Polynuclear Carbonyl Complexes of Cobalt containing Isocyanides and Other Ligands

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Isocyanides, RNC (R = alkyl but usually Me or Bu^t), displace up to five carbonyl ligands from $[Co_4(CO)_{12}]$, $[(\pi\text{-}C_5H_5)NiCo_3(CO)_9]$, $[YCCo_3(CO)_9]$ (Y = Cl, Me, or Ph), $[SCo_3(CO)_9]$, and $[SCo_2Fe(CO)_9]$. The reactions usually take place under mild conditions with retention of the pseudotetrahedral XCo_3 or SCo_2Fe cluster (X = Co, Ni, C, or S). With octacarbonyldicobalt, the products are derivatives of $[Co_4(CO)_{12}]$ or $[(RNC)_5Co][Co(CO)_4]$, but never of $[Co_2(CO)_8]$. $[\{LCo(CO)_3\}_2Hg]$ (L = tertiary phosphine or CO) and $[(R_3P)_2Co(CO)_3][Co(CO)_4]$ salts undergo similar CO replacement reactions. The structures of the products are discussed on the bases of their i.r. spectra.

THE replacement of carbon monoxide in various polynuclear cobalt carbonyls by Group VA ligands may take place with (*a*) retention of the cluster,[1] or (*b*) its fragmentation into simpler units.[2] The related reactions using organoisocyanide ligands have received far less attention. The investigations described in the present paper show that they are much less likely to take place by route (*b*), and in some instances occur with polymerisation of dicobalt to tetracobalt species. Previous work has shown that under vigorous conditions octacarbonyldicobalt and methyl isocyanide give $[(MeNC)_5Co][Co(CO)_4]$.[3]

EXPERIMENTAL

Published methods were used to prepare the organoisocyanides,[4] $[Co_4(CO)_{12}]$,[5] $[(\pi\text{-}C_5H_5)NiCo_3(CO)_9]$,[6] $[SCo_3(CO)_9]$,[7] $[SFeCo_2(CO)_9]$,[8] $[MeCCo_3(CO)_9]$,[9] $[PhCCo_3(CO)_9]$,[9] $[ClCCo_3(CO)_9]$,[9] $[\{Ph_3PCo(CO)_3\}_2]$,[10] $[\{Bu^n{}_3PCo(CO)_3\}_2]$,[11] $[\{Co(CO)_4\}_2Hg]$,[12] $[\{Ph_3PCo(CO)_3\}_2Hg]$,[13] and $[\{Bu_3PCo(CO)_3\}_2Hg]$.[13] Other chemicals were purchased.

All reactions were carried out in purified solvents under an atmosphere of nitrogen at room temperature using *ca.* 1—2 g of the metal carbonyl complex unless it is stated otherwise. They were monitored by i.r. spectroscopy. When the reactions were complete, the products were separated by chromatography on alumina using benzene–hexane mixtures as eluants, or by crystallization. They were purified by recrystallization.

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Melting points, analyses, and infrared spectra (1700—2200 cm^{-1}) of compounds described in the text

