

Reactions of Tin(II) Halides with Hexacarbonylbis(tri-n-butylphosphine)-dicobalt

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Six types of compound have been isolated from the reactions of tin(II) halides, SnX_2 ($X = \text{F}, \text{Cl}, \text{Br}, \text{or I}$), with $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\}$; $[\text{Bu}^n_3\text{PCo}(\text{CO})_3\text{SnX}_3]$, $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{SnX}_2\}$, $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{SnX}\}$, $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{SnH}\}$, $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{Sn}\}$, and $[(\text{Bu}^n_3\text{P})_2\text{Co}(\text{CO})_2\text{X}]$. Their relative importances depend on X, the mole ratio of reactants, and the reaction conditions. It is proposed that these reactions proceed either by the direct insertion of SnX_2 into the Co-Co bond, or by the scission of this bond to give $[\text{Bu}^n_3\text{PCo}(\text{CO})_3\text{SnX}_3]$ which may react further with $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\}$. This last step has been utilized in the reactions of octacarbonyldicobalt with various halogenotin derivatives of the transition metals to prepare mixed metal complexes such as $\{[\text{Ph}_3\text{PFe}(\text{CO})_2\text{NO}\}\{\text{Co}(\text{CO})_4\}\text{SnCl}_2\}$ in high yields.

ALTHOUGH the insertion of tin(II) halides into metal-metal bonds has been known for more than a decade,¹ we have shown recently that their reaction with various dimers $\{[(\pi\text{-dienyl})\text{Fe}(\text{CO})_2]_2\}$ ² and $\{[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]_2\}$ ³ (dienyl = C_5H_5 , MeC_5H_4 , or C_9H_7 ; $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$) is far more complicated than had previously been assumed. It appears to take place by a 'direct' route with no detectable intermediates, or by an 'indirect' route with the initial formation of $[(\pi\text{-dienyl})\text{Fe}(\text{CO})_2\text{SnX}_3]$ or $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{SnX}_3]$ which react further with excess dimer. A wide variety of products have been isolated from these reactions, e.g. $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}]$, $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnX}_3]$, $\{[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnX}_2\}$, or $\{[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_3\text{SnX}\}$ depending on X (F, Cl, Br, or I), the transition metal, the mole ratio of reactants, and the reaction conditions.

Although octacarbonyldicobalt and tin(II) halides readily form the 'insertion' compounds $\{[\text{Co}(\text{CO})_4]_2\text{SnX}_2\}$,⁴ Bigorgne and Quintin have shown that $\{[\text{Co}(\text{CO})_4]_2\text{SnCl}\}$ and $\{[\text{Co}(\text{CO})_4]_2\text{Sn}\}$ may also be obtained in tetrahydrofuran.⁵ Thus it appeared likely that these reactions also proceed by 'direct' and/or 'indirect' routes and would yield a variety of products. Because of the relative instability of cobalt carbonyl, we decided to investigate the similar reactions of its derivative $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\}$. We obtained the previously reported $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{SnX}_2\}$ ($X = \text{Cl}$ or Br)⁶ as well as up to five other carbonyl-containing products. We have also prepared a number of compounds containing the $\text{Co}(\text{CO})_4$ moiety as one of the groups bonded to tin(IV).

EXPERIMENTAL

Literature methods were used to prepare $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\}$,⁷ $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnCl}_3]$,² $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnBr}_3]$,² $[(\pi\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\text{SnCl}_3]$,² $[(\pi\text{-C}_7\text{H}_9)\text{Fe}(\text{CO})_2\text{SnCl}_3]$,⁸ $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{SnCl}_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$)³ $[\text{Ph}_3\text{PFe}(\text{CO})_2(\text{NO})\text{SnCl}_2]$,⁹ and $\{[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnCl}_2\}$.¹ Other chemicals were purchased. All reactions were carried out under an atmosphere of nitrogen in purified solvents.

The reactions of $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\}$ (ca. 1 mmol) with the tin(II) halides in a suitable solvent (50 ml) were brought about by heating or by u.v. irradiation with a Philips HPR 25 W lamp at a distance of ca. 2 in. They were monitored by i.r. spectroscopy. The products were separated by frac-

tional crystallization or, occasionally, chromatography on alumina. Difficulties in eluting the halogenotin derivatives prevented the latter technique from being used more extensively. Purification of the separated products was achieved by recrystallization from an alcohol or from toluene-light petroleum mixtures.

