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Subvalent group 14 metal compounds

XI *. Complexes with group 14 metal–iron bonds: the synthesis and characterisation of the complexes $[FeCp(CO)_2\{M(X)R_2\}]$ ($R = CH(SiMe_3)_2$, $Cp = \eta$-C_5H_5; M = Sn and X = H, F, Cl, Br, I, or OMe; or M = Pb and X = I)

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Abstract

The tin(II) or lead(II) alkyl MR_2 reacts with $[FeCp(CO)_2(X)]$ to form the insertion product $[FeCp(CO)_2\{M(X)R_2\}]$ [$R = CH(SiMe_3)_2$, $Cp = \eta^5$-C_5H_5; M = Sn and X = I (**1**), Br (**2**), or Cl (**3**); or M = Pb and X = I (**4**)]. The iodide **1** or bromide **2** undergoes nucleophilic substitution at tin upon treatment with NaOMe, $K[BHEt_3]$, or $[NBu^n_4]F$ supported on silica gel, to yield $[FeCp(CO)_2\{Sn(OMe)R_2\}]$ (**6**), $[FeCp(CO)_2\{Sn(H)R_2\}]$ (**7**), or $[FeCp(CO)_2\{Sn(F)R_2\}]$ (**5**), respectively. Complex **7** serves as a hydride transfer agent, and is capable, for example, of transforming benzoyl chloride into benzaldehyde with concomitant production of $[FeCp(CO)_2$-$\{Sn(Cl)R_2\}]$. Each of the complexes **1**–**7** has been characterised by IR, elemental analysis, mass spectrometry, NMR (including, except for **4**, ^{119}Sn NMR), and ^{119}Sn (except for **4**) and ^{57}Fe Mössbauer spectroscopy. For complexes **1**–**3** and **5**–**7** there is an approximately linear correlation between the ^{119}Sn chemical shift and the appropriate Taft σ_I constant for X. The ^{119}Sn Mössbauer data are interpreted in terms of monomeric tetrahedral structures for each member of the $[FeCp(CO)_2\{Sn(X)R_2\}]$ series.

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* For Part X, see ref. 3. No reprints available.

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Introduction

For some time we have been interested in heavy group 14 metal analogues of carbenes MX_2 {M = Ge, Sn, or Pb; X = a bulky monohapto ligand such as $\overline{C}H(SiMe_3)_2$ (abbreviated as $\overline{R}$), $\overline{N}(SiMe_3)_2$, $\overline{O}C_6H_2Bu^t_2$-2,6-R′-4 (R′ = H, Me, or Bu^t), $SC_6H_2Bu^t_3$-2,4,6, or [Mo(η-C_5Me_5)$(CO)_3$]}; for a brief review, se ref. 2; $Pb(Mo^{II})_2$ complexes are described in ref. 3. The alkyl-germanium(II) and -tin(II) compounds MR_2 have been shown to have an extensive transition metal coordination chemistry, capable of (i) terminally ligating unsaturated transition metal (M′) fragments to form [L_nM'=MR_2] complexes, as in [$Cr(CO)_5(MR_2)$], and (ii) inserting into transition metal (M′)–X bonds to give L_nM'–$M(X)R_2$ derivatives such as [$MoCp(CO)_3\{Sn(H)R_2\}$]; in each of processes (i) and (ii) the product contains a transition metal–main group metal (M′–M) bond.

The transition metal chemistry of the germanium(II) and tin(II) bis(trimethylsilyl)amides $M(NR'_2)_2$ (R′ = $SiMe_3$) has been studied most extensively [4]. The following additional types of ligating behaviour have been recognised: (iii) $M(NR'_2)_2$ as a bridging ligand, e.g., in [$(Pt\{\mu\text{-}Sn(NR'_2)_2\}(CO))_3$] [5]; (iv) deprotonated $Ge(NR'_2)_2$ as a chelating or bridging ligand, cf. [$\{CH_2Me_2SiN(R')(NR'_2)$-$Ge\}HIr(\mu\text{-}Cl)_2\{Ge(NR'_2)N(R')SiMe_2CH_2\}IrH\{Ge(NR'_2)_2\}$] [6]; and (v) deprotonated $GeCl(NR'_2)_2$ as a chelating ligand (formed by insertion into an M′–Cl bond), cf. [$Ir\{GeCl(NR'_2)N(R')SiMe_2CH_2\}(CO)_2H\{Ge(NR'_2)_2\}$] [6]. Reviews have been published on coordination compounds of transition metals having M^{II} complexes as ligands (M = Si, Ge, Sn, or Pb) [7], and complexes having MM′ bonds (M′ = a transition metal) [8].

