ORGANOMETALLICS
Article

*Organometallics* **2010,** *29,* 6329–6333 6329
DOI: 10.1021/om100737v

# N-Heterocyclic Carbene Stabilized Dichlorosilaimine $\mathrm{IPr \cdot Cl_2Si{=}NR}$

Rajendra S. Ghadwal,[†] Herbert W. Roesky,*[,†] Carola Schulzke,[‡] and Markus Granitzka[†]

[†]*Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D 37077 Göttingen, Germany, and* [‡]*School of Chemistry, Trinity College Dublin, Dublin 2, Ireland*

*Received July 27, 2010*

N-Heterocyclic carbene stabilized dichlorosilaimine $\mathrm{IPr \cdot Cl_2Si{=}N(Diip)}$ (**2**) has been synthesized by the reaction of dichlorosilylene $\mathrm{IPr \cdot SiCl_2}$ (**1**) with bis(2,6-diisopropylphenyl)carbodiimide (IPr = :C[N(2,6-$i$-$\mathrm{Pr_2}$-$\mathrm{C_6H_3}$)CH]$_2$, Diip = 2,6-$i$-$\mathrm{Pr_2}$-$\mathrm{C_6H_3}$). Reaction of **1** with terphenyl azides also affords dichlorosilaimines $\mathrm{IPr \cdot Cl_2Si{=}N(2,6\text{-}Diip_2\text{-}C_6H_3)}$ (**3**) and $\mathrm{IPr \cdot Cl_2Si{=}N(2,6\text{-}Triip_2\text{-}C_6H_3)}$ (**4**) (Triip = 2,4,6-$i$-$\mathrm{Pr_3}$-$\mathrm{C_6H_2}$). Compounds **2**−**4** are stable under an inert atmosphere and were characterized by elemental analysis and NMR spectroscopic studies. The molecular structures of **2**−**4** were determined by single-crystal X-ray analysis.

## Introduction

Silylenes are key intermediates in numerous thermal and photochemical reactions[1] of organosilicon compounds. Silylene chemistry has been in focus over the last two decades.[2] After the isolation of room-temperature-stable silylenes their reactivity toward a wide range of unsaturated organic and organometallic substrates has been examined,[3,4] which is diverse and dependent on the substituents on the silicon atom and the nature of the substrates. Reactions of N-heterocyclic silylenes (NHSis) with organic azides are reported that show significant difference in their reactivity. Although a THF adduct of a silaimine was reported by West[3] et al. by the reaction of a NHSi with a bulky azide, most of the reactions of NHSis with organic azides resulted in the formation of either azidosilane[3,4] or silatetrazolines.[3,4] On the basis of this, the involvement of initial formation of an unstable silaimine as an intermediate in these reactions was proposed, which further reacts with another molecule of organic azide to form azidosilane or silaterazoline.[3,4]

The search for the formation of multiply bonded silicon compounds[5] has been attracting attention throughout the last decades and is still one of the most interesting topics for silicon chemists. Dialkylsilaimines are compounds with a silicon−nitrogen double bond, which were first isolated independently by Wiberg[6] and Klingebiel[7] in 1986 by thermal salt elimination through multistep reactions.

Moreover, direct methods for silaimine synthesis are still scarce, and there is no reported example of a dihalosilaimine because of the unavailability of suitable starting materials. Gaseous dihalosilylenes, $\mathrm{SiX_2}$ (X = F or Cl), have been known for many years;[8] however at room temperature they condense to polymeric $\mathrm{(SiX_2)}_n$ or disproportionate to Si and $\mathrm{SiX_4}$. There are a number of theoretical investigations[9] reporting the reactivity of silylenes. However, the only available experimental evidence[10] involves $\mathrm{SiCl_2}$, which was generated

---

*To whom correspondence should be addressed. E-mail: hroesky@gwdg.de.

[1] (a) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Apeloig, Y., Eds.; John Wiley & Sons: Chichester, U.K., 1998; Vol. *2*, pp 2463−2568. (b) Tokitoh, N.; Ando, W. In *Reactive Intermediate Chemistry*; Moss, R. A.; Platz, M. S.; Jones, M., Jr., Eds.; John Wiley & Sons: New York, 2004; pp 651−715. (c) du Mont, W.-W.; Gust, T.; Seppälä, E.; Wismach, C. *J. Organomet. Chem.* **2004**, *689*, 1331–1336.

