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# Synthesis of Zirconium Complexes That Contain a Tridentate Diamido Ligand

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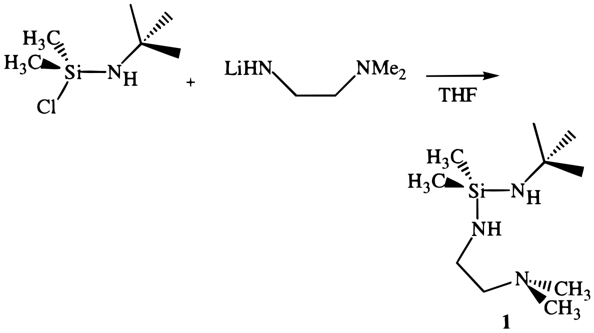
*Summary: The triamine t-BuNHSiMe$_2$NHCH$_2$CH$_2$NMe$_2$ (**1**; =H$_2$[NSiN$_2$]) was synthesized from LiNHCH$_2$CH$_2$NMe$_2$ and t-BuNHSiMe$_2$Cl and used without purification to produce [NSiN$_2$]Zr(NMe$_2$)$_2$ (**2**) from Zr(NMe$_2$)$_4$. Addition of excess trimethylsilyl chloride to **2** gave [NSiN$_2$]ZrCl$_2$ (**3**). Dialkyl complexes of the type [NSiN$_2$]ZrR$_2$ (R = CH$_2$SiMe$_3$, CH$_2$Ph, CH$_2$CHMe$_2$) were prepared readily by alkylation of **3**. The structure of a magnesium chloride adduct of the diisobutyl derivative showed it to be a dimer, {[NSiN$_2$]Zr(CH$_2$CHMe$_2$)$_2$MgCl$_2$}$_2$, which contains a ZrN(Cl)MgCl$_2$MgN(Cl)Zr backbone. [NSiN$_2$]Zr(CH$_2$CHMe$_2$)$_2$ proved to be inactive for the polymerization of 1-hexene when activated by either [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] or [Ph$_3$C][B(C$_6$F$_5$)$_4$] in chlorobenzene at 0 °C.*

## Introduction

Over the last 15 years enormous progress has been made in the development and design of “single-site” catalysts for the polymerization of α-olefins,[1−3] the vast majority of which are metallocenes. Complexes containing bridging monocyclopentadienyl−amide ligand systems have also been employed successfully.[4−7] Most recently, complexes that contain chelating diamido ligand systems have been the focus of attention as potential catalysts.[8−22] Some dialkyl diamido complexes yield polyolefins in a living manner when activated in ways analogous to those employed for metallocenes.[8,9] Since the number of possible chelating diamido catalysts that one might envision is large, it is important to explore the synthesis and efficacy of a variety of diamido ligands for group 4 catalyst activity. Here we report a silicon-bridged diamido system, [*t*-BuNSiMe$_2$NCH$_2$CH$_2$NMe$_2$]$^{2-}$ ([NSiN$_2$]$^{2-}$), and several dialkylzirconium complexes containing it.

The parent triamine, *t*-BuNHSiMe$_2$NHCH$_2$CH$_2$NMe$_2$ (**1**; =H$_2$[NSiN$_2$]), was synthesized from LiNHCH$_2$CH$_2$NMe$_2$ and *t*-BuNHSiMe$_2$Cl in a manner analogous to methods described for related aminosilanes reported in the literature[23] (eq 1). It was isolated in essentially quantitative yield as a colorless oil from pentane and was used in subsequent reactions without further purification.