Compound [a]			M.p. [b]	Analyses [c]								Absorption bands [d]							
				Found (%)			Others and M	Calculated (%)			Others and M								
R	n	Y		C	H	N		C	H	N									
$[Co_4(CO)_{12-n}(CNR)_n]$																			
Me	1		142—144	26·3	0·6	2·8		26·7	0·5	2·5		1845sh	1850 (9·3)	1860 (10)	1888 (0·2)	2012sh	2014 (5·5)	2020 (5·2)	2030sh
Et	1		dec. 200	27·1	0·9	2·2		28·0	0·8	2·3		1844sh	1848 (9·6)	1857 (10)	1886 (0·2)	2009sh	2012 (4·8)	2020 (4·8)	2032sh
Bu^t	1		106—108	30·6	1·4	2·4	M = 638	30·6	1·4	2·2	M = 627	1845sh	1850 (9·0)	1860 (10)	1888 (0·5)	2012sh	2014(4·8)	2020 (4·8)	2031sh
Cy	1		115—117	32·6	2·0	2·1		33.1	1·7	2·1		1845sh	1849 (9·4)	1857 (10)	1887 (0·2)	2009sh	2012 (5·0)	2020 (5·6)	2032sh
$PhCH_2$	1		dec. 270	33·8	1·6	2·3		34·5	1·1	2·1		1845sh	1850 (7·0)	1858 (10)	1886 (0·2)	2012sh	2015 (5·2)	2021 (4·8)	2032sh
Me	2		128—130	27·8	1·0	4·8		28·1	1·0	4·7		1832 (10)	1844 (8·4)	1875 (0·5)		1998 (8·0)	2014 (15·4)	2028 (29·0)	2066 (6·1)
Et	2		50—51	30·4	1·6	4.5		30·6	1·6	4·5		1835 (10)	1844 (9·2)	1876 (0·5)		1996 (7·5)	2014 (14·5)	2028 (27·0)	2065 (6·6)
Bu^t	2		87—89	35·2	2·7	4·1	M = 688	35·2	2·6	4·1	M = 682	1836 (10)	1844 (9·3)	1876 (0·4)		1996 (8·7)	2013 (15·0)	2027 (40·0)	2063 (6·9)
Cy	2		66—68	39·6	3·3	4·0		39·3	3·0	3·8		1835 (10)	1842 (9·3)	1876 (0·7)		1996 (8·3)	2012 (14·7)	2028 (31·0)	2064 (7·0)
$PhCH_2$	2		40—42	41·4	2·2	3·6		41·6	1·8	3·7		1836 (9·4)	1845 (10)	1876 (0·4)		2000 (8·3)	2016 (15·7)	2027 (35·7)	2065 (7·7)
Me	3		80—81	29·4	1·6	7·2		29·4	1·5	6·9		1825 (9·2)	1833 (10)	1865 (0·5)		1985 (9·0)	2005 (16·3)	2014 (27·0)	2045 (6·5)
Bu^t	3		137—139	38·9	3·7	5·6	M = 745	39·1	3·7	5·7	M = 737	1823 (9·5)	1831 (10)	1864 (0·5)		1984 (9·1)	2002 (18·7)	2011 (30·4)	2039 (6·5)
Cy	3		82—83	43·7	4·5	5·3		44·2	4·1	5·2		1822 (9·3)	1830 (10)	1864 (0·5)		1982 (9·3)	2002 (16·8)	2012 (23·0)	2041 (6·2)
Me	4		dec. 200	30·3	1·9	9·1		30·8	1·9	9·0		1794sh	1803 (10)	1843 (0·05)		1967sh	1977sh	1988 (19·0)	1997 (19·0)
Bu^t	4		dec. 156	42·3	4·6	7·0	M = 802	42·4	4·6	7·1	M = 792	1813 (9·8)	1820 (10)			1968 (8·4)	1976 (10·8)	1990 (9·2)	1997 (13·6)
Cy	4		96—98	48·1	4·9	6·0		48·2	4·9	6·2		1810 (10)	1817 (9·8)			1967 (10)	1975 (10·7)	1991 (11·5)	1997 (13·6)
Bu^t	5 [e]		177—178	44·9	5·3	8·1	M = 843	45·3	5·3	8·2	M = 847	1784sh	1793sh	1802 (10)	1816sh	1957 (13·0)	1967 (13·0)	1975sh	1992 (12·4)
$[(\pi\text{-}C_5H_5)NiCo_3(CO)_{9-n}(CNR)_n]$																			
Me	1											1830sh	1838 (4·7)	1845 (4·3)		2006 (6·8)	2013 (6·2)	2029 (1·0)	2057 (4·0)
