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

I. COBALT OR COBALT AND IRON COMPLEXES

C. COMBES, R.J.P: CORRIU, G. DABOSI, B.J.L. HENNER and M. MARTINEAU

Laboratoire des Organométalliques et laboratoire d'Electrochimie organique, laboratoire associé au CNRS n°349, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex (France)

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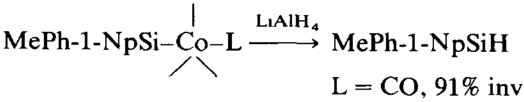
Summary

The complexes $Ph_3ECo(CO)_3L$ (E = Si, Ge; L = CO, PPh_3, $P(OPh)_3$) have been studied by electrochemistry. The reduction potential of these derivatives is less affected by the nature of the ligand L than in the case of $[Co(CO)_3L]_2$. The electrochemical reduction of the tin complexes $[Co(CO)_4]_n[Fe(CO)_2Cp]_{3-n}SnCl$ (n = 1–3) showed that the formation of the radical anion occurred with tin–cobalt rather than tin–chloride bond rupture. Electrolysis of these tin derivatives did not give any distannane containing transition metal groups. However it can be noted that the $Fe(CO)_2Cp$ group stabilized these tin complexes.

Introduction

In a previous paper we have shown that the stereochemistry of cleavage of the Co–E bond (E = Si, Ge) was strongly dependent on the nature of the ligand attached to the cobalt atom [1]; the replacement of a carbonyl group by a less electron-attracting ligand changed the stereochemistry of the silicon–cobalt bond cleavage from inversion to retention of the configuration; for example, when L is an electron-attracting group (L = CO) inversion of configuration is observed. On the other hand with σ-donating groups (phosphines, carbenes), retention of configura-



$$\text{MePh-1-NpSi–}\overset{|}{\text{Co}}\text{–L} \xrightarrow{\text{LiAlH}_4} \text{MePh-1-NpSiH}$$

L = CO, 91% inversion
L = PPh_3, 68% inversion
L = P(cyclohexyl)$_3$, 58% retention

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tion occurred. The electronic character of the Si–Co (or Ge–Co) bond changed with the nature of the ligand bonded to the cobalt atom in the apical position opposite to the Si–Co (or Ge–Co) bond.

We thought that electrochemistry could give us interesting information on the Co–E bond (E = Si, Ge, Sn), according to the nature of the ligand at cobalt, and we have studied the electrochemical behaviour of several cobalt derivatives.

In the first part of this work the electrochemical reduction values for the series of compounds $Ph_3ECo(CO)_3L$ (E = Si, Ge, Sn; L = CO, PPh_3, $P(OPh)_3$) is presented.

In the second part, we studied the electrochemical behaviour of tin complexes containing both tin–cobalt and tin–chlorine bonds and also some with tin–iron bonds. We have considered the electrochemical reduction products and their chemical generation corresponding to the competition between Sn–Cl and Sn–Co bond breaking.

Results and discussion

Table 1 shows the half-wave reduction potentials ($E_{1/2}$) of the complexes $Ph_3ECo(CO)_3L$. The potential decreased in the order Sn ≫ Ge > Si, corresponding to the higher polarisability of the Co–E bond (E = Si, Ge, Sn) and the decreasing ease of reduction. The stannyl compounds are more easily reduced than their silyl or germyl analogs, and this fact is certainly due to the possible adsorption of these compounds on the mercury drop [2]. The same observation has been made in the case of triorgano halogeno compounds [3]:

$$\begin{array}{lclcl} Ph_3SnCl & \gg & Ph_3GeCl & > & Ph_3SiCl \\ (E_{1/2}\ -0.9\ V) & & (E_{1/2}\ -2.1\ V) & & (E_{1/2}\ -2.4\ V)(\text{vs. SCE}) \end{array}$$

For the same Group IV elements, the replacement of a carbonyl by a phosphine group on the cobalt atom gave a more negative potential for the first reduction wave.

