Derivatives of Bivalent Germanium, Tin, and Lead. Part VII.[1] Chromium, Molybdenum, and Tungsten Pentacarbonyl Complexes of Tin(II) Bis(β-ketoenolates)

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Bis(β-ketoenolato)tin(II)–metal pentacarbonyl complexes, $[(O{:}CR'{\cdot}CH{:}CR{\cdot}O^-)_2SnM(CO)_5]$ ($R = R' = Me$ or CF_3; $R = Me$, $R' = Ph$ or CF_3; M = Cr, Mo, or W), have been synthesised by photolysis of the Group 6 metal hexacarbonyl and tin(II) bis(β-ketoenolate) in tetrahydrofuran (thf). The i.r. spectra indicate that chelation of the β-ketoenolate residues does not change significantly on complex formation. The complexes exhibit very low isomer shifts (1.80—2.11 mm s^{-1}), usually assumed to be characteristic of tin(IV) compounds, and demonstrate the invalidity of the use of the isomer shift of β-tin (2.56 mm s^{-1}) as the arbitrary dividing line between the two oxidation states. The n.m.r. and Mössbauer data have been interpreted in terms of synergic ($\sigma + \pi$) interactions along the tin–transition metal axis.

THE interaction of bivalent derivatives of germanium, tin, and lead with transition-metal carbonyl complexes is of interest since it provides suitable models for the more inaccessible analogues, carbenes and silylenes. *A priori*, there are two modes of reaction possible: (*i*) insertion of the bivalent species into a reactive M–M or M–X bond (formal oxidative addition at the Group 4 metal centre); and (*ii*) formation of a Lewis acid–Lewis base complex in which the bivalent metal functions as a two-electron donor molecule. Insertion reactions of germanium(II) and tin(II) dihalides into M–M bonds (M = Fe, Co, Ni, Mn, Cr, Mo, or W) to yield $M{-}M^{IV}X_2{-}M$ linkages have been known for a long time.[2-5]

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However, recent kinetic [6] and product-analysis studies [7] have shown that these reactions are more complex than the overall stoicheiometry suggests.

Although carbene–transition-metal complexes have been investigated in depth, analogous complexes of silylenes, germylenes, stannylenes, and plumbylenes have been studied relatively little. The nature of the trihalogenostannate(II) group as a donor has been a topic of controversy because of the anomalously low tin-119m Mössbauer isomer shifts exhibited by complexes containing this group. However, neutral complexes involving simple Ge^{II} and Sn^{II} dihalides as donors towards Group 6 metal pentacarbonyl moieties have only recently been synthesised by irradiation of the metal hexacarbonyl and metal(II) dihalide in tetrahydrofuran (thf).[8] In some cases stabilisation of the complexes was achieved by co-ordination of a solvent molecule to the Group 6 metal. Irradiation of pentane solutions of $W(CO)_6$ and Si_2I_6 leads to formation of the iodine-bridged dimer $[\{I_2SiW(CO)_5\}_2]$, which, when dissolved in thf, gives the monomeric species $[I_2SiW(CO)_5]\cdot thf$.[9] Similar complexes of isolable organometallic Sn^{II} species such as $[Sn\{CH(SiMe_3)_2\}_2]$ and $[Sn(cp)_2]$ (cp = cyclopentadienyl) may also be synthesised by photolytic methods.[10,11] In addition, complexes of unstable dialkyl-germylenes and -stannylenes have been obtained by indirect routes as thf, dimethyl sulphoxide (dmso), or pyridine (py) adducts.[12] An *X*-ray crystallographic investigation of one of the complexes, $[Bu^tSnCr(CO)_5]\cdot py$, has confirmed the presence of a direct tin–chromium bond and C_{4v} 'local' symmetry for the $Cr(CO)_5$ moiety.[13] The interaction of bivalent tin species with enneacarbonyldi-iron generally leads to formation of $[\{X_2SnFe(CO)_4\}_2]$ dimers which contain tin in the formal oxidation state IV. On addition of oxygen or nitrogeneous bases, however, rapid homolytic fission of the iron–tin bonds results leading to monomeric $[X_2SnFe(CO)_4]\cdot L$ complexes in which the tin formally has an oxidation state of II. Again a solvating molecule of base is necessary for stabilisation of the complexes.[14] Ylide-type contributions to the overall electronic structure have been proposed for these dialkyltin–chromium and –iron complexes in order to rationalise tin-119m Mössbauer and tin $3d_{\frac{5}{2}}$ photoelectron spectroscopic data.[14]

In Part V [15] of this series we described the synthesis and spectroscopic properties of tin(II) bis(β-ketoenolates). The hypothesis of lone-pair stereochemical activity for this family of complexes was later confirmed by an *X*-ray diffraction study of bis(4-phenylbutane-1,3-dionato)-tin(II), which was shown to possess a distorted trigonal-bipyramidal structure with the lone pair of electrons occupying an equatorial site.[1] In this paper we demonstrate the basicity of tin in these complexes by synthesis of Group 6 metal pentacarbonyl derivatives.

