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Preliminary communication

REINVESTIGATION OF THE REACTIONS OF TIN(II) HALIDES WITH $[CpFe(CO)_2]_2$ AND $[CpMo(CO)_3]_2$

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Summary

Contrary to a recent report, when moisture and oxygen are excluded, the halides SnX_2 (X = Cl, Br, I) react straightforwardly with $[CpFe(CO)_2]_2$ in tetrahydrofuran to give the insertion compounds $X_2Sn[Fe(CO)_2Cp]_2$.

The reaction between tin(II) halides and $[CpFe(CO)_2]_2$ in refluxing methanol or tetrahydrofuran is a well-known route to the "insertion" compounds $X_2Sn[Fe(CO)_2Cp]_2$ [1,2]. Rate studies on the thermal reactions with anhydrous $SnCl_2$ and $SnBr_2$ were interpreted in terms of a two-stage mechanism which involves, first, the formation of a singly carbonyl-bridged intermediate, and then nucleophilic attack by the tin(II) halides on this species [3]. A more recent report, however, questioned the straightforward nature of the reaction, and two competing synthetic pathways were proposed [4]. For SnF_2, and to a lesser extent $SnCl_2$, the "direct" reaction 1

$$[CpFe(CO)_2]_2 + SnX_2 \rightarrow X_2Sn[Fe(CO)_2Cp]_2 \qquad (1)$$

predominates, but for $SnBr_2$, and particularly SnI_2, the "indirect" route (involving, first, the formation of $XFe(CO)_2Cp$ and $X_3SnFe(CO)_2Cp$ in equal amounts, followed by the reaction of the latter with $[CpFe(CO)_2]_2$ to give the insertion product) is the more important. The disagreement between these reports, together with the difficulty of understanding why, in the indirect reaction, the tin(II) halide appears to react in the same fashion as a tin(IV) halide, prompted us to reinvestigate the system.

In our experiments, in tetrahydrofuran solution at various temperatures, we monitored the reactions of $[CpFe(CO)_2]_2$ with anhydrous SnX_2, (X = Cl, Br, or I) by scanning the cyclopentadienyl region of the ^1H NMR spectrum of the mixture and the carbonyl stretching region of the IR spectrum. Air

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and moisture were excluded as rigorously as possible by use of Schlenk techniques. We find, as reported earlier [3], that the reactions are markedly enhanced by diffuse light, but that, both in the light and in the dark, the so-called direct insertion reaction predominates (>98%) for all halides. We believe that the "indirect" process is unimportant, and probably represents a number of side reactions which are induced by either oxygen, water, tin(IV) impurities in the tin(II) halides, or by the use of hydrated tin(II) halides. It is impossible to define completely the several side reactions, but we would note that the amount of $X_3Sn[Fe(CO)_2Cp]$ produced increases on introduction of oxygen, with decrease in the overall concentration of the reactants (oxygen impurities in solvent) and with an increase in the molar ratio of SnX_2 to $[CpFe(CO)_2]_2$ (higher relative amount of tin(IV) impurity). In each case the side reaction is probably that of a tin(IV) species with $[CpFe(CO)_2]_2$, and it proceeds much faster than the thermal insertion reaction. The insertion reaction proceeds only slowly if the hydrated species $SnCl_2 \cdot 2H_2O$ and $SnBr_2 \cdot 2H_2O$ are used, possibly because of their limited solubility in tetrahydrofuran. A significant side reaction has been observed which involves the formation of both $XFe(CO)_2Cp$ and $X_3SnFe(CO)_2Cp$ (but not initially in equal amounts, as previously reported [4]). It may be by the formation, in the presence of water, of hydrogen halide, which then cleaves the iron—iron bond of the dimer. We agree with Hackett and Manning [4] that the reaction of $X_3SnFe(CO)_2Cp$ with unreacted $[CpFe(CO)_2]_2$ can lead to the insertion product in refluxing butanol, but we have shown that, under the normal conditions of the experiment (refluxing tetrahydrofuran), its rate is insignificant.

Our kinetic studies, at ca. 0.3 *M* concentration and using 1:1 ratios of reactants, gave approximate 2nd order kinetic plots for the thermal reaction. The rate of reaction with $SnBr_2$ ($t_{1/2}$(40°C) 2.5 h, $t_{1/2}$(56°C) 0.25 h) was faster than that with $SnCl_2$ ($t_{1/2}$(40°C) 3.5 h, $t_{1/2}$(56°C) 0.35 h). Comparative studies with SnF_2 and SnI_2 were not possible because of their limited solubility. The higher reactivity of the bromide is much less pronounced than was observed by Barrett and Sun [3]. In their work, both very dilute solutions of $[CpFe(CO)_2]_2$ ($\sim 10^{-3}$ *M*) and approximately 100-fold excesses of tin(II) halide were used, and we suspect that their technique of measurement (visible spectrophotometry) would not allow for rigorous air-exclusion. Under these conditions oxidative and hydrolytic side reactions could have been pronounced, but, in our experience, would not have been detectable spectrophotometrically at 550 nm. Their results, and the proposed mechanism, should, in our opinion, be regarded cautiously.

Reactions of SnX_2 (X = Cl, Br, or I) with $[CpMo(CO)_3]_2$ give $X_2Sn[Mo(CO)_3Cp]_2$ as the major product, and again are light-enhanced. Side reactions proceed to a slightly greater extent (approximately 5% at the lower concentration (0.05 *M*) used), but we have not observed the "indirect" process which has also been proposed for this reaction [5].

It is clear that if oxygen and moisture are excluded and anhydrous halides used, the insertion reaction is straightforward, and offers a clean synthetic route to the compounds $X_2Sn[Fe(CO)_2Cp]_2$ and $X_2Sn[Mo(CO)_3Cp]_2$. Our detailed mechanistic study of these and related reactions is continuing.

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References

1 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 179.
2 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 5 (1966) 1405.
3 P.F. Barrett and K.K.W. Sun, Canad. J. Chem., 48 (1970) 3300.
4 P. Hackett and A.R. Manning, J. Chem. Soc. Dalton, (1972) 1487.
5 P. Hackett and A.R. Manning, J. Chem. Soc. Dalton, (1972) 2434.