The following transition metal complexes derived from SnR_2 [R = $CH(SiMe_3)_2$] have been described previously: [$M'(CO)_5(SnR_2)$] (M′ = Cr or Mo) [9,10], *trans*-[$M'(CO)_4(SnR_2)_2$] [10,11], [$MoCp(CO)_3\{Sn(X)R_2\}$] (X = H or Me) [9,10,11], [$FeCp(CO)(\mu\text{-}CO)_2FeCp(SnR_2)$] [9,11], [$FeCp(CO)_2\{Sn(X')R_2\}$] (X′ = Cl or Me) [9,10], [$\{Fe(CO)_4\}_2(\mu\text{-}SnR_2)$] [9,10,12], [$\{Fe(CO)_3(\mu\text{-}SnR_2)\}_2$] [12], [$Os_3Sn(\mu\text{-}H)_2(CO)_{10}R_2$] [13], [$M'(CO)_9(\mu\text{-}CO)(\mu\text{-}SnR_2)_2$] (M′ = Ru or Os) [12], [$Os_3(CO)_8(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}SnR_2)_2$] [14], *cis*-[$RhCl(PPh_3)_2(SnR_2)$] [9,11], *cis*- or *trans*-[$PtCl(PEt_3)SnR_2)(SnClR_2)$] [9,10,11,15], and *trans*-[$\{Pt(\mu\text{-}Cl)(PEt_3)(SnClR_2)\}_2$] [15].

This report concerns the preparation and characterisation of group 14 metal–iron complexes of the general formula [$FeCp(CO)_2\{M(X)R_2\}$] [M = Sn and X = I (**1**), Br (**2**), or Cl (**3**) ; or M = Pb and X = I (**4**)], obtained by insertion of MR_2 into the appropriate [$FeCp(CO)_2(X)$] substrate. The [$FeCp(CO)_2\{M(X)R_2\}$] series has been extended by nucleophilic substitution reactions at tin to yield the further complexes [$FeCp(CO)_2\{Sn(F)R_2\}$] (**5**), [$FeCp(CO)_2\{Sn(OMe)R_2\}$] (**6**), and [$FeCp(CO)_2\{Sn(H)R_2\}$] (**7**). A further objective of this study was to identify trends in the spectral properties, especially in ^{119}Sn NMR and Mössbauer spectra, among this collection of compounds, and draw comparisons with existing data for related species. Although two members of the [$FeCp(CO)_2\{Sn(X)R_2\}$] series had been reported previously (X = Cl or Me), these were characterised, for the most part, only by elemental analysis, low-field hydrogen-1 NMR spectra [9], and ^{119}Sn Mössbauer [10] data.

Experimental

Materials and procedures. All manipulations were performed by standard Schlenk techniques either in vacuo or under argon. Solvents were dried over appropriate desiccants (potassium benzophenone ketyl for diethyl ether, toluene, tetrahydrofuran, or benzene; potassium metal for hexane; lithium tetrahydridoaluminate for pentane; and magnesium turnings for methanol), distilled under nitrogen, and subjected to three freeze-evacuate-thaw cycles prior to use. The compounds [FeCp(CO)$_2$(Cl)] [3a], [FeCp(CO)$_2$(Br)] [3b], [FeCp(CO)$_2$(I)] [3c], SnR$_2$ [3d], PbR$_2$ [3d], and [NBu$^n_4$]F supported on silica gel [3e] were prepared according to literature methods. Sodium methoxide was freshly prepared immediately prior to use from methanol and sodium metal; acetone, benzoyl chloride, and deuteriated solvents were obtained commerically, and used without further purification. The product yields reported were not optimised.

Physical measurements. IR spectra were recorded as Nujol mulls on either a Perkin–Elmer 597 or a Perkin–Elmer 1710 FT spectrophotometer. ^{1}H NMR spectra were recorded on either a Bruker WP 80 (^{1}H at 80 MHz) or a Bruker WM 360 (^{1}H at 360 MHz) instrument and referenced to SiMe$_4$. ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were recorded on a Bruker WM 360 instrument (^{13}C at 90.6, ^{29}Si at 71.5, and ^{119}Sn at 134.3 MHz) and referenced to SiMe$_4$ and SnMe$_4$, respectively. The ^{19}F NMR spectra were recorded at 75.3 MHz on a Bruker WP 80 spectrometer and referenced to external CFCl$_3$. Gas chromatography was carried out with a Hewlett–Packard HP 5890 instrument using a 50 meter capillary column with OV101 packing. Mass spectra were recorded with a Kratos MS 80 spectrometer. Elemental analyses were carried out by Butterworth Laboratories Ltd. Mössbauer spectra were obtained with samples cooled to ca. 80 K and with the sources (Ca^{119}SnO$_3$ or ^{57}Co/Rh) at ambient temperature, in conventional transmission geometry; the spectra were fitted to Lorentzian peaks.

Synthesis of [FeCp(CO)$_2${Sn(I)R$_2$}] (1). In a typical reaction a 100 ml Schlenk flask was charged with [FeCp(CO)$_2$(I)] (0.43 g, 1.42 mmol) and C$_6$H$_6$ (10 ml), and SnR$_2$ (0.62 g, 1.42 mmol) was added in portions during 10 min. The mixture was stirred for a further 2 h and the solvent then removed in vacuo. The residual yellow paste was extracted with hexane (40 ml) and the extract was filtered. The filtrate was concentrated in vacuo to ca. 5 ml and kept for ca. 12 h at $-20\,^\circ$C. Yellow crystals of [FeCp(CO)$_2${Sn(I)R$_2$}] (**1**) (80%) which had separated were filtered off and dried in vacuo. IR: ν(CO) 2000s, 1955s; ρ(Si–C–Si) 842s cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 4.29 (s, 5H, C$_5$H$_5$), 1.07 [s, 2H, C*H*(SiMe$_3$)$_2$], 0.52 (s, 18H, SiMe$_3$), 0.26 (s, 18H, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 214.8 (CO), 85.9 (C$_5$H$_5$), 17.3 [*C*H(SiMe$_3$)$_2$], 5.4 (SiMe$_3$), 4.8 (SiMe$_3$). ^{119}Sn (C$_6$D$_6$): δ 228.8. MS (EI) [m/z (assignment)]: 727 $(P-\text{CH}_3)^+$, 686 $(P-2\text{CO})^+$, 615 $(P-\text{I})^+$; MS (FAB): 615 $(P-\text{I})^+$. Found: C, 34.0; H, 5.94. C$_{21}$H$_{43}$FeIO$_2$Si$_4$Sn calc.: 34.0; H, 5.86%.

