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ELECTROCHEMICAL REDUCTION OF TRANSITION METAL-SUBSTITUTED SILICON, GERMANIUM AND TIN DERIVATIVES

II *. IRON DERIVATIVES. SYNTHESIS OF DISTANNANES CONTAINING $Cp(CO)_2Fe$ GROUPS

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Summary

The electrochemical reduction of the complexes $Cp(CO)_2FeER_3$ (E = Si, Ge, Sn; R = alkyl, aryl) have been studied. The radical anion is formed, followed by rupture of the Fe–E bond with formation of the $Cp(CO)_2Fe^-$ anion. As expected, the relative ease of reduction of these derivatives was in the order Sn > Ge > Si. Some other complexes having Sn–Fe and Sn–Cl bonds have been studied: i.e. $[Cp(CO)_2Fe]_nPh_{3-n}SnCl$ ($n = 0$–3), $[Cp(CO)_2Fe]_2SnCl_2$. The exhaustive electrolysis of these derivatives provided the synthesis of four new distannanes, substituted with $Cp(CO)_2Fe$ groups.

Introduction

The electrochemical study of organometallic derivatives is of great interest, especially for the synthesis of new complexes by reduction or oxidation. The reduction of chloro- or bromo-silanes, -germanes and -stannanes, has been studied intensively [1–12] but derivatives of the Group IVb elements substituted with a transition metal moiety have been less studied. However some R_3EMLn (E = Sn, Pb; R = Me, Ph; MLn = $Fe(CO)_2Cp$, $Mn(CO)_5$, $Co(CO)_4$, $Mo(CO)_3Cp$) complexes were studied by Dessy et al. [13] and the same authors prepared $Cp(CO)_2FeEPPh_3$ (E = Sn, Pb) by the reaction of the electrochemically-generated anion with the corresponding chloro triphenyl compound [14] (eq. 1).

$$Cp(CO)_2Fe^- + Ph_3SnCl \rightarrow Ph_3SnFe(CO)_2Cp \qquad (1)$$

We are interested in the influence of transition metal groups on the reduction

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* For Part I see ref. 15.

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potentials of silicon, germanium and tin derivatives: (i) to compare the behaviour of silicon, germanium and tin analogs: (ii) to synthesize anions electrochemically; and (iii) to analyse the chemical generation of the radical anions formed in the preparation of new complexes.

The previous paper [15] dealt with complexes having at least one cobalt moiety at Si, Ge or Sn. This paper is concerned with complexes having Fe(CO)LCp moieties as the only transition metal group bonded to Si, Ge or Sn.

Results and discussion

We first studied the electrochemical reduction of the $Cp(CO)LFeSiR_3$ derivatives in order to analyse the electrochemical behaviour in two ways: (i) when the R group at silicon is changed from methyl to phenyl, and (ii) when the ligand, L = CO, is replaced by an arsine, a phosphine or a phosphite. Table 1 summarizes the results obtained with $Cp(CO)_2FeSiR_3$ ($R_3 = Me_3$, $MePh_2$, Ph_3) and $Cp(CO)LFeSiPh_3$ ($L = AsPh_3$, PPh_3, $P(OEt)_3$).

With the first family of complexes no significant change of the reduction potential was observed when the methyl group at silicon was replaced by a phenyl group: all three complexes showed a reversible, single-electron first wave.

However when the ligand, L = CO, is replaced by an arsine, phosphine or phosphite, two main changes were observed: (i) a change in the electron transfer process, which is reversible when L = CO, and irreversible with $L = AsPh_3$, PPh_3, $P(OEt)_3$; (ii) a change in the values of the reduction potential. As expected from the study of De Montauzon and Poilblanc on $[Co(CO)_3L]_2$ [16], a shift towards less negative potential was observed in the case of $AsPh_3$ and PPh_3, while a shift in the other direction was observed with $P(OEt)_3$.

