Complexes of 2-Chloroethoxybis(trifluoromethyl)phosphine with Carbonyls of Manganese, Iron, and Cobalt

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The compound $P(CF_3)_2(OCH_2CH_2Cl)$, L, can be prepared in high yield by the reaction of $P(CF_3)_2Cl$ with 2-chloroethanol. The ligand displaces CO or PF_3 from $[Co(CO)_3(NO)]$, $[CoH(PF_3)_4]$, and $[MnH(CO)_5]$, but $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ gives a little $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(CF_3)_2\}]$ as the only isolable organometallic product. Treatment of $[MnH(CO)_4L]$ with CCl_4 gives a mixture of $[MnCl(CO)_4L]$ and $[Mn_2Cl_2(CO)_8]$. The complex *cis*-$[Mn(CO)_4(\eta\text{-}C_2H_4)\{P(CF_3)_2O\}]$ is formed by a novel rearrangement in the reaction of $[MnH(CO)_4L]$ with NMe_3 or of $[MnCl(CO)_4L]$ with sodium amalgam.

RECENT work has shown that it is possible to synthesize heterocyclic transition-metal alkyl complexes in which one end of the alkyl chain is anchored to the metal atom by a phosphine [1] or arsine [2] ligand. We now report an attempt to prepare an analogous complex by a novel route, which led instead to an unusual rearrangement.

RESULTS AND DISCUSSION

Preparation of the Ligand.—The phosphinite ester $P(CF_3)_2(OCH_2CH_2Cl)$, L, was prepared by the elimination of HCl from a mixture of $P(CF_3)_2Cl$ and 2-chloroethanol in a manner analogous to earlier reactions.[3] The HCl liberated in the reaction shows no tendency to attack at the C–O bond as it does in $P(CF_3)_2(OBu^t)$.[4] Hydrolysis of L by aqueous alkali yields fluoroform quantitatively. As found for related species,[4] L does not spontaneously rearrange to a phosphine oxide $P(CF_3)_2(CH_2CH_2Cl)O$.

Ligand Action of L.—Treatment of $[Co(CO)_3(NO)]$ with L at 40 °C results in the formation of a deep red monosubstituted species $[Co(CO)_2(NO)L]$, closely resembling the previously reported $[Co(CO)_2(NO)\{P(CF_3)_2X\}]$ (X = Cl, Br, or I).[5] The i.r. (vapour-phase) and ^{19}F n.m.r. (CCl_3F solution) spectra strongly support the monosubstituted species (see Table), but there is some evidence in the mass spectrum for the existence of trace amounts of $[Co(CO)(NO)L_2]$.

Compound L expels 1 mol of PF_3 from $[CoH(PF_3)_4]$ to form the monosubstituted $[CoH(PF_3)_3L]$ as a colourless liquid.

With $[MnH(CO)_5]$ a single carbonyl group is replaced, to form $[MnH(CO)_4L]$, an involatile yellow oil stable up to 70 °C. In the ^1H n.m.r. spectrum (C_6F_6–C_6H_6 solution) a Mn–H resonance occurs at τ 18.38 [$^2J(PH)$ 55 Hz], which contributes 90% of the expected intensity. By analogy with the known trifluoromethylphosphine complexes of $[MnH(CO)_5]$,[6] this must correspond to the *trans* isomer: the Mn–H resonance due to *cis*-$[MnH(CO)_4L]$, in which the phosphine shares no bonding orbitals with the hydride ligand, would be expected to have a much smaller value of $^2J(PH)$, as has been observed in related systems.[6] The ^1H chemical shift, moreover, is similar to that of the earlier *trans* complexes. No Mn–H resonance due to *cis*-$[MnH(CO)_4L]$ is observed, presumably because of its relatively low intensity and quadrupole broadening. The ^{19}F n.m.r. spectrum shows resonances due to both the *cis* (12%) and *trans* (88%) isomers.

Treatment of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ with L produces a mixture of at least 10 products, according to the complexity of the ^{19}F n.m.r. spectrum. Only one product, a small amount of the known complex [7] $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(CF_3)_2\}]$, could be isolated.

