TRANSACTIONS, ILL. STATE ACAD. SCI.
Vol. 67, No. 3 (1974)

INFRARED SPECTRA OF SOME ORGANOMETALLIC COMPOUNDS WITH TIN-COBALT BONDS

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ABSTRACT--The syntheses and infrared spectra of a series of compounds containing the (triphenylphosphinetricarbonylcobalt) derivatives of tin with general formulas $Y_{4-n}Sn[Co(CO)_3PPh_3]_n$ (where Y = Cl, Br, I, CH_3, C_4H_9, or C_6H_5 and n = 1, 2, or 3) are reported. The infrared spectra in the carbonyl stretching region of these compounds are discussed.

INTRODUCTION

Recently, there is a great deal of interest in organometallic compounds with metal-to-metal bonds. In the present work, a detailed study is made on a series of compounds containing the triphenylphosphinetricarbonylcobalt derivatives of tin. The compounds are prepared by one of the following methods: (1) Displacement of a neutral carbon monoxide molecule on a tetracarbonylcobalt derivative by triphenylphosphine, (2) Substitution of a chloride ion on tin by a triphenylphosphinetricarbonylcobalt anion, or (3) Insertion of an anhydrous tin(II) halide molecule into the triphenylphosphinetricarbonylcobalt dimer.

METHODS AND MATERIALS

All reactions were carried out under a static nitrogen atmosphere, and solid products were handled with minimum exposure to air. Tetrahydrofuran (THF) was purified by distillation from lithium aluminum hydride. Solutions of sodium triphenylphosphinetricarbonylcobaltate(I) were prepared by stirring THF solutions of triphenylphosphinetricarbonylcobalt dimer with excess 1% sodium amalgam for 10 to 12 hours.

The infrared spectra in the carbonyl stretching region were measured in 0.5 mm cells in methylene chloride solution using a

Perkin-Elmer 337 grating spectrometer and recorded on a Texas Instruments Serro-Riter with calibrations as described by Jetz (1966).

Microanalyses were performed by the Alfred Bernhardt Mikroanalytisches Laboratorium. Analytical data for the compounds are given in TABLE 1.

TABLE 1. Analytical Data.

COMPOUND	CALCD %			FOUND %		
	C	H	X	C	H	X
$Cl_3SnCo(CO)_3PPh_3$	40.02	2.40	16.87	40.83	2.71	15.85
$Cl_2Sn[Co(CO)_3PPh_3]_2$	50.44	3.02	7.09	50.70	2.91	7.08
$ClSn[Co(CO)_3PPh_3]_3$	55.22	3.31	2.60	55.73	3.73	2.47
$Br_3SnCo(CO)_3PPh_3$	33.03	1.98	31.39	34.94	2.36	30.37
$Br_2Sn[Co(CO)_3PPh_3]_2$	46.32	2.78	14.68	46.26	3.12	13.31
$BrSn[Co(CO)_3PPh_3]_3$	53.50	3.21	5.65	53.42	3.32	6.15
$I_3SnCo(CO)_3PPh_3$	27.88	1.67	42.08	27.34	1.94	43.13
$I_2Sn[Co(CO)_3PPh_3]_2$	42.64	2.56	21.45	42.20	1.93	20.48
$ISn[Co(CO)_3PPh_3]_3$	51.76	3.10	8.69	51.90	3.38	8.98
$Me_3SnCo(CO)_3PPh_3$	50.66	4.25	---	51.62	4.42	---
$Me_2Sn[Co(CO)_3PPh_3]_2$	55.09	3.78	---	56.19	3.94	---
$MeSn[Co(CO)_3PPh_3]_3$	56.96	3.58	---	56.78	3.91	---
$Bu_2Sn[Co(CO)_3PPh_3]_2$	57.56	4.64	---	57.25	3.97	---
$BuSn[Co(CO)_3PPh_3]_3$	57.83	3.91	---	58.64	4.14	---
$Ph_3SnCo(CO)_3PPh_3$	62.27	4.00	---	61.04	4.41	---
$Ph_2Sn[Co(CO)_3PPh_3]_2$	59.87	3.72	---	59.44	3.75	---
$PhSn[Co(CO)_3PPh_3]_3$	58.48	3.59	---	58.64	3.82	---

X = Cl, Br, or I.

