Reactions of Bis(trifluoromethyl)phosphine with some Organocobalt Complexes

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The reaction of $(CF_3)_2PH$ with the complex $[Co_2(CO)_8]$ can lead either to $[Co(CO)_3\{P(CF_3)_2\}]_2$ or a polymeric red solid, depending on the presence or absence of solvent. With $[Co(CO)_3NO]$, the monomeric complex $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ is formed in high yield which on pyrolysis gives $[Co(CO)(NO)\{P(CF_3)_2\}]_2$ and $[Co(NO)_2\{P(CF_3)_2\}]_3$. When $(CF_3)_2PH$ is heated (80 °C) with a mixture of the complexes $[Co(CO)_3NO]$ and $[Fe(CO)_2(NO)_2]$, $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ is again produced. At higher temperatures, the products include $[FeCo(CO)(NO)_3\{P(CF_3)_2\}_2]$. A complex reaction occurs between $(CF_3)_2PH$ and $[(cp)Co(CO)_2]$ (cp = π-cyclopentadienyl), giving $[Co(CO)_3\{P(CF_3)_2\}]_2$, $[(cp)Co\{P(CF_3)_2\}]_2$, and $[(cp)Co(CO)\{P(CF_3)_2\}Co(CO)_3]$: at the same time, reduction of the co-ordinated cp ligand to C_5H_6 is followed by addition of the phosphine or of hydrogen to give $C_5H_7P(CF_3)_2$ and C_5H_8 respectively as additional products. Spectroscopic data for all the complexes prepared are discussed and reaction mechanisms proposed.

DURING the past few years several reports [1-8] of reactions of secondary phosphines with metal carbonyl complexes and their derivatives have appeared. Secondary phosphines undergo varied and interesting reactions which are important in the synthesis of complexes containing the phosphino-group, PR_2. For example, the reaction of $[Fe_2(CO)_9]$ with bis(trifluoromethyl)phosphine, $(CF_3)_2PH$ gives $[Fe(CO)_4\{P(CF_3)_2H\}]$, which yields [8] the dihydride $[H_2Fe_2(CO)_6\{P(CF_3)_2\}_2]$ on pyrolysis. With dicarbonyldinitrosyliron, the phosphine gives a diphosphino-bridged complex $[Fe(NO)_2\{P(CF_3)_2\}]_2$, with elimination of hydrogen. The investigation of the ligand $(CF_3)_2PH$ has now been extended to cobalt complexes.

RESULTS AND DISCUSSION

Excess of bis(trifluoromethyl)phosphine reacted at room temperature with a solution of octacarbonyldicobalt to give the complex $[Co_2(CO)_6\{P(CF_3)_2\}_2]$, (I), previously prepared [9] from iodobis(trifluoromethyl)phosphine and $Hg[Co(CO)_4]_2$. Without solvent the reaction was vigorous at 0 °C giving a deep red insoluble, polymeric solid, all the hydrogen from the phosphine being evolved as H_2. Although sublimation of the red solid gave only traces of (I) and a complex tentatively identified as $[Co_3(CO)_6\{P(CF_3)_2\}_3]$, (II), heating in solution gave (I) in good yield along with some carbon

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[1] W. Hieber and E. Winter, *Chem. Ber.*, 1964, **97**, 1037.

[2] M. Green, A. Taunton-Rigby, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1875.

[3] J. G. Smith and D. T. Thompson, *J. Chem. Soc.* (*A*), 1967, 1694.

[4] P. M. Treichel, W. K. Dean, and W. M. Douglas, *Inorg. Chem.*, 1972, **11**, 1609.

[5] P. M. Treichel, W. M. Douglas, and W. K. Dean, *Inorg. Chem.*, 1972, **11**, 1615.

[6] P. M. Treichel, W. K. Dean, and W. M. Douglas, *J. Organometallic Chem.*, 1972, **42**, 145.

[7] M. Cooke, M. Green, and D. Kirkpatrick, *J. Chem. Soc.* (*A*), 1968, 1507.

[8] R. C. Dobbie, M. J. Hopkinson, and D. Whittaker, *J.C.S. Dalton*, 1972, 1030.

[9] J. Grobe and H. Stierand, *Z. anorg. Chem.*, 1969, **371**, 99.

monoxide. Reactions of $[Co_2(CO)_8]$ with other phosphines give ionic complexes of the form $[Co(CO)_3L_2]$-$[Co(CO)_4]$ (L = phosphine) at low temperatures, but on heating form the binuclear products $[Co_2(CO)_6L_2]$.[10] As found for other phosphines, bis(trifluoromethyl)phosphine forms a monosubstituted derivative, $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$, (III), with $[Co(CO)_3NO]$. The carbonyl and nitrosyl stretching bands in the i.r. spectrum (Table 1) were not much shifted from those of $[Co(CO)_3NO]$, suggesting that CO and $(CF_3)_2PH$ have similar bonding requirements. Comparison of the n.m.r. parameters (Table 1) with those of $(CF_3)_2PH$ and its $[Fe(CO)_4]$ and $[Ni(CO)_3]$ complexes shows that the ligand has been co-ordinated intact in all three complexes, *i.e.* oxidative addition has not occurred. Co-ordination results in an upfield shift of the ^{19}F resonance and an increase in $^2J_{FP}$, as found for the ligands $(CF_3)_2PX$ (X = F, Me, and CF_3).[11a,b]