Spectroscopic properties of some complexes of $P(CF_3)_2(OCH_2CH_2Cl)$

	L [a]	$[Co(CO)_2(NO)L]$ [b]	$[MnH(CO)_4L]$ [c]	$[MnCl(CO)_4L]$ [d]	$[MnCl(CO)_3(NMe_3)L]$ [e]
$\tilde{\nu}(CO)/cm^{-1}$		2 082s	2 093s	2 110m	2 100vw
		2 040s	2 020m (sh)	2 052s (sh)	2 015vs
			1 993vs	2 036s	1 995vs (sh)
			1 980m (sh)	2 015m (sh)	1 975s
				1 997s (sh)	1 942s
				1 993s	1 919s (sh)
$\tilde{\nu}(^{13}CO)?/cm^{-1}$			1 964w	1 979w	
δ_F/p.p.m.[f]	64.6	68.6	66.1 (*trans*)	62.7	65.2
			66.3 (*cis*)	63.6	68.9
$^2J(PF)$/Hz	86	95	85 (*trans*)	80	96
			86 (*cis*)	83	81
τ_H	5.75	5.7	5.62	5.12	6.2
	6.30	6.3	6.34	6.10	6.1
$^3J(PH)$/Hz	9	10	6	*g*	*g*
$^3J(HH)$/Hz	6	6	4	*g*	*g*

[a] In CCl_3F solution. [b] I.r. in vapour phase, n.m.r. in CCl_3F. I.r. in hexane, n.m.r. in C_6H_6–C_6F_6; hydride at τ 18.38, $^2J(PH)$ 55 Hz. [d] In $CHCl_3$ solution. [e] In CH_2Cl_2 solution, NMe_3 at τ 7.2. [f] Relative to CCl_3F. [g] Not resolved.

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Chlorination of $[MnH(CO)_4L]$.—Treatment of $[MnH(CO)_4L]$ with CCl_4 at room temperature results in the formation of $[MnCl(CO)_4L]$ (76%) and $[Mn_2Cl_2(CO)_8]$ (23%). The reaction is more rapid than that reported for $[MnH(CO)_3\{P(OPh)_3\}_2]$,[8] proceeding to completion in 30 min. The origin of the $[Mn_2Cl_2(CO)_8]$ is obscure, neither free L nor CO being detected in the reaction products. The major product exists as a mixture of *cis* and *trans* isomers, according to i.r. and ^{19}F n.m.r. spectra. A marked shift to higher frequency of the a_1 vibration of *cis*-$[MnCl(CO)_4L]$ with respect to *cis*-$[MnH(CO)_4L]$ is indicative of the electron-withdrawing property of the chloride ligand.

Given the rapidity of the reaction of $[MnH(CO)_4L]$ with CCl_4, it is perhaps surprising that no intra- or inter-molecular reaction with the alkyl chloride residue of L occurs for $[MnH(CO)_4L]$ even in 14 d at 70 °C or over a period of several months at room temperature. The carbon in the ligand is presumably much less electrophilic than that in CCl_4, however.

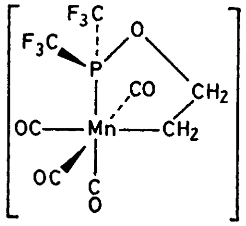
The Reaction of $[MnH(CO)_4L]$ *with* NMe_3.—When a solution of $[MnH(CO)_4L]$ in cyclohexane is treated with NMe_3 at room temperature a precipitate of $[NMe_3H]Cl$ starts to form immediately. After *ca.* 1 min a bright red viscous liquid begins to separate from solution. The oil, virtually insoluble in non-polar solvents but soluble in polar solvents, is involatile. The i.r. spectrum (CH_2Cl_2 solution) shows four bands in the carbonyl region [2 008s, 1 995m (sh), 1 980s (sh), and 1 970s cm^{-1}]. The ^{19}F n.m.r. spectrum has a sharp doublet (δ 69.8 p.p.m.) with a coupling constant [^2J(PF) 66 Hz] quite different from those of the complexes of L, but resembling, for example, that of $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(CF_3)_2O\}]$ [7] [δ 70.5 p.p.m., ^2J(PF) 66 Hz]. The ^1H n.m.r. spectrum [$(CD_3)_2CO$ solution] has only a single resonance at τ 7.8, with a peak width at half-height of 20 Hz at 303 K, broadening to 38 Hz at 253 K. No Mn–H resonance is present, and, since the same complex can also be prepared from $[MnCl(CO)_4L]$ and sodium amalgam, a metal hydride complex is not likely.

