

THE PREPARATION AND PHYSICAL PROPERTIES OF SOME IRON-TIN COMPOUNDS

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SUMMARY

The preparation of $\text{CpFe}(\text{CO})_2\text{SnPh}_n\text{Cl}_{3-n}$ ($n=0, 1, 2, 3$) by the reaction $\{\text{Na}[\text{CpFe}(\text{CO})_2] + \text{Ph}_n\text{SnCl}_{2-n} \rightarrow\}$ are reported and their IR, NMR, and mass spectra discussed.

INTRODUCTION

The use of sodium dicarbonyl- π -cyclopentadienylferrate in the synthesis of compounds of the type $\text{CpFe}(\text{CO})_2\text{M}^{\text{IV}}\text{R}_3$ has been known for several years since Gorsich first used it to prepare $\text{CpFe}(\text{CO})_2\text{SnPh}_3$ ^{1,2}. However, the preparation of the other compounds in the series $\text{CpFe}(\text{CO})_2\text{SnPh}_n\text{Cl}_{3-n}$ ($n=0-2$) by this technique has not previously been reported.

One of us briefly reported the preparation of $\text{CpFe}(\text{CO})_2\text{SnCl}_3$ and $\text{CpFe}(\text{CO})_2\text{SnPhCl}_2$ by the novel reaction³:



A variety of other methods of preparing $\text{CpFe}(\text{CO})_2\text{SnCl}_3$ has been used: $[\text{CpFe}(\text{CO})_2]_2\text{SnCl}_2 + \text{SnCl}_4$ (ref. 4), $\text{CpFe}(\text{CO})_2\text{SnPh}_3 + \text{HCl}$ (ref. 1), $\text{CpFe}(\text{CO})_2\text{HgCl} + \text{SnCl}_2$ (ref. 5), $\text{CpFe}(\text{CO})_2\text{X} + \text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{X}=\text{I}$, ref. 6 and $\text{X}=\text{Cl}$, ref. 4).

DISCUSSION

We find that sodium dicarbonyl- π -cyclopentadienylferrate^{2,7} readily reacts with a 1/1 molar ratio of the corresponding chloro-tin compound in tetrahydrofuran solution in an inert atmosphere. The sodium chloride is filtered and the product easily crystallises from methylene chloride/petroleum ether or ethanol to yield well-formed yellow to red crystals in reasonable yields (32-60%).

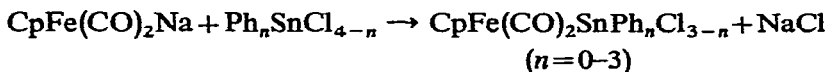


TABLE I

THE IR SPECTRA OF $\text{CpFe}(\text{CO})_2\text{SnPh}_n\text{Cl}_{3-n}$ (KBr Disc)

Assignment	$\text{CpFe}(\text{CO})_2\text{SnCl}_3$	$\text{CpFe}(\text{CO})_2\text{SnPhCl}_2$	$\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$	$\text{CpFe}(\text{CO})_2\text{SnPh}_3$
$\nu(\text{C-H})\text{C}_5\text{H}_5$	3114 w	3115 w	3108 w	3121 vw
$\nu(\text{C-H})\text{C}_6\text{H}_5$	{ 3099 (sh)	{ 3098 (sh) 3076 vw 3033 vw	{ 3055 w 3021 w	{ 3064 w
$\nu(\text{CO})$	{ A' 2051 vs 2039 (sh) A'' 1989 vs 1965 w	{ 2024 vs 2015 (sh) 1965 vs	{ 2006 vs 1999 vs 1956 vs 1926 w 1874 vw	{ 1993 vs 1988 vs 1939 vs 1929 vs 1900 vw 1573 vw 1477 w 1426 m 1412 w
	1426 m 1417 m	1479 w 1426 m 1416 w	1477 w 1428 m 1412 w 1331 vw 1301 vw 1262 vw 1191 vw 1159 vw	1295 vw 1256 vw 1183 vw 1070 w
	1014 vw 1001 vw	1069 w 1023 vw 997 w	1069 w 1022 vw 997 w 912 vw 871 vw	1067 w 1021 w 998 w 873 vw 857 vw
$\delta(\text{C-H})\text{C}_5\text{H}_5$	862 m	858 w 837 vw	850 m 837 (sh)	844 m 834 w
$\delta(\text{C-H})\text{C}_6\text{H}_5$	{	{ 728 m 693 w	{ 732 m 697 m 654 vw	{ 728 s 698 s
$\delta(\text{M-C-O})$ region	{ 608 m 577 s 557 m	{ 618 m 588 s 573 m	{ 627 m 588 s 578 s	{ 635 m 588 s
$\nu(\text{M-C})$ region	{ 497 w	{ 463 w 443 m	{ 514 w 458 vw 447 m 443 m	{ 524 w 517 w 460 vw 450 m 443 w 437 w
$\nu(\text{Sn-Cl})$	342 m 319 s	379 vw 312 s 254 w	392 vw 299 vw 290 vw 250 m	351 w 303 vw 290 vw 253 m