Synthesis of [FeCp(CO)$_2${Sn(Br)R$_2$}] (2). Yellow crystals of compound **2** (92%) were obtained similarly from [FeCp(CO)$_2$(Br)] and SnR$_2$. IR: ν(CO) 2006s, 1961s; ρ(Si–C–Si) 840s cm^{-1}. ^{1}H NMR (C$_6$D$_5$CD$_3$): δ 4.32 (s, 5H, C$_5$H$_5$), 0.73 [s, 2H, C*H*(SiMe$_3$)$_2$], 0.39 (s, 18H, SiMe$_3$), 0.22 (s, 18H, SiMe$_3$). ^{13}C NMR (C$_6$D$_5$CD$_3$): δ 214.4 (CO), 85.3 (C$_5$H$_5$), 19.8 [*C*H(SiMe$_3$)$_2$], 5.2 (SiMe$_3$), 4.7 (SiMe$_3$). ^{119}Sn NMR (C$_6$D$_5$CD$_3$): δ 292.2. MS (EI) [m/z (assignment)]: 679 $(P-\text{CH}_3)^+$, 615 $(P-\text{Br})^+$; MS (FAB): 615 $(P-\text{Br})^+$. Found: C, 36.4; H, 5.99. C$_{21}$H$_{43}$BrFeO$_2$Si$_4$Sn calc.: C, 36.3; H, 6.25%.

Synthesis of [FeCp(CO)$_2${Sn(Cl)R$_2$}] (3). Yellow crystals of compound **3** (80%) were obtained from [FeCp(CO)$_2$(Cl)] and SnR$_2$. IR: ν(CO) 2006s, 1961s; ρ(Si–C–Si) 841s cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.32 (s, 5H, C_5H_5), 0.66 [s, 2H, CH(SiMe$_3$)$_2$], 0.46 (s, 18H, SiMe$_3$) 0.30 (s, 18H, SiMe$_3$). ^{13}C NMR (C_6D_6): δ 212.0 (CO), 84.7 (C_5H_5), 20.9 [*C*H(SiMe$_3$)$_2$], 5.1 (SiMe$_3$), 4.7 (SiMe$_3$). ^{119}Sn NMR (C_6D_6): δ 310.5. MS (EI) [*m/z* (assignment)]: 635 $(P-\mathrm{CH_3})^+$, 615 $(P-\mathrm{Cl})^+$. Found: C, 39.05; H, 6.64. $\mathrm{C_{21}H_{43}ClFeO_2Si_4Sn}$ calc.: C, 38.8; H, 6.68%.

Synthesis of [FeCp(CO)$_2${Pb(I)R$_2$}] (4). Red crystals of compound **4** (20%) were prepared similarly from [FeCp(CO)$_2$(I)] and PbR$_2$. IR: ν(CO) 2010s, 1970s; ρ(Si–C–Si) 895s cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.42 (s, 5H, C_5H_5), 1.03 (s, 2H, C*H*(SiMe$_3$)$_2$], 0.43 (s, 18H, SiMe$_3$), 0.11 (s, 18H, SiMe$_3$). ^{13}C NMR (C_6D_6): δ 212.0 (CO), 85.7 (C_5H_5), 7.4 [*C*H(SiMe$_3$)$_2$], 6.5 (SiMe$_3$). Found: C, 30.15; H, 4.92. $\mathrm{C_{21}H_{43}FeIO_2PbSi_4}$ calc.: C, 30.4; H, 5.23%.