RESULTS AND DISCUSSION

Treatment of chromium, molybdenum, and tungsten pentacarbonyl thf adducts (formed by u.v. irradiation of the appropriate hexacarbonyl in thf until gas evolution ceased) with tin(II) bis(pentane-2,4-dionate), $[Sn(pd)_2]$, bis(4-phenylbutane-2,4-dionate), $[Sn(pbd)_2]$, bis(4-trifluoromethylbutane-2,4-dionate), $[Sn(tbd)_2]$, or bis[1,3-bis(trifluoromethyl)propane-1,3-dionate], $[Sn(bpd)_2]$, resulted in formation of the bis(β-ketoenolato)tin(II)–metal carbonyl complexes, (I), as coloured amorphous solids or oils (X = tbd, M = Mo or W; X = bpd, M = W). Yields of the chromium and tungsten complexes

$$M(CO)_6 \xrightarrow[thf]{Light} M(CO)_5\cdot thf \xrightarrow[-thf]{SnX_2} \underset{(I)}{[X_2SnM(CO)_5]} \quad (1)$$

were satisfactory (58—82%), but the molybdenum complexes could only be obtained in poor (20—32%) yield. All the complexes are sensitive to oxygen and moisture, and also decomposed on attempted sublimation *in vacuo*. The solubility of the complexes in dry deoxygenated solvents such as thf, acetonitrile, benzene, chloroform, and dichloromethane is generally high, but decomposition occurs when traces of oxygen or water are present.

The i.r. spectra of the complexes in the region below 1 800 cm^{-1} differed only slightly from those of the parent tin(II) bis(β-ketoenolates), indicating that negligible perturbation of the chelating β-ketoenolate groups takes place on complex formation and consistent with the formulation of the complexes as (A) involving a co-ordinate tin–transition-metal bond. Dissolution of the complexes $[(pbd)_2SnM(CO)_5]$ (M = Cr or Mo) in the donor solvent pyridine, however, produced a band at 1 710 cm^{-1}, which may be assigned to unco-ordinated carbonyl groups of the now unidentate β-ketoenolate residue, any vacant co-ordination sites at tin presumably being occupied by py.[15] In the metal–carbonyl stretching region the complexes usually exhibited three bands in the

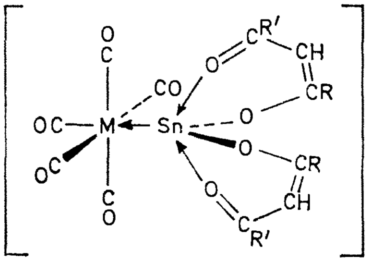

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TABLE 1

Carbonyl-stretching bands of the M(CO)$_5$ residue (cm^{-1}) [a]

