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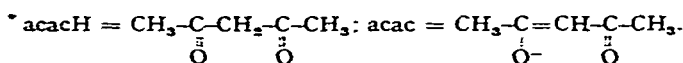
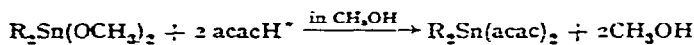
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## Organometal complexes

### II. Organotin and organolead bis(acetylacetonates)

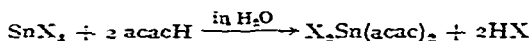
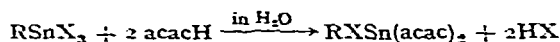
Many stable complexes have been obtained by the reaction of dialkyltin dihalides with 8-hydroxyquinoline<sup>1,2</sup>, 2,2'-bipyridine<sup>2,3</sup> and 1,10-phenanthroline<sup>2,3</sup>. Although these complexes have been reported to have a chelate structure containing hexa-coordinated tin, further stereochemical study seems to be rather difficult, for the ligands are too complicated<sup>2</sup>. Infrared, Raman and NMR spectra studies have suggested that dimethylbis(acetylacetonato)tin<sup>1,5</sup> or -lead<sup>4</sup> have the methyl groups in *trans*-configuration. In order to study the electronic effect of substituents on tin on the acetylacetonate ligand through the tin atom, we have prepared a series of disubstituted bis(acetylacetonato)tin compounds (Table I).

Diorganobis(acetylacetonato)tin compounds were obtained by the reaction of the diorganotin dichloride and sodium methoxide in methanol, followed by the addition of acetylacetone.



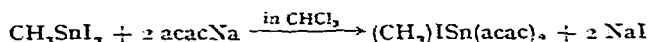
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Organobis(acetylacetonato)tin halides,  $RXSn(acac)_2$ , or bis(acetylacetonato)tin dihalides,  $X_2Sn(acac)_2$  ( $X = Cl, Br$ ), were prepared by the reaction of acetylacetonato organotin trihalides or tin tetrahalides in water.



The compounds  $X_2Sn(acac)_2$  ( $X = Cl, Br$ ) were previously prepared by Morgan *et al.*<sup>6</sup>

Although we could not obtain the corresponding iodides,  $(CH_3)ISn(acac)_2$  and  $Sn(acac)_2$ , by this procedure, these compounds could be prepared by the reaction of methyltin triiodide or tin tetraiodide with sodium acetylacetonate in chloroform:



The bis(acetylacetonato)tin dihalides react easily with methanol to lose one acetylacetonate ring, giving dimeric methoxy(acetylacetonato)tin dihalides,  $[X_2Sn(acac)(OCH_3)]_2$ , as we have reported elsewhere<sup>7</sup>.

TABLE I

MELTING POINT AND ANALYTICAL DATA OF BIS(ACETYLACETONATO)TIN COMPLEXES OF THE TYPE  $(R)XSn(acac)_2$

$R$	$X$	M.p. ( $^{\circ}C$ )	% C Found (Calcd.)	% H Found (Calcd.)	% Sn Found (Calcd.)
$CH_3$	$CH_3$	177-178 <sup>a</sup>	41.03 (41.54)	5.83 (5.81)	34.25 (34.21)
$C_2H_5$	$C_2H_5$	86.5-87.0	44.31 (44.84)	9.47 (9.45)	31.73 (31.65)
$C_2H_5$	$C_2H_3$	87-88	44.83 (45.32)	5.41 (5.43)	(31.99)
$C_6H_5$	$C_6H_5$	125-126 <sup>b</sup>			25.54 (25.19)
$CH_3$	Cl	135-136	35.56 (35.95)	4.64 (4.66)	32.28 (32.31)
$CH_3$	Br	129	31.90 (31.80)	4.16 (4.66)	28.70 (28.82)
$CH_3$	I	115-116			25.60 (25.87)
$C_2H_5$	Br	94.5	33.76 (33.84)	4.46 (4.46)	27.54 (27.87)
$C_6H_5$	Cl	149-152	44.86 (44.75)	4.31 (4.46)	27.83 (27.64)
Cl	Cl	202-203 <sup>c</sup>			30.42 (30.61)
Br	Br	186-187 <sup>d</sup>			24.77 (24.90)
I	I	179-180	21.06 (21.05)	2.20 (2.47)	20.95 (20.80)