Table 2 gives the electrochemical values for the reduction of the germanium derivatives $Cp(CO)_2FeGeR_3$ ($R_3 = Ph_3$, Et_3, MePh-1-Np). These compounds

TABLE 1

ELECTROCHEMICAL DATA FOR THE REDUCTION OF THE $Cp(CO)LFeSiR_3$ DERIVATIVES

Compounds	$-E_{1/2}$(V/SCE) [a]	Cyclic voltammetry $-E_p$ (V/SCE)		Reversibility [b]	Calc. [c] slope (mV)	Coulometry (F/mol)
		Red.	Ox. [d]			
$Cp(CO)_2FeSiMe_3$	$\underline{2.15}$	2.2	1.95	R	60	1
$Cp(CO)_2FeSiMePh_2$	$\underline{2.05}$, 2.9	2.6	1.5	R	64	> 2
$Cp(CO)_2FeSiPh_3$	$\underline{2.05}$, 2.9	2.2	1.6	R	60	> 2
$Cp(CO)AsPh_3FeSiPh_3$	1.7, 2.25, $\underline{2.8}$			I★		
$Cp(CO)PPh_3FeSiPh_3$	1.85, 2.3, $\underline{2.8}$			I★		
$Cp(CO)P(OEt)_3FeSiPh_3$	$\underline{2.2}$			I★	30	

[a] Results were obtained in dry DME with $n\text{-}Bu_4NClO_4$ as the electrolyte, working with a dropping and hanging drop mercury electrode for polarographic and cyclic voltammetry measurements, respectively. The potentials are given vs. a saturated calomel electrode (SCE). Principal waves are underlined. [b] R, reversible; I, irreversible; ★ sweep speed 100 mV s^{-1}. [c] Slope of the equation $E = f\left(\log \frac{i_D - i}{i}\right)$, coming from the Nernst equation $E = E^\circ + \frac{0.059}{n} \log \frac{ox}{red}$, which gave n, the number of electrons for an ideal solution. When $n = 1$, the slope is 0.059 V. [d] Sweep speed 3 V s^{-1}.

TABLE 2

ELECTROCHEMICAL DATA FOR THE REDUCTION OF THE $Cp(CO)_2FeGeR_3$ DERIVATIVES

Compound (yield)[a]	$-E_{1/2}$ (V/SCE)[b]	Reversibility[b]	Cyclic voltammetry[b] $-E_p$ (V/SCE) Red.	Ox.
$Cp(CO)_2FeGePh_3$[c] (33%)	$\underline{1.95}$	R	2.2	1.8
$Cp(CO)_2FeGeEt_3$ (46%)	$\underline{2.15}$	R	2.2	2.0
$Cp(CO)_2FeGeMePh$-1-Np (44%)	$\underline{2.05}$, 2.5	R	2.4	2.0

[a] Prepared by the electrolysis of $Cp(CO)_2FeCl$ in the presence of the corresponding bromogermane. [b] See footnotes to Table 1. Cyclic voltammetry, sweep speed 3 V s^{-1}. [c] Slope of the Nernst equation, 62 mV.

showed a reversible wave near −2.0 V (vs. SCE). This wave was for a single-electron in the case of $Cp(CO)_2FeGePh_3$ (slope of the Nernst equation, 62 mV). This fact can reasonably be extended to the derivatives $Cp(CO)_2FeGeR_3$ with $R_3 = Et_3$ or MePh-1-Np. The values obtained for silyl (cf. Table 1) and germyl derivatives (cf. Table 2) are very similar: one reversible wave near −2V (vs. SCE). They can also be compared with the value obtained under the same conditions with $Cp(CO)_2FeSnPh_3$ (−1.95 V vs. SCE) (Dessy et al. [13] found −2.6 V vs. Ag/Ag^+ which corresponds to −2 V vs. SCE). It can be inferred that the mechanism of the reduction process is the same for these silyl, germyl and stannyl derivatives: i.e. Fe–E bond rupture leading to the $Cp(CO)_2Fe$ anion (Scheme 1).

