OPF_2)_2$	111.1	−44.5	1 329	121.3[e]	148.0[e]	117.8[e]	130.6					135.3[e]	

n.o. = not observed, n.s. = not studied.

[a] Spectra recorded in $CDCl_3$ or CD_2Cl_2 solutions at 298 K. Chemical shifts (in p.p.m.) to high frequency of 85% H_3PO_4, CCl_3F, or $SiMe_4$. Coupling constants in Hz. [b] $^2J(PC)$ 4.5, $^3J(PC)$ 5.0, and $^3J(FC)$ 5.0 Hz. [c] $^2J(PC)$ 4.6, $^3J(PC^1)$ 4.7, $^3J(PC^4)$ 4.9, and $^3J(FC)$ 5.0 Hz. [d] $^2J(PC)$ 4.4, $^3J(PC)$ 4.6, and $^3J(FC)$ 5.0 Hz. [e] Splittings due to coupling with ^{31}P and/or ^{19}F observed.

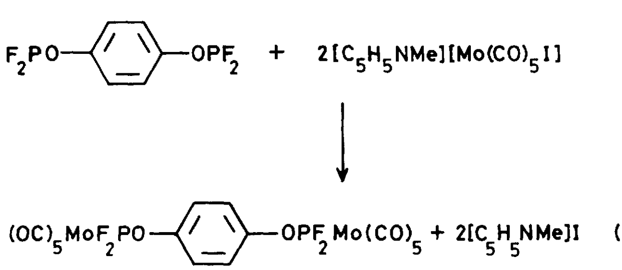
Parameters are listed in Table 1. In each case the ^{31}P and ^{19}F chemical shifts are close to 110 and −44 p.p.m. respectively, and $^1J(PF)$ is *ca.* 1 330 Hz, typical values for aromatic OPF_2 compounds. In aliphatic OPF_2 compounds $^1J(PF)$ is significantly smaller, around 1 290 Hz.[1] In the ^{13}C spectra, couplings from ^{19}F and ^{31}P to the carbon atom bearing the OPF_2 substituent were observed, and from ^{31}P to the adjacent carbon atoms. Proton spectra for the 1,2 and 1,3 compounds were second order, with resonances centred near δ 7, while the spectrum of the 1,4 compound consisted of a single peak at δ 7.2 p.p.m.

Similar reactions were carried out using 2,2′- and 4,4′-dihydroxybiphenyl, 1- and 2-naphthol, and seven different naphthalenediols. Most reactions were simply studied in n.m.r. tubes, and the products subsequently allowed to react to form molybdenum pentacarbonyl complexes, although one ligand, the 1,7-naphthalenediol derivative, was isolated. There is no doubt that all the ligands can easily be obtained in essentially 100% yield, although it is important to use an excess of $S(PF_2)_2$ and to ensure that the reaction time is long enough (10 min is normally sufficient) for complete substitution to occur. In the cases of the unsymmetrical 1,3- and 1,7-naphthalenediols the intermediate monosubstituted compounds were studied, but in both cases the two isomers were formed in equal quantities, and there is no evidence that substitution occurs preferentially in one site.

The stability of the $-PF_2$ derivative of 2,3-naphthalenediol is apparently greater than that of 1,2-$C_6H_4(OPF_2)_2$, and only very weak resonances that might be attributed to the naphthodioxaphosphole, formed by elimination of PF_3 [δ(P) 124.0, δ(F) −37.4 p.p.m., $^1J(PF)$ 1 310 Hz], were observed. However, when the ligand was treated with $[Mo(CO)_5I]^-$ a large amount of PF_3 was formed, and both ^{31}P and ^{19}F n.m.r. spectra included new doublets [δ(P) 169.7, δ(F) −1.8 p.p.m., $^1J(PF)$ 1 266 Hz] which could be assigned to the $Mo(CO)_5$ phosphole complex, as well as peaks due to the expected complex 2,3-$C_{10}H_6[OPF_2Mo(CO)_5]_2$. The ligand derived from 2,3-naphthalenediol is therefore as yet the most stable one with $-OPF_2$ groups on adjacent carbon atoms.

