Derivatives of Bivalent Germanium, Tin, and Lead. Part XIX.[1] Reactions of Bis(β-Ketoenolato)tin(II) Compounds with Metal Carbonyls: the Octacarbonyldicobalt System

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The reaction of bis(β-ketoenolato)tin(II) compounds, [SnX_2], with octacarbonyldicobalt in benzene at room temperature yields products of composition [$\{Co(CO)_4\}_2SnX_2$], [$Co_2(CO)_7(SnX_2)$], or [$Co(CO)_4(SnX)$] depending on the nature of the β-ketoenolato-residue X. Infrared data indicate that the β-ketoenolato-groups chelate tin in all cases, and also the presence of both terminal and bridging carbonyl groups in [$Co_2(CO)_7(SnX_2)$]. Tin-119m Mössbauer data for [$\{Co(CO)_4\}_2SnX_2$] are very similar to those of [$Co_2(CO)_7(SnX_2)$], which have the same structure as that determined for [$\{Co(CO)_4\}_2Sn(pd)_2$] (pd = pentane-2,4-dionate), demonstrating that the tetracarbonylcobalt groups occupy *cis* positions at octahedrally co-ordinated tin. The Mössbauer isomer shifts of [$Co(CO)_4(SnX)$] fall in the range 3.35—3.68 mm s^{-1}, above those of the corresponding [SnX_2] compounds, and structures involving [$Co(CO)_4$]$^-$ anions co-ordinated to [SnX]$^+$ cations *via* the carbonyl oxygen atom are proposed. The mechanisms of formation of the complexes are discussed.

THE interaction of bivalent tin derivatives with transition-metal carbonyls has recently been an area of intensive activity.[2] In previous papers we described the formation of pentacarbonyl-chromium, -molybdenum, and -tungsten complexes of [$Sn(C_5H_5)_2$], [$Sn(C_5H_4Me)_2$],[3] and several bis(β-ketoenolato)tin(II) compounds,[2] as well as dicarbonyl(methylcyclopentadienyl)manganese complexes of the latter.[4] With enneacarbonyldi-iron a different mode of reaction is observed. Initial displacement of [$Fe(CO)_5$] is accompanied by a rapid dimerisation yielding [$\{Fe(CO)_4(SnX_2)\}_2$] complexes seemingly regardless of the nature of X, although complexes with bulky β-ketoenolato-groups are essentially monomeric in solution at room temperature. All the complexes are dimers at 77 K, but monomeric species are stabilised by pyridine as solvate.[5]

The insertion reactions of tin(II) halides with [$L(OC)_3CoCo(CO)_3L$] (L = CO or phosphine) have been studied extensively,[6-9] but the reaction of [$Sn(C_5H_4Me)_2$] with [$Co_2(CO)_8$] in cyclohexane at room temperature yielded [$\{Co(CO)_4\}_4Sn$] as the only detectable tin-containing product.[3] Among tin(II)–oxygen derivatives, only the reaction of tin(II) acetate with [$Co_2(CO)_8$] has been investigated, and both [$\{Co(CO)_4\}_2Sn(CO_2Me)_2$] and [$\{Co(CO)_4\}_3Sn(CO_2Me)$] were identified as products.[8] In this

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[1] Part XVIII, P. F. R. Ewings, P. G. Harrison, A. Morris, and T. J. King, *J.C.S. Dalton*, preceding paper.

[2] A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 1486 and refs. therein.

[3] A. B. Cornwell, P. G. Harrison, and J. A. Richards, *J. Organometallic Chem.*, 1976, **108**, 47.

[4] A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1976, 1054.

[5] A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 2017.

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

[7] F. Bonati, S. Cenini, D. Morelli, and R. Vgo, *J. Chem. Soc.* (*A*), 1966, 1052.

[8] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 771.

[9] P. F. Barrett and A. J. Poë, *J. Chem. Soc.* (*A*), 1968, 429.

paper we report the reactions of bis(β-ketoenolato)tin(II) compounds with $[Co_2(CO)_8]$.