Synthesis of [FeCp(CO)$_2${Sn(F)R$_2$}] (5). A 100 ml Schlenk flask was charged with [FeCp(CO)$_2${Sn(I)R$_2$}] (0.37 g, 0.50 mmol) and [NBu$^n_4$]F (0.55 g, 0.55 mmol) supported on silica gel. Tetrahydrofuran (30 ml) was added and the mixture was heated under reflux for 12 h. The solvent was evaporated, the residue was extracted with benzene, and the extract filtered. The solvent was removed from the filtrate in vacuo. The residue was extracted into a small amount of hexane and chromatographed on a Florisil column with hexane/benzene (1/1) as the eluent. A pale yellow fraction was collected and was concentrated in vacuo to a paste, which was dissolved in pentane. The solution was cooled to −80 °C, and complex **3** (60%) separated out as a pale yellow powder. IR: ν(CO) 2005s, 1960s; ρ(Si–C–Si) 840s cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.26 (s, 5H, C_5H_5), 0.55 [d, ^3J(FH) 2.4 Hz, 2H, C*H*(SiMe$_3$)$_2$], 0.42 [d, ^5J(FH) 0.7 Hz, 18H, SiMe$_3$], 0.25 (s, 18H, SiMe$_3$). ^{13}C NMR (C_6D_6): δ 214.1 (CO), 83.4 (C_5H_5), 23.2 [d, ^2J(FC) 7.0 Hz *C*H(SiMe$_3$)$_2$], 4.5 (br, SiMe$_3$). ^{119}Sn NMR (C_6D_6): δ 321.6 [d, ^1J(SnF) 2489 Hz]. ^{19}F NMR (C_6D_6): δ −154 [^1J(^{117}SnF) 2377 Hz, ^1J(^{119}SnF) 2489 Hz]. ^{29}Si NMR (C_6D_6): δ 0.17 (brs), −0.73(s). MS (EI) [*m/z* (assignment)]: 619: $(P-\mathrm{CH_3})^+$. Found: C, 39.3; H, 6.91. $\mathrm{C_{21}H_{43}FFeO_2Si_4Sn}$ calc.: C, 39.8; H, 6.86%.

Synthesis of [FeCp(CO)$_2${Sn(OMe)R$_2$}] (6). A 100 ml Schlenk flask was charged with [FeCp(CO)$_2${Sn(I)R$_2$}] (0.66 g, 0.89 mmol) and methanol (30 ml) and an excess of sodium methoxide was added. The mixture was heated for 10 h under reflux and the solvent then removed in vacuo. The residue was extracted with hexane, and the extract was filtered through Celite. The solvent was removed from the filtrate in vacuo. The residual yellow oil thus obtained was triturated in methanol (5 ml) at ca. −70 °C to give a fine powder. The solid complex **6** (70%) was filtered off and dried in vacuo. IR: ν(CO) 2000s, 1955s; ρ(Si–C–Si) 843s cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.32 (s, 5H, C_5H_5), 3.67 [s, ^3J(SnH) 45 Hz, 3H, OCH$_3$], 0.47 (s, 18H, SiMe$_3$), 0.38 (s, 18H, SiMe$_3$). ^{13}C NMR (C_6D_6): δ 214.7 (CO), 83.0 (C_5H_5), 53.8 (OCH$_3$), 19.7 [*C*H(SiMe$_3$)$_2$], 4.6 (SiMe$_3$), 4.4 (SiMe$_3$). ^{119}Sn NMR (C_6D_6): δ 267.7 MS (EI) [*m/z* (assignment)]: 631 $(P-\mathrm{CH_3})^+$, 615 $(P-\mathrm{OCH_3})^+$; MS (FAB): 615 $(P-\mathrm{OCH_3})^+$. Found: C, 40.45; H, 7.08. $\mathrm{C_{22}H_{46}FeO_3Si_4Sn}$ calc.: C, 40.9; H, 7.20%.

Synthesis of [FeCp(CO)$_2${Sn(H)R$_2$}] (7). A 100 ml Schlenk flask was charged with [FeCp(CO)$_2${Sn(I)R$_2$}] (0.22 g, 0.30 mmol) and tetrahydrofuran (20 ml). The mixture was cooled to −80 °C and a THF solution of potassium triethylborohydride (0.5 ml, 1.0 *M*) was added dropwise. After 40 min the mixture was warmed to room temperature, the solvent removed in vacuo, and the residue extracted into benzene. The extract was filtered through Celite and the solvent removed in vacuo. The residual thick yellow oil was dissolved in a minimum of pentane and the solution was cooled to −80 °C. Yellow blocks of complex **7** (60%) which precipitated were filtered off and dried in vacuo. IR: ν(CO) 1997s, 1951s; ν(Sn–H) 1763m, ρ(Si–C–Si) 844s cm^{-1}. ^{1}H NMR (C_6D_6): δ 5.69 (s, 1H, SnH), 4.15 (s, 5H, C_5H_5), 1.32 [s, 2H, C*H*$(SiMe_3)_2$], 0.34 (brs, 36H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 215.5 (CO), 83.2 (C_5H_5), 6.9 [*C*H$(SiMe_3)_2$], 4.3 ($SiMe_3$), 3.9 ($SiMe_3$). ^{119}Sn NMR (C_6D_6): δ 35.1 [dt, ^1J(SnH) 1366 Hz, ^2J(SnH) 75 Hz]. MS (EI) [*m/z* (assignment)]: 616 $(P)^+$, 601 $(P - CH_3)^+$. Found: C, 41.0; H, 7.31. $C_{21}H_{44}FeO_2Si_4Sn$ calc.: C, 41.0; H, 7.22%.

Reactions of [FeCp(CO)$_2${Sn(H)R$_2$}] (7). (i) With aqueous HCl. A solution containing [FeCp(CO)$_2${Sn(H)R$_2$}] (0.06 g, 0.01 mmol) in acetone (10 ml) was treated with aqueous hydrogen chloride (9 ml of a 6 *M* solution). The acetone was then allowed to evaporated slowly under vacuum, and the yellow crystals of [FeCp(CO)$_2${Sn(Cl)R$_2$}], which separated were filtered off and dried in vacuo. Authentic IR, ^{1}H NMR, and ^{119}Sn NMR spectra were recorded.

