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SYNTHESIS AND CRYSTAL STRUCTURE OF THE NOVEL TRANSITION-METAL SUBSTITUTED TIN HYDRIDE $H_2Sn_2[Mn(CO)_5]_4$*

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Summary

Dicyclopentadienyltin reacts with manganese pentacarbonyl hydride to give the first transition-metal substituted ditin dihydride, $H[Mn(CO)_5]_2Sn{-}Sn[Mn(CO)_5]_2H$, the structure of which has been determined by X-ray analysis.

The compound crystallizes in the monoclinic space group $C2/c$ with four molecules in a unit cell of dimensions $a = 15.71$, $b = 17.18$, $c = 12.51$ Å and $\beta = 107.3°$.

Reaction of the dihydride with CCl_4 and CBr_4 gives $Cl_2Sn_2[Mn(CO)_5]_4$ and $Br_2Sn_2[Mn(CO)_5]_4$, respectively. With acrylonitrile the hydrostannation product is formed.

Introduction

Recent studies have shown that the reaction of dicyclopentadienyltin with proton-active compounds offers a suitable route to monocyclopentadienyltin(II) compounds (eqn. 1) [2], as well as inorganic and organic tin(II) compounds (eqn. 2) [3-5].

$$(C_5H_5)_2Sn + HX \rightarrow C_5H_5SnX + C_5H_6 \quad (1)$$

(X = Cl, Br, OPh)

$$(C_5H_5)_2Sn + 2HX \rightarrow SnX_2 + 2C_5H_6 \quad (2)$$

(X = inorganic or organic radical)

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[*] For a preliminary account of this work see ref. 1.

Compounds containing a tin—transition metal bond have attracted much attention [6]. Among the great variety of compounds reported, those of the type $RSn^{II}ML_n$ or $Sn^{II}[ML_n]_2$ are notable absent. The reaction of dicyclopentadienyltin(II) with transition metal hydrides having a sufficiently low pK_a in principle offers a route to such compounds. Recently, Harrison and Stobart [4] have reported that the reaction of bis(methylcyclopentadienyl)tin with the tungsten hydride $(\pi\text{-}C_5H_5)(CO)_3WH$ gives rise to the formation of a tetravalent tin compound, tentatively suggested to be polymeric $[Sn\{W(CO)_3(\pi\text{-}C_5H_5)\}_2]_n$.

We describe below the unexpected formation of a transition-metal substituted ditin dihydride from the reaction of dicyclopentadienyltin with manganese pentacarbonyl hydride.

Results and discussion

Reaction of dicyclopentadienyltin with manganese pentacarbonyl hydride both in a 1/1 and 1/2 molar ratio in benzene at room temperature gives an orange crystalline product, initially presumed to be bis(pentacarbonylmanganese)-tin, $Sn[Mn(CO)_5]_2$. However, the Mössbauer data (cf. Table 1) showed the tin to be in the tetravalent instead of the divalent state (I.S. = 1.85 mm s^{-1} relative to SnO_2). Molecular weight determinations in THF yielded a value of about 1065. The mass spectrum shows a polyisotope parent peak pattern with the most abundant peak at 1020 rather than at 1018 as expected for the dimer $[Sn\{Mn(CO)_5\}_2]_2$. This result, together with the analytical data (cf. Table 1) pointed to the presence of two hydrogen atoms in the molecule.

Chemical evidence for the presence of a metal—hydrogen bond was obtained from the reaction with carbon tetrachloride, which gave chloroform (see below).

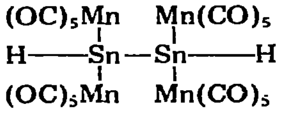
On the basis of these data the product was concluded to be the new transition-metal substituted ditin dihydride (I).