The n.m.r. parameters for the biphenyl and naphthalene derivatives are included in Table 1. The ^{31}P chemical shifts for $-OPF_2$ groups in positions adjacent to ring-junction positions are consistently higher than usual (112—114 compared with 110—112 p.p.m.) while the ^{19}F resonances are also slightly shifted (from *ca.* −44.5 to −43.5 p.p.m.). The ^{13}C chemical shifts and assignments are also given in Table 1. Some peaks could easily be recognised by observation of couplings to phosphorus and fluorine, whilst resonances due to carbon atoms at ring-junction positions were of lower intensity. It was then found that the effects of the $-OPF_2$ groups on chemical shifts of naphthalene derivatives were additive, as they are for the benzene derivatives, and after full analysis of all the data the assignments in Table 1 were made, with few uncertainties. In Table 2 the individual effects of $-OPF_2$ groups in different positions on ^{13}C chemical shifts are given, and these may be valuable for the identification of compounds other than those we have made.

Reactions of Ligands with N-*Methylpyridinium Pentacarbonyliodomolybdate*.—The reactions of the ligands 1,2-, 1,3-, and 1,4-$C_6H_4(OPF_2)_2$, 2,2′-$(C_6H_4OPF_2)_2$, and five isomers of $C_{10}H_6(OPF_2)_2$ with $[Mo(CO)_5I]^-$ were monitored by n.m.r. spectroscopy. As was found for the other PF_2O ligands,[1] the ^{31}P chemical shifts moved to higher frequency on complex formation, from *ca.* 110 to *ca.* 150 p.p.m. The ^{19}F chemical shifts also moved to higher frequency, from *ca.* −44 to *ca.* −12 p.p.m., with an associated decrease of *ca.* 80 Hz in the $^1J(PF)$ coupling constant. These changes in the n.m.r. parameters are only consistent with the bidentate ligands co-ordinating to the molybdenum at one metal site *via* each phosphorus, as in



(4)

equation (4). Most of these reactions went cleanly, but care had to be taken to ensure that complete replacement of –OH by –OPF_2 groups had occurred, and that the subsequent reaction to form the molybdenum complex was also complete. Many of the n.m.r. spectra showed the presence of minor impurities which could be attributed to incomplete reactions.

Reactions with 1,2-$C_6H_4(OPF_2)_2$ and 2,3-$C_{10}H_6(OPF_2)_2$ showed that there is no difficulty in accommodating $Mo(CO)_5$ groups on two adjacent sites, but in the case of 2,3-$C_{10}H_6(OPF_2)_2$, PF_3 was eliminated, and resonances which we assign to the $Mo(CO)_5$ complex of the naphthodioxaphosphole were observed. In this case the yield of the bis $Mo(CO)_5$ complex was only *ca.* 70%, compared with the usual 90%. The only other low yield was given by 2,2′-$(C_6H_4OPF_2)_2$, and here the reaction was incomplete after 2 h at room temperature. Some PF_3 was formed, as well as a black solid which may be metallic molybdenum, and the n.m.r. spectra contained many peaks in addition to those of the expected complex. It seems likely that in this case the formation of the bis $Mo(CO)_5$ complex is hindered sterically, and it is possible that the resonances which we have observed are in fact due to a complex with one $Mo(CO)_5$ group and one free –OPF_2 group.

Table 2. Effects of –OPF_2 substituents on ^{13}C chemical shifts of benzene and naphthalene

		Naphthalene	
Δδ/p.p.m.	Benzene	1-OPF_2 substituent	2-OPF_2 substituent
C(1)	+19.5	+17.5	−6.9
C(2)	−7.0	−10.0	+21.0
C(3)	+1.0	+0.5	−8.4
C(4)	−3.3	−2.3	+1.8
C(5)		−0.3	+0.4
C(6)		+1.8	+0.4
C(7)		+1.3	+1.1
C(8)		−6.0	−0.2
C(9)		−6.3	+0.8
C(10)		+2.0	−2.0

Most of the metal complexes were isolated as yellow oils which were insensitive to both air and moisture. They were identified primarily by their n.m.r. parameters, which are listed in Table 3. Mass spectra were recorded for the benzene derivatives, which were slightly volatile and thus more easily handled. The mass spectra confirm the proposed structures, and show parent ions and a sequence of ions formed by loss of up to ten CO groups (Table 4).