(ii) With benzoyl chloride. A 20 ml Schlenk flask was charged with [FeCp(CO)$_2${Sn(H)R$_2$}] (ca. 0.1 mmol) and a benzene solution of benzoyl chloride (0.30 ml, 1.23 *M*) was added. After ca. 20 min at ambient temperature, the solution was analysed by GC/MS; this showed the presence of benzaldehyde (confirmed by co-elution with an authentic sample). The mixture was evaporated to leave a yellow paste, the ^{1}H NMR spectrum of which in C_6D_6 showed the presence of [FeCp(CO)$_2${Sn(Cl)R$_2$}] and unchanged [FeCp(CO)$_2${Sn(H)R$_2$}].

Results

NMR spectral properties. The cyclopentadienyl hydrogens in the series of compounds [FeCp(CO)$_2${M(X)R$_2$}] (**1**–**7**) gave rise to a singlet resonance near 4.3 ppm (Table 1). The $SiMe_3$ hydrogens of the $CH(SiMe_3)_2$ groups afforded two singlet signals near zero ppm for each member of the series except [FeCp(CO)$_2${Sn(H)R$_2$}] (**7**), for which there was a broad resonance at 0.34 ppm. The broad signal at 5.69 ppm in **7** is assigned to the hydrogen bound directly to tin; three-bond coupling to the C*H*$(SiMe_3)_2$ hydrogens was not resolved. The complexes **1**–**7** revealed ^{13}C resonances near 212 ppm (CO) and near 85 pm (C_5H_5). Signals appropriate for the $CH(SiMe_3)_2$ group were detected; in most cases there were two resonances for the $SiMe_3$ groups at ca. 4 ppm.

The ^{119}Sn NMR chemical shifts for compounds **1**–**3** and **5**–**7** are listed in Table 1 and range from 35 to 322 ppm. The ^{119}Sn spectrum of [FeCp(CO)$_2${Sn(F)R$_2$}] (**5**) showed a doublet, with $^1J(^{119}Sn^{19}F)$ 2489 Hz; while that of [FeCp(CO)$_2${Sn(H)R$_2$}] (**7**) revealed a doublet of triplets, $^1J(^{119}Sn^1H)$ 1366 Hz and $^2J(^{119}Sn^1H)$ 75 Hz. The ^{19}F NMR spectrum of [FeCp(CO)$_2${Sn(F)R$_2$}] (**5**) showed a singlet at −154 ppm flanked by ^{117}Sn and ^{119}Sn satellites, $^1J(^{117}Sn^{19}F)$ 2377 Hz and $^1J(^{119}Sn^{19}F)$ 2489 Hz.

Infrared spectral properties. The carbonyl stretching mode data for the series of compounds [FeCp(CO)$_2${M(X)R$_2$}] (**1**–**7**) are shown in Table 1. For each of **1**–**7** there were two ν(CO) absorptions of nearly equal intensity between 2010 and 1955 cm^{-1}. A medium intensity band at 1793 cm^{-1} in [FeCp(CO)$_2${Sn(H)R$_2$}] (**7**) is assigned to ν(Sn–H). The intense band around 840 cm^{-1} found in each spectrum is assigned to the $Me_3Si–C–SiMe_3$ asymmetric bending mode, ρ(Si–C–Si).

Table 1

Selected IR and NMR data for the series of compounds $[FeCp(CO)_2\{M(X)R_2\}]$

Compound	ν(CO) (cm^{-1}) [a]	$\delta(^1H)$ for η-C_5H_5 (ppm) [b]	$\delta(^{119}Sn)$ (ppm) [b]
$[FeCp(CO)_2\{Sn(F)R_2\}]$ (5)	2005, 1960	4.26	321.6
$[FeCp(CO)_2\{Sn(Cl)R_2\}]$ (3)	2006, 1961	4.32	310.5
$[FeCp(CO)_2\{Sn(Br)R_2\}]$ (2)	2006, 1961	4.32 [c]	292.2 [c]
$[FeCp(CO)_2\{Sn(I)R_2\}]$ (1)	2000, 1955	4.29	228.8
$[FeCp(CO)_2\{Sn(H)R_2\}]$ (7)	1997, 1961	4.15	35.1
$[FeCp(CO)_2\{Sn(OMe)R_2\}]$ (6)	2000, 1955	4.32	267.7
$[FeCp(CO)_2\{Pb(I)R_2\}]$ (4)	2010, 1970	4.42	–

[a] Recorded as Nujol mulls; ±4 cm^{-1}. [b] In C_6D_6, unless otherwise noted; ±3 ppm. [c] In $C_6D_5CD_3$.

Mass spectrometry. Selected members of the $[FeCp(CO)_2\{M(X)R_2\}]$ series were characterised by low resolution mass spectrometry. Electron impact (EI) gave ions corresponding to $(P - CH_3)^+$ and $(P - X)^+$, whilst fast atom bombardment (FAB) gave ions corresponding to $(P - X)^+$ as the principal species in the high molecular weight region of the spectrum.