TABLE 1

HALF-WAVE REDUCTION POTENTIALS OF THE COMPLEXES $Ph_3ECo(CO)_3L$

No.	Complex	$-E_{1/2}$ [a] (V)	1st wave slope [b] (mV)	E_{pa} [c] (V)
1	$Ph_3SiCo(CO)_4$	1.70 [d]	70	−1.2 +0.3
2	$Ph_3SiCo(CO)_3P(Ph)_3$	1.87 2.76	56	−1.3 +0.3
3	$Ph_3SiCo(CO)_3P(OPh)_3$	1.95 2.80	87	−1.1 +0.3
4	$Ph_3GeCo(CO)_4$	1.53	70	−1.1 +0.3
5	$Ph_3GeCo(CO)_3PPh_3$	1.78 2 78	68	−1.1 +0.4
6	$Ph_3GeCo(CO)_3P(OPh)_3$	1.85 2.83	70	−1.1 +0.4
7	$Ph_3SnCo(CO)_4$	1.0		
8	$Co_2(CO)_8$	0 3		+0 3

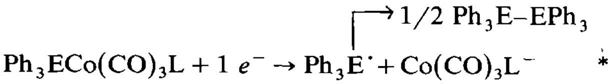
[a] Results are obtained in dry THF with $n\text{-}Bu_4NClO_4$ as electrolyte, with a dropping or hanging mercury electrode. The potentials are given vs. a saturated calomel electrode (SCE). [b] Slope of the equation $E = f(\log \frac{i_D - i}{i})$ (for an ideal reversible single-electron mechanism the slope is 59 mV.) [c] Voltammetric curves show the irreversibility of these reductions, but the presence of anodic peaks are noted here. [d] In anisole as solvent; the product is unstable in other solvents.

The effect of the nature of the ligand was similar to that obtained by other workers who studied the effect of the basicity of a ligand on the carbonyl stretching frequency [4], or on the half-wave reduction potential [5,6]. With $[Co(CO)_3L]_2$ and $Hg[Co(CO)_4]_2$, De Montauzon and Poilblanc [6] have shown that the increasing basicity of the ligand L gave a shift to more negative reduction potential. However the difference between the reduction potentials of compounds in which $L = PPh_3$ and $L = P(OPh)_3$, observed by these authors, is higher ($\Delta E_{1/2}$ 0.4 V) than that which we obtained with $R_3ECo(CO)_3L$ ($\Delta E_{1/2} < 0.1$ V). This difference would be explained by the occurence of two different reduction mechanisms:

(a) A two-electron reduction process, analogous to that found with $Co_2(CO)_8$ [7] was proposed in the case of the reduction of $[Co(CO)_3L]_2$ ($L = P(OPh)_3$, PPh_3, $P(OEt)_3$, PMe_3, PEt_3) by De Montauzon and Poilblanc [6]. These complexes are reduced in a potential range of -0.9 to -1.8 V vs. Ag/Ag^+ (which correspond to -0.4 to -1.3 V vs. SCE), according to the following mechanism:

$$[Co(CO)_3L]_2 + 2e^- \rightleftharpoons 2Co(CO)_3L^-$$

(b) On the other hand the $Ph_3ECo(CO)_3L$ complexes (E = Si, Ge) being studied are reduced at a very negative potential $-1.9 < E_{1/2} < -1.5$ V (vs. SCE) by an irreversible, single-electron process (cf. Table 1). Furthermore, these complexes present a second reduction wave near -2.7 V (vs. SCE), which is close to the phosphine reduction potential [8]. The following reduction scheme can be proposed:

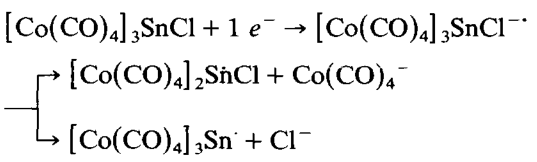


$$Ph_3ECo(CO)_3L + 1\ e^- \rightarrow \underset{\llcorner\rightarrow 1/2\ Ph_3E\text{–}EPh_3}{Ph_3E^{\cdot}} + Co(CO)_3L^- \quad *$$

$$Co(CO)_3L^- + 1\ e^- \xrightarrow[-2.7\ \text{V/SCE}]{} L^{-\cdot} + Co(CO)_3{}^-$$

The reduction potentials of $Ph_3ECo(CO)_3L$ (E = Si, Ge) (cf. Table 1) showed that with L = CO the complex accepted one electron more easily than the complex with $L = PPh_3$. Between these two derivatives, the electron environment is different enough to affect the stereochemistry of the Co–E bond rupture, as previously stated (vide supra).