Mixed-metal Complexes of 1,3- *and* 1,4-$C_6H_4(OPF_2)_2$.—It was noted that if 1:1 mixtures of 1,3- or 1,4-$C_6H_4(OH)_2$ and $S(PF_2)_2$ were allowed to react, about 60% yield of the monodentate ligand $C_6H_4(OH)(OPF_2)$ could be obtained, contaminated with $C_6H_4(OPF_2)_2$ and unchanged $C_6H_4(OH)_2$. Treatment of this mixture with $[M(CO)_5I]^-$ (M = Mo or W) yielded a solution containing mainly $C_6H_4(OH)[OPF_2M(CO)_5]$, plus the expected by-products, such as $C_6H_4[OPF_2Mo(CO)_5]_2$, identified by its n.m.r. parameters. Further reaction with $S(PF_2)_2$ then led to the formation of a free –OPF_2 group, and a second treatment with $[M(CO)_5I]^-$ gave the

Table 3. N.m.r. parameters for molybdenum and tungsten complexes[a]

Complex	$\delta(^{31}P)$	$\delta(^{19}F)$	$^1J(PF)$	$\delta(^{31}P')$	$\delta(^{19}F')$	$^1J(P'F')$
1,2-$C_6H_4[OPF_2Mo(CO)_5]_2$	149.9	−12.6	1 254			
1,3-$C_6H_4[OPF_2Mo(CO)_5]_2$	150.9	−11.2	1 253			
1,4-$C_6H_4[OPF_2Mo(CO)_5]_2$	149.9	−13.1	1 252			
1,3-$C_6H_4(OH)[OPF_2Mo(CO)_5]$	152.4	−14.0	1 251			
1,4-$C_6H_4(OH)[OPF_2Mo(CO)_5]$	153.0	−14.9	1 246			
1,3-$C_6H_4(OH)[OPF_2W(CO)_5]$[b]	125.5	−14.2	1 231			
1,4-$C_6H_4(OH)[OPF_2W(CO)_5]$[b]	126.8	−16.2	1 227			
1,3-$C_6H_4(OP'F'_2)[OPF_2Mo(CO)_5]$	150.6	−12.8	1 253	108.9	−44.3	1 332
1,4-$C_6H_4(OP'F'_2)[OPF_2Mo(CO)_5]$	150.8	−13.6	1 250	109.8	−45.0	1 329
1,3-$C_6H_4(OP'F'_2)[OPF_2W(CO)_5]$[b]	124.9	−15.3	1 232	109.1	−44.8	1 332
1,4-$C_6H_4(OP'F'_2)[OPF_2W(CO)_5]$[b]	125.1	−15.7	1 230	108.9	−44.9	1 327
1,3-$C_6H_4[OPF_2Mo(CO)_5][OP'F'_2W(CO)_5]$[c]	149.9	−13.3	1 252	124.1	−15.2	1 230
1,4-$C_6H_4[OPF_2Mo(CO)_5][OP'F'_2W(CO)_5]$[d]	147.3	−13.6	1 252	124.5	−15.8	1 230
2,2′-$[C_6H_4OPF_2Mo(CO)_5]_2$	147.6	−17.0	1 250			
1,4-$C_{10}H_6[OPF_2Mo(CO)_5]_2$	151.7	−15.2	1 250			
1,5-$C_{10}H_6[OPF_2Mo(CO)_5]_2$	152.1	−15.0	1 249			
2,3-$C_{10}H_6[OPF_2Mo(CO)_5]_2$	153.0	−11.2	1 250			
2,6-$C_{10}H_6[OPF_2Mo(CO)_5]_2$	151.1	−15.8	1 250			
2,7-$C_{10}H_6[OPF_2Mo(CO)_5]_2$	151.0	−13.0	1 250			
$\{1,3\text{-}C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_2$[e]	149.8	−12.3	1 250			
$\{1,3\text{-}C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_n$[f]	149.5	−12.5	1 250			
$\{1,4\text{-}C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_2$[g]	151.5	−8.9	1 248			
$\{1,4\text{-}C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_3$[h]	150.2	−12.4	1 251			
$\{1,4\text{-}C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_n$[i]	149.8	−12.6	1 250			
$\{2,7\text{-}C_{10}H_6[OPF_2Mo(CO)_4F_2PO]\}_2$[j]	151.3	−12.2	1 255			
$\{2,7\text{-}C_{10}H_6[OPF_2Mo(CO)_4F_2PO]\}_3$	150.9	−12.4	1 251			

