Trifluoromethylphosphine Complexes of Tricarbonylnitrosylcobalt

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The reaction of $P(CF_3)_nX_{3-n}$ (L; n = 1 or 2, X = F, Cl, Br, or I) with $[Co(CO)_3(NO)]$ at room temperature gives $[Co(CO)_2(NO)L]$ as the major product in all cases except $P(CF_3)I_2$. The chloro- and fluoro-phosphines can additionally form $[Co(CO)(NO)L_2]$ and the fluorophosphines give intermediates of sufficient thermal stability to allow total substitution of CO under more forcing conditions, giving $[Co(NO)L_3]$. Exchange reactions between free ligand (L′) and the co-ordinated phosphine (L) in $[Co(CO)_2(NO)L]$ enable the construction of the following displacement series: $P(CF_3)F_2 \sim P(CF_3)_2F > P(CF_3)Cl_2 \sim P(CF_3)_2Cl > PBr(CF_3)_2 > P(CF_3)H_2 > P(CF_3)_2I > PBr_2(CF_3)$. The reactivity of the P–X bond in the co-ordinated phosphines is much lower than that in the corresponding free phosphine.

COMPLEXES of the general formula $[Co(CO)_{3-n}(NO)L_n]$ (n = 1 or 2; L = an aryl-phosphine, -arsine, or -stibine) have been known since 1957.[1] Complexes containing alkyl- and halogen-substituted phosphines have also been prepared,[2] and more recently some trifluoromethylphosphines have been investigated as ligands towards $[Co(CO)_3(NO)]$.[3-5]

We now report a detailed study of the substitution of CO by $P(CF_3)_nX_{3-n}$ (X = halogen; n = 1 or 2) in $[Co(CO)_3(NO)]$ including an examination of the relative tendency of a ligand to replace another which is already co-ordinated.

RESULTS AND DISCUSSION

Preparation of the Complexes.—Monosubstituted complexes, $[Co(CO)_2(NO)L]$, have been obtained for all the ligands $P(CF_3)X_2$ and $P(CF_3)_2X$, with the exception of $P(CF_3)I_2$, by the room-temperature reaction of the ligands with tricarbonylnitrosylcobalt. However, the fluoro- and chloro-phosphines also give more highly substituted products. Prolonged heating of $P(CF_3)_2Cl$ with $[Co(CO)_2(NO)\{P(CF_3)_2Cl\}]$ gave $[Co(CO)(NO)\{P(CF_3)_2Cl\}_2]$ in low yield, and the corresponding disubstituted complex of $P(CF_3)Cl_2$ was prepared by the further reaction of the ligand with $[Co(CO)_2(NO)\{P(CF_3)Cl_2\}]$. The disubstituted derivatives form a significant portion of the products from mixtures of $P(CF_3)F_2$ or $P(CF_3)_2F$ and $[Co(CO)_3(NO)]$ at room temperature, and the tris(phosphine) complexes can be prepared by heating reaction mixtures containing excess of the appropriate ligand, to 60 °C for $P(CF_3)F_2$ and 120 °C for $P(CF_3)_2F$. The more forcing conditions required for complete substitution by $P(CF_3)_2F$ parallel those for substitution of the same two fluorophosphines in $[Ni(CO)_4]$.[6] The previous explanation of steric inhibition in the case of the bulkier $P(CF_3)_2F$ seems correct, especially as it has been reported that $[Co(CO)(NO)\{P(CF_3)_3\}_2]$ can be prepared but $[Co(NO)\{P(CF_3)_3\}_3]$ cannot.[3] The trifluoromethylphosphine complex $[Co(CO)_2(NO)\{P(CF_3)H_2\}]$ was also required for comparison purposes, and was formed by the action of the appropriate phosphine on $[Co(CO)_3(NO)]$ as reported in the literature.[5] Some properties of the complexes are given in the Table.

