Derivatives of Bivalent Germanium, Tin, and Lead. Part XIII.[1] Dicarbonyl(methylcyclopentadienyl)stanniomanganese Complexes

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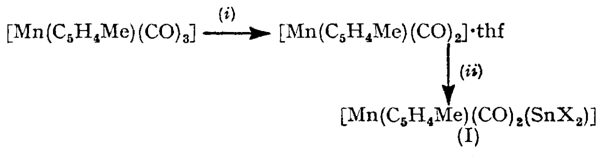
Complexes of composition $[Mn(C_5H_4Me)(CO)_2(SnX_2)]$ (X = various β-diketonate ligands) have been synthesised by photolysis of $[Mn(C_5H_3Me)(CO)]$ and the appropriate bivalent tin compound in tetrahydrofuran.

PREVIOUSLY we have reported the synthesis and properties of bis(β-ketoenolato)tin(II)–chromium, –molybdenum, and –tungsten pentacarbonyl complexes involving tin(II)→transition-metal co-ordinate bonds.[2] Attempts to prepare similar tetracarbonyliron complexes always resulted in the formation of dimeric $[\{Fe(CO)_4(SnX_2)\}_2]$ species involving a central Fe_2Sn_2 four-membered ring. Monomeric species were however obtained by base-induced fragmentation of the ring.[3] We now report the results of our investigations concerning complex formation between bivalent tin(II) donor molecules and methylcyclopentadienylmanganese tricarbonyl.

RESULTS AND DISCUSSION

Treatment of the tetrahydrofuran (thf) adduct of methylcyclopentadienylmanganese dicarbonyl 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), $[Sn(tbd)_2]$, bis[1,3-bis(trifluoromethyl)propane-1,3-dionate], $[Sn(bpd)_2]$, bis(1,3-bisphenylpropane-1,3-dionate), $[Sn(bppd)_2]$, bis(2-hydroxycyclohepta-2,4,6-trienonate), $[Sn(hct)_2]$, or anhydrous tin(II) chloride or bromide resulted in the formation of the bis(β-ketoenolato)stannio- or dihalogenostanniodicarbonyl(methylcyclopentadienyl)manganese complexes, (I), as coloured solids, except for the $[Sn(pbd)_2]$ complex which was a very viscous orange-red oil (Scheme). No sensible products were obtained using bis(cyclopentadienyl)tin(II), bis(methylcyclopentadienyl)tin(II), or tin(II) iodide. Yields of the complexes were quite satisfactory (50—80%). All the complexes are extremely sensitive to atmospheric



$$\begin{tikzcd}[Mn(C_5H_4Me)(CO)_3] \arrow[r, "(i)"] & {[Mn(C_5H_4Me)(CO)_2]\cdot thf} \arrow[d, "(ii)"] \\ & {[Mn(C_5H_4Me)(CO)_2(SnX_2)]} \\ & (I)\end{tikzcd}$$

SCHEME (*i*), light, thf; (*ii*), SnX_2 — thf

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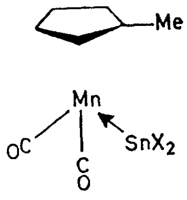
[1] Part XII, P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S. Dalton*, 1975, 2097.

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

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

moisture and oxygen, and are only very sparingly soluble in common organic solvents such as benzene, chloroform, or dichloromethane, thus precluding the gathering of n.m.r., solution i.r., or colligative data.

Like the analogous Group 6 metal pentacarbonyl complexes,[2] the i.r. spectra of the β-ketoenolato-complexes are essentially unchanged from that of the free ligands in the region below 1 800 cm^{-1}. In the metal-carbonyl stretching region, all the complexes exhibit two principal bands in the 1 920—1 940 and 1 850—1 870 cm^{-1} regions, although in a few cases additional weaker bands were observed, most probably due to solid-state effects (Table). We thus formulate the complexes as