[a] Spectra recorded in CD_2Cl_2 solutions at 298 K. Chemical shifts (in p.p.m.) to high frequency of 85% H_3PO_4 or CCl_3F. Coupling constants in Hz. [b] $^1J(WP)$ 495 and $^2J(WF)$ 30 Hz. [c] $^1J(WP)$ 470 and $^2J(WF)$ 30 Hz. [d] $^1J(WP)$ 475 and $^2J(WF)$ 30 Hz. [e] $^2J(PP)$ 54 and $^3J(PF)$ 3 Hz. [f] $n \geqslant 3$, $^2J(PP)$ 53 and $^3J(PF)$ 4 Hz. [g] $^2J(PP)$ 46 and $^3J(PF)$ 4 Hz. [h] $^2J(PP)$ 54 and $^3J(PF)$ 4 Hz. [i] $n \geqslant 4$, $^2J(PP)$ 47 and $^3J(PF)$ 3 Hz. [j] $^3J(PF)$ 9.3 and $^2J(PP)$ 53.4 Hz.

Table 4. Relative abundances* of ions in the mass spectra of molybdenum complexes

Complex	$[M]^+$	$[M-\mathrm{CO}]^+$	$[M-2\mathrm{CO}]^+$	$[M-3\mathrm{CO}]^+$	$[M-4\mathrm{CO}]^+$	$[M-5\mathrm{CO}]^+$	$[M-6\mathrm{CO}]^+$	$[M-7\mathrm{CO}]^+$	$[M-8\mathrm{CO}]^+$	$[M-9\mathrm{CO}]^+$	$[M-10\mathrm{CO}]^+$
1,2-$C_6H_4[OPF_2Mo(CO)_5]_2$	50	20	0	29	7	32	100	50	57	50	25
1,3-$C_6H_4[OPF_2Mo(CO)_5]_2$	100	4	23	0	33	94	61	39	29	19	42
1,4-$C_6H_4[OPF_2Mo(CO)_5]_2$	93	0	10	0	20	78	100	33	55	18	60
1,3-$C_6H_4[OPF_2Mo(CO)_5]$-$[OPF_2W(CO)_5]$	100	6	28	61	61	89	75	64	67	19	36
1,4-$C_6H_4[OPF_2Mo(CO)_5]$-$[OPF_2W(CO)_5]$	100	6	21	14	57	100	46	53	64	43	64
$\{$1,3-$C_6H_4[OPF_2Mo(CO)_4$-$F_2PO]\}_2$	27	0	8	0	6	21	15	100	12		
$\{$1,4-$C_6H_4[OPF_2Mo(CO)_4$-$F_2PO]\}_2$	100	0	23	10	47	13	21	24	42		

* Ionizing voltage 70 eV (1.12×10^{-17} J): the abundance given is the total for the group of ions containing different isotopes of Mo (and W).

mixed-metal complex, containing both $Mo(CO)_5$ and $W(CO)_5$ groups. The n.m.r. parameters for the products and all the intermediate compounds are given in Table 3, and details of mass spectra in Table 4. No attempt was made to separate the Mo/W from the Mo/Mo and W/W species, but it is clear that this is a fairly general method of preparing compounds containing two different metal centres in reasonably high yield, and with suitable compounds separation by chromatographic methods would be possible.

