Full paper / Mémoire

Neutron diffraction analysis of the first stable hydride derivative of a divalent group-14 metal

Thomas F. Koetzle [a,*], Arthur J. Schultz [a], Robert Henning [a], Alberto Albinati [b], Wim T. Klooster [c], Barrett E. Eichler [d], Philip P. Power [d]

[a] *Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL 60439, USA*
[b] *Department of Structural Chemistry, University of Milan, Via Venezian 21, and INFM, UdR Milan, I-20133 Milan, Italy*
[c] *Bragg Institute, Australian Nuclear Science and Technology Organization, Lucas Heights, NSW, Australia*
[d] *Department of Chemistry, University of California Davis, One Shields Avenue, Davis, CA 95616, USA*

Abstract

A single-crystal neutron diffraction study at 20 K has revealed accurate hydride ligand positions in the first stable hydride derivative of a divalent group-14 metal, $[2,6\text{-Trip}_2C_6H_3Sn(\mu\text{-H})]_2\cdot4C_6H_6$, Trip = 2,4,6-tri-isopropylphenyl [B.E. Eichler, P.P. Power, *J. Am. Chem. Soc.* 122 (2000) 8785]. In the solid state this dimeric complex assumes a *trans* C_{2h} geometry with two bridging hydrides (Sn–H 1.943(7) Å, ∠C–Sn–H 92.4(2)°, ∠Sn–H–Sn′ 106.9(3)°, ∠H–Sn–H′ 73.1(3)°). The bulky Trip ligand serves to stabilize the Sn–H bonds. The tin atoms carry lone pairs, and, as determined previously by X-ray diffraction and reported by Eichler and Power, the tin coordination accordingly is pyramidal as evidenced by the sum of the three bond angles around tin of 257°. To our knowledge this is the first neutron diffraction study of a tin hydride complex to be reported. The neutron diffraction measurements were carried out using the time-of-flight Laue SCD instrument at the Argonne Intense Pulsed Neutron Source. ***To cite this article: T.F. Koetzle et al., C. R. Chimie 8 (2005).***

Résumé

L'étude d'un monocristal par diffraction de neutrons à 20 K a révélé de manière précise les positions des ligands hydrures dans le premier hydrure stable d'un métal divalent du groupe 14, $[2,6\text{-Trip}_2C_6H_3Sn(\mu\text{-H})]_2\cdot4C_6H_6$, Trip = 2,4,6-tri-isopropylphényl [B. E. Eichler, P. P. Power, *J. Am. Chem. Soc.* 122 (2000) 8785]. À l'état solide, ce complexe dimère présente une géométrie C_{2h} *trans*, avec deux hydrures pontants (Sn–H 1.943(7) Å, ∠C–Sn–H 92.4(2)°, ∠Sn–H–Sn′ 106.9(3)°, ∠H–Sn–H′ 73.1(3)°). L'encombrement stérique provoqué par chaque ligand Trip stabilise les liaisons Sn–H. Chaque centre Sn porte une paire d'électrons célibataires et, comme déterminé précédemment par diffraction aux rayons X et reporté par Eichler et Power, la coordination de l'étain est pyramidale, la somme des angles formés par les trois liaisons autour de l'étain étant égale à 257°. A notre connaissance il s'agit de la première étude par diffraction de neutrons d'un hydrure d'étain à l'état de complexe. Les

---

* Corresponding author.

E-mail address: tkoetzle@anl.gov (T.F. Koetzle).

mesures de diffraction de neutrons ont été obtenues en utilisant le diffractomètre SCD de la source de neutrons pulsée par spallation (IPNS) à Argonne, grâce à la méthode du temps de vol Laue. ***Pour citer cet article : T.F. Koetzle et al., C. R. Chimie 8 (2005)***.

1. Introduction

Organotin hydrides are important reducing agents used in organic synthesis [1]. Like all tin hydrides reported to date, they generally have tin in the formal +4 oxidation state. Until recently there were no stable, well-characterized, divalent tin +2 hydrides, and no equivalent stable hydrides of other group 14 elements had been reported. However, there is now a relatively large body of data showing that low-coordinate, divalent organic derivatives of the group-14 elements can be stabilized by bulky substituents [3]. Reasoning that lower valent hydride derivatives of these elements might be stabilized in an analogous way, Eichler and Power [2] have prepared the first known example of a Sn(II) hydride, [2,6-Trip$_2$C$_6$H$_3$Sn(μ-H)]$_2$·4 C$_6$H$_6$ (**1**), Trip = 2,4,6-tri-isopropylphenyl, which they have stabilized through the use of the bulky Trip substituent. In view of the novel nature of **1** it was deemed to be important to carry out a neutron diffraction study to locate the hydrides accurately and to give precise Sn–H distances. IR spectroscopy had suggested that, while **1** has a dimeric structure in the solid, it is monomeric in solutions with hydrocarbon solvents. The X-ray structure of **1** at 90 K [2] shows the tin hydride complex to have a dimeric structure with essentially symmetrical hydride bridges and a long Sn–Sn separation, of 3.12 Å, indicative of very little direct tin-tin interaction.