SCHEME 1

$$Cp(CO)_2FeER_3 \overset{1e^-}{\rightleftharpoons} [Cp(CO)_2FeER_3]^{-\cdot}$$

$$\rightarrow Cp(CO)_2Fe^- + R_3E^{\cdot}$$

$$\hookrightarrow \tfrac{1}{2}R_3EER_3$$

$$(E = Si, Ge, Sn)$$

A second class of iron complex having a Si–Cl bond was studied; these derivatives gave a shift of the first wave towards less negative potentials and a change from a reversible to an irreversible process. Table 3 summarizes the results obtained with

TABLE 3

ELECTROCHEMICAL DATA FOR THE REDUCTION OF THE $[Cp(CO)_2Fe]_nSiH_mX$ DERIVATIVES

Compound	$-E_{1/2}$(V/SCE)[a]	Reversibility[a] 1st wave	Calc.[a] slope (mV)
$Cp(CO)_2FeSiHCl_2$	1.2[b], $\underline{1.6}$, $\underline{2.10}$	I	61
$[Cp(CO)_2Fe]_2SiHCl$	$\underline{1.8}$, $\underline{2.03}$, 2.3	I	42
$[Cp(CO)_2Fe]_2SiCl_2$	$\underline{1.7}$, $\underline{2.0}$	I	42

[a] See footnotes to Table 1. [b] This small wave belongs to the HCl released by partial hydrolysis of this very moisture sensitive compound.

$Cp(CO)_2FeSiHCl_2$, $[Cp(CO)_2Fe]_2SiHCl$ and $[Cp(CO)_2Fe]_2SiCl_2$. The cyclic voltammograms of the last two derivatives showed an oxidation peak at −1.1 V (vs. SCE), which corresponded to the second wave. This oxidation peak may be attributed to the oxidation of the $Cp(CO)_2Fe^-$ anion as previously observed by Miholová and Včlek (−1.18 V vs. SCE, THF as solvent) [17] (eq. 2).

$$Cp(CO)_2Fe^- \xrightarrow{-1\,e^-} Cp(CO)_2Fe^{\cdot} \xrightarrow{1/2Hg} 1/2[Cp(CO)_2Fe]_2Hg \qquad (2)$$

A partial Si–Fe bond rupture was then observed, near −2 V (vs. SCE).

It is well known that Ph_3SnCl easily gives the $Ph_3Sn^{\cdot}$ radical and it was shown that electrochemistry was a good route for the preparation of the distannane starting from Ph_3SnCl [18] (Scheme 2).

SCHEME 2

$$Ph_3SnCl \xrightarrow{+1e^-} [Ph_3SnCl]^{-\cdot} \rightarrow Ph_3Sn^{\cdot} + Cl^-$$
$$\hookrightarrow 1/2Ph_3SnSnPh_3$$

This reaction should allow the synthesis of new distannanes substituted with transition metal groups. These derivatives are difficult to prepare chemically and only one family of derivatives is known: viz. $\{[(CO)_5Mn]_2SnX\}_2$ (X = H, Cl, Br). They were prepared by Noltes et al. according to eq. 3 [19].

$$Cp_2Sn + HMn(CO)_5 \rightarrow \{[(CO)_5Mn]_2SnH\}_2 \qquad (3)$$

We have studied the tin derivatives $[Cp(CO)_2Fe]_nPh_{3-n}SnCl$ (n = 0–3) and $[Cp(CO)_2Fe]_2SnCl_2$. Table 4 gives the electrochemical values of these compounds and Table 5 lists the products obtained by controlled potential electrolysis. They showed two principal waves near −1.5 and −2.3 V (vs. SCE); the replacement of the first phenyl in Ph_3SnCl by a $Cp(CO)_2Fe$ moiety greatly affected the first wave potential (−0.9 to −1.5 V), but further replacement of phenyl groups by $Cp(CO)_2Fe$ did not alter the reduction potential. The mechanism of the electron transfer of the

TABLE 4

ELECTROCHEMICAL DATA FOR THE TIN DERIVATIVES

Compound	$-E_{1/2}$(V/SCE) [a]	Reversibility 1st wave [a]	Calc. slope (mV) [a]
Ph_3SnCl	$\underline{0.9}$, $\underline{2.3}$	R	
$[Cp(CO)_2Fe]Ph_2SnCl$	$\underline{1.5}$, 1.95, $\underline{2.3}$	I	80 [b]
$[Cp(CO)_2Fe]_2PhSnCl$	$\underline{1.45}$, 2.1, $\underline{2.4}$	I	50 [c]
$[Cp(CO)_2Fe]_3SnCl$	$\underline{1.4}$, 2.0, $\underline{2.4}$		63 [d]
$[Cp(CO)_2Fe]_2SnCl_2$	$\underline{1.2}$, $\underline{1.4}$, 1.9, 2.3	I	[e]