Reactions of Ligands with Tetracarbonyl(norbornadiene)-molybdenum.—The reactions of 1,3- and 1,4-$C_6H_4(OPF_2)_2$ and 2,7-$C_{10}H_6(OPF_2)_2$ with $[Mo(nbd)(CO)_4]$ were studied initially by n.m.r. spectroscopy. There were two products of the reaction of 1,3-$C_6H_4(OPF_2)_2$, both of which exhibited $[AX_2]_2$ resonance patterns in the ^{31}P and ^{19}F n.m.r. spectra and had almost identical n.m.r. parameters, with δ(P) *ca.* 149, δ(F) *ca.* −12.5 p.p.m., and ^1J(PF) 1 250 Hz (Table 3). The higher-frequency set of resonances was the more intense by a factor of three. The ^{31}P n.m.r. spectrum was very similar to that observed for the reaction of $(F_2P)O(CH_2)_6O(PF_2)$ with $[Mo(nbd)(CO)_4]$.[1] This implied that the major product was $\{$1,3-$C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_2$ and that the minor product could be assigned as $\{$1,3-$C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_n$, where $n \geqslant 3$, rather than the monomeric species which would have significantly different n.m.r. parameters. Mass spectroscopy showed that the parent ion corresponded to the dimer (Table 4), and no ions derived from the monomeric complex were observed. It was not possible to observe the parent ion of the higher oligomer because of the limits of the mass spectrometer, and the assignment of the n.m.r. peaks to such a species must therefore be tentative.

The reaction of 1,4-$C_6H_4(OPF_2)_2$ with $[Mo(nbd)(CO)_4]$ yielded four products, one of which was precipitated with chloroform and did not dissolve in any common solvent. The soluble products all exhibited $[AX_2]_2$ resonances in the ^{31}P and ^{19}F n.m.r. spectra, with very similar ^{31}P and ^{19}F chemical shifts of *ca.* 149 and −12 p.p.m. respectively and ^1J(PF) *ca.* 1 250 Hz (Table 3). By comparison with results obtained with other ligands we assign the resonance with δ(P) 151.5 p.p.m. to a dimeric complex, which may exhibit some steric strain. We assign the other resonances to higher oligomers, probably the trimer and tetramer, and believe that the insoluble product is a polymer. The relative amounts of the complexes with chemical shifts 151.5, 150.2, and 149.8 p.p.m. are *ca.* 1:2:1, and we assign the second of these chemical shifts to the trimer, which is therefore the most abundant product. The mass spectrum of the soluble sample showed a parent ion corresponding to $[$1,4-$C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_2{}^+$ (Table 4). Ions whose isotope distribution pattern corresponded to a fragment containing three molybdenum atoms were also detected. In an attempt to obtain a better yield of the dimeric complex, the experiment was repeated with the reactants highly diluted in chloroform. A pale yellow solution was obtained, with no solids present. However, when this solution was concentrated a polymeric complex precipitated. It would appear that the dimeric complex is less stable than oligomeric or polymeric complexes. This is not surprising, as the positions of the two $-OPF_2$ groups at opposite ends of the ring must make the formation of fairly small ring structures more difficult than with 1,3-$C_6H_4(OPF_2)_2$.

Reaction of 2,7-$C_{10}H_6(OPF_2)_2$ with $[Mo(nbd)(CO)_4]$ in chloroform gave one major soluble product (about 90%), with small amounts of a second and a trace of a third. Some insoluble material was also precipitated. The ^{19}F and ^{31}P n.m.r. spectra of at least the two major soluble products were characteristic of molybdenum complexes with two PF_2O ligands in *cis* positions, and we assign the strongest peaks to the dimeric complex, with relatively small amounts of higher oligomers being formed.

Although the number of bonds separating the phosphorus atoms is greater in the 2,7-naphthalenediol derivative than in 1,4-$C_6H_4(OPF_2)_2$, the bond lengths and angles are such that the former can more readily become part of a fairly small ring than the latter, and this is demonstrated by the reactions with $[Mo(nbd)(CO)_4]$. The ligands we have described, and others which can be made in the same way, cover a great range of distances between the phosphorus donor sites, and may be useful in a wide variety of situations. All the complexes described in this paper were viscous liquids, and we hope to continue studies of these ligands with different metal systems, and to obtain crystalline products which can be characterised more completely, particularly by *X*-ray diffraction.

Experimental

All volatile compounds were handled using a Pyrex-glass vacuum line fitted with glass stopcocks, greased with Apiezon N. Bis(difluorophosphino) sulphide was prepared from bromodifluorophosphine and bis(tributylstannyl) sulphide,[6] and was purified by fractional condensation. Its purity was checked spectroscopically. Molybdenum and tungsten carbonyl complexes were prepared by standard methods,[7] and the phosphine complexes were handled under a purified nitrogen atmosphere.

