Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 3461–3464 **3461**
DOI: 10.1021/ic100031d

An Efficient Route for the Synthesis of a Tin(II) Substituted Carbodiimide from a Diazo Compound

Anukul Jana,[†] Herbert W. Roesky,[*,†] Carola Schulzke,[‡] and Prinson P. Samuel[†]

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

Received January 6, 2010

The reaction of β-diketiminate substituted tin(II) chloride, LSnCl (**1**; L = HC{(CMe)(2,6-iPr$_2$C$_6$H$_3$N)}$_2$), with the lithium salt of trimethylsilyl diazomethane (LiC(N$_2$)SiMe$_3$) is described. In the course of the reaction, the exclusive formation of tin(II) substituted carbodiimide LSnNCNSiMe$_3$ (**2**) is observed in good yield. This reaction occurs at room temperature without any side products. Furthermore, we reacted diiron nonacarbonyl, Fe$_2$(CO)$_9$, with compound **2** to confirm the carbodiimide skeleton (N=C=N) without rearrangement. The latter reaction leads to the tin(II) coordinate iron carbonyl complex LSnNCNSiMe$_3$Fe(CO)$_4$ (**3**). Compounds **2** and **3** were investigated by microanalysis and multinuclear NMR spectroscopy and were further characterized by X-ray structural analysis.

Introduction

The chemistry of transition metals with diazoalkanes is well documented,[1] although the corresponding chemistry with main group elements has not been extensively studied.[2] Trialkylsilyl diazomethane derivatives are established for the synthesis of chemical building blocks,[3] and they also possess six known or suspected structural isomers including nitrilimine and carbodiimide. In synthetic organic chemistry compounds containing the carbodiimide functionality are used as dehydration agents, and to activate carboxylic acids toward amide or ester formation. For this purpose especially, dicyclohexylcarbodiimide (DCC) with additives, such as N-hydroxybenzotriazole, is applied for peptide synthesis in biochemistry.[4] In the literature there are reports on the synthesis of carbodiimides from diazo compounds at very high temperatures or in the presence of a metal catalyst.[5] Herein, we report our efforts to explore diazoalkane main group chemistry with β-diketiminate substituted tin(II) chloride, LSnCl.[6] The reaction of lithiated trimethylsilyl diazomethane with LSnCl leads to carbodiimide that reacts further with diiron nonacarbonyl to form the tin(II) coordinate iron carbonyl complex, without rearrangement. Recently, we reported on the unprecedented end-on nitrogen insertion of a diazo compound into a germanium(II) hydrogen bond,[7] and furthermore we showed the C−H bond cleavage of trimethylsilyl diazomethane, when this was reacted with a N-heterocyclic germylene.[8]

Results and Discussion

The reaction of LSnCl (**1**; L = HC{(CMe)(2,6-iPr$_2$C$_6$H$_3$-N)}$_2$), with lithiated trimethylsilyl diazomethane, obtained from nBuLi and Me$_3$SiCHN$_2$ in THF, resulted in the formation of LSnNCNSiMe$_3$ (**2**; Scheme 1). The reaction proceeds at ambient temperature without using any additional catalyst. The formation of the diazo compound LSnC(N$_2$)SiMe$_3$ (**2a**) or nitrilimine compound LSnNNCSiMe$_3$ (**2b**) was not observed on the basis of analytical and structural data. In this context it is worth mentioning that the synthesis of diazo germylene and stannylene compounds was previously reported using ArGeCl (Ar = 2,6-(CH$_2$NR$_2$)$_2$C$_6$H$_3$, R = Et, iPr) and Ar^{1}SnCl (Ar^1 = 2,6-Tip$_2$C$_6$H$_3$, Tip = 2,4,6-iPr$_3$C$_6$H$_2$).[9,10]

---

*To whom correspondence should be addressed. Fax: +49-551-393373. E-mail: hroesky@gwdg.de.

[1] (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29. (b) Schrock, R. R. *Angew. Chem.* **2006**, *118*, 3832–3844. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748−3759. (c) Grubbs, R. H. *Angew. Chem.* **2006**, *118*, 3845–3850. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760−3765.

