Instant Ligands. Part 4.[1] Preparation of some Difluorophosphinite Ligands from Unsaturated Hydroxy Compounds, and their Reactions to form Molybdenum Complexes *

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The compounds $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$ and $(F_2P)OCH_2CH_2CN$ have been prepared by the reaction of $S(PF_2)_2$ with the appropriate alcohols, and have been characterised by n.m.r. and i.r. spectroscopy. The reactions of these compounds with some molybdenum(o) complexes have been studied using n.m.r. spectroscopy. The reaction of $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$ with *N*-methylpyridinium pentacarbonyliodomolybdate gives a compound with two $Mo(CO)_5$ groups linked by the ligand and with tetracarbonyl(norbornadiene)molybdenum, $[Mo(CO)_4(nbd)]$, an apparently polymeric product is obtained. The reaction of $(F_2P)OCH_2CH_2CN$ with $[C_5H_5NMe][Mo(CO)_5I]$ gives a mixture of complexes of the types $Mo(CO)_5L$ and $Mo(CO)_4L_2$, while with $[Mo(CO)_4(nbd)]$ the sole product is the $Mo(CO)_4L_2$ type complex. In all these cases the ligand appears to be co-ordinated to the metal by the phosphorus atom.

Difluorophosphinites have been known for many years[2] and are of interest both for their structures and their potential as ligands. Co-ordination to a metal by the phosphorus atom would be expected to stabilise low oxidation states of the metal since the PF_2O group is a good π acceptor. A number of such ligands have been used to prepare molybdenum(0)[3–5] and tungsten(0)[5] complexes. Some chromium(0),[6] nickel(0),[3] rhodium(I),[7] and ruthenium(II)[8] complexes have also been prepared.

If the ligand also contains a second type of potential co-ordination site then this may also bind to a metal atom, possibly of a different element giving the possibility of mixed-metal complexes. For example, alkynes will react with $[Co_2(CO)_8]$ by displacing two carbonyl groups and, acting as four-electron donors, bridge the cobalt atoms.[9,10] The $-C{\equiv}N$ group forms complexes with a variety of metal atoms.

Therefore we have prepared two compounds, 1,4-bis(difluorophosphinoxy)but-2-yne, $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$, and 3-difluorophosphinoxypropionitrile, $(F_2P)OCH_2CH_2CN$. We describe here their preparation and characterisation, and some representative reactions with molybdenum complexes. The displacement of I^- or bicyclo[2.2.1]heptadiene (norbornadiene, nbd) from suitable complexes by difluorophosphinites occurs readily under mild conditions[4,5] and thus such complexes were used here. Some unsuccessful attempts to form mixed-metal complexes are also described.

Results and Discussion

Preparation.—Both the compounds were prepared by reaction of $S(PF_2)_2$ with the appropriate alcohol, but-2-yne-1,4-diol or 3-hydroxypropanonitrile [equations (1) and (2)].

$$HOCH_2C{\equiv}CCH_2OH + 2S(PF_2)_2 \longrightarrow (F_2P)OCH_2C{\equiv}CCH_2O(PF_2) + 2PF_2HS \quad (1)$$

$$HOCH_2CH_2CN + S(PF_2)_2 \longrightarrow (F_2P)OCH_2CH_2CN + PF_2HS \quad (2)$$

This is a convenient method[4] since the alcohols are available commercially and the products are easily separated from the much more volatile $S(PF_2)_2$ and PF_2HS and the much less volatile alcohol. The reaction, separation, and purification were carried out using standard vacuum-line techniques.[11] The product of reaction (1) is a clear liquid, with a vapour pressure of *ca.* 3 Torr at 293 K and a melting point of 222 K, obtained in 92% yield. The product of the second reaction is also a clear liquid with a vapour pressure of *ca.* 1 Torr at 293 K and a melting point of 225 K. It was obtained in 94% yield.

