

REACTIVITY OF METAL-METAL BONDS

II. EXCHANGE REACTIONS OF TRIMETHYLTIN DERIVATIVES OF MANGANESE AND IRON

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SUMMARY

The reactivity of $\text{Me}_3\text{SnMn}(\text{CO})_5$, $(\text{CH}_2=\text{CHCH}_2)_3\text{SnMn}(\text{CO})_5$, $\text{Me}_3\text{SnFeCp}(\text{CO})_2$, and $\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$ has been investigated with respect to iodine, organomercury chlorides, trialkyl- and triarylchlorosilane, inorganic chlorides (SiCl_4 , SnCl_4 , TiCl_4 , ZnCl_2 , HgCl_2) and $\text{Mn}_2(\text{CO})_{10}$.

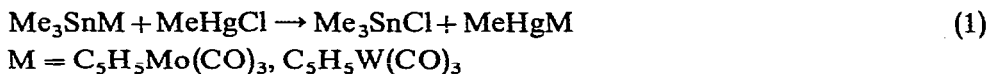
Iodination proceeded with dominant metal-metal bond cleavage in all solvents used, as was the case in most of the subsequent reactions, with the exception of the triallyltin derivative where carbon-metal bond fission occurred.

$\text{Me}_3\text{SnFeCp}(\text{CO})_2$ reacted with MeHgCl in a 1/1 ratio in $\text{DMSO}-d_6$ to give initially $\text{MeHgFeCp}(\text{CO})_2$ and Me_3SnCl which subsequently gave Me_4Sn , Me_2Hg , $\text{Hg}[\text{FeCp}(\text{CO})_2]_2$ and $\text{ClHgFeCp}(\text{CO})_2$. In contrast with the phenyl analogue, the intermediate $\text{MeHgFeCp}(\text{CO})_2$ was not stable enough to be isolated. $\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$ reacted similarly but secondary reactions yielded Me_3SnCl and, using excess MeHgCl , Me_2SnCl_2 . Reaction of $\text{Me}_3\text{SnMn}(\text{CO})_5$ followed similar patterns but in this instance $\text{MeHgMn}(\text{CO})_5$ appeared much more stable than $\text{PhHgMn}(\text{CO})_5$.

Pathways accounting for all the products are discussed. Evidence is also presented for a range of exchange reactions with a variety of inorganic and organometallic chlorides.

INTRODUCTION

In a previous paper¹, new organomercury derivatives of molybdenum and tungsten were synthesised by the following exchange reaction



The mercurials were found to decompose by reaction (2)



The purpose of the present work is to investigate the generality of the above behaviour by examining the corresponding derivatives of manganese and iron, and extending the range of the exchanging reagent.

RESULTS AND DISCUSSION

The compounds chosen for the investigation were $\text{Me}_3\text{SnMn}(\text{CO})_5$, $\text{Me}_3\text{-SnFeCp}(\text{CO})_2$, and $\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$, mainly because of their accessibility. The new allylic derivative, $(\text{CH}_2=\text{CHCH}_2)_3\text{SnMn}(\text{CO})_5$, was also synthesised.

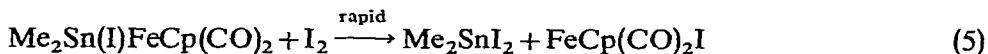
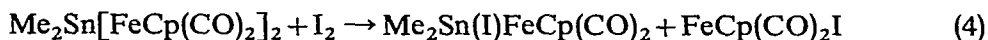
The following reagents were used in the exchange reactions: (a) iodine, (b) organomercury halides, (c) trialkyl- and triarylchlorosilanes, (d) various inorganic chlorides, (e) $\text{Mn}_2(\text{CO})_{10}$.

(a). Iodination reactions

Reactions were carried out in solvent CDCl_3 , MeOD and $(\text{CD}_3)_2\text{SO}$, and followed by NMR using 0.1 M solutions. In contrast with the molybdenum and tungsten analogues, no effervescence was observed even in polar solvents^{1,2}. For both trimethyltin-manganese and -iron compounds, metal-metal bond cleavage was almost quantitative (Table 1).