Bu^t	1		114—115	35·1	2·3	2·1		35·5	2·3	2·3		1830sh	1838 (5·0)	1845 (4·0)		2004 (6·6)	2012 (6·8)	2028 (1·0)	2055 (3·3)
$[YCCo_3(CO)_{9-n}(CNR)_n]$																			
Me	1	Me	55—56	31·2	1·3	3·0		30·8	1·3	3·0					1987 (0·5)	1992 (0·6)	2000 (0·8)	2010 (2·9)	2016 (3·1)
Bu^t	1	Ph	80—82	42·1	2·4	2·5		41·9	2·4	2·4								1944 (0·4)	2015 (3·1)
Me	1	Cl	68—69	26·5	0·4	2·9		27·0	0·6	2·9					2003 (0·8)	2014sh	2019sh	2025 (3·7)	2038 (7·1)
Me	2	Me	37—38	31·9	1·8	5·7		32·4	2·1	5·8					1972 (1.6)	1983 (1·8)	1988 (2·5)	1995 (3·8)	2006sh
Bu^t	2	Ph	78—79	45·6	3·5	4·2		45·9	3·7	4·4					1975 (1·4)	1982 (1·4)	1995 (2·5)	2006 (5·0)	2016 (10)
Me	2	Cl	44—46	29·2	1·3	5·4		28·7	1·2	5·6					1987 (1·7)	1995 (2·2)	2006 (4·4)	2017 (5·5)	2031 (10)
Bu^t	2	Cl	23—24	36·5	3·6	4·6		36·8	3·1	4·8					1983 (1·3)	1991 (2·1)	2002 (4·0)	2012 (5·0)	2027 (10)
Me	3	Me	88—89	33·4	2·4	8·4		33·9	2·4	8·5					1957sh	1965 (4·4)	1980 (6·6)	1984 (6·8)	1997 (10)
Bu^t	3	Me	133—134	44·6	4·6	6·7		44·4	4·8	6·8					1955sh	1962 (4·4)	1977 (6·8)	1979 (6·8)	1994 (10)
Bu^t	3	Ph	72—74	49·9	4·2	5·8		49·2	4·7	6·1					1960sh	1968 (3·4)	1984 (6·1, br)		1996 (10)
Me	3	Cl [f]	200	34·4	3·8	7·5		34·4	2·7	7·5					1972sh	1979 (5·9)	1993 (7·1)	1998 (7·1)	2008 (10)
Bu^t	3	Cl	103—104	41·5	4·5	6·5		41·2	4·4	6·5					1968sh	1974 (5·4)	1987 (6·8)	1990 (6·8)	2004 (10)
Bu^t	4	Ph	94—96	52·9	5·2	7·4		52·0	5·5	7·6						1948sh	1954 (8·7)	1969 (8·9)	1980 (10)
Bu^t	4	Cl	88—89	44·3	4·7	7·6		44·8	5·2	8·0						1956sh	1962 (9·7)	1974 (1·0)	1987 (9·3)
$[SFeCo_2(CO)_{9-n}(CNR)_n]$																			
Bu^t	2		85—86	35·4	4·0	4·7	S = 5·3	35·9	3·2	4·9	S = 5·6				1948 (2·2)	1984 (2·0)	1999 (4·0)	2006 (8·2)	2020 (10)
Bu^t	3		90—91	40·4	4·4	6·5	S = 4·4	40·4	4·3	6·7	S = 5·1	1823 (1·4)	1831 (1·6)	1864 (0·05)	1931 (3·4)	1970 (3·2)	1983 (7·1)	1996 (7·6)	2002 (10)
$[(Ph_3P)_2Co(CNR)_3][Co(CO)_4]$																			
Me [g]			174—176	63·0	4·8	4·4		62·9	4·5	4·8					1873s	1882s			
Et [g]			162—164	63·6	5·3	4·5		64·0	4·9	4·6					1880s	1880s			
Cy [g]			138—139	67·2	5·6	3·8		67·7	5·8	3·9					1877s	1886sh			
$[(Bu^n_3P)_2Co(CNR)_3][BPh_4]$																			
Me [e]			122—124	72·8	9·8	4·4		71·6	9·2	4·6									
$[Y_2Co_2(CO)_{6-n}(CNR)_nHg]$																			
Me	2	CO [e]	127—128	20·6	0·8	4·8		21·2	1·1	4·9						1962 (10)	2007sh		2014 (1·0)
Me	1	Bu^n_3P [e]	76—78	41·8	6·6	1·6		41·2	6·3	1·6						1985sh	1912 (4·2)	1917sh	1934 (1·0)
Bu^t	2	Ph_3P [e]	216—219	53·7	4·4	2·4		53·6	4·3	2·5						1894 (10)	1927 (7·4)		1940 (4·8)

