

Notes

A Triamidostannate(II) as a “Spectator Ligand” in an Organozirconium Complex: Insertion of CO into a Zr–CH₃ Fragment in the Presence of a Zr–Sn Bond

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Summary: Reaction of the previously characterized triamidostannate complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)] (1) with [Cp₂Zr(CH₃)Cl] in toluene yielded the Zr–Sn complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η⁵-C₅H₅)₂(CH₃)] (2) possessing a Zr–Sn bond [3.0397(2) Å]. Upon pressurizing a solution of 2 with CO (50 bar) at 50 °C, it was completely converted to the acylzirconium complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η⁵-C₅H₅)₂(η²-OCCH₃)] (3) by CO insertion into the Zr–CH₃ bond, while the Sn–Zr bond remains intact.

Introduction

We have recently begun to explore the coordination chemistry of triamidometalates(II) of the heavy group 14 elements, which are stabilized by a tripodal triamide.^{1,2} The combination of the thermodynamic stabilization of the triamidometalates by their integration into a rigid molecular cage structure along with the well-defined orientation and high variability of the peripheral N-substituents has established the tripodal triamidometalates as a versatile new class of “ligands” in the coordination chemistry of the transition metals. The electronegative N-substituents at the divalent metal atoms render these less oxidizable as would be expected for alkyl- or aryl-substituted derivatives. The latter not only allowed the synthesis of stable Ag(I)–Sn or Au(I–III)–Sn compounds³ but provided the access to stannate(II) complexes of the early transition metals, in particular the tetravalent group 4 elements, without degradative single-electron transfer.^{4,5}

This redox chemical degradation pathway was completely suppressed in the reaction of the triamido-

stannate complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)]^{3c} with the metallocene dichlorides [Cp₂MCl₂] of all three titanium group metals to give the corresponding Sn–M complexes [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–M(η⁵-C₅H₅)₂(Cl)].⁴ These new complexes were found to be thermally highly stable and the M–Sn bonds particularly inert toward displacement of the stannate from the group 4 metal. To assess the possibility of using the tin(II) ligand as an ancillary ligand in organometallic transformations, we decided to investigate the reactivity of mixed alkyl(stannyl)zirconium complexes toward CO insertion. We note that Tilley and co-workers observed CO insertion into Zr–Si bonds some 15 years ago,⁶ however, we are unaware of a similar experiment using Zr–Sn complexes. A system that is chemically somewhat related to ours was described by Arnold et al. in their work on [Cp₂Zr(CH₃){TeSi(SiMe₃)₃].⁷ This complex was found to insert CO exclusively into the Zr–C bond to give the corresponding acyl complex.

Results and Discussion

Reaction of the previously characterized triamidostannate complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)] (1) with [Cp₂Zr(CH₃)Cl]⁸ in toluene yielded, after work-up, the deep orange Zr–Sn complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η⁵-C₅H₅)₂(CH₃)] (2) (Scheme 1).

The elemental analysis and the NMR spectra are consistent with the structure depicted in Scheme 1, and