TABLE 1

ANALYTICAL AND PHYSICAL DATA

Compound	Analytical data: found (calcd.) (%)					M.p. (°C)	Mössbauer data	
	C	H	Cl/Br	Sn	Mn		I.S. [a] (mm/s)	Q.S. (mm/s)
$H_2Sn_2[Mn(CO)_5]_4$	23 63 (23.56)	0.28 (0.20)		23.1 (23.29)	21.31 (21.56)	150 (dec.)	1.85	0.63
$Cl_2Sn_2[Mn(CO)_5]_4$	22.26 (22.07)	0.20 (0.0)	6.44 (6.51)	22.16 (21.81)	 (20.19)	180-190 (dec.)	2.04	1.84
$Br_2Sn_2[Mn(CO)_5]_4$	20.48 (20.41)	0.10 (0.0)	13.54 (13.58)	20.26 (20.17)	18.60 (18.67)	165-170 (dec.)	2.06	1.80

[a] Recorded at 77 K. The I.S. values are relative to SnO_2.



$$\begin{array}{ccc} (OC)_5Mn & & Mn(CO)_5 \\ | & & | \\ H\text{---}Sn & \text{---} & Sn\text{---}H \\ | & & | \\ (OC)_5Mn & & Mn(CO)_5 \end{array}$$

(I)

The formation of I has been confirmed by a single-crystal structure determination. The crystals are built up from discrete $H_2Sn_2[Mn(CO)_5]_4$ molecules having C_2 symmetry. Figure 1 shows the molecular structure and the atom-labelling scheme. Figure 2 gives a view along the tin—tin axis. For a stereoscopic drawing see Fig. 3. The atomic parameters defining the crystal structure of the molecule are given in Table 2. In Table 3 are listed the various bond lengths and bond angles. The manganese atoms, which are surrounded by five carbonyl groups and one tin atom, are in an octahedral environment with bond angles of about 90°. This precludes a direct bonding between the hydrogen atoms and the manganese atoms.

The tin atoms are in a strongly distorted tetrahedral environment (the Mn—Sn—Mn bond angle is 119.8°, the Mn—Sn—Sn bond angles are 107.7 and 121.9°, respectively). This is not unexpected because in transition metal—tin

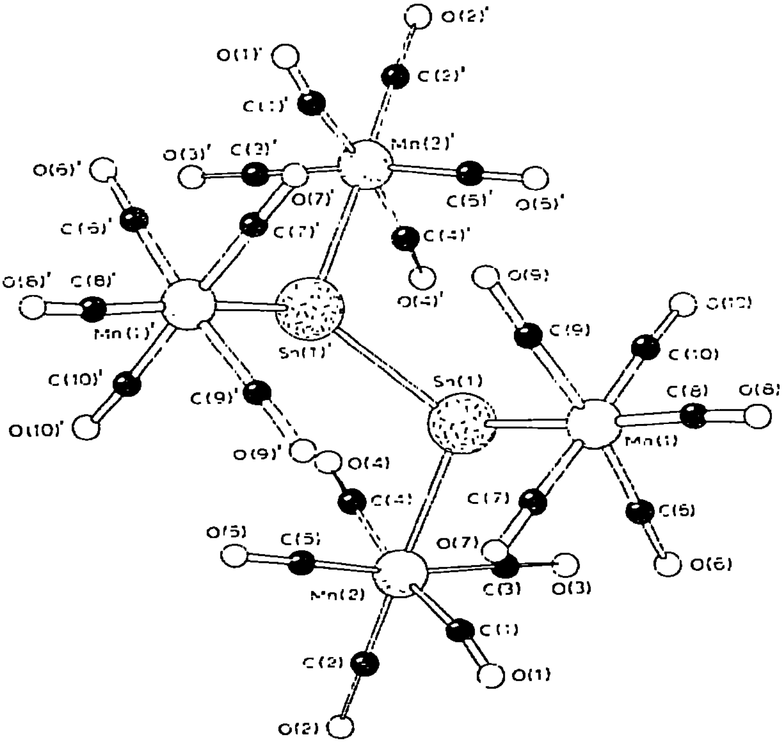


Fig. 1. A general view of the molecular structure of $H_2Sn_2[Mn(CO)_5]_4$ indicating the numbering scheme adopted. The two hydrogen atoms have been omitted.