Compound [a]			Absorption bands [d]						
R	n	Y							
$[Co_4(CO)_{12-n}(CNR)_n]$									
Me	1		2040 (31·0)	2046 (37·0)	2087 (6·1)			2181sh	2192 (3·3)
Et	1		2039 (30·0)	2045 (34·5)	2085 (6·5)			2172sh	2177 (2·8)
Bu^t	1		2040 (29·0)	2046 (34·0)	2087 (6·2)			2150sh	2168 (3·1)
Cy	1		2039 (35·6)	2045 (39·4)	2084 (5·6)			2159sh	2171 (5·0)
$PhCH_2$	1		2041 (31·0)	2045 (37·0)	2087 (7·0)			2166sh	2176 (3·7)
Me	2		2070 (5·6)					2171 (5·5)	2177 (5·8)
Et	2		2069 (6·6)					2159 (5·4)	2164 (5·5)
Bu^t	2		2067 (6·8)					2154 (6·5)	2163 (4·1)
Cy	2		2067 (7·0)					2149 (4·7)	2158 (4·7)
$PhCH_2$	2		2069 (8·3)					2143 (6·8)	2175 (5·0)
Me	3						2156sh	2167 (9·1)	2175sh
Bu^t	3						2133sh	2142 (9·5)	2160sh
Cy	3						2141 (9·3)	2148 (9·3)	2163sh
Me	4		2025 (16·0)				2149sh	2169 (19·0)	2187sh
Bu^t	4		2021 (6·4)				2122sh	2133 (10·8)	2149sh
Cy	4		2018 (5·8)				2123sh	2136 (12·0)	2156sh
Bu^t	5 [e]		1997 (12·4)	2020 (2·3)			2073 (3·5)	2121 (18·0)	2134sh
$[(\pi\text{-}C_5H_5)NiCo_3(CO)_{9-n}(CNR)_n]$									
Me	1		2065 (1·0)					2184 (2·2)	
Bu^t	1		2064 (0·8)					2153 (2·2)	
$[YCCo_2(CO)_{9-n}(CNR)_n]$									
Me	1	Me	2030 (8·0)	2037 (10)	2076 (0·8)	2082 (2·0)		2181 (1·6)	
Bu^t	1	Ph	2030 (9·1)	2038 (10)	2076sh	2081 (3·9)		2155 (1·0)	
Me	1	Cl	2047 (1·0)	2085sh	2089 (2·9)			2185 (1·3)	
Me	2	Me	2010 (5·3)	2018 (10)	2056 (2·6)	2059 (2·6)	2164 (2·4)		2176sh
Bu^t	2	Ph	2020sh	2053 (3·8)	2056 (4·9)		2139 (2·9)		2159sh
Me	2	Cl	2062sh	2066 (3·5)	2069 (3·5)		2175 (2·4)		2185sh
Bu^t	2	Cl	2057sh	2061 (2·9)	2064 (2·9)		2147 (2·5)		2162sh
Me	3	Me	2003sh	2021 (3·6)	2032 (4·0)		2140sh		2153 (6·4)
Bu^t	3	Me	2000sh	2017 (2·6)	2027 (4·2)		2113sh	2126 (6·3)	2146sh
Bu^t	3	Ph	1999sh	2019 (4·1)	2031 (5·1)		2118 (4·4)	2131 (6·8)	2148 (1·7)
Me	3	Cl [f]	2012sh	2034 (3·4)	2044 (3·7)		2151sh	2165 (6·5)	2181sh
Bu^t	3	Cl	2011sh	2011sh	2037 (4·0)		2120sh		2135 (6·8)
Bu^t	4	Ph	1994 (7·8)				2078 (3·1)	2112sh	2121 (11·4)
Bu^t	4	Cl	2007 (7·3)				2117sh	2128 (11·4)	2135sh
$[SFeCo_2(CO)_{8-n}(CNR)_n]$									
Bu^t	2		2027sh	2054 (3·1)	2062sh		2136sh	2152 (2·3)	2164 (1·4)
Bu^t	3		2016 (5·8)	2029 (5·0)	2039 (1·4)		2130 (3·9)	2141 (5·9)	2157 (2·0)
$[(Ph_3P)_2Co(CNR)_3][Co(CO)_4]$									
Me [g]							2100m		2140w
Et [g]							2028sh	2087m	2114sh
Cy [g]							2049m		2088m
$[(Bu^n{}_2P)_2Co(CNR)_3][BPh_4]$									
Me [e]							2071sh	2088 (1·0)	2122 (4·8)
$[Y_2Co_2(CO)_{6-n}(CNR)_nHg]$									
Me	2	CO [e]	2035 (1·3)				2143sh		2160 (2·0)
Me	1	$Bu^n{}_3P$ [e]	1944 (8·9)	2986 (0·5)	1995 (1·7)				2099 (0·9)
Bu^t	2	Ph_3P [e]	2059 (1·1)						2100 (3·7)