Complex	Solid [b]	Solution [c]
[(pd)$_2$SnCr(CO)$_5$]	2 060ms, 1 980s, 1 935vs,br, 1 910(sh)	2 070m, 1 970s, 1 940vs,br
[(pd)$_2$SnMo(CO)$_5$]	2 070w, 1 985s, 1 930ms,br	2 075m, 1 980s(sh), 1 940s,br
[(pd)$_2$SnW(CO)$_5$]	2 080ms, 1 980s, 1 925vs,br	2 080m, 1 975m(sh), 1 940vs,br
[(pbd)$_2$SnCr(CO)$_5$]	2 065ms, 1 980m, 1 940, 1 920s,br	1 060s, 1 980ms(sh), 1 925vs,br
[(pbd)$_2$SnMo(CO)$_5$]	2 090ms, 1 990w(sh), 1 950vs,br, 1 925s	2 080ms, 1 985m(sh), 1 940, 1 920vs,br
[(pbd)$_2$SnW(CO)$_5$]	2 080ms, 1 980s, 1 950, 1 930vs,br	2 080m, 1 980m(sh), 1 940vs,br
[(tbd)$_2$SnCr(CO)$_5$]	2 070m, 1 985m(sh), 1 940s,br	2 060s, 1 980ms(sh), 1 940vs,br
[(tbd)$_2$SnMo(CO)$_5$]	2 080ms,[d] 1 985(sh),[d] 1 925vs,br [d]	2 075m, 1 980m, 1 930vs,br
[(tbd)$_2$SnW(CO)$_5$]	2 085m,[d] 1 990(wsh),[d] 1 930vs,br [d]	2 085m, 1 990w(sh), 1 945vs,br
[(bpd)$_2$SnCr(CO)$_5$]	2 075ms, 1 985s, 1 935vs,br	2 070m, 1 980s, 1 940vs,br
[(bpd)$_2$SnMo(CO)$_5$]	2 080m, 1 980s, 1 940s,br	2 085m, 1 980ms, 1 935s,br
[(bpd)$_2$SnW(CO)$_5$]	2 085ms,[d] 1 990m(sh),[d] 1 940vs,br [d]	
[Me$_2$SnCr(CO)$_5$]·thf [e]		2 038w, 1 941m, 1 920s
[Bu$^t_2$SnCr(CO)$_5$]·thf [e]		2 031s, 1 938m, 1 918s
[Cl$_2$SnCr(CO)$_5$]·thf [f]		2 063 m, 1 982(sh), 1 958vs, 1 945(sh)
[Cl$_3$SnCr(CO)$_5$]$^-$ [f]		2 060ms, 1 946vs
[Cl$_2$SnMo(CO)$_5$] [f]		2 080ms, 1 985vs, 1 958(sh)
[Cl$_3$SnMo(CO)$_5$]$^-$ [f]		2 076m, 1 918(sh), 1 951vs
[Cl$_2$SnMo(CO)$_5$] [f]		2 075m, 1 975(sh), 1 950vs
[Cl$_3$SnW(CO)$_5$]$^-$ [f]		2 075ms, 1 948vs

[a] w = Weak, m = medium, ms = medium strong, s = strong, vs = very strong, sh = shoulder, and br = broad. [b] Nujol mull. [c] In chloroform. [d] Liquid film. [e] Hexane solution; ref. 14. [f] Acetonitrile solution; ref. 8.

regions 2 060—2 085, 1 980—1 990, and 1 920—1 950 cm^{-1}, the latter being very broad and sometimes split into two components. Spectra recorded in the solid phase and in dichloromethane were essentially identical. ' Local ' C_{4v} symmetry for the M(CO)$_5$ fragment would predict three i.r.-active carbonyl-stretching modes ($2A_1 + E$). Although the bands at 2 060—2 085 and 1 920—1 950 cm^{-1} may be assigned to A_1 and E modes, respectively, those at 1 980—1 990 cm^{-1} occur at too high energy to be the second A_1 mode. This band is more appropriately assigned to a B_1 mode, inactive in C_{4v} symmetry, indicating a lowering of the symmetry towards overall C_2. Bands in similar regions have also been observed for the [X$_2$SnM(CO)$_5$] and [X$_3$SnM(CO)$_5$] (X = halogen; M = Cr, Mo, or W) species.[8] The complexes, [R$_2$SnCr(CO)$_5$]·thf (R = Me or Bu^t), on the other hand, exhibit bands at 2 031—2 038, 1 938—1 941, and 1 918—1 920 cm^{-1}, quite consistent with ' local ' C_{4v} symmetry.[12]

TABLE 2

^{1}H and ^{19}F N.m.r. and ^{119m}Sn Mössbauer data

	N.m.r.			Mössbauer [a]	
Complex	τ(CH)	τ(CH$_3$)	δ(CF$_3$)/ p.p.m.	I.s.	Q.s.
[(pd)$_2$Sn] [b]	4.87	8.28		3.12	1.89
[(pd)$_2$SnCr(CO)$_5$]	4.52	7.95		1.81	2.28
[(pd)$_2$SnMo(CO)$_5$]	4.49	8.06		1.82	2.30
[(pd)$_2$SnW(CO)$_5$]	4.12	8.00		1.80	2.35
[(pbd)$_2$Sn] [c]	3.93	8.02		3.07	1.98
[(pbd)$_2$SnCr(CO)$_5$]	3.84	7.83		2.02	2.07
[(pbd)$_2$SnMo(CO)$_5$]	3.87	7.83		1.93	2.51
[(pbd)$_2$SnW(CO)$_5$]	3.86	7.92		1.90	2.39
[(tbd)$_2$Sn] [b]	4.22	7.88	76.58	3.40	1.87
[(tbd)$_2$SnCr(CO)$_5$]	4.12	7.77	77.27	1.95	2.29
[(tbd)$_2$SnMo(CO)$_5$]	4.10	7.74	77.33	1.93	2.42
[(tbd)$_2$SnW(CO)$_5$]	4.06	7.73	77.19	2.00	2.31
[(bpd)$_2$Sn] [b]	4.02		77.54	3.60	1.66
[(bpd)$_2$SnCr(CO)$_5$]	3.75		76.60	1.99	2.60
[(bpd)$_2$SnMo(CO)$_5$]	3.74		76.46	2.03	2.45
[(bpd)$_2$SnW(CO)$_5$]	3.76		76.51	2.13	2.56
[Bu$^t_2$SnCr(CO)$_5$]·thf [d]				2.11	1.44
[Bu$^t_2$SnCr(CO)$_5$]·dmso [d]				1.98	3.60
[Bu$^t_2$SnCr(CO)$_5$]·py [d]				2.01	3.44