Trichloro(triphenylphosphinetricarbonylcobalt)tin(IV), $Cl_3SnCo(CO)_3PPh_3$. Triphenylphosphine (0.065 g, 0.25 mmoles) was added to 0.1 g (0.25 mmoles) of $Cl_3SnCo(CO)_4$ dissolved in benzene. Vigorous CO evolution ensued and the solution was magnetically stirred for 20 min. Precipitation of solid occurred and this was completed by addition of hexane. The precipitate was recrystallized in benzene and precipitated by hexane. The tribromo and triiodo compounds, $Br_3SnCo(CO)_3PPh_3$ and $I_3SnCo(CO)_3PPh_3$, were similarly prepared.

Dichlorobis(triphenylphosphinetricarbonylcobalt)tin(IV), $Cl_2Sn[Co(CO)_3PPh_3]_2$. This compound was prepared by insertion reaction as described by Patmore (1966). The dibromo and diiodo compounds, $Br_2Sn[Co(CO)_3PPh_3]_2$ and $I_2Sn[Co(CO)_3PPh_3]_2$, were similarly prepared.

Chlorotris(triphenylphosphinetricarbonylcobalt)tin(IV), $ClSn[Co(CO)_3PPh_3]_3$. Anhydrous $SnCl_4$ (0.19 g, 1 mmole) and 1.22 g (1.5 mole) of $[Ph_3PCo(CO)_3]_2$, prepared by the method of Hieber (1957), were refluxed for 12 hours in 80 ml of dry THF. Solvent was removed at reduced pressure and the residue extracted with methylene chloride. Addition of *n*-pentane to the extract followed by cooling in dry ice-acetone mixture afforded red crystals. Recrystallization was done in methylene chloride and precipitated by *n*-pentane followed by cooling in dry ice-acetone mixture. The bromo and iodo compounds, $BrSn[Co(CO)_3PPh_3]_3$ and $ISn[Co(CO)_3PPh_3]_3$, were prepared in a similar manner.

Triphenyl(triphenylphosphinetricarbonylcobalt)tin(IV), $Ph_3SnCo(CO)_3PPh_3$. Triphenyl tin chloride (0.75 g, 2 mmole) was added to 100 ml of THF solution containing 4 mmoles of $Na[Co(CO)_3PPh_3]$. The reaction mixture was stirred at room temperature for 30 min. Solvent was removed at reduced pressure and the residue was extracted with minimum amount of methylene chloride. Slow addition of *n*-pentane followed by cooling in dry ice-acetone mixture gave pale yellow crystals. Recrystallization was done in methylene chloride followed by addition of *n*-pentane and cooling in dry ice-acetone mixture. $Me_3SnCo(CO)_3PPh_3$ was prepared in a similar manner.

Diphenyl-, dimethyl-, and dibutylbis(triphenylphosphinetricarbonylcobalt)tin(IV), $Ph_2Sn[Co(CO)_3PPh_3]_2$, $Me_2Sn[Co(CO)_3PPh_3]_2$, and $Bu_2Sn[Co(CO)_3PPh_3]_2$; and phenyl-, methyl-, and butyltris(triphenylphosphinetricarbonylcobalt)tin(IV), $PhSn[Co(CO)_3PPh_3]_3$, $MeSn[Co(CO)_3PPh_3]_3$ and $BuSn[Co(CO)_3PPh_3]_3$ were prepared by refluxing the corresponding tin chlorides in THF solutions of

$Na[Co(CO)_3PPh_3]$ for 30 min. The general procedure was the same as that for the $Ph_3SnCo(CO)_3PPh_3$.