[a] See footnotes to Table 1. Cyclic voltammetry, sweep speed 100 mV s^{-1}. [b] Coulometry measurement, 1.1 ± 0.2 F mol^{-1}. [c] Small oxidation peak at −1.1 V in the cyclic voltammogram. [d] Cyclic voltammogram: red. −1.55//ox. −1.1 V. Coulometry measurement 1.2 ± 0.2 F mol^{-1}. [e] The waves at −1.9 V and −2.3 V are ill-defined; cyclic voltammetry gave oxidation peaks at −1.2 V which corresponded to the 3rd or 4th waves and −0.55 V which was associated with the 1st wave.

TABLE 5

PRODUCTS OBTAINED BY POTENTIAL ELECTROLYSIS

Compound	Potential electrolysis (V/SCE)	Product	Yield (%)
$[Cp(CO)_2Fe]SnPh_2Cl$	−1.5	$\{[Cp(CO)_2Fe]SnPh_2\}_2$	47
$[Cp(CO)_2Fe]_2SnPhCl$	−1.45	$\{[Cp(CO)_2Fe]_2SnPh\}_2$	7
$[Cp(CO)_2Fe]_3SnCl$	−1.4	–	
$[Cp(CO)_2Fe]_2SnCl_2$	−1.25	$\{[Cp(CO)_2Fe]_2SnCl\}_2$	31
$[Cp(CO)_2Fe]_2SnCl_2$ $+ Ph_3SnCo(CO)_4$	−1.15	$Ph_3SnSn(Cl)[Fe(CO)_2Cp]_2$	25

first wave for Ph_3SnCl is reversible but became irreversible as soon as a $Cp(CO)_2Fe$ group replaced a phenyl group. The second principal reduction wave is not affected by the change from phenyl to $Cp(CO)_2Fe$. The polarogram of $[Cp(CO)_2Fe]_2SnCl_2$ showed two principal waves (−1.2 and −1.4 V vs. SCE) plus two ill-defined waves (−1.9 and −2.3 V vs. SCE). Cyclic voltammetry indicated two oxidation peaks: one at −1.2 V (vs. SCE), which corresponded to the third or fourth peak and suggested tin–iron bond rupture leading to $Cp(CO)_2Fe^-$ (vide supra); the second oxidation peak at −0.55 V (vs. SCE) came from the first reduction step. These two facts suggested that the first reduction step might result in tin–chloride bond rupture and allow the preparation of the corresponding distannane (vide infra).

When $[Cp(CO)_2Fe]Ph_2SnCl$ was electrolysed at −1.5 V (vs. SCE) an orange solid precipitated and after 1 Faraday per mol gave the distannane $\{[Cp(CO)_2Fe]Ph_2Sn\}_2$; the formation of this product is explained by the dimerisation of the tin radical (Scheme 3).

SCHEME 3

$$\begin{tikzcd}
Cp(CO)_2FePh_2SnCl \arrow[r, "+1e"] & \{[Cp(CO)_2Fe]Ph_2SnCl\}^{-\cdot} \arrow[d] \\
1/2\{[Cp(CO)_2Fe]Ph_2Sn\}_2 & {[Cp(CO)_2Fe]Ph_2Sn^{\cdot} + Cl^-} \arrow[l]
\end{tikzcd}$$

However a competitive process would be the formation of the mercury derivative, followed by its decomposition (Scheme 4), as proposed by Feasson and Devaud [11] and by Blaukat and Neumann [20] for the reduction of Ph_3SnCl at a mercury pool, in methanol as solvent.

SCHEME 4

$$2[Cp(CO)_2Fe]Ph_2Sn^{\cdot} \rightarrow 2[Cp(CO)_2Fe]Ph_2Sn^{\cdot}\ (\text{adsorbed})$$

$$\xrightarrow{Hg} 2[Cp(CO)_2Fe]Ph_2SnHg^{\cdot} \rightarrow$$

$$\{[Cp(CO)_2Fe]Ph_2Sn\}_2Hg + Hg$$

$$\xrightarrow{\qquad\qquad} \{[Cp(CO)_2Fe]Ph_2Sn\}_2 + Hg$$

Both mechanisms may occurred in the preparation of the distannane but the dimerisation of the radical is certainly the main route.