[a] Cy = cyclohexyl. [b] Determined in sealed tubes. dec. = decomposed without melting. [c] M = molecular weight determined cryoscopically in benzene. [d] Peak positions (cm^{-1}) with relative peak heights in parentheses. Hexane solution unless stated otherwise. sh = shoulder, s = strong, m = medium, and w = weaker. [e] I.r. spectrum in chloroform solution. [f] Crystallizes as $[ClCo_3(CO)_6(CNMe)_3],\frac{1}{2}C_6H_{14}$. [g] I.r. spectrum of Nujol mull.

The reactions between $[Co_4(CO)_{12}]$ and the isocyanide RNC were carried out in benzene with the slow, dropwise addition of a solution of the ligand to a well-stirred solution of the complex. They were virtually instantaneous and proceeded by stepwise substitution. Thus the use of RNC : $[Co_4(CO)_{12}]$ mole ratios of n : 1 gave nearly pure $Co_4(CO)_{12-n}(CNR)_n$ in yields of 60—70% for $n = 1$—4. The procedure prevented the formation of the $[(RNC)_5Co][Co(CO)_4]$ salts which otherwise took place at higher concentrations. $[Co_4(CO)_7(CNBu^t)_5]$ was obtained from $[Co_4(CO)_8(CNBu^t)_4]$ and Bu^tNC (mole ratio 1 : 6).

Octacarbonyldicobalt and RNC (mole ratio 2 : n) gave $[Co_4(CO)_{12-n}(CNR)_n]$ ($n = 2$—4). There was no evidence for the formation of any other products except $[(RNC)_5Co][Co(CO)_4]$. Even very low concentrations of isocyanide gave no more than traces of $[Co_4(CO)_{11}(CNR)]$.

In contrast, when solutions or suspensions of $[\{LCo(CO)_3\}_2]$ in benzene (L = Ph_3P or Bu^n_3P) were refluxed with isocyanides for 1 h (mol ratio 1 : 3), yellow salts $[L_2Co(CNR)_3][Co(CO)_4]$ were obtained (R = Me, Et, or C_6H_{11}). They were isolated as such or as $[L_2Co(CNR)_3][BPh_4]$ by crystallization from acetone (yields 70—80%). When L = Bu^n_3P, there was evidence for the formation of cations containing carbonyl ligands.

