

A convenient electrosynthesis of new complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$ and their spectroscopic characterization

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Abstract

New complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$, which have been identified by FTIR, mass spectroscopy, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR, were obtained easily in high yield (70–80%) by electroreduction of a series of water-soluble or water-insoluble complexes $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]$. The mechanistic aspects of the synthesis are discussed.

Keywords: Tin; Cobalt; Phosphine; Water-soluble phosphines; Phosphine complexes; Electrochemistry

1. Introduction

We have recently reported the electrosynthesis and structure of a mixed tin–cobalt carbonyl compound $[\text{Sn}\{\text{Co}(\text{CO})_4\}_4]$ [1]. This compound has interesting catalytic properties in olefin hydroformylation, hydrolysis of propylene carbonate, consecutive double carbonylation and aldol condensation of organic halides, and isomerization of epoxides [2]. In an attempt to test related compounds as catalyst in homogeneous and in biphasic aqueous/organic media. We have undertaken the synthesis of phosphorus derivatives of $[\text{Sn}\{\text{Co}(\text{CO})_4\}_4]$ by using phosphines, phosphites and water-soluble phosphines which are currently attracting considerable attention [3]. Only one complex of this kind has already been synthesized, by Schmid and Etzrodt [4]. The product $[\text{Sn}\{\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3\}_4]$ was obtained by the reaction of $[\text{Sn}\{\text{Co}(\text{CO})_4\}_4]$ with triphenylphosphine.

In this work, we have chosen a different route to complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$ which is similar to the one we have used for synthesizing $[\text{Sn}\{\text{Co}(\text{CO})_4\}_4]$. This synthesis is based on the electroreduction of $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]$ using a tin anode.

2. Experimental section

All reactions were carried out under purified dinitrogen using standard inert-atmosphere techniques. Solvents were purified by conventional methods. Dicobaltoctacarbonyl (Strem Chemicals), tin anodes (Johnson Matthey) and tetrabutylammonium hexafluorophosphate (Fluka) were used without further purification. The hydrophobic phosphines were purchased from Aldrich and used as received. The trisodium (tris(3-sulfonato)phenyl)phosphine (TPPTS) and the (sodium(3-sulfonato)phenyl) diphenylphosphine (TP-PMS) were synthesized by the sulfonation of triphenylphosphine according to published procedures [5].

Infrared spectra were determined with a Nicolet 510 FT-IR spectrometer. Standard deviations of the repeated measurements were 0.05 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 25°C on a Brüker AC-300 spectrometer (121.49 MHz). Phosphorus-31 chemical shifts were referenced to external 85% H_3PO_4 . $^{119}\text{Sn}\{^1\text{H}\}$, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained at 25°C on a Brüker AM-400 NMR spectrometer at observation frequencies of 149.28, 400.13 and 100.61 MHz, respectively. ^{119}Sn chemical shifts were referenced to external $\text{Sn}(\text{CH}_3)_4$. Mass spectra were obtained on a MS-50 RF KRATOS apparatus using the fast atom bombardment technique (FAB, Ar, 8 keV);

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data were collected on a MCA (multichannel analysis) station with a resolution of 1500; nitrobenzylalcohol and/or trichlorobenzene were used as matrices. Cyclic voltammetry was performed on a 100-1X Solea-Tacusel potentiostat. CV curves were recorded on a Sefram TGM 101 X-Y recorder with a CV cell which functioned under dinitrogen. The working electrode consisted of a platinum disk (1 mm²). The counter electrode was a platinum gauze and the SCE reference electrode was separated from the catholyte by a glass frit. Elemental analyses were performed by Mikroanalytisches Labor Pascher.

2.1. Preparation of [Co₂(CO)₆(PR₃)₂] (PR₃ is a hydrophobic phosphine or phosphite)

These products were prepared as described in the literature [6]. For example, a mixture of 1.47 g (4.3 mmol) of [Co₂(CO)₈] and 2.67 g of P(OC₆H₅)₃ (8.6 mmol) in 50 ml of toluene was heated to reflux under dinitrogen for 3 h. The solution was concentrated in vacuo, and 3.48 g (3.8 mmol) of red [Co₂(CO)₆{P(OC₆H₅)₃}₂] were isolated by filtration. For selected spectroscopic data, see Table 1.