The complex $[MnH(CO)_4L]$ would be expected to be sufficiently acidic to lose a proton to NMe_3 [equation (1)] to form $[Mn(CO)_4L]^-$. This ion could also result from the reaction of $[MnCl(CO)_4L]$ with sodium amalgam [equation (2)]. Loss of chloride ion from $[Mn(CO)_4L]^-$ might be expected to occur either in an intermolecular-displacement reaction, yielding a polymer $[\{\text{-}Mn(CO)_4\text{-}[P(CF_3)_2(OCH_2CH_2\text{-})\}_n]$, or in an intramolecular reaction to give the cyclic product (1), but neither of these products is consistent with the ^1H n.m.r. spectrum observed.

$$[MnH(CO)_4L] + NMe_3 \longrightarrow [Mn(CO)_4L]^- + [NMe_3H]^+ \quad (1)$$

$$[MnCl(CO)_4L] + 2Na \longrightarrow Na[Mn(CO)_4L] + NaCl \quad (2)$$

Possibly (1) is formed as an intermediate in the reaction, but undergoes an intramolecular rearrangement to form the final product, *cis*-$[Mn(CO)_4(\eta\text{-}C_2H_4)\text{-}\{P(CF_3)_2O\}]$, identified by the similarity of its ^{19}F n.m.r. spectrum to that of $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(CF_3)_2O\}]$. The i.r. spectrum indicates the *cis*-$[Mn(CO)_4X(Y)]$ structure required by this reaction if the product is stereochemically rigid, and the ^1H n.m.r. chemical shift is within the range observed for ethene complexes.[9] The 900—1 300 cm^{-1} range of the i.r. spectrum (liquid film) is less helpful, but there is a band at 1 212 cm^{-1}, which could be ν(P=O) (*cf.*[7] 1 210 cm^{-1} for $[Fe(\eta\text{-}C_5H_5)(CO)_2\text{-}\{P(CF_3)_2O\}]$). The absence of ν(P–OR) at *ca.* 1 050 cm^{-1} is not significant, since this band, although strong for the free ligand L, is rather weak in all the complexes studied. The broadness of the ^1H n.m.r. resonance could be due to restricted rotation about the metal–alkene bond, but quadrupole broadening by the ^{55}Mn nucleus (spin $\frac{5}{2}$) seems more likely.



(1)

The complex $[MnCl(CO)_4L]$ reacts with NMe_3 to give $[MnCl(CO)_3(NMe_3)L]$ without affecting the ligand L, providing additional evidence that the first stage of the reaction between $[MnH(CO)_4L]$ and NMe_3 is unlikely to involve L directly. Only three of the four possible isomers of $[MnCl(CO)_3(NMe_3)L]$ are apparent in the ^{19}F n.m.r. spectrum. Replacement of one CO ligand by NMe_3 results, as expected, in a large shift to lower frequency of the remaining carbonyl-stretching vibrations.

The complex $[CoH(PF_3)_3L]$ is unaffected by chlorinating solvents even after prolonged exposure, but treatment with NMe_3 leads to complete breakdown of the complex, forming cobalt(II) species.