TABLE 2

FINAL REFINED ATOMIC COORDINATES AND THERMAL PARAMETERS [a] FOR $H_2Sn_2[Mn(CO)_5]_4$

The atomic coordinates have been multiplied by 10^4. The anisotropic factors β_{ij} are multiplied by 10^4. The β_{ij} coefficients are given by the expression: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{13}$
Sn(1)	621(1)	1424(1)	1847(2)	54	46	95	4	0	38
Mn(1)	644(3)	2565(2)	402(4)	62	40	83	4	7	24
Mn(2)	2188(3)	804(2)	3146(3)	52	37	78	0	1	25
C(1)	2775(20)	1666(17)	2715(24)	55	46	88	−25	−57	50
C(2)	3160(24)	325(20)	3928(28)	88	47	100	26	−6	77
C(3)	2146(21)	325(18)	1822(27)	77	36	85	21	41	55
C(4)	1428(21)	64(18)	3386(25)	69	48	60	−14	15	11
C(5)	2041(22)	1355(19)	4301(28)	66	46	116	−33	26	53
C(6)	1560(21)	2013(17)	152(24)	54	46	97	−10	13	54
C(7)	1422(22)	3134(19)	1456(27)	97	23	101	4	28	72
C(8)	583(28)	3283(24)	−689(35)	90	82	81	31	−18	25
C(9)	−260(26)	2991(22)	844(31)	65	54	130	41	6	−8
C(10)	−140(26)	1926(22)	−595(31)	53	70	115	25	−12	50
O(1)	3225(17)	2063(14)	2559(21)	83	70	121	−55	30	66
O(2)	3839(20)	31(16)	4480(23)	67	68	200	77	39	18
O(3)	2140(18)	20(15)	1052(23)	143	70	65	33	−22	53
O(4)	1017(16)	−450(14)	3477(20)	83	53	126	−34	34	26
O(5)	1961(16)	1729(14)	5038(21)	84	62	138	−13	−65	80
O(6)	2121(15)	1674(12)	13(18)	73	49	123	−30	10	110
O(7)	1908(18)	3492(15)	2114(22)	105	58	128	−36	−22	28
O(8)	594(21)	3744(18)	−1329(26)	187	81	104	24	127	80
O(9)	−855(20)	3254(17)	1113(24)	78	92	176	61	−19	52
O(10)	−603(18)	1549(16)	−1249(23)	57	82	145	−9	−47	−18

[a] Numbers in parentheses here and in the other tables are standard deviations of the last significant figures