Nuclear Magnetic Resonance Spectra.—N.m.r. spectroscopy (^{31}P, ^{19}F, ^{1}H, and ^{13}C) was used to ascertain the identities of the compounds and to characterise them. Most of the spectra are first order and the majority of the parameter values (Table 1) are similar to those found previously for difluorophosphinites.[4,5,12–15] The value of $^3J(FC)$ is slightly higher and that of $^2J(PC)$ lower than the equivalent couplings (9—10 and 3—4 Hz respectively) found for other PF_2O compounds.[4,15].

There is only one signal in the ^1H n.m.r. spectrum, with a chemical shift of δ *ca.* 4.8, higher than the value of 4.1 found for the CH_2 groups adjacent to the PF_2O groups in $(F_2P)O(CH_2)_4O(PF_2)_4$,[4] and this can be attributed to the effect of the alkyne group. Close examination, using narrow spectral widths, of both the ^1H and ^{31}P (central part of triplet) n.m.r. spectra revealed centrosymmetric second-order patterns consistent with the X and A atom spectra of an $[AX_2]_2$ spin system. The proton-coupled fluorine n.m.r. spectrum shows no resolvable F–H coupling.

The equations of Harris[16] which describe the X spectrum of an $[AX_2]_2$ spin system, while predicting a spectrum of superficial similarity to that found here, do not fit the peak positions well. These equations assume that the X–X′ coupling is zero and that it is the A–A′ coupling which is the more important long-range coupling. However, the reverse is probably true here and thus these equations are not valid for this system. Full simulation[17] of both the ^1H and ^{31}P (central part of triplet) n.m.r. spectra gave good comparison with the experimental spectra when values of 1.87 Hz for $J(XX')$ and zero for both $J(AA')$ and $J(AX')$ were used in the calculations. That a five-bond H–H coupling is observable is quite unusual and can be attributed to efficient spin transfer by the $C{\equiv}C$ bond.

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* *Non-S.I. unit employed:* Torr ≈ 133 Pa.

Vibrational Spectra.—Infra-red spectra were recorded for both the gaseous (pressure *ca.* 3 Torr) and liquid phases of $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$ and the Raman spectrum was also recorded for the liquid phase. The i.r. spectrum was recorded for the liquid phase of $(F_2P)OCH_2CH_2CN$, but a satisfactory gas-phase spectrum could not be obtained due to the very low vapour pressure of this compound. The peak positions obtained from these spectra are summarised in Tables 2 and 3 together with tentative assignments, based on group frequencies and reported assignments for similar compounds.[4,14,18]

Table 1. N.m.r. parameters for $(F_2P)OCH_2CCCH_2O(PF_2)$ and $(F_2P)OCH_2CH_2CN$

Parameter[a]	$(F_2P)OCH_2CCCH_2O(PF_2)$[b]	$(F_2P)OCH_2CH_2CN$[b]
δ(P)	113.3	111.7
δ(F)	−48.9	−49.1
δ(H)	4.75	4.26
δ(H′)	—	2.73
δ[C(1)]	50.9	57.8
δ[C(2)]	81.7	20.0
δ[C(3)]	—	116.7
^1J(PF)	1 299	1 297
^1J[C(1)H]	155	154
^1J[C(2)H′]	—	137
^2J[PC(1)]	2.3	4.1
^2J[C(1)H′]	—	4.9
^2J[C(2)H]	—	2.3
^3J[PC(2)]	n.s.[c]	3.4
^3J[FC(1)]	12.3	10.5
^3J(PH)	7.3	6.3
^3J(HH′)	—	6.2
^4J[C(1)H]	1.1	—
^5J(PH′)	—	0.7
^5J(HH)	1.87	—

[a] Chemical shifts (δ) are positive to high frequency in p.p.m. relative to 85% H_3PO_4 for ^{31}P, CCl_3F for ^{19}F, and $SiMe_4$ for ^1H and ^{13}C. Coupling constants (J) are absolute values in Hz. All spectra were recorded in CCl_2D_2 solution at room temperature. [b] Atom labelling: $(F_2P)OC(1)H_2C(2)C(2)C(1)H_2O(PF_2)$; $(F_2P)OC(1)H_2C(2)H'_2C(3)N$. [c] Not studied.