Equimolar solutions of $\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$ [$\delta(\text{Me})$ 0.54, $\delta(\text{Cp})$ 5.00] and I_2 in $\text{DMSO}-d_6$ showed six singlet resonances (δ 0.52, 0.82, 1.05, 5.00, 5.14, 5.35 ppm), two of which corresponded to unreacted starting material. From the previous cleavage of $\text{Me}_3\text{SnFeCp}(\text{CO})_2$, $\text{FeCp}(\text{CO})_2\text{I}$ showed a singlet at 5.35 ppm, identical with that of one of the observed products. It was concluded that the following reaction sequence had occurred



On using a two-fold excess of iodine, only two singlets were observed at 5.35 and 1.07 ppm. in the ratio 5/2.9, which strongly supported the above stoichiometry. The resonances at 0.82 and 5.14 ppm can be assigned to $\text{Me}_2\text{Sn}(\text{I})\text{FeCp}(\text{CO})_2$.

TABLE 1

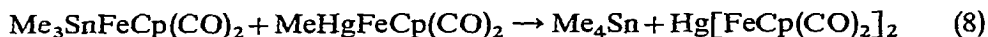
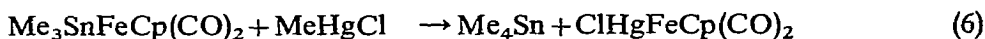
PROTON RESONANCES (δ in ppm) OF PRODUCTS OF IODINATION OF $\text{Me}_3\text{SnMn}(\text{CO})_5$, $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ AND $\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$ (0.1 M in organometal and iodine) IN VARIOUS SOLVENTS

Compound	Solvent	Me_3Sn	Cp	Me_3SnI^a	MeI^a
$\text{Me}_3\text{SnMn}(\text{CO})_5$	CDCl_3	0.87		0.87	2.14
$\text{Me}_3\text{SnMn}(\text{CO})_5$	MeOD	0.79		0.79	2.16
$\text{Me}_3\text{SnMn}(\text{CO})_5$	$(\text{CD}_3)_2\text{SO}$	0.57		0.59	2.18
$\text{Me}_3\text{SnFeCp}(\text{CO})_2$	CDCl_3	0.85	5.03	0.87	2.14
$\text{Me}_3\text{SnFeCp}(\text{CO})_2$	MeOD	0.78	5.00	0.79	2.16
$\text{Me}_3\text{SnFeCp}(\text{CO})_2$	$(\text{CD}_3)_2\text{SO}$	0.58	5.35	0.59	2.18
$\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$	$(\text{CD}_3)_2\text{SO}^b$	1.05	5.35	0.59	2.18
$\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$	$(\text{CD}_3)_2\text{SO}^b$	0.82	5.14	0.59	2.18
$\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$	$(\text{CD}_3)_2\text{SO}^b$	0.52	5.00	0.59	2.18
$\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$	$(\text{CD}_3)_2\text{SO}^c$	1.07	5.35	0.59	2.18