$[\text{Bu}^n_3\text{PCo}(\text{CO})_3\text{SnCl}_3]$ was obtained by stirring $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\}$ (0.69 g) with tin(IV) chloride (1 ml) in benzene (50 ml) at room temperature for 15 min. The solvent was removed and the residue recrystallized from methanol to give the product in 35% yield.

A solution of $\text{Na}[\text{Bu}^n_3\text{PCo}(\text{CO})_3]$ in diglyme (40 ml) was prepared by the reduction of $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\}$ (1.4 g) with sodium amalgam. To it was added a solution of tin(II) sulphate (3.0 g) in water (100 ml). The mixture was stirred for 15 min, extracted with ether, and the ether layer washed repeatedly with water. The ether solution was dried over sodium sulphate and the solvent removed. The residue was recrystallized from methanol to give $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{SnH}\}$. The deuteride $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{SnD}\}$ was obtained by replacing water with deuterium oxide. The ether layer was not washed, but only dried, and the product recrystallized from pentane.

The reactions between octacarbonyldicobalt (1 mmol) and the tin(IV) halide derivative, e.g. $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3\text{SnCl}_3]$ (0.5 mmol) were carried out in tetrahydrofuran (25 ml) at room temperature. After ca. 10 min, the solvent was removed and the residue recrystallized from toluene-light petroleum to give the product, e.g. $\{[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{Co}(\text{CO})_4\text{SnCl}_2\}$. Yields were usually ca. 70%.

The melting points, analyses, and i.r. spectra of the products in the C-O stretching region are summarized in the Table. Spectra were obtained on a Perkin-Elmer 337 spectrometer fitted with a Hitachi-Perkin-Elmer readout recorder. They were calibrated with DCl/DBr mixtures.¹⁰ Peak positions are accurate to within $\pm 1 \text{ cm}^{-1}$.

RESULTS

When solutions of $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\}$ and SnX_2 ($X = \text{Cl}$ or Br ; mole ratio = 1 : 1 or 1 : 10) in tetrahydrofuran were refluxed for ca. 3 h in the absence of light, the only products were $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{SnX}_2\}$ (yields = ca. 70%). No other compounds could be detected in the course of the reaction. When $X = \text{I}$ and equimolar quantities of the reactants were used, $\{[\text{Bu}^n_3\text{PCo}(\text{CO})_3]_2\text{SnI}_2\}$ (yield = 65%) was the only product, but an intermediate, $[\text{Bu}^n_3\text{PCo}(\text{CO})_3\text{SnI}_3]$, could be

* F. Bonati, S. Cenini, D. Morelli, and R. Ugo, *J. Chem. Soc. (A)*, 1966, 1052.

⁷ A. R. Manning, *J. Chem. Soc. (A)*, 1968, 1135.

⁸ P. O'Neill and A. R. Manning, unpublished work.

⁹ M. Casey and A. R. Manning, *J. Chem. Soc. (A)*, 1971, 256.

¹⁰ 'Tables of Wavenumbers for the Calibration of Infrared Spectrometers,' Butterworths, London, 1961.

¹ F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179.

² P. Hackett and A. R. Manning, *J.C.S. Dalton*, 1972, 1487.

³ P. Hackett and A. R. Manning, *J.C.S. Dalton*, 1972, 2434.

⁴ D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, 5, 1405.

⁵ M. Bigorgne and A. Quintin, *Compt. rend.*, 1967, C264, 2055.

detected by i.r. spectroscopy. This was the only product (yield = 35%) if the large excess of tin(II) iodide was used. When X = F, $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_2\text{SnF}_2]$ and $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnF}]$ are both formed. The mixture could not be separated when the reactant mole ratio was 1 : 1 but when a 1 : 10 excess of tin(II) fluoride was used, $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_2\text{SnF}_2]$ was the major product.

