Reaction of $[HFeCo_3(CO)_{12}]$ with Phosphorus Donor Ligands

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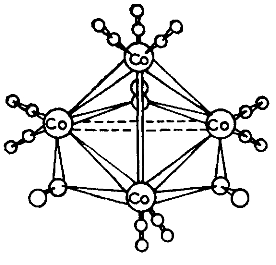
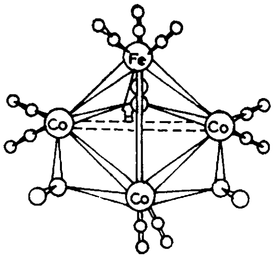
The reaction of organophosphine and organophosphite ligands with $[HFeCo_3(CO)_{12}]$ gives a series of substitution complexes of general formula $[HFeCo_3(CO)_{12-x}L_x]$ ($L = Ph_3P$, Ph_2MeP, Et_3P, $(PhO)_3P$ or $(PrO)_3P$ where depending on the substituent ($x = 1$—3). Only with the chelating phosphine bisdiphenylphosphinoethane (dppe) could more than three CO groups per molecule be displaced. Some corresponding derivatives of $[Co_4(CO)_{12}]$ have also been synthesised for comparative purposes. The i.r. and ^{57}Fe Mössbauer spectra of the substituted iron–cobalt complexes have been recorded and are discussed. The Mössbauer data show that substitution takes place preferentially at cobalt and that the complexes $[HFeCo_3(CO)_{12-x}L_x]$ ($x = 1$—3) are formed by successive substitution of one CO group at each cobalt atom. The complex $[HFeCo_3(CO)_8(dppe)_2]$ exists as a mixture of two isomers and in one of which a carbonyl group on the iron atom has been substituted.

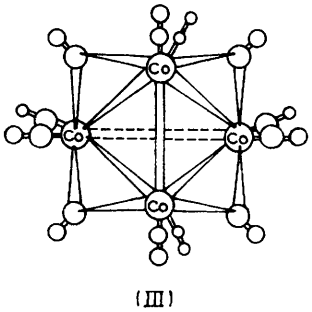
THE mixed-metal cluster $[HFeCo_3(CO)_{12}]$ is isoelectronic with $[Co_4(CO)_{12}]$ and its structure has been inferred from spectroscopic data [1,2] as being similar to that of $[Co_4(CO)_{12}]$ in the solid state [3] (I), with the hydrogen atom located at the centroid of the metal atom skeleton (II). It seemed likely, however, that the substitution of a cobalt atom by an HFe unit would render the chemistry of this complex rather different from that of $[Co_4(CO)_{12}]$. In order to obtain some information about this point, we have studied the reaction of $[HFeCo_3(CO)_{12}]$ with some phosphorus donor ligands. This is a reaction which has already been studied by other workers for $[Co_4(CO)_{12}]$ [4] but we have prepared some new substitution products of this latter molecule to aid our comparison, and these are also described.



(I)



(II)



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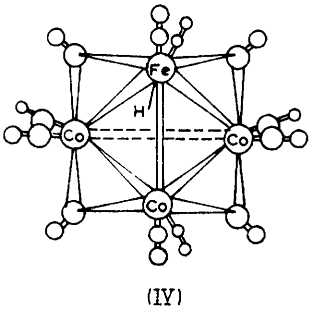

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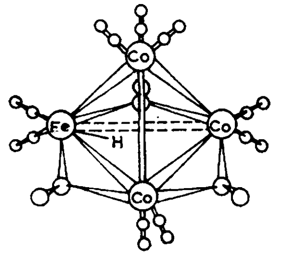

(V)

RESULTS AND DISCUSSION

Preparation of the Complexes.—The reaction of $[HFeCo_3(CO)_{12}]$ with phosphorus donor ligands in chloroform solution leads in every case to a complex mixture of products being obtained. The yields of the various products are very dependent on the reaction conditions employed. In general it is possible by an appropriate choice of conditions to substitute up to three CO groups and hence to obtain the complexes $[HFeCo_3(CO)_{12-x}L_x]$ ($x = 1$—3). Only with the chelating phosphine bisdiphenylphosphinoethane (dppe) in acetone solution was it possible to substitute more than three CO groups per molecule. In addition to products of the type $[HFeCo_3(CO)_{12-x}L_x]$, ionic products of formula $[FeCo_3(CO)_{12}][Co(CO)_3L_2]$ were also obtained in reactions with the stronger bases. These ionic products must arise from initial deprotonation of $[HFeCo_3(CO)_{12}]$ by R_3P. Once deprotonated, the polynuclear anion is

[1] G. Bor, *Spectrochim. Acta*, 1963, **19**, 1209.