(1)

**1**

H$_2$[NSiN$_2$]

The reaction between **1** and Zr(NMe$_2$)$_4$ yielded [NSiN$_2$]Zr(NMe$_2$)$_2$ (**2**) in 79% isolated yield. Proton NMR data suggest that the yield of **2** is essentially quantitative, but the high solubility of **2** evidently prevents it from being isolated in higher yield. Addition of excess trimethylchlorosilane to **2** gave [NSiN$_2$]ZrCl$_2$ (**3**) in 98% isolated yield (eq 2). The most convenient synthesis of **3** in an overall yield of 88% is a one-pot synthesis

$$\mathbf{1} + \mathrm{Zr(NMe_2)_4} \xrightarrow[\text{pentane}]{} \underset{\mathbf{2}}{[\mathrm{NSiN_2}]\mathrm{Zr(NMe_2)_2}} \xrightarrow[\text{pentane}]{\mathrm{Me_3SiCl}} \underset{\mathbf{3}}{[\mathrm{NSiN_2}]\mathrm{ZrCl_2}} \qquad (2)$$

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(1) Kaminsky, W.; Ardnt, M. *Adv. Polym. Sci.* **1997**, *127*, 144.

(2) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(3) Bochmann, M. *J. Chem. Soc., Dalton Trans* **1996**, 255.

(4) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789.

(5) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649.

(6) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

(7) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649.

(8) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008.

(9) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830.

(10) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343.

(11) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25.

(12) Guérin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085.

(13) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1996**, *15*, 5586.

(14) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 3154.

(15) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

(16) Horton, A. D.; de With, J. *Chem. Commun.* **1996**, 1375.

(17) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478.

(18) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.

(19) Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923.

(20) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333.

(21) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562.

(22) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 1491.

(23) Wannagat, U.; Schreiner, G. *Monatsh. Chem.* **1965**, *96*, 1889.

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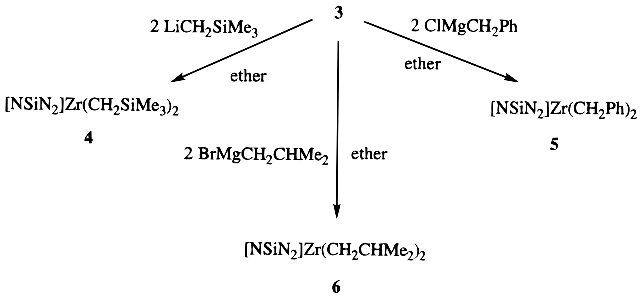
**Scheme 1. Dialkyl Complexes of the Type [NSiN$_2$]ZrR$_2$**



directly from **1** (without isolating **2**). $^1$H and $^{13}$C NMR spectra of **2** and **3** are consistent with molecules that have a single plane of symmetry. On the basis of a recent unpublished structure of a related diamido/donor zirconium dichloride derivative,[24] we believe that **3** is likely to be a dimer in the solid state with a pseudooctahedral arrangement around each Zr.

Although **3** could not be alkylated cleanly with 2 equiv of LiMe or MeMgBr, a series of other dialkyl complexes can be prepared easily, as shown in Scheme 1. Compound **4** appears to be produced cleanly, according to NMR studies, but all attempts to crystallize it failed. Compound **5** was obtained in 76% yield as a yellow, crystalline solid, while **6** was isolated in 78% yield as colorless crystals. Compound **6** is unusual at first glance, since the alkyl ligands contain $\beta$-hydrogen atoms, and dialkylmetallocenes or homoleptic alkyl complexes of such alkyls are typically not stable toward $\beta$-hydride elimination.[25] However, several stable Zr or Hf diamido complexes containing alkyl ligands that contain $\beta$-protons are known,[26−29] and the stability of diamido group 4 complexes to $\beta$-elimination now appears to be more often the rule rather than the exception.