In the second part of this work we studied the electrochemical behaviour of heteropolymetallic complexes containing a tin–chlorine and tin–cobalt or tin–iron bonds. These complexes correspond to the step-by-step replacement of a $Co(CO)_4$ group in $[Co(CO)_4]_3SnCl$ by a $Fe(CO)_2Cp$ moiety. They are good examples for the study of the competitive cleavage of Sn–Cl and Sn–$Co(CO)_4$ bonds (Scheme 1).



$$[Co(CO)_4]_3SnCl + 1\ e^- \rightarrow [Co(CO)_4]_3SnCl^{-\cdot} \begin{cases} \rightarrow [Co(CO)_4]_2Sn^{\cdot}Cl + Co(CO)_4{}^- \\ \rightarrow [Co(CO)_4]_3Sn^{\cdot} + Cl^- \end{cases}$$

SCHEME 1

This competition between tin–cobalt and tin–chloride bond rupture is suggested

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* Dessy et al. [7] proposed an anologous mechanism for the case of $Ph_3SnCo(CO)_4$.

by the close values of the reduction potentials observed with the following two compounds: (i) the reduction of $Ph_3SnCo(CO)_4$ (-1.0 V vs. SCE) (see Table 1), which led to rupture of the tin–cobalt bond; (ii) the reduction of Ph_3SnCl (-0.9 V vs. SCE) (see Table 2) which gave rupture of the tin–chlorine bond, leading to the stannyl radical which dimerised giving the distannane [9] (Scheme 2).

$$Ph_3SnCl \underset{-0\ 9\ V/SCE}{\overset{+1\,e^-}{\rightleftharpoons}} [Ph_3SnCl]^{-\cdot} \rightarrow Ph_3Sn^{\cdot} + Cl^-$$

$$\hookrightarrow 1/2\ Ph_3SnSnPh_3$$

SCHEME 2

The observed results are summarized in Table 2. The values for the first wave showed that the energy required for the one-electron reduction depended on the number of $Co(CO)_4$ groups in the molecule. The ease of reduction was found to be in the following order:

$$[Co(CO)_4]_3SnCl > [Co(CO)_4]_2[Fe(CO)_2Cp]SnCl > [Co(CO)_4][Fe(CO)_2Cp]_2SnCl.$$

The value of -0.7 V vs. SCE observed in the case of $[Fe(CO)_2Cp]$-$[Co(CO)_4][Ni(CO)Cp]SnCl$ showed that the replacement of $Co(CO)_4$ by a $Ni(CO)Cp$ group did not alter very much the reduction potential of the complex.

Table 2 also indicates that the first wave was a single-electron one (slope about 59 mV) and that all these complexes show an oxidation peak at $+0.3$ V.

The difference observed between the values of the first reduction wave of $[Co(CO)_4]_3SnCl$ (-0.3 V) and Ph_3SnCl (-0.9 V) suggest that the radical anion formed in both cases may evolve by different routes. The value of -0.3 V in the case of $[Co(CO)_4]_3SnCl$ is identical with the value observed by Dessy et al. in the case of the two-electron reduction of $Co_2(CO)_8$ leading to $Co(CO)_4^-$ [7] (-0.9 V vs. Ag/Ag^+ or -0.3 V vs.SCE).

$$Co_2(CO)_8 \xrightarrow[-0\ 9\ V\ vs\ Ag/Ag^+]{+2\,e} 2Co(CO)_4^-$$

This suggested that the one-electron reduction of $[Co(CO)_4]_3SnCl$ gave tin–cobalt rather than tin–chlorine bond rupture (see Scheme 1). The formation of $Co(CO)_4^-$

TABLE 2 [a]

HALF-WAVE REDUCTION POTENTIALS OF THE COMPLEXES

No.	Complex	$-E_{1/2}$ (V)	1st wave slope (mV)	E_{pa} (V)
9	Ph_3SnCl	$\underline{0.9}$ $\underline{2.3}$		
10	$[(CO)_4Co]_3SnCl$	$\underline{0.3}$	70 [b]	0.3 -0.05
11	$[(CO)_4Co]_2[Fe(CO)_2Cp]SnCl$	$\underline{0.65}$ 1.2 2.0	57	0.3 -0.05 (-0.15)
12	$[(CO)_4Co][Fe(CO)_2Cp]_2SnCl$	$\underline{0.9}$ 1.2 1.45 $\underline{1\ 9}$	55	0.3 -0.05 (-0.15)
13	$[(CO)_4Co][Fe(CO)_2Cp][Ni(CO)Cp]SnCl$	$\underline{0.7}$ 1.1 1.4	65	0 3 -0.05 (-0.7)