2.2. Preparation of [Co₂(CO)₆(TPPMS)₂]

A mixture of 0.31 g (0.91 mmol) of Co₂(CO)₈ and 0.6 g (1.64 mmol) of TPPMS in toluene (50 ml) was heated to reflux under dinitrogen for 60 min. After cooling, a brown-red precipitate was filtered off and washed with three 10-ml portions of toluene and dried under vacuum to give 0.75 g (0.74 mmol) of [Co₂(CO)₆(TPPMS)₂]. For electrochemical and ³¹P NMR data, see Table 1 FTIR (KBr, cm⁻¹): ν(CO) 1978 (sh), 1949

(vs), ν(SO) 1222 (sh), 1194 (m), 1038 (m). ¹H NMR δ (DMF-d₇): 7.4–8.1 (br m). ¹³C NMR δ (DMF-d₇): 202.91, 135.05, 134.42, 133.92, 133.49, 131.74, 130.93, 130.33, 129.63, 129.37, 129.17. MS/FAB⁻ (nitrobenzylalcohol/trichlorobenzene; *m/z*, relative intensity): 1014 (M, 15%), 991 (M – Na, 63%), 935 (M – Na – 2CO, 55%), 907 (M – Na – 3CO, 100%), 879 (M – Na – 4CO, 20%).

2.3. Preparation of [Co₂(CO)₆(TPPTS)₂]

This was prepared as described by Herrmann et al. [8]. For example, a toluene solution (10 ml) of 0.1 g (0.29 mmol) of [Co₂(CO)₈] and an aqueous solution (10 ml) of 0.4 g (0.7 mmol) of TPPTS were stirred under dinitrogen at room temperature during 12 h. During this time the aqueous phase gradually became red-brown. The aqueous layer was collected and washed with 2 × 5 ml of toluene. The water was removed under vacuum and 0.30 g (0.21 mmol) of brown-red [Co₂(CO)₆(TPPTS)₂] was isolated. For selected spectroscopic data, see Table 1.

2.4. Syntheses of complexes [Sn{Co(CO)₃PR₃}₄] where [PR₃ = (P(OC₆H₅)₃, P(OCH₃)₃, or P(CH₂CH₂-CH₂CH₃)₃)]

For example, [Co₂(CO)₆{P(OC₆H₅)₃}₂] (250 mg, 0.275 mmol), (NBu₄)(PF₆)₃ (10 mg, 0.025 mmol) and 25 ml of solvent (acetone) were introduced into an undivided glass cell, monitored with two electrodes (platinum cathode, tin anode). Electrolysis was performed at controlled current density (3 mA/cm²) until 1.4F/[Co₂(CO)₆{P(OC₆H₅)₃}₂] had passed. The solu-

Table 1
FTIR, ³¹P{¹H} NMR and electrochemical data for complexes [Co₂(CO)₆L₂]

No.	Complex	Electronic parameter χ ^j	FTIR ^a ν(CO) (cm ⁻¹)	³¹ P{ ¹ H} NMR δ (ppm)	Electroreduction E _c V (vs SCE)	Electrooxidation E _a V (vs SCE)
1	[Co ₂ (CO) ₈]	–	1831(vs), 1843(sh) 2020(vs), 2074(sh)	–	–0.50 ^b	0.20 ^b
2	[Co ₂ (CO) ₆ {P(OCH ₃) ₃ } ₂]	27	1951(vs)	173.4 ^c	–1.21 ^b	–0.18 ^b
3	[Co ₂ (CO) ₆ {P(OC ₆ H ₅) ₃ } ₂]	29	1967(vs), 1991(sh)	168.3 ^d	–0.90 ^b	0.04 ^b
4	[Co ₂ (CO) ₆ (PBu ₃) ₂]	5.25	1936(vs), 1963(sh)	52.2 ^d	–1.60 ^b	–0.51 ^b
5	[Co ₂ (CO) ₆ (TPPMS) ₂]	14.01 ^k	1949(vs), 1978(sh)	68.4 ^e	–0.95 ^f	–0.21 ^f
6	[Co ₂ (CO) ₆ (TPPTS) ₂]	15.55	1955(vs), 1987(sh)	67.1 ^g	–1 < ^{h,i}	–0.25 ^h

^a Carbonyl stretching frequencies in KBr.

^b Cyclic voltammetry in acetone.

^c NMR solvent, CD₃COCD₃.

^d NMR solvent, C₆D₅CD₃.