^a Calibrants. ^b 0.1 M I_2 , ^c 0.2 M I_2

(b). Reactions with organomercury halides

Again NMR techniques were used to follow the course of reaction. Chemical shifts of reactants and products appear throughout in parentheses (δ ppm). The intermediate RHgM was isolated and characterised where possible. Reaction of equimolar concentrations (0.1 M) of $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ and MeHgCl in $\text{DMSO}-d_6$ resulted in the original signals from the starting materials, $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ (4.95, 0.31), MeHgCl (0.82), being replaced by singlets at 4.91, 0.56 and 0.53 ppm. The last, showing tin satellites, was assigned to Me_3SnCl (0.55) and hence the first two were attributed to $\text{MeHgFeCp}(\text{CO})_2$. However, significant changes occurred in the spectrum on standing; the signals due to the methyl groups in $\text{MeHgFeCp}(\text{CO})_2$ decreased in intensity, and two new peaks gradually appeared at 0.15 and 0.07 ppm; the first showed $^{199}\text{Hg}-^1\text{H}$ satellites ($J \sim 105$ Hz) and was tentatively attributed to Me_2Hg . The chemical shift of the latter in this solvent was found to be 0.23 ppm. Independent experiments showed that solutions containing equimolar quantities of Me_2Hg and $\text{Hg}[\text{FeCp}(\text{CO})_2]_2$ [the other product of symmetrisation step (2)] had NMR spectra comprising two resonances at 4.90 (Cp) and 0.15 ppm (MeHg)*. Since the chemical shifts of the other reaction products did not differ appreciably from those of the appropriate calibrants in $\text{DMSO}-d_6$, it appears that there is some specific interaction or even complex formation between Me_2Hg and $\text{Hg}[\text{FeCp}(\text{CO})_2]_2$. The second resonance (0.07 ppm) displayed attendant tin satellites and a chemical shift close to that of Me_4Sn . The C_5H_5 signal remained sensibly constant throughout. The yield of Me_2Hg based on (1) and (2) was $\approx 60\%$ indicating that either $\text{MeHgFeCp}(\text{CO})_2$ was not quantitatively formed in the initial reaction due to a different mode of cleavage, e.g. (6), or that it subsequently decomposed by a route other than (2), possibly via (7) or (8).



All three possibilities would account for the formation of Me_4Sn , however, route (8) would result in residual MeHgCl , whereas consumption of both reactants was complete. The ultimate yield of Me_3SnCl (190 min at 40°) was $\approx 85\%$, and is certainly compatible with that of Me_4Sn ($\approx 15\%$) as determined in a necessarily rather crude manner from the NMR spectra (standard deviation $\approx 5\%$). An alternative explanation for the unexpected appearance of Me_4Sn is that it results from a disproportionation of Me_3SnCl , but this can be discarded because such a reaction normally occurs only under forcing conditions, and no Me_2SnCl_2 was detected. Routes (6) and (7) should yield $\text{ClHgFeCp}(\text{CO})_2$ (5.23) but no signal was observed in this region.

A synthetic mixture of reaction products was made up in $\text{DMSO}-d_6$ in accordance with the observed yields, and the spectrum of the resulting solution was found to be exactly superposable on that of the original product solution. The cyclopentadienyl singlet was noticeably broader than those observed for calibrant solutions of either $\text{ClHgFeCp}(\text{CO})_2$ or $\text{Hg}[\text{FeCp}(\text{CO})_2]_2$. It appears, therefore, that a rapid

* Values of 4.90 and 0.19 ppm. were obtained for solvent acetone- d_6 (cf. corresponding reaction of $\text{Me}_3\text{SnMoCp}(\text{CO})_5$ in ref. 1).

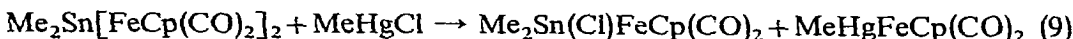
exchange of C_5H_5 occurs between these two species resulting in a broadening of the signal due to $ClHgFeCp(CO)_2$ (already in low concentration) to an extent that it is lost in the noise level.

The initial yield (4 min at 40°) of Me_3SnCl was $\approx 95\%$, significantly higher than the final yield. No Me_4Sn was detected at this stage. This supports route (7). $MeHgFeCp(CO)_2$ can, therefore, be lost by two competitive processes (2) and (7). Attempts to isolate the intermediate failed, the main product being identified as $Hg[FeCp(CO)_2]_2$.