<sup>a</sup> Ref. 5 reports that this compound does not melt or decompose below 300 $^{\circ}$ . <sup>b</sup> Ref. 5 reports m.p. 125 $^{\circ}$ . <sup>c</sup> Ref. 6 reports m.p. 202-203 $^{\circ}$ . <sup>d</sup> Ref. 6 reports m.p. 187 $^{\circ}$ .

*Experimental*

$R_2Sn(acac)_2$  ( $R = CH_3, C_2H_5, C_2H_5, C_6H_5$ ). Dimethyltin dichloride (4.4 g, 0.02 mole) was added to 100 ml of methanol solution, in which 0.5 g of sodium and 4 g of acetylacetonate (0.04 mole) had been dissolved. Sodium chloride precipitated immediately and was filtered. On standing for a few hours, the resulting white precipitate was recrystallized from methanol to give small, transparent crystals of dimethylbis(acetylacetonato)tin (yield 80 %). The other diorganotin derivatives were obtained by this general method. These compounds are stable in air, excepting diethyltin and divinyltin compounds. The dimethyltin compound is soluble in hot methanol, but not in other common organic solvents, and the other three are soluble in benzene, chloroform or dichloroethane. Results are shown in Table 1.

$(CH_3)_2XSn(acac)_2$ ,  $(C_2H_5)_2BrSn(acac)_2$ ,  $(C_6H_5)_2ClSn(acac)_2$  ( $X = Cl, Br$ ). To a suspension of methyltin oxide<sup>8,9</sup> (0.005 mole) in 10 ml of water was added concentrated HCl (1.6 g) (or HBr); all the oxide dissolved on standing for a day. To this solution was added acetylacetonate (1.0 g, 0.01 mole) with stirring. A white precipitate appeared within a few minutes. Recrystallization from benzene- or dichloromethane-ligroin (adding a small amount of acetylacetonate to avoid decomposition of the product) gave transparent crystals (yield ca. 60 %). The other compounds were prepared similarly from trihalides dissolved in water. It was observed in the case of phenyl compounds that the addition of a little excess of acetylacetonate accelerates crystallization of the product.

$(CH_3)_2I_2Sn(acac)_2$  and  $I_2Sn(acac)_2$ . Sodium acetylacetonate (6.1 g, 0.05 mole) prepared from sodium ethoxide and acetylacetonate, was added to a solution of tin tetraiodide (15.6 g, 0.025 mole) in 80 ml of chloroform. After refluxing for 2 h, the mixture was filtered. The filtrate was evaporated to about 10 ml, and 50 ml of ligroin was added. The yellow precipitate obtained was recrystallized from dichloromethane-ligroin to give crystals of bis(acetylacetonato)tin diiodide (yield 15 %). Methylbis(acetylacetonato)tin iodide was obtained from methyltin triiodide by the same procedure.

*Dimethylbis(acetylacetonato)lead*. Dimethyllead dichloride<sup>10</sup> (10.2 g, 0.033 mole) was suspended in 100 ml of ethyl acetate solution of acetylacetonate (6.7 g, 0.067 mole). By adding aqueous ammonia slowly to this solution, dimethyl lead dichloride was dissolved. After the solvent was evaporated to 30 ml and cooled, white precipitate appeared. It was recrystallized from methanol to give transparent, pale blue crystal of dimethylbis(acetylacetonato)lead, m.p. 163-163.5°. (Found; C, 33.10; H, 4.58; Pb, 47.53.  $C_{12}H_{20}O_4Pb$  calcd.: C, 33.10; H, 4.58; Pb, 47.58 %.)

*Determination of molecular weight*. Molecular weight was determined cryscopically in benzene for two representative compounds. The results are: calcd. for  $(C_6H_5)_2Sn(CH_3COCHCOCH_3)_2$  471.1, observed 487, 467, 460 at concentrations of 1.10, 1.06 and 0.74 wt. %, respectively; calcd. for  $I_2Sn(CH_3COCHCOCH_3)_2$  570.7, observed 581, 569, 552 at concentrations of 1.19, 1.62 and 2.04 wt. %, respectively.