RESULTS AND DISCUSSION

Bis(β-ketoenolato)tin(II) compounds reacted slowly with octacarbonyldicobalt in benzene at room temperature giving products which varied with the nature of the β-ketoenolato-residue. Reaction with tin(II) bis(1,3-diphenylpropane-1,3-dionate), $[Sn(bppd)_2]$, afforded $[\{Co(CO)_4\}_2Sn(bppd)_2]$ (I) after 24 h, whilst tin(II) bis(4-phenylbutane-2,4-dionate), $[Sn(pbd)_2]$, and tin(II) bis(cyclohepta-2,4,6-triene-2,7-dionate), $[Sn(chtd)_2]$, gave the complexes $[Co_2(CO)_7(SnX_2)]$ (IIa; X = pbd) and (IIb; X = chtd) after 5 d. The reactions with tin(II) bis(pentane-2,4-dionate), $[Sn(pd)_2]$, bis(4-trifluoromethylbutane-2,4-dionate), $[Sn(tbd)_2]$, and bis[1,3-bis(trifluoromethyl)propane-1,3-dionate], $[Sn(bpd)_2]$, afforded complexes of composition $[Co(CO)_4(SnX)]$ (IIIa; X = pd), (IIIb; X = tbd), and (IIIc; X = bpd) after stirring the reaction mixtures for 72 h. Physical and spectroscopic data for the products are collected in Tables 1 and 2. Complexes (I), (IIa), and (IIb), obtained in >80% yield, are brown or red-brown air-stable powders, but (IIIa)—(IIIc) were isolated in much lower yield (40—54%) as black [(IIIa)] or purple [(IIIb) and (IIIc)], very hygroscopic, powders. All the complexes decompose without melting at elevated temperatures.

TABLE 1

Spectroscopic data for (I)—(III) and related complexes

Compound	Tin-119m Mössbauer (mm s^{-1})		I.r. (cm^{-1}) [a]							
			Terminal CO bands							Bridging CO bands
	i.s.	q.s.								
$[\{Co(CO)_4\}_2Sn(bppd)_2]$	1.27	1.67		2 090w(sh)	2 070m	2 030m(sh)			19 965br	
$[\{Co(CO)_4\}_2Sn(pd)_2]$ [b]			2 101w	2 091m	2 069s	2 023s	2 020m(sh)	2 013s	2 003s	
$[\{Co(CO)_4\}_2SnCl_2]$ [c,d]	1.83	1.43	2 115w	2 098s	2 057m	2 038s	2 023m			
	1.74	1.42								
$[\{Co(CO)_4\}_2SnBr_2]$ [d]	1.73	1.42	2 112m	2 095s	2 054m	2 036m	2 020m	2 014w(sh)	1 992vw	
$[Co_2(CO)_7\{Sn(pbd)_2\}]$	1.28	1.48		2 090s		2 045vs	2 010vs	1 995vs	1 985vs	1 805s
$[Co_2(CO)_7\{Sn(chtd)_2\}]$	1.31	1.58		2 100s	2 060vs	2 038vs	2 010vs		1 972vs	1 805s
$[Co_2(CO)_7\{Sn(pd)_2\}]$ [b]				2 076m		2 036s	2 013s	2 004m	1 994m	1 836m
$[Co(CO)_4\{Sn(pd)\}]$	3.35	1.93	2 100m(sh)	2 075s	2 040m(sh)				1 980vs,vbr	
$[Co(CO)_4\{Sn(tbd)\}]$	3.58	1.82	2 110m		2 060mw(sh)		2 010s,vbr			
$[Co(CO)_4\{Sn(bpd)\}]$	3.68$_5$	1.65	2 105m		2 040mw(sh)		2 010s,vbr			
$[Co(CO)_3(NO)]$ [e]			2 100				2 033			
$[Sn(bppd)_2]$ [f]	3.31	1.80								
$[Sn(pbd)_2]$ [f]	3.07	1.98								
$[Sn(chtd)_2]$ [f]	2.91	1.95								
$[Sn(pd)_2]$ [g]	3.10	2.02								
	3.12	1.89								
$[Sn(tbd)_2]$ [g]	3.40	1.87								
$[Sn(bpd)_2]$ [g]	3.60	1.66								

[a] w = Weak, mw = medium weak, m = medium, s = strong, vs = very strong, br = broad, and sh = shoulder. [b] Ref. 10. [c] S. R. A. Bird, J. D. Donaldson, A. F. LeC. Holding, S. Cenini, and B. Ratcliffe, *Inorg. Chim. Acta*, 1974, **8**, 149. [d] Ref. 6. [e] Ref. 15. [f] Ref. 18. [g] Ref. 17.