[2] (a) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692. (b) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaser, D. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1931–1932. (c) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722–9723. (d) Haaf, M.; Schmedake, T. A.; Paradise, B. J.; West, R. *Can. J. Chem.* **2000**, *78*, 1526–1533. (e) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C.; Lentz, D. *J. Am. Chem. Soc.* **2006**, *128*, 9628–9629. (f) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948–3950. *Angew. Chem.* **2006**, *118*, 4052−4054.

[3] Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 10813–10814.

[4] (a) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785–788. (b) Hill, N. J.; Moser, D. F.; Guzei, I. A.; West, R. *Organometallics* **2005**, *24*, 3346–3349. (c) Tomasik, A. C.; Mitra, A.; West, R. *Organometallics* **2009**, *28*, 378–381. (d) Xiong, Y.; Yao, S.; Driess, M. *Chem.—Eur. J.* **2009**, *15*, 8542–8547.

[5] (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419–509. (b) West, R. *Polyhedron* **2002**, *21*, 467–472.

[6] (a) Wiberg, N.; Schurz, K.; Fischer, G. *Angew. Chem., Int. Ed.* **1985**, *24*, 1053–1054. *Angew. Chem.* **1985**, *97*, 1058−1059. (b) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *Chem. Communn.* **1986**, 591–592.

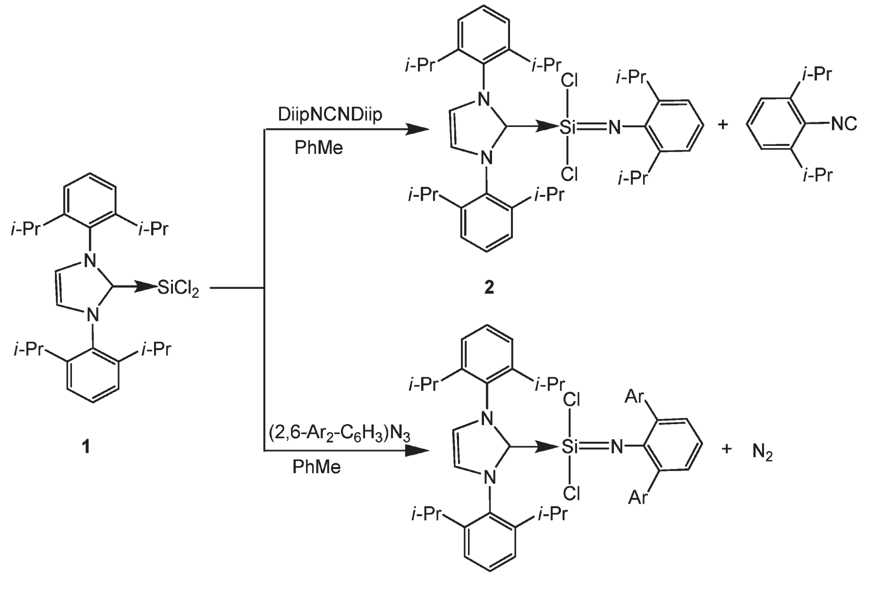
[7] Hesse, M.; Klingebiel, U. *Angew. Chem., Int. Ed.* **1986**, *25*, 649–650. *Angew. Chem.* **1986**, *98*, 638−639.

[8] (a) Schmeisser, M.; Voss, P. *Z. Anorg. Allg. Chem.* **1964**, *334*, 50–56. (b) Schenk, V. P. W.; Bloching, H. *Z. Anorg. Allg. Chem.* **1964**, *334*, 57–65. (c) Timms, P. L. *Inorg. Chem.* **1968**, *7*, 387–389. (d) Schwarz, V. R.; Meckbach, H. *Z. Anorg. Allg. Chem.* **1937**, *232*, 241–248. (e) Schwarz, V. R.; Köster, A. *Z. Anorg. Allg. Chem.* **1952**, *270*, 2–15. (f) Hengge, V. E.; Kovar, D. *Z. Anorg. Allg. Chem.* **1979**, *458*, 163–167. (g) Koe, J. R.; Powell, D. R.; Buffy, J. J.; Hayase, S.; West, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1441–1442. *Angew. Chem.* **1998**, *110*, 1514−1515.