2. Results and discussion

Fig. 1 illustrates the essential features of the molecular structure of the tin hydride complex in **1**. To our knowledge this is the first neutron diffraction study of a tin hydride complex to be reported. The dimeric complex in **1** sits on a crystallographic center of inversion

assuming a *trans* geometry with two bridging hydrides. Significantly the two independent Sn–H bonds are found to be of essentially equal length, 1.943(7) Å and 1.941(7) Å, and the effective molecular symmetry of the complex is C_{2h}. The tin atoms carry lone pairs, as has been reported by Eichler and Power [2], and the angles around tin sum to 257° pointing to the pyramidal nature of the coordination at these centers. A listing of important distances and angles in **1** from the neutron diffraction study is included in Table 1. In general, all distances and angles fall within expected limits and are close to their corresponding X-ray values. For an ORTEP [4] drawing of **1**, see Fig. 2.

The neutron diffraction study confirms that **1** contains tin in the +2 oxidation state. Most significantly, no evidence was found in the final difference Fourier synthesis for terminal hydrides on tin.
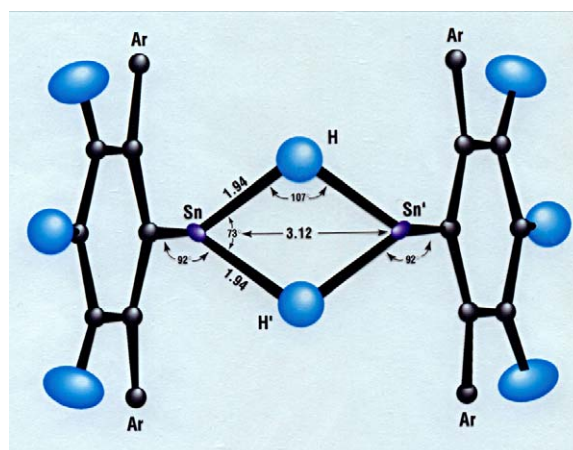

Fig. 1. View of **1** along a direction perpendicular to the Sn$_2$H$_2$ plane. The Trip ligand is denoted Ar.

Table 1

Important distances and angles in **1** from neutron diffraction at 20 K, with the corresponding parameters determined by X-ray diffraction at 90 K [2]

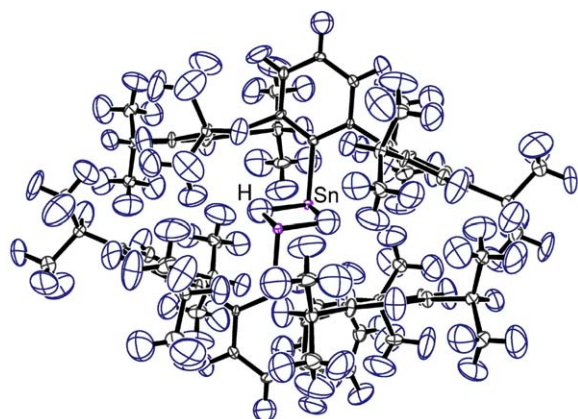| Distance	Neutron Diffraction	X-ray Diffraction
Sn–H	1.943(7) Å	1.89(3) Å
Sn–H′	1.941(7)	1.95(3)
Sn–C	2.193(4)	2.210(3)
Sn–Sn′	3.120(5)	3.1192(3)
H–H′	2.31(1)	2.24(18)
Angle		
C–Sn–H	92.4(2) °	91.7(9) °
C–Sn–H′	91.6(2)	93.6(9)
Sn–H–Sn′	106.9(3)	108.7(9)
H–Sn–H′	73.1(3)	71.3(9)

Fig. 2. ORTEP [4] diagram of **1** viewed approximately normal to the Sn–C bonds to highlight the pyramidal coordination at the tin atoms. Thermal ellipsoids are plotted at 90% probability.

3. Experimental

3.1. Synthesis and crystal preparation

Crystals of **1** were obtained from a preparation in which a di-isobutylaluminum hydride solution was added drop wise to a solution of 2,6-Trip$_2$C$_6$H$_3$SnCl in diethyl ether at –78 °C. The initially orange solution became green, and subsequently upon warming to ca. 30 °C the color changed to dark blue. After further warming to room temperature, the diethyl ether was removed, and the remaining blue solid was extracted with benzene. Filtration and concentration of the blue solution produced orange crystals of **1**.