[2] J. W. White and C. J. Wright, *J. Chem. Soc.* (*A*), 1971, 2843.

[3] C. H. Wei, *Inorg. Chem.*, 1969, **8**, 2384.

[4] D. Labroue and R. Poilblanc, *Inorg. Chim. Acta*, 1972, **6**, 387.

more difficult to substitute than the neutral complex,[5] whilst the cobalt cation presumably results from the decomposition of some of the neutral cluster. Higher ligand : cluster ratios and the use of non-polar solvents favour the formation of ionic compounds. Of the many reactions we have carried out, two, those with the ligands Ph_2MeP and dppe, are described in detail in the Experimental section. Experimental conditions for all other reactions attempted are summarised in Table 1 and analytical and infrared data for all the products obtained are given respectively in Tables 2 and 5.

TABLE 1

Reaction of $[HFeCo_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$ with Group V ligands (L) in $CHCl_3$

Reactants	Ratio	t/°C	Time	Product	Chromatography		Crystallisation solvent (t/°C)	Colour	Yield (%)
					First eluant (n-hexane–CH_2Cl_2)	Second eluant (n-hexane–CH_2Cl_2)			
PPh_3,$[HFeCo_3(CO)_{12}]$	3 : 1	20	½ h	$[HFeCo_3(CO)_{11}L]$	4 : 1	9 : 1	n-Pentane (−20)	Purple	70
				$[HFeCo_3(CO)_{10}L_2]\cdot 0{\cdot}25Me_2CO$	4 : 1	9 : 3	Me_2CO–n-pentane (−20)	Green	30
PPh_3,$[HFeCo_3(CO)_{12}]$	3 : 1	60	3 h	$[HFeCo_3(CO)_{10}L]\cdot Me_2CO$	4 : 1	9 : 3	Me_2O–n-pentane (−20)	Green	95
Et_3P,$[HFeCo_3(CO)_{12}]$	2 : 1	20	½ min	$[HFeCo_3(CO)_{11}L_2]$	9 : 1	9 : 1	n-Pentane (−20)	Purple	20
				$[HFeCo_3(CO)_{10}L_2]$	9 : 1	4 : 1	n-Pentane–Et_2O (−20)	Violet	30
				$[FeCo_3(CO)_{12}][Co(CO)_3L_2]$			Et_2O–n-pentane (−20)	Red	20
$(PrO)_3P$,$[HFeCo_3(CO)_{12}]$	2 : 1	60	3½ h	$[HFeCo_3(CO)_{11}L]$	9 : 1	9 : 1	n-Pentane (−20)	Purple	90
$(PrO)_3P$,$[HFeCo_3(CO)_{11}P(OPr)_3]$	2 : 1	60	3½ h	$[HFeCo_3(CO)_{10}L_2]$	4 : 1	9 : 1	n-Pentane–Et_2O (−20)	Violet	70
$(PhO)_3P$,$[HFeCo_3(CO)_{12}]$	3 : 1	60	2 h	$[HFeCo_3(CO)_{11}L]$	9 : 1	9 : 1	n-Pentane (−20)	Purple	70
$(PhO)_3P$,$[HFeCo_3(CO)_{11}P(OPh)_3]$	3 : 1	60	2½ h	$[HFeCo_3(CO)_{10}L_2]$	9 : 1	4 : 1	n-Pentane (−20)	Violet	20
Ph_2MeP,$[Co_4(CO)_{12}]$	2 : 1	20	1 min	$[Co_4(CO)_{11}L]$	9 : 1	9 : 1	n-Pentane (−20)	Dark brown	90
Ph_2MeP,$[Co_4(CO)_{12}]$	2 : 1	60	10 min	$[Co_4(CO)_{10}L_2]$	9 : 1	9 : 1	n-Pentane (−20)	Dark brown	50
Et_3P,$[Co_4(CO)_{12}]$	2 : 1	20	1 min	$[Co_4(CO)_{11}L]$	9 : 1	9 : 1	n-Pentane (−20)	Dark brown	70
$(PrO)_3P$,$[Co_4(CO)_{12}]$	2 : 1	20	1 h	$[Co_4(CO)_{11}L]$	9 : 1	9 : 1	n-Pentane (0)	Dark brown	80
				$[Co_4(CO)_{10}L_2]$	9 : 1	9 : 1	n-Pentane (0)	Dark brown	5
$(PhO)_3P$,$[Co_4(CO)_{12}]$	2 : 1	20	1 h	$[Co_4(CO)_{11}L]$	9 : 1	9 : 1	n-Pentane (0)	Dark brown	80
$(PhO)_3P$,$[Co_4(CO)_{12}]$	3 : 1	60	5 h	$[Co_4(CO)_{11}L]$	9 : 1	9 : 1	n-Pentane (0)	Dark brown	10
				$[Co_4(CO)_{10}L_2]$	4 : 1	4 : 1	Et_2O–n-Pentane (−20)	Dark brown	30
				$[Co_4(CO)_9L_3]$	4 : 1	4 : 1	Et_2O–n-Pentane (−20)	Dark brown	50