TABLE 2

THE m.p., $\nu(\text{CO})$ (IN CH_2Cl_2 SOLUTION) AND τ VALUES (IN CDCl_3 SOLUTION) FOR $\text{CpFe}(\text{CO})_2\text{SnPh}_n\text{Cl}_{3-n}$

Compound	m.p. (°C)	$\nu(\text{CO})$ A' (cm^{-1})	$\nu(\text{CO})$ A'' (cm^{-1})	$\tau(\text{C}_5\text{H}_5)$	$\tau(\text{C}_6\text{H}_5)$
$\text{CpFe}(\text{CO})_2\text{SnCl}_3$	159-160	2046	2007	4.74	
$\text{CpFe}(\text{CO})_2\text{SnPhCl}_2$	116-117	2029	1984	4.87	ca. 2.4
$\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$	100-101	2010	1961	5.07	ca. 2.6
$\text{CpFe}(\text{CO})_2\text{SnPh}_3$	139-141	1993	1942	5.21	ca. 2.6

These compounds form a useful series in which the effect of replacing a phenyl group by a chlorine atom can be examined using physical methods, notably IR and NMR spectroscopy. Parts of the IR spectra of the compounds $\text{CpFe}(\text{CO})_2\text{-SnCl}_3$ and -SnPh_3 have been studied, especially in the $\nu(\text{CO})$ region, by several workers^{3,4,6-12}. However the complete spectra of these compounds in the region $4000\text{-}250\text{ cm}^{-1}$ have not previously been reported. The spectra were taken as KBr discs and are tabulated in Table 1. The $\nu(\text{CO})$ frequencies were also measured in CH_2Cl_2 solution (Table 2). The expanded scale facility on the instrument was utilized for the measurements of $\nu(\text{CO})$ with calibration provided by carbon monoxide or atmospheric absorptions.

The binary carbonyl stretching vibrations⁸ expected around 4000 cm^{-1} were either extremely weak or beyond the limits of the instrument. The carbonyl stretching vibrations show an approximately constant difference between each of the compounds in the series (Fig. 1). The increase in frequency on replacing a phenyl group by a chlorine atom has been interpreted as being due to the greater π -bonding of -SnCl_3 compared with -SnPh_3 ⁸. However, other workers believe that it is predominantly an induction effect on a very polarisable σ bond¹⁰. The $\nu(\text{M-C})$ and $\delta(\text{M-C-O})$ occur around $400\text{-}700\text{ cm}^{-1}$ (ref. 9). The 4 expected $\delta(\text{MCO})$ are believed to occur at higher

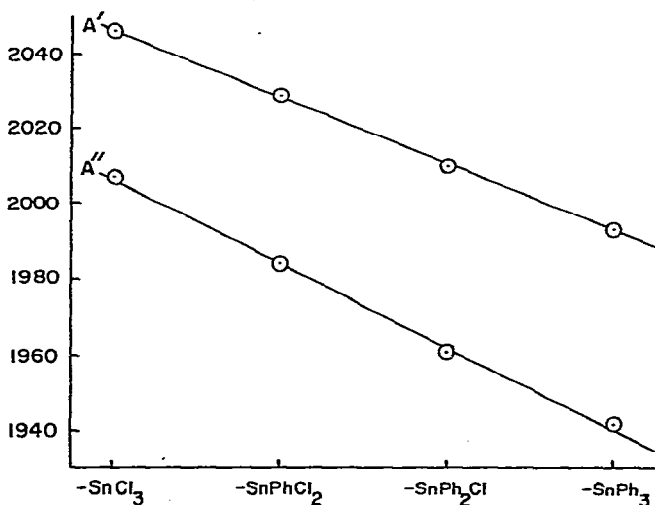


Fig. 1. Variation of $\nu(\text{CO})$ in CH_2Cl_2 solution with substituents on tin in the compounds $\text{CpFe}(\text{CO})_2\text{SnPh}_n\text{Cl}_{3-n}$. Ordinate: $\nu(\text{CO})$ (cm^{-1}).