$[(\pi\text{-}C_5H_5)NiCo_3(CO)_9]$ (0·3 g) and Bu^tNC (0·6 ml) in benzene (25 ml) were stirred for 2 h to give $[(\pi\text{-}C_5H_5)NiCo_3(CO)_8(CNBu^t)]$ (50% yield) and $[Co_4(CO)_{12-n}(CN^tBu)_n]$ (n = 2 or 3). The direct reaction of $[\{(\pi\text{-}C_5H_5)Ni(CNC_6H_{11})\}_2]$ and $Co_2(CO)_8$ gave $[Co_4(CO)_{12-n}(CNC_6H_{11})_n]$ and $[Ni(\pi\text{-}C_5H_5)_2]$.

Although $[SCo_3(CO)_9]$ reacted with Bu^tNC, no product could be isolated. However with the more stable $[SFeCo_2(CO)_9]$, $[(Bu^tNC)Fe(CO)_4]$ and $[SFeCo_2(CO)_{9-n}(CNBu^t)_n]$ (n = 2 or 3) were obtained.

When hexane solutions of $[MeCCo_3(CO)_9]$ (0·5 g) and RNC (R = Me or Bu^t), mol ratio 1 : 6, were refluxed for 1—1½ h, mixtures $[MeCCo_3(CO)_{9-n}(CNR)_n]$ (n = 1—3) were obtained. Yields of the purified products were 15—50%.

$[PhCCo_3(CO)_{9-n}(CNBu^t)_n]$, ($n$ = 1—4) could be prepared similarly or by stirring the reaction mixtures for 20 h. $[ClCCo_3(CO)_9]$ reacted rapidly with isocyanides in hexane. By using suitable proportions of reactants, pure $[ClCCo_3(CO)_{9-n}(CNR)_n]$ could be isolated without the aid of chromatography in yields of 30—40% (n = 1—4; R = Me or Bu^t).

Methyl isocyanide and $[\{Co(CO)_4\}_2Hg]$ (mol ratio 2 : 1) reacted rapidly in benzene to give $[\{(MeNC)Co(CO)_3\}_2Hg]$ (yield *ca.* 40%). Under the same conditions, $[\{Bu^n_3PCo(CO)_3\}_2Hg]$ and MeNC, or $[\{Ph_3PCo(CO)_3\}_2Hg]$ and Bu^tNC gave $[\{Bu^n_3PCo(CO)_3\}Hg\{Co(CO)_2(CNMe)PBu^n_3\}]$ or $[\{Ph_3P(Bu^tNC)Co(CO)_2\}_2Hg]$ respectively in yields of *ca.* 70%. All three products were yellow solids which were recrystallized from benzene–hexane mixtures.

The complexes which have been isolated are listed in the Table together with their melting points, analyses, and i.r. spectra. The spectra were obtained as described previously.[14]

RESULTS AND DISCUSSION

Whereas the ionic products and the derivatives of mercury cobalt carbonyl are yellow, air-stable solids, the polynuclear compounds are deeply coloured solids or liquids; $[Co_4(CO)_{12-n}(CNR)_n]$ (R = alkyl; n = 1—5) are dark brown, $[(\pi\text{-}C_5H_5)NiCo_3(CO)_8(CNBu^t)]$ is green, $[YCCo_3(O)_{9-n}(CNR)_n]$ (Y = Me, Ph or Cl) purple, and $[SFeCo_2(CO)_{9-m}(CMR)_m]$ (m = 2 or 3) are brown. All are at least as stable as their unsubstituted precursors towards thermal and oxidative decomposition. Although this increase in stability is especially marked for the derivatives of dodecacarbonyltetracobalt, the ability of isocyanide ligands to stabilize clusters of the first-row transition metals appears to be widespread.[15]

