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Preliminary communication

REACTIONS OF POLYNUCLEAR MANGANESE AND IRON CARBONYL COMPLEXES WITH ORGANOISOCYANIDES

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Summary

The preparations of $(RNC_nMn_2(CO)_{10\text{-}n}$ (R = Me or t-Bu; n = 1-4) $\{(PhO_3P\}_2$-(t-BuNC)$Mn_2(CO)_7$, and $(RNC)_mFe_3(CO)_{12\text{-}m}$ (R = Me or t-Bu; m = 1-3) are reported; many of these complexes exist as mixtures of isomers in solution and appear to be fluxional.

In continuation of our study of the reactions of polynuclear metal carbonyls with isocyanides [1], we describe here the products obtained from MeNC or t-BuNC, and $Mn_2(CO)_{10}$, $\{(PhO)_3P\}_2Mn_2(CO)_8$, or $Fe_3(CO)_{12}$.

Triiron dodecarbonyl undergoes CO substitution isocyanides in hexane at room temperature to form the known $(RNC)Fe(CO)_4$ [2] as well as $(RNC)_m$-$Fe_3(CO)_{12\text{-}m}$ (m = 1 or 2 when R = Me, and m = 1, 2 or 3 when R = t-Bu) and a red unidentified product. Attempts to obtain compounds where m is larger than 2 (R = Me) or 3 (R = t-Bu) resulted in breakdown of the cluster.

By contrast, the reactions of RNC with $Mn_2(CO)_{10}$ or $\{(PhO)_3P\}_2Mn_2(CO)_8$ required UV irradiation or refluxing toluene for their completion. The products included $(RNC)_nMn_2(CO)_{10\text{-}n}$ (n = 1-4 when R = Me or n = 1-3 when R = t-Bu), and $\{(PhO)_3P\}_2$(t-BuNC)$Mn_2(CO)_7$. Related complexes which have been reported previously are $(PhNC)_xMn_2(CO)_{10\text{-}x}$ (x = 1 or 2) [3] and $(MeNC)_3Mn_2(CO)_7$ [4].

The IR spectra of solutions of these compounds show more absorption bands due to ν(CO) and ν(CN) vibrations than expected, and many are asymmetric e.g. for (t-BuNC)$_2Fe_3(CO)_{10}$ in hexane $\nu(CO)_\mu$ = 1793(sh), 1800(0.7), 1841(0.2; ν(CO) = 1979(sh), 1982(3.3), 1990(sh), 2007(8.9), 2012(10), 2014(sh), 2024(4.4), 2056(1.7); ν(CN) = 2141(1.1), 2151(sh), 2167(sh) cm^{-1}, and for (MeNC)Mn_2-$(CO)_9$ in hexane ν(CO) = 1962(3.5), 1972(2.8), 1982(1.6), 1998(10, asymm.), 2009(3.9), 2028(6.8), 2087(sh), 2090(1.5); ν(CN) = 2.69(sh), 2184(0.6) cm^{-1}. Absorption bands due to ν(CO) are only weak in the spectra of the $Fe_3(CO)_{12}$ derivatives, and are not observed for the manganese compounds. There is no evidence for bridging isocyanide ligands in either series. It is probable that in

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many instances mixtures of isomers are present and that the molecules are fluxional. It is consistent with this supposition that the proton NMR spectrum of $(MeNC)_2Fe_3(CO)_{10}$ shows only a single resonance at room temperature. Thus the complexes resemble $Fe_3(CO)_{12}$ [5], and $(MeNC)_3Mn_2(CO)_7$ [4] in their behaviour. This is being further investigated.

References

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