

Synthesis, Characterization, and Molecular Structure of $[\{\text{Sn}(\mu\text{-NBu}^t)_2\text{W}(\text{NBu}^t)_2\}_2]$

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Summary: The preparation and characterization of $[\{\text{Sn}(\mu\text{-NBu}^t)_2\text{W}(\text{NBu}^t)_2\}_2]$ **1**, obtained by reacting $[\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}]$ with SnCl_2 , is described. X-ray diffraction revealed that **1** exists in the solid state as a centrosymmetric dimer. Compound **1** was studied by multinuclear NMR, and the results are presented and discussed.

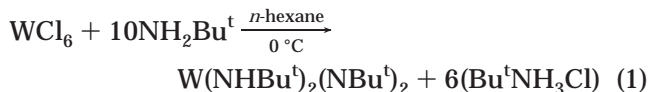
Introduction

Little has been done to investigate the ability of $[\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}]$ as an ambidentate ligand. To date, a few derivatives have been structurally characterized. Other than some compounds utilizing group 13 elements, $[\text{W}\{\mu\text{-NBu}^t)_2\text{MCl}_2\}_2]$ $\{\text{M} = \text{Al and Ga}\}$, only one example of a transition metal complex, $[\{\text{W}_2\text{Cu}_5(\text{NBu}^t)_2(\mu\text{-NBu}^t)_6(\text{NHBu}^t)_2\}\text{BF}_4]$, has been reported.² No investigations have been carried out on group 14 elements derivatives.

This paper reports the preparation and characterization of a new example of a heterometallic amido tin(II) compound, $[\{\text{Sn}(\mu\text{-NBu}^t)_2\text{W}(\text{NBu}^t)_2\}_2]$ **1**, which was obtained by reacting $[\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}]$ with SnCl_2 .

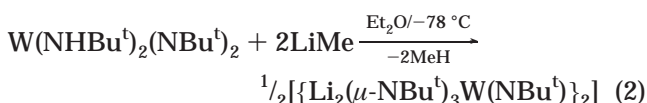
Results and Discussions

The starting material for the ligand, $[\text{W}(\text{NHBu}^t)_2(\text{NBu}^t)_2]$, known for about 20 years, was prepared by treating a suspension of WCl_6 in hexane with an excess of NH_2Bu^t (1:10). After stirring the solution for 48 h, $\text{Bu}^t\text{NH}_3\text{Cl}$ was separated by filtration and the volatiles were removed under vacuum. Recrystallization from hexane at -30°C yielded $[\text{W}(\text{NHBu}^t)_2(\text{NBu}^t)_2]$ as a colorless, moisture- and air-sensitive crystalline product (eq 1).³



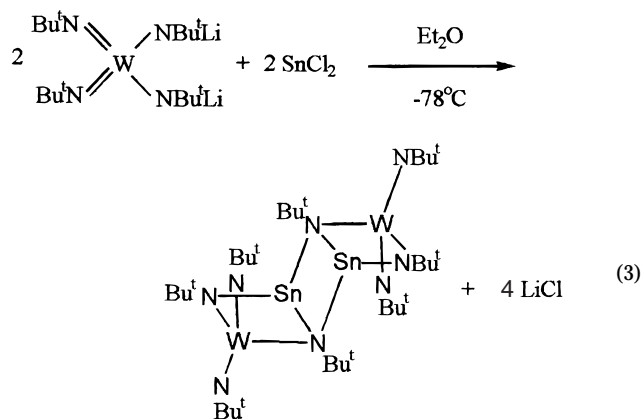
The identity of this compound was confirmed by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

In a second step the reaction of $[\text{W}(\text{NHBu}^t)_2(\text{NBu}^t)_2]$ with LiMe in Et_2O provided the lithiated species $[\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}]$ (eq 2).



The molecular structure of the latter has been determined previously by a single-crystal X-ray diffraction study which showed that this compound exists in the solid state as a dimer that possesses three bridging and one terminal NBu^t group.⁴

The Sn(II) derivative was obtained by treating 1 equiv of $[\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}]$ with SnCl_2 in Et_2O at -78°C (eq 3). There was a color change to orange on warming the reaction mixture to ambient temperature with concomitant formation of a white precipitate. After 12 h of stirring the solution was filtered and the solvent removed under vacuum. Compound **1** was extracted into benzene as an air- and moisture-sensitive orange solid. X-ray quality crystals were obtained after recrystallization from benzene/hexane.



