Journal of Organometallic Chemistry, 64 (1974) 223–227

REACTIONS OF TIN(II) HALIDES WITH COMPOUNDS CONTAINING A TRANSITION METAL—CARBON σ-BOND

B.J. COLE, J.D. COTTON and D. McWILLIAM
Department of Chemistry, University of Queensland, St. Lucia, Queensland 4067 (Australia)
(Received May 15th, 1973)

Summary

Tin(II) chloride inserts into the iron—carbon σ-bond in $MeFe(CO)_2Cp$ (Cp = cyclopentadienyl), in refluxing methanol or THF, to give $MeCl_2SnFe(CO)_2$-Cp and traces of $Cl_3SnFe(CO)_2Cp$, but, with $EtFe(CO)_2Cp$, a mixture of the insertion product, $Cl_3SnFe(CO)_2Cp$, and $Cl_2Sn[Fe(CO)_2Cp]_2$ is formed. Insertion of tin(II) chloride was not observed for $MeMo(CO)_3Cp$ and $MeMn(CO)_5$; in these reactions, and in those between tin(II) bromide and $MeFe(CO)_2Cp$, $EtFe(CO)_2Cp$ and $MeMo(CO)_3Cp$, mixtures of halo—metal carbonyls and halotin—metal carbonyls result.

Introduction

"Insertion" reactions of tin(II) and germanium(II) halides into a variety of transition metal—halogen bonds and transition metal—transition metal bonds have been widely investigated and often provide convenient syntheses of compounds containing a transition metal bound to a Group IVB element [1]. Although many reports of the insertion of sulphur dioxide and other small molecules into transition metal—carbon σ-bonds have appeared [2], similar insertion reactions of the Group IVB dihalides have received little attention. Recently Nesmeyanov et al. reported that germanium(II) chloride reacted with the compounds $RFe(CO)_2Cp$ (R = Me, Et, n-Pr, i-Pr and CH_2Ph), under mild conditions in dioxane or THF solution, to give $RCl_2GeFe(CO)_2Cp$ species in high yield [3]. $MeCl_2GeFe(CO)_2Cp$ has also been prepared from $MeFe(CO)_2Cp$ and $CsGeCl_3$ in THF [4].

In an attempt to extend the scope of this insertion process, we have studied the reactions of tin(II) chloride and bromide with $MeFe(CO)_2Cp$, $EtFe(CO)_2Cp$, $MeMn(CO)_5$ and $MeMo(CO)_3Cp$.

Results and discussion

The only example, in the systems studied, of a preparatively useful and reasonably clean insertion into a transition metal—carbon σ-bond occurred in the reaction between excess anhydrous $SnCl_2$ or $SnCl_2 \cdot 2H_2O$ and $MeFe(CO)_2Cp$ in refluxing THF or methanol. $MeCl_2SnFe(CO)_2Cp$ was formed in good yields together with a small amount of $Cl_3SnFe(CO)_2Cp$ ($< 5\%$), and the reaction course thus parallels closely that reported [3] for $GeCl_2$ and $MeFe(CO)_2Cp$. The reaction between $EtFe(CO)_2Cp$ and $SnCl_2$ was significantly slower and more complex. In the early stages, the insertion compound $EtCl_2SnFe(CO)_2Cp$ was the major product, but, after long reflux, $Cl_2Sn[Fe(CO)_2Cp]_2$ and $Cl_3SnFe(CO)_2Cp$ predominated. The slower reaction of the ethyl derivative is in contrast with the comparable reactions with $GeCl_2$ for which a reactivity order: i-Pr > n-Pr > Et > Me > CH_2Ph, was observed. The product distribution observed for the $SnCl_2$ reactions with $MeFe(CO)_2Cp$ and $EtFe(CO)_2Cp$ is markedly different from that of the $GeCl_2$ reactions in which $Cl_3GeFe(CO)_2Cp$ alone was obtained as a by-product, with the amount ranging only from 5% for the methyl to 9% for the isopropyl derivative.

Insertion compounds were not detected in the reactions of $MeMn(CO)_5$ and $MeMo(CO)_3Cp$ with $SnCl_2$. With $MeMn(CO)_5$, the major products in solution were $[ClMn(CO)_4]_2$, $Cl_3SnMn(CO)_5$, and, in the early stages, $ClMn(CO)_5$. The lack of reaction between $MeMo(CO)_3Cp$ and $SnCl_2$ in refluxing methanol was surprising in view of the reported reaction between $MeW(CO)_3Cp$ and $SnCl_2$ in refluxing acetone which gave $Cl_3SnW(CO)_3Cp$ [5]. However, reaction proceeded slowly under weak UV irradiation giving, initially, $ClMo(CO)_3Cp$, with traces of $Cl_3SnMo(CO)_3Cp$, and, on continued irradiation, an increasing relative amount of $Cl_3SnMo(CO)_3Cp$. Stronger irradiation increased the reaction rate markedly and gave $Cl_2Sn[Mo(CO)_3Cp]_2$ as a further product.