[2] Barnier, J.-P.; Blanco, L. *J. Organomet. Chem.* **1996**, *514*, 67–71.

[3] Bertrand, G. *Organosilicon Chemistry III: From Molecules to Materials*; Wiley-VCH: New York, 1998; pp 223−236.

[4] (a) Rebek, J.; Feitler, D. *J. Am. Chem. Soc.* **1973**, *95*, 4052–4053. (b) Carpino, L. A. *J. Am. Chem. Soc.* **1993**, *115*, 4397–4398. (c) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149–2154. (d) Veneziani, G.; Shimada, S.; Tanaka, M. *Organometallics* **1998**, *17*, 2926–2929.

[5] Veneziani, G.; Réau, R.; Bertrand, G. *Organometallics* **1993**, *12*, 4289–4290.

[6] Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Power, P. P. *Organometallics* **2001**, *20*, 1190–1194.

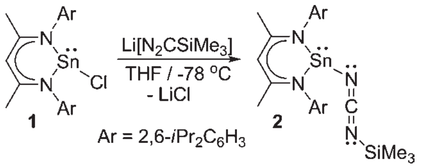
[7] Jana, A.; Sen, S. S.; Roesky, H. W.; Schulzke, C.; Dutta, S.; Pati, S. K. *Angew. Chem.* **2009**, *121*, 4310–4312. *Angew. Chem., Int. Ed.* **2009**, *48*, 4246−4248.

[8] Jana, A.; Objartel, I.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2009**, *48*, 7645–7649.

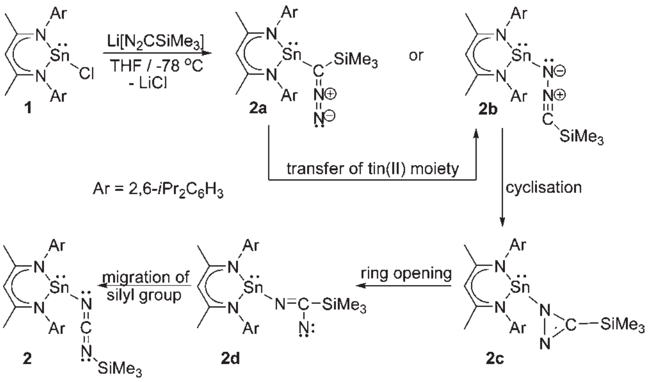
[9] Bibal, C.; Mazières, S.; Gornitzka, H.; Couret, C. *Angew. Chem.* **2001**, *113*, 978–980. *Angew. Chem., Int. Ed.* **2001**, *40*, 952−954.

[10] (a) Setaka, W.; Hirai, K.; Tomioka, H.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **2004**, *126*, 2696–2697. (b) Setaka, W.; Hirai, K.; Tomioka, H.; Sakamoto, K.; Kira, M. *Chem. Commun.* **2008**, 6558–6560.

Scheme 1. Preparation of **2**



Scheme 2. Proposed Pathway for the Formation of **2**



Furthermore, N-bound silyl products, $[(MeC_5H_4)TiCl(\mu\text{-}NSiMe_3)]_2$,[11] and $[(C_5Me_5)_2Ln\{\mu\text{-}N(SiMe_3)NC\}]_2$ (Ln = Sm, La)[12] have been previously observed in the reaction of $Li[Me_3SiCN_2]$ with $(MeC_5H_4)TiCl_3$ and $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ (Ln = Sm, La), respectively, with migration of the silyl group. However, compound **2** represents the first structurally characterized carbodiimide of heavier group 14 elements containing the Sn(II) motif.

It is well-known that the reaction of lithium salts of substituted diazomethane with different electrophiles generates diazo or nitrilimine compounds.[13] Therefore, the present observation of a carbodiimide formation requires an unprecedented rearrangement. Wentrup and co-workers reported the evidence for nitrilimine to carbodiimide rearrangement through an isodiazirine and imidoylnitrene intermediate, based on the nature of the products obtained in the pyrolysis of different nitrilimine precursors at 500 to 960 °C.[14] Subsequently, Bertrand and co-workers mentioned the direct evidence for the nitrilimine to imidoylnitrene rearrangement by the isolation of a unusual nitrene complex.[15] Considering all the facts, we propose the following pathway for the formation of **2** (Scheme 2).