[a] Data obtained in the solvent DME, under the same condition as those given in Table 1. Principal waves are underlined. See footnotes to Table 1. [b] Coulometry: $1.2 \pm 0\ 2\ F\ mol^{-1}$.

was proved by two routes:

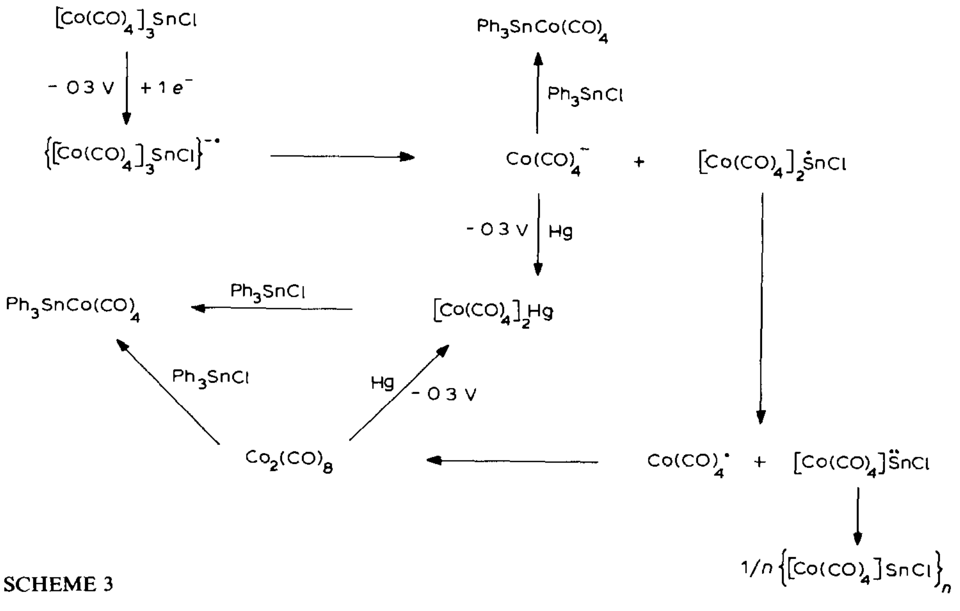
(a) The cyclic voltammetry of $[Co(CO)_4]_3SnCl$ (Fig. 1) showed an oxidation peak at +0.3 V (vs.SCE) which was also observed in the case of $Co_2(CO)_8$. This value corresponds to the oxidation of $Co(CO)_4^-$ to $Co(CO)_4^{\cdot}$, as found previously by Vlček [10] (+0.12 V vs. SCE with Pt electrode) and Gross et al. [11] (+0.2 V vs.SCE with Au electrode, in CH_3CN or propylene carbonate).

(b) The electrolysis of $[Co(CO)_4]_3SnCl$ at −0.3 V (vs.SCE) in the presence of an excess of Ph_3SnCl led to the formation of 1.3 mol (isolated) of $Ph_3SnCo(CO)_4$ per mol $[Co(CO)_4]_3SnCl$.

Scheme 3 gives the postulated mechanism for the reduction of $[Co(CO)_4]_3SnCl$ at −0.3 V (vs.SCE). The first step is the formation of the radical anion, which would be followed by rupture of the tin–cobalt bond, giving the $Co(CO)_4^-$ anion and the tin radical. The anion would react with Ph_3SnCl to give the substitution product, or with the mercury pool to give $Hg[Co(CO)_4]_2$, which could react further with Ph_3SnCl and so lead to $Ph_3SnCo(CO)_4$. The generation of $[Co(CO)_4]_2\dot{S}nCl$ through $Co(CO)_4^{\cdot}$ is a possible route suggested by the formation of 1.3 mol of $Ph_3SnCo(CO)_4$ per mol of $[Co(CO)_4]_3SnCl$. This means that the generated radical $[Co(CO)_4]_2SnCl^{\cdot}$ gives an active $Co(CO)_4$ group (radical or anion), which reacts with Ph_3SnCl to give the product $Ph_3SnCo(CO)_4$.