Reaction of $[Co_4(CO)_{12}]$ with organophosphines and organophosphites has been reported to give complexes of the type $[Co_4(CO)_{12-x}L_x]$, where x can take values up to four.[4] We have carried out some substitution reactions of $[Co_4(CO)_{12}]$ using the same ligands as in our study of $[HFeCo_3(CO)_{12}]$. A significant difference noticed was that, in general, substitution of CO groups occurred much more rapidly with $[Co_4(CO)_{12}]$ than with $[HFeCo_3(CO)_{12}]$, although the rate is clearly ligand dependent and some reactions proceeded too fast to allow any differences in reaction times to be observed. This difference in reaction rate suggests that there is a higher kinetic barrier to CO substitution in the case of the heteronuclear complex. More conclusive evidence that this is the case is provided by ^{13}CO exchange experiments. Thus whereas ^{13}CO exchange with $[Co_4(CO)_{12}]$ gives *ca.* 50% enrichment after 24 h at room temperature (n-hexane solution; excess of *ca.* 88% enriched ^{13}CO gas)[6] $[HFeCo_3(CO)_{12}]$ is only *ca.* 3% enriched (estimated mass spectroscopically) under these conditions.

Once formed, the substituted $[HFeCo_3(CO)_{12-x}L_x]$

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[5] M. J. Mays and C. G. Cooke, *J. Organometallic Chem.*, 1974, **74**, 449.

[6] J. Evans, personal communication.

complexes are kinetically less labile than their $[Co_4(CO)_{12-x}L_x]$ analogues. For example, the prolonged standing of a pure compound of general formula $[Co_4(CO)_{11}L]$ in n-hexane solution resulted in a mixture of complexes of formula $[Co_4(CO)_{12-x}L_x]$ ($x = 0$—3) being formed, whereas the complexes $[HFeCo_3(CO)_{12-x}L_x]$ were found not to disproportionate in this way.

Spectroscopic Studies.—Infrared spectra. The solution i.r. spectrum of $[Co_4(CO)_{12}]$ has been interpreted[1] in terms of structure (I) (C_{3v} symmetry) being present and this structure is also favoured by ^{59}Co n.m.r. data.[7,8] A less well-resolved spectrum showing fewer ν_{CO} bands has, however, been interpreted in terms of the more symmetrical structure (III) (D_{2d} symmetry). For $[HFeCo_3(CO)_{12}]$ a distinction between the various structural possibilities on the basis of i.r. data alone is easier to make, since all structures other than shown on (II) have no higher than C_s symmetry and at least eight terminal ν_{CO} bands and three bridging ν_{CO} bands are predicted for such structures. The observed spectrum exhibits six well-resolved terminal and two bridging ν_{CO} bands which is exactly as predicted for structure (II) (C_{3v} symmetry). Although the six terminal CO bands in the spectrum of $[Co_4(CO)_{12}]$[1] are less well-resolved than for $[HFeCo_3(CO)_{12}]$ the two spectra are very similar, and this may be taken as further evidence that $[Co_4(CO)_{12}]$ adopts structure (I) rather than (III) in solution.

The i.r. spectra of the monosubstituted derivatives $[HFeCo_3(CO)_{11}L]$ in n-hexane solution are very similar to those of corresponding $[Co_4(CO)_{11}L]$ derivatives. In particular they all exhibit three bands in the ν_{CO} bridging region. This is as expected for structures derived from those of the parent compounds by replacing one of the terminal CO groups by the ligand L. The spectra are not compatible with structures of type (**III**) and (IV) for which four ν_{CO} bridging bands would be expected.

TABLE 2

Analytical data (%)