When dioxane was omitted from the synthetic procedure leading to the isolation of **6**, a few crystals were obtained (compound **7**) that proved to be insoluble in pentane at room temperature, in contrast to the high solubility of **6**. An X-ray diffraction study of **7** showed it to be a dimeric magnesium chloride adduct of **6**, i.e., $\{[NSiN_2]Zr(CH_2CHMe_2)_2MgCl_2\}_2$ (Tables 1 and 2; Figure 1). (The two ends of the molecule are similar, so only bond lengths and angles at one end will be discussed.) A MgCl fragment has been "inserted" between the dimethylamino donor (N(13)) and zirconium and also binds to N(12), turning Zr(1)−N(12) (2.212(3) Å) into a pure dative bond whose bond length should be compared to the relatively short Zr(1)−N(11) bond length (2.074(4) Å) typical of an amido ligand that is $\pi$-bound to the metal in the expected manner. Consequently N(12) is approximately tetrahedral, while the sum of all angles around N(11) is 359.3°. Magnesium(1) then becomes five-coordinate via bridging chlorides (Cl(3) and Cl(4)) to Mg(2), forming (very approximately) a trigonal-bipyramidal coordination sphere in which N(12) and Cl(4) are axial in the coordination geometry about Mg(1); the Mg(1)−Cl(4) bond length (2.511(2) Å) is approximately 0.15 Å longer than the Mg(1)−Cl(3) bond length. The two Zr−C bond lengths at a given Zr are statistically the same and are typical of a Zr−C$_{alkyl}$ bond. The range in the Zr−C($\alpha$)−C($\beta$) angles (~10°) can be attributed to different degrees of steric interactions between isobutyl groups and the rest of the molecule.

**Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for $\{[NSiN_2]Zr(CH_2CHMe_2)_2MgCl_2\}_2$ (7)**

| | |
|---|---|
| empirical formula | $C_{18}H_{43}Cl_2MgN_3SiZr$ |
| fw | 516.07 |
| cryst color | colorless |
| cryst dimens (mm) | 0.39 × 0.28 × 0.22 |
| cryst syst | triclinic |
| $a$ | 12.082(3) Å |
| $b$ | 13.395(3) Å |
| $c$ | 18.240(5) Å |
| $\alpha$ | 107.304(13)° |
| $\beta$ | 104.22(2)° |
| $\gamma$ | 93.31(2)° |
| $V$ | 2704.5(12) Å$^3$ |
| space group | $P\bar{1}$ |
| $Z$ | 4 |
| $D_{calc}$ | 1.267 g/cm$^3$ |
| $F_{000}$ | 1088 |
| diffractometer | Siemens SMART/CCD |
| $\lambda$(Mo K$\alpha$) | 0.710 73 Å |
| scan type | $\omega$ scans |
| temp | 183(2) K |
| total no. of unique reflns | 7003 |
| no. of variables | 479 |
| $R$ | 0.0399 |
| $R_w$ | 0.1040 |
| GOF | 1.206 |

**Table 2. Selected Interatomic Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of $\{[NSiN_2]Zr(CH_2CHMe_2)_2MgCl_2\}_2$ (7)**

| Bond Lengths | | | |
|---|---|---|---|
| Zr(1)−N(11) | 2.074(4) | Zr(2)−N(21) | 2.074(4) |
| Zr(1)−N(12) | 2.212(3) | Zr(2)−N(22) | 2.228(4) |
| Zr(1)−Cl(1) | 2.600(2) | Zr(2)−Cl(2) | 2.615(2) |
| Zr(1)−C(11) | 2.235(5) | Zr(2)−C(21) | 2.229(5) |
| Zr(1)−C(31) | 2.250(4) | Zr(2)−C(41) | 2.237(6) |
| Mg(1)−N(12) | 2.196(4) | Mg(2)−N(22) | 2.159(4) |
| Mg(1)−N(13) | 2.173(4) | Mg(2)−N(23) | 2.178(4) |
| Mg(1)−Cl(1) | 2.4426(19) | Mg(2)−Cl(2) | 2.4313(19) |
| Mg(1)−Cl(3) | 2.359(2) | Mg(2)−Cl(3) | 2.546(2) |
| Mg(1)−Cl(4) | 2.511(2) | Mg(2)−Cl(4) | 2.358(2) |

| Bond Angles | | | |
|---|---|---|---|
| N(11)−Zr(1)−N(12) | 74.05(15) | N(21)−Zr(2)−N(22) | 73.89(15) |
| Zr(1)−C(11)−C(12) | 120.8(4) | Zr(2)−C(21)−C(22) | 130.2(3) |
| Zr(1)−C(31)−C(32) | 127.8(6) | Zr(2)−C(41)−C(42) | 128.3(4) |
| Cl(4)−Mg(1)−N(12) | 167.88(10) | Cl(4)−Mg(1)−Cl(1) | 89.68(7) |
| Cl(3)−Mg(1)−Cl(1) | 118.23(8) | Cl(4)−Mg(1)−Cl(3) | 85.87(7) |
| N(13)−Mg(1)−Cl(1) | 120.58(12) | Cl(4)−Mg(1)−N(13) | 91.87(11) |
| N(13)−Mg(1)−Cl(3) | 121.13(12) | | |