N.m.r. spectra were obtained using Bruker WH360 (^1H), WP200 (^{13}C), and WP80 (^{19}F) and JEOL FX60 (^{31}P) spectrometers; mass spectra were recorded using an AEI MS902 spectrometer, with an ionizing potential of 40 eV (6.4×10^{-18} J), at temperatures of 370—400 K.

Preparation of 1,3- *and* 1,4-$C_6H_4(OPF_2)_2$.—Bis(difluorophosphino) sulphide (4.0 mmol) was condensed into a glass ampoule (50 cm^3) containing 1,3- or 1,4-$C_6H_4(OH)_2$ (1.5 mmol) in chloroform or Et_2O (2 cm^3). The mixture was warmed to room temperature and left for 4 h, although much shorter reaction times could be used. The volatile products were distilled into the vacuum line and passed through a bath held at 195 K, at which temperature the ligands $C_6H_4(OPF_2)_2$ were retained and all other products were volatile.

Preparation of Other Bidentate Difluorophosphine Ligands.—In a typical reaction, bis(difluorophosphino) sulphide (0.3 mmol) was condensed into a 5-mm n.m.r. tube containing a naphthalenediol (0.1 mmol) and deuteriochloroform (0.5 cm^3). The tube was warmed to room temperature and the reaction was monitored by n.m.r. spectroscopy, being essentially complete in 10 min. In some cases the solution of ligand was then treated with a metal carbonyl complex without further purification, and in others the solvent and other volatile compounds were removed, leaving the involatile ligand, to which fresh solvent was added.

Reactions of Bidentate Ligands with N-*Methylpyridinium Pentacarbonyliodomolybdate.*—In a typical reaction, *N*-methylpyridinium pentacarbonyliodomolybdate (0.2 mmol) and a bidentate ligand (0.1 mmol) were allowed to react at room temperature in CD_2Cl_2 or $CDCl_3$ solvent for 1—3 h, in a vessel which had been sealed under vacuum. A white precipitate of *N*-methylpyridinium iodide was formed, leaving a yellow solution. The vessel was opened and the contents were filtered, and the solution was then sealed in an n.m.r. tube. The complexes could be isolated, simply by pumping off the solvent and any other volatile materials, as yellow, air-sensitive oils. The oils solidified on cooling, but despite considerable efforts we were unable to obtain any crystalline material suitable for a single-crystal *X*-ray diffraction study.

Reactions of Bidentate Ligands with Tetracarbonyl(norbornadiene)molybdenum.—Typically, a solution of tetracarbonyl(norbornadiene)molybdenum (0.1 mmol) in $CDCl_3$ (0.5 cm^3) was mixed with 1,3-$C_6H_4(OPF_2)_2$ (0.1 mmol) in an n.m.r. tube. The reaction was monitored by ^{31}P n.m.r. spectroscopy, and was essentially complete after 3 h at room temperature. The tube was then opened and the solvent and free norbornadiene were removed under vacuum, leaving a pale yellow oily liquid containing a small amount of solid. The soluble portion was extracted with chloroform, and was shown to contain low-order oligomers $\{1,3\text{-}C_6H_4[OPF_2Mo(CO)_4F_2PO]\}_n$.

Preparation of Mixed Molybdenum–Tungsten Complexes.—Bis(difluorophosphino) sulphide (0.1 mmol) was condensed into an n.m.r. tube containing 1,3-$C_6H_4(OH)_2$ (0.1 mmol) and CD_2Cl_2 (0.5 cm^3). The tube was sealed and warmed to room temperature for 5 min. After opening the tube, the contents were added to *N*-methylpyridinium pentacarbonyliodotungstate (0.1 mmol) in a fresh n.m.r. tube, and the reaction was monitored by ^{31}P n.m.r. spectroscopy until it was complete (3 d). A further portion of bis(difluorophosphino) sulphide was then added, and this reacted in 10 min at room temperature. Finally, the solution was added to *N*-methylpyridinium pentacarbonyliodomolybdate (0.1 mmol), and this stage of the procedure was completed in 30 min at room temperature. The metal complexes were isolated by filtration, followed by removal of volatile material under vacuum. The same procedure was used with 1,4-$C_6H_4(OPF_2)_2$, and worked equally well if the molybdenum pentacarbonyl group was introduced first and the tungsten pentacarbonyl second.

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