RESULTS AND DISCUSSION

IR Spectra of Mono(triphenylphosphinetricarbonylcobalt) Derivatives. In compounds of general formula $Y_3SnCo(CO)_3PPh_3$, there are two structural possibilities. The triphenylphosphine group can be either *trans* to tin (C_{3v} point group) or *cis* to tin (C_s point group). In the former case, two IR-active modes are expected, (A_1 + E); in the latter case, three IR-active nondegenerate modes should be observed. It has been suggested by El-Sayed (1962) that, in any vibrational mode, the intensity should be proportional to the square of the vector sum of the local dipoles. Thus E modes are expected to be more intense than any nondegenerate A modes. Since only one intense broad band and a weak band at higher frequency are observed in all the carbonyl stretching region of the mono(triphenylphosphinetricarbonylcobalt) derivatives, the triphenylphosphine group is *trans* to tin. The selection rules enable assignment of the single intense band to the E mode and the weak band at higher frequency to the A_1 mode. The assignments of the mono(triphenylphosphinetricarbonylcobalt) derivatives in the carbonyl stretching region are summarized in TABLE 2.

TABLE 2. C-O Stretching Frequencies of $Y_3SnCo(CO)_3PPh_3$.

COMPOUND	A_1	E
$Cl_3SnCo(CO)_3PPh_3$	2058(0.2)	2009(10)
$Br_3SnCo(CO)_3PPh_3$	2058(0.3)	2005(10)
$I_3SnCo(CO)_3PPh_3$	2058(0.3)	2002(10)
$Ph_3SnCo(CO)_3PPh_3$	2015(0.5)	1956(10)
$Me_3SnCo(CO)_3PPh_3$	2015(0.3)	1946(10)

When the IR-active carbonyl stretching modes in $Y_3SnCo(CO)_3PPh_3$ and $Y_3SnCo(CO)_4$ are compared, the A_1 mode (C_{3v} point group) in

the former can be related to the $A_1^{(2)}$ mode (C_{3v} point group) in the latter (Patmore, 1967). When the spectra for the carbonyl stretching region of two analogous compounds are compared, it is observed that both the A_1 and E modes in $Y_3SnCo(CO)_3PPh_3$ are shifted to lower frequencies with respect to the $A_1^{(2)}$ and E modes in $Y_3SnCo(CO)_4$ and the relative intensities of A_1 to E in the former is much less than those of $A_1^{(2)}$ to E in the latter. The lowering in frequencies is due to the poor T-accepting property of the triphenylphosphine group as suggested by Graham (1968). The A_1 mode in $Y_3SnCo(CO)_3PPh_3$ and the $A_1^{(2)}$ mode in $Y_3SnCo(CO)_4$ are the symmetrical stretch of the equatorial carbonyl groups and should be almost IR-forbidden. The fact that the relative intensity of $A_1^{(2)}$ to E (C_{3v}) is much larger than that of A_1 to E (C_{3v}) suggests strong coupling between the $A_1^{(2)}$ mode and the $A_1^{(1)}$ mode in $Y_3SnCo(CO)_4$. The $A_1^{(1)}$ mode is the stretching vibration of the terminal CO group. When this terminal CO group is replaced by triphenylphosphine, no coupling can be expected.

<u>IR Spectra of Bis- and Tris(triphenylphosphinetricarbonylcobalt) Derivatives</u>. Assuming the equatorial arrangement of the carbonyl groups persists in the bis- and tris(triphenylphosphinetricarbonylcobalt) derivatives of tin, compounds of general formulas $Y_2Sn[Co(CO)_3PPh_3]_2$ and $YSn[Co(CO)_3PPh_3]_3$ have respectively C_{2v} and C_{3v} molecular symmetry. The group theory predicts five IR-active carbonyl stretching modes, ($2A_1 + 2B_1 + B_2$), for the former class of compounds and also five IR-active modes, ($2A_1 + 3E$), for the latter. In all the IR spectra of the compounds (TABLE 3 and TABLE 4), the predicted number of bands, including shoulders, are counted. Representative spectra are displayed in FIGURE 1 and FIGURE 2.