We tested complex **6** as a precursor to cationic complexes that could serve as olefin polymerization catalysts, since we felt that the isobutyl ligand is the most similar to the growing chain in a system in which an $\alpha$-olefin reacts with a ZrR$^+$ center in a 1,2-manner. However, no polymer could be obtained upon addition of 1-hexene to a mixture of **6** and either $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene at 0 °C,

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(24) Baumann, R.; Schrock, R. R.; Davis, W. M. To be submitted for publication.

(25) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.

(26) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424.

(27) Andersen, R. *Inorg. Chem.* **1979**, *18*, 2928.

(28) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16.

(29) Erker, G.; Schlund, R.; Krüger, C. *Organometallics* **1989**, *8*, 2349.

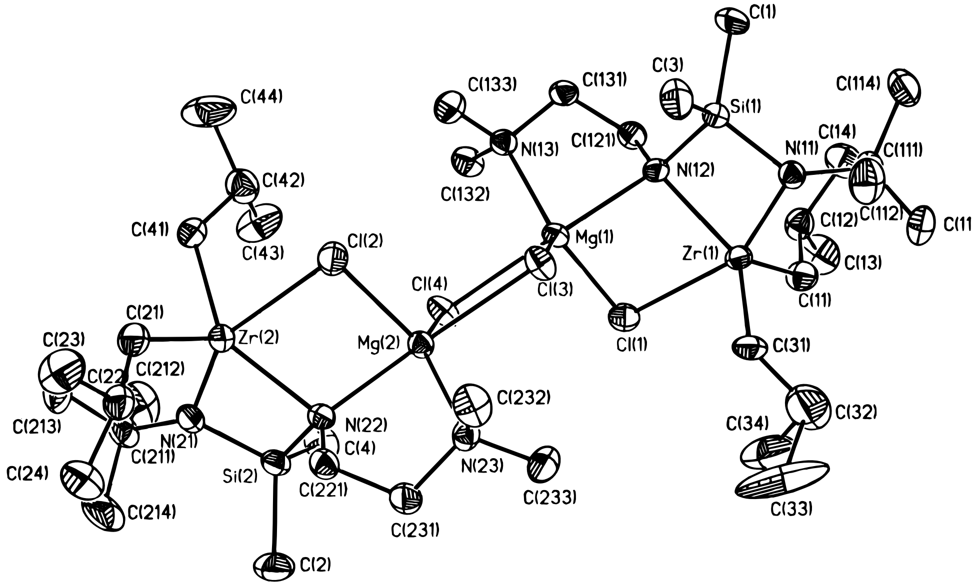

**Figure 1.** X-ray crystal structure of $\{[NSiN_2]Zr(CH_2CHMe_2)_2MgCl_2\}_2$ (**7**).

conditions that have led to the living polymerization of 1-hexene in a system that contains a $[(t\text{-BuN-}o\text{-}C_6H_4)_2O]^{2-}$ ligand system.[9] Since the X-ray study of **7** suggests that the dimethylamino nitrogen and the amido nitrogen that does not contain a bulky *tert*-butyl group are both susceptible to electrophilic attack, we were not surprised to find that polymerization catalysts in fact could not be prepared and suggest that the $[NSiN_2]^{2-}$ ligand in general will not be "innocent" enough. Although much work exploring diamido ligand chemistry remains to be done, we conclude that if a diamido donor ligand is considered, it should contain the donor in the *central* position and the amido nitrogens sterically and electronically deactivated toward electrophiles as much as possible, as found in the successful $[(t\text{-BuN-}o\text{-}C_6H_4)_2O]^{2-}$ ligand system,[9] if relatively well-behaved olefin polymerization activity is the goal.