Discussion

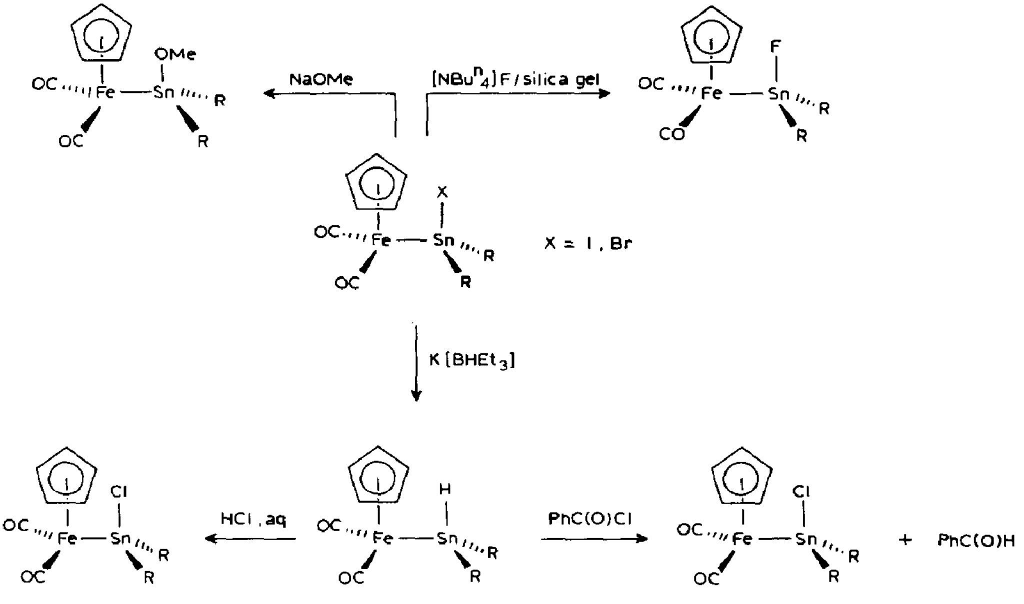
Syntheses. Addition of SnR_2 or PbR_2 to a benzene solution of the appropriate complex $[FeCp(CO)_2(X)]$ (X = I, Br, or Cl) resulted in rapid formation of $[FeCp(CO)_2\{M(X)R_2\}]$ in which the tin or lead had expanded its coordination number from two to four (eq. 1). Yields for these transformations were in the 80–90% range except for the lead compound (20%). Participation of SnR_2 in insertion reactions involving a variety of substrates, including transition metal halides, halogenocarbons, or carboxylic acid chlorides or anhydrides has been documented [2,9,11,15,17] but such behaviour for the lead analogue was previously unknown. Earlier attempts to carry out insertion reactions involving PbR_2 and either HCl or methyl iodide resulted in formation of lead(II) chloride or iodide, respectively [9].

(1)

(M = Sn and X = Cl, Br, or I; or M = Pb and X = I)

In Scheme 1 are summarised the reactions of the compounds $[FeCp(CO)_2\{Sn(X)R_2\}]$ which have been investigated. It is evident that despite the presence of sterically demanding ligands at tin, nucleophilic substitution at tin is facile, suggesting that the Sn–X linkage is either strongly polarised (e.g., X = Cl) or is susceptible to homolysis (X = H). Yields for these transformations were in the range 60–70%.

A feature of this nucleophilic substitution method, which has synthetic value, is that it provides access to three FeSn compounds for which the appropriate



Scheme 1.

[FeCp(CO)$_2$(X)] precursor (e.g. X = H) is not readily available.

Compounds **1**–**7** are of additional interest because analogues which are likewise prochiral at Sn (or Ge) were often previously found to suffer redistribution. For example, [FeCp(CO){Sn(Cl)Br$_2$}] was unstable in warm tetrahydrofuran, yielding [FeCp(CO)$_2${SnBr$_3$}], eq. 2 [18]. Similarly, {[FeCp(CO)$_2$}$_2${μ-Ge(Ph)(Cl)}] decomposed even at low temperatures, eq. 3 [19]. No such decomposition was observed for any of the [FeCp(CO)$_2${Sn(X)R$_2$}] series **1**–**3** or **5**–**7**, even after several hours in refluxing THF. Presumably ligand redistribution is disfavoured because of the bulk of the alkyl groups, which inhibits associative decomposition pathways.

$$3[\mathrm{FeCp(CO)_2\{Sn(Cl)Br_2\}}] \longrightarrow 2[\mathrm{FeCp(CO)_2(SnBr_3)}] + [\mathrm{FeCp(CO)_2(SnCl_3)}] \qquad (2)$$

$$[\{\mathrm{FeCp(CO)_2}\}_2\{\mu\text{-}\mathrm{Ge(Cl)Ph}\}] \longrightarrow [\{\mathrm{FeCp(CO)_2}\}_2(\mu\text{-}\mathrm{GeCl_2})] + \tfrac{1}{2}n(\mathrm{GePh_2})_n \qquad (3)$$

The hydrido complex [FeCp(CO)$_2${Sn(H)R$_2$}] (**7**) manifested a reaction pattern common to many tin(IV) hydrides. Thus, **7** cleanly afforded [FeCp(CO)$_2${Sn(Cl)R$_2$}] upon treatment with hydrogen chloride. The ability of **7** to serve as a hydride transfer agent is illustrated by its reaction with benzoyl chloride, which provided benzaldehyde along with [FeCp(CO)$_2${Sn(Cl)R$_2$}].