The most characteristic peaks are those due to P–F stretching modes (820—770 cm^{-1}) and the peaks at *ca.* 1 030 cm^{-1}, usually assigned[19] to O–C or antisymmetric P–O–C stretching modes. The position of the P–O or symmetric P–O–C stretching mode is not as certain but has been assigned[4,19] to peaks between 930 and 990 cm^{-1} and peaks in this range are present for other difluorophosphinites.[14,15] However, PF_2OCH_3 has no strong peak in this region and a peak at 785 cm^{-1} has been assigned to this mode.[18]

The regions 3 000—2 800 and 1 500—1 100 cm^{-1} correspond to C–H stretching and deformation modes respectively, though some peaks due to C–C stretching could lie in the latter region. For $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$ there are no peaks readily assignable to C–C stretching but for $(F_2P)OCH_2CH_2CN$ the peaks at 1 074 and 1 008 cm^{-1} might correspond to such modes.

The peak at 2 253 cm^{-1} in the Raman spectrum of $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$ is at about the highest frequency normally found for a C≡C bond, usually between[20] 2 260 and 2 100 cm^{-1}, while no corresponding peak is apparent in the i.r. spectrum. The moderately strong peak at 2 330 cm^{-1} is probably an overtone from the band at 1 162 cm^{-1} in Fermi resonance with the C≡C stretching mode. The small peaks between 2 500 and 1 500 cm^{-1} in the i.r. spectrum are probably overtones or combination bands since they are fairly broad and of low intensity.

The peaks below 600 cm^{-1} are difficult to assign as the frequencies for the various modes expected here are quite variable. The assignments suggested are made merely by comparison with other reported assignments[4,18] and are very uncertain.

Unfortunately it is not possible to deduce much about the symmetry of the molecule. The absence of an absorption for the C≡C stretching mode in the i.r. spectrum suggests an inversion centre, but it is also possible that the dipole change caused by this vibration is so small that the peak is simply too weak to be

Table 2. Vibrational frequenices (cm^{-1}) for $(F_2P)OCH_2CCCH_2O(PF_2)$

I.r.			
Gas	Liquid	Raman liquid	Suggested assignment
2 950w	2 948m	2 957m, p	C–H stretch
2 883vw	2 878w	2 880w, p	
	2 820vw		Combination (1 452 + 1 370)
		2 330m, p	Overtone (1 162)
		2 253vs, p	C≡C stretch
	1 820w, br		Combination (1 033 + 790)
	1 580vw, br		Combination (815 + 778)
1 457vw	1 452m	1 455s	C–H deformation
1 370m	1 370s	1 378s	
1 260w	1 256m	1 262m	
1 158m	1 159s	1 162w	
1 022s	1 020vs	1 033vs, p	O–C stretch
993s	985vs	990s, p	P–O stretch?*
865w			
829s	815vs	818s, p	P–F stretch
800s	778vs	790s	
	553m		
530w	530m		PF_2 wag?*
		445m, br, p	PF_2 deformation?*
—	368m	370s	PF_2 rock?*
—	338w	342m	
—		293m, br	

Abbreviations: w = weak, m = medium, s = strong, br = broad, v = very, and p = polarised.

* See text.

Table 3. Vibrational frequencies (cm^{-1}) for $(F_2P)OCH_2CH_2CN$

I.r., liquid	Suggested assignment
3 130m, br	Impurity
2 970m	C–H stretch
2 915m	
2 800w	
2 252m	C≡N stretch
1 762w, br	Combination (1 008 + 755)
1 725w, br	Combination (933 + 805)
1 468m	C–H deformation
1 410s	
1 387m	
1 336m	
1 261m	
1 223m	
1 074s	C–C stretch?*
1 040vs	O–C stretch
1 008s	C–C stretch?*
933s	P–O stretch?*
805vs	P–F stretch
775vs	
577m	
546m	
526s	
499m	
470m	
374m, br	
305m	

Abbreviations: w = weak, m = medium, s = strong, br = broad, and v = very.