## Experimental Section

General experimental details can be found elsewhere.[21] Routine NMR coupling constants are not reported. Spectra were obtained at room temperature unless otherwise noted. X-ray data were collected on a SMART/CCD diffractometer as described elsewhere.[30] Crystallographic data, collection parameters, and refinement parameters can be found in Table 1. (See also the Supporting Information.) All commercial reagents were used without further purification unless specified otherwise. $ClMe_2SiNH(t\text{-Bu})$[23] was prepared as reported in the literature.

***t*-BuNHSiMe$_2$NHCH$_2$CH$_2$NMe$_2$ (1).** Solid $LiNHCH_2CH_2NMe_2$ (5.67 g, 60.3 mmol) was added over 10 min to a solution of $ClMe_2SiNH(t\text{-Bu})$ (10 g, 60.3 mmol) in THF at −30 °C. The reaction mixture was stirred overnight at room temperature. All solvents were removed in vacuo, and the residue was extracted with pentane. Removal of solvents in vacuo gave **1** as a colorless oil (12.3 g, 93%), which was used without further purification: $^1H$ NMR ($CDCl_3$) $\delta$ 2.79 (q, 2, $NHCH_2$), 2.26 (t, 2, $CH_2NMe_2$), 2.19 (s, 6, $NMe_2$), 1.13 (s, 9, $CMe_3$), 0.81 (br t, 1, $CH_2NH$), 0.68 (br, 1, *t*-BuN*H*), 0.00 (s, 6, $SiMe_2$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 63.2 ($NHCH_2$), 49.0 ($CMe_3$), 45.6 ($NMe_2$), 39.0 ($CH_2NMe_2$), 33.6 ($CMe_3$), 0.6 ($SiMe_2$).

**[*t*-BuNSiMe$_2$NCH$_2$CH$_2$NMe$_2$]Zr(NMe$_2$)$_2$ (2).** A solution of **1** (3.89 g, 17.9 mmol) in pentane (5 mL) was added over 10 min to a solution of $Zr(NMe_2)_4$ (4.25 g, 17.9 mmol) in pentane (10 mL) at room temperature. After the reaction mixture stood at room temperature for 5 h, it was concentrated to about 6 mL and stood at −30 °C. Analytically pure crystals were isolated, and upon further concentration and cooling of the mother liquor a second crop was obtained: total yield 5.6 g (79%); $^1H$ NMR ($C_6D_6$) $\delta$ 3.40 (t, 2, $SiNCH_2$), 2.92 (s, 12, $ZrNMe_2$), 2.15 (t, 2, $CH_2NMe_2$), 1.87 (s, 6, $NMe_2$), 1.47 (s, 9, $CMe_3$), 0.51 (s, 6, $SiMe_2$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 65.3 ($SiNCH_2$), 54.9 ($CMe_3$), 46.7 ($CH_2NMe_2$), 46.1 ($NMe_2$), 43.0 ($ZrNMe_2$), 36.4 ($CMe_3$), 4.8 ($SiMe_2$). Anal. Calcd for $C_{14}H_{37}N_5SiZr$: C, 42.59; H, 9.45; N, 17.74. Found: C, 42.68; H, 9.74; N, 18.03.

**[*t*-BuNSiMe$_2$NCH$_2$CH$_2$NMe$_2$]ZrCl$_2$ (3).** Neat $Me_3SiCl$ (1.87 g, 17.2 mmol) was added to a solution of **2** (1.7 g, 4.3 mmol) in 10 mL of pentane at room temperature. The reaction mixture was allowed to stand overnight at room temperature and then placed in a refrigerator at −30 °C for 2 h. Colorless crystals were obtained: yield 1.6 g (98%); $^1H$ NMR ($C_6D_6$) $\delta$ 3.22 (t, 2, $SiNCH_2$), 2.41 (t, 2, $CH_2NMe_2$), 2.24 (s, 6, $NMe_2$), 1.50 (s, 9, $CMe_3$), 0.34 (s, 6, $SiMe_2$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 65.4 ($SiNCH_2$), 57.5 ($CMe_3$), 48.1 ($CH_2NMe_2$), 47.2 ($NMe_2$), 34.3 ($CMe_3$), 3.2 ($SiMe_2$). Anal. Calcd for $C_{10}H_{25}Cl_2N_3SiZr$: C, 31.81; H, 6.67; N, 11.13. Found: C, 31.98; H, 6.75; N, 10.98.