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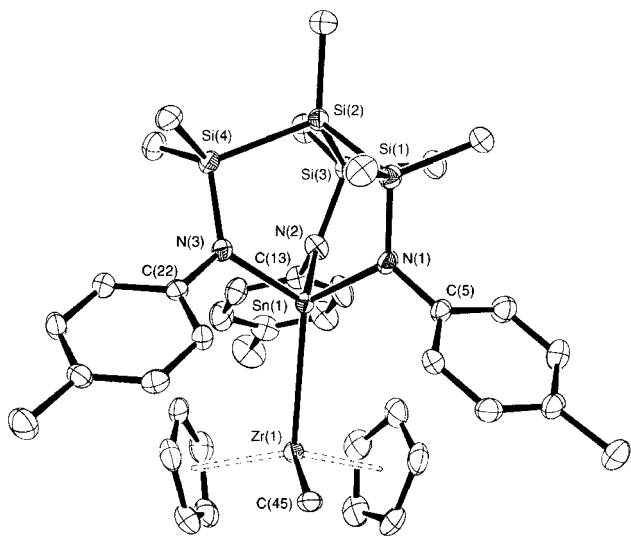
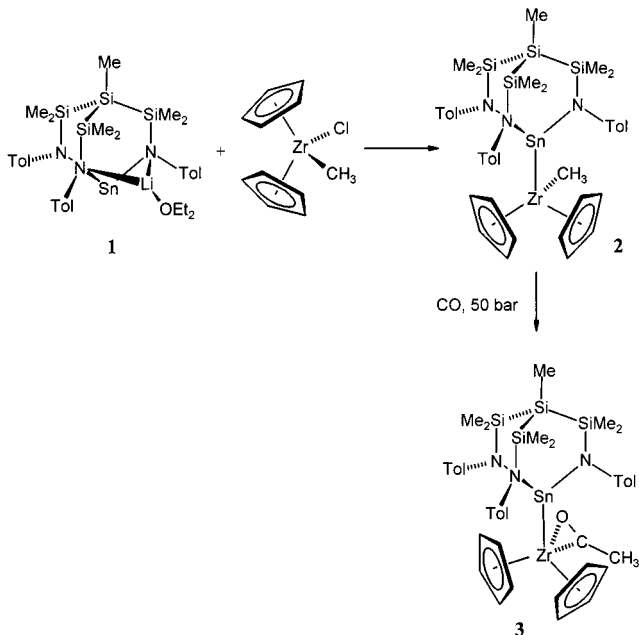


Figure 1. Molecular structure of compound **2**. Principal bond lengths [Å] and interbond angles [deg]: Sn(1)–N(1) 2.0930(18), Sn(1)–N(2) 2.0892(18), Sn(1)–N(3) 2.1012(17), Sn(1)–Zr(1) 3.0397(2), Zr(1)–C(45) 2.281(2), N(1)–Sn(1)–N(2) 97.97(7), N(1)–Sn(1)–N(3) 101.07(8), N(2)–Sn(1)–N(3) 100.27(7), N(1)–Sn(1)–Zr(1) 119.93(5), N(2)–Sn(1)–Zr(1) 114.94(5), N(3)–Sn(1)–Zr(1) 118.92(5), Sn(1)–Zr(1)–C(45) 101.27(5).

Scheme 1. Synthesis of the Zr–Sn Complex 2 and Its Conversion to the Acylzirconium Derivative 3 by CO Insertion into the Zr–CH₃ Bond



the effective local 3-fold symmetry of the stannate fragment, as is evident from the signal patterns in the NMR spectra, indicates a free internal rotation around the Zr–Sn axis. The ¹¹⁹Sn NMR resonance observed at $\delta -12.9$ displays a considerable coordination shift with respect to the lithium stannate **1** ($\delta -96.3$).⁹ An X-ray diffraction study of compound **2** confirmed its molecular structure, which is shown in Figure 1. The crystals of **2** were found to be isomorphous to those of the previously characterized chlorozirconium complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η^5 -C₅H₅)₂(Cl)}], and the structural features of both compounds therefore are practically

identical. The Zr–Sn bond in **2** [3.0397(2) Å] is slightly longer than that found in the chloro complex [3.0231(2) Å]⁴ and significantly longer the sum of the covalent radii of the two metals as given by Pauling (~ 2.85 Å).¹⁰

Upon pressurizing a solution of **2** with CO (50 bar) in an autoclave at 50 °C for 1 h, it is completely converted to the product of CO insertion into the Zr–CH₃ bond, while the Sn–Zr bond remains intact. The formation of the acylzirconium complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η^5 -C₅H₅)₂(η^2 -OCCH₃)] (**3**) (Scheme 1) was first evidenced by the ¹³C NMR resonance at δ 305.9 ppm and the infrared band at 1498 cm⁻¹ and confirmed by a single-crystal X-ray structure analysis.¹¹ Compound **3** crystallizes in the centrosymmetric monoclinic space group *C*₂, and its structure comprises two independent molecules in the asymmetric unit. The molecular structure is depicted in Figure 2 along with the principal bond lengths and angles.