Compound	Found				Required			
	C	H	P	Fe	C	H	P	Fe
$[HFeCo_3(CO)_{11}PPh_3]$	43·6	2·2	3·75	7·05	43·28	1·99	3·86	6·96
$[HFeCo_3(CO)_{10}(PPh_3)_2]\cdot 1/4Me_2CO$	53·9	3·4	5·8		53·31	3·09	5·89	
$[HFeCo_3(CO)_{11}PMePh_2]$	39·1	1·95	4·15		38·82	1·89	4·18	
$[HFeCo_3(CO)_{10}(PMePh_2)_2]$	47·5	3·2	6·6	6·5	47·26	2·95	6·78	6·13
$[HFeCo_3(CO)_9(PMePh_2)_3]$	53·25	3·7	8·9		54·04	3·66	8·73	
$[HFeCo_3(CO)_{10}(dppe)]$	47·55	2·8	6·8		47·37	2·74	6·80	
$[HFeCo_3(CO)_8(dppe)_2]$	56·95	3·75	9·9		57·42	3·91	9·89	
$[HFeCo_3(CO)_{11}PEt_3]$	30·85	2·7	4·0	8·5	30·91	2·42	4·70	8·49
$[HFeCo_3(CO)_{10}(PEt_3)_2]$	35·3	4·0	7·75	7·3	35·20	4·13	8·27	7·74
$[HFeCo_3(CO)_{11}\{P(OPr)_3\}]$	31·9	2·75	3·95		32·00	2·93	4·13	
$[HFeCo_3(CO)_{10}\{P(OPr)_3\}_2]$	36·1	4·5	6·45		36·12	4·62	6·67	
$[HFeCo_3(CO)_{11}\{P(OPh)_3\}]$	41·1	1·9	3·35	6·75	40·85	1·88	3·64	6·57
$[HFeCo_3(CO)_{10}\{P(OPh)_3\}_2]$	48·8	3·0	5·5	5·1	48·67	2·73	5·47	4·94
$[Co(CO)_{11}PMePh_2]$	38·15	1·9	3·95		38·71	1·75	4·17	
$[Co_4(CO)_{10}(PMePh_2)_2]$	47·55	2·95	6·0		47·16	2·84	6·77	
$[Co_4(CO)_{11}PEt_3]$	30·4	2·3	4·6		30·81	2·27	4·68	
$[Co_4(CO)_{11}\{P(OPr)_3\}]$	32·05	2·95	4·25		31·99	2·79	4·12	
$[Co_4(CO)_{10}\{P(OPr)_3\}_2]$	36·35	4·4	6·35		36·05	4·51	6·65	
$[Co_4(CO)_{11}\{P(OPr)_3\}]$	40·55	1·9	3·85		40·73	1·76	3·63	
$[Co_4(CO)_{10}\{P(OPh)_3\}_2]$	49·1	2·85	5·15		48·59	2·64	5·46	
$[Co_4(CO)_9\{P(OPh)_3\}_3]$	53·9	3·3	6·4		53·31	3·17	6·56	
$[FeCo_3(CO)_{12}][Co(CO)_3(PMePh_2)_2]$	44·45	2·6	5·7		44·25	2·34	5·58	
$[FeCo_3(CO)_{12}][Co(CO)(dppe)_2]$	53·65	3·35	8·9		54·46	3·35	8·66	

TABLE 3

I.r. spectra of $[M_4(CO)_{12-x}L_x]$ (M = Rh, Ir, Co, L = Ph_3P)

Compound	Ref.	ν(C–O)/cm^{-1}
$[Rh_4(CO)_{11}PPh_3]$	9	2087s, 2057vs, 2053vs, 2031s, 2020m, 2009w, 1902vw, 1871m, 1851m,
$[Co_4(CO)_{11}PPh_3]$	4	2082s, 2041vs, 2036vs, 2010s, 2003m, 1990w, 1877w, 1851s, 1834s,
$[HFeCo_3(CO)_{11}PPh_3]$		2077m, 2041vs, 2033vs, 2010s, 1995s, 1972m, 1935vw, 1891w, 1866m, 1847m,
$[Rh_4(CO)_{10}(PPh_3)_2]$	9	2069s, 2044s, 2018m, sh, 2021m, 2002m, 1850m, 1815m,
$[Ir_4(CO)_{10}(PPh_3)_2]$	9	2060s, 2030s, 2000s, 1830s, 1790s,
$[HFeCo_3(CO)_{10}(PPh_3)_2]$		2051vs, 2018vs, 1986vs, 1951m, sh, 1865w, 1832s

The disubstituted derivatives $[HFeCo_3(CO)_{10}L_2]$ were insufficiently soluble in hydrocarbon solvents for their i.r. spectra to be recorded. In more polar solvents, band broadening did not permit the resolution of three i.r. bands in the ν_{CO} bridging region except in the case of $[HFeCo_3(CO)_{10}(dppe)]$. The spectra are, however, similar to those previously obtained for $[Co_4(CO)_{10}L_2]$, $[Rh_4(CO)_{10}L_2]$, and $[Ir_4(CO)_{10}L_2]$ derivatives[9] (Table 3), and this suggests that all these derivatives are isostructural in solution.

Mössbauer spectra. The i.r. spectra of the derivatives $[HFeCo_3(CO)_{12-x}L_x]$ show that the structures are

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[7] H. Haas and R. K. Sheline, *J. Inorg. Nuclear Chem.*, 1967, **29**, 693.

[8] E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc.* (*A*), 1967, 148.