Alternatively, a solution of **1** (4.80 g, 22.0 mmol) in pentane (10 mL) was added over 10 min to a solution of $Zr(NMe_2)_4$ (5.90 g, 22.0 mmol) in pentane (20 mL) at room temperature. The reaction mixture stood at room temperature for 6 h, and neat $Me_3SiCl$ (9.6 g, 88.0 mmol) was then added. The reaction mixture was allowed to stand overnight at room temperature. After the mixture stood at −30 °C for several hours, colorless crystals were filtered off; yield 7.3 g (88% overall).

**[*t*-BuNSiMe$_2$NCH$_2$CH$_2$NMe$_2$]Zr(CH$_2$SiMe$_3$)$_2$ (4).** A solution of $LiCH_2SiMe_3$ (205 mg, 2.17 mmol) in diethyl ether (3 mL) was added over a period of 1 min to a solution of **3** (400 mg, 1.06 mmol) in ether (5 mL) at −30 °C. Within seconds a fine precipitate appeared. The reaction mixture was warmed to room temperature, stirred for 20 min, and filtered through Celite. The solvents were removed in vacuo to give a colorless oil quantitatively that was at least 95% pure according to its NMR spectrum: $^1H$ NMR ($C_6D_6$) $\delta$ 3.30 (t, 2, $SiNCH_2$), 2.32 (t, 2, $CH_2NMe_2$), 2.06 (s, 6, $NMe_2$), 1.51 (s, 9, $CMe_3$), 0.41 (s, 6, $SiMe_2$), 0.18 (d, 2, $ZrCH_2$), −0.01 (d, 2, $ZrCH_2$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 66.1 ($SiNCH_2$), 56.0 ($CMe_3$), 49.1 ($ZrCH_2$), 47.1 ($NMe_2$), 46.8 ($CH_2NMe_2$), 35.9 ($CMe_3$), 4.9 ($SiMe_2$), 4.5 ($SiMe_3$).

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[30] Rosenberger, C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1997**, *36*, 123.

**[*t*-BuNSiMe$_2$NCH$_2$CH$_2$NMe$_2$]Zr(CH$_2$Ph)$_2$ (5).** A solution of ClMgCH$_2$Ph (1.0 M in ether, 6.5 mL, 6.5 mmol) was added to a solution of **3** (1.2 g, 3.18 mmol) in diethyl ether (10 mL) at −30 °C. Almost immediately a fine precipitate formed. The mixture was warmed to room temperature over a period of 15 min and was filtered through Celite. All solvents were removed in vacuo and the residue was extracted with pentane. On standing at −30 °C, the extract gave yellow crystals: yield 1.18 g (76%); $^1$H NMR (C$_6$D$_6$) $\delta$ 7.11 (t, 4, H$_m$), 6.98 (d, 4, H$_o$), 6.83 (t, 2, H$_p$), 3.14 (t, 2, SiNCH$_2$), 2.18 (d, 2, ZrCH$_2$), 2.07 (d, 2, ZrCH$_2$), 1.94 (t, 2, C*H*$_2$NMe$_2$), 1.66 (s, 6, NMe$_2$), 1.33 (s, 9, C*Me*$_3$), 0.36 (s, 6, SiMe$_2$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 147.5 (C$_{ipso}$), 129.5 (C$_o$), 127.3 (C$_m$), 121.7 (C$_p$), 65.7 (SiNCH$_2$), 59.9 (ZrCH$_2$), 56.6 (*C*Me$_3$), 46.9 (*C*H$_2$NMe$_2$), 45.5 (NMe$_2$), 35.5 (C*Me*$_3$), 4.4 (SiMe$_2$). Anal. Calcd for C$_{24}$H$_{39}$N$_3$SiZr: C, 58.96; H, 8.04; N, 8.59. Found: C, 58.66; H, 8.23; N, 8.58.