In a preliminary publication, the $[Co_4(CO)_{12-n}(CNR)_n]$ complexes were formulated as derivatives of octacarbonyldicobalt, $[Co_2(CO)_{8-m}(CNR)_m]$.[16] * Their true natures were confirmed by molecular-weight measurements (cryoscopic in benzene [17]), whilst their i.r. spectra are consistent with molecular structures based on that of $[Co_4(CO)_{12}]$.[18,19] The isocyanide molecules do not act as bridging ligands in these complexes (or in any other described here), but there are three types of terminal co-ordination positions which they may occupy. Thus although isomerism is possible, the simplicity of the spectra in the terminal C–O stretching region and the sharpness of most absorption bands suggests that one isomer predominates over the others in all complexes except those of the type $[Co_4(CO)_{10}(CNR)_2]$. With these, the terminal ν(CO) absorption band of highest frequency has two components which may be due to isomers (*cf.* $[Co_4(CO)_{10}(PEt_3)_2]$ and $[Co_4(CO)_9(PMe_2Ph)_3]$ [20]). The intense absorption bands in the $\nu(CO\mu)$ region of all spectra are probably due to the *e* vibrations of the $Co_3(\mu\text{-}CO)_3$ moiety which have been split into two components by the lowering of the molecular symmetries which take place on CO substitutions. The weak absorption band at higher frequency in many spectra is attributed to the $\nu(CO\mu)$ mode of a_1 symmetry.

The structure of $[(\pi\text{-}C_5H_5)NiCo_3(CO)_9]$ is similar to that of $[Co_4(CO)_{12}]$ but with the apical $Co(CO)_3$ moiety being replaced by $(\pi\text{-}C_5H_5)Ni$.[6] In the spectra of $[(\pi\text{-}C_5H_5)NiCo_3(CO)_8(CNR)]$, the two components of the *e* $\nu(CO\mu)$ mode have a separation comparable to that observed for $[Co_4(CO)_{11}(CNR)]$. This implies that in both series of compounds the isocyanide ligands are co-ordinated to a cobalt atom of the triangular $Co_3(\mu\text{-}CO)_3$ array. $[(\pi\text{-mesitylene})CO_4(CO)_9]$ [21] undergoes a similar substitution reaction, but no product was isolated.

The pseudotetrahedral XCo_3 framework found in

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* It is only when R = Me that the expected analyses for $[Co_2(CO)_{8-m}(CNR)_m]$ and $[Co_4(CO)_{12-n}(CNR)_n]$ ($n = 2m$) differ to any great extent.

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$[Co_4(CO)_{12}]$ and $[(\pi\text{-}C_5H_5)NiCo_3(CO)_9]$ is retained in the $[YCCo_3(CO)_9]$ complexes, but these last do not possess bridging carbonyl groups.[22] As they have two types of terminal ligands, isomers are possible on CO substitution. They are probably responsible for the relative complexity of the i.r. spectra of those $[YCCo_3(CO)_{9-n}(CNR)_n]$ derivatives where $n = 1$—4 which often show more absorption bands due to their ν(CO) vibrations than they have CO ligands. In other instances two components are observed for the absorption bands at highest frequency which are almost certainly due to the singly degenerate, fully symmetric, ν(CO) vibrations of two different species which cannot be separated by chromatography. Isomerism is also exhibited by various $[YCCo_3(CO)_{9-n}L_n]$ complexes (L = tertiary phosphine or arsine), but for these C–O bridged isomers are often important.[23] Although no μ-CO species have been observed in solutions of the isocyanide derivatives, $[MeCCo_3(CO)_6(CNR)_3]$ (R = Me or Bu^t) crystallize in a purple form having only terminal carbonyl groups and an orange form with terminal and bridging CO ligands.*

$[SFeCo_2(CO)_9]$ has a structure similar to those of the methynyl complexes.[24] The Mössbauer spectra of its derivatives $[SFeCO_2(CO)_{9-n}(PPh_3)_n]$ ($n = 1$ or 2) show that substitution takes place on the cobalt atoms,[25] and the similarity of the i.r. spectra of $[SFeCo_2(CO)_7(PPh_3)_2]$ and $[SFeCo_2(CO)_7(CNBu^t)_2]$ suggests that the two have similar structures. $[SFeCo_2(CO)_6(CNBu^t)_3]$ exists as mixtures of isomers in solution; at least one has μ-CO ligands.

Although $[SCo_3(CO)_9]$ undergoes CO substitution reactions with isocyanides, the products appear to be less stable than the precursor.