The complexes are all liquids at room temperature with low vapour pressures so that all could be handled using vacuum-line techniques. They vary in colour from pale yellow $[Co(NO)\{P(CF_3)F_2\}_3]$ to deep red for the iodo- and bromo-complexes. The thermal stability is greatest for the fluorophosphine complexes which survive heating to 100 °C. All the other complexes slowly lose CO at room temperature, the rate of loss being highest for the complexes of $P(CF_3)_2I$ and $PBr_2(CF_3)$. However, under a pressure of CO the phosphine ligand can be replaced and $[Co(CO)_3(NO)]$ reformed from the monosubstituted complexes.

The absence of observed disubstituted products other than for chlorophosphine and fluorophosphine ligands can be attributed to weaker Co–P bonding with these ligands, although it could also be interpreted as due to the more rapid thermal decomposition of these complexes competing successfully with further substitution.

A useful method of identification of the more volatile complexes in mixtures is the ν(NO) overtone band at *ca.* 3 600 cm^{-1} which is more easily resolved into its components than the fundamental at *ca.* 1 800 cm^{-1}. The

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[1] L. Malatesta and A. Araneo, *J. Chem. Soc.*, 1957, 3803.

[2] W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, 1963, **2**, 723.

[3] A. B. Burg and I. H. Sabherwal, *Inorg. Chem.*, 1970, **9**, 974.

[4] I. H. Sabherwal and A. B. Burg, *Inorg. Chem.*, 1972, **11**, 3138.

[5] I. H. Sabherwal and A. B. Burg, *Inorg. Chem.*, 1973, **12**, 697.

[6] A. B. Burg and G. B. Street, *Inorg. Chem.*, 1966, **5**, 1532.

polysubstituted complexes gave the symmetrical ^{19}F n.m.r. spectra anticipated from chemically equivalent but magnetically inequivalent nuclei for both phosphorus and fluorine, although accurate values of J_{PP} cannot be obtained from the ^{19}F spectra because the limiting case is approached and J_{PP} is small compared to $^{2}J_{FP}$.

Spectroscopic properties of some fluorocarbon–phosphine derivatives of $[Co(CO)_3(NO)]$

	Infrared data (cm^{-1}) [a]					^{19}F N.m.r. data [b]	
Complex	L	ν(CO)		ν(NO)	2ν(NO)	δ/p.p.m.[c]	$^{2}J_{FP}$/Hz
$[Co(NO)L_3]$	$P(CF_3)F_2$			1 852	3 672	79.8 (80.7)	122 [d] (87.2)
	$P(CF_3)_2F$			1 854		68.6 (66.5)	107 [d] (89.6)
$[Co(CO)(NO)L_2]$	$P(CF_3)F_2$	2 065		1 840	3 658	79.8 (80.7)	116 [d] (87.2)
	$P(CF_3)_2F$	2 072		1 842	3 664	68.7 (66.5)	102 [d] (89.6)
	$P(CF_3)Cl_2$ [e]					75.7 (72.1)	105.5 [f] (79.9)
	$P(CF_3)_2Cl$	2 062		1 838		65.7 (61.3)	96 [d] (85)
$[Co(CO)_2(NO)L]$	$P(CF_3)F_2$	2 087	2 045	1 831	3 640	79.4 (80.7)	110 [d] (87.2)
	$P(CF_3)_2F$	2 085	2 045	1 832	3 643	69.0 (66.5)	99 [g] (89.6)
	$P(CF_3)Cl_2$	2 082	2 042	1 829	3 632	75.9 (72.1)	102 (79.9)
	$P(CF_3)_2Cl$	2 082	2 043	1 830	3 636	66.3 (61.3)	94 (85)
	$PBr_2(CF_3)$	2 081	2 042	1 827		73.7 (67.8)	93 (69.6)
	$PBr(CF_3)_2$	2 083	2 044	1 829	3 628	64.6 (59.0)	90 (81)
	$P(CF_3)_2I$	2 082	2 042	1 825		62.2 (55.4)	82 (73.2)
	$PBr(CF_3)Cl$ [e]					74.7 (70.0)	98 (75)
	$P(CF_3)H_2$	2 073	2 027	1 813	3 600	52.1 [h] (42.4)	64.5 (48.5)