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## PRELIMINARY NOTES

### Koordinationsverbindungen von Aluminiumboranaten mit Äther und Tetrahydrofuran

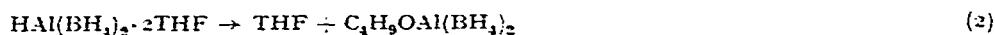
Das Koordinationsverhalten von Äthern gegenüber Aluminiumboranaten  $\text{AlH}_{3-n}(\text{BH}_4)_n$  wird bevorzugt von sterischen Effekten bestimmt. So bildet Diäthyläther mit  $\text{Al}(\text{BH}_4)_3$  ein farbloses, flüssiges, im Hochvakuum schwerflüchtiges  $\text{Al}(\text{BH}_4)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2^{1,2}$ , das man leicht aus  $\text{AlH}_3$  und Diboranüberschuss in Äther synthetisieren kann. Ein Hydridoaluminium-bis(boranat) erhält man gemäss (1) in Äther. Aus der Ätherlösung kristallisiert in der Kälte instabiles  $\text{HAl}(\text{BH}_4)_2 \cdot 2\text{O}(\text{C}_2\text{H}_5)_2$



aus, das bei  $\sim 10^\circ$  schmilzt und im Vakuum sehr leicht 1 Mol Äther unter  $\text{HAl}(\text{BH}_4)_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ -Bildung abspaltet. Das hydrolyseempfindliche Monoätherat kann im Hochvakuum transportiert werden. Analog zu (1) erhält man auch ein  $\text{H}_2\text{AlBH}_4$  in Äther.

Die Umsetzung der genannten Monoätherate oder ihrer Ätherlösungen mit 1 Mol Tetrahydrofuran (THF) führt unter Verdrängung des gebundenen Äthers durch THF zu den Aluminiumboranat-Tetrahydrofuran-Komplexen  $\text{H}_2\text{AlBH}_4 \cdot \text{THF}$  (Schmp.  $55-58^\circ$ , in Benzollösung assoziiert),  $\text{HAl}(\text{BH}_4)_2 \cdot \text{THF}$  (Schmp.  $-6^\circ$ , in Benzol monomer löslich) und  $\text{Al}(\text{BH}_4)_3 \cdot \text{THF}$  (Schmp.  $24-26^\circ$ )\*. Diese THF-Addukte sind nicht aus den Tetrahydrofuranlösungen von  $\text{AlH}_{3-n}(\text{BH}_4)_n$  zugänglich; aus den Lösungen kristallisieren vielmehr  $\text{H}_2\text{AlBH}_4 \cdot 2\text{THF}$  (Schmp.  $79-80^\circ$ ) bzw.  $\text{HAl}(\text{BH}_4)_2 \cdot 2\text{THF}$  (Schmp.  $78^\circ$ ).  $\text{Al}(\text{BH}_4)_3 \cdot 2\text{THF}$  ist aus den Lösungen nicht zugänglich, da es sich sehr leicht unter  $\text{BH}_3$ -Abspaltung, insbesondere in Gegenwart von überschüssigem THF zersetzt.

Die Ditetrahydrofuran-Komplexe besitzen bei Raumtemperatur einen geringen THF-Dampfdruck. Der Abbau zu den 1:1-Addukten gelingt jedoch nicht, da dieser stets von einer hydrierenden Ringöffnung des koordinativ gebundenen THF begleitet wird. So zerfällt z.B.  $\text{HAl}(\text{BH}_4)_2 \cdot 2\text{THF}$  bei  $50-70^\circ$  im Vakuum nach (2)\*\*.



\* Schmp.  $33.5^\circ$  (Ref. 1). Das Schmelzen aller THF-Addukte verläuft unter Zersetzung.

\*\* Die Zersetzung unter dem eigenen Dampfdruck bzw. bei Normaldruck verläuft unübersichtlicher.