TABLE 2

Physical data for the complexes

Complex		Appearance	Yield (%)	Decomposition temperature (θ_c/°C)	Microanalysis (%) *		
					C	H	Co
$[\{Co(CO)_4\}_2Sn(bppd)_2]$	(I)	Red-brown powder	80	130	50.05 (50.3)	2.50 (2.45)	12.8 (13.0)
$[Co_2(CO)_7\{Sn(pbd)_2\}]$	(IIa)	Red-brown powder	81	140	42.4 (42.85)	2.70 (2.40)	15.65 (15.55)
$[Co_2(CO)_7\{Sn(chtd)_2\}]$	(IIb)	Brown powder	90	145	36.95 (37.35)	1.55 (1.50)	17.15 (17.45)
$[Co(CO)_4\{Sn(pd)\}]$	(IIIa)	Black powder	51	150	27.95 (27.8)	1.95 (1.80)	14.95 (15.15)
$[Co(CO)_4\{Sn(tbd)\}]$	(IIIb)	Purple powder	54	160	23.85 (24.4)	1.30 (0.90)	13.45 (13.3)
$[Co(CO)_4\{Sn(bpd)\}]$	(IIIc)	Purple powder	40	170	21.5 (21.75)	0.05 (0.20)	12.2 (11.85)

* Calculated values are given in parentheses.

The i.r. spectra of all the complexes in the <1 800 cm^{-1} region were essentially unchanged from those of the corresponding bis(β-ketoenolato)tin(II) compounds, indicating that the chelation of the β-ketoenolato-residue to tin is preserved on complex formation. Patmore and Graham [10] isolated both $[\{Co(CO)_4\}_2Sn(pd)_2]$ and $[Co_2(CO)_7\{Sn(pd)_2\}]$ by substitution of *cis*-$[SnCl_2(pd)_2]$ by the $[Co(CO)_4]^-$ anion, the particular product obtained depending on the rate of addition of the $[Co(CO)_4]^-$ solution.

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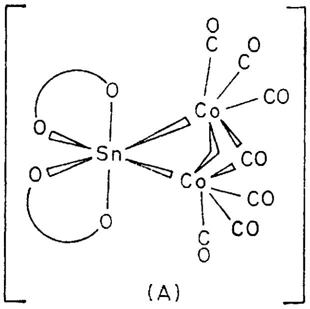
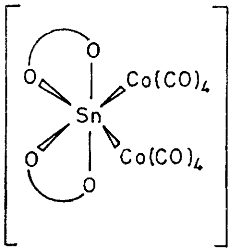
[10] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1967, **6**, 1879.

The structure of the complex $[\mathrm{Co_2(CO)_7\{Sn(pd)_2\}}]$ has been determined by *X*-ray diffraction, and contains a central $\mathrm{Co_2Sn}$ three-membered ring with each cobalt atom bearing three terminal carbonyl groups, whilst the seventh carbonyl group bridges both cobalt atoms.[11] Six-co-ordination at tin is completed by two chelating pd groups. The i.r. spectra of (IIa) and (IIb) in the metal–carbonyl stretching region are very similar to that of $[\mathrm{Co_2(CO)_7\{Sn(pd)_2\}}]$.[10] All three complexes exhibited five bands in the terminal metal–carbonyl stretching region and a further band at 1 805—1 836 $\mathrm{cm^{-1}}$ attributable to a bridging carbonyl group, consistent with structure (A).

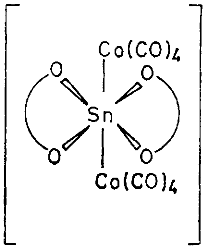
The similarity of the Mössbauer parameters for (I), (IIa), and (IIb) indicate that the *cis* geometry, (B), at tin, which is necessarily imposed on the metal for (IIa) and (IIb), also occurs for (I). However, Patmore and Graham,[10] on the basis of inconclusive mass-spectroscopic data, postulated the alternative *trans* geometry (C) for the $[\mathrm{\{Co(CO)_4\}_2Sn(pd)_2}]$ homologue. This possibility may be excluded in the present case since a value for the quadrupole splitting of *ca.* 3 mm $\mathrm{s^{-1}}$ (twice the *cis* value) would be expected for the *trans* isomer.



(A)

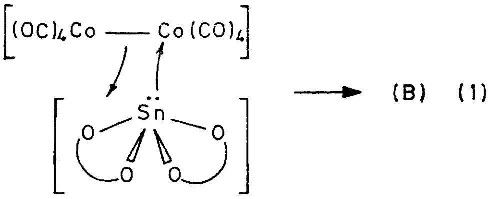


(B)

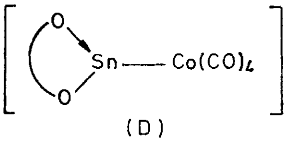


(C)