In the presence of u.v. light, an acetone solution of

A larger molar excess of $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_2]$ (3 : 1) and longer reaction times (24 h in boiling ethanol) gave a mixture of products. Small amounts of $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnF}]$ and $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnCl}]$ and a ca. 30% yield of brown $[(\text{Bu}^n_3\text{P})_2\text{Co}(\text{CO})_2\text{I}]$ were obtained using respectively tin(II) fluoride, chloride, and iodide. However, in all instances red $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_4\text{Sn}]$ and yellow $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnH}]$ were among the products.

Melting points, analyses, and i.r. spectra (1700—2100 cm^{-1}) for some compounds with Co-Sn bonds

Compound ^a	M.p. ^b ($^{\circ}\text{C}$)	Analyses						Absorption bands ^c
		Found (%)			Required (%)			
		C	H	X	C	H	X	
$[\text{Bu}_3\text{PCo}(\text{CO})_3\text{SnCl}_3]$	140 (d)	31.3	4.7	18.7	31.6	4.7	18.8	1995 (10), 2056 (0.2)
$[\text{Bu}_3\text{PCo}(\text{CO})_3\text{SnBr}_3]$	133 (d)	26.0	3.9	33.9	25.6	3.8	34.0	1992 (10), 2053 (0.5)
$[\text{Bu}_3\text{PCo}(\text{CO})_3\text{SnI}_3]$	144 (d)	21.8	3.1	45.1	21.3	3.2	45.1	1984 (10), 2051 (1.0)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_2\text{SnF}_2]$	166—168	41.3	6.3		42.5	6.4		1963 (3.2), 1976 (10), 2022 (1.7)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_2\text{SnCl}_2]$	98—99							1966 (2.7), 1977 (10), 2021 (1.9)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_2\text{SnBr}_2]$	126—127							1959 (3.0), 1975 (10), 2022 (2.1)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_2\text{SnI}_2]$	dec. 134	34.0	5.1	24.0	33.9	5.1	23.9	1960 (2.6), 1975 (10), 2019 (2.1)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_3\text{SnF}]$	139—140	46.2	7.2	2.1	46.0	6.9	1.6	1935 (1.4), 1958 (10), 2005 (2.1), 2034 (0.4)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_3\text{SnCl}]$	193—195	45.4	6.7	3.3	45.4	6.8	3.0	1931 (1.6), 1959 (10), 2006 (2.6), 2033 (0.3)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_3\text{SnBr}]$	210—212	43.9	6.6	6.3	43.7	6.6	6.5	1930 (1.6), 1959 (10), 2005 (2.7), 2033 (0.3)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_3\text{SnI}]$	205—207	42.3	6.4		42.2	6.3		1932 (1.5), 1960 (10), 2007 (3.1), 2034 (0.2)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_3\text{SnH(D)}]$ ^d	168—170	46.6	7.3		46.7	7.0		1932 (1.2), 1952 (7.2), 1958 (10), 2001 (1.5), 2031 (0.2)
$[(\text{Bu}_3\text{PCo}(\text{CO})_3)_4\text{Sn}]$	190 (d)	48.3	7.4		48.0	7.2		1919 (0.5), 1948 (10), 1990 (3.3)
$[(\pi\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2\{\text{Co}(\text{CO})_4\}\text{SnCl}_2]$	108—110	24.5	1.1	13.4	24.6	0.9	13.2	1984 (1.8), 1998 (3.5), 2013 (4.7), 2029 (10), 2041 (3.9), 2095 (3.9)
$[(\pi\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2\{\text{Co}(\text{CO})_4\}\text{SnBr}_2]$	112—113	21.2	1.3	25.1	21.0	0.8	25.5	1972 (1.5), 1993 (3.8), 2019 (7.6), 2028 (10), 2039 (3.5), 2096 (4.6)
$[(\pi\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2\{\text{Co}(\text{CO})_4\}\text{SnCl}_2]$	dec. 160	30.8	1.1	12.3	30.6	1.2	12.1	1980 (1.8), 1999 (2.7), 2014 (5.5), 2029 (10), 2034 (3.2), 2098 (4.1)
$[(\pi\text{-C}_7\text{H}_5)\text{Fe}(\text{CO})_2\{\text{Co}(\text{CO})_4\}\text{SnCl}_2]$	120—123	27.7	1.5	12.8	27.6	1.6	12.5	1975 (2.4), 2002 (4.1), 2015 (6.6), 2025 (10), 2041 (3.4), 2097 (4.9)
$[(\pi\text{-C}_5\text{H}_5)_3\text{Cr}(\text{CO})_3\{\text{Co}(\text{CO})_4\}\text{SnCl}_2]$	118—120	25.3	1.0	12.4	25.2	0.9	12.7	1943 (3.7), 1966 (2.4), 2013 (2.7), 2026 (sh), 2031 (10), 2042 (2.4), 2099 (2.4)
$[(\pi\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_3\{\text{Co}(\text{CO})_4\}\text{SnCl}_2]$	134—136	23.5	1.3	11.8	23.8	0.8	11.7	1943 (3.7), 1967 (1.9), 2010 (2.3), 2027 (sh), 2032 (10), 2045 (2.5), 2099 (2.8)
$[(\pi\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_3\{\text{Co}(\text{CO})_4\}\text{SnBr}_2]$	118—119	20.1	0.5	25.0	20.7	0.7	25.8	1934 (4.1), 1958 (2.7), 1995 (1.4), 2015 (10), 2030 (6.7), 2046 (2.4), 2101 (3.4)
$[(\pi\text{-C}_5\text{H}_5)_3\text{W}(\text{CO})_3\{\text{Co}(\text{CO})_4\}\text{SnCl}_2]$	144—145	20.5	0.8	10.0	20.7	0.7	10.3	1933 (5.3), 1956 (2.8), 2014 (2.8), 2025 (9.7), 2029 (10), 2044 (2.8), 2100 (2.8)
$[(\text{Ph}_3\text{PFe}(\text{CO})_2\text{NO})\{\text{Co}(\text{CO})_4\}\text{SnCl}_2]$ ^e	dec. 160	37.5	2.1	9.9	38.4	2.0	9.5	1754 (2.5), 1773 (2.3), 1963 (4.2), 2005 (6.5), 2024 (10), 2042 (4.9), 2097 (5.4)
$[(\text{Ph}_3\text{PCo}(\text{CO})_3)\{\text{Ph}_3\text{AsCo}(\text{CO})_3\}\text{SnCl}_2]$	dec. 180	48.7	3.3	6.5	48.2	2.9	6.8	1971 (3.1), 1995 (10), 2030 (1.4)
$[(\pi\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2\{\text{Co}(\text{CO})_4\}\text{SnCl}]$	125—127	31.4	1.7	5.5	31.8	1.5	5.2	1952 (sh), 1959 (5.6), 1964 (sh), 1974 (3.8), 1994 (8.6), 1999 (10), 2011 (8.6), 2020 (8.2), 2026 (sh), 2074 (7.5)