* See text.

observed. Neither is it possible to decide whether there is overall exclusion between the i.r. and Raman since the difference in frequency between modes which are symmetric or antisymmetric with respect to the two ends of the molecule will, in most cases, be slight.

The very broad peak at 3 130 cm^{-1} in the spectrum of $(F_2P)OCH_2CH_2CN$ is due to an impurity, probably a hydrolysis product as the intensity of this peak increases upon deliberate exposure of the sample to air. The peak at 2 252 cm^{-1} is due to C≡N stretching and there is a peak in the same position in the i.r. spectrum of $HOCH_2CH_2CN$.

Reaction of $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$ *with* $[Mo(CO)_5I]^-$.—The reaction was carried out in an n.m.r. tube using a ratio of 2 mol of complex to one of the ligand. After 1 h at room temperature the ^{31}P-$\{^1H\}$ n.m.r. spectrum showed unreacted ligand as a triplet at 113 p.p.m. and two co-ordinated species with very similar shifts of *ca.* 154 p.p.m. After 3 h the intensity of the signal due to the species at slightly lower frequency had decreased with respect to that of the other species and there was very little free ligand left unreacted. Further small signals were observed in the second spectrum and these were assigned to PF_3, both free and complexed, which was confirmed by the fluorine n.m.r. spectrum.

The co-ordinated species at slightly lower chemical shift probably contains a ligand with only one PF_2 group co-ordinated while in the other species both PF_2 groups are co-ordinated. As the reaction proceeds the signal of the former species diminishes as its free end becomes co-ordinated, giving the latter species whose signal consequently grows. The signal due to apparently free ligand may be largely due to the unco-ordinated PF_2 groups of ligands attached by only one end as the peaks from these two species must overlap.

The main product of the reaction has the n.m.r. parameters $\delta(P) = 154$, $\delta(F) = -19.2$ p.p.m., and $^1J(PF) = 1\,240$ Hz, all of which are consistent with the most likely product, $[\{Mo(CO)_5\}_2\{(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)\}]$. Unfortunately it was not possible to confirm that the C≡C bond was not co-ordinated. The sample was too weak to allow observation of quaternary carbon atoms in the ^{13}C n.m.r. spectrum and the C≡C stretch of the free ligand was not observed in the i.r. spectrum so its absence in the spectrum of the complex would be of little significance. An attempt to record a solution Raman spectrum failed due to boiling of the yellow solution. However, it seems unlikely that the C≡C bond is co-ordinated since, unless CO were eliminated, there would be insufficient complex for complete reaction with the PF_2 groups and more apparently unreacted ligand would be observed in the ^{31}P n.m.r. spectrum.

Preparation and isolation of $[\{Mo(CO)_5\}_2\{(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)\}]$ was attempted and a brown oil was obtained by complete evaporation of the solvent. A solid could not be obtained despite attempts to precipitate the complex from CCl_2H_2 solution by adding another solvent and reducing the solution volume by evaporation. Several common solvents were tried but an oil was always deposited. Solutions in CCl_2H_2 and diethyl ether were cooled to approximately 250 K and left for a week but no precipitation of solid occurred.

The reaction of $[\{Mo(CO)_5\}_2\{(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)\}]$ with $[Co_2(CO)_8]$ was attempted using the solution of complex obtained in the n.m.r. tube reaction described above. However, a paramagnetic species, probably from an impurity in the cobalt octacarbonyl, was found to be present in the tube and no spectrum could be obtained.