A single-crystal X-ray diffraction study⁵ (Table 1) showed that compound **1** is dimeric in the solid state (Figure 1) with bridging and terminal NBu^t units.

There are three almost identical Sn–N interactions in each monomer, two intramolecular, Sn–N(1) 2.276(5) Å, Sn–N(2) 2.290(5) Å, and one intermolecular, Sn'–

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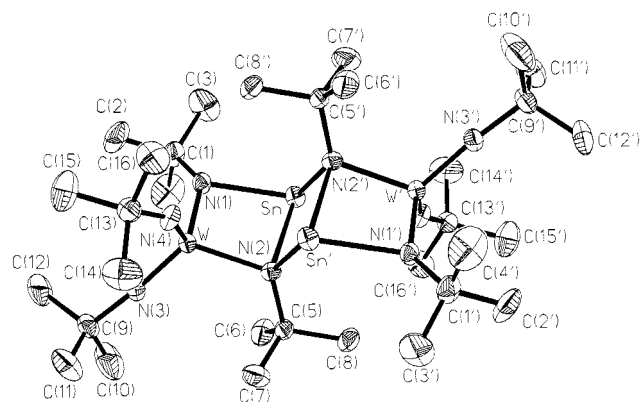


Figure 1. Molecular structure of $[\{\text{Sn}(\mu\text{-NBu})_2\text{W}(\text{NBu})_2\}_2]$ **1** and atom-numbering scheme with selected bond lengths (Å) and angles (deg): W–N(3) 1.753(5), W–N(4) 1.799(5), W–N(1) 1.890(5), W–N(2) 2.050(5), Sn–N(1) 2.276(5), Sn–N(2) 2.290(5), Sn–N(2') 2.289(5), Sn'–N(2) 2.289(5); W–N(1)–C(1) 139.2(4), W–N(2)–C(5) 120.3(3), W–N(3)–C(9) 170.2(5), W–N(4)–C(13) 153.7(4).

Table 1. Crystal Data and Structure Refinement for Compound 1

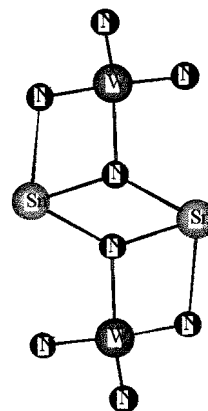
empirical formula	$\text{C}_{16}\text{H}_{36}\text{N}_4\text{SnW}$
fw	587.03
temperature	200(2) K
wavelength	0.710 73
crystal system	orthorhombic
space group	<i>Pbca</i>
unit cell dimens	$a = 10.387(2)$ Å; $b = 16.760(3)$ Å; $c = 24.957(5)$ Å; $\alpha = \beta = \gamma = 90^\circ$
volume	$4345(2)$ Å ³
<i>Z</i>	8
density (calc)	1.795 Mg m ^{−3}
absorp coeff	6.444 mm ^{−1}
<i>F</i> (000)	2272
crystal size	$0.15 \times 0.10 \times 0.10$ mm
θ range for data collection	1.63 – 28.73°
index ranges	$-13 \leq h \leq 12$, $-21 \leq k \leq 21$, $-26 \leq l \leq 33$
no. of rflns collected	24 760
no. of indep rflns	5269 [<i>R</i> (int) = 0.0631]
no. of rflns with $I > 2\sigma(I)$	3875
structure solution	direct methods
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	5269/0/199
goodness-of-fit on F^2	1.133
final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0409$, $wR_2 = 0.0747$
<i>R</i> indices (all data)	$R_1 = 0.0735$, $wR_2 = 0.0846$
largest diff peak and hole	0.844 and -1.435 e Å ^{−3}

N(2), 2.289(5) Å. These Sn–N distances are longer than in normal amido tin(II) compounds, e.g., $[\text{Sn}(\mu\text{-NBu})_2(\text{SiMe}_2)]$, 2.091(8) Å;⁶ however, they are comparable to