TABLE 1

N.m.r. parameters for some complexes of $(CF_3)_2PH$

Compound	δ [a]/p.p.m.	$^2J_{FP}$/Hz	$^3J_{FH}$/Hz	τ	$^1J_{HP}$/Hz
$[Fe(CO)_4\{P(CF_3)_2H\}]$	57·2	79	6·9	3·87	356
$[Ni(CO)_3\{P(CF_3)_2H\}]$	55·4	77	7·2	4·40	327
$[Co(CO)_2(NO)$-$\{P(CF_3)_2H\}]$	53·4	78	6·8	3·82	344
$(CF_3)_2PH$ [b]	47·5	69	9·7	5·45	218

[a] Relative to internal $CFCl_3$. [b] K. J. Packer, *J. Chem. Soc.*, 1963, 960.

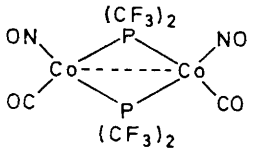
TABLE 2

I.r. spectra of some cobalt complexes

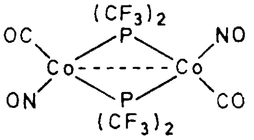
Complex	Absorption bands (cm^{-1})		
	ν(C–O)	ν(N–O)	ν(C–F)
$[Co(CO)_2\{P(CF_2)_3\}]_3$ ' (II) [a,b]	2 090m, 2 062vs, 2 053msh		1 183m, 1 167s, 1 150m, 1 136m
$[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ (III) [c]	2 076s, 2 035vs, 2 000w	1 187vs	1 202s, 1 180s, 1 144s, 1 130m
$[Co(CO)_2(NO)\{P(CF_3)_2D\}]$ [c]	2 076s, 2 035vs, 2 000w	1 815vs	1 205s, 1 179s, 1 148s, 1 132m
$[Co(CO)(NO)\{P(CF_3)_2\}]_2$ (IV) [a]	2 090m, 2 067s	1 847s, 1 830vs	1 182s, 1 153m, 1 138s
$[Co(NO)_2\{P(CF_3)_2\}]_3$ (V) [a]		1 863s, 1 830s	1 172s, 1 146m, 1 128m
$[(cp)Co_2(CO)_4\{P(CF_3)_2\}]$ (VII) [a,b]	2 065vs, 2 026m, 1 998s, 1 994s		1 176s, 1 137s
$[(cp)Co\{P(CF_3)_2\}]_2$ (VIII) [a]			1 164s, 1 137s

[a] In CCl_4 solution. [b] Tentative identification (see text). [c] Gas-phase spectrum. [d] ν(C–O) Region in cyclohexane solution.

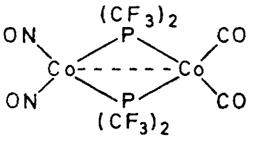
In view of the decomposition of the complex $[Fe(CO)_4\{P(CF_3)_2H\}]$ on heating to give the iron dihydride, $[H_2Fe_2(CO)_6\{P(CF_3)_2\}_2\}$,[8] the pyrolysis of $[Co(CO)_2NO\{P(CF_3)_2H\}]$ was examined. Non-condensable gas (H_2 and CO) was formed and $[Co(CO)_3NO]$ and $(CF_3)_2PH$ were recovered as volatile products. The solid products of the reaction were $[Co(CO)(NO)\{P(CF_3)_2\}]_2$, (IV), and $[Co(NO)_2\{P(CF_3)_2\}]_3$, (V), both of hitherto unreported structural types. Analysis and mass spectrometry established the molecular formula of (IV). The fragmentation of the parent ion in the mass spectrum was similar to that of other complexes, such as $[Fe(NO)_2$-$\{P(CF_3)_2\}]_2$, known to have bridging $P(CF_3)_2$ groups.[12] The i.r. spectrum in solution (see Table 2) shows two terminal ν(C–O) and two terminal ν(N–O) bands, in each case the higher-frequency band being much less intense.



(IVa)



(IVb)



(IVc)

Neglecting coupling across the Co_2P_2 ring, (IVa) and (IVb) would each show a single ν(C–O) and ν(N–O) absorption. The asymmetric structure (IVc) would give two bands in each region of approximately equal intensity, as in the i.r. spectrum of the isoelectronic complex $[Fe(NO)_2\{P(CF_3)_2\}]_2$. The ^{19}F n.m.r. spectrum (Table 3) showed a doublet and other partially overlapping resonances. Limited solubility of the complex prevented a complete n.m.r. study. The evidence suggests that the complex exists as a mixture of isomers, probably of structures (IVa) and (IVb).