TABLE 3

BOND LENGTHS AND ANGLES FOR $H_2Sn_2[Mn(CO)_5]_4$

Bond lengths (Å)		Bond angles (degrees)	
Sn(1)—Sn(1)'	2.894(5)	Mn(1)—Sn(1)—Mn(2)	119.8(1)
Sn(1)—Mn(1)	2.675(5)	Mn(1)—Sn(1)—Sn(1)'	121.9(1)
Sn(1)—Mn(2)	2.730(5)	Mn(2)—Sn(1)—Sn(1)'	107.7(1)
Mn(1)—C(6)	1.83(3)	Sn(1)—Mn(2)—C(2)	175.0(10)
Mn(1)—C(7)	1.80(3)	Sn(1)—Mn(1)—C(8)	174.3(10)
Mn(1)—C(8)	1.82(4)	Sn(1)—Mn(2)—C(1)	87.4(9)
Mn(1)—C(9)	1.82(4)	Sn(1)—Mn(2)—C(3)	81 6(10)
Mn(1)—C(10)	1.83(3)	Sn(1)—Mn(2)—C(4)	81.5(10)
Mn(2)—C(1)	1.91(3)	Sn(1)—Mn(2)—C(5)	87.9(11)
Mn(2)—C(2)	1 76(4)	Sn(1)—Mn(1)—C(6)	84.6(10)
Mn(2)—C(3)	1.83(3)	Sn(1)—Mn(1)—C(7)	92.7(11)
Mn(2)—C(4)	1.83(3)	Sn(1)—Mn(1)—C(9)	85.5(12)
Mn(2)—C(5)	1.80(4)	Sn(1)—Mn(1)—C(10)	83.1(12)
C(1)—O(1)	1.04(4)		
C(2)—O(2)	1.19(5)	Mn(1)—C(6)—O(6)	179.2(26)
C(3)—O(3)	1.09(5)	Mn(1)—C(7)—O(7)	179.8(28)
C(4)—O(4)	1.12(4)	Mn(1)—C(8)—O(8)	175.9(35)
C(5)—O(5)	1.16(5)	Mn(1)—C(9)—O(9)	178.5(31)
C(6)—O(6)	1.11(4)	Mn(1)—C(10)—O(10)	176.3(33)
C(7)—O(7)	1.12(4)		
C(8)—O(8)	1.13(6)	Mn(2)—C(1)—O(1)	167.0(26)
C(9)—O(9)	1.17(5)	Mn(2)—C(2)—O(2)	177.2(28)
C(10)—O(10)	1.12(5)	Mn(2)—C(3)—O(3)	177.6(26)
		Mn(2)—C(4)—O(4)	171.6(26)
		Mn(2)—C(5)—O(5)	177.9(28)
		C(6)—Mn(1)—C(7)	90.6(15)
		C(6)—Mn(1)—C(10)	88.6(16)
		C(9)—Mn(1)—C(7)	88.9(17)
		C(9)—Mn(1)—C(10)	91 2(17)
		C(8)—Mn(1)—C(6)	95.3(17)
		C(8)—Mn(1)—C(7)	93.1(17)
		C(8)—Mn(1)—C(9)	94.8(18)
		C(8)—Mn(1)—C(10)	91.2(18)
		C(1)—Mn(2)—C(3)	89.1(14)
		C(1)—Mn(2)—C(5)	90.4(15)
		C(4)—Mn(2)—C(5)	89.3(15)
		C(4)—Mn(2)—C(3)	89.2(14)
		C(2)—Mn(2)—C(1)	95.9(15)
		C(2)—Mn(2)—C(3)	94.7(15)
		C(2)—Mn(2)—C(4)	95.1(15)
		C(2)—Mn(2)—C(5)	95.8(16)
		C(1)—Mn(2)—C(4)	168.9(15)
		C(3)—Mn(2)—C(5)	169.5(16)
		C(7)—Mn(1)—C(10)	175.7(16)
		C(6)—Mn(1)—C(9)	170.0(17)

compounds the tin—transition metal bond has strong *s*-character with the remaining bonds accordingly having stronger *p*-character (for a review see ref. 7). The asymmetric distribution of the *s*-electron density around the tin atoms is reflected in the occurrence of a quadrupole splitting in the Mössbauer spectrum. In the IR spectrum the absorption at 1725 cm^{-1}, which is notably absent in the

IR spectrum of $Cl_2Sn_2[Mn(CO)_5]_4$, is assigned to the Sn—H stretching frequency. The low value of ν(Sn—H), in fact the lowest value so far reported for a tin hydride [8], may be explained by the enhanced *p*-character of the Sn—H bond in this transition metal—tin hydride.

The bond length between the two tin atoms (2.89 Å) is somewhat greater than that in the cyclic hexamer of diphenyltin (Sn—Sn = 2.78 Å) [9] and that in hexaphenylditin (Sn—Sn = 2.77 Å) [10]. The tin—manganese distances (2.67 and 2.73 Å) are not considerably different from those in $Me_3SnMn(CO)_5$ (Sn—Mn = 2.67 Å) [11] and in $Ph_3SnMn(CO)_5$ (Sn—Mn = 2.67 Å) [12]. The positions of the hydrogen atoms could not be determined. Although most distances between the oxygen atoms of neighbouring manganese pentacarbonyl groups in the same molecule are about 3.2 Å or larger, two oxygen—oxygen distances of 2.98 Å have been found [viz. the O(5)—O(10)' and the O(10)—O(5)' distances].

Notwithstanding the shielding of the hydrogen atoms by the large manganese pentacarbonyl groups, the hydride reacts fast with carbon tetrachloride or tetrabromide, resulting in the formation of the corresponding dichloride or dibromide, respectively (eqn. 3).