**[*t*-BuNSiMe$_2$NCH$_2$CH$_2$NMe$_2$]Zr(CH$_2$CHMe$_2$)$_2$ (6).** A solution of BrMgCH$_2$CHMe$_2$ (2.51 M in ether, 3.0 mL, 7.55 mmol) was added to a solution of **3** (1.39 g, 3.67 mmol) in diethyl ether (15 mL) at −30 °C. The mixture was warmed to room temperature and was held at room temperature for 15 min. Dioxane (663 mg, 7.55 mmol) was then added. After 20 min all solvents were removed in vacuo and the residue was extracted with pentane. The extract was reduced in volume to ~2 mL and allowed to stand at −30 °C to give yellow crystals: yield 1.2 g (78%); $^1$H NMR (C$_6$D$_6$) $\delta$ 3.35 (t, 2, SiNCH$_2$), 2.29 (t, 2, C*H*$_2$NMe$_2$), 2.24 (m, 2, CH$_2$C*H*Me$_2$), 2.03 (s, 6, NMe$_2$), 1.55 (s, 9, C*Me*$_3$), 1.18 (d, 6, CH$_2$CH*Me*$_2$), 1.15 (d, 6, CH$_2$CH*Me*$_2$), 0.78 (d, 2, ZrCH$_2$), 0.54 (d, 2, ZrCH$_2$), 0.43 (s, 6, SiMe$_2$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 72.1 (ZrCH$_2$), 65.9 (SiNCH$_2$), 55.9 (*C*Me$_3$), 46.8 (*C*H$_2$NMe$_2$), 46.5 (NMe$_2$), 35.9 (C*Me*$_3$), 30.5 (CH$_2$*C*HMe$_2$), 29.9 (CH$_2$CH*Me*$_2$), 29.7 (CH$_2$CH*Me*$_2$), 4.4 (SiMe$_2$). Anal. Calcd for C$_{18}$H$_{43}$N$_3$SiZr: C, 51.37; H, 10.30; N, 9.98. Found: C, 51.45; H, 10.53; N, 9.94.

When dioxane was omitted from the synthetic procedure, a few crystals were obtained that proved to be insoluble in pentane at room temperature in the extraction step. These were shown to be {[*t*-BuNSiMe$_2$NCH$_2$CH$_2$NMe$_2$]Zr(CH$_2$CHMe$_2$)$_2$-MgCl$_2$}$_2$ (**7**) in an X-ray study. Compound **7** was not characterized further.

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**Supporting Information Available:** Tables of crystal data and structure refinement, final positional parameters, final thermal parameters, and bond lengths and angles for {[NSiN$_2$]Zr(CH$_2$CHMe$_2$)$_2$MgCl$_2$}$_2$ (5 pages). Ordering information is given on any current masthead page.

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# *Additions and Corrections*

## 1998, Volume 17

**Charles S. Weinert, Ilia A. Guzei, Arnold L. Rheingold, and Lawrence R. Sita*:** Heterocumulene Metathesis of Pb[N(SiMe$_3$)$_2$]$_2$. High-Yield Syntheses of the Heteroleptic Dimer {Pb[N(SiMe$_3$)$_2$($\mu$-SOiMe$_3$)}$_2$ and the Novel Lead(II) Oxo Cluster Pb$_7$($\mu_3$-O)($\mu_4$-O)($\mu$-SiMe$_3$)$_{10}$.

Page 500. The following description of the Supporting Information available for this paper was omitted in the Web edition published January 22, 1998, as well as in the print edition.

**Supporting Information Available:** Full tables of the data collection parameters, isotropic and anisotropic temperature factors, and bond distances and bond angles for compounds **2** and **4** (15 pages). Ordering information is given on any current masthead page.

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