Insertion into a transition metal—carbon bond was likewise not observed in any reaction with $SnBr_2 \cdot 2H_2O$. With $MeFe(CO)_2Cp$ and $EtFe(CO)_2Cp$, the major product in the early stages was $BrFe(CO)_2Cp$, but $Br_3SnFe(CO)_2Cp$ was predominant after long reflux. With $MeMo(CO)_3Cp$, the reaction product was mainly $BrMo(CO)_3Cp$ but traces of $Br_3SnMo(CO)_3Cp$ were also formed.

The eventual fate of the alkyl group in the non-insertion reactions seems mainly to be as a dialkyltin dihalide, which was identified in several reactions, but the severe problems encountered in separation do not rule out the possible formation of other alkyltin systems. Overall, the reaction thus formally involves an oxidation from Sn^{II} to Sn^{IV}, but it is probably better considered in terms of changes in the valence state of tin [6]. In a recent detailed study of the reactions of tin(II) halides with $[Fe(CO)_2Cp]_2$, where the initial reaction course was that expected for a Sn^{IV} species, the possible disproportionation of Sn^{II} to give metallic tin and Sn^{IV}, and the possibility of contamination of the purge gas by oxygen were considered [7]. However, we have in no case observed the formation of metallic tin, and consider that the probable preferential reaction with oxygen of the transition metal—alkyl systems, leading to their subsequent decomposition, would make the second explanation unlikely.

Our present data do not allow us to comment definitively on possible mechanisms for the non-insertion reactions. However, the observation of halo—

metal carbonyls, in all except the $RFe(CO)_2Cp$ reactions with $SnCl_2$, may imply a different reaction path in these cases. The relative distributions of halo—metal carbonyls and halotin—metal carbonyls possibly reflect the relative rates of insertion of tin(II) halides into the respective transition metal—halogen bonds, but the formation of the halotin—metal carbonyl species by an additional route cannot be eliminated at this stage.

The rapid conversion of $Cl_3SnFe(CO)_2Cp$ to $Br_3SnFe(CO)_2Cp$ on treatment with a 10-fold excess of $SnBr_2$ in refluxing methanol [8], suggested that a similar exchange might lead to the previously inaccessible $RBr_2SnFe(CO)_2Cp$ species. Surprisingly, the reaction of $MeCl_2SnFe(CO)_2Cp$ with $SnBr_2$ proceeded very slowly, and only traces of $Br_3SnFe(CO)_2Cp$ and $BrFe(CO)_2Cp$ were detected. The reaction of $MeCl_2SnFe(CO)_2Cp$ with anhydrous HCl resulted in slow cleavage of the Sn—C bond, and formation of $Cl_3SnFe(CO)_2Cp$, in accord with previous work [9]. $MeCl_2SnFe(CO)_2Cp$ partially decomposed during sublimation to give $Cl_2Sn[Fe(CO)_2Cp]_2$ and Me_2SnCl_2. Several thermal redistribution reactions of this type are now known for tin—transition metal complexes [10].

Experimental

All reactions were carried out under an atmosphere of nitrogen. $SnCl_2$, $SnCl_2 \cdot 2H_2O$ and $SnBr_2 \cdot 2H_2O$ (BDH laboratory reagent grade) were used without further purification. $MeFe(CO)_2Cp$, $EtFe(CO)_2Cp$, $MeMn(CO)_5$, and $MeMo(CO)_3Cp$ were prepared by literature methods [11].

The reactions were monitored by scanning the carbonyl stretching region of the infrared spectrum of extracted samples, in cyclohexane solution, and solution species were identified by IR comparisons with the spectra of authentic samples. Spectra were recorded on a Perkin - Elmer 225 spectrophotometer. Proton NMR spectra were measured on a Jeolco Minimar MH100 spectrometer. A Hanovia photochemical reactor was used for internal irradiation of samples using either a low (4 W) or medium pressure (125 W) mercury lamp and a silica jacket. Microanalyses were performed by Mr. J. Kent of this Department, or by the Australian Microanalytical Service, C.S.I.R.O., Melbourne.