The *cis* geometry is also that which would be expected on mechanistic grounds. No kinetic data are available for insertion reactions into the Co–Co bond of $[\mathrm{Co_2(CO)_8}]$, but Barrett and Poë [9] studied the kinetics of both the thermal and photochemical insertion reactions of tin(II) chloride and bromide and $[\mathrm{Co_2(CO)_6(PBu_3)_2}]$. In view of the strongly nucleophilic character of the tin lone pair in bis(β-ketoenolato)tin(II) derivatives,[12] a bimolecular process similar to that proposed for the thermal reaction of $\mathrm{SnBr_2}$ and $[\mathrm{Co_2(CO)_6(PBu_3)_2}]$ [equation (1)] would lead to the *cis* isomer (B), although a mechanism involving $[\mathrm{Co_2(CO)_8}]$ in an electronically excited state in which the Co–Co bond is stretched, or even homolytically broken, cannot be excluded. The loss of a CO group to produce (IIa) and (IIb) may occur during the initial insertion reaction *via* the carbonyl-bridged isomer of $[\mathrm{Co_2(CO)_8}]$, or may be a secondary process due to the longer reaction times involved.



The reactions of $[\mathrm{Co_2(CO)_8}]$ with $[\mathrm{Sn(pd)_2}]$, $[\mathrm{Sn(tbd)_2}]$, and $[\mathrm{Sn(bpd)_2}]$ obviously take a different course, in which one β-ketoenolate residue is displaced from tin giving the complexes (IIIa)—(IIIc) of composition $[\mathrm{Co(CO)_4(SnX)}]$ (X = pd, tbd, or bpd). Surprisingly, the Mössbauer isomer shifts of the three products (IIIa)—(IIIc) showed a marginal but distinct increase from the starting bis(β-ketoenolato)tin(II) compounds. Thus, a formulation for these complexes involving a direct tin–cobalt bond, *e.g* (D), may be ruled out, since tin(II)–transition-metal bond formation is accompanied by a decrease of >1.5 mm $\mathrm{s^{-1}}$ in the isomer shift, due to increased shielding of the tin 5*s* electrons arising from $(d\rightarrow d)\pi$ multiple-bonding interactions along the tin–transition metal axis.[2,3,5] The isomer-shift values are, however, not inconsistent with the ionic formulation $[\mathrm{SnX}][\mathrm{Co(CO)_4}]$, since the increase in nuclear charge on tin due to the loss of one β-ketoenolate group would cause a contraction of the tin 5*s* orbital, and so increase $\psi_{5s}(0)$. Discrete isolated cationic species are unlikely, since the tin would be co-ordinatively unsaturated whilst bearing a high effective nuclear charge. Moreover, the absence [13] of a band at 1 886 $\mathrm{cm^{-1}}$ shows that isolated tetrahedral $[\mathrm{Co(CO)_4}]^-$ anions are also not present. However, transition-metal carbonyls and carbonyl anions are well known to complex *via* the carbonyl oxygen atom with $\mathrm{Al^{III}}$, $\mathrm{Ga^{III}}$, and $\mathrm{Eu^{III}}$ Lewis acids.[14] As (β-ketoenolato)tin(1+) species would be expected to be strongly Lewis acidic, we propose a structure for (IIIa)—(IIIc) in which $[\mathrm{Co(CO)_4}]^-$ anions co-ordinate to tin *via* the oxygen of one carbonyl group, thus completing pyramidal three-co-ordination at $\mathrm{Sn^{II}}$, (E). Such an arrangement would relax the ' local '



(D)

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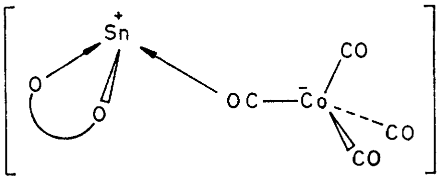
[11] R. D. Ball and D. Hall, *J. Organometallic Chem.*, 1973, **56**, 209.

[12] P. F. R. Ewings, P. G. Harrison, and T. J. King, *J.C.S. Dalton*, 1975, 1455.

[13] W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *J. Amer. Chem. Soc.*, 1960, **82**, 1254.

[14] D. F. Shriver, *Chem. in Britain*, 1972, **8**, 419.