The initial products from the reactions of $[Co_2(CO)_8]$ with isocyanides are the $[Co_4(CO)_{12-n}(CNR)_n]$ derivatives. If an excess of ligand and more vigorous conditions are used, the $[Co(CNR)_5][Co(CO)_4]$ salts are obtained.[3] The only products obtained from $[\{LCo(CO)_3\}_2]$ and RNC (L = Ph_3P or Bu^n_3P) were the salts $[L_2Co(CNR)_3][Co(CO)_4]$ in which the cation has *trans* trigonal bipyramidal co-ordination about the cobalt atom.[26] In these reactions there was i.r. spectroscopic evidence for the formation of cations containing both carbonyl and isocyanide ligands.

The i.r. spectrum of $[\{Co(CO)_3(CNMe)\}_2Hg]$ is more complicated than that of $[\{Et_3PCo(CO)_3\}_2Hg]$ [27] where it is known that there is trigonal bipyramidal co-ordination about each cobalt atom and that the P–Co–Hg–Co–P system is linear.[28] Therefore it is probable that the methyl isocyanide ligands occupy at least one of the equatorial co-ordination positions of a $[\{Co(CO)_4\}_2Hg]$-type of molecule.[29] It is probable that the linear P–Co–Hg–Co–P structure is retained in $[\{(Ph_3P)Co(CO)_2(CNBu^t)\}_2Hg]$ and the single absorption band due to its ν(CN) vibration implies a centrosymmetric molecule. The complexity of the i.r. spectrum of $[\{(Bu^n_3P)Co(CO)_3\}Hg\{Co(CO)_2(CNMe)(PBu^n_3)\}]$ suggests that isomers are present (*cf.* $[Co_2(CO)_5(PMe_3)_3Hg]$ in ref. 30).

The observed changes in the frequencies of the various absorption bands in the i.r. spectra of the compounds may be interpreted using the accepted model of the bonding between metal atoms and either carbonyl or isocyanide ligands. As RNC are weaker π-acceptors and/or stronger σ-donors than CO groups, replacement of the latter by the former causes a decrease in the frequency of both ν(CO) and ν(CN) vibrations.[31] The absolute frequencies of ν(CN) decrease along the series R = Me > n-alkyl > sec-alkyl > tert-alkyl and as the mass of R increases. The large band widths of these absorption bands, as compared with those due to ν(CO) modes, is also due to the presence of R. Similar behaviour is observed for absorption bands due to ν(CO) when the carbonyl group acts as Lewis base towards Lewis acids such as BF_3,[32] or hydrogen bonds to alcohol solvents.[33]

An important feature of the properties of isocyanide ligands which has emerged in this work is their ability to stabilize polynuclear complexes. This is especially well illustrated by their reactions with octacarbonyldicobalt. Whereas phosphines, arsines, and stibines bring about a breakdown of this binuclear compound to salts, *e.g.* $[(Ph_3P)_2Co(CO)_3][Co(CO)_4]$,[2] under similar, mild conditions isocyanides cause a polymerisation to tetracobalt complexes. The almost total absence of $[Co_4(CO)_{11}(CNR)]$ from such reactions even when very low concentrations of isocyanides are used suggest that $[Co_2(CO)_7(CNR)]$ are formed first and rapidly dimerise to $[Co_4(CO)_{10}(CNR)_2]$. $[SCo_3(CO)_9]$ is the only compound which appears to be destabilized when its carbonyl ligands are replaced by RNC molecules. It has been suggested that in it the unpaired electron occupies a σ* molecular orbital of the SCo_3 framework.[34] If replacement of CO by CNR causes an increase in the energy separation between the σ and σ* orbitals, *i.e.* stabilizes the former, then the behaviour of $[SCo_3(CO)_9]$ is not unexpected nor is it inconsistent with the other observations.

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* The i.r. spectrum of the orange crystals of $[MeCCo_3(CO)_6(CNBu^t)_3]$ as a Nujol mull shows absorption bands at 1800sh, 1834s, 1867w, 1967vs, 2004s, 2145s, and 2163m cm^{-1}.

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