Group VI Transition Metal Carbonyl Derivatives of Manganese

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Summary The complexes, $[C_5H_5M(CO)_3]_2Mn(py)_4$ (M = Cr, Mo, W), prepared from $Hg[M(CO)_3C_5H_5]_2$ and manganese metal, have i.r. spectra consistent with the presence of M–CO–Mn bonds.

Until recently all of the compounds which have been isolated, structurally characterized, and shown to contain an oxygen-co-ordinated carbonyl ligand have had aluminium[1] or magnesium[2] as the acceptor. Marks *et al.*[3] have attributed shifts in the ^1H n.m.r. spectrum of (phen)-$[Ph_3P]_2Mo(CO)_2$ in the presence of $Eu(fod)_3$ to O-co-ordination of a carbonyl group to europium. In contrast, a report[4] on a complex formulated as $Er[Co(CO)_4]_3 \cdot 4THF$ suggests the presence of cobalt–erbium bonds.

We describe here the preparation and characterization of some Group VI metal carbonyl derivatives of manganese which are the first isolable complexes that give evidence for metal carbonyls O-co-ordinated to a transition metal.

A solution of $Hg[Mo(CO)_3C_5H_5]_2$[5] in THF was stirred with a tenfold excess of manganese metal at room temperature for 5 h to produce an extremely air-sensitive, white solid which was recrystallized from pyridine to give yellow crystals of $[C_5H_5Mo(CO)_3]_2Mn(py)_4$, (**1**) (63%), m.p. 206—212° (decomp). The analogous chromium and tungsten compounds (**2**) and (**3**) were prepared in a similar fashion with manganese metal activated by pretreatment with a THF solution of mercuric chloride; fourteen-hour reaction times were employed. All three complexes gave satisfactory analyses.

Table. *I.r. spectra of* $[C_5H_5M^1(CO)_3]_2M^2(py)_4$ *complexes*

	M^2	M^1	Carbonyl stretching frequencies (cm^{-1})[a]
(**1**)	Mn	Mo	1905, 1808, 1650
(**2**)	Mn	Cr	1902, 1805, 1652
(**3**)	Mn	W	1902, 1797, 1647
(**4**)[b]	Mg	Mo	1918, 1828, 1667

[a] Nujol mull prepared under nitrogen. [b] From ref. 2.

The i.r. spectra of the new complexes (Table) contain three strong absorptions in the carbonyl stretching region with one of these being conspicuously lower than the other two. Of particular interest is the similarity of the spectra to that of $[C_5H_5Mo(CO)_3]_2Mg(py)_4$, (**4**), which has been shown by *X*-ray diffraction to consist of magnesium octahedrally co-ordinated by four equatorial pyridine ligands (average Mg–N distance 2·233 Å) and two axial carbonyl oxygen atoms (Mg–O distance 2·047 Å), one from each h^5-$C_5H_5Mo(CO)_3$ group.[2] By analogy with the spectral assignments made for (**4**), in which the C–O bond length of the O-co-ordinated carbonyl [1·189(3) Å] was conspicuously longer than that of the terminal carbonyls [1·157(3) Å], the low frequency absorptions in complexes (**1**)—(**3**) are attributed to carbonyls co-ordinated to manganese by the oxygen atom; the high frequency absorptions are associated with the terminal carbonyls. Since the average carbonyl frequency in a particular complex is nearly the same as that of $C_5H_5M(CO)_3^-Na^+$,† the new compounds may be viewed as manganese(II) complexes of pyridine and the metal carbonyl anion. The observed magnetic moment, μ_{eff} = 4·8 B.M. for (**1**) in toluene–pyridine at ambient temperature[6] is in reasonable accord with this interpretation.

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† In pyridine the i.r. spectrum of $C_5H_5Mo(CO)_3^-Na^+$ contains strong carbonyl absorptions at 1893, 1775, and 1749(sh) cm^{-1}, S. W. Ulmer, Ph.D. Thesis, Cornell University, 1972.

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