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# A Study of the Basicity of Metal–Metal Bonding in [$\mu$-$SCH_3Fe(CO)_2L]_2$ Complexes. II. Interaction with Mercuric Chloride

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In a recent publication [1] we showed by protonation that the metal–metal bond in [$\mu$-$SCH_3Fe(CO)_2L]_2$ acts as the nucleophilic center. These results, deduced from infrared and n.m.r. spectroscopic data, have recently been confirmed by X-ray structure determination [2]. Moreover, this study revealed that the nucleophilicity of the metal–metal bond towards $H^+$ is strongly dependent on the basicity of the ligand L. We now report a study of the action of $HgCl_2$ on [$\mu$-$(SCH_3)Fe(CO)_2L]_2$ with L = $P(CH_3)_3$, $P(C_6H_5)_3$, $P(OCH_3)_3$. These three cases were chosen to determine whether the basicity of the ligands plays here as prominent a part as it does in protonation.

## Results and Discussion

The addition of solution of $HgCl_2$ in acetone to a solution of [$\mu$-$SCH_3Fe(CO)_2L]_2$ [3] causes the immediate precipitation of [$\mu$-$SCH_3Fe(CO)_2L]_2 \cdot HgCl_2$ (I) or [$\mu$-$SCH_3Fe(CO)_2L]_2 \cdot 2HgCl_2$ (II) depending on the $HgCl_2$/complex ratio used, except for L = $P(OCH_3)_3$ where the complexes remain in solution. In this last case they are crystallized in methanol. The reactions are always nearly quantitative.

One of the problems in formulating a structure is whether or not the halide ion of mercuric chloride has been displaced [4, 5]. Conductivity measurements (Table I) showed that these compounds are non conducting in nitrobenzene and support their formulation as simple adducts.

Three infrared active bands were observed in the $\nu$(CO) stretching region for complexes I and II (Table I) from which one can conclude that the $C_{2v}$ point group of the starting molecule [6] is preserved. The increase in frequency as compared to the starting compounds is about 40 $cm^{-1}$, which is smaller than that found for monomolecular complexes of group VIA [4] or of iron [7], or in the protonation of these dinuclear complexes [1]. The structure hypothesis is corroborated by proton n.m.r. in $CH_2Cl_2$ in the case of the most soluble adducts (L = $P(OCH_3)_3$), in which there is one signal for the $P(OCH_3)_3$ ligand ($\delta$ = 3.86 ppm, J = 10 Hz (complex I); $\delta$ = 3.91 ppm,

TABLE I. Infrared $\nu$(C–O) Spectra and Analytical Data for [$\mu$-$SCH_3Fe(CO)_2L]_2 \cdot x\ HgCl_2$ Complexes

| x | L | $\nu$CO $cm^{-1}$ [a] | Analysis | | | | | | | | Colour | Melting Point, °C | $\Lambda_M$ [b] $ohm^{-1}\ cm^2\ mol^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calcd. | | | | Found | | | | | | |
| | | | C | H | P | Cl | C | H | P | Cl | | | |
| 1 | $P(CH_3)_3$ | 2027m, 2009s, 1977s | 19.42 | 3.23 | 8.36 | 9.57 | 20.22 | 3.36 | 8.69 | 9.38 | Carmine | 137 dec | 1.37 |
| | $P(C_6H_5)_3$ | 2023m, 2007s, 1976s | 45.26 | 3.23 | 5.56 | 6.37 | 43.86 | 3.27 | 5.57 | 6.29 | Black | 130 dec | c |
| | $P(OCH_3)_3$ | 2041m, 2022s, 1995s | 17.19 | 2.86 | 7.40 | 8.48 | 17.04 | 2.91 | 7.44 | 8.37 | Red | 105 | 2.84 |
| 2 | $P(CH_3)_3$ | 2036m, 2016s, 1985s | 14.21 | 2.36 | 6.12 | 14.01 | 14.66 | 2.35 | 6.54 | 13.60 | Bright Red | 145 dec | 0.64 |
| | $P(C_6H_5)_3$ | 2030m, 2015s, 1982s | 36.83 | 2.59 | 4.47 | 10.25 | 36.42 | 2.66 | 4.67 | 9.94 | Black | 126 dec | c |
| | $P(OCH_3)_3$ | 2048m, 2032s, 2000s | 12.98 | 2.16 | 5.59 | 12.80 | 13.32 | 2.05 | 5.77 | 12.75 | Orange | 122 | 1.05 |

[a] Measured in $CH_2Cl_2$ solutions. [b] Molar conductivity in nitrobenzene at 25°C for a $10^{-3}M$ concentration. [c] Too insoluble to be measured.

J = 10 Hz (complex II) and one for $SCH_3$ group ($\delta$ = 1.75 ppm (complex I); $\delta$ 1.70 ppm (complex II)).

From these observations we can conclude that in complexes of type I, $HgCl_2$ is fixed "on the metal–metal bond" to give a three-center donor–acceptor bond as was initially suggested for $Co_2CO_8 \cdot AlBr_3$ [8] even though, in this latter case, it has been shown that $AlBr_3$ interacts with a bridging CO group [9]. The structure of type II products is more difficult to establish. However, two observations seem to indicate that the second molecule of $HgCl_2$ does not interact directly with the iron complex.

First, the increase in CO frequencies from complex I to complex II is very small (less than 10 $cm^{-1}$). Secondly, the first stage of the addition of triphenyl phosphine to complex II is the regeneration of complex I and then, more slowly, of the starting material. From a recent study of the crystal structure of $C_6H_3(CH_3)_3Mo(CO)_3 \cdot 2HgCl_2$ [10] it seems reasonable to assume that the second $HgCl_2$ molecule interacts with a chlorine atom of the coordinated $HgCl_2$.

In conclusion, we have shown that mercuric chloride adds onto the metal–metal bond of the $[\mu\text{-}SCH_3Fe(CO)_2L]_2$ complexes and that, in these reactions, the basicity of the ligand plays a less important role than in protonation. The addition of a Lewis base such as triphenylphosphine causes a slow regeneration of the starting material.

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