(II)

having the structure (II), involving tin(II)-manganese co-ordinate bonds, and similar to that proposed for the analogous amine,[4–6] phosphine,[5,7–9] arsine,[5,10] and stibine [11] donor molecules, and deduced crystallographically for μ-*o*-phenylene-tetracarbonylbis(dimethylarsine)(η-methylcyclopentadienyl)dimanganese.[12]

Physical data for the $[Mn(C_5H_4Me)(CO)_2(SnX_2)]$ complexes

X	Appearance	M.p. (θ_c/°C)	Yield (%)	Microanalysis (%) C	H	Halogen	$\tilde{\nu}$(M–CO)/cm^{-1}		Tin-119m Mössbauer data (mm s^{-1}) I.s.	Q.s.
Cl	Red-brown powder	Decomp. >140	80	23.8 (23.55)	1.85 (1.75)	17.15 (17.4)	1 970m (sh), 1 940s, br	1 870m, br	1.77	1.81
Br	Red-brown powder	Decomp. >150	50	21.1 (20.5)	1.75 (1.50)	34.65 (34.1)	1 970m (sh), 1 930s, br	1 870m, br	2.03	1.65
bppd	Orange-yellow powder	135	51	60.0 (60.45)	3.90 (3.85)		1 930m, br	1 865m, br	1.96	2.55
pbd	Yellow crystalline powder	Decomp. <120	58	53.6 (53.1)	4.30 (4.00)		1 940s, 1 920m (sh)	1 865m, 1 850m	1.99	2.40
tbd	Cream-yellow powder	88—89	50	35.05 (35.15)	2.55 (2.45)		1 970w (sh), 1 940m, br	1 870m, br	1.92	2.62
bpd	Yellow-brown powder	99—101	65	30.35 (29.9)	1.60 (1.25)		1 965w (sh), 1 940m, br	1 865s, br	1.89	2.77
pd	Orange-red oil		68	42.1 (42.65)	3.85 (4.20)		1 930s, vbr	1 865s, br	1.93	2.48
chtd	Orange crystalline powder	Decomp. >140	51	47.9 (47.95)	3.45 (3.10)		1 920s, br	1 855s, br	1.88	2.26

The tin-119m Mössbauer spectra for the β-ketoenolato-complexes (Table) consisted of quadrupole-split doublets with isomer shifts in the narrow range 1.88—1.99 mm s^{-1} and quadrupole splittings varying from 2.26 to 2.77 mm s^{-1}. The isomer shifts of the halide complexes were similar, but the quadrupole splittings were significantly lower. As in the case of the $[M(CO)_5(SnX_2)]$ (M = Cr, Mo, or W) [2] and $[Fe(CO)_4(SnX_2)]\cdot B$ complexes,[3] the reduction of the isomer shift and increase in quadrupole splitting on complex formation can be attributed to synergic ($\sigma + \pi$) interactions along the tin–manganese axis.

EXPERIMENTAL

All manipulations were made under an atmosphere of dry argon or nitrogen. Infrared spectra were recorded as Nujol mulls using a Perkin-Elmer 457 spectrophotometer calibrated with a polystyrene film. 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 line shapes was effected by the usual least-squares methods. U.v. irradiations were made with a medium-pressure arc (*ca.* 180—256 nm) (Hanovia Ltd.). The tin(II) bis(β-ketoenolate) derivatives were synthesised as described earlier.[3,13] Methylcyclopentadienylmanganese tricarbonyl was obtained from the Ethyl Corporation Ltd.

Preparation of the Complexes.—The synthesis of all the complexes was essentially the same. Generally $[Mn(C_5H_4Me)(CO)_3]$ (1.2—9.2 mmol) was irradiated in dry oxygen-free thf (*ca.* 150 cm^3) under an atmosphere of argon until the evolution of carbon monoxide ceased. The appropriate quantity of the bivalent tin compound dissolved in thf (10—30 cm^3) was then added and the mixture stirred for *ca.* 24 h during which time a colour change from dark purple to dark or light orange took place. Crystallisation of the *complexes* occurred as the volume of the solvent was reduced. Pertinent physical data are listed in the Table.

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