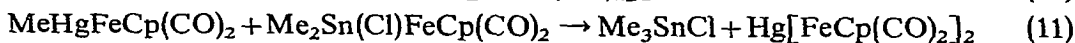
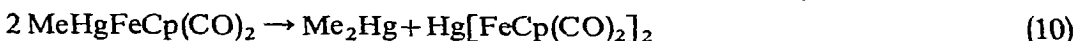
Similar behaviour was observed using acetone- d_6 , but the analysis was hindered by the masking of the methyl-protons of $MeHgFeCp(CO)_2$ by Me_3SnCl . The corresponding reaction with $PhHgCl$ in $DMSO-d_6$ gave a solution whose spectrum showed a complex multiplet at 7.7–7.2 ppm (Ph) and sharp singlets at 4.95 (C_5H_5) and 0.53 ppm (Me_3SnCl), and did not vary with time. The phenyl resonance was almost superposable on that obtained for $PhHgMoC_5H_5(CO)_3$ ¹. Integration of the Me_3SnCl signal showed reaction (1) to be quantitative. The absence of step (2) indicates that, as for the molybdenum and tungsten derivative, the phenyl compound has a much greater stability than the methyl analogue and it was subsequently isolated by the precipitation method in good yields.

The reaction of $Me_2Sn[FeCp(CO)_2]_2$ with $MeHgCl$ in $DMSO-d_6$ was also complex. When reagent solutions of equal concentrations were used, the signals due to starting materials $Me_2Sn[FeCp(CO)_2]_2$ (4.99, 0.56) and $MeHgCl$ (0.82), were replaced after about 5 min by singlets at (a) 5.08, (b) 4.89, (c) 0.79, (d) 0.58 and (e) 0.14 ppm. Peaks (a) and (b) (C_5H_5) were of almost equal intensity; peaks (b) and (d) (ratio $\approx 5/3$) corresponded well with those obtained previously for $MeHgFeCp(CO)_2$; peaks (a) and (c) (ratio 5/6.5) were assigned to $Me_2Sn(Cl)FeCp(CO)_2$; peak (e), initially very small, was assigned to Me_2Hg .

On standing (a), (c) and (d) decreased as (b) and (e) increased, and a new singlet appeared at 0.54 ppm, which increased in intensity and was identified as Me_3SnCl . This suggests that the first step is the normal cleavage (9)



followed by the decomposition of both products by the routes (10) and (11)



The latter process is analogous to (7) in the cleavage of $Me_3SnFeCp(CO)_2$. $Hg[FeCp(CO)_2]_2$ and $MeHgFeCp(CO)_2$ have almost identical cyclopentadienyl resonances and thus this part of the spectrum will not change with time. Integration gave yields of $Me_2Sn(Cl)FeCp(CO)_2$, Me_2Hg , and Me_3SnCl of 61%, 31% and 37% respectively which is consistent with 61% reaction via (10) and 37% via (11).

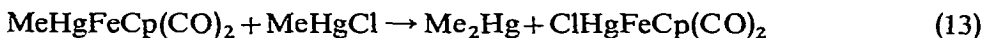
When a twofold excess of $MeHgCl$ is used, the reagent is completely consumed and the same general reaction pattern is observed, except that yields of $Me_2Sn(Cl)FeCp(CO)_2$ and Me_3SnCl are reduced whilst those of Me_2Hg are increased and appreciable quantities of Me_2SnCl_2 are formed, probably by route (12).



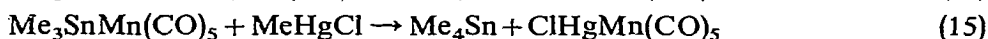
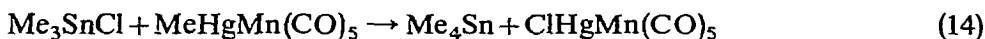
Thus the intermediate $Me_2Sn(Cl)FeCp(CO)_2$ is competed for by $MeHgCl$ and $MeHg-$

FeCp(CO)₂. By measuring the quantities of Me₂Sn(Cl)FeCp(CO)₂, Me₂SnCl₂ and Me₃SnCl formed, it was possible to assess the relative contributions of (10), (11) and (12) as being 25, 20 and 55%. No Me₄Sn was detected and hence Me₂SnCl₂ and Me₃-SnCl were not formed by a redistribution process.