[a] Measured in the vapour phase. [b] The values in parentheses refer to the free ligand and are taken from ref. 7 and from K. J. Packer, *J. Chem. Soc.*, 1963, 960. [c] Resonance of the CF_3 group, measured relative to CCl_3F. [d] For the separation of the peak centres which approximates closely to $^{2}J_{FP}$ when the other coupling constants are small. [e] Detected by n.m.r. spectroscopy but not obtained pure. [f] $^{4}J_{FP}$ 4.5 Hz. [g] $^{3}J_{FF}$ 4.5 Hz for complex, $^{3}J_{FF}$ 3.5 Hz for free ligand. [h] $^{3}J_{FH}$ 8.0 Hz for complex, $^{3}J_{FH}$ 12.2 Hz for free ligand.

Reactions leading to Decomposition.—Di-iodo(trifluoromethyl)phosphine expelled *ca.* 2 mol of CO from $[Co(CO)_3(NO)]$ to give a brown solid with i.r. absorption bands at 1 856 and 1 798 cm^{-1} but no terminal CO bands. The mass spectra of the solids gave no useful information. Similar solids were formed in trace amounts [up to 20% for $P(CF_3)_2I$] in the preparation of the other complexes, and were also formed on pyrolysis of the monosubstituted products. It appears reasonable to suppose that these solids are analogous to the trimer, $[\{Co(CO)(NO)[P(CF_3)_2]\}_3]$, found to result from the pyrolysis of $[Co(CO)_2(NO)\{P(CF_3)_3\}]$,[3] as the ligand appears to be intact in the solid product.

Ligand-exchange Reactions.—A series of exchange reactions [equation (1)] has been examined. No mixed

$$[Co(CO)_2(NO)L] + L' \rightleftharpoons [Co(CO)_2(NO)L'] + L \quad (1)$$

complexes of the form $[Co(CO)(NO)(L)L']$ were observed, suggesting that the incoming phosphine ligand expelled the co-ordinated phosphine in preference to CO.

Further, in the exchange of $[Co(CO)_2(NO)\{P(CF_3)_2Cl\}]$ with $P(CF_3)Cl_2$, the amount of $P(CF_3)_2Cl$ displaced after 5 months was equal, within experimental error, to the amount of $[Co(CO)_2(NO)\{P(CF_3)Cl_2\}]$ formed, which would be unlikely if CO had been produced during the reaction. The following displacement series summarises the results: $P(CF_3)F_2 \sim P(CF_3)_2F > P(CF_3)Cl_2 \sim P(CF_3)_2Cl > PBr(CF_3)_2 > P(CF_3)H_2 > P(CF_3)_2I > PBr_2(CF_3)$. Ligands early in the series will partially displace those later in the series. The fluorophosphines, in addition to displacing other phosphine ligands, tend also to displace CO, forming $[Co(CO)(NO)L_2]$, and the free CO will in turn form $[Co(CO)_3(NO)]$, preventing accurate work. Redistribution involving only the complexes $[Co(CO)_n(NO)L_{3-n}]$ does not occur. The overall change in the remainder of the series is such that an equilibrium constant of *ca.* 100 is obtained when $P(CF_3)_2Cl$ is added to $[Co(CO)_2(NO)\{PBr_2(CF_3)\}]$.

A complication is that the phosphine expelled from the co-ordination sphere (L) may undergo a redistribution reaction with excess of L',[7] *e.g.* equations (2) and (3).

$$[Co(CO)_2(NO)\{P(CF_3)Cl_2\}] + PBr_2(CF_3) \rightleftharpoons [Co(CO)_2(NO)\{PBr_2(CF_3)\}] + P(CF_3)Cl_2 \quad (2)$$

$$PBr_2(CF_3) + P(CF_3)Cl_2 \rightleftharpoons 2PBr(CF_3)Cl \quad (3)$$

The mixed bromochlorophosphine formed according to equation (3) might then be expected to attack at cobalt to give a new complex. Of the possible mixed species, only $PBr(CF_3)Cl$ and $PBr(CF_3)I$ were detected, formed at a rate comparable with the exchange reaction (1). Neither of these mixed phosphines was observed as a complex in the exchange reactions, presumably because of their relatively low concentrations and unfavourable equilibrium constants with respect to the preferred ligand. It was, however, established that the mixed species did form complexes by allowing $PBr(CF_3)Cl$, prepared from $P(CF_3)Cl_2$ and $PBr_2(CF_3)$, to react with $[Co(CO)_3(NO)]$ when $[Co(CO)_2(NO)\{PBr(CF_3)Cl\}]$ was formed.