Reactions of $MeFe(CO)_2Cp$

(a) With $SnCl_2$. $MeFe(CO)_2Cp$ (1.0 g, 5.2 mmol) and anhydrous $SnCl_2$ (2.0 g, 10.5 mmol) in refluxing methanol (25 ml) reacted completely over 100 h to give $MeCl_2SnFe(CO)_2Cp$ and a small amount (< 5%) of $Cl_3SnFe(CO)_2Cp$. Removal of solvent on a rotary evaporator followed by extraction with methylene chloride and addition of 60/80° petroleum ether gave orange crystals (1.7 g) of $MeCl_2SnFe(CO)_2Cp$ (85% yield, m.p. 110 - 112°). (Found: C, 25.1; H, 2.1; Cl, 18.9; Fe, 14.3%; mol.wt. (osmometric in $CHCl_3$), 398. $C_8H_8Cl_2FeO_2Sn$ calcd.: C, 25.2; H, 2.1; Cl, 18.6; Fe, 14.6%; mol.wt., 382.) The ^1H NMR spectrum ($CDCl_3$ solution, rel. to internal TMS) showed two resonances at τ 4.75 (C_5H_5) and 8.58 ppm (CH_3). Infrared spectrum (C_6H_{12} solution) in the carbonyl stretching region: 2030 m, 2020 s, 1985 m and 1977 s cm^{-1}.

A similar reaction of $MeFe(CO)_2Cp$ (1.0 g, 5.2 mmol) and anhydrous

$SnCl_2$ (2.0 g, 10.5 mmol) in refluxing THF for 48 h gave a 70% yield. A 43% yield was obtained from $SnCl_2 \cdot 2H_2O$ (1.4 g, 6.5 mmol) and $MeFe(CO)_2Cp$ (0.85 g, 4.4 mmol) in methanol and an 18 h reflux. No change in the reaction course was observed using a 6-fold excess of $SnCl_2$.

(b) With $SnBr_2$. The reaction between $MeFe(CO)_2Cp$ (1.0 g, 5.2 mmol) and $SnBr_2 \cdot 2H_2O$ (1.9 g, 6.0 mmol) in refluxing tetrahydrofuran (25 ml) was approximately 50% complete after 12 h giving mainly $BrFe(CO)_2Cp$ with a trace of $Br_3SnFe(CO)_2Cp$. On complete reaction (48 h) the major product was $Br_3SnFe(CO)_2Cp$. Extraction and recrystallization as before gave red-brown crystals (0.1 g) of $Br_3SnFe(CO)_2Cp$.

Reactions of $EtFe(CO)_2Cp$

(a) With $SnCl_2$. $EtFe(CO)_2Cp$ (1.0 g, 4.9 mmol) and anhydrous $SnCl_2$ (1.5 g, 7.9 mmol) were refluxed in THF (25 ml). After 5 h, only slight conversion to $EtCl_2SnFe(CO)_2Cp$ had occurred. After 56 h, the mixture contained approximately equal amounts of $EtCl_2SnFe(CO)_2Cp$ and $Cl_2Sn[Fe(CO)_2Cp]_2$. After 104 h with reaction about 50% complete, $Cl_2Sn[Fe(CO)_2Cp]$ and $Cl_3SnFe(CO)_2Cp$ were the major products.

Reaction of a larger excess of $SnCl_2$ (7.0 g, 37 mmol) with $EtFe(CO)_2Cp$ (1.3 g, 6.3 mmol) in refluxing methanol (25 ml) for 36 h gave $EtCl_2SnFe(CO)_2Cp$, $Cl_3SnFe(CO)_2Cp$ and $Cl_2Sn[Fe(CO)_2Cp]_2$ in approximately equivalent amounts. Solvent was removed on a rotary evaporator, and unreacted $EtFe(CO)_2Cp$ (ca. 0.3 g) by distillation (70°/0.1 mmHg). Extraction and fractional crystallization as before gave Et_2SnCl_2 (0.05 g), $EtCl_2SnFe(CO)_2Cp$ (0.10 g, 4% yield, m.p. 76 - 78°), $Cl_3SnFe(CO)_2Cp$ (0.13 g) and $Cl_2Sn[Fe(CO)_2Cp]_2$ (0.15 g). (Found for $EtCl_2SnFe(CO)_2Cp$: C, 27.3; H, 2.6; Cl, 18.4. $C_9H_{10}Cl_2FeO_2Sn$ calcd.: C, 27.3; H, 2.6; Cl, 17.9%.) Infrared spectrum (C_6H_{12} solution) in carbonyl stretching region: 2030 m, 2019 s, 1983 m and 1976 s cm^{-1}.

(b) With $SnBr_2$. $EtFe(CO)_2Cp$ (1.0 g, 4.9 mmol) and $SnBr_2 \cdot 2H_2O$ (1.9 g, 6.0 mmol), in refluxing THF, reacted slowly to give $BrFe(CO)_2Cp$ (after 5 h), an approximately 1/3 mixture of $BrFe(CO)_2Cp$ and $Br_3SnFe(CO)_2Cp$ (after 50 h), and almost completely to give $Br_3SnFe(CO)_2Cp$ (after 100 h). Solvent and unreacted starting material (0.1 g) were distilled off and Et_2SnBr_2 (0.2 g), identified by IR spectroscopy and melting point, was sublimed (85°/0.1 mmHg) from the residual brown oil. Work up, as before, gave orange crystals of $Br_3SnFe(CO)_2Cp$ (0.2 g).