In agreement with these suggestions we note that $Ph_3SnCo(Co)_4$ is easily obtained by the chemical reaction of $Co_2(CO)_8$ on Ph_3SnCl in methanol [12]. The $[Co(CO)_4]_2Hg$ derivative may be prepared by electrochemical reduction of $Co_2(CO)_8$ at a mercury pool at −0.3 V (vs.SCE) [5]. A mixture of $[Co(CO)_4]_3SnCl$ and Ph_3SnCl, stirred at room temperature in DME, gave no reaction; this means that no chemical redistribution reaction occurred (vide infra).

These results may be extended to the complexes $[Co(CO)_4]_2[Fe(CO)_2Cp]SnCl$, $[Co(CO)_4][Fe(CO)_2Cp]_2SnCl$ and $[Co(CO)_4][Fe(CO)_2Cp][Ni(CO)Cp]SnCl$. These



SCHEME 3

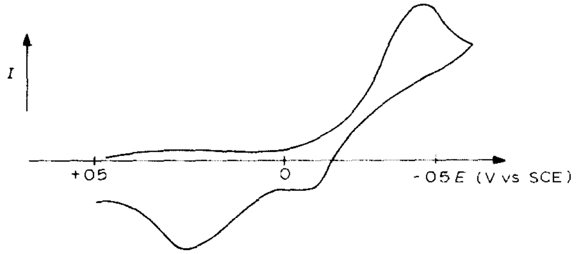


Fig. 1. Cyclic voltammogram of $[Co(CO)_4]_3SnCl$ in 0.1 *M* TBAP DME solution with a hanging mercury drop cathode. Scan rate 50 mV s^{-1}

complexes showed the oxidation peak for $Co(CO)_4^-$ between +0.3 and +0.2 V (vs.SCE) (see Table 2); however a fast chemical redistribution reaction was also observed between $[Co(CO)_4]_2[Fe(CO)_2Cp]SnCl$ or $[Co(CO)_4][Fe(CO)_2Cp]_2SnCl$ and Ph_3SnCl, according to the following equations:

$$[Co(CO)_4]_2[Fe(CO)_2Cp]SnCl + Ph_3SnCl \rightarrow Ph_3SnCo(CO)_4 + [Co(CO)_4][Fe(CO)_2Cp]SnCl_2$$

$$[Co(CO)_4][Fe(CO)_2Cp]_2SnCl + Ph_3SnCl \rightarrow Ph_3SnCo(CO)_4 + [Fe(CO)_2Cp]_2SnCl_2$$

These reactions make invalid the proof of the presence of $Co(CO)_4^-$ in the medium using Ph_3SnCl as reactant, but they show that the tin–cobalt bond is also more easy to break chemically than the tin–chloride bond in the complexes $[Co(CO)_4]_2[Fe(CO)_2Cp]SnCl$ and $[Co(CO)_4][Fe(CO)_2Cp]_2SnCl$. It is interesting to stress that the ease of rupture of the tin–cobalt bond depends on the number of iron groups in the molecule for $[Co(CO)_4][Fe(CO)_2Cp]_2SnCl$ gave the faster reaction with Ph_3SnCl, while $[Co(CO)_4]_3SnCl$ gave no reaction at all:

$$[Co(CO)_4]_3SnCl \ll [Co(CO)_4]_2[Fe(CO)_2Cp]SnCl < [Co(CO)_4][Fe(CO)_2Cp]_2SnCl$$

Exhaustive electrolysis of $[Co(CO)_4]_3SnCl$, $[Co(CO)_4]_2[Fe(CO)_2Cp]SnCl$ and $[Co(CO)_4][Fe(CO)_2Cp]_2SnCl$ at the first-wave potential did not give any isolable product. This fact can be explained by the rapid decomposition of the species which is formed during electrolysis.

Conclusion

The particular behaviour of complexes like $Ph_3ECo(CO)_3L$ (L = carbonyl, phosphine, phosphite; E = Si, Ge, Sn) towards the electronic effect of ligands is explained by the occurence of a reduction mechanism different from that observed for $[Co(CO)_3L]_2$. The electrochemical reduction study of tin complexes substituted with chlorine, cobalt and iron groups showed that the generation of the radical anion formed occurred through tin–cobalt rather than tin–chloride bond rupture. Exhaustive electrolysis of these complexes did not give any distannanes substituted with transition metal moieties. However it can be noted that the $Cp(CO)_2Fe$ group stabilized these complexes.