In solvent acetone-*d*₆ equimolar reaction mixtures gave almost quantitative yields of Me₂Sn(Cl)FeCp(CO)₂, indicating that (11) and (12) were inoperative. When a two-fold excess of MeHgCl was used, yields of Me₂Hg in excess of that predicted from the disproportionation of MeHgFeCp(CO)₂ were obtained together with some ClHgFeCp(CO)₂ (broad \approx 5.25). This could be accounted for by reaction (13) though why this exchange occurs in acetone instead of (12) as in DMSO is unclear.



The reaction of Me₃SnMn(CO)₅ with MeHgCl in acetone-*d*₆ yielded Me₃SnCl, Me₂-Hg and Me₄Sn. The intermediate MeHgMn(CO)₅ was isolated by precipitation and shown to have $\delta(\text{Me})$ of 0.57 ppm, close enough to be partially masked by the intense Me₃SnCl signal. There was no evidence of any Me₂SnCl₂ and thus Me₄Sn could not have resulted from a redistribution process. Yields of Me₂Hg [44% based on (2)] were low, suggesting that MeHgMn(CO)₅ was being lost by similar routes, *viz.* (14), (15), to those postulated for the iron analogue.

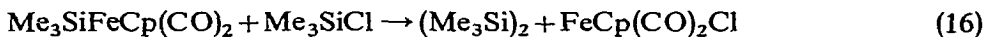


The actual yield of MeHgMn(CO)₅ (73%) obtained by rapid quenching of reaction mixtures is nicely complimentary to the yields of Me₄Sn (22%) and Me₃SnCl (77%) obtained from NMR measurements at comparable reaction times (5 min at 40°). The fact that yields of Me₃SnCl [and MeHgMn(CO)₅] decreased with time in the initial period of reaction (up to 15 min at 40°) at approximately the same rate as Me₄Sn was formed, no Me₂Hg being formed during this period, suggests that route (14) is indeed operative.

All attempts to isolate PhHgMn(CO)₅ resulted in the formation of Hg[Mn(CO)₅]₂ in good yields, this being in marked contrast to the phenyl derivatives of molybdenum, tungsten and iron.

(c). *Reactions with R₃MCl (R = Me, Ph; M = Si, Sn)*

The reaction of Me₃SiCl with Me₃SnFeCp(CO)₂ in 1/1 ratio gave 35% Me₃SiCl after 50 h at 20° in acetone-*d*₆, but the reaction solution showed signs of decomposition. Using a tenfold excess of Me₃SiCl, 88% Me₃SnCl was formed, together with what was assumed to be Me₃SiFeCp(CO)₂ (Cp, 5.23, Me₃Si 0.30 ppm). Attempts to prepare the latter using excess Me₃SiCl resulted in the isolation of FeCp(CO)₂Cl, formed possibly via (16).



Silicon-iron bonds have been shown to be very reactive towards electrophilic species³. However, no reaction occurs with Ph₃SiCl under the above conditions. The analogous reactions of Me₃SnMn(CO)₅ yielded 52 and 80% Me₃SnCl using equimolar and tenfold excess Me₃SiCl respectively. The reactions were much more rapid than those of the iron derivatives. Again no Me₃SiMn(CO)₅ could be isolated from reaction

mixtures, but appreciable yields of $\text{Mn}(\text{CO})_5\text{Cl}$ (characterised by its ready transformation into the more stable $\text{Cl}_2\text{Mn}_2(\text{CO})_8$) were obtained.