[9] (a) Schlegel, H. B.; Skancke, P. N. *J. Am. Chem. Soc.* **1993**, *115*, 10916–10924. (b) Morgon, N. H.; Argenton, A. B.; da Silva, M. L. P.; Riveros, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 1708–1716. (c) Becerra, R.; Cannady, J. P.; Walsh, R. *J. Phys. Chem. A* **1999**, *103*, 4457–4464. (d) Ikeda, H.; Inagaki, S. *J. Phys. Chem. A* **2001**, *105*, 10711–10718. (e) Tian, C.; Yu, H.; Lu, X. *J. Mol. Struct.* (*THEOCHEM*) **2008**, *861*, 39–45. (f) Lu, X. H.; Yu, H. B.; Che, X.; Xiang, P. P. *Int. J. Quantum Chem.* **2008**, *108*, 1114–1122.

[10] (a) Benkeser, R. A. *Acc. Chem. Res.* **1971**, *4*, 94–100. (b) Kang, S. H.; Han, J. S.; Lee, M. E.; Yoo, B. R.; Jung, I. N. *Organometallics* **2003**, *22*, 2551–2553.

**Scheme 1**



**3**: Ar = Diip = 2,6-*i*-Pr$_2$-C$_6$H$_3$,
**4**: Ar = Triip = 2,4,6-*i*-Pr$_3$-C$_6$H$_2$

*in situ* and trapped by reagents to form Si(IV) compounds. Very recently, we generated and stabilized SiCl$_2$ by N-heterocyclic carbene (NHC) and isolated IPr·SiCl$_2$ (**1**) at room temperature.[11] Reaction of **1** with 1-azidoadamantane yielded a functionalized NHC[12] via the formation of unstable dichlorosilaimine as an intermediate. Silaimines contain polarized Si=N bonds, and the presence of an alkyl or aryl group on the nitrogen atom plays a very important role in their stabilization. In view of the above results, we expected the reaction of **1** with aryl azides to lead to NHC-stabilized dichlorosilaimines. Furthermore, no reaction of stable silylene with a carbodiimide has appeared so far. Herein, we report on the synthesis and characterization of dichlorosilaimines IPr·Cl$_2$Si=N(Diip) (**2**), IPr·Cl$_2$Si=N(2,6-Diip$_2$-C$_6$H$_3$) (**3**), and IPr·Cl$_2$Si=N(2,6-Triip$_2$-C$_6$H$_3$) (**4**) (IPr = :C[N(2,6-*i*-Pr$_2$-C$_6$H$_3$)CH]$_2$, Diip = 2,6-*i*-Pr$_2$-C$_6$H$_3$, Triip = 2,4,6-*i*-Pr$_3$-C$_6$H$_2$) by reacting **1** with bis(2,6-diisopropylphenyl)carbodiimide or terphenyl azides. Silaimines **2**−**4** should serve as suitable precursors for the preparation of differently substituted silaimines and silanitriles or silaisonitriles, which are currently under investigation.

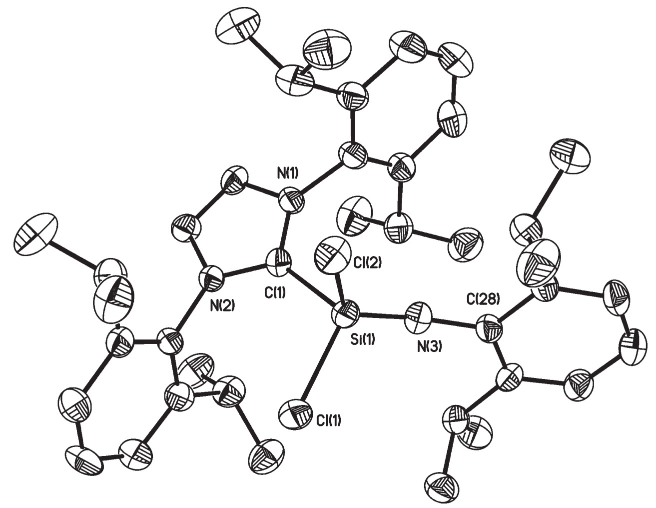


**Figure 1.** Molecular structure of **2**. Anisotropic displacement parameters are depicted at the 50% probability level. The toluene solvent molecule and H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−Cl(1) 2.0717(18), Si(1)−Cl(2) 2.095(2), Si(1)−C(1) 1.917(5), Si(1)−N(3) 1.563(4), N(3)−C(28) 1.366(6); Cl(1)−Si(1)−Cl(2) 100.10(8), Cl(1)−Si(1)−C(1) 106.36(16), Cl(2)−Si(1)−C(1) 99.77(16), Cl(1)−Si(1)−N(3) 116.51(18), Cl(2)−Si(1)−N(3) 122.69(17), C(1)−Si(1)−N(3) 109.2(2).