An alternative route to the mixed cobalt–molybdenum complex envisaged above would be to treat $[Co_2(CO)_6(HOCH_2C{\equiv}CCH_2OH)]$ with $S(PF_2)_2$, to replace the hydroxy groups by PF_2O, then with $[Mo(CO)_5I]^-$ to give co-ordination to molybdenum. Therefore the reaction of $[Co_2(CO)_6(HOCH_2C{\equiv}CCH_2OH)]$ with $S(PF_2)_2$ was tried on a small scale in an n.m.r. tube. After 30 min at room temperature a solid had formed in the tube and a fluorine n.m.r. spectrum showed PF_2HS as the only major soluble product. As this is an expected product from the reaction of $S(PF_2)_2$ with a hydroxy group it appears that such a reaction has occurred, but since the other phosphorus-containing product does not appear in the spectrum it must be very insoluble. One possibility is that the resulting PF_2O groups have displaced carbonyl groups from other molecules, giving polymers. Replacement of CO in $[Co_2(CO)_6(RC{\equiv}CR')]$ compounds by various phosphines has been observed,[21] though heating was required. However, reaction of $Ph_2PC{\equiv}CCF_3$ with $[Co_2(CO)_8]$ at room temperature has been found to result in co-ordination of phosphine and alkyne.[22]

Reaction of $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$ *with* $[Mo(CO)_4(nbd)]$.—This reaction was carried out in an n.m.r. tube using a 1:1 ratio of ligand to metal complex in CCl_2D_2 solvent. After 10 min at room temperature a brown precipitate rapidly formed. No signal could be found in the phosphorus n.m.r. spectrum, suggesting that all the ligand had reacted to give a very insoluble product, probably a polymer. This is not surprising as the ligand is capable of bridging and, since there are two available co-ordination sites on the substrate, this bridging could continue indefinitely. The results are in agreement with those of Bell[23] who tried this reaction using the products from the direct reaction of $HOCH_2C{\equiv}CCH_2OH$ and $S(PF_2)_2$ without isolation and purification of the ligand.

Reaction of $(F_2P)OCH_2CH_2CN$ *with* $[Mo(CO)_5I]^-$.—The ligand and metal complex were mixed in equimolar proportions in an n.m.r. tube together with CCl_3D and the reaction was followed by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy. After an hour at room temperature the spectrum showed unreacted ligand and several species at higher chemical shift, indicating co-ordinated species. After 13 h the triplet at 144 p.p.m. (species A) had diminished relative to the signals at 151 (species B) and 152 p.p.m. (species C). After 2 weeks all free ligand had disappeared, as had species A, leaving only the triplet from species B and the second-order pattern from species C, together with a very weak, second-order signal at *ca.* 155 p.p.m. (species D). The second-order patterns from species C and D were similar and resembled that obtained from the A nuclei of an $[AX_2]_2$ spin system.

The $^{19}F-\{^1H\}$ n.m.r. spectrum shows a doublet which, from the coupling, corresponds to species B in the phosphorus spectrum. Thus this species has n.m.r. parameters $\delta(P) = 151$ p.p.m., $\delta(F) = -20.3$ p.p.m., and $^1J(PF) = 1\,239$ Hz, which are consistent with those expected for $[Mo(CO)_5(F_2POCH_2CH_2CN)]$, the predicted product of this reaction. The fluorine n.m.r. spectrum also shows one second-order pattern consistent with the X spectrum for an $[AX_2]_2$ system, which thus corresponds to species C. Therefore this species seems to have two ligands attached to the metal centre. The second-order pattern was analysed[16] and the n.m.r. parameters for species C are $\delta(P) = 152$, $\delta(F) = -19.7$ p.p.m., $^1J(PF) = 1\,234$, $^2J(PP) = 53$, and $^3J(PF) = 3$ Hz, which are consistent with those expected for $[Mo(CO)_4(F_2POCH_2CH_2CN)_2]$. The small value of $^3J(PF)$ suggests that the complex is the *cis* isomer.[13] There is no clear signal corresponding to species D in the fluorine spectrum, but the signal was very weak in the phosphorus spectrum anyway. This species could be the *trans* isomer of species C or perhaps a complex similar to C but with a carbonyl group replaced by some other group not co-ordinated *via* a phosphorus atom.