When $[Cp(CO)_2Fe]_2PhSnCl$ was electrolysed at the first-wave potential, the corresponding distannane was obtained in only 7% yield. With $[Cp(CO)_2Fe]_3SnCl$ the electrolysis did not gave any isolable and identifiable product. But with $[Cp(CO)_2Fe]_2SnCl_2$ the electrolysis gave $\{[Cp(CO)_2Fe]_2SnCl\}_2$ in 31% yield (cf. Table 5). Furthermore the first reduction potentials of $[Cp(CO)_2Fe]_2SnCl_2$ (-1.2 V vs. SCE) and $Ph_3SnCo(CO)_4$ (-1.0 V vs. SCE) (see Part I) are close enough to allow the possible synthesis of the unsymmetrical distannane according to Scheme 5. The electrolysis of a 1 : 1 mixture of both reactants gave the unsymmetrical distannane $Ph_3SnSn(Cl)[Fe(CO)_2Cp]_2$ in 25% yield (cf. Table 5). The same distannane was obtained by electrolysis at -1.15 V (vs. SCE) with $Ph_3SnCo(CO)_4$ replaced by Ph_3SnCl ($E_{1/2}$ -0.9 V vs. SCE).

SCHEME 5

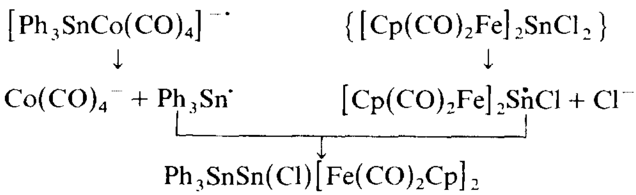
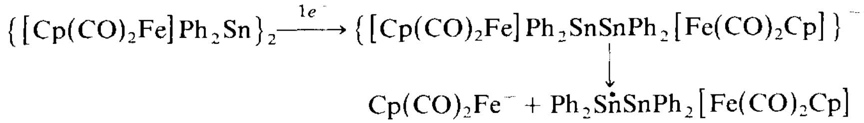


Table 6 gives the electrochemical values obtained with the distannane substituted by $Cp(CO)_2Fe$ moieties. These four complexes have several waves, the first of which, between -1.35 and -1.65 V (vs. SCE) shows an oxidation peak near -1.1 V (vs. SCE) in cyclic voltammetry. As shown before (vide supra) this value corresponds to the oxidation of the $Cp(CO)_2Fe^-$ anion. Accordingly, the first reduction wave of these four distannanes corresponded to the rupture of one tin–iron bond, leading to the $Cp(CO)_2Fe^-$ anion, as pictured in Scheme 6.

SCHEME 6



The results show that electrochemical reduction of $Cp(CO)_2FeER_3$ ($E = Si$, Ge, Sn; $R =$ alkyl, aryl) leads to the Fe–E bond cleavage with formation of the $Cp(CO)_2Fe^-$ anion. As expected, the ease of reduction of $Cp(CO)_2FeER_3$ was in

TABLE 6

ELECTROCHEMICAL DATA FOR THE SUBSTITUTED DISTANNANES

Compound	$-E_{1/2}$ (V/SCE) [a]	Calc. slope (mV) [a]
$\{[Fe(CO)_2Cp]SnPh_2\}_2$	1.65, 2.0, 2.4	53
$\{[Fe(CO)_2Cp]_2SnPh\}_2$	1.7, 2.2, 2.5	72
$Ph_3SnSn(Cl)[Fe(CO)_2Cp]_2$	1.4, 2.3	
$[\{Fe(CO)_2Cp]_2SnCl\}_2$	1.35, 2.25	

[a] See footnotes to Table 1. Cyclic voltammetry, sweep speed 100 mV s^{-1} All these complexes had an oxidation peak at -1.1 V, corresponding to the first wave.

the order Sn > Ge > Si. When the complexes had both Sn–Fe and Sn–Cl bonds, the first reduction wave corresponded to the tin–chlorine bond rupture. The exhaustive electrolysis of these derivatives allowed the synthesis of four new distannanes substituted with iron groups.