^e NMR solvent, DCON(CD₃)₂.

^f Cyclic voltammetry in DMF.

^g NMR solvent, D₂O.

^h Cyclic voltammetry in water.

ⁱ The signal is too close to the cathodic limit of the solvent.

^j Electronic character of the phosphorus ligand defined by Tolman [7].

^k Calculated electronic character [7].

tion was filtered and the filtrate was evaporated and dried under vacuum to give 0.19 g (0.098 mmol) of a reddish powder of $[\text{Sn}\{\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3\}_4]$ (72% yield). For spectroscopic data, see Table 2. MS/FAB⁺ (nitrobenzylalcohol/trichlorobenzene; m/z , relative intensity): 1478.8 (M - Co(CO)₃P(OC₆H₅)₃, 40%). The FAB⁺ spectrum displayed signals (isotopic ratios) which are characteristic of a compound containing one tin atom. Anal. Calc. for C₈₄H₆₀Co₄O₂₄P₄Sn: C, 52.22; H, 3.14; O, 19.88; P, 6.41. Found: C, 50.26; H, 3.52; O, 19.00; P, 6.53%. The oxygen was determined by pyrolysis in a graphite capsule at 2000–3000°C in vacuo, and the CO generated determined by an IR analyser.

2.5. Synthesis of complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$ ($\text{PR}_3 = \text{TPPMS}$ or TPPTS).

$[\text{Co}_2(\text{CO})_6(\text{TPPMS})_2]$ (325 mg, 0.32 mmol) and 25 ml of solvent (*N,N*-dimethylformamide) were introduced in an undivided glass cell, monitored with two electrodes (platinum cathode, tin anode). Electrolysis was performed under controlled intensity until 1.4F/ $[\text{Co}_2(\text{CO})_6(\text{TPPMS})_2]$ had passed. The solution was filtered and the filtrate was evaporated to dryness under vacuum to give 0.26 g (0.121 mmol) of $[\text{Sn}\{\text{Co}(\text{CO})_3\text{TPPMS}\}_4]$ (76% yield). For NMR data, see Table 2. FTIR (KBr, cm⁻¹): $\nu(\text{CO})$ 1999 (w), 1954 (vs), 1928 (sh) $\nu(\text{SO})$ 1223 (sh), 1196 (m), 1036 (m). MS/FAB⁻ (nitrobenzylalcohol; m/z , relative intensity): 2147.7 (M, 12%), 2121.8 (M - Na, 70%); 2103.3 (M - 2Na, 100%), 2080.3 (M - 3Na, 20%), 1784.6 (M - TPPMS, 60%). The FAB⁻ spectrum displayed signals (isotopic ratios) which are characteristic of a compound containing one tin atom.

This compound slowly decomposes in solution (8 days) presumably to give $[\text{Sn}\{\text{Co}(\text{CO})_3\text{TPPMS}\}_3][(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{C}_6\text{H}_4\text{SO}_3]$. FTIR (KBr, cm⁻¹): $\nu(\text{CO})$ 2011 (w), 1958 (vs), 1935 (sh) $\nu(\text{SO})$ 1229 (sh), 1222 (sh), 1198 (m), 1195 (m), 1036 (m). ³¹P{¹H} NMR (DMF-*d*): δ 59.4 [s + 2 satellites], 28.1 [s]. ¹¹⁹Sn{¹H}

NMR (DMF-*d*₇): δ 546 [quartet], ² $J(^{119}\text{Sn}-^{31}\text{P})$ 254 Hz; MS/FAB⁻ (nitrobenzylalcohol; m/z , relative intensity) 1997.8 (M, 23%), 1974.8 (M - Na, 80%), 1952.8 (M - 2Na, 100%), 1928.8 (M - 3Na, 30%). The FAB⁻ spectrum displayed signals (isotopic ratios) which are characteristic of a compound containing one tin atom.