Species A appears to contain just one co-ordinated PF_2 group on each metal atom, since it gives a simple triplet with $^1J(PF)$ coupling of 1 235 Hz, but it has a chemical shift *ca.* 7 p.p.m. lower than that of species B. The most likely reason for this difference in chemical shift is the effect of some other ligand co-ordinated to the metal atom, either I^-, solvent, or C≡N. If it is C≡N which is co-ordinated this may be from the same ligand as the PF_2 group, that is a chelated ligand, or from a different ligand. In the latter case either or both of the other ends of the ligand may be co-ordinated to another metal centre. Unfortunately we have insufficient information to differentiate between these various possibilities.

The presence of species C suggests that the ligand is capable of displacing a carbonyl group from the molybdenum complex at room temperature. This is rather unusual for a difluorophosphinite, as elevated temperatures or radiation are normally required[13] for such reactions. To test this possibility, $(F_2P)OCH_2CH_2CN$ was treated with an equimolar quantity of molybdenum hexacarbonyl in an n.m.r. tube at room temperature. Species corresponding to B and C were observed in both the phosphorus and fluorine n.m.r. spectra and therefore either the PF_2 or the C≡N group must be capable of displacing CO directly at room temperature.

Detecting C≡N co-ordination by ^{13}C n.m.r. spectroscopy is difficult since the quaternary carbon atom in this group, like those in C≡C, is not easy to observe because of its long relaxation time. In principle, observation of a change in the C≡N stretching frequency in the i.r. spectrum could be used[24] to detect co-ordination of this group. However, the solution available here appeared to be too weak for this method, as no peak could be observed in the C≡N stretching region.

Reaction of $(F_2P)OCH_2CH_2CN$ *with* $[Mo(CO)_4(nbd)]$.—The reaction was carried out in an n.m.r. tube using a 1:2 ratio of metal complex to ligand in CCl_2D_2 solvent. After 1 h the $^{31}P-\{^1H\}$ n.m.r. spectrum showed unreacted ligand and two co-ordinated species at higher chemical shift. The signal at 148 p.p.m. was either a triplet with $^1J(PF)$ *ca.* 1 240 Hz or a second-order pattern. The signal at 153 p.p.m. appeared to be from an $[AX_2]_2$ spin system. After 2 d only the species at 153 p.p.m. was in evidence. The second-order pattern of this species was identical with that of species C obtained from the reaction with $[Mo(CO)_5I]^-$. Since this is the expected product, *cis*-$[Mo(CO)_4(F_2POCH_2CH_2CN)_2]$, from the reaction with $[Mo(CO)_4(nbd)]$ this also lends support to the *cis* assignment for this species. However, the stereochemistry of product and starting complex need not be the same,[25] since rearrangements could occur.

There appeared to be a transient species of a similar nature to that of species A in the reaction of $(F_2P)OCH_2CH_2CN$ with $[Mo(CO)_5I]^-$. Jones and Coskran[26] found that reaction of ligands of the type R_2PCN in a 2:1 ratio with $[Mo(CO)_4(nbd)]$ in n-hexane at room temperature gave $[\{Mo(CO)_4(R_2PCN)\}_2]$ with the ligands bridging. On refluxing the bridges broke to give $[Mo(CO)_4(R_2PCN)_2]$. A similar reaction could be occurring here, though the bridged species would need to be less stable since it converts even at room temperature.

An attempt to isolate $[Mo(CO)_4(F_2POCH_2CH_2CN)_2]$ was not successful due to problems similar to those encountered when trying to isolate $[\{Mo(CO)_5\}_2\{(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)\}]$. The oil obtained was apparently unstable with respect to either air or moisture since on exposure to the atmosphere the colour changed from pale yellow to blue within a couple of hours. A similar instability has been noted[26] for $[Mo(CO)_4(R_2PCN)_2]$ compounds. The i.r. spectrum showed many overlapping, broad bands in the carbonyl region, probably because of the impurity of the product, and therefore gave no useful information about the identity of the product.