## Results and Discussion

Reaction of IPr·SiCl$_2$ (**1**) with bis(2,6-diisopropylphenyl)carbodiimide (Scheme 1) affords NHC-stabilized dichlorosilaimine IPr·Cl$_2$Si=N(Diip) (**2**). **1** reacts with an equimolar amount of 2,6-Diip$_2$-C$_6$H$_3$N$_3$ or 2,6-Triip$_2$-C$_6$H$_3$N$_3$ with clean formation of dichlorosilaimines IPr·Cl$_2$Si=N(2,6-Diip$_2$-C$_6$H$_3$) (**3**) and IPr·Cl$_2$Si=N(2,6-Triip$_2$-C$_6$H$_3$) (**4**), respectively.

Dichlorosilaimines **2**−**4** are yellow crystalline compounds that are stable under an inert atmosphere and soluble in common organic solvents. **2**−**4** were characterized by single-crystal X-ray diffraction, elemental analyses, and $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopic studies. $^1$H and $^{13}$C NMR spectra of **2**−**4** show resonances for the IPr ligand coordinated to the silicon atom along with the resonances due to the aryl group attached to the imine nitrogen atom. $^{29}$Si NMR resonances for **2**, **3**, and **4** appear at $\delta$ −107.07, −99.95, and −99.70 ppm, respectively, which are shifted upfield with respect to **1** ($\delta$ 18 ppm)[11] due to higher coordinate silicon atoms and are consistent with Si(IV) compounds.[13]

---

(11) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683–5686. *Angew. Chem.* **2009**, *121*, 5793−5796.

(12) Ghadwal, R. S.; Roesky, H. W.; Granitzka, M.; Stalke, D. *J. Am. Chem. Soc.* **2010**, *132*, 10018–10020.

(13) Ghadwal, R. S.; Sen, S. S.; Roesky, H. W.; Granitzka, M.; Kratzert, D.; Merkel, S.; Stalke, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 3952–3955. *Angew. Chem.* **2010**, *122*, 4044−4047.

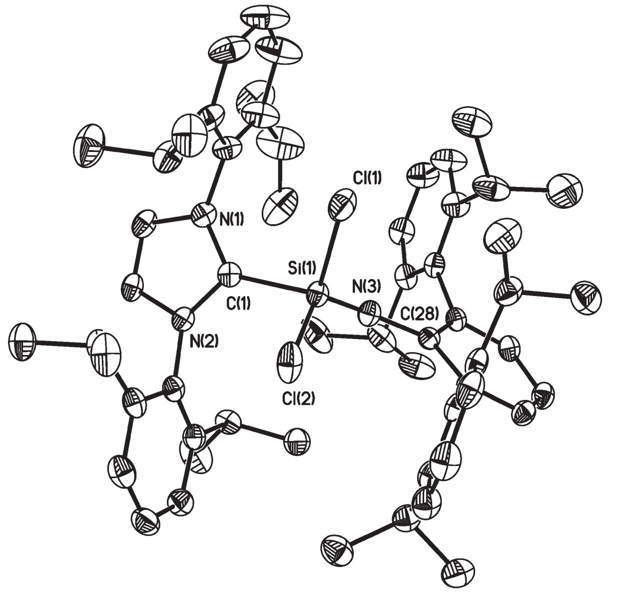


**Figure 2.** Molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50% probability level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−Cl(1) 2.0649(10), Si(1)−Cl(2) 2.0653(10), Si(1)−C(1) 1.953(2), Si(1)−N(3) 1.588(2), N(3)−C(28) 1.376(3); Cl(1)−Si(1)−Cl(2) 102.08(4), Cl(1)−Si(1)−C(1) 103.25(8), Cl(2)−Si(1)−C(1) 99.33(8), Cl(1)−Si(1)−N(3) 114.18(8), Cl(2)−Si(1)−N(3) 122.17(8), C(1)−Si(1)−N(3) 113.26(10).

