

# 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  $\text{SnCl}_2$ , 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.

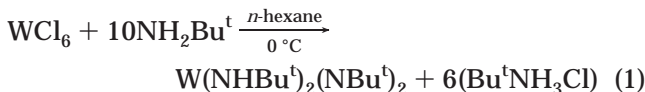
## Introduction

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, [ $\text{W}\{(\mu\text{-NBu}^t)_2\text{MCl}_2\}_2$ ] {M = 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.<sup>2</sup> 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  $\text{SnCl}_2$ .

## 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  $\text{WCl}_6$  in hexane with an excess of  $\text{NH}_2\text{Bu}^t$  (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  $-30^\circ\text{C}$  yielded [ $\text{W}(\text{NHBu}^t)_2(\text{NBu}^t)_2$ ] as a colorless, moisture- and air-sensitive crystalline product (eq 1).<sup>3</sup>



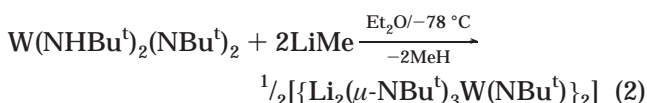
The identity of this compound was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and mass spectrometry.

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(2) Danopoulos, A. A.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2753.

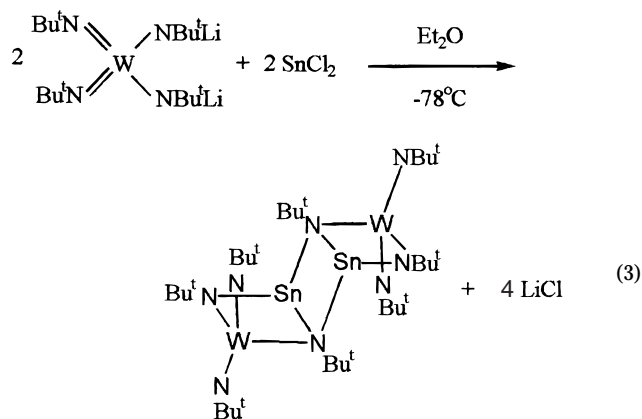
(3) (a) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1980**, *19*, 777. (b) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965.

In a second step the reaction of [ $\text{W}(\text{NHBu}^t)_2(\text{NBu}^t)_2$ ] with  $\text{LiMe}$  in  $\text{Et}_2\text{O}$  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  $\text{NBu}^t$  group.<sup>4</sup>

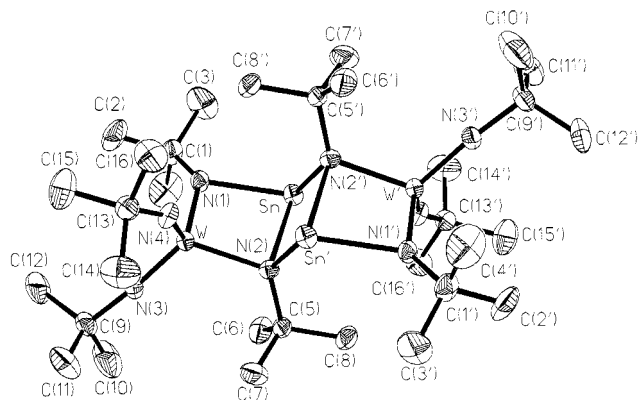
The Sn(II) derivative was obtained by treating 1 equiv of [ $\{\text{Li}_2(\mu\text{-NBu}^t)_3\text{W}(\text{NBu}^t)_2\}$ ] with  $\text{SnCl}_2$  in  $\text{Et}_2\text{O}$  at  $-78^\circ\text{C}$  (eq 3). There was a color change to orange on warming the reaction mixture to ambient temperature with 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 study<sup>5</sup> (Table 1) showed that compound **1** is dimeric in the solid state (Figure 1) with bridging and terminal  $\text{NBu}^t$  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'–

(4) Danopoulos, A. A.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1989**, 896.



