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Preliminary communication

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

K.D. BOS, E.J. BULTEN, J.G. NOLTES
Institute for Organic Chemistry TNO, Utrecht (The Netherlands)
and A.L. SPEK
Department of Structural Chemistry, State University of Utrecht, Utrecht (The Netherlands)
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Summary

The preparation and structural characterization of the novel transition metal substituted tin hydride $H_2Sn_2[Mn(CO)_5]_4$ is reported.

The recent finding that the reaction of dicyclopentadienyltin(II) with proton-active compounds represents a useful synthesis of monocyclopentadienyltin(II) [1] as well as inorganic and organic tin(II) compounds [2–4] has led us to study the possibility of obtaining hitherto unknown transition metal–tin(II) derivatives of the type $RSn^{II}ML_n$ or $Sn^{II}(ML_n)_2$ via the reaction of $(C_5H_5)_2Sn^{II}$ with transition metal hydrides having sufficiently low pK_a's. Recently Harrison and Stobart reported the formation of the four-valent tin compound $\{Sn^{IV}[W(CO)_3(\pi\text{-}C_5H_5)]_2\}_n$ from the reaction of $(MeC_5H_4)_2Sn^{II}$ with $(\pi\text{-}C_5H_5)(CO)_3WH$ [3]. Also relevant is the very recently reported formation of $[n\text{-}Bu_3PCo(CO)_3]_3SnH$ from the reaction of a tin(II) halide and $[n\text{-}Bu_3PCo(CO)_3]_2$ [5].

Reaction of $(C_5H_5)_2Sn^{II}$ with $HMn(CO)_5$ in a 1/1 and 1/2 molar ratio in benzene solution at room temperature afforded an orange-coloured crystalline product, with m.p. 150° dec. The possibility that this was $Sn[Mn(CO)_5]_2$ was excluded by the Mössbauer spectrum (*IS* 1.85 mm/s relative to SnO_2). Based on the analytical data, the mass spectrum (polyisotope parent peak pattern with the most abundant peak at 1020) and chemical evidence (formation of $CHCl_3$ upon reaction with CCl_4, and of a bis-hydrostannation product with acrylonitrile) this compound was concluded to be $HSn[Mn(CO)_5]_2\text{—}Sn[Mn(CO)_5]_2H$. Reaction with CCl_4 gives the corresponding dichlorodistannane (m.p. 180–190° dec.; polyisotope parent peak pattern around 1088; *IS* 2.04 mm/s).

The formation of $HSn[Mn(CO)_5]_2\text{—}Sn[Mn(CO)_5]_2H$ has been confirmed by an X-ray structure determination. Crystals (from benzene) are monoclinic with *a* 15.71(5), *b* 17.18(5), *c* 12.51(5) Å, β 107.4(1)°; space group *C2/c*; *Z* = 4. The structure was solved by Patterson and Fourier techniques and refined by blockdiagonal anisotropic least squares to a *R* value of 0.20 using 2968 independent reflections.

The compound has C_2 symmetry in the crystal, its stereochemistry being illustrated in Fig. 1. The tin atoms are in a strongly distorted tetrahedral environment (Mn(1)—Sn(1)—Mn(2), 119.8°; Mn(1)—Sn(1)—Sn(1)', 121.9°; Mn(2)—Sn(1)—Sn(1)', 107.7°). The tin—manganese bond lengths (Sn(1)—Mn(1), 2.67 Å; Sn(1)—Mn(2), 2.73 Å) are comparable to the values reported for other tin—manganese compounds (2.67 Å in $Me_3SnMn(CO)_5$ [6]; 2.74 Å in $ClSn[Mn(CO)_5]_3$ [7]). The tin—tin distance is rather long (2.89 Å; 2.78 Å in $Ph_3SnSnPh_3$ [8]).

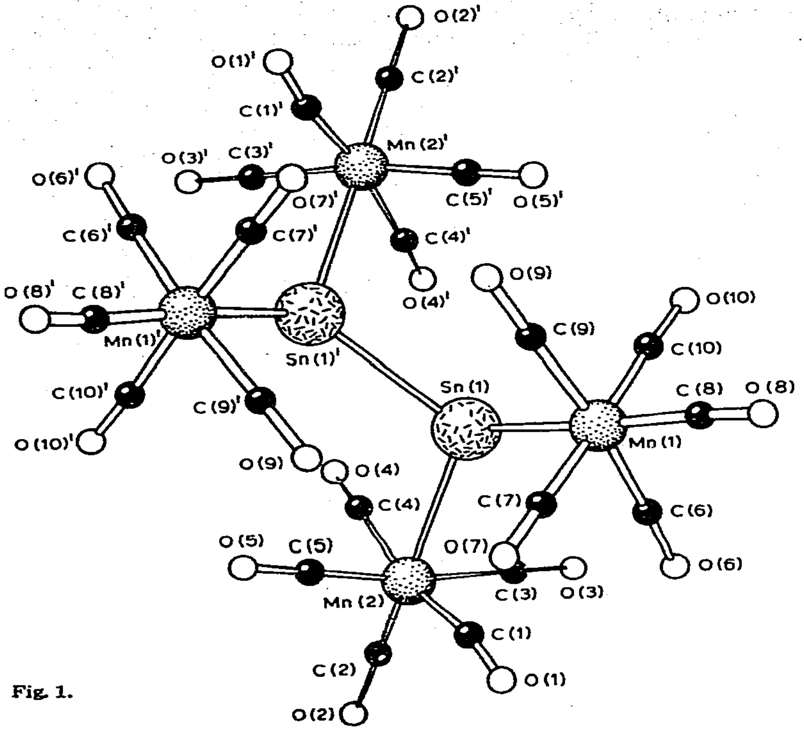

Fig. 1.

Noteworthy is the very low frequency (1725 cm^{-1}) of the Sn—H stretching absorption, the lowest so far reported.

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