Experimental

General

All manipulations were carried out under nitrogen using Schlenk techniques. All solvents were dried and degassed before use. IR spectra were recorded on a Perkin–Elmer 298 spectrophotometer with CaF_2 cells and various solvents. Proton NMR spectra were recorded on a Varian EM 360 or EM 390 instrument with TMS as internal standard. Mass spectra were recorded on a JEOL JMS-D 100 spectrometer. Mass spectra simulation programme was written by J.M. Thierry (C.E.N. Cadarache, France). Melting points were determined in capillaries using an oil circulating apparatus and are uncorrected.

Ph_3SnCl was purchased from Fluka; $[Fe(CO)_2Cp]_2$, from Pressure Chemicals, was recrystallized from CH_2Cl_2-pentane. Ph_2SnCl_2 [21], Et_3GeBr [22], Ph_3GeBr [23], MePh-1-NpGeBr [24], $Cp(CO)_2FeCl$ [25], $[Fe(CO)_2Cp]SnCl_3$ [26], $Ph_3SnCo(CO)_4$ [27], $[Fe(CO)_2Cp]_2SnCl_2$ [28], $[Fe(CO)_2Cp]_3SnCl$ [29], $[Fe(CO)_2Cp]SnPh_2Cl$ [30], $[Fe(CO)_2Cp]_2SnPh_2$ [31], $Cp(CO)_2FeSiMe_3$ [32], $Cp(CO)_2FeSiMePh_2$ [33], $Cp(CO)_2FeSiPh_3$ [33], $Cp(CO)(AsPh_3)FeSiPh_3$ [34], $Cp(CO)LFeSiPh_3$ ($L = PPh_3$, $P(OEt)_3$) [33], $Cp(CO)_2FeSiHCl_2$ [35], $[Cp(CO)_2Fe]_2SiHCl$ [36], $[Cp(CO)_2Fe]_2SiCl_2$ [36] were prepared according to published methods.

Electrochemical measurements

1,2-Dimethoxyethane (DME), Baker Analysed reagent, was refluxed for 1 day over $LiAlH_4$ and distilled under nitrogen before use. Tetrabutylammonium perchlorate (TBAP), Fluka A.G. purum, was crystallized from water and dried under vacuo with P_2O_5 for one week.

Potentials were measured against an aqueous saturated calomel electrode (SCE), separated from the non-aqueous solution by a salt bridge containing the same solvent (DME) and supporting electrolyte (0.1 *M* TBAP) as the solution being studied in order to prevent water diffusion in the medium. The working electrodes, besides a platinum wire anode, were a dropping mercury cathode (t 0.75 s, h 37 cm) in the polarographic measurements, a hanging mercury cathode in the case of voltammetry, and a mercury pool cathode in the controlled potential electrolysis. The supporting electrolyte concentration in the electrolysis experiment was 0.2 *M* in TBAP. These electrolysis were carried out in a Moinet's cell [37] with anodic and cathodic compartments separated by a sintered glass disc (porosity 4). Tetrabutylammonium chloride was used in the anodic compartment to prevent diffusion from cathode into the anode.

Polarograms were recorded using a Tacussel PRT 10-0.5 L potentiostat associated with a pilot UAP 3. A 10 mV s^{-1} speed was used. Voltammograms were generated using a Tacussel GSTP 3 unit and recorded with an EPL 2 instrument of the same manufacturer, or with a Tektronix oscilloscope R 5103 N single beam storage D11. A Tacussel PRT 100-1 X potentiostat associated with a Tacussel IG-5-L N integrator was used in controlled potential electrolysis. All experiments were performed at room temperature under nitrogen. The concentrations range was 1–5 × 10^{-3} *M* for polarographic measurements and 0.8–1.4 × 10^{-1} *M* for electrolysis.