frequency ($550\text{--}650\text{ cm}^{-1}$) than the 2 expected $\nu(\text{M-C})$ modes ($440\text{--}550\text{ cm}^{-1}$). The spectra of several simple phenyl tin compounds have been analysed and several bands characteristic of the phenyl group have been tabulated¹³. Most of these are observed with $\text{CpFe}(\text{CO})_2\text{SnPh}_{3-n}\text{Cl}_n$, though the intensities of the absorptions, as expected, increase with the number of phenyl groups in the molecule.

One feature of the IR spectra of cyclopentadienyl compounds which seems to have been overlooked or ignored by most workers is the variation in the CH deformation mode at ca. 850 cm^{-1} [$\delta(\text{CH})$ of the cyclopentadienyl group]. As with the $\nu(\text{CO})$, the $\delta(\text{CH})$ increases in the series $-\text{SnCl}_3 > -\text{SnPh}_3$ and thus it seems reasonable to suppose that the CH and CO bonds are subject to similar electronic influences. The chemical shifts of π -cyclopentadienyl compounds have been shown to have a linear relationship to the $\nu(\text{CO})$ frequency for first row transition elements¹⁴. If this shift is primarily due to a through bond interaction or if in similar compounds any other ring current effects¹⁵ can be ignored, then the chemical shift and $\delta(\text{CH})$ would be expected to be directly related to each other as shown in Fig. 2*. The τ values are tabulated in Table 3.

The mass spectra were obtained using the direct insertion probe at temperatures of $100\text{--}140^\circ$ and an ionising beam of 70 eV . The spectra ($m/e > 56$) are tabulated in Table 3. The spectrum of $\text{CpFe}(\text{CO})_2\text{SnPh}_3$ compares favorably with the reported spectrum¹⁹. As with many carbonyl complexes the parent ion is relatively weak and fragment ions form the base peak. An interesting feature of the spectra of the chlorine-containing compounds is the presence of peaks at m/e greater than the parent ion and also of greater abundance than the parent. This appears to indicate that catalytic

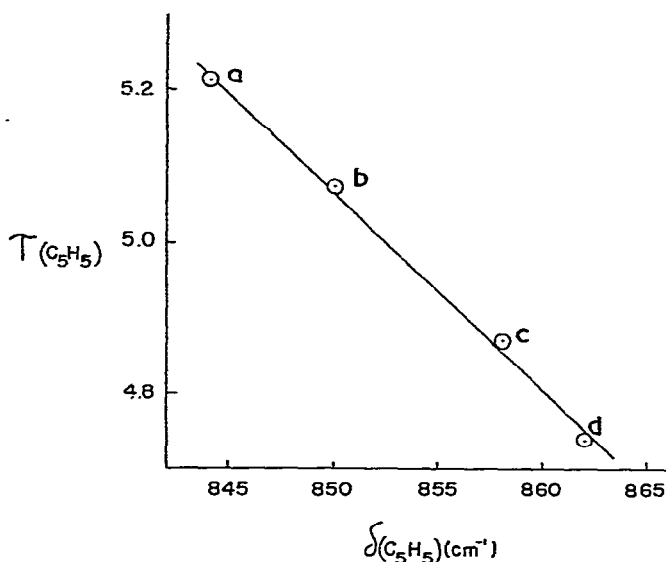


Fig. 2. Plot of $\delta(\text{C}_5\text{H}_5)$ (KBr disc) against $\tau(\text{C}_5\text{H}_5)$ (CDCl_3 soln.) for $\text{CpFe}(\text{CO})_2\text{SnPh}_n\text{Cl}_{3-n}$. a: $\text{CpFe}(\text{CO})_2\text{SnCl}_3$; b: $\text{CpFe}(\text{CO})_2\text{SnPhCl}_2$; c: $\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$; d: $\text{CpFe}(\text{CO})_2\text{SnPh}_3$.

* A referee has pointed out that comparison of $\delta(\text{CH})$ from solution spectra with τ would be better than the comparison of $\delta(\text{CH})$ from KBr discs with τ as shown here.