Experimental

Volatile compounds were handled in a conventional Pyrex-glass vacuum line[11] with ground-glass taps and joints lubricated by Apiezon N and L grease respectively. Each time the line was cleaned it was dried in an oven before being assembled, left under vacuum for 24 h, and treated with $SiClMe_3$ vapour. The line was then, and at frequent intervals, exposed to a sample of $S(PF_2)_2$ to ensure that no water or other OH groups remained on the surface of the glass to react with any other PF_2 compounds. Reactions were carried out in Pyrex-glass ampoules fitted with 'Sovirel' greaseless taps and connected to the vacuum line by ground-glass joints. Transition-metal complexes were handled under dry nitrogen in Schlenk tubes or ampoules using a conventional Schlenk line.[11] The n.m.r. tubes used were of 5 mm diameter and were attached to the vacuum line *via* ground-glass joints and sealed once filled.

The reagent $S(PF_2)_2$ was prepared from the reaction of $PBrF_2$ with $S(SnBu_3)_2$ but it was not possible to obtain it without some PF_2HS as an impurity. ^{31}P N.m.r. spectroscopy was used to ensure that the level of this impurity was less than 5% so that this could be allowed for in the quantities of the reagent used in reactions, which were normally excesses anyway. The complex $[Co(CO)_6(HOCH_2C{\equiv}CCH_2OH)]$ was prepared by the literature method.[10] Solvents were either distilled, or dried and deoxygenated, using standard methods.[27]

Infra-red spectra were recorded in the range 4 000—200 cm^{-1} using a Perkin-Elmer 598 spectrophotometer. Gaseous samples were contained in a 100-mm cell fitted with KBr windows and liquid samples were placed between CsI plates. The Raman spectrum was recorded on a Spex Ramalab spectrometer, using an argon-ion laser with a wavelength of 541.5 nm, with the sample held in a glass capillary. N.m.r. spectra were recorded on various spectrometers: JEOL FX60Q and FX90Q (^{31}P), Bruker WP80SY (^{19}F, ^1H), Bruker WP200SY (^{31}P, ^{13}C, ^1H), and Bruker WH360 (^{31}P, ^1H).

Preparation of $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$.—A sample of $HOCH_2C{\equiv}CCH_2OH$ (426 mg, 4.95 mmol) was placed in an ampoule which was then evacuated and left open to the pump for 2 h. Then $S(PF_2)_2$ (10.9 mmol) was condensed into the ampoule which was sealed and warmed to room temperature. After 30 min the volatile products were transferred to a trap on the vacuum line. The products were first fractionated through a trap held at 177 K. The material retained in this trap was fractionated through a trap at 227 K, which then contained the pure product. The identity and purity of the product were checked by i.r. and n.m.r. spectroscopy. Elemental analyses could not be obtained because the compound is very sensitive to air and moisture and is also slightly volatile.

Preparation of $(F_2P)OCH_2CH_2CN$.—A quantity of $HOCH_2CH_2CN$ (419 mg, 5.89 mmol) was placed in an ampoule which was then evacuated and left open to the pump for 30 min. The sample was left under vacuum for a further 16 h before being briefly exposed to the pump again. A measured quantity of $S(PF_2)_2$ (6.5 mmol) was condensed into the ampoule which was then sealed and warmed to room temperature. After 1 h the volatile products were transferred to a trap on the vacuum line. The products were fractionated through a trap at 177 K and then the retained material further fractionated through a trap held at 236 K. The product retained in this trap still contained small amounts of impurities. With the trap closed the contents were warmed to room temperature and then the trap was opened very briefly to the pump. After repeating this procedure once, the product remaining in the trap was pure. Its identity and purity were checked as for $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$.