[9] R. Whyman, *J.C.S. Dalton*, 1972, 1375.

derived from that of the parent compound by substitution of terminal CO groups, but do not give any indication as to whether substitution takes place on iron or cobalt. In an attempt to resolve this question we have studied the ^{57}Fe Mössbauer spectra of the series of complexes $[HFeCo_3(CO)_{12-x}(PMePh_2)_x]$ (x = 0—3). The data are recorded in Table 4 together with those for the anion $[FeCo_3(CO)_{12}]^-$.

TABLE 4

Mössbauer data [a]

Compound	δ [b]	Δ	Γ
$[Et_4N][FeCo_3(CO)_{12}]$	0·05	0·14	0·30
$[HFeCo_3(CO)_{12}]$	0·12	0·08	0·30
$[HFeCo_3(CO)_{11}PMePh_2]$	0·10	0·36	0·30
$[HFeCo_3(CO)_{10}(PMePh_2)_2]$	0·12	0·35	0·30
$[HFeCo_3(CO)_9(PMePh_2)_3]$	0·11	0·10	0·25
$[HFeCo_3(CO)_9(dppe)_2]$	0·11	0·11	0·30
$[HFeCo_3(CO)_8(dppe)_2]$ (A)	0·13	0·39	0·32
$[HFeCo_3(CO)_8(dppe)_2]$ (B)	0·08	1·01	0·31

[a] Parameters in mm/sec. [b] Quoted relative to natural iron foil at 295 K with the sample at 80 K.

There is little information that can be extracted from the isomer-shift data. The decrease in isomer shift in going from $[HFeCo_3(CO)_{12}]$ to $[FeCo_3(CO)_{12}]^-$ indicates an increased s-electron density at the iron nucleus, and is entirely consistent with the trend in the series $[Fe(CO)_5]$, $[HFe(CO)_4]^-$, and $[Fe(CO)_4]^{2-}$, where the progressive increase in anionic charge is accompanied by a similar decrease in isomer shifts.[10] The isomer shifts of the substituted complexes are all very similar. This is consistent with substitution at either the iron or the cobalt atoms, since there are much data to indicate that the isomer shifts in iron carbonyl complexes are insensitive to phosphine substitution at the iron atom.[11,12] A similar insensitivity in isomer shift values in the series of complexes $[Co_2FeS(CO)_{9-x}L_x]$ ($L = Ph_3P$; x = 0—2) has been attributed to substitution taking place at the cobalt atoms [13] but this conclusion is almost certainly not justified.

If the iron atom in $[FeCo_3(CO)_{12}]^-$ were octahedrally co-ordinated by the three cobalt atoms and the three CO groups it might reasonably be expected to show no quadrupole splitting, since $V_{xx} = V_{yy} = V_{zz} = 0$ for such a molecule.[14] The low quadrupole splitting observed for $[Et_4N][FeCo_3(CO)_{12}]$ is therefore in accord with a structure of the type shown in (II) (without the hydrogen atom). The fact that a quadrupole splitting is observed at all could either be due to the presence of the counter ion or to the fact that the co-ordination of the iron atom is not perfectly octahedral.

The quadrupole splitting for $[HFeCo_3(CO)_{12}]$ is also very small, and this suggests that there is no radical change of structure on protonation. It also lends support to the proposal [2] that the hydrogen atom occupies a symmetrical position on the three-fold axis of the cluster.

