The Ionic Dissociation of Pentacarbonylmanganese-indium Complexes in Acetonitrile Solution

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Summary Cationic metal–metal bonded species are present in acetonitrile solutions of pentacarbonylmanganese-indium complexes, and crystalline complexes containing such cations have been isolated.

THE ionisation of organometallic complexes containing transition-metal–main-group-metal bonds has recently been shown to take place more readily than had previously been realised.[1] In particular, the ionisation of complexes containing transition metals bonded to Group IIB or Group IVB metals in dimethylformamide (dmf) solution has been studied, and it has been shown that the mode of ionisation in this solvent is such that the transition metal is invariably present as part of the anion. For example $Zn[Co(CO)_4]_2$ is almost completely ionised in dmf to give the $Co(CO)_4^-$ anion.[1] The nature of the counterion has not been investigated but is presumably the solvated main-group-metal ion.

In the course of an investigation of complexes containing transition-metal–Group IIIB metal bonds we have studied the ionisation of some pentacarbonylmanganese-indium complexes of the type $X_nIn[Mn(CO)_5]_{3-n}$ (X = Cl or Br,[2] n = 0—2).† In dmf solution the i.r. spectra of all of these complexes show relatively strong absorptions due to the $Mn(CO)_5^-$ anion[1] and, apart from weak shoulders, no other carbonyl bands are observed, indicating that all the complexes are extensively ionised in the manner already described. In acetonitrile solution, however, a different pattern of behaviour is observed. The i.r. spectrum of $In[Mn(CO)_5]_3$ contains peaks due to the $Mn(CO)_5^-$ ion at 1899 w and 1862 m cm^{-1} but, in addition, four other absorptions to higher frequency at 2089 w, 2061 mw, 1988 vs, and 1960 msh are present (Figure, a). The i.r. spectra of the remaining complexes, *e.g.* $Cl_2InMn(CO)_5$ and $ClIn[Mn(CO)_5]_2$, do not show any absorptions due to the $Mn(CO)_5^-$ ion but

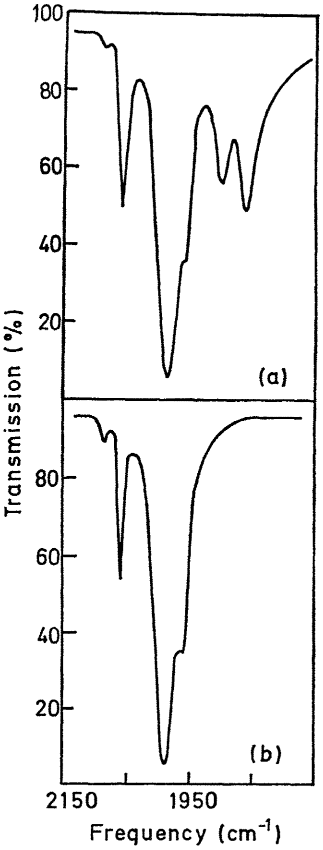

FIGURE. (a) *I.r. spectrum of* $In[Mn(CO)_5]_3$ *in acetonitrile solution.* (b) *I.r. spectra of* (i) $ClIn[Mn(CO)_5]_2$, (ii) $Cl_2InMn(CO)_5$, *or* (iii) $(MeCN)_2In[Mn(CO)_5]_2^+$ *in acetonitrile solution.*

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† Satisfactory analytical data have been obtained for all the new complexes reported in this note.

are otherwise identical with that of $In[Mn(CO)_5]_3$ (Figure, b).

Possible ionisation schemes which would account for these results are shown in equations (1), (2), and (3).

$$In[Mn(CO)_5]_3 \rightleftharpoons In[Mn(CO)_5]_2^+ + Mn(CO)_5^- \quad (1)$$

$$XIn[Mn(CO)_5]_2 \rightleftharpoons In[Mn(CO)_5]_2^+ + X^- \quad (2)$$

$$2X_2InMn(CO)_5 \rightleftharpoons In[Mn(CO)_5]_2^+ + InX_4^- \quad (3)$$

If ionisation takes place in this manner it would suggest that the cation $In[Mn(CO)_5]_2^+$ possesses considerable stability in acetonitrile solution and, in accordance with this, we have been able to isolate it as an acetonitrile adduct, $(MeCN)_2In[Mn(CO)_5]_2^+$ by treatment of $XIn[Mn(CO)_5]_2$ with silver perchlorate [equation (4)]

$$XIn[Mn(CO)_5]_2 + AgClO_4 \xrightarrow{MeCN} \{(MeCN)_2In[Mn(CO)_5]_2\}^+ ClO_4^- \quad (4)$$

or by the metathetical reaction (5)

$$2X_2InMn(CO)_5 + Me_4N^+ClO_4^- \longrightarrow \{(MeCN)_2In[Mn(CO)_5]\}_2^+ClO_4^- + Me_4N^+InX_4^- \quad (5)$$

The i.r. spectrum of this complex in acetonitrile solution in the carbonyl stretching region is identical with that of the complex $X_nIn[Mn(CO)_5]_{3-n}$ ($n = 1$—2) (Figure, b) providing strong support for the ionisation schemes in equations (1), (2), and (3).

The above evidence shows that not only does the *extent* of ionisation of metal–metal bonded complexes in solution depend upon the nature of the solvent (as previously demonstrated[1]) but that the *mode* of ionisation may also be influenced. In addition, the formation of the cation $\{(MeCN)_2In[Mn(CO)_5]_2\}^+$ in acetonitrile solution provides a useful intermediate for the preparation of other cationic metal–metal bonded species. Thus the crystalline adducts $\{py_2In[Mn(CO)_5]_2\}^+ClO_4^-$ and $\{(phen)_2In[Mn(CO)_5]_2\}^+ClO_4^-$ may be prepared by addition of an excess of the appropriate ligand to an acetonitrile solution of $\{(MeCN)_2In[Mn(CO)_5]_2\}^+ClO_4^-$.

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[1] J. M. Burltich, *J. Amer. Chem. Soc.*, 1969, **91**, 4562.

[2] J. Hoyano, D. J. Patmore, and W. A. G. Graham, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 201.