(5) (a) The data were collected using a Siemens 3 circle diffractometer equipped with a SMART CCD area detector, graphite-monochromated Mo K α radiation. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were inserted at calculated positions and fixed. The structure was solved by direct methods using SHELXTL^{5(b)} version 5.0, and the refinements were carried out using SHELXTL96^{5(c)} software, minimizing on the weighted *R* factor wR_2 . Residuals were calculated using the following formulas: $R = \sum |F_o - F_c| / \sum F_o$ (for $F_o \geq 4\sigma(F_o)$), $(wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$ for all data); a weighting scheme of the form $w^{-1} = \sigma^2(F_o^2) + aP + bP$ was used, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, where $\max(F_o^2, 0)$ indicates that the larger of F_o^2 or 0 is taken, *a* and *b* are values set by the program. All non-H atoms were anisotropic. Additional material is available from the Cambridge Crystallographic Data Centre {117980}. Atom positions were refined, and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$. (b) Sheldrick, G. M. *SHELXL 5.0*; Siemens Analytical Instruments: Madison, WI, 1994. (c) Sheldrick, G. M. *SHELXL 96*; University of Cottengen, 1996. (6) Veith, M. Z. *Naturforsch.* **1978**, 33B, 7.

the Sn–N bond length found in $[\text{Sn}\{\mu\text{-NSiMe}_3\}_2(\text{PPh}_2)_2]$,⁷ 2.233 (av) Å (Table 2).

The SnN_3 fragment describes a trigonal pyramidal geometry, which implies the presence of a stereochemically active lone pair at the Sn(II) atom.



Regarding the ligand framework, the two terminal W–N bonds are not very different, W–N(3) 1.753(5) Å and W–N(4) 1.799(5) Å. These bond lengths compare well with the W–N (terminal) distance observed in $[\{\text{Li}_2(\mu\text{-NBu})_3\text{W}(\text{NBu})_2\}_2]$,⁴ 1.747 (av) Å (Table 2).

The angles W–N(3)–C(9), 170.2(5)°, and W–N(4)–C(13), 153.7(4)°, suggest that the hybridization at N(3) and N(4) is approximately *sp*. In contrast, the W–N contacts of the bridging NBu^t groups are quite different, W–N(1), 1.890(5) Å, and W–N(2), 2.050(5) Å. The W–N(1) distance is comparable to that found in both the lithium derivative, 1.876 (av) Å, and aluminum complex, $[\{\text{AlMe}_2\}_2\text{W}(\mu\text{-NBu})_4]$,² 1.845 (av) Å (Table 2). The geometry at N(1) is close to trigonal planar, as the sum of the three angles around this atom is almost 360° and thus may be considered as *sp*² hybridized. Finally the geometry at N(2) is distorted tetrahedral.

The ¹¹⁹Sn NMR spectrum of **1** displayed in solution a resonance at δ −839. This signal appears at a higher field compared with a similar systems, $[\text{Sn}\{\mu\text{-NSiMe}_3\}_2(\text{PPh}_2)_2]$,⁷ which displays a signal at δ −247. Due to the presence of ¹⁴N (*S* = 1), which broadened the Sn resonance, no coupling to the W atom was detected in the ¹¹⁹Sn NMR spectrum. Broad signals also were observed in the ¹³C, δ 36.8, 64.7, and ¹H NMR, δ 1.5, spectra in solution as a consequence of a fast exchange between terminal and bridging Bu^t groups. This process was slowed by cooling a CDCl_3 solution of **1** to −30 °C, allowing the signals in the ¹³C NMR spectrum to be separated into δ 35.7/37.2 for the Me group and δ 58.3/70.5 for the quaternary carbon. On the other hand, the protons signals were not separated, possibly due to there being only a small difference in chemical shift.

Experimental Section

Experimental work was carried out under an atmosphere of dry nitrogen. All manipulations were conducted using Schlenk techniques, employing a vacuum/nitrogen line or using a glovebox under an atmosphere of nitrogen (<1 ppm H₂O, <1 ppm O₂). Solvents were distilled from K or Na suspension and kept in Schlenk flasks with K or Na mirror. Solution-state

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Table 2. Selected Bond Lengths and Angles for Some Cyclic Amido Compounds

compound	W–N/Å	Sn–N/Å	N–Sn–N/deg	W–N–C/deg	ref
[$\{\text{Sn}(\mu\text{-NBu}^t)_2\text{W}(\text{NBu}^t)_2\}_2$]	1.776 (av) ^a	2.276(5) ^b	79.3(2) ^d	170.2(5) ^a	this work
	1.890(5) ^b	2.289(5) ^c	81.5(2) ^c	153.7(4) ^a	
	2.050(5) ^c				
[$\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}_2$]	1.747 (av) ^a			177.6 (av) ^a	4
	1.876 (av)				
[$\{\text{AlMe}_2\}_2\text{W}(\mu\text{-NBu}^t)_4$]	1.845 (av)			143.5 (av)	2
[$\text{Sn}(\mu\text{-NBu}^t)_2(\text{SiMe}_2)$]		2.091(8)	70(4)		6
[$\text{Sn}\{\mu\text{-NSiMe}_3\}_2(\text{PPh}_2)_2$]		2.233 (av)	65.6 (av)		7