[a] Measured at 77 K; mm s^{-1} relative to SnO$_2$. [b] Ref. 15. [c] Ref. 32. [d] Ref. 14.

N.m.r. data are listed in Table 2. The methine and methyl group protons are deshielded on complex formation by 0.07—0.75 and 0.11—0.33 p.p.m., respectively. The CF$_3$ resonances of the bpd complexes were also deshielded by *ca.* 1 p.p.m., but in the tbd complexes the shielding actually increased somewhat. Participation of the tin lone pair in co-ordination to the transition metal would be expected to increase the effective nuclear charge on the tin, causing electron drift away from the β-ketoenolate residue towards the metal and resulting in *greater* shielding of the methine proton. The observed trends may be rationalised by the presence of retrodative chromium→tin ($d \rightarrow d$) π bonding. Such a mechanism would transfer electron density *via* the metal *d* orbitals to the π-resonance system of the β-ketoenolate residues, resulting in an increase in ring current and the deshielding observed. Such tin–transition metal ($d \rightarrow d$) π interactions have received support in previous years from chemical,[16] i.r.,[17-23] and n.m.r. data,[24,25] and also from theoretical calculations.[26]

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The tin-119m Mössbauer data (Table 2) are most interesting. The free bivalent tin ligands exhibited isomer shifts in the range 3.07—3.60 mm s^{-1}, well above that of β-tin (2.56 mm s^{-1}), the empirical dividing line between the two oxidation states of tin.[27] Complex formation resulted in a lowering of the isomer shift to the range 1.80—2.11 mm s^{-1}, in the ' tin(IV) ' region. Since there is no reason to suppose that simultaneous oxidation of tin takes place on complex formation, this series of complexes illustrates the invalidity of the use of such an empirical dividing line for the two oxidation states. Bancroft and Butler [28] attributed the lowering in isomer shift in the $SnCl_3$ moiety in a number of isocyanide(trichlorotin)iron(II) complexes to donation of the tin lone pair of the $[SnCl_3]^-$ ion to iron. The formation of such complexes is accompanied by a rehybridisation of tin from p^3 in the $[SnCl_3]^-$ anion (Cl–Sn–Cl 86.9—92.3°)[29] towards sp^3 in the complexes (Cl–Sn–Cl 92.8—103.7°)[30] which would be expected to contribute to the lowering of the isomer shift. However, since formation of a simple σ bond does not necessarily change the 5*s*-electron density at tin {Mössbauer parameters for $[Sn(cp)_2]$ and its boron trifluoride complex are identical within experimental error [31]}, some additional mechanism must be operative in the present case to lower the effective $[\psi_{5s}(0)]^2$ on complex formation. Transition metal→tin ($d \rightarrow d$) π interactions would place electron density in vacant tin *d* orbitals and lower the effective $[\psi_{5s}(0)]^2$ by shielding. The magnitude of such π interactions has been calculated from force-constant data to be not inconsiderable in the case of pentacarbonylmanganese–tin derivatives.[22,23] This effect would be expected to be synergic, the greater the electron withdrawal along the σ framework the greater the back donation *via* *d*-orbital overlap. Thus it would appear that the lowering of the isomer shift (Δδ 1.05—1.71 mm s^{-1}) comprises of contributions from both σ and π effects. The magnitude of the quadrupole splitting also increases [Δ(Δ) 0.09—0.94 mm s^{-1}] consistent with this model.