TABLE 5

I.r. spectra

Compound	Solvent *	ν(C–O)/cm^{-1}
$[HFeCo_3(CO)_{11}PMePh_2]$	1	2076m, 2040s, 2031vs, 2008s, 1996m, sh, 1970m, 1935vw, 1891w, 1865m, 1846m
$[Co_4(CO)_{11}PMePh_2]$	1	2082s, 2043vs, sh, 2037vs, 2027s, 2004m, 1992m, sh, 1970w, 1953vw, 1873w, 1845m, 1824m
$[HFeCo_3(CO)_{11}PEt_3]$	1	2080w, sh, 2074m, 2033s, sh, 2029vs, 2006s, 1995m, sh, 1979w, sh, 1972m, 1938vw, 1892w
$[Co_4(CO)_{11}PEt_3]$	1	2083s, 2038vs, 2027s, 2002m, 1985m, 1962vw, 1873m, 1846s, 1825s, 1865s, 1845s
$[HFeCo_3(CO)_{11}P(OPr)_3]$	1	2080m, 2044s, 2036vs, 2012s, 2000m, sh, 1982w, sh, 1971s, 1939w, 1895w, 1865s, 1846s
$[Co_4(CO)_{11}P(OPr)_3]$	1	2086m, 2046vs, sh, 2041vs, sh, 2026s, 2008m, 1990m, 1978w, sh, 1948vw, 1976w 1845m, 1827m
$[HFeCo_3(CO)_{11}P(OPh)_3]$	1	2082m, 2046s, sh, 2040vs, 2023s, 2016s, sh, 1977s, 1899w, 1875s, 1863m, sh
$[Co_4(CO)_{11}P(OPh)_3]$	1	2089m, 2051vs, 2044vs, 2033s, 2010m, 1970vw, 1883w, 1853m, 1838m
$[HFeCo_3(CO)_{10}(PMePh_2)_2]$	2	2050vs, 2017vs, 1991vs, 1951m, sh, 1866w, sh, 1826m, vbr
$[Co_4(CO)_{10}(PMePh_2)_2]$	1	2063s, 2026vs, 2014vs, 1990m, 1982m, sh, 1967m, sh, 1855w, 1817m, 1797m
$[HFeCo_3(CO)_{10}(dppe)]$	2	2057vs, 2020vs, 2008vs, sh, 1952m, 1869w, sh, 1837m, 1820m
$[HFeCo_3(CO)_8(dppe)_2]$	2	2004vs, 1973vs, 1926s, 1880m, 1830vw, 1772s, vbr, 1741s, vbr
$[HFeCo_3(CO)_{10}(PEt_3)_2]$	2	2074m, 2028vs, 2005s, 1965m, 1888w, 1859s, 1843s
$[HFeCo_3(CO)_{10}\{P(OPh)_3\}_2]$	1	2058s, 2027sh, vs, 2020vs, 2001s, sh, 1987vs, 1979m, sh, 1957m, 1875vw, 1839m, br
$[Co_4(CO)_{10}\{P(OPh)_3\}_2]$	1	2066s, 2030vs, 2015vs, 2009vs, sh, 1995s, 1986w, sh, 1976m, 1853w, 1819m, 1804m, sh
$[HFeCo_3(CO)_{10}\{P(OPh)_3\}_2]$	1	2065s, 2030vs, 2008vs, 1976vw, 1965s, 1930w, sh, 1920w, 1886w, 1849m, vbr
$[Co_4(CO)_{10}\{P(OPh)_3\}_2]$	1	2089w, 2075s, 2050w, sh, 2039vs, 2024vs, 2011m, sh, 1997w, sh, 1867w, 1835m, br
$[HFeCo_3(CO)_9(PMePh_2)_3]$	2	2032s, 1971s, br, 1942m, sh, 1844w, br, 1803,m, br
$[HFeCo_3(CO)_9(dppe)_2]$	1	2072vw, 2058s, 2052s, sh, 2022vs, 2004vs, sh, 1996s, sh, 1967w, 1835m, br
$[Co_4(CO)_9\{P(OPh)_3\}_3]$	2	2032s, 1986s, br, 1941m, sh, 1841w, br, 1800m, vbr, 1786m, vbr
$[FeCo_3(CO)_{12}][Co(CO)_3(PMePh_2)_2]$	2	2062w, 2001vs, 1946m, sh, 1920m, sh, 1848vw, 1802m, br
$[FeCo_3(CO)_{12}][Co(CO)(dppe)_2]$	2	2016w, 1999vs, 1960m, br, 1924m, br, 1846w, sh, 1802s, br

* 1 n-hexane, 2 chloroform.

The change in quadrupole splitting for the series of complexes $[HFeCo_3(CO)_{12-x}(PMePh_2)_x]$ (x = 0—3) shows that there is a large distortion of the electric field gradient for x = 1—2 and that the symmetry round the iron atom is in some way restored for x = 3. This can be interpreted either in terms of successive substitution of all three CO groups on the iron atom by phosphine

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[10] K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1969, 2339.

[11] R. L. Collins and R. Pettit, *J. Chem. Phys.*, 1963, **39**, 3433.

[12] R. L. Collins and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 2332.

[13] K. Burger, L. Korecz, and G. Bor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1527.

[14] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem.*, *Radiochem.*, 1972, **15**, 208.

ligands or, alternatively, by stepwise replacement of one carbonyl group on each of the cobalt atoms. The first of these alternatives can be rejected on electronic grounds, and in any case does not correspond to the pattern of substitution observed in homonuclear clusters. For example, *X*-ray diffraction studies on $[Fe_3(CO)_9(PMe_2Ph)_3]$[15] and $[Ir_4(CO)_9(PPh_3)_3]$[16] show that the phosphine ligands are all on different metal atoms.