The electroreduction of $[\text{Co}_2(\text{CO})_6(\text{TPPTS})_2]$ was carried out in water as described. The unstable $[\text{Sn}\{\text{Co}(\text{CO})_3\text{TPPTS}\}_4]$ observed by ³¹P{¹H} NMR spectroscopy (D₂O, δ 60.4 [s + 2 satellites], ² $J(^{119}\text{Sn}-^{31}\text{P})$ 152 Hz), was mainly decomposed during the electrolysis into Na₂[Sn{Co(CO)₃TPPTS]₃ [(NaSO₃C₆H₄)₂-P(O)(C₆H₄SO₃)]. FTIR (KBr, cm⁻¹): $\nu(\text{CO})$ 2012 (w), 1960 (vs); ³¹P{¹H} NMR (D₂O): δ 61.8 [s + 2 satellites], 35.9 [s]; ¹¹⁹Sn{¹H} NMR (D₂O): δ 542 [quartet], ² $J(^{119}\text{Sn}-^{31}\text{P})$ 255 Hz.

3. Discussion

3.1. Synthesis and characterization of precursors of $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]$

As described in the literature [6], treatment of dicobaltoctacarbonyl with a phosphine gives rise to the corresponding substituted compound $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]$ (see Section 2). For each complex, FTIR, ³¹P NMR and electrochemical data are given in Table 1. Of the species studied, $[\text{Co}_2(\text{CO})_6(\text{TPPMS})_2]$ has not yet been described. The FTIR and NMR data confirmed the expected similarity in structure to other known compounds.

Cyclic voltammetry of each of these complexes exhibited a two-electron-reduction wave corresponding to the formation of carbonylcobaltate anions and a one-electron wave due to the oxidative dimerization of these anions in the reverse scan [9]. The characteristic cyclic voltammogram for $[\text{Co}_2(\text{CO})_6\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$ is shown in Fig. 1.

The FTIR spectra of the precursors exhibit CO peaks in the region 1900–2000 cm⁻¹. As expected,

Table 2
FTIR, ³¹P{¹H} and ¹¹⁹Sn{¹H} NMR data for complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$

No.	Complex	FTIR ^a $\nu(\text{CO})$ (cm ⁻¹)	³¹ P{ ¹ H} NMR δ (ppm)	¹¹⁹ Sn{ ¹ H} NMR	
				δ (ppm)	² $J(^{119}\text{Sn}-^{31}\text{P})$ (Hz)
1	$[\text{Sn}\{\text{Co}(\text{CO})_4\}]$	2085(s), 2003(vs), 1978(m)	–	775.0	–
2	$[\text{Sn}\{\text{Co}(\text{CO})_3\text{P}(\text{OCH}_3)_3\}_4]$	1935(sh), 1962(vs), 2008(m)	168.6 ^c	738.3 ^c	286 ^c
3	$[\text{Sn}\{\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3\}_4]$	1956(sh), 1981(vs), 2021(m)	162.0 ^b	793.5 ^b	300 ^b
4	$[\text{Sn}\{\text{Co}(\text{CO})_3\text{PBu}_3\}_4]$	1917(sh), 1944(vs), 1989(m)	42.5 ^c	756.8 ^c	135 ^c
5	$[\text{Sn}\{\text{Co}(\text{CO})_3\text{TPPMS}\}_4]$	1928(sh), 1954(vs), 1999(w)	57.7 ^d	826.3 ^d	152 ^d

^a Carbonyl stretching frequencies in KBr.

^b NMR solvent CD₃COCD₃.

^c NMR solvent, C₆D₅CD₃.

^d NMR solvent, DCON(CD₃)₂.