^a Bu = n-butyl. ^b Measured in sealed tubes. dec. = decomposes without melting, and (d) = melts with decomposition. ^c Peak positions (cm^{-1}) with relative peak heights in parentheses. Measured in carbon disulphide solution. ^d Found %P = 7.7, required = 8.0. Molecular weight found = 1100 (benzene solution), required = 1155. ^e Found %N = 1.7, required = 1.9.

$[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_2]$ and SnBr_2 (mole ratio = 1 : 10) at 0 $^{\circ}\text{C}$ gave a 46% yield of $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnBr}_3]$. However, the course of the reactions of the other tin(II) halides were not affected. $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnCl}_3]$ could only be prepared from $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_2]$ and tin(IV) chloride.

The 'insertion' compounds $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_2\text{SnX}_2]$ were intermediates in the reactions of $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_2]$ with SnX_2 when their mole ratio was 2 : 1. The final products in refluxing ethanol after ca. 4—6 h were $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnX}]$ in yields of 30—40%.

The stannane, which we have reported previously,¹¹ was prepared in high yields from $\text{Na}[\text{Co}(\text{CO})_3\text{PBu}^n_3]$ and tin(II) sulphate in aqueous diglyme. Replacement of water by deuterium oxide afforded $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnD}]$. Boiling carbon tetrachloride converted the stannane into $[(\text{Bu}^n_3\text{PCo}(\text{CO})_3)_3\text{SnCl}]$ (yield 60%) with no detectable side reactions.