^a Terminal. ^b Bridging W and Sn. ^c Bridging W and two Sn. ^d N(1) and N(2).

NMR spectra were recorded at 100.13 MHz (¹³C) and 149.21 MHz (¹¹⁹Sn) using a Bruker DMX-400 spectrometer. The ¹³C shifts are reported relative to SiMe₄ and ¹¹⁹Sn shifts relative to SnMe₄.

Synthesis of [$\text{W}(\text{NHBu}^t)_2(\text{NBu}^t)_2$]. To a Schlenk flask charged with WCl₆ (10 g, 0.025 mol) suspended in hexane (200 mL) at 0 °C was added NH₂Bu^t (30 mL, 0.25 mol). After 48 h, the pale yellow solution was filtered and the volatiles were removed under vacuum, leaving the crude product. Further recrystallization from hexane afforded [$\text{W}(\text{NHBu}^t)_2(\text{NBu}^t)_2$] as a moisture- and air-sensitive, colorless, crystalline product in 62% yield (7.3 g, 0.016 mol). ¹H NMR (C₆D₆, 400.13 MHz): δ 1.34 (6 Me), 1.53 (6 Me), 5.3 (br, 2 NH). ¹³C{¹H} NMR (C₆D₆, 100.61 MHz): δ 33.3 (6 Me₃CNH), 33.5 (6 Me₃CN), 53.2 (2 Me₃CNH) and 65.9 (2 Me₃CN). Mp: 87–88 °C. EI-MS: M⁺ *m/z* 470, M⁺ – Me 455, M⁺ – Me – Bu^t 397.

Synthesis of [$\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}_2$]. To a Schlenk flask charged with [$\text{W}(\text{NHBu}^t)_2(\text{NBu}^t)_2$] (2 g, 4.3 mmol) suspended in Et₂O (75 mL) at –78 °C was added LiMe (8.6 mmol) dissolved in Et₂O. After 3 h of stirring, the solvent was removed and a crystalline product was isolated. Recrystallization from hot hexane afforded colorless needles of [$\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}_2$] in 69% yield (1.4 g, 2.97 mmol). Mp > 200 °C. ⁷Li NMR (pyridine, 400.13 MHz): δ 2.1.

Synthesis of [$\{\text{Sn}(\mu\text{-NBu}^t)_2\text{W}(\text{NBu}^t)_2\}_2$]. To a Schlenk flask charged with [$\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}_2$] (1.4 g, 2.97 mmol) dissolved in Et₂O (100 mL) at –78 °C was added SnCl₂ (0.56 g, 2.97 mmol) in Et₂O. There was a color change to orange on warming the solution to ambient temperature. The solution was stirred for 12 h, and an orange solid was isolated after removing the Et₂O and extracting with hot benzene. Recrystallization from benzene/hexane (3:1) afforded orange plates of [$\{\text{Sn}(\mu\text{-NBu}^t)_2\text{W}(\text{NBu}^t)_2\}_2$] in 72% yield (1.25 g, 2.12 mmol). Mp: 230 °C (d). ¹H NMR (C₆D₆, 400.13 MHz): δ 1.5 (very broad). ¹³C{¹H} NMR (C₆D₆, 100.61 MHz): δ 36.8 (br), 64.7 (br). ¹¹⁹Sn{¹H} NMR (C₆D₆, 149.21 MHz): δ –838.7. EI-MS: M⁺ – Sn($\mu\text{-NBu}^t)_2\text{W}(\text{NBu}^t)_2$ *m/z* 587, M⁺ – Sn($\mu\text{-NBu}^t)_2\text{W}(\text{NBu}^t)_2$ – Me 571. Anal. Calcd (found) for C₃₂H₇₂N₈W₂Sn₂: C 31.71 (32.74), H 6.11 (6.18), and N 9.44 (9.54).

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