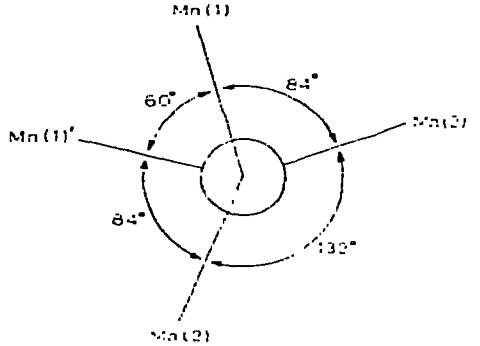


Fig. 2. A view of the molecule in projection down the Sn(1)—Sn(1)' axis.

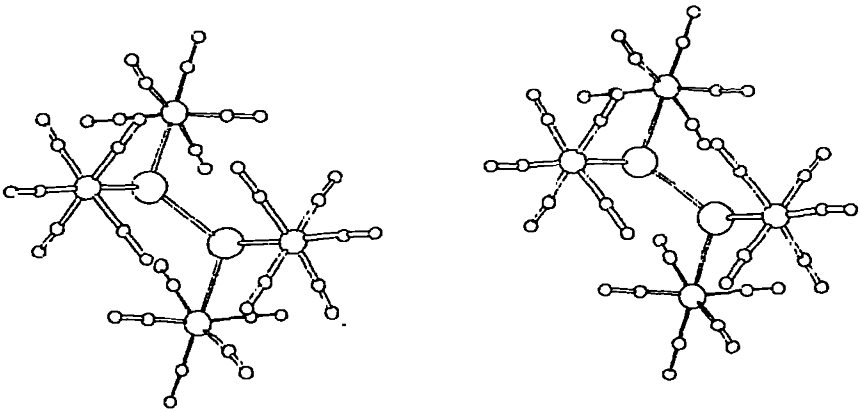


Fig. 3. Stereoscopic pair of the $H_2Sn_2[Mn(CO)_5]_4$ molecule.

$$H_2Sn_2[Mn(CO)_5]_4 \xrightarrow[-CHX_3]{CX_4} X_2Sn_2[Mn(CO)_5]_4 \quad (3)$$

(X = Cl, Br)

The Mössbauer data of these products are given in Table 1. The crystal structure determination of $Br_2Sn_2[Mn(CO)_5]_4$ is in its final stages. The molecular structure of this dibromide is very similar to that of the dihydride [13].

Analogous to the more familiar types of organotin hydrides [14], compound I reacts smoothly with acrylonitrile to give the corresponding bis-adduct.

The formation of unexpected tetravalent tin derivatives in the reaction of tin(II) compounds with transition metal carbonyl derivatives is not without precedent. Hacket and Manning recently isolated $Sn[Co(CO)_3PBu_3]_4$ and $HSn[Co(CO)_3PBu_3]_3$ from the reaction of $SnBr_2$ with $[Co(CO)_3PBu_3]_2$ [15], whereas Cornwell, Harrison and Richards observed the formation of $Sn[Co(CO)_4]_4$ from the reaction of bis(methylcyclopentadienyl)tin with $Co_2(CO)_8$ [16].

Experimental

General

The reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use from $LiAlH_4$ under nitrogen.

The mass spectra were run on AEI MS 9 and MS 902 instruments at the Laboratory for Analytical Chemistry of the State University, Utrecht. Elemental analyses were carried out under supervision of W.J. Buis by the Element Analytical Department of the Institute for Organic Chemistry TNO. The Mössbauer spectra were recorded at the Interuniversitair Reactor Instituut at Delft. The spectrometer has been described [17].

Sampling of the crystal for X-ray analysis and the mounting in a Lindemann capillary was performed using the apparatus described by van Koten and Boersma [18].

Structure determination

For the crystal structure determination the intensities of 2968 independent reflexions ($\theta \leqslant 25°$) were collected with a computer equipped Nonius four-circle diffractometer (CAD-4), using Mo-K_α-radiation (ω-scan technique). A graphite monochromator was used $2\theta_m = 12.6°$. No absorption correction was applied. The crystal structure was solved with standard Patterson techniques and refined by block-diagonal anisotropic least-squares. Scattering factors were taken from the International Tables for X-ray Crystallography [21]. The applied corrections for the anomalous scattering of Sn were $\Delta f' = -0.6$ and $\Delta f'' = 1.9$ and for Mn $\Delta f' = 0.4$ and $\Delta f'' = 0.9$.

