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Preliminary communication

Some binuclear complexes of iron and cobalt with isocyanide ligands

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SUMMARY

Whereas $Co_2(CO)_8$ and RNC (R = Me, Et, and Cy) react to give mixtures of $[(RNC)_5Co][Co(CO)_4]$ and the covalent, carbonyl-bridged $[(RNC)_mCo_2(CO)_{8-m}]$ derivatives (m = 1–3), $[(\pi\text{-dienyl})Fe(CO)_2]_2$ give only $[(\pi\text{-dienyl})_2Fe_2(CO)_{4-n}(CNR)_n]$ complexes (dienyl = C_5H_5, MeC_5H_4 and C_9H_7; n = 1–2) that exist in solution as mixtures of *cis*- and *trans*-CO- and RNC-bridged tautomers with the μ-RNC species decreasing in importance as the bulk of R increases.

We have reinvestigated the reaction of $Co_2(CO)_8$ with isocyanides, and have found that at room temperature a series of $[(RNC)_mCo_2(CO)_{8-m}]$ complexes are formed as well as the previously reported $[(RNC)_5Co][Co(CO)_4]$ salts[1,2] (R = Me, Et, and Cy; m = 1–3). The covalent compounds contain terminal CO, bridging CO, and terminal RNC ligands (Table 1). $Co_4(CO)_{12}$ gives a range of similar complexes as well as others which we have not identified, but with $[(Ph_3P)Co(CO)_3]_2$, only $[(Ph_3P)_2Co(CNR)_3][Co(CO)_4]$ salts were obtained.

Isocyanides will replace one[3–5], or two CO ligands of $[(\pi\text{-dienyl})Fe(CO)_2]_2$ compounds. In solution, the $[(\pi\text{-dienyl})_2Fe_2(CO)_{4-n}(CNR)_n]$ derivatives (dienyl = C_5H_5, MeC_5H_4, or C_9H_7; n = 1 or 2) exist as mixtures of tautomers in equilibria which depend on the solvent, temperature, and R (Table 1). Increasing the bulk of R brings about a decrease in the importance of those isomers of the monosubstituted complexes which have a bridging RNC group as these would be destabilized by the increasing steric interaction of R with a $(\pi\text{-}C_5H_5)Fe(CO)$ moiety. When the isocyanide is terminally coordinated, such an interaction is not possible. A similar effect appears to operate when n = 2. In the case of $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBz)]$, it is probably the electronic

TABLE 1

INFRARED SPECTRA OF SOME COBALT AND IRON COMPLEXES WITH ISOCYANIDE LIGANDS IN HEXANE SOLUTION

Compound [b]	*Absorption bands* [a]								
$(CyNC)Co_2(CO)_7$	1835(10)	1842(9.3)	1876(0.7)	1996(8.3)	2014(14.7)	2028(31.0)	2064(7.0)	2067(7.0)	2156(4.2, br) [c]
$(CyNC)_2Co_2(CO)_6$	1822(9.3)	1830(10)	1863(0.5)	1982(9.3)	2002(16.8)	2012(23.0)	2041(6.2)		2143(8.3, br) [c]
$(CyNC)_3Co_2(CO)_5$	1810(10)	1817(9.8)		1967(10)	1975(10.7)	1991(11.5)	1997(13.6)	2018(5.8)	2129(12.0, br) [c]
$\{(CyNC)_5Co\}\{Co(CO)_4\}$					1889(8.0)		2122(7.7) [c]	2153(10) [c]	2179(5.6) [c]
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBz)$	1720(12.0) [d]		1772(10)	1803(19.5) [d]		1953(33.2)	1999(37.4) [d]		2119(1.1, br) [c]
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNMe)$	1737(5.9) [d]		1774(10)	1802(4.7) [d]		1953(14.8)	1999(11.3) [d]		2134(2.7, br) [c]
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNEt)$	1741(2.0) [d]		1773(10)	1799(3.1) [d]		1953(11.3)	1998(7.2) [d]		2127(2.7, br) [c]
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu\text{-}i)$	1731(1.4) [d]		1775(10)	1798(2.1) [d]		1953(8.7)	1997(4.3) [d]		2122(1.9, br) [c]
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNCy)$	1740(0.5) [d]		1772(10)	1801(1.0) [d]		1952(6.3)	1996(1.7) [d]		2112(1.6, br) [c]
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu\text{-}t)$			1771(10)	1796(sh)		1952(6.8)		2072(1.0) [c]	2108(1.7, br) [c]
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(CNMe)_2$	1720(21.4) [d,e]			1784(10) [d]	1944(15.3)	1953(13.2) [a]	1990(29.0) [e]		2127(4.4, br) [c,d]
$(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(CNCy)_2$	1697(10.1) [d,e]			1783(10) [d]	1941(13.4)	1951(7.1) [e]	1987(4.7) [e]		2111 (5.2, br) [c,d]

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses. [b] Cy = cyclohexyl, i-Bu = isobutyl, t-Bu = tert-butyl and Bz = benzyl. [c] Due to terminal ν(CN) vibrations; br = broad. [d] Due solely or in past to species containing one bridging isocyanide ligand. [e] Due solely or in part to species containing two bridging isocyanide ligands.

effects of the benzyl group which cause the μ-RNC species to be so important. The shapes of the absorption bands due to the terminal and bridging ν(CN) vibrations of the monosubstituted complexes are consistent with *cis* and *trans* forms of both the terminal and bridged isocyanide species. In the spectrum of $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu\text{-}t)]$, the terminal ν(CN) absorption band may be resolved into its two components.

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