3.2. Neutron diffraction measurements

A large single crystal of **1**, prepared at Davis, was estimated to be of dimensions 1 × 3 × 5 mm, or approximately 15 mm^3 in volume. Crystals of **1** are triclinic, $P\bar{1}$, $a = 12.995(1)$, $b = 13.093(1)$, $c = 13.199(1)$ Å, $\alpha = 93.552(8)$, $\beta = 97.607(8)$, $\gamma = 115.801(8)$ °, $V = 1986.0(4)$ Å^3 at $T = 20$ K, $Z = 1$, with 111 independent atoms.

The crystal was handled in a glove bag under N$_2$ where it was coated with fluorocarbon grease to protect it from contact with air. It was then molded into an aluminum foil pack that was glued to the end of an aluminum pin with DEVCON® 5 minute® epoxy adhesive. The mounted sample was placed in the DISPLEX® closed-cycle refrigerator on the IPNS SCD instrument [5] and was cooled to 20 K.

At IPNS neutrons are produced by a pulsed (30 Hz) spallation source. The SCD time-of-flight Laue instrument, with its time- and position-sensitive detector, accumulates data in x,y,t-histogram form and uses the entire thermal spectrum of neutrons from each pulse. A detailed description of the SCD instrument and data collection and analysis procedures has been published [6,7].

The crystal was indexed based on a preliminary data histogram. The unit cell that was obtained at 20 K approximately matched the 90-K X-ray cell [2], indicating that the neutron crystal was an authentic sample of **1**.

Data collection runs of approximately 5–6 h per histogram were initiated arranged at χ and ϕ values suitable to cover a unique hemisphere of reciprocal space (Laue symmetry $\bar{1}$). In total 44 histograms were completed during 11 days of measurement on SCD. Altogether, some 27 542 reflections were sampled. Counting statistics were excellent with approximately 100 peaks per histogram observed with $I/\sigma(I) > 10$.

The recorded histograms were indexed and integrated using individual orientation matrices for each histogram to allow for any misalignment of the sample. Bragg peaks were integrated in three dimensions about their predicted locations and were corrected for the incident neutron spectrum, detector efficiency, and dead-time loss. A Lorentz correction was also applied. The intensities were corrected for the wavelength-dependent absorption assuming a spherical crystal of radius 1.5 mm.

Structure refinements were carried out with the GSAS system [8], starting with the atomic positions taken from the 90-K X-ray study. All atoms were refined with anisotropic displacement parameters with the exception of four organic hydrogen atoms, for which the displacement parameters tended to become non-positive definite, which were therefore refined isotropically. This model refined satisfactorily, based on the reflections observed above 3σ in intensity, including a Type I Gaussian extinction correction. Outliers for which F_o and F_c differed by a factor greater than 2 were assumed to be affected by systematic errors and were accordingly discarded. Final agreement indices are as follows: $Rw(F) = 0.076$, GOF = 2.64, for $n_o = 9,932$ and $n_v = 1,024$. Extinction was found to be of minimal significance; the maximum correction for strong reflections did not exceed 6%.

A final difference–Fourier synthesis did not show any residual peaks at chemically reasonable positions. In particular, no evidence was found for terminal hydrides on tin. The height of the largest positive residual peak was observed to be approximately 4% of a typical carbon Fourier peak while the height of the largest negative residual peak was approximately 15% of a typical hydrogen Fourier peak.

Acknowledgements

References

[1]   M. Pereyre, J.-P. Quintard, A. Rahm, Tin in Organic Synthesis, Butterworths, London, UK, 1987.

[2]   B.E. Eichler, P.P. Power, J. Am. Chem. Soc. 122 (2000) 8785.

[3]   K. Klinkhammer, in: Z. Rappaport (Ed.), The Chemistry of Organic Germanium, Tin and Lead Compounds, 2nd Edition, Vol. 2, John Wiley and Sons, New York, USA, 2002, Part 1, p. 283.

[4]   C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976.

[5]   A.J. Schultz, Trans. Am. Crystallogr. Assoc. 29 (1993) 29.

[6]   A.J. Schultz, D.G. Van Derveer, D.W. Parker, J.E. Baldwin, Acta Crystallogr, Sect. C C46 (1990) 276.

[7]   A.J. Schultz, Trans. Am. Crystallogr. Assoc 23 (1987) 61.

[8]   A.C. Larson, R.B. Von Dreele, GSAS General Structural Analysis System, Los Alamos National Laboratory, Los Alamos, NM, USA, 2000.