The tripod-amide-tin unit is characterized by its rigid cage structure as found in related tin complexes previously characterized by us. The peripheral tolyl groups adopt a “lamp shade” arrangement to make space for the Cp₂Zr(η^2 -OCCH₃) fragment to which it is bonded. The acyl group is bonded as expected with the orientation of the η^2 -carbonyl group toward the second ligand at the zirconocene unit, the triamidostannate. As a consequence of the CO insertion into the Zr–CH₃ bond, the Zr–Sn bond length in **3** has slightly decreased to an average value of 3.014 Å, as compared to **2**. The distances and angles within the ZrOC triangle (average values for the two independent molecules in the asymmetric unit: Zr–O 2.273, Zr–C 2.201, C–O 1.237 Å) lie in the range previously observed for acylzirconium compounds.¹¹

Concerning the mechanism of the CO insertion reaction, it was conceivable that a reversible CO insertion into the Sn–Zr bond precedes the irreversible insertion into the Zr–C bond. To test this possibility, we pressurized the chloro complex [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η^5 -C₅H₅)₂(Cl)}], which does not contain a Zr–C bond, with CO under the reaction conditions indicated above. The absence of any reaction under these conditions suggests that the insertion takes place directly into the Zr–C bond without involving the metal–metal bond.

Conclusion

In conclusion the Zr–Sn bond proved to be completely inert toward CO insertion under pressure which occurred exclusively at the adjacent Zr–C bond in complex **2**. This implies that the stannate(II) cages developed

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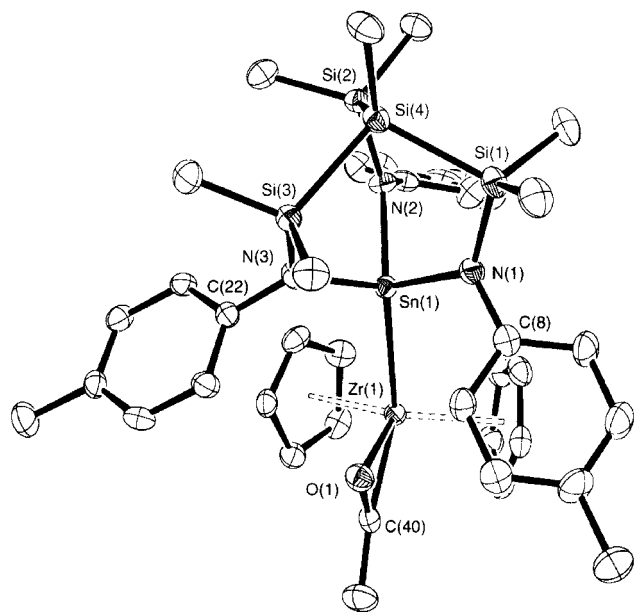


Figure 2. Molecular structure of compound **3**. Principal bond lengths [Å] and interbond angles [deg]: molecule 1: Sn(1)–N(1) 2.108(3), Sn(1)–N(2) 2.104(3), Sn(1)–N(3) 2.093(3), Sn(1)–Zr(1) 3.0155(4), Zr(1)–C(40) 2.202(4), Zr(1)–O(1) 2.278(3), C(40)–O(1) 1.245(4), C(40)–C(39) 1.479(5), N(1)–Sn(1)–N(2) 100.2(1), N(1)–Sn(1)–N(3) 99.8(1), N(2)–Sn(1)–N(3) 98.1(1), O(1)–Zr(1)–C(40) 32.2(1), Sn(1)–Zr(1)–C(40) 113.5(1), Sn(1)–Zr(1)–C(1) 81.3(1), Zr(1)–C(40)–C(39) 161.0(3); molecule 2: Sn(1B)–N(1B) 2.111(3), Sn(1B)–N(2B) 2.104(3), Sn(1B)–N(3B) 2.093(3), Sn(1B)–Zr(1B) 3.0121(4), Zr(1B)–C(40B) 2.200(4), Zr(1B)–O(1B) 2.268(3), C(40B)–O(1B) 1.228(5), C(40B)–C(39B) 1.493(6), N(1B)–Sn(1B)–N(2B) 100.8(1), N(1B)–Sn(1B)–N(3B) 98.5(1), N(2B)–Sn(1B)–N(3B) 98.5(1), O(1B)–Zr(1B)–C(40B) 31.9(1), Sn(1B)–Zr(1B)–C(40B) 113.3(1), Sn(1B)–Zr(1B)–C(1B) 81.5(1), Zr(1B)–C(40B)–C(39B) 160.4(3).

recently may serve as ancillary ligands in reactions requiring relatively forced conditions. We are currently investigating to what extent this finding may be employed in the application of these systems as ligands in catalytic conversions of the early and late transition elements.