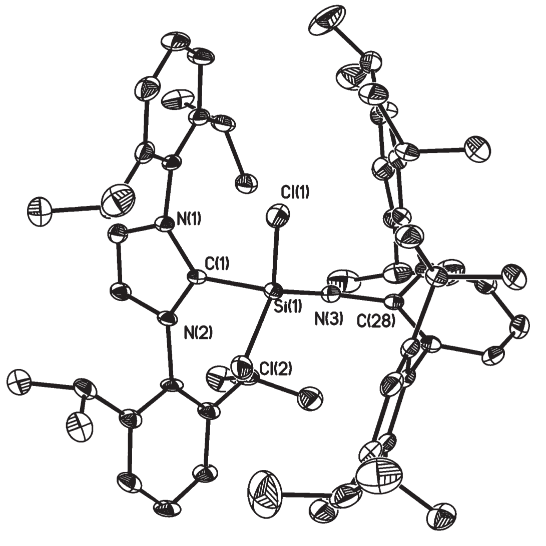


**Figure 3.** Molecular structure of **4**. Anisotropic displacement parameters are depicted at the 50% probability level. The second molecule, toluene solvent molecules, and H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−Cl(1) 2.0612(9), Si(1)−Cl(2) 2.0668(9), Si(1)−C(1) 1.938(2), Si(1)−N(3) 1.594(2), N(3)−C(28) 1.376(3); Cl(1)−Si(1)−Cl(2) 101.59(4), Cl(1)−Si(1)−C(1) 104.67(8), Cl(2)−Si(1)−C(1) 98.12(7), Cl(1)−Si(1)−N(3) 114.46(8), Cl(2)−Si(1)−N(3) 124.76(8), C(1)−Si(1)−N(3) 110.57(10).

**Single-Crystal X-ray Structures.** The molecular structures of compounds **2**, **3**, and **4** were established by single-crystal X-ray crystallography and are shown in Figures 1−3. Silaimines **2**−**4** were obtained as yellow crystals, containing toluene molecules in the lattice. Crystallographic data for **2**−**4** are summarized in Table 1. The molecular structure of **2** is shown in Figure 1. Compound **2** crystallizes in the monoclinic space group $P2_1/c$. The silicon atom in **2** exhibits a distorted tetrahedral geometry. Two coordination sites of the silicon atom are occupied by the two chlorine atoms, the third one is occupied by the C atom of the NHC, and the fourth site is occupied by one N atom of the imine moiety.

Silaimine **3** crystallizes in the monoclinic space group $C2/c$, whereas **4** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. The silicon atom in each of **3** and **4** is four-coordinate, and the sum of the bond angles around silicon exhibits a distorted tetrahedral geometry (Figures 2 and 3). The NHC ligand, the Cl atoms, and imine N atom in **3** and **4** are arranged in a similar fashion to those in **2**. The Si=N bond lengths for **2**−**4** (av 1.565(4) Å) are consistent with those reported[3,6] for silaimine THF adducts. The Si←C bond distances for **2** (1.917(5) Å), **3** (1.953(2) Å), and **4** (1.938(2) Å) are only marginally shorter than that of **1** (1.985(4) Å). The average Si−Cl bond length (2.0708(18) Å) in **2**−**4** is noticeably shorter than that of **1** (2.1664(16) Å) and in agreement with that of four-coordinate[14] silicon in IPr·SiCl$_2$·B(C$_6$F$_5$)$_3$.

## Conclusion

In this article we presented two methods for the preparation of dichlorosilaimines stabilized by a NHC ligand. (i) NHC-stabilized dichlorosilylene **1** reacts with bis(2,6-diisopropylphenyl)carbodiimide in a unexpected way to afford dichlorosilaimine **2**. The reaction of a stable silylene with carbodiimide is reported for the first time. (ii) NHC-stabilized dichlorosilaimines **3** and **4** have been prepared by the reaction of **1** with terphenyl azides. The availability of easily replaceable and reducible chlorine atoms in compounds **2**−**4** on the silicon atom makes them interesting starting materials for preparing a variety of silicon compounds, which are presently under further investigation.