TABLE 3 MASS SPECTRA OF $\text{CpFe}(\text{CO})_2\text{SnPh}_n\text{Cl}_{3-n}$

$\text{CpFe}(\text{CO})_2\text{SnCl}_3$, inlet temp. 140°			$\text{CpFe}(\text{CO})_2\text{SnPhCl}_2$, inlet temp. 100°		
<i>m/e</i>	Abund.(%)	Assignment	<i>m/e</i>	Abund.(%)	Assignment
436	0.22		506	0.83	P + Cl, CO
402	0.22	P	488	0.69	P + (CO) ₂
390	1.2	P - C	478	1.3	P + Cl
367	2.5	P - Cl	460	6.9	P + O
346	3.9	P - (CO) ₂	444	0.83	P
304	2.5		432	11	P - C
276	2.7		416	23	P - CO
256	4.0		388	28	P - (CO) ₂
248	3.0		352	12	P - (CO) ₂ HCl
228	5.7		261	100	PhSnC ₅ H ₄
212	18	CpFe(CO) ₂ Cl	198	51	PhSnH
200	12	CpFeCO ₂ Cl	197	61	PhSn
185	27	CpSn	185	56	CpSn
184	33	CpFe(CO)Cl	155	27	SnCl
177	19	CpFe(CO) ₂	149	35	CpFe(CO)
156	53	CpFeCl	121	23	CpFe
149	20	CpFeCO	120	42	Sn
121	100	CpFe	78	43	PhH
120	14	Sn	56	72	Fe
65	79	Cp			
56	59	Fe			
Metastable peaks			Metastable peaks		
<i>m/e</i>	Transition		<i>m/e</i>	Transition	
159.7	212→184		362	416→388	
132.3	184→156		318	388→352	
125.5	177→149		176	388→261	
			167		
			149.5	261→198	
$\text{CpFe}(\text{CO})_2\text{SnPh}_2\text{Cl}$, inlet temp. 100°			$\text{CpFe}(\text{CO})_2\text{SnPh}_3$, inlet temp. 120°		
<i>m/e</i>	Abund.(%)	Assignment	<i>m/e</i>	Abund.(%)	Assignment
502	4.6	P + O	528	1.4	P
486	0.93	P	500	20	P - (CO)
474	7.0	P - C	472	9.5	P - (CO) ₂
458	26	P - CO	395	25	CpFeSnPh ₂
430	33	P - (CO) ₂	351	100	SnPh ₃
397	6.7		275	18	CpFePh ₂
353	38	CpFeSnPhCl	261	11	PhSnC ₅ H ₄
288	23	FeSnPhCl	252	7.6	FeSnC ₆ H ₄
275	17	CpFePh ₂	197	38	PhSn
274	30		185	44	CpSn
261	71	PhSnC ₅ H ₄	176	15	FeSn
197	100	PhSn	149	29	CpFeCO
185	66	CpSn	141	22	
120	59	Sn	120	34	Sn
78	53	PhH	78	53	PhH
56	48	Fe	56	28	Fe

(continued)

TABLE 3 (continued)

Metastable peaks		Metastable peaks	
<i>m/e</i>	Transition	<i>m/e</i>	Transition
448	502→474	472.5	528→500
429	486→458	445.0	500→472
288	430→353	329.5	472→395
		194	351→261

effects^{16,17} on the surfaces of the ion source are occurring with the formation of these unusual ions. Simple thermal decomposition in the direct inlet is unlikely since the compounds seem to be stable up to their melting points, the probe temperature being kept below this. The formation of the $P + O^+$ and $P - C^+$ ions is particularly unusual in that carbonyl groups attached to the first row transition elements do not usually fragment by splitting of $C-O$ ¹⁸.

EXPERIMENTAL

The preparation of a solution of sodium dicarbonyl- π -cyclopentadienyliron in tetrahydrofuran was achieved using the standard procedure in which a solution of bis(dicarbonyl- π -cyclopentadienyliron) is added to excess sodium amalgam⁷. The tetrahydrofuran was freshly distilled from sodium prior to use and reactions were carried out under nitrogen although the crystalline products appear to be stable towards atmospheric oxygen.

Element analyses were carried out by the Alfred Bernhardt Microanalytical Laboratories, West Germany. IR spectra were recorded on a Perkin-Elmer model 457 and for NMR spectra a Varian A60 was used. For mass spectroscopy a Perkin-Elmer-Hitachi RMU-6E was employed using the direct insertion probe.