Experimental

General

All manipulations were carried out under nitrogen using Schlenk techniques. All solvents were dried and degassed before use. IR spectra were recorded in various solvents on a Perkin–Elmer 298 spectrophotometer with CaF_2 cells. ^1H 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. The mass spectra simulation programme was written by J.M. Thierry (C.E.N. Cadarache, France). M.p. were determined in capillaries using an oil circulating apparatus, and are uncorrected.

Ph_3SnCl was purchased from Fluka and $Co_2(CO)_8$ from Strem Chemicals; $[Fe(CO)_2Cp]_2$, from Pressure Chemicals, was recrystallized from CH_2Cl_2-pentane. $Ph_3SiCo(CO)_4$ [13], $Ph_3SiCo(CO)_3PPh_3$ [14], $Ph_3SiCo(CO)_3P(OPh)_3$ [1], $Ph_3GeCo(CO)_4$ [15], $Ph_3GeCo(CO)_3PPh_3$ [16], $Ph_3GeCo(CO)_3P(OPh)_3$ [16], $Ph_3SnCo(CO)_4$ [12], $[Fe(CO)_2Cp]SnCl_3$ [17], $[Fe(CO)_2Cp]_2SnCl_2$ [18], $[Co(CO)_4][Fe(CO)_2Cp]SnCl_2$ [19], $[Co(CO)_4][Fe(CO)_2Cp]_2SnCl$ [19], $[Co(CO)_4]_2[Fe(CO)_2Cp]SnCl$ [20], $[Co(CO)_4]_3SnCl$ [21] $[Co(CO)_4]$-$[Fe(CO)_2Cp][Ni(CO)Cp]SnCl$ [20] were prepared according to published methods.

Electrochemical measurements

1,2-Dimethoxyethane (DME), Baker Analysed reagent, was refluxed for one 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.

Potential 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 into 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 electrolyses were carried out in a Moinet's cell [22] 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 the 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 concentration range was $1-5 \times 10^{-3}$ *M* for the polarographic measurements and $0.8-1.4 \times 10^{-1}$ *M* for the electrolysis.

The identities of the products were confirmed by comparison with authentic samples.

Electrolysis of $[Co(CO)_4]_3SnCl$ *(**10**)*

Compound **10** (600 mg, 0.9 mmol) was added to a 0.2 *M* solution of TBAP in DME (12 ml) and electrolysed at −0.3 V. After completion of the reaction, the mixture was transferred to a Schlenk tube and an equal volume of ether added to precipitate the TBAP. The mixture was filtered and the solvent removed under vacuo. Several attemps at crystallization in toluene did not give any identifiable products.

Electrolysis of $[Co(CO)_4]_2[Fe(CO)_2Cp]SnCl$ *(**11**)*

Compound **11** (440 mg, 0.65 mmol) was added to a 0.2 *M* solution of TBAP in DME (12 ml) and electrolysed at −0.7 V. The reaction gave a red solution and stopped after the passage of 81 C. The polarogram of the solution had 3 waves, at −0.8, −1.15 and −1.35 V (vs.SCE). Column chromatography (acidic alumina, toluene) gave complete decomposition, and attempts at crystallization in toluene, hexane or mixtures of these solvents, did not give any identifiable products.

Electrolysis of $[Co(CO)_4][Fe(CO)_2Cp]_2SnCl$ *(**12**)*

Compound **12** (450 mg, 0.66 mmol) was added to a 0.2 *M* solution of TBAP in DME (12 ml) and electrolysed at −0.95 V. The reaction stopped after the passage of 50 C. The polarogram of the solution had 3 waves, at −1.2, −1.45 and −1.9 V (vs. SCE). Column chromatography (acidic alumina, CH_2Cl_2) did not give any identifiable products.

Electrolysis of $[Co(CO)_4]_3SnCl$ *(**10**) with* Ph_3SnCl *(**9**)*

Compound **10** (420 mg, 0.63 mmol) and **9** (740 mg, 1.92 mmol) were dissolved in 12 ml of a 0.2 *M* solution of TBAP in DME and electrolysed at −0.65 V. The reaction gave a red solution and stopped after the passage of 69 C. Column chromatography (acidic alumina, CH_2Cl_2) gave a light yellow solution. The solvent was removed to give 426 mg (0.83 mmol) of **7**, m.p. 109–119 °C, that is 1.3 mol of **7** per mol of **10**.