N.M.R. Tube Reactions between Ligands and Metal Complexes.—A weighed sample of the complex (*ca.* 0.1 mmol) was placed in an n.m.r. tube which was then evacuated and left open to the pump for 30 min. The required quantity of ligand was measured out using the following procedure. A small, evacuated glass ampoule was weighed and then a quantity of the ligand was condensed in and the ampoule reweighed to give the amount of ligand present. Ligand was then added or removed, on the vacuum line, and the ampoule reweighed until the required quantity of ligand was present. Solvent (0.5 cm^3) was condensed into the tube followed by the previously measured quantity of ligand. The tube was sealed, warmed to room temperature, and the reaction followed by ^{31}P n.m.r. spectroscopy. For reactions with $[C_5H_5NMe][Mo(CO)_5I]$ and $[Mo(CO)_6]$ the solvent used was CCl_3D whereas for $[Mo(CO)_4(nbd)]$ it was CCl_2D_2.

Attempted Preparation of Difluorophosphinite Complexes.—A solution of the molybdenum starting material in CCl_2H_2 (4 cm^3) was placed in a greaseless tap ampoule, the required quantity of ligand condensed in, and the ampoule sealed. The reaction mixture was stirred at room temperature and then filtered. The solvent was removed by evaporation to leave an oily residue. This residue was dissolved in CCl_2H_2 (1 cm^3) and then diethyl ether (1 cm^3) was added dropwise with stirring. The volume was reduced by evaporating solvent from the mixture, which resulted in an oil separating out. This procedure was repeated using n-pentane, cyclohexane, and toluene, but each time an oil separated from the solution. Finally all the solvent was again removed to leave the oily residue.

For the preparation of $[Mo(CO)_4(F_2POCH_2CH_2CN)_2]$, 56 mg (0.187 mmol) of complex and 47 mg (0.382 mmol) of ligand were used and the reaction time was 45 h. For $[\{Mo(CO)_5\}_2\{(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)\}]$, 192 mg (0.420 mmol) of complex and 45 mg (0.203 mmol) of ligand were used and the reaction was left for 5 h. For the latter reaction further attempts to obtain a solid were made in the following manner. Diethyl ether (5 cm^3) was added to the residue giving a pale yellow solution but leaving at least half of the residue undissolved. The solution was separated from the residue which was then dissolved in a minimum quantity of CCl_2H_2 (*ca.* 0.5 cm^3). The solutions were placed into separate glass tubes which were then evacuated, sealed, and placed in a refrigerator at approximately 250 K for 1 week. The tubes were then examined for the presence of any solid, but none was apparent.

Reaction of $[\{Mo(CO)_5\}_2\{(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)\}]$ *with* $[Co_2(CO)_8]$.—The n.m.r. tube from the reaction of $(F_2P)OCH_2C{\equiv}CCH_2O(PF_2)$ (13 mg, 0.059 mmol) with $[C_5H_5NMe][Mo(CO)_5I]$ (53 mg, 0.116 mmol) was opened and the solvent evaporated. The residue was then dissolved in CCl_2D_2 (0.5 cm^3), filtered, and the filtrate transferred to an n.m.r. tube containing $[Co_2(CO)_8]$ (14 mg, 0.041 mmol). This tube was then evacuated, sealed, and left at room temperature for 15 min before being examined by n.m.r. spectroscopy.

Reaction of $[Co_2(CO)_6(HOCH_2C{\equiv}CCH_2OH)]$ *with* $S(PF_2)_2$.—A sample of $[Co_2(CO)_6(HOCH_2C{\equiv}CCH_2OH)]$ (36 mg, 0.097 mmol) was placed in an n.m.r. tube which was then evacuated and the contents immediately cooled to 77 K. Solvent (CCl_3D, 0.5 cm^3) was condensed into the tube, followed by $S(PF_2)_2$ (0.20 mmol), and the tube sealed. The tube was warmed to room temperature and left for 30 min before being examined.

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