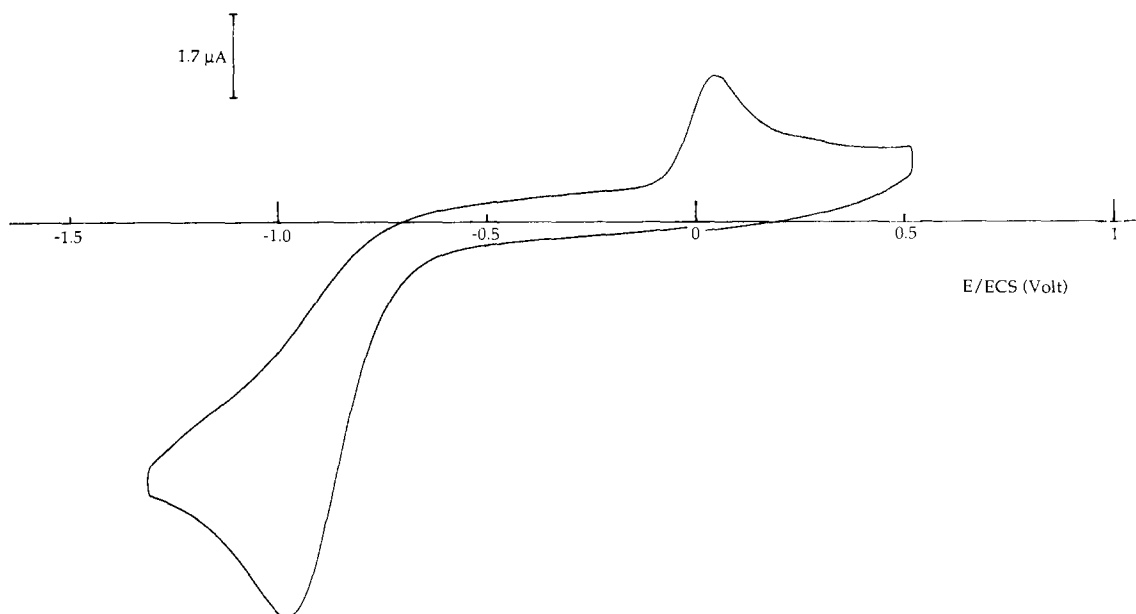
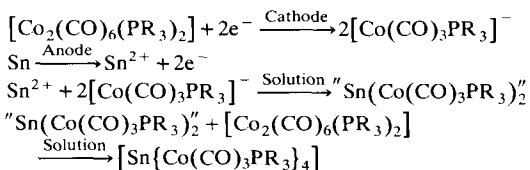


Fig. 1. Cyclic voltammogram of $[\text{Co}_2(\text{CO})_6\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2](10^{-3} \text{ M})$ in CH_3COCH_3 (30 ml) with $(\text{NBu}_4)\text{PF}_6$ (0.1 M), scan rate: 100 mV s^{-1} .

$\nu(\text{CO})$ decreases with increasing the σ donor power of the coordinated phosphine which can be measured by the electronic character χ defined by Tolman [7]. The position of TPPTS phosphine compared with triphenylphosphine is consistent with that reported by Hanson et al. [10]. The value of $\nu(\text{CO})$ of the $\text{P}(\text{OCH}_3)_3$ complex is abnormally low here, in the solid state but this was not found for the spectrum in solution. We have not found a solvent to dissolve both lipophilic and hydrophilic complexes. Such a solvent would allow us to obtain the FTIR spectra of each complex in solution and to classify soluble phosphines among lipophilic phosphines.

3.2. Synthesis and characterization of complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$

As already mentioned, the only complex of this kind described in the literature is $[\text{Sn}\{\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3\}_4]$, obtained from reaction of $[\text{Sn}\{\text{Co}(\text{CO})_4\}_4]$ with triphenylphosphine. From our standpoint, this route had three main drawbacks if it was to be extended to other types of PR_3 : (i) the low yield (< 15%); (ii) the long reaction time (6 days); and (iii) the poor solubility of $[\text{Sn}\{\text{Co}(\text{CO})_4\}_4]$ in most of organic solvents as well as total insolubility in aqueous phases, which prevented the synthesis of complexes with water-soluble phosphines.



Scheme 1. Proposed mechanism for the formation of $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$.

In this study, the complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$ were obtained easily by electroreduction of $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]$ in a 30-ml electrochemical cell, although they can be obtained on a bigger scale without any problem.

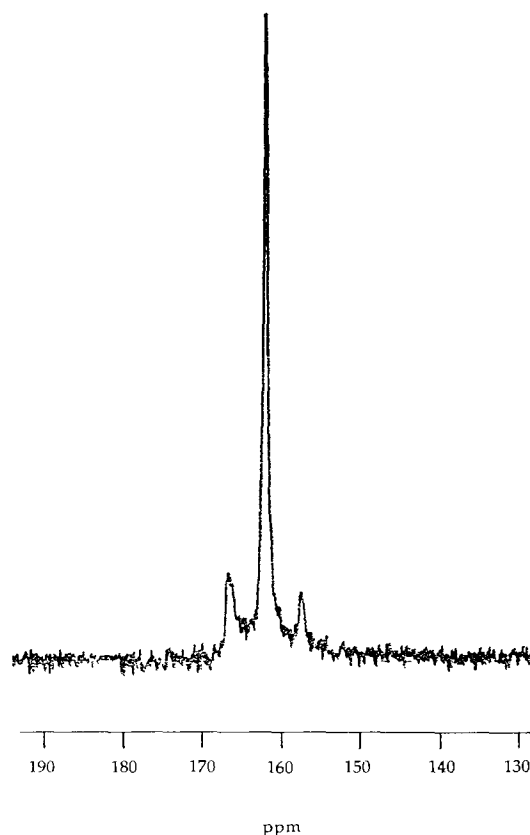


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Sn}\{\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3\}_4]$ in CD_3COCD_3 at 25°C .