Crystallographic data for $H_2Sn_2[Mn(CO)_5]_4$: mol. wt. = 1019.36, monoclinic, space group $C2/c$; cell dimensions $a = 15.71(5)$, $b = 17.18(5)$, $c = 12.51(5)$ Å; $\beta = 107.3(2)°$. $V = 3226$ Å^3. Four molecules in the unit cell ($Z = 4$). $d_{calcd.} = 2.08$ g cm^{-3}; $d_{exp.} = 2.11$ g cm^{-3}; μ(Mo-K_α) = 31.62 cm^{-1}. The R-factor is 0.20. A final difference Fourier map showed no significant features, except for some peaks near the tin atoms. The reason for this is that no absorption correction due to experimental difficulties was applied. The crystal was poorly defined and mounted in a glass capillary (under nitrogen). Most of the crystallographic calculations were carried out with the X-RAY System [22] on the CDC-Cyber 72 at the computer centre of the State University of Utrecht.

$H_2Sn_2[Mn(CO)_5]_4$

To a solution of 1.5 g $(C_5H_5)_2Sn$ (6.0 mmol) in 7 ml benzene 1.9 ml $HMn(CO)_5$ (14 mmol) [19, 20] was added. The mixture was stored at 5° overnight. The solution was separated from the orange crystals formed. The crystals were washed twice with 2 ml pentane and dried in vacuo. Yield 1.5 g; m.p. 150° (dec.). Treatment of the mother liquid with pentane raised the total yield of product to 2.5 g.

The mass spectrum shows the polyisotope peak patterns of the ions of $H_2Sn_2[Mn(CO)_5]_4$, $HSn_2[Mn(CO)_5]_3$, $HSn[Mn(CO)_5]_2$, $SnMn_2$, $HMn(CO)_5$, $Mn(CO)_5$, and several fragments which may be formed by loss of one or more CO groups from the above ions.

$Cl_2Sn_2[Mn(CO)_5]_4$

To an orange solution of 0.37 g $H_2Sn_2[Mn(CO)_5]_4$ (0.36 mmol) in 13 ml THF was added 0.2 ml (2.1 mmol) carbon tetrachloride. The mixture became dark-red within a few seconds. After standing for two hours at room temperature the mixture was evaporated in vacuo to a volume of 3 ml and to complete the crystallization it was cooled in ice. The liquid was removed by a syringe. The red crystals were washed with 1 ml of benzene and dried in vacuo. Yield 0.3 g; m.p. 180-190° (dec.). The mass spectrum shows the polyisotope peak patterns of the ions of $Cl_2Sn_2[Mn(CO)_5]_4$, $Cl_2Sn_2[Mn(CO)_5]_3$, $Sn_2[Mn(CO)_5]_3$, $ClSn[Mn(CO)_5]_2$, $SnMn(CO)_5$, $ClSnMn_2$, $SnMn_2$, $ClSnMn$, $Mn(CO)_5$ and several fragments which may be formed by loss of one or more CO groups from the above ions.

$Br_2Sn_2[Mn(CO)_5]_4$

The ditin dibromide was prepared from the ditin hydride and carbon tetrabromide. The crude product was recrystallized from a THF/pentane mixture yielding dark-red crystals, m.p. 165-170° (dec.).

$(NCC_2H_4)_2Sn_2[Mn(CO)_5]_4$

0.20 ml (3.0 mmol) acrylonitrile was added to a suspension of 0.22 g (0.2 mmol) $H_2Sn_2[Mn(CO)_5]_4$ in 2 ml acetonitrile. The mixture was stirred for one week. The colour of the undissolved compound gradually changed from orange-yellow to yellow. The liquid was removed, the yellow product was washed with pentane and dried in vacuo (found: C, 27.39; H, 0.98. $C_{26}H_8Mn_4N_2O_{20}Sn_2$ calcd.: C, 27.75; H, 0.72%).

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