TABLE 3

N.m.r. parameters for some compounds containing the $P(CF_3)_2$ group

Compound	δ^a/p.p.m.	$^2J_{FP}$/Hz	$^4J_{FF}$/Hz
$[Co(CO)(NO)\{P(CF_3)_2\}]_2$ (IV)	51·8	88 [b]	
$[Co(NO)_2\{P(CF_3)_2\}]_3$ (V)	48·9	68 [b]	
$[(cp)Co_2(CO)_4\{P(CF_3)_2\}]$ (VII) [c]	53·6 52·4	74·5 71·0	8·0
$(3\text{-}C_5H_7)P(CF_3)_2$ (IX) [d]	54·4 53·8	66·0 67·0	7·6
$(4\text{-}C_5H_7)P(CF_3)_2$ (X) [e]	53·8	67·4	

[a] Relative to internal CCl_3F. [b] The second-order spectrum was not fully resolved and $^2J_{FP}$ is taken as the separation of the doublet. [c] ^1H N.m.r. shows a singlet at τ 4·85. [d] ^1H N.m.r. shows multiplets at τ 3·99 (1H), 4·24(1H), 6·47(1H), 7·61(2H), and 7·85(2H). [e] R. C. Dobbie, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1881.

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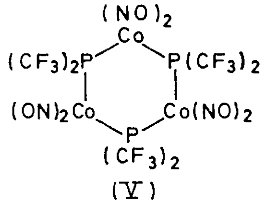
[10] R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 657.

[11] (*a*) R. C. Dobbie, *J. Chem. Soc.* (*A*), 1971, 230; (*b*) J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363.

[12] R. C. Dobbie and D. Whittaker, unpublished work.

The complex $[Co(NO)_2\{P(CF_3)_2\}]_3$, (V), was characterised by analysis and mass spectrometry. The fragmentation pattern was consistent with bridging phosphino-groups: breakdown of the phosphorus ligands was mainly by loss of $P(CF_3)_2$, $P(CF_3)(CF_2)$, and F fragments, as found for similar complexes.[12] In the i.r. spectrum, two equally intense bands were observed in the region expected for terminal nitrosyl groups. The ^{19}F n.m.r. spectrum showed a symmetrical resonance indicative of a second-order spin system. The simplicity of the observed spectra suggests the symmetrical structure (V). Below room temperature, additional fine structure was observed in the n.m.r. spectrum, suggesting that (V) is non-rigid on an n.m.r. time scale. The equivalence of the two CF_3 groups attached to each phosphorus atom was maintained down to −20 °C, the lowest temperature studied. The trimeric carbonyl complex (II) may have an analogous structure to (V) with the addition of Co–Co bonds, thus satisfying the inert-gas rule. Isolation of a complex with two NO groups bonded to each cobalt atom from the thermal decomposition of $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ is unexpected. Its formation probably involves disproportionation rather than reco-ordination of free NO, as NO was not found amongst the reaction products.



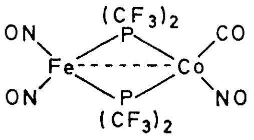
(V)

Thermal decomposition of the complex $[Co(CO)_2(NO)\{P(CF_3)_3\}]$ gives a trimer with bridging carbonyl groups, $[Co(CO)(NO)\{P(CF_3)_3\}]_3$.[13] This illustrates the importance of P–H bond cleavage in reactions of coordinated secondary phosphines.

When a mixture of the complexes $[Co(CO)_3NO]$ and $[Fe(CO)_2(NO)_2]$ was heated with $(CF_3)_2PH$ (2 days, 80 °C), the only product was $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$, (III); the iron complex was not attacked. The substituted cobalt complex (III) reacted at 110 °C with $[Fe(CO)_2(NO)_2]$ to give $[Co(CO)_3NO]$ and an inseparable mixture of $[Fe(NO)_2\{P(CF_3)_2\}]_2$,[8] and $[FeCo(CO)(NO)_3\{P(CF_3)_2\}_2]$, (VI). Equilibrium (1) may be established during both reactions. Below 80 °C, the equilibrium

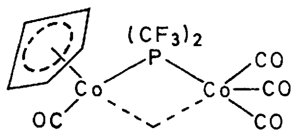
$$[Co(CO)_2(NO)\{P(CF_3)_2H\}] + [Fe(CO)_2(NO)_2] \rightleftharpoons [Co(CO)_3NO] + [Fe(CO)(NO)_2\{P(CF_3)_2H\}] \quad (1)$$

must lie to the left as no substituted iron nitrosyl complex could be detected. However, at 110 °C, the equilibrium is driven to the right by rapid dimerisation of $[Fe(CO)(NO)_2\{P(CF_3)_2H\}]$ to $[Fe(NO)_2\{P(CF_3)_2\}]_2$. Attack by $[Fe(CO)(NO)_2\{P(CF_3)_2H\}]$ on (III) would explain the formation of the mixed-metal complex (VI) which appears from spectroscopic evidence to have $P(CF_3)_2$ bridging groups and terminal CO and NO groups (see Table 1). Heating the monomeric complex $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ with $[Co_2(CO)_8]$ gave $[Co(CO)_3NO]$, the red polymeric solid isolated from the reaction of bis(trifluoromethyl)phosphine with $[Co_2(CO)_8]$, and a trace of $[Co_3(CO)_6\{P(CF_3)_2\}_3]$, (II). Thus the complex $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ can act as a source of the phosphine.