The rates of the exchange reactions appear to depend on the bulk of the ligands, as reactions involving $P(CF_3)_2X$ were much slower than those of $P(CF_3)X_2$. In view of the likelihood of a trigonal-bipyramidal intermediate[8] in the displacement, this can be explained in terms of steric crowding in the transition state.

Reactions of the P–X *Bond.*—Because of the known reactivity of $P(CF_3)_2I$, some reactions of $[Co(CO)_2(NO)\{P(CF_3)_2I\}]$ were attempted. In sharp contrast to the

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[7] R. C. Dobbie and P. Gosling, *J.C.S. Dalton*, 1975, 2368.

[8] F. Basolo, *Chem. in Britain*, 1969, 505.

free ligand, the complex did not react with mercury, mercury(II) chloride, or antimony trifluoride, and it was decomposed by aqueous alkali and KF in tetrahydrothiophene 1,1-dioxide, in the latter case giving at least some of the normal thermolysis product without attack at the P–I bond. Further, although $P(CF_3)Cl_2$ and $PBr_2(CF_3)$ exchange fairly quickly to form an equilibrium mixture with $PBr(CF_3)Cl$, $[Co(CO)_2(NO)\{P(CF_3)Cl_2\}]$ does not exchange with $[Co(CO)_2(NO)\{PBr_2(CF_3)\}]$. Presumably the reactions of the free phosphine involve an intermediate with increase in co-ordination number at phosphorus to four, which is the ground-state co-ordination number of the co-ordinated ligand. However, $[Fe(CO)_4(PBrF_2)]$ has been reported to react with $Ag[SCN]$, $Ag[N_3]$, or KF to replace the bromine with the relevant pseudohalogen or fluorine,[9] and five-co-ordination would be feasible for phosphorus.

EXPERIMENTAL

All the volatile compounds were handled by standard vacuum-line techniques. ^{19}F N.m.r. spectra were recorded at 84.66 MHz on a Bruker Spectrospin with CCl_3F as internal standard. Infrared spectra were obtained on a Perkin-Elmer 457 spectrometer in the gas phase for the complexes and in chloroform solution for the decomposition products. Tricarbonylnitrosylcobalt was prepared by the direct action of NO on $[Co_2(CO)_8]$ at 40 °C (24 h), giving yields of *ca.* 80% and forming no other volatile product. The ligands were prepared from $P(CF_3)I_2$ or $P(CF_3)_2I$ by the established routes.[10]

Preparation of the Complexes.—In a typical reaction, $P(CF_3)_2I$ (2.10 mmol) reacted at 20 °C with $[Co(CO)_3(NO)]$ (2.0 mmol) over a period of 6 d, with periodic removal of CO (2.43 mmol), to give $[Co(CO)_2(NO)\{P(CF_3)_2I\}]$ (1.60 mmol, 80%) which was trapped at -22 °C by vacuum fractionation. The monosubstituted complexes of $P(CF_3)Cl_2$, $P(CF_3)_2Cl$, $PBr_2(CF_3)$, and $PBr(CF_3)_2$ were prepared in a similar manner. In the reaction with $P(CF_3)Cl_2$, the monocarbonyl $[Co(CO)(NO)\{P(CF_3)Cl_2\}_2]$ was observed as a trace product in the -22 °C trap together with the predominant dicarbonyl product. The action of excess of $P(CF_3)_2Cl$ on $[Co(CO)_2(NO)\{P(CF_3)_2Cl\}]$ at 60 °C (7 d) gave $[Co(CO)(NO)\{P(CF_3)_2Cl\}_2]$, isolated by prolonged fractionation with pumping at -22 °C, when the dicarbonyl slowly passed but the monocarbonyl remained.