The complexes $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]$ were reduced in a polar solvent, allowing their dissolution and the electrolyses were performed in an undivided cell with a sacrificial tin anode until 1.4 F/mol had passed.

The mechanism involved was the same as that described in the case of $[\text{Sn}\{\text{Co}(\text{CO})_4\}_4]$. Carbonylcobaltate anions were produced at the cathode by reduction of $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]$. Concomitantly, the tin anode underwent an oxidation leading to the formation of the assumed intermediate $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_2]$ which could react in solution with the dicobalt compound to form the required tin–cobalt product (Scheme 1).

The complexes were obtained in good yield (70–80%), except with TPPTS. The complex $[\text{Sn}\{\text{Co}(\text{CO})_3\text{TPPTS}\}_4]$ was too unstable in the electrolysis solution to be isolated. The same phenomenon was observed with TPPMS, but the change was far slower (8 days, checked by ^{31}P NMR spectroscopy). From the data collected on water-soluble complexes, it appears that substitution of one cobalt moiety $\text{Co}(\text{CO})_3\text{PR}_3$ by a sulfonato group of an oxidized phosphine was involved (see Section 2).

All complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$ exhibited in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra a central peak with two satellites as broad shoulders, due to the $^{31}\text{P}-^{119}\text{Sn}/^{117}\text{Sn}$ coupling (Fig. 2). The accurate value for $^2J(\text{Sn}/\text{P})$ was obtained from the well-resolved quintets in the $^{119}\text{Sn}\{^1\text{H}\}$ spectrum where the neighbouring ^{59}Co does not influence the Sn nucleus, as shown for compounds $[(\text{CH}_3)_3\text{SnCo}(\text{CO})_3\text{PR}_3]$ (Fig. 3) [11].

4. Conclusion

We have demonstrated that the electroreduction of complexes $[\text{Co}_2(\text{CO})_6(\text{PR}_3)_2]$ in the presence of tin anode is a general and convenient way to synthesize the complexes $[\text{Sn}\{\text{Co}(\text{CO})_3\text{PR}_3\}_4]$ in high yields. At present the value of these new complexes in olefin hydroformylation and epoxide isomerization is being studied.

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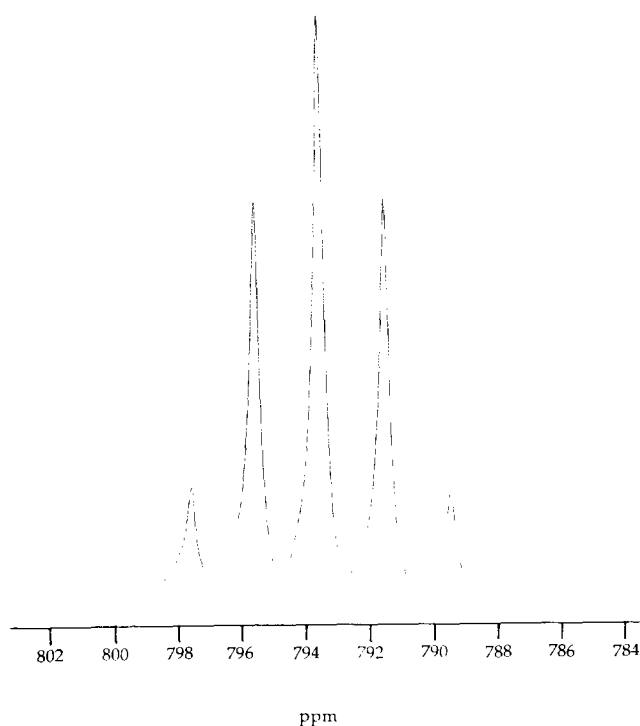


Fig. 3. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $[\text{Sn}\{\text{Co}(\text{CO})_3\text{P}(\text{OC}_6\text{H}_5)_3\}_4]$ in CD_3COCD_3 at 25°C.