(VI)

A complex reaction occurred between bis(trifluoromethyl)phosphine and $[(cp)Co(CO)_2]$ at room temperature, giving three solid products. The first was identified as $[Co(CO)_3\{P(CF_3)_2\}]_2$, (I),[9] previously prepared in this work from $[Co_2(CO)_8]$. The second complex, molecular formula $C_5H_5Co_2(CO)_4P(CF_3)_2$, showed four distinct C–O stretching bands in the terminal region of the i.r. spectrum (Table 1) in non-polar solvents, suggesting a molecule of low symmetry. The structure (VII) follows from a singlet cp resonance in the ^1H n.m.r. spectrum, and two resonances of equal intensity, each a doublet of quartets, in the ^{19}F spectrum. The inequivalence of the CF_3 groups attached to phosphorus can best be explained if the co-ordination number of the cobalt atom is five for the $Co(CO)_3$ group and six for the (cp)Co(CO) group. This implies that the observed diamagnetism of the complex results from a bent metal–metal bond. If the metal–metal bond was not sterically active, the complex would probably have a plane of symmetry so as to make the CF_3 groups equivalent. The structure of the third product, $[C_5H_5Co\{P(CF_3)_2\}]_2$, (VIII), a dark green crystalline solid, is probably analogous to that of the diphenylphosphino-complex.[14]



(VII)

Cyclopentene, C_5H_8, was identified amongst the volatile products of the reaction and in addition a cyclopentene derivative, $C_5H_7P(CF_3)_2$, (IX), was characterised by spectroscopic methods. In the ^{19}F n.m.r. spectrum (Table 3), the CF_3 groups are inequivalent, the F–F coupling constant being almost the same as that in $[(cp)Co_2(CO)_4\{P(CF_3)_2\}]$, (VII). In the ^1H n.m.r. spectrum, the vinyl hydrogen atoms are inequivalent and the hydrogen attached to the same carbon atom as the $P(CF_3)_2$ substituent was shifted downfield from the

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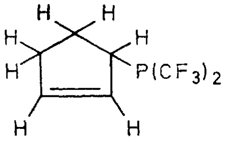
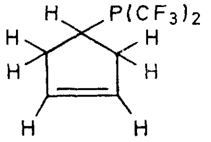
[13] A. B. Burg and I. H. Sabherwal, *Inorg. Chem.*, 1970, **9**, 974.

[14] J. M. Coleman and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 542.

remaining hydrogen atoms. Thus the complex has structure (IX) rather than (X). The more symmetrical



(IX)



(X)

isomer (X) is a product of the reaction of $(CF_3)_2PH$ with bis(π-cyclopentadienyl)nickel,[15] whereas the addition of the phosphine to cyclopentadiene, C_5H_6, is much slower and gives both isomers. No interconversion of pure samples of (IX) and (X) could be detected in several months under ambient conditions. The use of labelled phosphine, $(CF_3)_2PD$, gave mainly $C_5H_5D_3$ and $C_5H_5D_2P(CF_3)_2$ in place of the hydrogenated products, confirming the source of the hydrogen added to the cp group. Hydrogen accumulated in the phosphine at the expense of deuterium, suggesting that there is an equilibrium between the hydrogen atoms of the co-ordinated cp or cyclopentadiene groups and $(CF_3)_2PH$. Between 20 and 100 °C, the variations in the stoicheiometry of the reaction are consistent with increased displacement of cp instead of carbonyl ligand at higher temperatures. Severance of metal–hydrocarbon bonds leads to increased yields of cyclopentenes and to formation of the complex $[Co(CO)_3\{P(CF_3)_2\}]_2$ rather than $[(cp)Co_2(CO)_4\{P(CF_3)_2\}]$.

In the reaction of $[(cp)_2Ni]$ with thiols, RSH, to produce $[(cp)NiSR]_2$ and cyclopentadiene, Ellgen and Gregory propose that initial co-ordination of the thiol is followed by transfer of hydrogen from sulphur to the cp ligand.[16] The rate is reduced when deuteriothiols are used, suggesting that the rate-determining step is cleavage of the S–H bond. The interaction of $(CF_3)_2PH$ with $[(cp)Co(CO)_2]$ may be initiated in the same way (see Scheme), to give intermediate (A) which dissociates with loss of CO to form (B). Formation of (A) is consistent with the suggestion [17] that ligand substitution in the complex $[(cp)Co(CO)_2]$ occurs by an S_N2 mechanism; although several phosphine analogues of (B) are known, they are unstable.[18] Again following Ellgen's mechanism in outline, P–H bond cleavage in intermediate (A) will give co-ordinated C_5H_6 (C). In this work, the reaction goes further and this is attributed to the much reduced nucleophilic character of the phosphine compared to the more basic thiols, making addition to the unsaturated ring feasible.

Addition of free bis(trifluoromethyl)phosphine or of hydrogen to (C) to give (D) and (E) is less probable than addition of co-ordinated $(CF_3)_2PH$, since it has been shown herein that the P–H bond is activated towards cleavage on co-ordination. Others [5] have demonstrated that $[Fe(CO)_4(PPh_2H)]$ is a stronger acid than PPh_2H. The co-ordinated phosphine could add to the C_5H_6 ligand by either an inter- or an intra-molecular mechanism, involving initial bonding of further $(CF_3)_2PH$ groups to the cobalt atom in (C). As no product contained more than two phosphino-groups, the intramolecular process, which would involve successive co-ordination of three phosphine ligands, is improbable. Free hydrogen is not implicated in the reaction as it is not detected amongst the products.