Preparation of $[Fe(CO)_2Cp]_2SnPhCl$

(a) A solution of 7.5 ml PhLi (0.7 *M*) in ether was added to 2.7 g (5 mmol) $[Fe(CO)_2Cp]_2SnCl_2$ dissolved in 120 ml of toluene and cooled to −60 °C. The mixture was allowed to warm to room temperature and the solvent removed. The residue was extracted with hot toluene, filtered and methanol added. 1.6 g (55% yield) of orange crystals of $[Cp(CO)_2Fe]_2SnPhCl$ were obtained after cooling at −20 °C and recrystallization from toluene/methanol (50/30). M.p. 118–120 °C, ^1H NMR, δ (ppm): 7.65, 7.25 (m, 5H), 4.80 (s, 10H); IR (Nujol) $\nu(C{\equiv}O)$ (cm^{-1}): 2020s, 1195m, 1970s, 1940s. Mass spectrum, *m/e* 586, 558, 530, 502, 474, 409, 353, 318, which fit $\{[Fe(CO)_2Cp]_2SnPhCl\}^+$ and the successive loss of 4 CO, Cp, Fe and Cl.

(b) The method described is an improvement over that published by Sasse and Ziegler [38] (1.5% yield). A mixture of 1.315 g (2.1 mmol) $[Fe(CO)_2Cp]_2SnPh_2$ and 1.140 g (2.1 mmol) $[Fe(CO)_2Cp]_2SnCl_2$ was heated at the melting point (165 °C) for 2 days. The residue was extracted with toluene, filtered, and an equal volume of MeOH added. Upon cooling the mixture to −20 °C, 610 mg (25% yield) of orange crystals were obtained, m.p. 123 °C, NMR ($CDCl_3$) identical with that from method (a) plus one impurity at 5.03 ppm (s).

Preparation of $\{[Fe(CO)_2Cp]Ph_2Sn\}_2$

A solution of 610 mg (1.26 mmol) of $Cp(CO)_2FePh_2SnCl$ in 12 ml of 0.2 *M* TBAP in DME was electrolysed under nitrogen at −1.5 V in a Moinet's cell. A yellow-orange solid precipitated. After 93 C (76% yield) the solid was filtered and recrystallized from toluene to give 260 mg (46% yield) of yellow-orange crystals of the expected distannane, m.p. 222–225 °C, ^1H NMR (C_6D_6), δ (ppm): 8.0 (m, 4H), 7.3 (m, 6H), 4.1 (s, 5H), IR (toluene) $\nu(C{\equiv}O)$ (cm^{-1}): 2000m, 1990s, 1945m, 1935sh. Found: C, 50.73; H, 3.36; Fe, 12.42. $C_{38}H_{30}O_4Fe_2Sn_2$ calcd.: C, 50.90; H, 3.42; Fe, 12.36%. Mass spectrum: *m/e* 816 $\{[Fe(CO)Cp]Ph_2{}^{119}Sn^{119}SnPh_2[FeCp]\}^+$, 723 $\{[FeCp]Ph_2{}^{119}Sn^{119}SnPh_2Fe\}^+$, 451, 395, 351 $\{[Fe(CO)_2Cp]Ph_2{}^{120}Sn\}^+$ and successive loss of 2 carbonyl groups.

Preparation of $\{[Fe(CO)_2Cp]_2PhSn\}_2$

A solution of 630 mg of $[Cp(CO)_2Fe]_2SnPhCl$ (1.07 mmol) in 12 ml of 0.2 *M* TBAP in DME was electrolysed under nitrogen at −1.5 V in a Moinet's cell. The solution turned deep red, after 120 C the solution was transferred to a Schlenk tube, the solvent removed and the residue extracted with 3 ml of toluene. The toluene extract was chromatographed under nitrogen, on a 5 cm silicic acid column with toluene as the solvent. The red solution obtained was concentrated and cooled to −20 °C to give 40 mg (0.036 mmol) (7% yield) of red crystals of the title compound, m.p. 254–258 °C, ^1H NMR ($CDCl_3$), δ (ppm): 7.15 (m, 5H), 4.4 (s, 10H), IR (toluene), $\nu(C{\equiv}O)$ (cm^{-1}): 1995s, 1975vs, 1930s, 1900m. Mass spectrum: *m/e* 551, 523, 495, 467 and 439 $\{[Fe(CO)_2Cp]_2{}^{120}SnPh\}^+$ and successive loss of 4 carbonyls.