EXPERIMENTAL

All the volatile compounds were handled by standard vacuum-line techniques. Most products were air-sensitive, and were identified by spectroscopic methods. N.m.r. spectra were recorded on a Brucker Spectrospin spectrometer operating at 90 MHz for ^1H and 84.66 MHz for ^{19}F nuclei, i.r. spectra on a Perkin-Elmer 457 spectrometer, and mass spectra on an A.E.I. MS9 instrument operating at an ionizing energy of 70 eV.*

Pentacarbonylhydridomanganese was prepared by an adaptation of the method of King,[10] using anhydrous HCl instead of phosphoric acid. Tricarbonylnitrosylcobalt was prepared by the direct action of NO on $[Co_2(CO)_8]$ at 40 °C (24 h). Other metal complexes were made available by

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* Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J; 1 Torr = (101 325/760) Pa.

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Dr. R. C. Dobbie. The compound $P(CF_3)_2Cl$ was prepared by the standard route from $P(CF_3)_2I$.[11]

Preparation of the Ligand L.—2-Chloroethanol (6.55 mmol) reacted with $P(CF_3)_2Cl$ (7.9 mmol) at 21 °C (2.5 h) with shaking. Vacuum fractionation trapped a trace amount of 2-chloroethanol at -22 °C, *2-chloroethoxybis-(trifluoromethyl)phosphine*, $P(CF_3)_2(OCH_2CH_2Cl)$ (5.95 mmol, 91%), at -63 °C, excess of $P(CF_3)_2Cl$ at -112 °C, and HCl (*ca.* 6.5 mmol) at -196 °C. Compound L is a colourless mobile liquid with a vapour pressure *ca.* 11 Torr at 21 °C. Alkaline hydrolysis with 20% aqueous K[OH] (24 h) yielded fluoroform,[12] CHF_3 (CF_3 liberated: 54.5%. Calc. for L: 55.5%). The mass spectrum showed a very weak molecular-ion peak, but strong peaks consistent with the loss of Cl, F, CF_3, and other fairly stable species; the strongest peak was assigned to $[C_2H_4{}^{35}Cl]^+$. The vapour-phase i.r. spectrum showed a P–O stretch at 1 042 cm^{-1}, and no P=O stretch. The ^{19}F n.m.r. parameters (Table) are consistent with three-co-ordinate phosphorus, and very different from those expected for a phosphine oxide.[7] The ^1H n.m.r. spectrum is consistent with the assigned formula.

Preparation of the Complexes.—Treatment of L (1.17 mmol) with $[Co(CO)_3(NO)]$ (1.18 mmol) at 45 °C (21 h) gave CO (0.79 mmol). The complex $[Co(CO)_2(NO)L]$ (0.74 mmol, 66%) was collected by vacuum fractionation at -22 °C. It is a deep red liquid with a vapour pressure *ca.* 0.1 Torr at 21 °C. Monosubstitution is indicated by the gas-phase i.r. and solution ^{19}F n.m.r. spectra, which closely resemble those of the previously reported $[Co(CO)_2(NO)\{P(CF_3)_2X\}]$ (X = Cl, Br, or I),[5] and differ considerably from those of $[Co(CO)(NO)\{P(CF_3)_2X\}_2]$.[5] Most peaks in the mass spectrum are assignable on the basis of this formula, but there are some weak signals with higher m/e values and isotope patterns corresponding to two Cl atoms, indicating a small proportion of the disubstituted $[Co(CO)(NO)L_2]$.

The complex $[MnH(CO)_5]$ (1.34 mmol) reacted with L (1.63 mmol) at 40 °C (3 d) to yield CO (1.13 mmol). Volatile products (0.139 g), chiefly excess of L, were recovered. The complex $[MnH(CO)_4L]$ (1.13 mmol, 85%) (Found: C, 22.9; H, 1.35; Mn, 12.9. Calc.: C, 23.05; H, 1.20; Mn, 13.2%) remained in the reaction tube as a highly involatile yellow oil, stable in air for a short time, and thermally stable to 70 °C.

The complex $[CoH(PF_3)_4]$ (0.95 mmol) and L (1.05 mmol) reacted at 50 °C (15 d), with periodic removal of PF_3 (total 0.90 mmol), to give $[CoH(PF_3)_3L]$, which was collected by fractionation at -22 °C. It is a colourless liquid with a very slight vapour pressure at 21 °C. Integration of the ^{19}F n.m.r. spectrum (CCl_3F solution) indicated a monosubstituted product; the presence of two signals for the fluorine atoms of L [68.1 and 69.1 p.p.m. with $^2J(PF)$ 113 and 116 Hz respectively; relative intensity 3 : 2] showed that the complex was a mixture of isomers, but the $^4J(PF)$ coupling was not sufficiently resolved to assign the isomers.

