Inorganic Tin(II) Derivatives

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Summary Protolysis of dicyclopentadienyltin(II) is a novel route to inorganic tin(II) derivatives; tin-119m Mössbauer spectra are reported.

WHEREAS general routes to functionally substituted tin(IV) compounds exist, standard syntheses of even the simplest tin(II) compounds are unavailable. Some tin(II) alkoxides^{1,2} and aryl oxides,²⁻⁴ and tin(II) bisbenzenethiolate^{4,5} have been prepared, but the routes used were specific or of low yield; tin(II) phthalocyanine⁶ is the only compound containing an unequivocal^{4,5} tin(II)-nitrogen bond yet prepared. Protolysis of the tin(II)-carbon bonds of dicyclopentadienyltin(II) offers a versatile synthesis, in high yield, of a wide range of tin(II) derivatives under very mild conditions, and tin(II) carboxylates, alkoxides, aryl oxides, oximes, hydroxylamines, metalloxanes, azoles, thiolates, and pseudohalides, some previously inaccessible, are conveniently obtained in this way. Reactions are typically conducted at room temperature in anhydrous benzene or tetrahydrofuran. The inorganic tin(II) derivatives, most of which are sensitive to oxygen and moisture, were characterised by microanalysis, and by ^{119m}Sn Mössbauer and i.r. spectroscopy (see Table). The Mössbauer isomer shifts, δ , are all greater than that of β -tin (2.65 mm s⁻¹) thus confirming the preservation of the lower oxidation state. Besides the obvious versatility, the method overcomes the problem, frequently encountered in previous syntheses,^{4,6} of further oxidation to tin(IV) species.

^{119m}Sn Mössbauer data⁸ for tin(II) compounds. All except Sn(OMe)₂ and Sn(SPh)₂ are novel.

Compound	$\delta/(mm \ s^{-1})^{a}$	$\Delta/(\text{mm s}^{-1})^{\mathbf{a}}$
Sn(OMe),	3.02	1.97
Sn(O·N:CHMe),	3.22	$2 \cdot 26$
$Sn(O \cdot N : CMe_2)_2$	3.27	2.09
$Sn(O \cdot N : CHPh)_2$	3.23	2.14
MeC: N·O·Sn·O·N : CMe	3.30	1.90
Sn(O·NH·CO·Ph) ₂	3.37	1.95
Sn(O·NPh·CO·Ph) ₂	3.23	2.09
	9.70	0.17
CH:N·O·Sn·O·C ₆ H ₄	3.70	2.17
$Sn(OSiPh_3)_2$	3.18	2.34
$(Ph_3SiOSn)_2O$	3.12	$2 \cdot 39$
Sn(imidazole) ₂	3.09	2.02
Sn(1,2,4-triazole),	3.60	$2 \cdot 14$
Sn(SPh).	3.51	1.60
$Sn(SC_2H_{15})_2$	3.28	1.69
Sn(SCH, CH, OH),	3.14	1.83
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ĊH₂·S·Sn·S·CH₂	3.27	1.71
$Sn(CN)_2$	3.28	$2 \cdot 23$

^a Recorded at 77 K vs. a Ba^{119m}SnO₃ source. Values given are considered to be accurate to ± 0.06 mm s⁻¹.

We thank the P.C.M.U. at Harwell for recording ^{119m}Sn Mössbauer spectra.

(Received, 6th March 1972; Com. 365.)

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