When the IR spectra in the carbonyl stretching region of similar compounds are compared, it is observed that the carbonyl stretching frequencies of compounds containing the $Co(CO)_3PPh_3$ group are shifted to lower frequencies with respect to compounds containing the $Co(CO)_4$ group, and that the two high energy bands for both the bis- and tris-$[Co(CO)_3PPh_3]$ derivatives are again smaller in relative intensities comparing with the corresponding compounds with $Co(CO)_4$ derivatives. Assignments for such complex spectra are difficult but it was suggested that the two high energy bands in all the bis-$[Co(CO)_4]$ derivatives are assigned the symmetric and asymmetric combination of the $A_1^{(2)}$

TABLE 3. C-O Stretching Frequencies of $Y_2Sn[Co(CO)_3PPh_3]_2$

COMPOUND	A_1(sym)	A_1(asym)	$2B_1 + B_2$		
$Cl_2Sn[Co(CO)_3PPh_3]_2$	2049(0.7)	2028(3.8)	2012sh(1.9)	1984(10)	1970(812)
$Br_2Sn[Co(CO)_3PPh_3]_2$	2046(1.0)	2028(4.9)	2012sh(2.4)	1984(10)	1972(8.0)
$I_2Sn[Co(CO)_3PPh_3]_2$	2043(0.7)	2025(5.3)	2012sh(1.4)	1983(10)	1970(8.0)
$Ph_2Sn[Co(CO)_3PPh_3]_2$	2025(0.7)	2009(2.0)	1962sh(9.7)	1953(10)	1940(7.6)
$Bu_2Sn[Co(CO)_3PPh_3]_2$	2022(0.3)	2007(0.7)	1960sh(8.7)	1953(10)	1942(5.5)
$Me_2Sn[Co(CO)_3PPh_3]_2$	2020(0.2)	2005(0.5)	1959sh(8.8)	1953(10)	1942(5.4)

TABLE 4. C-O Stretching Frequencies of $YSn[Co(CO)_3PPh_3]_3$

COMPOUND	A_1(sym)	A_1(asym)	3E		
$ClSn[Co(CO)_3PPh_3]_3$	2039(1.3)	2013(3.5)	1973sh(9.8)	1967(10)	1943(2.9)
$BrSn[Co(CO)_3PPh_3]_3$	2039(1.3)	2015(3.6)	1974sh(9.7)	1968(10)	1942(3.0)
$ISn[Co(CO)_3PPh_3]_3$	2038(1.3)	2016(3.5)	1974sh(9.8)	1968(10)	1943(3.2)
$PhSn[Co(CO)_3PPh_3]_3$	2038(1.2)	2018(2.6)	1975sh(9.6)	1968(10)	1957(7.9)
$BuSn[Co(CO)_3PPh_3]_3$	2035(1.6)	2015(2.9)	1972sh(9.6)	1965(10)	1951(7.1)
$MeSn[Co(CO)_3PPh_3]_3$	2035(1.0)	2015(2.5)	1970sh(9.5)	1962(10)	1950(7.0)

modes of the individual $Co(CO)_4$ group (Patmore, 1967). Observations in the present work for the bis-$[Co(CO)_3PPh_3]$ derivatives lends support to assignments by Patmore (1967). The band with the highest energy in bis-$[Co(CO)_3PPh_3]$ derivatives is assigned the symmetric combination of the A_1 modes of the individual