(d). *Reactions with inorganic halides*

(i). *With MX_4 ($M = \text{Si}, \text{Sn}, \text{Ti}$; $X = \text{Cl}$)*. SiCl_4 reacted with $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ in $\text{DMSO}-d_6$ to give yields of Me_3SnCl of 26% (20 min) and 50% (48 h). $\text{Cl}_3\text{SiFeCp}(\text{CO})_2$ formed during the reaction showed a cyclopentadienyl resonance at 4.89 ppm (cf. 4.88, ref. 5). Similar reaction with SnCl_4 gave 7% and 45% Me_3SnCl together with $\text{Cl}_3\text{SnFeCp}(\text{CO})_2$ (5.07, cf. 5.18 in CDCl_3 , ref. 6). TiCl_4 reacted very rapidly to give a dark red solution and quantitative yields of Me_3SnCl and $\text{Cl}_3\text{TiFeCp}(\text{CO})_2$ (5.31). The order of reactivity of halides is thus $\text{TiCl}_4 > \text{SiCl}_4 > \text{SnCl}_4$.

(ii). *With MX_2 ($M = \text{Zn}, \text{Hg}$; $X = \text{Cl}$)*. Anhydrous zinc chloride reacted with $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ and $\text{Me}_3\text{SnMn}(\text{CO})_5$ in dry THF to give 25% and 19% yields of Me_3SnCl respectively in 48 h.

Dominant metal-metal bond fission was again found to occur for the reactions of $\text{Me}_3\text{SnMn}(\text{CO})_5$ and $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ with HgCl_2 in acetone, yielding $\text{ClHgMn}(\text{CO})_5$ (76%) and $\text{ClHgFeCp}(\text{CO})_2$ (64%) respectively. Allylmercury chloride was identified as one of the major products from the corresponding cleavage of $(\text{CH}_2=\text{CHCH}_2)_3\text{SnMn}(\text{CO})_5$; as with the tungsten analogue¹, carbon-tin bond fission becomes dominant where a labile organic group is bound to tin. $\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$ and HgCl_2 in acetone- d_6 gave almost quantitative yields of $\text{ClHgFeCp}(\text{CO})_2$ (5.27) and $\text{Me}_2\text{Sn}(\text{Cl})\text{FeCp}(\text{CO})_2$ (5.19, 0.86)* after 5 min at 20°. In contrast to the iodination reaction, the reaction appeared to stop after fission of one Fe-Sn bond, probably due to formation of $[\text{Me}_2\text{SnFeCp}(\text{CO})_2]^+ [\text{HgCl}_3]^-$.

(e). *Reactions with $\text{Mn}_2(\text{CO})_{10}$*

$\text{Me}_3\text{SnFeCp}(\text{CO})_2$ did not react with $\text{Mn}_2(\text{CO})_{10}$ in 100 h at 20° in acetone- d_6 during which time appreciable broadening of the spectrum of the former occurred with much decomposition.

Structure of $(\text{CH}_2=\text{CHCH})_3\text{SnMn}(\text{CO})_5$

The $\nu(\text{C}=\text{C})$ of this compound (1622 cm^{-1}) did not vary appreciably from that of tetraallyltin⁷ which has an unperturbed olefinic double bond, from which it is concluded that no Mn-olefin interactions occur.

EXPERIMENTAL

Purification of materials

Solvents carbon tetrachloride, THF⁸, acetone, methanol and DMSO were purified by standard procedures. Iodine was resublimed prior to use. Mercury salts were recrystallised from acetone/methanol mixtures. Chloroform- d_1 , acetone- d_6 and DMSO- d_6 were obtained from Ryvan Chemicals Ltd. Methanol- d_1 was supplied by Koch-Light Laboratories Ltd. $[\text{Mn}(\text{CO})_5]_2$ and $[\text{FeCp}(\text{CO})_2]_2$ were supplied by Strem Chemicals Inc.

* Cf. values obtained in cleavage of $\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$ by MeHgCl in the same solvent: $\text{ClHgFeCp}(\text{CO})_2$ (5.25), $\text{Me}_2\text{Sn}(\text{Cl})\text{FeCp}(\text{CO})_2$ (5.15, 0.82).