## Experimental Section

**General Procedures.** All reactions and manipulations were performed under an inert atmosphere using standard Schlenk line techniques or a glovebox. The solvents used were purified by MBraun solvent purification system MB SPS-800. The N-heterocyclic carbene, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr),[15] and IPr·SiCl$_2$ (**1**)[11] were prepared by literature methods. Bis(2,6-diisopropylphenyl)phenyl azide and bis(2,4,6-triisopropylphenyl)phenyl azide were prepared according to reported methods.[16] C$_6$D$_6$ was dried over Na metal and distilled under nitrogen prior to use. $^1$H, $^{13}$C, and $^{29}$Si NMR spectra were recorded using Bruker Avance DPX 200 or Bruker Avance DRX 500 spectrometers. Tetramethylsilane (TMS) was used as an internal ($^1$H and $^{13}$C NMR) or an external ($^{29}$Si NMR) reference. Elemental analyses were obtained from the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were measured in sealed capillary tubes under nitrogen.

**Synthesis of IPr·Cl$_2$Si=N(Diip) (2).** To a mixture of **1** (1.03 g, 2.11 mmol) and bis(2,6-diisopropylphenyl)carbodiimide (0.77 g,

---

(14) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Stalke, D. *Chem.—Eur. J.* **2010**, *16*, 85–88.

(15) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49–54.

(16) (a) Twamley, B.; Hwang, C. S.; Hardman, N. J.; Power, P. P. *J. Organomet. Chem.* **2000**, *609*, 152–160. (b) Gavenonis, J.; Tilley, T. D. *Organometallics* **2004**, *23*, 31–43.

**Table 1. Crystallographic Data and Structure Refinement for Compounds 2−4**

| | **2**·$C_6H_5CH_3$ | **3** | **4**·0.75$C_6H_5CH_3$ |
|---|---|---|---|
| formula | $C_{46}H_{61}Cl_2N_3Si$ | $C_{57}H_{73}Cl_2N_3Si$ | $C_{273}H_{364}Cl_8N_{12}Si_4$ |
| CCDC no. | 746183 | 780073 | 780074 |
| fw | 754.97 | 899.17 | 4209.72 |
| cryst size/mm | 0.50 × 0.20 × 0.05 | 0.17 × 0.10 × 0.08 | 0.30 × 0.25 × 0.10 |
| cryst syst | monoclinic | monoclinic | triclinic |
| space group | $P2_1/c$ | $C2/c$ | $P\bar{1}$ |
| $a$/Å | 18.146(4) | 18.674(3) | 13.0796(16) |
| $b$/Å | 13.126(3) | 14.193(2) | 21.796(3) Å |
| $c$/Å | 18.957(4) | 38.194(6) | 22.043(3) |
| α/deg | 90 | 90 | 90.581(2) |
| $\beta$/deg | 104.39(3) | 93.331(2) | 92.462(2) |
| $\gamma$/deg | 90 | 90 | 100.942(2) |
| $V$/Å$^3$ | 4373.3(15) | 10105(3) | 6163.0(13) |
| $D_{calcd}$/g cm$^{-3}$ | 1.147 | 1.182 | 1.134 |
| $Z$ | 4 | 8 | 4 |
| abs coeff/mm$^{-1}$ | 0.210 | 0.192 | 0.167 |
| $\theta$ range/deg | 1.16 to 26.00 | 2.45 to 24.71 | 1.31 to 24.71°. |
| reflns collected/ indep reflns | 26 102/8478<br>[$R$(int) = 0.1307] | 92 428/8602<br>[$R$(int) = 0.0922] | 75 367/21023<br>[$R$(int) = 0.0617] |
| max. and min. transmn | 0.9868 and 0.9238 | 0.7452 and 0.6190 | 0.9874 and 0.7649 |
| final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0893, $wR_2$ = 0.1727 | $R_1$ = 0.0475, $wR_2$ = 0.1026 | $R_1$ = 0.0480, $wR_2$ = 0.1124 |
| $R$ indices (all data) | $R_1$ = 0.1721, $wR_2$ = 0.2054 | $R_1$ = 0.0758, $wR_2$ = 0.1163 | $R_1$ = 0.0817, $wR_2$ = 0.1285 |
| largest diff peak and hole/e Å$^3$ | 0.608 and −0.458 | 0.933 and −0.464 | 0.711 and −0.367 |