Experimental Section

All manipulations were performed under nitrogen (desiccant P₄O₁₀, Granusic, J.T. Baker) on a high-vacuum line using standard Schlenk techniques or in a glovebox. All reaction flasks were heated prior to use using three evacuation–refill cycles. Solvents and solutions were transferred by needle-septa techniques. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive “freeze–pump–thaw” cycles and stored over 4 Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite. The ¹H, ¹³C, ²⁹Si, and ¹¹⁹Sn NMR spectra were recorded on Bruker AC 200, Bruker Avance 250, and Bruker AMX 400 FT-NMR spectrometers. ¹H and ¹³C NMR data are listed in parts per million [ppm] relative to tetramethylsilane and were referenced using the residual protonated solvent peak (¹H) or the carbon resonance (¹³C). ²⁹Si NMR data are listed in ppm relative to tetramethylsilane as an external standard. ¹¹⁹Sn NMR data are listed in ppm relative to tetramethyltin as an external standard. Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out with a Leco

Table 1. X-ray Experimental Data of Compounds **2** and **3**

	2	3
formula	C ₃₉ H ₅₅ N ₃ Si ₄ SnZr·C ₆ D ₆	C ₄₀ H ₅₅ N ₃ O ₃ Si ₄ SnZr
molecular weight	972.27	916.14
cryst syst	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> _c
<i>a</i> (Å)	12.40710(10)	11.73910(10)
<i>b</i> (Å)	17.62050(10)	21.8360(2)
<i>c</i> (Å)	21.0788(2)	34.2254(3)
β (deg)		98.6732(3)
<i>V</i> (Å ³)	4608.23(6)	8672.84(13)
<i>Z</i>	4	8
ρ _{calc} (g cm ⁻³)	1.401	1.403
<i>F</i> 000	1992	3760
μ (mm ⁻¹)	0.906	0.960
temperature (K)	173	150
wavelength (Å)	0.71073	0.71073
radiation	Mo Kα	Mo Kα
no. of data measd	66 918	53 989
no. of data with <i>I</i> > 2σ(<i>I</i>)	13 381	15 863
no. of variables	496	614
<i>R</i>	0.0291	0.0294
<i>wR</i> ₂	0.0572	0.0635

CHNS-932 microanalyzer and a CE-instruments EA 1110 CHNS-O microanalyzer, respectively. (η^5 -C₅H₅)₂Zr(Me)Cl and MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂) were prepared according to published procedures.^{3,8} All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η^5 -C₅H₅)₂(CH₃)] (2). Toluene (15 mL) was added at –78 °C to a stirred mixture of (η^5 -C₅H₅)₂Zr(Me)Cl⁸ (371 mg, 1.37 mmol) and MeSi{SiMe₂N(4-CH₃C₆H₄)₃SnLi(OEt₂)^{3a,c} (1.00 g, 1.37 mmol). The orange reaction mixture was warmed over a period of 3 h to room temperature, and the LiCl precipitate was removed by filtration through Celite. The solvent volume was reduced to about 1 mL, and the solution was stored at –35 °C to give a deep-orange powder. ¹H NMR (250.13 MHz, C₆D₆, 295 K): δ –0.25 (s, 3H, ZrCH₃), 0.28 (s, 3H, SiCH₃), 0.63 (s, 18H, Si(CH₃)₂), 2.20 (s, 9H, CH₃C₆H₄), 5.37 (s, 10H, C₅H₅), 6.99 (d, ³J_{HH} = 8.3 Hz, 6H, H^{2,6} of CH₃C₆H₄), 7.15 (d, ³J_{HH} = 8.3 Hz, 6H, H^{3,5} of CH₃C₆H₄). ¹³C{¹H} NMR (62.9 MHz, C₆D₆, 295 K): δ –14.2 (SiCH₃), 3.9 (Si(CH₃)₂), 20.8 (CH₃C₆H₄), 60.6 (ZrCH₃), 110.2 (C₅H₅), 127.9 (C^{2,6}), 129.8 (C^{3,5}), 129.9 (C⁴), 151.8 (C¹). ²⁹Si{¹H} NMR (39.8 MHz, C₆D₆, 295 K): δ –85.3 (SiCH₃), 0.6 (Si(CH₃)₂). ¹¹⁹Sn{¹H} NMR (149.2 MHz, C₆D₆, 295 K): δ –12.9 (N₃SnZr). Anal. Calcd for C₃₉H₅₅N₃Si₄SnZr (888.14): C 52.74, H 6.24, N 4.73. Found: C 52.77, H 6.13, N 4.65.