Accordingly the addition of $(CF_3)_2PH$ or of hydrogen occurs by interaction of (C) with (A) and (B) respectively. The other product of the reaction of (B) with (C) is $[(cp)Co\{P(CF_3)_2\}]$ which would dimerise to give the observed complex (VIII). Rupture of the metal–olefin bond in (D) or (E) by carbon monoxide gives $[Co(CO)_3\{P(CF_3)_2\}]$, which may dimerise to (I) or react with the starting material to give $[(cp)Co(CO)\{P(CF_3)_2\}Co(CO)_3]$, (VII). Alternatively, but less probably, (VII) could be formed by the direct action of (B) on $[(cp)Co(CO)_2]$ followed by addition of CO, the cyclopentadiene eliminated being reco-ordinated to cobalt prior to further reduction. This step follows from elimination of propene in the reaction of $[Fe(CO)_4(PPh_2H)]$ with π-allyl metal complexes.[19] The reaction of $(CF_3)_2PH$ with $[(cp)_2Ni]$ may proceed by a similar, though less complex, mechanism. Formation of the isomeric cyclopentene (X) rather than (IX) may be explained by postulating that a variation in electron density between the ring carbon atoms in the cyclopentadiene co-ordinated to nickel and to cobalt alters the orientation of addition of the phosphine.

In conclusion, the secondary phosphine $(CF_3)_2PH$ reacts initially with metal carbonyl complexes to substitute carbon monoxide, normally forming a mono-substituted phosphine derivative. Complexes of this type include $[Fe(CO)_4L]$,[8] $[Co(CO)_2(NO)L]$, and $[Ni(CO)_3L]$ $[L = P(CF_3)_2H]$.[12] However, co-ordination of the phosphine polarises the P–H bond, making the hydrogen atom more acidic. Probably for this reason, the monomeric complexes are thermally unstable, giving dimers or trimers containing bridging $P(CF_3)_2$ groups. Hydrogen is commonly lost as H_2, as found in the reaction of the phosphine with $[Fe(CO)_2(NO)_2]$ and $[Co_2(CO)_8]$, or as in the thermal decomposition of $[Fe(CO)_4L]$ and $[Co(CO)_2(NO)L]$. However, the hydrogen can be transferred either to the metal to give a stable hydride, as in the reaction of $(CF_3)_2PH$ with $[Fe(CO)_5]$ and $[Mn_2(CO)_{10}]$, to give $[H_2Fe_2(CO)_6P\{(CF_3)_2\}]$ [8] and $[HMn_2(CO)_8\{P(CF_3)_2\}]$ [12] respectively, or to another ligand, as in the reaction with $[(cp)Co(CO)_2]$ and $[(cp)_2Ni]$.[15] Considerable similarity thus exists in the activation of P–H and C–H bonds by organometallic complexes.

EXPERIMENTAL

Volatile compounds were handled in a Pyrex vacuum system by standard techniques. The amount of non-condensable gases was measured using a Toepler pump.

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[15] R. C. Dobbie, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1881.

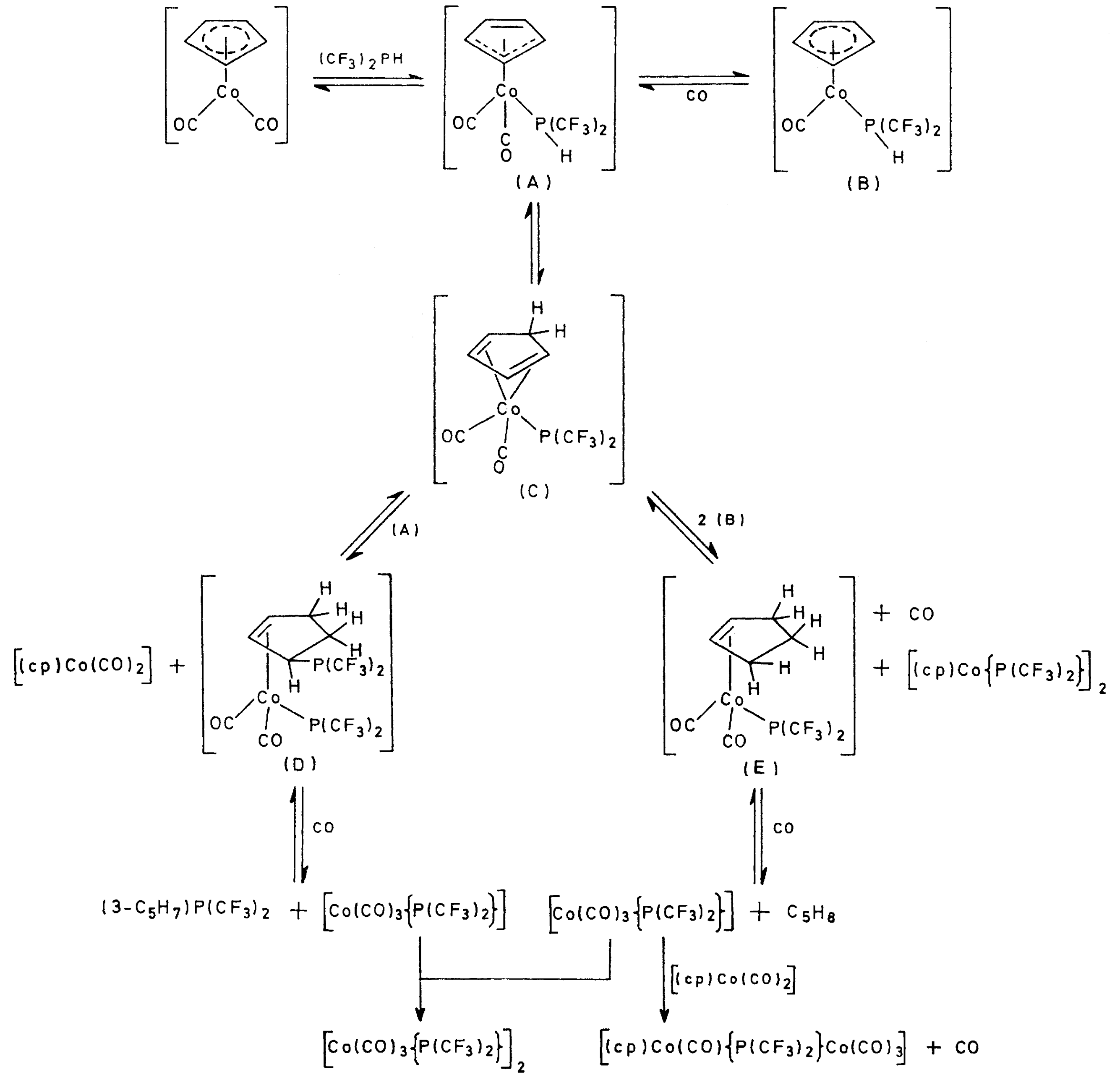
[16] P. C. Ellgen and C. D. Gregory, *Inorg. Chem.*, 1971, **10**, 980.