2.12 mmol) was added precooled toluene (60 mL) at −78 °C. The yellow reaction mixture was brought to room temperature and turned red after 2 h. After overnight stirring, all volatiles were removed under vacuum to obtain a pale yellow solid. The byproduct 2,6-diisopropylphenyl isonitrile was extracted with *n*-hexane (2 × 30 mL) and characterized by NMR spectroscopy. The residue was dissolved in 20 mL of toluene and stored at −35 °C for 2 days. Yellow crystals of **2** were obtained (0.89 g, 63%). Mp: 170 (dec) °C. Anal. Calcd (%) for $C_{39}H_{53}Cl_2N_3Si$ (M = 662.85): C, 70.67; H, 8.06; N, 6.34. Found (%): C, 70.56; H, 8.10; N, 6.25. $^1$H NMR (200.13 MHz, $C_6D_6$, 298 K): $\delta$ 0.92 (d, $J$ = 6.87 Hz, 12H, CH*Me*$_2$), 1.31 (dd, $J$ = 6.99 Hz, 24H, CH*Me*$_2$), 2.79 (m, 4H, C*H*Me$_2$), 3.21 (m, 2H, C*H*Me$_2$), 6.23 (s, 2H, NC*H*), 7.00−7.27 (m, 9H, $C_6H_3$) ppm. $^{13}$C{$^1$H} NMR (125.76 MHz, $C_6D_6$, 298 K): $\delta$ 22.73, 23.35, (CH(*C*H$_3$)$_2$), 25.35, 25.64 (CH(*C*H$_3$)$_2$), 28.74, 29.50 (*C*H(CH$_3$)$_2$), 123.42 (N*C*H), 124.36, 125.40 (*m*-*C*$_6$H$_3$), 131.60, (*p*-*C*$_6$H$_3$), 134.26 (*o*-*C*$_6$H$_3$), 145.45, 146.25 (*ipso*-*C*$_6$H$_3$) ppm. $^{29}$Si NMR (99.36 MHz, $C_6D_6$, 298 K): $\delta$ −107.07 ppm.

**Synthesis of IPr·Cl$_2$Si=N(2,6-Diip$_2$-C$_6$H$_3$) (3).** To a 100 mL Schlenk flask containing **1** (0.56 g, 1.15 mmol) and bis(2,6-diisopropylphenyl)phenyl azide (0.51 g, 1.16 mmol) was added toluene (50 mL), and the resulting yellow solution was stirred for 5 h and then concentrated to 10 mL. Storing the solution at 4 °C for 2 days afforded yellow crystals of **3** (0.71 g, 69%). Mp: 235 (dec) °C. Anal. Calcd (%) for $C_{57}H_{73}Cl_2N_3Si$ (M = 899.23): C, 76.14; H, 8.18; N, 4.67. Found (%): C, 76.09; H, 8.24; N, 4.15. $^1$H NMR (200.13 MHz, $C_6D_6$, 298 K): $\delta$ 0.72 (d, $J$ = 6.60 Hz, 12H, CH*Me*$_2$), 1.10 (d, $J$ = 6.20 Hz, 12H, CH*Me*$_2$), 1.21 (dd, $J$ = 6.22 Hz, 24H, CH*Me*$_2$), 2.42 (m, 2H, C*H*Me$_2$), 2.85 (m, 2H, C*H*Me$_2$), 3.34 (m, 4H, C*H*Me$_2$), 6.02 (s, 2H, NC*H*), 6.69 (t, $J$ = 6.80 Hz, 1H, *p*-C$_6$*H*$_3$) 6.92−7.27 (m, 14H, C$_6$*H*$_3$) ppm. $^{13}$C{$^1$H} NMR (125.76 MHz, $C_6D_6$, 298 K): $\delta$ 22.98, 23.14, 23.37 (CH(*C*H$_3$)$_2$), 24.15, 24.25, 25.59, 25.82 (CH(*C*H$_3$)$_2$), 29.83, 30.24, 30.38, 30.56, 30.72 (*C*H(CH$_3$)$_2$), 122.66 (N*C*H), 124.22, 125.42 (*m*-*C*$_6$H$_3$), 130.20, 130.63, 132.80, 132.89 (*p*-*C*$_6$H$_3$), 134.48 (*o*-*C*$_6$H$_3$), 144.50, 145.04, 147.01, 147.66 (*ipso*-*C*$_6$H$_3$) ppm. $^{29}$Si NMR (99.36 MHz, $C_6D_6$, 298 K): $\delta$ −99.95 ppm.