Preparations

$\text{Me}_3\text{SnMn}(\text{CO})_5$ was prepared in 66% yield from $\text{NaMn}(\text{CO})_5$ and Me_3SnCl in dry THF⁸. $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ was synthesised in 60% yield using the same method⁹. In each case 10% Na amalgam was used instead of the recommended 1%, enabling the mixtures to be agitated with a magnetic stirrer rather than the more cumbersome Hg seal stirrer.

$(\text{CH}_2=\text{CHCH}_2)_3\text{SnMn}(\text{CO})_5(\text{nc})$ was prepared in 48% yields by the same route. It was a yellow oil whose IR spectrum in CCl_4 (3 mg/10 ml) showed absorptions at 3085 w, 3055 vw, 3000 w, 2970 m, 2915 m, 2860 w, 2091 s, 2075 w, 1997 vs, 1962 ms, 1782 w, 1622 s, 1462 w, 1445 m, 1391 m, 1297 w, 1190 s, 1088 s, 1029 s, 987 ms, 965 ms, 890 vs cm^{-1} and whose NMR spectrum (CCl_4) showed a complex multiplet at 6.50–5.50 ppm, a triplet centred at 4.89 ppm, and a doublet centred at 2.21 ppm (J 8.5 Hz), these resonances being typical of a σ bonded allylic system. (Found: C, 38.64; H, 3.59; O, 18.15. $\text{C}_{14}\text{H}_{15}\text{MnO}_5\text{Sn}$ calcd.: C, 38.50; H, 3.44; O, 38.31%). The compound decomposed in CCl_4 on standing.

$[\text{FeCp}(\text{CO})_2]_2\text{SnCl}_2$ was prepared in 72% yield from $[\text{FeCp}(\text{CO})_2]_2$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, and then converted to $\text{Me}_2\text{Sn}[\text{FeCp}(\text{CO})_2]_2$ (43%), m.p. 105–106° by reaction with MeMgI in dry ether¹⁰. Attempts to prepare the allyl analogue resulted in the isolation of a small quantity of $(\text{CH}_2\text{CH}=\text{CH}_2)\text{Sn}(\text{Cl})[\text{FeCp}(\text{CO})_2]_2$.

In an attempt to find an alternative route to $\text{Me}_3\text{SnFeCp}(\text{CO})_2$, $[\text{FeCp}(\text{CO})_2]_2\text{SnCl}_2$ was converted to $[\text{FeCp}(\text{CO})_2]\text{SnCl}_3$ (50%) by SnCl_4 in dry benzene. Treatment of $[\text{FeCp}(\text{CO})_2]\text{SnCl}_3$ with MeMgI in dry ether, however, did not yield any of the desired product.

*Synthesis of organomercury derivatives of iron and manganese**

The method used has already been reported in detail¹. PhHgCl and $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ (1.00 mmole of each) in DMSO (3 ml) gave $\text{PhHgFeCp}(\text{CO})_2(\text{nc})$ (82%), orange crystals, in 2 min, m.p. 101°. (Found: C, 34.37; H, 2.08; O, 6.96. $\text{C}_{13}\text{H}_{10}\text{FeHgO}_2$ calcd.: C, 34.35; H, 2.21; O, 7.04%). The IR spectrum in CCl_4 (3 mg/10 ml) showed the following absorptions: 3068 w, 3050 w, 3020 vw, 2990 vw, 2057 m, 2017 m, 1994 s, 1969 vs, 1943 vs, 1480 m, 1429 m, 1412 w, 1112 w, 1085 m, 1062 vw, 1026 m, 1002 w, 997 m, 698 s, 635 s cm^{-1} . The NMR spectrum in CDCl_3 comprised a multiplet at 7.4–7.2 ppm (Ph) and a singlet at 4.68 ppm (Cp). In DMSO- d_6 the cyclopentadienyl resonance occurred at 4.99 ppm.