The polarogram and IR spectrum of a 1 : 1 mixture of **10** and Ph_3SnCl in DME indicated no change after 1.5 h.

Reaction of $Co_2(CO)_8$ *with* Ph_3SnCl *in DME*

The reaction is analogous to that in MeOH described previously [12]. $Ph_3SnCo(CO)_4$, m.p. 120–123 °C, as off-white crystals were obtained in 47% yield after two recrystallizations from hexane.

Reaction of $[Co(CO)_4]_2[Fe(CO)_2Cp]SnCl$ *(**11**) with* Ph_3SnCl *(**9**)*

Compounds **11** (15 mg, 22 μmol) and Ph_3SnCl (10 mg, 26 μmol) were dissolved in 1 ml DME and the reaction followed by IR spectroscopy. After 20 min the spectrum was analogous to that of a 1 : 1 mixture of $[Fe(CO)_2Cp][Co(CO)_4]SnCl_2$ and $Ph_3SnCo(CO)_4$.

Reaction of $[Co(CO)_4][Fe(CO)_2Cp]_2SnCl$ *(**12**) with* Ph_3SnCl *(**9**)*

Ph_3SnCl (113.4 mg, 0.20 mmol) and **12** (200 mg) were dissolved in 10 ml DME. After 5 min, the IR spectrum was identical with the spectrum of a 1 : 1 mixture of $[Fe(CO)_2Cp]_2SnCl_2$ and $Ph_3SnCo(CO)_4$ in DME. Evaporation of the solvent gave a yellow-orange solid. NMR (C_6D_6): δ 4.3 ppm (s,Cp). (c.f. $[Fe(CO)_2Cp]_2SnCl_2$ (C_6D_6): δ 4.3 ppm(s).

References

1 G. Cerveau, E. Colomer and R.J.P. Corriu, J. Organomet. Chem., 236 (1982) 33.
2 C. Feasson and M. Devaud, Bull. Soc. Chim. Fr., (1983) I-40.
3 R.J.P. Corriu, G. Dabosi and M. Martineau, J. Organomet. Chem., 188 (1980) 63.
4 M. Bigorgne, Bull. Soc. Chim. Fr., (1960) 1986.
5 G. Cardaci, S.M. Murcia and G. Paliani, J. Organomet. Chem., 77 (1974) 253.
6 D. de Montauzon and R. Poilblanc, J. Organomet. Chem., 104 (1976) 99.
7 R.E. Dessy, D.M. Weissman and R.L. Pohl, J. Am. Chem. Soc., 88 (1966) 5117.
8 K.S.V. Santhanam and A.J. Bard, J. Am. Chem. Soc., 90 (1968) 1118.
9 G.A. Mazzocchin, R. Seeber and G. Bontempelli, J. Organomet. Chem., 121 (1976) 55.
10 A.A. Vlček, Collect. Czech. Chem. Commun., 24 (1959) 1748; Chem. Listy, 52 (1958) 1460; A.A. Vlček, Z. Anorg. Chem., 298 (1959) 270.
11 A. Giraudeau, P. Lemoine, M. Gross and P. Braunstein, J. Organomet. Chem., 202 (1980) 455, and refs. cited therein.
12 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 6 (1967) 981.
13 A.J. Chalk and J.F. Harrod, J. Am. Chem. Soc., 89 (1967) 1640.
14 M.D. Curtis, Inorg. Nucl. Chem. Lett., 6 (1970) 859.
15 E. Colomer and R.J.P. Corriu, J. Organomet. Chem., 133 (1977) 159.
16 G. Cerveau, E. Colomer, R.J.P. Corriu and J.C. Young, J. Organomet. Chem., 205 (1981) 31.
17 R.C. Edmondson and M.J. Newlands, Chem. Ind. (London), (1966) 1888.
18 F. Bonati and G. Wilkinson, J. Chem. Soc. A, (1964) 179.
19 P. Hackett and A.R. Manning, J. Chem. Soc., Dalton Trans., (1974) 2257.
20 F.H. Carre, R.J.P. Corriu and B.J.L. Henner, J. Organomet. Chem., 228 (1982) 139.
21 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 5 (1966) 2222.
22 C. Moinet and D. Peltier, Bull. Soc. Chim. Fr., (1969) 690.