[17] F. Basolo, *Chem. in Britain*, 1969, **5**, 505.

[18] R. B. King, *Inorg. Chem.*, 1966, **5**, 82.

[19] B. C. Benson, R. Jackson, K. K. Joshi, and D. T. Thompson, *Chem. Comm.*, 1968, 1506.

Solids and their solutions were protected where necessary by an atmosphere of nitrogen. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer and mass spectra on an A.E.I. MS9 spectrometer operating at an ionising voltage of 70 eV. N.m.r. spectra were recorded on a Bruker Spectrospin HFX instrument operating at 90·00 MHz for ^1H and 84·66 MHz for ^{19}F nuclei, with Me_4Si and CCl_3F as internal standards. Bis(trifluoromethyl)phosphine,[20] [^2H]bis(trifluoromethyl)phosphine,[8] and π-dicarbonylcyclopentadienylcobalt [21] were prepared and characterised by literature methods. Using a modification of Mond's original method of preparation,[22] tricarbonylnitrosylcobalt was prepared directly from octacarbonyldicobalt and nitrogen oxide by reaction in sealed tubes at 40 °C (12 h). After vacuum fractionation yields of up to 93% {based on $[Co_2(CO)_8]$} were obtained.



SCHEME

Reactions.—$[Co_2(CO)_8]$ *with* $(CF_3)_2PH$. The carbonyl complex (0·645 g, 1·88 mmol) reacted vigorously with $(CF_3)_2PH$ (1·00 g, 5·88 mmol), below room temperature in a sealed tube of volume 50 cm^3, releasing H_2 (2·25 mmol) and CO (3·40 mmol), identified by mass spectrometry. The only remaining volatile product was excess of $(CF_3)_2PH$ (0·343 g, 2·02 mmol). A small part of the red residue in the reaction

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[20] R. G. Cavell and R. C. Dobbie, *J. Chem. Soc.* (*A*), 1967, 1308.

[21] R. B. King, *Organometallic Synth.*, 1965, **1**, 114.

[22] R. L. Mond and A. E. Wallis, *J. Chem. Soc.*, 1922, **32**.

tube was soluble in CCl_4, giving i.r. bands characteristic of $[Co(CO)_3\{P(CF_3)_2\}]_2$.[9] Attempted sublimation of the residue gave soft black crystals (0·012 g), ν(CO) at 2 090m, 2 062s, and 2 053m,sh cm^{-1}, tentatively identified as $[Co(CO)_2\{P(CF_3)_2\}]_3$ (Found: *m*/*e*, 851·6616. Calc. for $C_{12}Co_3F_{18}O_6P_3$ *m*/*e*, 851·6616). When a sample (0·494 g) of the original red residue was heated in a sealed tube with toluene at 110 °C, a small amount (0·26 mmol) of CO was liberated and $[Co(CO)_3\{P(CF_3)_2\}]_2$ was recovered in high yield, and identified spectroscopically. The reaction of $[Co_2(CO)_8]$ (0·483 g, 1·41 mmol) and $(CF_3)_2PH$ (0·925 g, 5·45 mmol) in the presence of dry cyclohexane at room temperature (2 days) gave H_2 (1·43 mmol), CO (2·41 mmol), excess of the phosphine (0·449 g, 2·64 mmol), and $[Co_2(CO)_6\{P(CF_3)_2\}_2]$ (0·342 g, 0·55 mmol).