Preparation of [MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η^5 -C₅H₅)₂(η^2 -OCCH₃)] (3). In a 100 mL autoclave equipped with a Teflon liner and stirring bar were placed MeSi{SiMe₂N(4-CH₃C₆H₄)₃Sn–Zr(η^5 -C₅H₅)₂(Me) (1) (0.75 g, 0.84 mmol) and toluene (2 mL). The autoclave was filled with CO (50 bar), and stirring was continued at elevated temperature (50 °C) for 1 h. After release of the pressure, the product was isolated as an off-white powder, which was filtered off, washed with pentane (3 × 10 mL), and dried in a vacuum to afford 460 mg (59%) of **3**. IR (KBr): 3088 w, 3016 w, 2955 w, 2938 w, 2889 w, 2728 vw, 2457 vw, 1888 vw, 1602 s, 1566 s, 1498 vs, 1430 m, 1408 w, 1365 w, 1343 vw, 1235 vs, 1181 m, 1173 m, 1137 m, 1111 w, 1103 m, 1069 m, 1041 vw, 1023 s, 1015 s, 1009 m, 947 s, 921 vs, 857 s, 815 s, 777 s, 746 s, 710 m, 688 w 670 vw cm⁻¹. ¹H NMR (250.13 MHz, C₆D₆, 295 K): δ 0.37 (s, 3H, SiCH₃), 0.73 (s, 18H, Si(CH₃)₂), 1.94 (s, 3H, COCH₃), 2.15 (s, 9H, CH₃C₆H₄), 4.78 (s, 10H, C₅H₅), 6.95 (d, ³J_{HH} = 8.0 Hz, 6H, H^{2,6} of CH₃C₆H₄), 7.40 (d, ³J_{HH} = 8.0 Hz, 6H, H^{3,5} of CH₃C₆H₄). ¹³C{¹H} NMR (62.9 MHz, C₆D₆, 295 K): δ –14.0 (SiCH₃), 4.1 (Si(CH₃)₂), 20.8 (CH₃C₆H₄), 32.7 (ZrCOCH₃), 104.5 (C₅H₅), 128.5 (C^{2,6}), 129.0 (C^{3,5}), 129.2 (C⁴), 152.4 (C¹), 305.9 (ZrCOCH₃). ²⁹Si{¹H} NMR (39.8 MHz, C₆D₆, 295 K): δ –88.3

(*SiCH*₃), -2.2 (*Si(CH*₃)₂). ¹¹⁹Sn{¹H} NMR (93.3 MHz, C₆D₆, 295 K): δ 15.7 (N₃SnZrCOMe). Anal. Calcd for C₄₀H₅₅N₃OSi₄SnZr (916.15): C 52.44, H 6.05, N 4.59. Found: C 51.96, H 6.08, N 4.26.

X-ray Crystallographic Study of Compounds 2 and 3.

The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The Denzo-Scalepack program package was used for cell refinements and data reduction.¹² A multiscan absorption correction, based on equivalent reflections (XPREP in SHELX-TL v5.1),¹³ was applied to the data of **2** (T_{\max}/T_{\min} 0.26648/0.21770) and **3**. Structures were solved by direct methods and

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refined using the SHELXS-97 program.¹⁴ In both compounds hydrogens were located from a difference Fourier map and refined isotropically. The crystallographic data of compounds **2** and **3** are summarized in Table 1.

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Supporting Information Available: Text detailing the structure determination and tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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