Octacarbonyldicobalt replaced a tin-halogen bond of various halogeno-derivatives of tin(IV) by a $\text{Sn}^{\text{IV}}\text{-Co}(\text{CO})_4$

¹¹ P. Hackett and A. R. Manning, *J. Organometallic Chem.*, 1974, **66**, C17.

moiety. The reactions were rapid in tetrahydrofuran at room temperature (*ca.* 10 min) but much slower in benzene (*ca.* 3 days). Yields were generally good.

The complexes containing tin-metal bonds were air-stable crystalline solids. Their colours varied from yellow to deep red. They deepened as the number of tin-metal bonds increased and as the atomic weights of any attached halogens increased.

DISCUSSION

The insertion of tin(II) halides into the metal-metal bond of $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_2]$ appears to take place by two different routes. As has previously been suggested for the comparable reactions of $[\{(\pi\text{-dienyl})\text{Fe}(\text{CO})_2\}_2]^2$ and $[\{(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\}_2]^3$ (dienyl = C_5H_5 , MeC_5H_4 , or C_9H_7 ; M = Cr, Mo, or W), one is direct, and gives $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_2\text{SnX}_2]$ with the formation of no detectable intermediates. The other is 'indirect' and proceeds *via* $[\text{Bu}^n_3\text{PCo}(\text{CO})_3\text{SnX}_3]$ which then reacts with more dimer to give $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_2\text{SnX}_2]$ and $[\text{Bu}^n_3\text{PCo}(\text{CO})_3\text{X}]$. This last may react further with SnX_2 , to give $[\text{Bu}^n_3\text{PCo}(\text{CO})_3\text{SnX}_3]$, or it may decompose.

The thermal reactions of tin(II) fluoride, chloride, or bromide take place solely by the 'direct' route. That of the iodide utilizes the 'indirect' route, but the yield of $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_2\}_2\text{SnI}_2]$ obtained with equimolar quantities of the reagents implies that the 'direct' one is not unimportant. The presence of u.v. radiation causes an increase in the importance of the 'indirect' route for tin(II) bromide but not for the chloride (*cf.* ref. 3).

The formation of $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_3\text{SnX}]$ (X = F, Cl,

* We are indebted to a referee for this suggestion.

¹² P. E. Potler, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1964, 524.

¹³ T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, 3, 104.

Br, or I) and $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_4\text{Sn}]$ obviously takes place by the replacement of one and then both halogens of $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_2\text{SnX}_2]$ by a $\text{Bu}^n_3\text{PCo}(\text{CO})_3$ group. This is similar to the second step of the 'indirect' route.

The stannane $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_3\text{SnH}]$ is formulated as such on the basis of its molecular weight in benzene solution (found = 1100, required = 1155), its p.m.r. spectrum in deuteriochloroform which shows a resonance at τ 5.84 due to the stannane proton,¹² and its reaction with carbon tetrachloride to give $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_3\text{SnCl}]$ (*cf.* ref. 13). The deuterium analogue $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_3\text{SnD}]$ has an i.r. spectrum which is identical with that of the stannane, but the resonance at τ 5.84 is absent from its p.m.r. spectrum. It is possible that the compound is $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_3\text{SnOH}]$,* but we feel that this is less likely. Even if such a hydroxide did not dehydrate to a stannoxane, it would be expected to undergo rapid H-D exchange with deuterium oxide. N.m.r. studies show that our product does not. Furthermore, it is unlikely that a hydroxide would react with CCl_4 to give a chloride. We attribute our inability to detect ¹¹⁷Sn-H or ¹¹⁹Sn-H coupling to the relatively low abundances of the relevant isotopes of tin and the limited solubility of the complex.

It is probable that the complexes contain tin-cobalt bonds and that the ligand distributions about these atoms are similar to those found in related compounds such as $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnCl}_3]$,¹⁴ $[\{\text{Co}(\text{CO})_4\}_2\text{-Hg}]$,¹⁵ and $[\{\text{Bu}^n_3\text{PCo}(\text{CO})_3\}_2\text{Hg}]$.¹⁶ The i.r. spectra (Table) are not inconsistent with these suppositions.

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¹⁴ P. T. Greene and R. F. Bryan, *J. Chem. Soc. (A)*, 1970, 1696.

¹⁵ G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc. (A)*, 1968, 1005.

¹⁶ R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316