$[Co(CO)_3NO]$ *with* $(CF_3)_2PH$. In a typical reaction the cobalt complex (0·472 g, 2·73 mmol) and $(CF_3)_2PH$ (0·912 g, 5·36 mmol) at 50 °C (20 h) in a small (12 cm^3) sealed tube gave carbon monoxide (1·27 mmol), $[Co(CO)_3NO]$ (0·206 g, 1·19 mmol), $[CF_3)_2PH$ (0·655 g, 3·85 mmol), and *[bis(trifluoromethyl)phosphine]dicarbonylnitrosylcobalt*, $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$, (0·457 g, 1·45 mmol, 96% yield) [Found: C, 15·35; H, 0·40; N, 4·55. *M* (Regnault's method), 310. *m*/*e*, 314·8925. Calc. for $C_4HCoF_6NO_3P$: C, 15·25; H, 0·30; N, 4·45%. *M*, 315. *m*/*e*, 314·8930]. Alternatively, the reaction could be carried out at 20 °C over several months. A trace of a dark solid always remained in the reaction tube after removal of the volatile products. This was shown by mass spectrometry to be a mixture of the two complexes formed by pyrolysis of $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ (see below). The reaction of $(CF_3)_2PD$ with $[Co(CO)_3NO]$ likewise gave $[Co(CO)_2(NO)\{P(CF_3)_2D\}]$ (Found: *m*/*e*, 315·9005. Calc. *m*/*e*, 315·8993) in high yield.

Pyrolysis of $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$. When the monomeric complex (0·872 g, 2·77 mmol) was heated *in vacuo* at 50 °C (7 days), with removal of non-condensable gas every second day, less than half (0·362 g, 1·15 mmol) was recovered. The volatile products of the pyrolysis were CO (0·056 g, 2·0 mmol), H_2 (0·008 g, 0·4 mmol), $(CF_3)_2PH$ (0·065 g, 0·38 mmol, 24% yield based on monomer consumed), and $[Co(CO)_3NO]$ (0·069 g, 0·40 mmol, 25% yield). All were identified by a combination of i.r. and mass spectrometry and molecular-weight measurements. The solid remaining in the tube was subjected to high-vacuum sublimation from which two pure products were isolated. The more volatile, m.p. 111 °C, was *di-μ-[bis(trifluoromethyl)phosphino]-dicarbonyldinitrosyldicobalt*, $[Co(CO)(NO)\{P(CF_3)_2\}]_2$ (0·162 g, 0·28 mmol, 35% yield) (Found: C, 12·5; H, 0·0; N, 4·9. *m*/*e*, 571·7823. Calc. for $C_6Co_2F_{12}N_2O_4P_2$: C, 12·6; H, 0·0; N, 4·9%. *m*/*e*, 571·7805). The minor product was obtained in trace quantities only, but it was identified as *tri-μ-[bis(trifluoromethyl)phosphino]-hexanitrosyltricobalt*, $[Co(NO)_2\{P(CF_3)_2\}]_3$ (Found: C, 8·4; H, 0·0; N, 9·8. *m*/*e*, 863·6831. Calc. for $C_6Co_3F_{18}N_6O_6P_3$: C, 8·3; H, 0·0; N, 9·7%. *m*/*e*, 863·6801). It was found that yields of up to 14% of the trimer could be obtained by repeating the pyrolysis of $[Co(CO)_2NO\{P(CF_3)_2H\}]$ at 70 °C (30 h) without removal of non-condensable gas.

$(CF_3)_2PH$ *with* $[Co(CO)_3NO]$ *and* $[Fe(CO)_2(NO)_2]$. The complexes $[Co(CO)_3NO]$ (0·609 g, 3·52 mmol) and $[Fe(CO)_2(NO)_2]$ (0·158 g, 0·92 mmol), and $(CF_3)_2PH$ (0·547 g, 3·22 mmol) were heated in a sealed tube (50 cm^3 volume) at 80 °C to give CO (2·96 mmol), excess of phosphine (0·204 g, 1·20 mmol), and of $[Co(CO)_3NO]$ (0·181 g, 1·04 mmol), and an inseparable mixture of $[Fe(CO)_2(NO)_2]$ and $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$, leaving only a trace of solid in the tube. All the products with the exception of CO were returned to the tube and heated at 110 °C (2 days), forming a further small amount of carbon monoxide (0·35 mmol). The volatile products were found to be $(CF_3)_2PH$ (0·182 g, 1·07 mmol), $[Co(CO)_3NO]$ (0·377 g, 2·17 mmol), and $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ (0·289 g, 0·92 mmol). No $[Fe(CO)_2(NO)_2]$ could be detected. The black, partially crystalline, solid (0·330 g) was sublimed at 30 °C to give black crystals, readily soluble in CCl_4. In addition to the features associated with $[Fe(NO)_2\{P(CF_3)_2\}]_2$, bands were observed in the i.r. spectrum at 2 075m, 1865m, and 1852m cm^{-1}, peaks in the mass spectrum at *m*/*e* 571 and 543, and new resonances in the ^{19}F n.m.r. spectrum. By precise mass measurement, the peaks in the mass spectrum were found to correspond to $[Fe(NO)_2\{P(CF_3)_2\}_2Co(CO)(NO)]^+$ (Found: *m*/*e*, 570·7878. Calc. *m*/*e*, 570·7853) and to $[Fe(NO)_2\{P(CF_3)_2\}_2Co(NO)]^+$ (Found: *m*/*e*, 542·7899. Calc. *m*/*e*, 542·7904) respectively. When the residue from the sublimation was resublimed at 60 °C, a small quantity of $[Co(NO)_2\{P(CF_3)_2\}]_3$ was found.