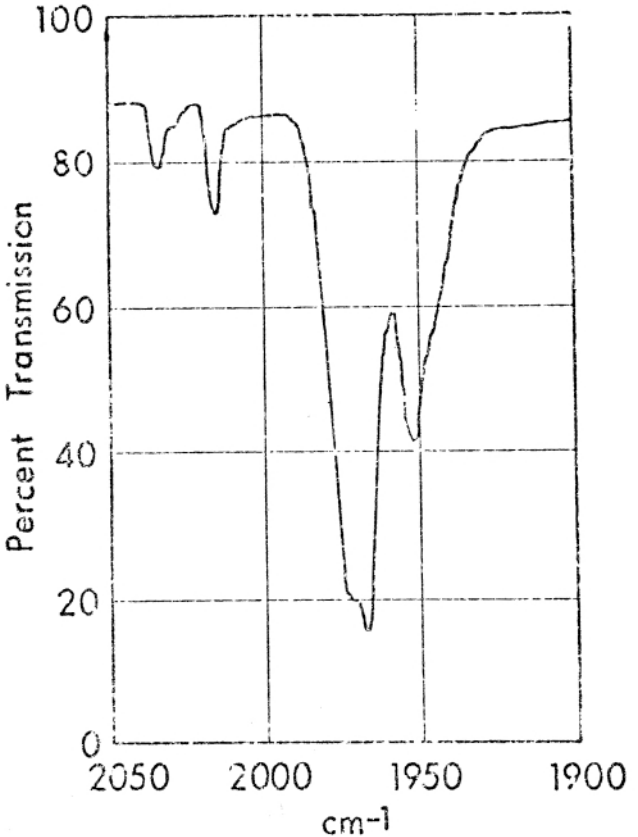

FIGURE 1. Infrared Spectrum of $Ph_2Sn[Co(CO)_3PPh_3]_2$.

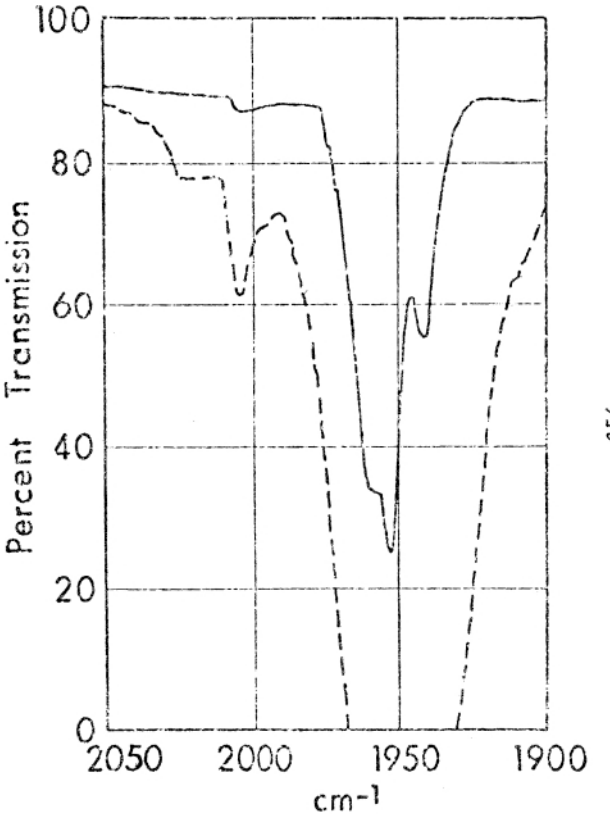

FIGURE 2. Infrared Spectra of $PhSn[Co(CO)_3PPh_3]_3$.

$Co(CO)_3PPh_3$ group and the band with the next highest energy is assigned the asymmetric combination of the A_1 modes, as illustrated in FIGURE 3. The two high energy bands in tris-$[Co(CO)_3PPh_3]$ derivatives are similarly assigned.

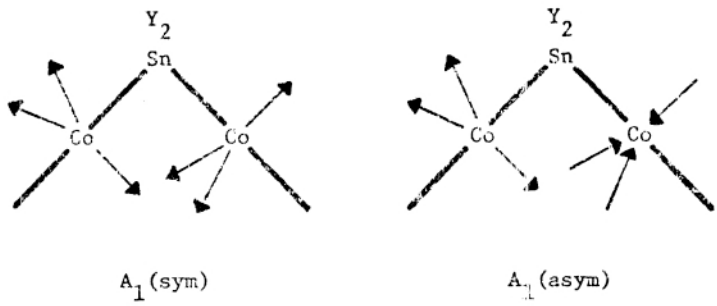

FIGURE 3. Symmetric and Asymmetric Combinations of A_1 Modes.

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