**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**

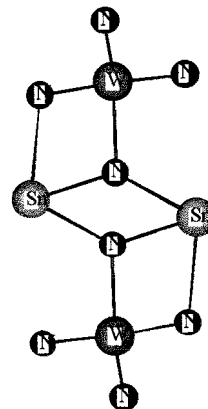
empirical formula	$\text{C}_{16}\text{H}_{36}\text{N}_4\text{SnW}$
fw	587.03
temperature	200(2) K
wavelength	0.710 73
crystal system	orthorhombic
space group	<i>Pbca</i>
unit cell dimens	$a = 10.387(2)$ Å; $b = 16.760(3)$ Å; $c = 24.957(5)$ Å; $\alpha = \beta = \gamma = 90^\circ$
volume	$4345(2)$ Å <sup>3</sup>
Z	8
density (calc)	$1.795$ Mg m <sup>-3</sup>
absorp coeff	$6.444$ mm <sup>-1</sup>
$F(000)$	2272
crystal size	$0.15 \times 0.10 \times 0.10$ mm
$\theta$ range for data collection	$1.63$ – $28.73^\circ$
index ranges	$-13 \leq h \leq 12$ , $-21 \leq k \leq 21$ , $-26 \leq l \leq 33$
no. of reflns collected	24 760
no. of indep reflns	5269 [ $R(\text{int}) = 0.0631$ ]
no. of reflns 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 $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0409$ , $wR2 = 0.0747$
$R$ indices (all data)	$R1 = 0.0735$ , $wR2 = 0.0846$
largest diff peak and hole	$0.844$ and $-1.435$ e Å <sup>-3</sup>

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;<sup>6</sup> 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 $\alpha$  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<sup>5(b)</sup> version 5.0, and the refinements were carried out using SHELXTL96<sup>5(c)</sup> software, minimizing on the weighted  $R$  factor  $wR2$ . Residuals were calculated using the following formulas:  $R = \sum |F_o - F_c| / \sum F_o$  (for  $F_o \geq 4\sigma(F_o)$ ),  $(wR2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$  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  $[\text{Sn}\{\mu\text{-NSiMe}_3\}_2(\text{PPh}_2)]_2$ ,<sup>7</sup> 2.233 (av) Å (Table 2).

The  $\text{SnN}_3$  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  $[\{\text{Li}_2(\mu\text{-NBu})_3\text{W}(\text{NBu})_2\}_2]$ ,<sup>4</sup> 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  $\text{NBu}^t$  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,  $[\{\text{AlMe}_2\}_2\text{W}(\mu\text{-NBu})_4]$ ,<sup>2</sup> 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 <sup>119</sup>Sn NMR spectrum of **1** displayed in solution a resonance at  $\delta$  –839. This signal appears at a higher field compared with a similar systems,  $[\text{Sn}\{\mu\text{-NSiMe}_3\}_2(\text{PPh}_2)]_2$ ,<sup>7</sup> which displays a signal at  $\delta$  –247. Due to the presence of <sup>14</sup>N ( $S = 1$ ), which broadened the Sn resonance, no coupling to the W atom was detected in the <sup>119</sup>Sn NMR spectrum. Broad signals also were observed in the <sup>13</sup>C,  $\delta$  36.8, 64.7, and <sup>1</sup>H NMR,  $\delta$  1.5, spectra in solution as a consequence of a fast exchange between terminal and bridging  $\text{Bu}^t$  groups. This process was slowed by cooling a  $\text{CDCl}_3$  solution of **1** to –30 °C, allowing the signals in the <sup>13</sup>C NMR spectrum to be separated into  $\delta$  35.7/37.2 for the Me group and  $\delta$  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 H<sub>2</sub>O, <1 ppm O<sub>2</sub>). Solvents were distilled from K or Na suspension and kept in Schlenk flasks with K or Na mirror. Solution-state

(7) Kilimann, U.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1993**, *443*, 35.