TABLE 3

Experimental details and physical properties of the complexes

Complex	Quantity of reagent (mmol)	Yield/%	Form	M.p. (θ_c/°C)	Analyses/% Found C	Found H	Calc. C	Calc. H
$[(pd)_2SnCr(CO)_5]$	3.0	80	Pale yellow-cream powder	87—88	35.6	2.50	35.4	2.80
$[(pd)_2SnMo(CO)_5]$	4.0	20	Brown powder	Decomp. >90	30.9	2.75	32.55	2.55
$[(pd)_2SnW(CO)_5]$	3.0	69	Pale cream powder	96—97	28.2	2.30	28.1	2.20
$[(pbd)_2SnCr(CO)_5]$	3.0	76	Lime-green powder	95—97	47.2	3.20	47.4	2.85
$[(pbd)_2SnMo(CO)_5]$	4.5	32	Purple-brown powder	105	44.25	2.50	44.35	2.70
$[(pbd)_2SnW(CO)_5]$	3.5	68	Cream powder	130	39.45	2.70	39.25	2.35
$[(tbd)_2SnCr(CO)_5]$	3.0	58	Pale green powder	Decomp. >120	29.25	1.30	2.96	1.30
$[(tbd)_2SnMo(CO)_5]$	4.0	21	Very viscous dark red-brown oil	Oil	27.25	1.05	27.6	1.25
$[(tbd)_2SnW(CO)_5]$	6.0	82	Bright orange-yellow oil	Oil	24.2	1.15	24.3	1.10
$[(pbd)_2SnCr(CO)_5]$	3.0	61	Pale green powder	Decomp. >120	25.1	0.65	24.85	0.30
$[(bpd)_2SnMo(CO)_5]$	4.0	30	Dark brown powder	Decomp. >130	23.8	0.50	23.45	0.25
$[(pbd)_2SnW(CO)_5]$	3.2	70	Red-purple oil	Oil	20.85	0.35	21.05	0.25

The isomer shifts of the related di-t-butylstannylene complexes, $[Bu^t_2SnCr(CO)_5]\cdot L$ (L = py, dmso, or thf) all fell in a similar range (1.98—2.11 mm s^{-1}) but exhibited quadrupole splittings substantially greater (3.44—4.14 mm s^{-1}).[14] In addition, i.r. data suggest that the $SnBu^t_2\cdot L$ groups are powerful π acceptors.[12] The crystal structure of the py complex shows that the tin is four-co-ordinated by the two t-butyl groups, the chromium atom, and the py nitrogen in a fashion which is intermediate between tetrahedral and trigonal pyramidal with the nitrogen atom in the apical position, but probably closer to the latter description.[13] However, in spite of the known stereochemistry, Grynkewich *et al.*[14] found it necessary to postulate sophisticated ylide structures in order to rationalise the large quadrupole splittings observed for these complexes.

EXPERIMENTAL

All manipulations were made under an atmosphere of dry argon or nitrogen.

I.r. spectra were recorded using a Perkin-Elmer 457 spectrophotometer calibrated with a polystyrene film. ^1H and ^{19}F N.m.r. spectra were obtained on a Varian HA-100 spectrometer using $SiMe_4$ (^1H) and $CFCl_3$ (^{19}F) as internal lock signals. Samples for examination were prepared by dissolution in either $CDCl_3$ (^1H) or $CHCl_3$ (^{19}F). Tin-119m Mössbauer spectra were obtained at 77 K using a Harwell spectrometer equipped with a 256 multichannel analyser against a $Ba^{119m}SnO_3$ source. Data reduction to Lorentzian lineshapes was effected by the usual least-squares methods. U.v. irradiations were effected with a medium-pressure arc (*ca.* 180—256 nm) (Hanovia Ltd).

The tin(II) derivatives of pentane-2,4-dione, 4-trifluoromethylbutane-2,4-dione, and 1,3-bis(trifluoromethyl)propane-1,3-dione were synthesised as described previously.[15]

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Bis(4-phenylbutane-1,3-dionato)tin(II) was prepared similarly from bis(methylcyclopentadienyl)tin(II) and 4-phenylbutane-2,4-dione in thf.[32]

Preparation of the Complexes.—The synthesis of all the complexes was essentially similar. Generally the Group 6 metal hexacarbonyl (3.0—6.0 mmol) was irradiated in dry oxygen-free thf (*ca*. 100 cm^3) until evolution of carbon monoxide ceased. The appropriate quantity of tin(II) bis(β-ketoenolate) also in thf (20 cm^3) was then added, usually producing a colour change in the reaction mixture. Reduction of the volume to a few cm^3 precipitated out a small amount of unchanged metal hexacarbonyl which was filtered off. The *complexes* crystallised out of solution on slow addition of a small amount of pentane. Essential experimental details and physical properties for the complexes are listed in Table 3.

[4/2383 *Received*, 14*th November*, 1974]

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