Treatment of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (1.03 mmol) with L (0.87 mmol) in CH_2Cl_2 (*ca.* 1.5 cm^3) at 45 °C (4 d) gave CO (0.54 mmol). A little L (0.105 mmol) was recovered, and a small amount of $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(CF_3)_2\}]$ (*ca.* 0.1 mmol; identified by comparison of its i.r. and ^{19}F and ^1H n.m.r. spectra with those of an authentic sample [7]) was isolated by pumping at room temperature. The remaining involatile brown solid consisted of a mixture of species, according to the complexity of the ^{19}F n.m.r. spectrum, but no other pure compounds could be separated, either by vacuum sublimation or by column chromatography.

Reactions of the Complexes.—Treatment of $[MnH(CO)_4L]$ (0.42 mmol) with CCl_4 (0.61 mmol) (21 °C, 70 min) resulted in the formation of $CHCl_3$ (*ca.* 0.44 mmol), which was distilled off and identified by its ^1H n.m.r. spectrum. A solid and a liquid component remained, which were separated by addition of more CCl_4 and filtration. The orange crystalline solid was found to be $[Mn_2Cl_2(CO)_8]$ [13] by a crystal-structure determination.[14] After removal of CCl_4 solvent, the pale yellow involatile oil was identified as $[MnCl(CO)_4L]$ by analysis of its i.r. and ^{19}F and ^1H n.m.r. spectra. No free ligand L or CO were detected in the reaction products.

A two-armed reaction vessel was used to mix NMe_3 (0.60 mmol) and a solution of $[MnH(CO)_4L]$ (0.48 mmol) in cyclohexane (*ca.* 2 cm^3) at room temperature. A white precipitate of $[NMe_3H]Cl$ (0.46 mmol) began to form at once, and after *ca.* 1 min a bright red viscous oil separated from solution. After 1 h, volatiles were removed *in vacuo*, the products washed with cyclohexane, and the oil removed in acetone solution. This involatile red oil was insoluble in non-polar solvents but soluble in polar solvents. It was identified by spectroscopic methods (see Results and Discussion) as *cis*-$[Mn(CO)_4(\eta\text{-}C_2H_4)\{P(CF_3)_2O\}]$.

The complex $[MnCl(CO)_4L]$ (0.23 mmol) was dissolved in dry tetrahydrofuran (*ca.* 15 cm^3) and shaken vigorously (30 min) with sodium amalgam under an atmosphere of nitrogen. After separation from the amalgam and removal of solvent, the products were dissolved in $(CD_3)_2CO$. The ^1H and ^{19}F n.m.r. spectra showed the presence of the same complex as prepared in the previous reaction (*ca.* 15% yield).

The complex $[MnCl(CO)_4L]$ (0.21 mmol) was dissolved in cyclohexane (*ca.* 1 cm^3) and NMe_3 (0.48 mmol) was added. After 20 h at 21 °C, CO (0.20 mmol) had been produced and NMe_3 (0.24 mmol) was recovered. The solid residue was washed with hexane under nitrogen, and $[MnCl(CO)_3(NMe_3)L]$ was obtained as a pale yellow, extremely air-sensitive, solid, soluble in polar but not in non-polar solvents, and identified by i.r. and ^1H and ^{19}F n.m.r. spectroscopy. The ^1H n.m.r. spectrum indicated a 1 : 1 L : NMe_3 ratio; the i.r. and ^{19}F n.m.r. spectra supported the formulation and suggested the presence of three of the four possible isomers in roughly equal amounts.

The complex $[CoH(PF_3)_3L]$ was inert to CCl_3F (8 months), but treatment of it (0.54 mmol) with NMe_3 (0.96 mmol) in hexane gave a pale green cobalt(II) species.

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