Reaction of $\text{Me}_3\text{SnMn}(\text{CO})_5$ and MeHgCl in acetone gave $\text{MeHgMn}(\text{CO})_5$ (73%), white crystals, m.p. 100°. (Found: C, 17.58; H, 0.89; O, 19.41. $\text{C}_6\text{H}_3\text{HgMnO}_5$ calcd.: C, 17.54; H, 0.73; O, 19.48%). IR spectrum had adsorptions at 2992 w, 2918 m, 2855 w, 2097 s, 2061 m, 1988 vs, 1957 (sh), 1450 vw, 1390 vw, 1370 vw, 1210 vw, 1152 s, 1088 w, 1035 w, 890 w cm^{-1} . The NMR spectrum in acetone- d_6 showed only one signal at 0.57 ppm, $J(^{199}\text{Hg}-\text{H})$ 127.4 Hz.

Attempts to prepare $\text{MeHgFeCp}(\text{CO})_2$ and $\text{PhHgMn}(\text{CO})_5$ resulted in the formation of $\text{Hg}[\text{FeCp}(\text{CO})_2]_2$ and $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ respectively in good yields.

Reactions with mercuric salts

Reaction of $\text{Me}_3\text{SnFeCp}(\text{CO})_2$ and HgCl_2 (1.0 mmole each) in acetone (3 ml)

* The synthesis of $\text{C}_6\text{F}_5\text{HgFeCp}(\text{CO})_2$ and $\text{C}_6\text{F}_5\text{HgMn}(\text{CO})_5$ has recently been reported¹⁵.

gave a dark orange solution which on cooling deposited golden yellow crystals of $\text{ClHgFeCp}(\text{CO})_2$ ¹¹, m.p. 114°. The product (64%) was identified from its IR spectrum¹¹ (CCl_4) which showed $\nu(\text{CO})$ at 2019 s, 1974 vs cm^{-1} . In a similar reaction $\text{Me}_3\text{SnMn}(\text{CO})_5$ gave 76% $\text{ClHgMn}(\text{CO})_5$, m.p. 170 dec., $\nu(\text{CO})$ (CHCl_3) 2115 m, 2052 w, 2025 vs cm^{-1} ^{12,13}. $(\text{CH}_2=\text{CHCH}_2)_3\text{SnMn}(\text{CO})_5$ gave nearly quantitative yields of $\text{CH}_2=\text{CHCH}_2\text{HgCl}$, m.p. 102–103°.

Reactions with $R_3\text{MCl}$

$\text{Me}_3\text{SnFeCp}(\text{CO})_2$ (1.0 g, 2.94 mmole) was dissolved in AR acetone (20 ml) and Me_3SiCl (10 ml, 79 mmole) added under N_2 . The whole was stirred for 3 h, then poured into ice-water (150 ml). The mixture was extracted with 2×100 ml CHCl_3 , dried and pumped down to a brown oil which on cooling gave brown crystals (0.49 g) whose IR spectrum showed $\nu(\text{CO})$ (CCl_4) 2058 s, 2015 cm^{-1} with intensities very similar to $\text{FeCp}(\text{CO})_2\text{Cl}$ ¹⁴ (79%). Similarly $\text{Me}_3\text{SnMn}(\text{CO})_5$ gave 75% $\text{ClMn}(\text{CO})_5$ identified by conversion to $\text{Cl}_2\text{Mn}_2(\text{CO})_8$ in refluxing CCl_4 ; $\nu(\text{CO})$ 2104 w, 2045 s, 2012 m, 1977 s cm^{-1} . The same products were obtained when water was excluded in the extraction procedure. No reaction was apparent with either Ph_3SnCl or Ph_3SiCl .

Spectra

NMR spectra were run on a Varian A60A spectrometer with the probe thermostatted at 40°. The known impurities in the deuteriated solvents (CHCl_3 , $\text{CD}_3\text{-COCD}_2\text{H}$, $\text{CD}_3\text{SOCD}_2\text{H}$) were used as internal references and chemical shifts quoted as δ in ppm relative to TMS. Infrared spectra of solutions were obtained using a Perkin-Elmer SP 257 instrument.

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