$[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ *with* $[Co_2(CO)_8]$. Freshly sublimed $[Co_2(CO)_8]$ (0·583 g, 1·71 mmol) and $[Co(CO)_2(NO)\{P(CF_3)_2H\}]$ (0·497 g, 1·58 mmol) liberated CO (1·30 mmol) and H_2 (0·59 mmol) at 50 °C (3 days). The only remaining volatile product was $[Co(CO)_3NO]$ (0·245 g, 1·42 mmol). The solid product remaining in the tube was identical in its properties to the polymeric solid obtained from the action of $(CF_3)_2PH$ on $[Co_2(CO)_8]$.

$[(cp)Co(CO)_2]$ *with* $(CF_3)_2PH$. The reaction was carried out under a variety of conditions. Two detailed examples of the reaction at 20 and 80 °C with excess of phosphine are given in Table 4. The volatile products contained CO, cyclopentene (C_5H_8), and *cyclopent-3-enyl-bis(trifluoromethyl)phosphine*, $(3\text{-}C_5H_7)P(CF_3)_2$ (i.r. absorptions in the gas phase at 3 078w, 2 958m, 2 863w, 2 350br,w, 1 191vs, 1 159vs, 1 142vs, 1 107s, 1 049w, 913w, 870w, 740w, and 705w cm^{-1}), but no hydrogen could be detected. The cyclopentenes were identified by i.r., n.m.r., and mass spectroscopy. The solid products of the reaction were separated by chromatography on a Florisil column under an atmosphere of nitrogen, giving the known complex $[Co(CO)_3\{P(CF_3)_2\}]_2$ and the new complexes di-μ-*[bis(trifluoromethyl)phosphino]-di-π-cyclopentadienyldicobalt*, $[(cp)Co\{P(CF_3)_2\}]_2$ (Found: C, 26·8; H, 1·65. *m*/*e*, 585·8746. Calc. for $C_{14}H_{10}Co_2F_{12}P_2$: C, 28·7; H, 1·7%. *m*/*e*,

TABLE 4

Quantitative details of the reaction of $(CF_3)_2PH$ with the complex $[(cp)Co(CO)_2]$

Reaction conditions		
t/°C	20	80
Time/days	2	5
Reactants		
$[(cp)Co(CO)_2]$/mmol	1·28	1·85
$[(CF_3)_2PH]$/mmol	1·98	3·64
Reactants consumed		
$[(cp)Co(CO)_2]$/mmol	1·28	1·85
$[(CF_3)_2PH]$/mmol	1·21	2·77
Products		
[CO]/mmol	0·5	0·24
$[H_2]$/mmol	0·00	0·00
$[C_5H_8]$/mmol	trace	0·33
$[(3\text{-}C_5H_7)P(CF_3)_2]$/mmol	0·08	0·30
$[Co_2(CO)_6\{P(CF_3)_2\}_2]$/mmo	trace	0·42
$[(cp)_2Co_2\{P(CF_3)_2\}_2]$/mmol	0·01	0·09
$[(cp)Co(CO)\{P(CF_3)\}_2Co(CO)_3]$/mmol	0·03	0·05

585·8730) and μ-[*bis(trifluoromethyl)phosphino*]-[*carbonyl(π-cyclopentadienyl)cobalt*][*tricarbonylcobalt*], [(cp)Co(CO)-{P$(CF_3)_2$}Co$(CO)_3$] (Found: C, 28·4; H, 1·10. *m/e*, 463·8486. Calc. for $C_{11}H_5Co_2F_6O_4P$: C, 28·4; H, 1·10%. *m/e*, 463·8493).

The reaction of $(CF_3)_2PD$ and [(cp)Co$(CO)_2$] was also investigated. Isotropic analysis of the mass spectrum of the unconsumed phosphine showed that it contained 92% $(CF_3)_2PH$. The major volatile products were $C_5H_5D_2P(CF_3)_2$ and $C_5H_5D_3$.

C_5H_6 *with* $(CF_3)_2PH$. Cyclopentadiene (0·069 g, 1·05 mmol), prepared by the thermal cracking of its dimer, was sealed with $(CF_3)_2PH$ (0·195 g, 1·15 mmol) in a tube of volume 10 cm³. After 3 days at 20 °C, a considerable quantity of C_5H_6 had dimerised, although some had reacted with the phosphine to give $C_5H_7P(CF_3)_2$ (*ca.* 0·03 mmol). After 45 days at room temperature, the volatile fraction still contained excess of phosphine (0·153 g, 0·90 mmol) and cyclopentadiene (0·03 g, 0·05 mmol). The less volatile fraction (0·045 g, 0·19 mmol) was shown by n.m.r. spectroscopy to be a mixture of the isomers (IX) and (X) of $C_5H_7P(CF_3)_2$ in the ratio 11 : 4.

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