**Synthesis of IPr·Cl$_2$Si=N(2,6-Triip$_2$-C$_6$H$_3$) (4).** Compound **4** was synthesized, adopting a similar method for the preparation to that of **3**, by reaction of **1** (0.79 g, 1.62 mmol) and bis(2,4,6-triisopropylphenyl)phenyl azide (0.85 g, 1.62 mmol) to yield yellow crystals of **4** (1.17 g, 73%). Mp: 235−236 (dec) °C. Anal. Calcd (%) for $C_{63}H_{85}Cl_2N_3Si$ (M = 983.36): C, 76.95; H, 8.71; N, 4.27. Found (%): C, 76.75; H, 8.78; N, 4.18. $^1$H NMR (200.13 MHz, $C_6D_6$, 298 K): $\delta$ 0.76 (d, $J$ = 6.80 Hz, 12H, CH*Me*$_2$), 1.12 (d, $J$ = 6.60 Hz, 12H, CH*Me*$_2$), 1.26 (d, $J$ = 6.80 Hz, 24H, CH*Me*$_2$), 1.38 (d, $J$ = 6.80 Hz, 12H, CH*Me*$_2$), 2.46 (m, $J$ = 6.80 Hz, 4H, C*H*Me$_2$), 2.92 (m, 2H, C*H*Me$_2$), 3.37 (m, $J$ = 6.80 Hz, 4H, C*H*Me$_2$), 6.03 (s, 2H, NC*H*), 6.66 (t, $J$ = 7.00 Hz, 1H, *p*-C$_6$*H*$_3$) 6.95−7.10 (m, 12H, C$_6$*H*$_3$) ppm. $^{13}$C{$^1$H} NMR (125.76 MHz, $C_6D_6$, 298 K): $\delta$ 23.48, 24.61, 26.34 (CH(*C*H$_3$)$_2$), 30.17, 30.67, 34.87 (*C*H(CH$_3$)$_2$), 120.90 (N*C*H), 125.63, 125.77 (*m*-*C*$_6$H$_3$), 129.27, 131.10, 133.27, 132.31 (*p*-*C*$_6$H$_3$), 134.92 (*o*-*C*$_6$H$_3$), 142.71, 145.51, 146.24, 147,87 (*ipso*-*C*$_6$H$_3$) ppm. $^{29}$Si NMR (99.36 MHz, $C_6D_6$, 298 K): $\delta$ −99.70 ppm.

**X-ray Structure Determination of Compounds 2−4.** A suitable crystal of **2** was mounted on a glass fiber, and data were collected on an IPDS II Stoe image-plate diffractometer (graphite-monochromated Mo Kα radiation, $\lambda$ = 0.71073 Å) at 133(2) K. The data were integrated with X-area and absorption corrected by X-red32. The data for **3** and **4** were collected from shock-cooled crystals at 100(2) K[17] and were measured on a Bruker TXS-Mo rotating anode with Helios mirror optics and an APEX II detector with a D8 goniometer. The diffractometer was equipped with a low-temperature device[17] and used Mo Kα radiation, $\lambda$ = 0.71073 Å. The data of **3** and **4** were integrated with SAINT[18] and an empirical absorption correction (SADABS) was applied.[19] The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against $F^2$ (SHELXL-97).[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their $U_{iso}$ values constrained to equal 1.5 times the $U_{eq}$ of their pivot atoms for terminal sp$^3$ carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were

---

(17) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619. (b) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178.

(18) *SAINT* v7.68A; Bruker AXS Inc.: Madison, WI, USA, 2009.

(19) Sheldrick, G. M. *SADABS* 2008/2; Göttingen, 2008.

(20) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

refined using bond length restraints and isotropic displacement parameter restraints. Due to the very low diffraction of the crystal of **2** and data collection time of one week, ice formed around the crystal and was frequently removed. But still, this had an impact on the *R*-values (in particular the internal *R*-value), which are comparatively high.

**Acknowledgment.** Financial support from the Deutsche Forschungsgemeinschaft is greatly acknowledged.

**Supporting Information Available:** Crystallographic data for complexes **2**−**4** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.