An approximately equimolar mixture of $P(CF_3)Cl_2$ (0.28 mmol) and $PBr_2(CF_3)$ (0.26 mmol) was allowed to equilibrate with $PBr(CF_3)Cl$ overnight. After $[Co(CO)_3(NO)]$ (0.87 mmol) had been added, the tube was heated (40 °C for 2 d), giving off CO (0.40 mmol). Examination by n.m.r. spectroscopy of the fraction trapped at -22 °C showed the presence of $[Co(CO)_2(NO)\{P(CF_3)Cl_2\}]$, $[Co(CO)_2(NO)\{PBr(CF_3)Cl\}]$, and $[Co(CO)_2(NO)\{PBr_2(CF_3)\}]$ in the ratio 7 : 7 : 9.

The complexes $[Co(CO)_n(NO)L_{3-n}]$ [$L = P(CF_3)F_2$ or $P(CF_3)_2F$; $n = 1$ or 2] were prepared by reaction (20 °C) of $[Co(CO)_3(NO)]$ with an equimolar amount of the appropriate fluorophosphine, again with periodic removal of CO over a period of 7 d. The mono- and di-substituted derivatives were separated with difficulty from each other and from the starting nitrosyl by repeated fractionation at -45 and -63 °C, the disubstituted complex being trapped at the former temperature and the monosubstituted complex at the latter. Heating $[Co(CO)_3(NO)]$ with excess of $P(CF_3)F_2$ at 60 °C until no more CO was given off formed $[Co(NO)\{P(CF_3)F_2\}_3]$, and $[Co(NO)\{P(CF_3)_2F\}_3]$ was prepared in a similar way at 120 °C. The mass spectra of the trisubstituted complexes were obtained, showing, in both cases, no ion above the parent ion $[Co(NO)L_3]^+$ and ions corresponding to $[Co(NO)L_2]^+$, $[Co(NO)L]^+$, $[Co(NO)]^+$, and also $[CoL_3]^+$, $[CoL_2]^+$, $[CoL]^+$, and L^+. Other ions were consistent with the breakdown of the complexes by loss of CF_3, F, and other stable fluorocarbon-containing fragments.

Exchange Reactions.—The exchange reactions were carried out by condensing pure samples of $[Co(CO)_2(NO)L]$, the competing ligand L′, and CCl_3F into an n.m.r. tube, which was then sealed and stored in the dark at 20 °C. Most of the equilibria were checked by making up samples of $[Co(CO)_2(NO)L']$ with L. The ^{19}F n.m.r. spectra were recorded shortly after mixing and then at weekly intervals until there was no further change or until the contents of the tube began to deteriorate.

Reactions of $[Co(CO)_2(NO)\{P(CF_3)_2I\}]$.—Small samples of the complex (*ca.* 0.5 mmol) in CCl_3F solution were shaken in separate reactions with Hg, $HgCl_2$, and SbF_3 for 24 h at 20 °C. In each case there was no reaction and the complex was recovered apart from slight loss attributable to thermal decomposition. The products of the reaction of the complex (0.40 mmol) and KF in tetrahydrothiophene 1,1-dioxide were also those of thermal decomposition, as shown by the i.r. spectrum of a pentane extract of the solid residue. After treatment with 20% K[OH] solution for 24 h at 20 °C, $[Co(CO)_2(NO)\{P(CF_3)_2I\}]$ (0.79 mmol) evolved CF_3H (1.05 mmol, 66% yield) but only small amounts of CO. No pure metal-containing product could be isolated.

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[9] W. M. Douglas and J. K. Ruff, *J. Chem. Soc.* (*A*), 1971, 3558.

[10] V. N. Kulakova, Yu. M. Zinov'ev, and L. Z. Soborovskii, *Zhur. obshchei Khim.*, 1959, **29**, 3957; A. B. Burg and G. Brendel, *J. Amer. Chem. Soc.*, 1958, **80**, 3198; F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565; K. J. Packer, *ibid.*, 1963, 960; R. G. Cavell and R. C. Dobbie, *J. Chem. Soc.* (*A*), 1967, 1308.