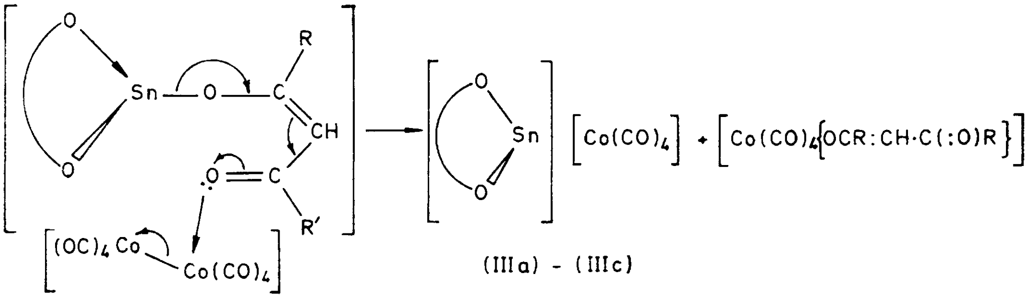
symmetry at cobalt from T_d to C_{3v}, in which point group three metal–carbonyl stretching bands ($2A_1 + E$) would be expected in the i.r. spectrum. Four bands (at 2 100, 2 075, 2 040, and 1 980 cm^{-1}) were observed for (IIIa),



(E)

whilst (IIIb) and (IIIc) exhibited three bands (at *ca.* 2 100, *ca.* 2 050, and 2 010 cm^{-1}). These values may be compared with those of [$Co(CO)_3(NO)$], which is also of C_{3v} symmetry, and exhibits the two expected modes at 2 100 and 2 033.[15]

The mechanism of formation of (IIIa)—(IIIc) could involve initial nucleophilic displacement of a [$Co(CO)_4$]$^-$ anion from [$Co_2(CO)_8$] by the tin(II) base, as proposed for the reaction of [$Sn(C_5H_4Me)_2$] with [$Co_2(CO)_8$].[3] However, the preferred mechanism involves a change in the mode of co-ordination of one β-ketoenolate group from bidentate to unidentate, followed by nucleophilic attack of the ' free ' carbonyl group at cobalt [equation (2)]. A similar mechanism has been proposed for pd group exchange between [$SnMe_2(pd)_2$] and [$SnPh_2(pd)_2$], in which the change of co-ordination of one pd group in the latter from bidentate to unidentate was identified as the rate-determining step of the process.[16] Such a mechanism would seem quite reasonable especially in the cases of [$Sn(tpd)_2$] and [$Sn(bpd)_2$], where perfluorination greatly increases the leaving ability of the dionato-ligands and the polarity of the tin–oxygen bonds. Attempts to obtain [$\{Co(CO)_4\}_2Sn(tpd)_2$] and [$\{Co(CO)_4\}_2Sn(bpd)_2$] by substitution of [$\{Co(CO)_4\}_2SnCl_2$] by the sodium salts of the β-diketones yielded only unidentifiable products.



(IIIa) - (IIIc)

EXPERIMENTAL

All the manipulations were under an atmosphere of dry argon or nitrogen, and all the solvents were dried and freed from oxygen by standard methods, and redistilled immediately prior to use.

Infrared spectra were recorded as Nujol mulls using Perkin-Elmer 457 and 521 spectrophotometers calibrated with polystyrene film. Tin-119m Mössbauer spectra were obtained at 77 K using a Harwell spectrometer with a $Ba^{119m}SnO_3$ source. Data reduction to Lorentzian lineshapes was effected by the usual least-squares methods. Values quoted in Table 1 for isomer shifts and quadrupole splittings are considered accurate to at least ± 0.05 and ± 0.10 mm s^{-1}, respectively. Cobalt analysis were by atomic absorption spectroscopy on samples initially digested in *aqua regia* before dilution with distilled water.

Octacarbonyldicobalt was obtained from Strem Chemicals, and stored at −10 °C. Bis(β-ketoenolato)tin(II) derivatives were synthesised as described previously.[17,18]

Preparation of Complexes (I)—(III).—The synthesis of the complexes were essentially similar. Generally, the tin(II) compound (1.0—3.0 mmol) in benzene (10 cm^3) was added to a solution of [$Co_2(CO)_8$] (1.0—3.0 mmol) also in benzene (30 cm^3), and the mixture was stirred for 24—120 h [(I) 24, (IIa) and (IIb) 120 h, (IIIa)—(IIIc) 72 h]. Unchanged [$Co_2(CO)_8$] was removed by filtration, and the ***product*** usually crystallised when the filtrate was concentrated to *ca.* 10 cm^3. Experimental details are collected in Table 2.

One of us (A. B. C.) thanks the S.R.C. for a studentship.

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[15] W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, 1963, **2**, 723.

[16] N. Serpone and R. Ishayek, *Inorg. Chem.*, 1974, **13**, 52.

[17] P. F. R. Ewings, P. G. Harrison, and D. E. Fenton, *J.C.S. Dalton*, 1975, 821.

[18] A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 1722.