Reactions of $MeMo(CO)_3Cp$

(a) With $SnCl_2$. No reaction occurred in a 25 h reflux of $MeMo(CO)_3Cp$ (1.0 g, 3.9 mmol) and $SnCl_2$ (1.5 g, 7.9 mmol) in methanol (25 ml), but, after 7 h of low pressure UV irradiation, a small amount of $ClMo(CO)_3Cp$ together with a trace of $Cl_3SnMo(CO)_3Cp$ was formed. On complete reaction (74 h), $Cl_3SnMo(CO)_3Cp$ was the major product.

Using the same conditions but with medium pressure irradiation, substantial formation of $Cl_3SnMo(CO)_3Cp$ together with a smaller amount of $ClMo(CO)_3Cp$ occurred after 2 h. After 7 h, all the starting material had reacted to give a mixture containing mainly $Cl_3SnMo(CO)_3Cp$ and $Cl_2Sn[Mo(CO)_3Cp]_2$.

(b) With $SnBr_2$. $MeMo(CO)_3Cp$ (1.0 g, 3.9 mmol) and $SnBr_2 \cdot 2H_2O$ (2.5 g, 7.9 mmol) in refluxing methanol (25 ml) gave, after 1 h, an approximately 10% yield of $BrMo(CO)_3Cp$. After 26 h, with reaction about 50% complete, small amounts of $Br_3SnMo(CO)_3Cp$ were also detected.

Reaction of $MeMn(CO)_5$

With $SnCl_2$. After a 3 h reflux in methanol (25 ml), $MeMn(CO)_5$ (0.72 g, 3.4 mmol) and $SnCl_2$ (1.3 g, 6.8 mmol) gave a complex mixture containing $ClMn(CO)_5$, $[ClMn(CO)_4]_2$, $Cl_3SnMn(CO)_5$ and other minor unidentified species. After 15 h, no $MeMn(CO)_5$ remained and the solution contained mainly $[ClMn(CO)_4]_2$ and $Cl_3SnMn(CO)_5$. Solvent was removed on a rotary evaporator, and traces of starting material and methyltin chlorides sublimed from the oily residue (90°/0.1 mmHg). $Cl_3SnMn(CO)_5$ (0.5 g) was isolated after the usual work-up.

Reactions of $MeCl_2SnFe(CO)_2Cp$

(a) With $SnBr_2$. $MeCl_2SnFe(CO)_2Cp$ (0.6 g, 1.6 mmol) and $SnBr_2 \cdot 2H_2O$ (5.0 g, 15.9 mmol), in refluxing methanol (30 ml), reacted slightly over 48 h to give traces of $BrFe(CO)_2Cp$ and $Br_3SnFe(CO)_2Cp$. Unreacted $MeCl_2SnFe(CO)_2Cp$ (0.5 g) was recovered.

(b) With hydrogen chloride. Dry hydrogen chloride, bubbled through a solution of $MeCl_2SnFe(CO)_2Cp$ (0.8 g, 2.1 mmol) in CH_2Cl_2 (25 ml) at room temperature over 17 h, produced about 5% conversion to $Cl_3SnFe(CO)_2Cp$.

Acknowledgement

We thank the Australian Reasearch Grants Committee for financial support.

References

1 J.F. Young, Advan. Inorg. Chem. Radiochem., 11 (1968) 91.
2 A. Wojcicki, Accounts Chem. Res., 4 (1971) 344.
3 A.N. Nesmeyanov, N.E. Kolobova, K.S. Anisimov and F.S. Denisov, Proc. Acad. Sci. USSR, 192 (1970) 813.
4 J.D. Cotton and R.M. Peachey, Inorg. Nucl. Chem. Lett., 6 (1970) 727.
5 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 179.
6 S.R.A. Bird, J.D. Donaldson, S.A. Keppie and M.F. Lappert, J. Chem. Soc. A, (1971) 1311.
7 P. Hackett and A.R. Manning, J. Chem. Soc. A, (1972) 1487.
8 M.J. Mays and S.M. Pearson, J. Chem. Soc. A, (1969) 136.
9 R.D. Gorsich, J. Amer. Chem. Soc., 84 (1962) 2486.
10 T.A. George, Inorg. Chem., 11 (1972) 77.
11 R.B. King, Organometallic Syntheses, Vol. 1, Academic Press, London, 1965.