Spectral properties. The ^{1}H and ^{13}C NMR spectra for complexes **1**–**7** were fully consistent with their [FeCp(CO)$_2${M(X)R$_2$}] formulation. Because of the prochirality at the group 14 metal centre, the SiMe$_3$ groups are expected to be pair-wise diastereotopic; this was reflected in the ^{1}H and ^{13}C NMR signals for the SiMe$_3$ hydrogens or carbons, where two equal intensity singlets were observed for most members of the series. Other consequences of diastereotopicity for [FeCp(CO)$_2$-{Sn(F)R$_2$}] included the observation of (i) two ^{29}Si signals and (ii) distinct coupling constants from the SiMe$_3$ protons.

Electronic effects associated with the X group are not apparently transmitted to the iron through the intervening tin or lead atom in the $[FeCp(CO)_2\{Sn(X)R_2\}]$ series. Thus, in **1**–**7**, there was insensitivity as a function of X of: (i) ^1H NMR chemical shifts of the cyclopentadienyl protons (a variation of less than 0.2 ppm; Table 1), (ii) CO stretching frequencies (Table 1), and (iii) ^{57}Fe Mössbauer parameters (vide infra). Items (i) and (ii) indicate that although the iron centre in $[FeCp(CO)_2\{Sn(I)R_2\}]$ is more electron-rich than that in $[FeCp(CO)_2\{Pb(I)R_2\}]$, differences between the electronic properties of the $\bar{P}b(I)R_2$ and the $\bar{S}n(I)R_2$ ligand are small. By contrast, a comparison of $\nu(CO)$ (cm^{-1}) IR data for $[FeCp(CO)_2\{SnCl_3\}]$ (2045, 2005) [18], $[FeCp(CO)_2\{SnBr_3\}]$ (2040, 2002) [18], $[FeCp(CO)_2\{Sn(Cl)R_2\}]$ (2006, 1961), and $[FeCp(CO)_2\{Sn(Br)R_2\}]$ (2006, 1961) reveals that replacement of the bis(trimethylsilyl)methyl groups on tin by Cl or Br substantially reduces the electron density at iron.

The ^{119}Sn NMR chemical shifts for compounds **1**–**3** and **5**–**7** do vary with the identity of X in $[FeCp(CO)_2\{Sn(X)R_2\}]$, Table 1. Deshielding of the tin nucleus followed the trend $X = X > Cl > Br > OMe > I > H$. Within a series of closely related compounds, $\delta(^{119}Sn)$ values are expected to correlate with a parameter sensitive to the degree of Sn–X bond polarisation [20]. Thus, approximately linear plots of $\delta(^{119}Sn)$ were obtained against (a) the electronegativity differences (between tin and the attached atom of the X group) [20a], and (b) the pK_a's of $R'COOH$ for a series of organotin carboxylates $R_3Sn(COOR')$ [20b]. In Fig. 1 the value of $\delta(^{119}Sn)$ for $[FeCp(CO)_2\{Sn(X)R_2\}]$ is plotted against the appropriate [21] Taft σ_I constant for X, and there is some approximation to linearity; the positive slope indicates that the tin nucleus is increasingly deshielded as the inductive donor ability of the X group falls. Deviations greater than can be ascribed to experimental error are evident, notably for X = OMe; no doubt the tin chemical shift is sensitive to other factors such as the extent of X–Sn π-interaction [20]. The equation of the line $a[\delta(^{119}Sn)] + b$ for X = H, F, Cl, Br, or I has a correlation coefficient of 0.998. Correlations between $\delta(^{119}Sn)$ and Mössbauer parameters have been observed previously for the organotin chalcogenides $(Me_3Sn)_2X$ and $(Ph_3Sn)_2X$ (X = S, Se, or Te) [9], but we found no such relationship for the $[FeCp(CO)_2\{Sn(X)R_2\}]$ series.

The ^{119}Sn Mössbauer data for $[FeCp(CO)_2\{Sn(X)R_2\}]$ are summarised in Table 2, along with those for some related compounds. The magnitudes of the isomer shifts (IS) and quadrupole splittings (QS) indicate monomeric pseudo-tetrahedral structures for all the compounds in Table 2, as suggested previously for the organotin halides R_3SnX (X = Cl, Br, or I) [10]. This indication is further supported by comparison of the QS data for $[FeCp(CO)_2\{Sn(OMe)R_2\}]$ (**6**) (1.19 mms^{-1}) with $R'_3Sn(OMe)$ [e.g., R′, IS (mm s^{-1}), QS (mm s^{-1}): Et, 1.41, 2.86; Pr^n, 1.40, 2.81; Bu^n, 1.38, 2.92] [23]. The values for the latter are far greater than can be accounted for by the replacement of an alkyl group R′ by the moiety $[FeCp(CO)_2]$. We attribute this to the fact that **6** (like all the other compounds in Table 2) is a monomer, whereas the alkoxides R'_3SnOMe are associated.