At first sight it may seem surprising that substitution at a cobalt atom should have such a marked effect on the quadrupole splitting observed for the iron atom. An *X*-ray diffraction study of $[CH_3CCo_3(CO)_8PPh_3]$,[17] however, shows that the methyl group attached to the apical carbon atom is bent away significantly from the cobalt atom to which the phosphine ligand is attached. It seems likely that a similar distortion in the co-ordination sphere of the Fe atom takes place in the complexes $[HFeCo_3(CO)_{12-x}(PMePh_2)_x]$ ($x = 1$ or 2) thereby removing the pseudo-octahedral symmetry and that this is at least as important as electronic effects transmitted *via* the metal–metal bonds in producing the observed large quadrupole splittings. Substitution of a CO group on all three cobalt atoms presumably restores the co-ordination geometry around the iron atom to approximately that of the unsubstituted complex and leads to a similarly low quadrupole splitting being observed.

Mössbauer spectra were also recorded for a black crystalline complex obtained by refluxing $[HFeCo_3(CO)_9(dppe)_2]$ in acetone for 30 min. This product analysed for $[HFeCo_3(CO)_8(dppe)_2]$ and eluted repeatedly as a single band on a t.l.c. plate. Its Mössbauer spectrum, however, revealed that it was a mixture of two compounds, since two quadrupole split doublets of approximate intensity ratio 1 : 3 were observed. It seems probable that these two compounds are isomers, and the Mössbauer data for each isomer (referred to as isomer A and B respectively) are presented in Table 4. It will be seen that the Mössbauer parameters for A are very similar to those for the complexes $[HFeCo_3(CO)_{12-x}(PMePh_2)_x]$ ($x = 1$ or 2). This suggests that the two dppe ligands chelate the three basal cobalt atoms and that, in consequence, one of the cobalt atoms is disubstituted. This would distort the co-ordination geometry round the iron atom in a similar way to that described previously. The more abundant isomer B has a quadrupole splitting which is very much larger than any of the other complexes examined herein. Such a marked change in the e.f.g. at the iron atom is indicative of a change in the primary co-ordination sphere of the iron atom. A probable explanation is that a CO group on the iron atom has been substituted by a phosphorus atom. The isomer shift of 0·34 mm/s is lower than those of the other phosphine-substituted complexes studied and is certainly compatible with phosphorus substitution on iron.

Mass spectra. Only one compound, $[HFeCo_3(CO)_{11}P(OC_3H_7)_3]$, was sufficiently volatile for its mass spectrum to be recorded. Two principal series of ions were observed, these being $[HFeCo_3(CO)_{11-x}P(OC_3H_7)_3]^+$ ($x = 0$—11; $x = 1$ of low intensity) and $[HFeCo_3(CO)_{11-x}\{P(OC_3H_7)_2(OC_2H_4)\}]^+$ ($x = 0$—11; $x = 1$ absent). Stepwise loss of carbonyl groups in both these series was shown by the presence of metastable peaks. This mass spectrum is useful in confirming the presence of the hydride ligand, since this could not be detected in the ^1H n.m.r. spectrum of either the unsubstituted[18] or any of the substituted complexes.

EXPERIMENTAL

Analyses were carried out by the Microanalytical Department of the University Chemical Laboratory. Proton n.m.r. spectra were recorded on a Perkin-Elmer R12 60 MHz spectrometer and i.r. spectra on a Perkin-Elmer 257 using carbon monoxide as calibrant and are quoted to an accuracy of ± 1 cm^{-1}. Mössbauer spectra were recorded at the P.C.M. unit at Harwell. The mass spectrum was recorded on an AEI MS12 spectrometer. Reactions were carried out under an atmosphere of dry nitrogen and solvents were degassed before use. T.l.c. plates were coated with silica gel. Light petroleum boiling in the range 40—60 °C was used as eluant. All organophosphines and organophosphites were commercial samples and were used as purchased. $[HFeCo_3(CO)_{12}]$ Was prepared by a literature method.[19]

$[HFeCo_3(CO)_{12-x}(PMePh_2)_x]$ ($x = 1$—2).—A two-fold excess of Ph_2MeP (0·4 g, 2 mmol) was stirred for ½ h with $[HFeCo_3(CO)_{12}]$ (0·5 g, 0·88 mmol) in chloroform (50 ml) at 20 °C. Chromatography on t.l.c. plates using a 9 : 1 light petroleum–CH_2Cl_2 mixture as eluant afforded two bands; a fast-moving purple and a slower-moving blue-green band together with an unmoved red ionic residue. Extraction of the bands was followed by rechromatography using the same eluant. Recrystallisation of the purple band from an n-pentane solution at −20 °C and of the blue-green band from n-pentane–diethyl ether solution at −20 °C afforded black crystals in each case which were formulated (from analytical data) respectively as $[HFeCo_3(CO)_{11}PMePh_2]$ (0·4 g, 60%) and $[HFeCo_3(CO)_{10}(PMePh_2)_2]$ (0·16 g, 20%). The yield of the disubstituted complex could be increased by extending the reaction time and/or heating to 60 °C. The ionic compound was recrystallised from n-pentane–diethyl ether solution at −20 °C to give black crystals of $[Co(CO)_3(PMePh_2)_2][FeCo_3(CO)_{12}]$ (0·1 g, 10%).