Electrolysis of $[Fe(CO)_2Cp]_3SnCl$

A solution of 700 mg (1.02 mmol) of $[Cp(CO)_2Fe]_3SnCl$ in 12 ml 0.2 *M* TBAP in

DME was electrolysed at −1.5 V. After 107 C, the solution was transferred to a Schlenk tube and the same volume of Et_2O added to precipitate the TBAP. The mixture was filtered, the solvent evaporated and the residue extracted with toluene. Attempts at crystallization using toluene, hexane or mixtures of these solvents, gave starting material as the only identifiable product.

Electrolysis of $[Cp(CO)_2Fe]_2SnCl_2 + Ph_3SnCo(CO)_4$ *mixture*

A solution of 410 mg (0.75 mmol) $[Cp(CO)_2Fe]_2SnCl_2$ and 390 mg (0.75 mmol) $Ph_3SnCo(CO)_4$ in 12 ml DME was electrolysed at −1.15 V. The electrolysis was stopped after 80 C. The red solution was transferred to a Schlenk tube and an equal volume of Et_2O added to precipitate the TBAP. Filtration, evaporation of the solvents and addition of MeOH to the residue gave 163 mg of an orange solid, $Ph_3SnSn(Cl)[Fe(CO)_2Cp]_2$ (25%); (concentration of the solution gave 33 mg of recovered $[Fe(CO)_2Cp]_2SnCl_2$). Recrystallization from MeOH gave orange-red crystals, m.p. 165–170 °C, IR (toluene) $\nu(C\equiv O)$ (cm^{-1}): 2025s, 1990s, 1965s, 1945sh; ^1H NMR (acetone-d_6), δ (ppm): 7.8 and 7.4 (m, 15H), 4.85 (s, 10H). Found: C, 44.72; H, 2.93; Cl, 4.15. $C_{32}H_{25}ClFe_2O_4Sn_2$ calcd.: C, 44.60; H, 2.90; Cl, 4.45. Polarogram: see Table 6.

Electrolysis of the $[Fe(CO)_2Cp]_2SnCl_2 + Ph_3SnCl$ *mixture*

A solution of 400 mg (0.73 mmol) of $[Fe(CO)_2Cp]_2SnCl_2$ and 285 mg (0.74 mmol) Ph_3SnCl [illegible] 12 ml DME was electrolysed at −1.1 V. The reaction stopped after 75 C and the deep-red solution was transferred to a Schlenk tube and an equal volume of Et_2O added to precipitate the TBAP. Filtration, evaporation of the solvents under vacuo, and addition of MeOH gave an orange-red solid. ^1H NMR (aceton-d_6), δ (ppm): 7.8 (m), 7.4 (m), 5.2 (s) and 4.9 (s); which corresponds to a 2 : 1 mixture of $[Fe(CO)_2Cp]_2SnCl_2$ and $Ph_3SnSn(Cl)[Fe(CO)_2Cp]_2$.

Preparation of $R_3GeFe(CO)_2Cp$ ($R_3 = Et_3$, Ph_3, *MePh-1-Np*)

A solution of 2.2 mmol $Cp(CO)_2FeCl$ and 2.2 mmol R_3GeX (i.e. Et_3GeCl, Ph_3GeBr, or MePh-1-NpGeBr) in 12 ml of 0.2 *M* TBAP in DME were electrolysed under nitrogen at −1.7 V in a Moinet's cell using 200 C. The solution was transferred to a Schlenk tube, the solvent was removed and the residue dissolved in a mixture of hexane and dichloromethane. The solution was chromatographed on acid alumina with a mixture of hexane-CH_2Cl_2 (80 : 20). Concentration of the solution gave the crystalline $R_3GeFe(CO)_2Cp$ derivative. Yields were 33% $R_3 = Ph_3$, 46% $R_3 = Et_3$ and 44% $R_3 =$ MePh-1-Np. NMR and IR spectra were identical to authentic samples prepared by the substitution of X by $Fe(CO)_2Cp^-$ in R_3GeX: $R_3 = Et_3$ [39]; $R_3 = Ph_3$ [40] and $R_3 =$ MePh-1-Np [41] (m.p. 125.5–127 °C dec.; $\nu(C\equiv O)$ (cyclohexane): 1948 and 1995 cm^{-1}).

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