The QS values for each of the halides $[FeCp(CO)_2\{Sn(X)R_2\}]$ (X = Cl, Br, or I) were closely similar, contrary to expectation. From the known partial QS values for the halides [25], the QS value for **3** (X = Cl) would have been expected to be ca. 0.34 mm^{-1} larger than that for **1** (X = I), whereas the observed difference was only 0.06 mms^{-1}, almost within experimental error. A similar effect was observed previously for R_3SnX [10], but not commented on. The probable cause is the steric pressure of

Table 2

^{119}Sn Mössbauer data for the series of compounds $[FeCp(CO)_2\{Sn(X)R_2\}]$ and related complexes

Compound	Isomer shift ^{a,b} (mm s^{-1})	Quadrupole Splitting ^{a} (mm s^{-1})	Linewidth (mm s^{-1}) ^{a}	Ref.
$[FeCp(CO)_2\{Sn(H)R_2\}]$ (7)	1.55	0.44	0.79, 0.89	This work
$[FeCp(CO)_2\{Sn(OMe)R_2\}]$ (6)	1.46	1.19	0.95, 0.90	This work
$[FeCp(CO)_2\{Sn(F)R_2\}]$ (5)	1.53	2.10	0.97, 0.84	This work
$[FeCp(CO)_2\{Sn(Cl)R_2\}]$ (3)	1.61	2.30	0.97, 0.97	This work
	1.54	2.37		10
$[FeCp(CO)_2\{Sn(Br)R_2\}]$ (2)	1.68	2.27	0.90, 0.90	This work
$[FeCp(CO)_2\{Sn(I)R_2\}]$ (1)	1.71	2.25	0.94, 0.90	This work
$[FeCp(CO)_2\{Sn(Me)R_2\}]$	1.48	0	1.34	10
$[FeCp(CO)_2\{SnMe_3\}]$	1.36	1.25		24
$[MoCp(CO)_3\{Sn(H)R_2\}]$	1.39	0.67		10
R_3SnCl	1.27	2.18		10
R_3SnBr	1.24	2.05		10
R_3SnI	1.48	2.24		10

^{a} ±0.02 mm s^{-1}. ^{b} Relative to SnO_2.

the bulky R and/or $[FeCp(CO)_2]$ groups on the Sn–X bond. Lengthening of the latter would decrease the effective electronegativity (x) of the halogen and diminish $\Delta x(= x_{Hal} - x_{Sn})$.

The systematic trend in the data for the halides $[FeCp(CO)_2\{Sn(X)R_2\}]$ did not extend to complex 5 (X = F), which had the smallest values of QS; on electronegativity grounds, this is unexpected. A similar trend had been noted previously in the series $Sn(X)[Co(CO)_4]_3$ and $Sn(X)[Co(CO)_3(PBu_3)]_3$ [26]. For the former, this was attributed to association in the fluoride involving unconventional *cis*-bridging, with one F^- ligand occupying an axial and the other an equatorial site in each trigonal bipyramidal $Sn(\mu\text{-}F)_2Co_3$ unit. In the $[FeCp(CO)_2\{Sn(X)R_2\}]$ series this explanation, involving increase in the coordination number of tin, is not plausible because

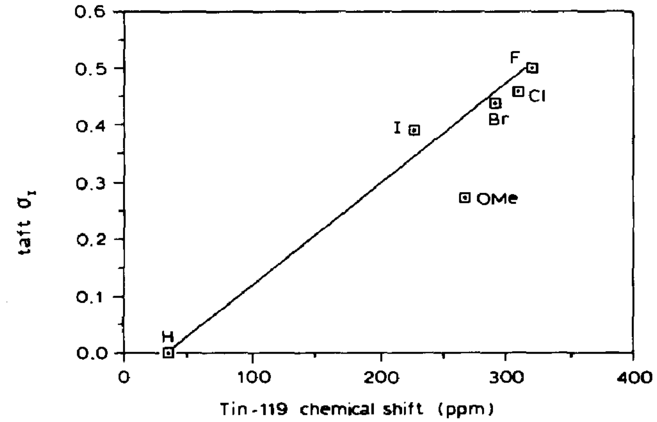


Fig. 1. Plot of ^{119}Sn NMR chemical shift (δ in ppm) vs Taft σ_I constant for the series $[FeCp(CO)_2\{Sn(X)R_2\}]$ (X, σ_I = H, 0.00; F, 0.50; Cl, 0.46; Br, 0.44; I, 0.39; OMe, 0.27).

of steric crowding. However, distortion from regular tetrahedral geometry, by an opening of the R–Sn–R angle, would be expected to decrease the contribution of the R groups to the electric field gradient (and hence to the QS) through the [3 $\cos^2 \theta - 1$] term.

For the hydride [FeCp(CO)$_2${Sn(H)R$_2$}], the value of QS is below the resolvable limit but is almost certainly real. The related derivative [MoCp(CO)$_3${Sn(H)R$_2$}] showed a splitting of 0.67 mm s^{-1} [10]; a change from a [MoCp(CO)$_3$] to a [FeCp(CO)$_2$] fragment would be expected to reduce the QS by about 0.2 mm s^{-1} on the basis of partial QS values [25].

The ^{57}Fe isomer shifts and quadrupolar splittings were found no to be sensitive to the identity of x in [FeCp(CO)$_2${Sn(X)R$_2$}]: the IS values were in the range 0.11–0.13 (±0.01) mm s^{-1}, and the QS values were in the range 1.76–1.81 (±0.01) mm s^{-1}. These data are in line with previous measurements for compounds of this type [27].

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