$[HFeCo_3(CO)_9(PMePh_2)_3]$.—This compound was prepared as above using a three-fold excess of Ph_2MeP and a reflux period of 3 h. Chromatographic separation using a 2 : 1 light petroleum–CH_2Cl_2 eluant gave $[HFeCo_3(CO)_{10}(PMePh_2)_2]$ in low yield and a slower-moving green band which was recrystallised from n-pentane–diethyl ether cooled to −20 °C to give (0·4 g) dark green crystals of $[HFeCo_3(CO)_9(PMePh_2)_3]$ in *ca.* 40% yield. ^1H N.m.r. of

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[15] W. S. McDonald, J. R. Moss, G. Raper, and B. L. Shaw, *Chem. Comm.*, 1969, 1295.

[16] V. Albano, P. Bellon, and V. Scatturin, *Chem. Comm.*, 1967, 730.

[17] M. D. Bruce, B. R. Penfold, W. T. Robinson, and S. R. Taylor, *Inorg. Chem.*, 1970, **9**, 362.

[18] M. J. Mays and R. N. F. Simpson, *J. Chem. Soc.* (*A*), 1968, 1444.

[19] P. Chini, L. Colli, and M. Peraldo, *Gazzetta*, 1960, **90**, 1005.

$[HFeCo_3(CO)_{11}PMePh_2]$ in $CDCl_3$ τ 2·6 (m), 8·0 (d) J(P–H) = 8 Hz, for 10, 3 protons respectively. ^1H N.m.r. of $[HFeCo_3(CO)_{10}(PMePh_2)_2]$ in $CDCl_3$ τ 2·7 (m), 8·5 (d), J(P–H) = 8 Hz, for 10, 3 protons respectively. ^1H N.m.r. of $[HFeCo_3(CO)_9(PMePh_2)_3]$ in $CDCl_3$ τ 2·8 (m), 8·4 (d) J(P–H) = 7·7 Hz, for 10, 3 protons respectively.

$[HFeCo_3(CO)_{10}(dppe)]$.—A two-fold excess of dppe (0·7 g, 1·8 mmol) reacted with $[Et_4N][FeCo_3(CO)_{12}]$ (0·5 g, 0·88 mmol) in refluxing acetone (50 ml) during 10 min to form $[Et_4N][FeCo_3(CO)_{10}(dppe)]$ (0·88 g, 96% yield). The product was freed from an excess of dppe by repeated recrystallisation from acetone–diethyl ether. Protonation of $[Et_4N][FeCo_3(CO)_{10}(dppe)]$ (0·5 g) in CH_2Cl_2 (50 ml) with concentrated HCl (5 ml) led to the rapid formation of $[HFeCo_3(CO)_{10}(dppe)]$ (0·77 g) in almost quantitative yield. The direct reaction of $[HFeCo_3(CO)_{12}]$ with dppe led to the isolation of $[HFeCo_3(CO)_{10}(dppe)]$ in low yield and the formation of $[FeCo_3(CO)_{12}][Co(CO)(dppe)_2]$ as the major product.

$[HFeCo_3(CO)_8(dppe)_2]$.—A two-fold molar excess of dppe (0·45 g, 1·1 mmol) reacted with $[HFeCo_3(CO)_{10}(dppe)]$ (0·5 g, 0·54 mmol) in acetone (50 ml) at 35 °C during 4 h to give a green product. An excess of dppe was removed from the product by repeated recrystallisation from acetone–n-pentane solution at −20 °C. The close similarity of the i.r. and Mössbauer spectra of this compound to those of $[HFeCo_3(CO)_9(PMePh_2)_3]$ suggests that it should be formulated as $[HFeCo_3(CO)_9(dppe)_2]$ where the second dppe molecule is unidentate. However, the compound gave consistently low analyses for C and H, although good phosphorus analyses were obtained.

The green compound $[HFeCo_3(CO)_9(dppe)_2]$ (0·77 g) was converted quantitatively into the dark black compound $[HFeCo_3(CO)_8(dppe)_2]$ in refluxing acetone during ½ h. The product was purified by repeated chromatography using an eluant mixture of 1 : 3 light petroleum–CH_2Cl_2; it was crystallised from an acetone–n-pentane solution at 0 °C giving 0·93 g of black crystals (95%). The complexes $[HFeCo_3(CO)_9(dppe)_2]$ and $[HFeCo_3(CO)_8(dppe)_2]$ were insufficiently soluble for their ^1H n.m.r. to be recorded.

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