(1). (Dicarbonyl- π -cyclopentadienyliron)triphenyltin(IV)

Triphenyltin chloride (47.2 g, 122 mmole) in tetrahydrofuran (500 ml) was added to a solution of sodium dicarbonyl- π -cyclopentadienyliron [prepared from 21.6 g, 60.9 mmole bis(dicarbonyl- π -cyclopentadienyliron)] in tetrahydrofuran (500 ml) and the mixture stirred at room temperature overnight (16 h). The solvent was removed under reduced pressure leaving a brownish solid which was taken up in methylene chloride (200 ml) and filtered. The filtrate was evaporated and the residue washed with petroleum ether (b.p. 60–80°, 200 ml) and then recrystallised from methylene chloride/petroleum ether (b.p. 60–80°) to yield pale yellow needles of (dicarbonyl- π -cyclopentadienyliron)triphenyltin (37.9 g, 71.9 mmole, 60% yield). m.p. 139–140° (lit.¹⁰ 140°, lit.^{1,2} 139–141°). (Found: C, 56.75; H, 3.93. $C_{25}H_{20}FeO_2Sn$ calcd.: C, 56.98; H, 3.83%.)

(2). (Dicarbonyl- π -cyclopentadienyliron)diphenyltin(IV) chloride

A solution of sodium dicarbonyl- π -cyclopentadienyliron [prepared from 3.56 g, 10.1 mmole bis(dicarbonyl- π -cyclopentadienyliron)] in tetrahydrofuran (50 ml) was added to a solution of diphenyltin dichloride (16.4 g, 47.6 mmole) in

tetrahydrofuran (100 ml) at ca. -60° . The mixture was allowed to come to room temperature (1 h) and stirred for a further 2 h. The mixture was filtered through celite and the filtrate evaporated to yield a red oil which on treatment with petroleum ether (b.p. $60-80^{\circ}$) and ethyl ether became an orange solid. Recrystallisation from ethanol afforded orange needles of (dicarbonyl- π -cyclopentadienyliron)diphenyltin(IV) chloride (3.17 g, 6.52 mmole, 32% yield) m.p. $100-101^{\circ}$. (Found: C, 47.00; H, 3.24; Cl, 7.15. $C_{19}H_{15}ClFeO_2Sn$ calcd.: C, 46.92; H, 3.10; Cl, 7.29%.)

(3). (Dicarbonyl- π -cyclopentadienyliron)phenyltin(IV) dichloride

A solution of sodium dicarbonyl- π -cyclopentadienyliron [prepared from 5.39 g, 15.2 mmole bis(dicarbonyl- π -cyclopentadienyliron)] in tetrahydrofuran (40 ml) was added to a solution of phenyltin trichloride (9.06 g, 30.0 mmole) in tetrahydrofuran (20 ml) and the mixture stirred at room temperature for 1 h. The solvent was removed under reduced pressure leaving a dark red oil which on treatment with petroleum ether (b.p. $60-80^{\circ}$, 40 ml) and ethyl ether (60 ml) became a yellow-brown solid. Methylene chloride was added and the mixture filtered. Evaporation of the filtrate gave a yellow solid which recrystallised from ethanol to yield orange crystals of (dicarbonyl- π -cyclopentadienyliron)phenyltin(IV) dichloride (6.36 g, 14.4 mmole 48% yield) m.p. $116-117^{\circ}$. (Found: C, 35.33; H, 2.48; Cl, 15.89. $C_{13}H_{10}Cl_2FeO_2Sn$ calcd.: C, 35.18; H, 2.27; Cl, 15.98%.)

(4). (Dicarbonyl- π -cyclopentadienyliron)tin(IV) trichloride

A solution of sodium dicarbonyl- π -cyclopentadienyliron [prepared from 5.40 g, 15.3 mmole bis(dicarbonyl- π -cyclopentadienyliron)] in tetrahydrofuran (40 ml) was added to a mixture of stannic chloride (4 ml, d 2.33, 34.3 mmole) in tetrahydrofuran (20 ml). The mixture was stirred at room temperature for 2 h before filtering through celite. The filtrate was evaporated to yield a yellowish solid which recrystallised from methylene chloride/petroleum ether (b.p. $60-80^{\circ}$) as reddish crystals of (dicarbonyl- π -cyclopentadienyliron)tin(IV) trichloride (5.41 g, 13.5 mmole, 44% yield) m.p. $159-160^{\circ}$ (lit.^{3,4} 137° , lit.¹⁰ 158° , lit.^{1,2}, 150° decompn.). (Found: C, 20.85; H, 1.42; Cl, 26.35. $C_7H_5Cl_3FeO_2Sn$ calcd.: C, 20.92; H, 1.25; Cl, 26.48%.)

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