New Examples of the Metal Basicity of Iron Pentacarbonyl

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Summary $Fe(CO)_5$, though a weak base, forms adducts with strong acid salts including $Cd(AsF_6)_2$, $Sn(SbF_6)_2$, and $Fe(SbF_6)_2$; in the adducts, the $Fe(CO)_5$ behaves as a weak Fe-donor ligand to the metal cation.

Though metal basicity of transition metal carbonyls is well-known,[1] very few adducts of $Fe(CO)_5$ with Lewis acids have been reported, a marked contrast with the extensive chemistry of the isoelectronic $[Mn(CO)_5]^-$. One of the main factors responsible for the limited acid–base chemistry of $Fe(CO)_5$ is undoubtedly its weak basicity which is exemplified by its protonation only in strong acids[2] and by the ease of dissociation of its $HgCl_2$ adduct.[3]

During our investigations of the interaction of weak bases with metal salts of strong acids we have found that $Fe(CO)_5$ has a much more extensive acid-base chemistry than the foregoing suggests, forming adducts with a wide range of metal cations in the weak donor solvent liquid sulphur dioxide. Thus, for example, the recently prepared[4] unsolvated hexafluoroarsenate of cadmium(II)† and hexafluoroantimonates of tin(II) and iron(II) react with $Fe(CO)_5$ in liquid SO_2;‡ the products are shown in the Table together with pertinent Mössbauer data. Using an excess of $Fe(CO)_5$, the pale yellow cadmium compound precipitates on mixing solutions of the components, insoluble $Sn(SbF)_6)_2$ is converted into the insoluble orange tin adduct on stirring and the SO_2-soluble brown iron product is isolated by, removal of volatile components *in vacuo*.

Table

Compound[a]		Mössbauer parameters[b] Centre shift	Quadrupole splitting
$[HFe(CO)_5]PF_6$		0·11	1·32[c]
$[Cd\{Fe(CO)_5\}_2](AsF_6)_2$		0·22	1·30[c]
$[Fe\{Fe(CO)_5\}_2](SbF_6)_2$	Fe^0	0·29	0·98[c]
	Fe^{II}	1·69	2·15[d]
$[Sn\{Fe(CO)_5\}](SbF_6)_2$	Fe^0	0·29	0·74[c]
	Sn^{II}	3·76[d]	1·40[d]

[a] All new compounds gave satisfactory analytical data. [b] In $mm\ s^{-1}$ at 80 °C. ^{57}Fe and ^{119}Sn centre shifts are given relative to sodium nitroprusside and barium stannate, respectively, at room temperature. Error $\pm 0{\cdot}01\ mm\ s^{-1}$ except where noted. [c] The QS of $[HFe(CO)_5]^+$ is probably negative (ref. 6a) and this is assumed to be the case for the other examples of co-ordinated $Fe(CO)_5$ also. [d] Error $\pm 0{\cdot}03\ mm\ s^{-1}$.

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† Cadmium(II) hexafluoroantimonate[4b] behaves similarly.

‡ In agreement with the work of other workers (W. Strohmeier, J. F. Guttenberger, and G. Popp, *Chem. Ber.*, 1965, **98**, 2248; E. H. Braye and W. Hubel, *Angew. Chem.*, 1963, **75**, 345), we find $Fe(CO)_5$ in SO_2 solution to be stable for a matter of hours.

The ^{57}Fe Mössbauer spectra demonstrate the equivalence of both pentacarbonyl units in the cadmium and iron compounds. In none of the products is the ^{57}Fe Mössbauer quadrupole splitting (QS) of the $Fe(CO)_5$ species large enough to be reasonably attributed to a five-co-ordinate iron [*cf.*, the reported [5a]QS of $Fe(CO)_5$ is 2·57 mm s^{-1}]. Rather the centre shifts (CS) and QS are of similar magnitude to those we find for $[HFe(CO)_5]^+$; the parameters for this cation are close to those expected[6a,b] for the usually assumed octahedral geometry, confirming its C_{4v} symmetry. Evidently the $Fe(CO)_5$ is bound to the cation *via* iron in the metal salts also. The variation in the ^{57}Fe Mössbauer parameters of the Fe-bound $Fe(CO)_5$ is consistent with $H^+ < [Cd\{Fe(CO)_5\}]^{2+} < [Fe\{Fe(CO)_5\}]^{2+} \sim Sn^{2+}$ being the order of σ-accepting ability,[6b] though this order will include any attenuation due to cation–anion interactions.

As expected the new compounds all have ν(CO) at higher frequencies than the parent $Fe(CO)_5$. In the common mulling agents, the i.r. spectra of all the products {and $[HFe(CO)_5]^+$} give evidence for some dissociation of $Fe(CO)_5$, showing the $Fe(CO)_5$ unit to be intact in them. None of the adducts have i.r. bands in the region where a carbonyl bound by both C and O might be expected to absorb;[1b] thus the iron atom of the $Fe(CO)_5$ is the only point of attachment.

The ^{57}Fe Mössbauer parameters of the iron cation in $[Fe\{Fe(CO)_5\}_2](SbF_6)_2$ are consistent with its being a quite ionic high-spin iron(II) ion, probably 6-co-ordinate.[6c] (This compound therefore contains an unusual metal–metal bond involving high-spin divalent iron; the co-ordination sphere of the Fe^{II} must be completed by fluorine-bridging with the anion). Similarly the ^{119}Sn Mössbauer CS of $[Sn\{Fe(CO)_5\}](SbF_6)_2$ is characteristic of a relatively ionic tin(II) compound.[5b] On the basis of these results it seems best to regard the $Fe(CO)_5$ adducts prepared here as complexes of the divalent metal ions in which $Fe(CO)_5$ is behaving as a weak Fe-donor ligand.

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