**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
[Sn( $\mu$ -NBu <sup>t</sup> ) <sub>2</sub> W(NBu <sup>t</sup> ) <sub>2</sub> ] <sub>2</sub>	1.776 (av) <sup>a</sup>	2.276(5) <sup>b</sup>	79.3(2) <sup>d</sup>	170.2(5) <sup>a</sup>	this work
	1.890(5) <sup>b</sup>	2.289(5) <sup>c</sup>	81.5(2) <sup>c</sup>	153.7(4) <sup>a</sup>	
	2.050(5) <sup>c</sup>				
[Li <sub>2</sub> ( $\mu$ -NBu <sup>t</sup> ) <sub>3</sub> W(NBu <sup>t</sup> ) <sub>2</sub> ] <sub>2</sub>	1.747 (av) <sup>a</sup>			177.6 (av) <sup>a</sup>	4
	1.876 (av)				
[AlMe <sub>2</sub> ] <sub>2</sub> W( $\mu$ -NBu <sup>t</sup> ) <sub>4</sub>	1.845 (av)			143.5 (av)	2
[Sn( $\mu$ -NBu <sup>t</sup> ) <sub>2</sub> (SiMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub>		2.091(8)	70(4)		6
[Sn( $\mu$ -NSiMe <sub>3</sub> ) <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub>		2.233 (av)	65.6 (av)		7

<sup>a</sup> Terminal. <sup>b</sup> Bridging W and Sn. <sup>c</sup> Bridging W and two Sn. <sup>d</sup> N(1) and N(2).

NMR spectra were recorded at 100.13 MHz (<sup>13</sup>C) and 149.21 MHz (<sup>119</sup>Sn) using a Bruker DMX-400 spectrometer. The <sup>13</sup>C shifts are reported relative to SiMe<sub>4</sub> and <sup>119</sup>Sn shifts relative to SnMe<sub>4</sub>.

**Synthesis of [W(NHBu<sup>t</sup>)<sub>2</sub>(NBu<sup>t</sup>)<sub>2</sub>].** To a Schlenk flask charged with WCl<sub>6</sub> (10 g, 0.025 mol) suspended in hexane (200 mL) at 0 °C was added NH<sub>2</sub>Bu<sup>t</sup> (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 [W(NHBu<sup>t</sup>)<sub>2</sub>(NBu<sup>t</sup>)<sub>2</sub>] as a moisture- and air-sensitive, colorless, crystalline product in 62% yield (7.3 g, 0.016 mol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta$  1.34 (6 Me), 1.53 (6 Me), 5.3 (br, 2 NH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta$  33.3 (6 Me<sub>3</sub>CNH), 33.5 (6 Me<sub>3</sub>CN), 53.2 (2 Me<sub>3</sub>CNH) and 65.9 ((2 Me<sub>3</sub>CN)). Mp: 87–88 °C. EI-MS: M<sup>+</sup> *m/z* 470, M<sup>+</sup> – Me 455, M<sup>+</sup> – Me – Bu<sup>t</sup> 397.

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

**Synthesis of [Sn( $\mu$ -NBu<sup>t</sup>)<sub>2</sub>W(NBu<sup>t</sup>)<sub>2</sub>]<sub>2</sub>.** To a Schlenk flask charged with [Li<sub>2</sub>( $\mu$ -NBu<sup>t</sup>)<sub>3</sub>W(NBu<sup>t</sup>)<sub>2</sub>] (1.4 g, 2.97 mmol) dissolved in Et<sub>2</sub>O (100 mL) at –78 °C was added SnCl<sub>2</sub> (0.56 g, 2.97 mmol) in Et<sub>2</sub>O. 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 Et<sub>2</sub>O and extracting with hot benzene. Recrystallization from benzene/hexane (3:1) afforded orange plates of [Sn( $\mu$ -NBu<sup>t</sup>)<sub>2</sub>W(NBu<sup>t</sup>)<sub>2</sub>]<sub>2</sub> in 72% yield (1.25 g, 2.12 mmol). Mp: 230 °C (d). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta$  1.5 (very broad). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta$  36.8 (br), 64.7 (br). <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 149.21 MHz):  $\delta$  –838.7. EI-MS: M<sup>+</sup> – Sn( $\mu$ -NBu<sup>t</sup>)<sub>2</sub>W(NBu<sup>t</sup>)<sub>2</sub> *m/z* 587, M<sup>+</sup> – Sn( $\mu$ -NBu<sup>t</sup>)<sub>2</sub>W(NBu<sup>t</sup>)<sub>2</sub> – Me 571. Anal. Calcd (found) for C<sub>32</sub>H<sub>72</sub>N<sub>8</sub>W<sub>2</sub>Sn<sub>2</sub>: C 31.71 (32.74), H 6.11 (6.18), and N 9.44 (9.54).

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