Compound **2** was characterized by multinuclear NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis (Figure 1). The ^1H NMR spectrum of **2** exhibits a singlet (δ 4.96 ppm) corresponding to the *C*H proton of the backbone of the C_3N_2Sn ring. Compound **2** has one $SiMe_3$ group and displays a singlet in the ^{29}Si NMR spectrum (δ −6.0 ppm) and shows only one type of ^{13}C satellite line due to the methyl groups with a coupling constant of 58.3 Hz. This is an indication that the $SiMe_3$ group binds to the N atom and not anymore to carbon. Moreover, the ^{29}Si NMR spectrum shows the resonances which are attributed to the ^{15}N satellite with a coupling constant of 16.8 Hz from the nitrogen atom of the carbodiimide backbone. The ratio of the two satellite lines matches well with their abundances. The ^{119}Sn NMR resonance of **2** arises at δ −321.4 ppm as a triplet ($J(^{119}Sn{-}^{14}N)$ = 250 Hz), which is upfield shifted when compared with that of the starting material LSnCl (**1**; δ −224 ppm). In the ^{14}N NMR spectrum, the signal at δ −329 ppm corresponds to the N atom bound to the silyl group, which was proven by the $^{15}N{-}^1H$ correlation experiment. The resonance of the N*C*N carbon is found in the ^{13}C NMR spectrum at δ 129.7 ppm (δ 131.0 ppm; $iPr_3SiNCNSnMe_3$).[5] In the EI mass spectrum, the molecular ion is observed at *m*/*z* 649 as the base peak for **2**.

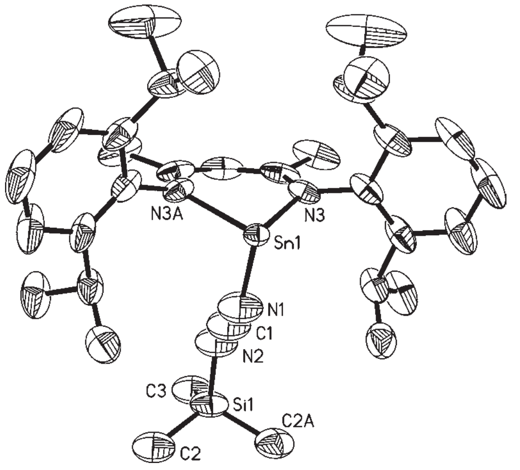


Figure 1. Molecular structure of **2**. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [deg]: Sn1−N1 2.121(7), N1−C1 1.124(10), C1−N2 1.239(11), N2−Si1 1.718(7), Sn1−N3 2.169(3); Sn1−N1−C1 152.5(8), N1−C1−N2 178.6(10), C1−N2−Si1 136.2(7), N1−Sn1−N3 90.35(18), N3−Sn1−N3A 86.5(2).

Compound **2** crystallizes from a saturated *n*-hexane solution at −30 °C after two days in the monoclinic space group *C*2/*m*, with one monomer in the asymmetric unit. The coordination around the tin atom features a distorted tetrahedral geometry with one lone pair (Figure 1). Crystallographic studies on **2** also indicate that the N-bound silyl group structure $LSn{-}N{=}C{=}N{-}SiMe_3$ was formed. All the bond lengths and bond angles are as expected. It is worth mentioning that in the solid state of **2** weak Sn−Sn interactions (3.708 Å) are observed which are below the sum of van der Waals radii of 4.40 Å for two tin atoms (Figure 2).[16]

From the multinuclear NMR and X-ray data, we formulated compound **2** as a carbodiimide derivative. To verify this skeleton, we reacted **2** with $Fe_2(CO)_9$ to show whether the lone pair on tin is still prone to complexation with $Fe(CO)_4$ (Scheme 3). In the course of the reaction, the tin(II) coordinate iron carbonyl complex $LSnNCNSiMe_3Fe(CO)_4$ (**3**) is formed with the same carbodiimde functionality.

Compound **3** was characterized by multinuclear NMR, EI mass spectrometry, and X-ray structural analysis. In the ^{29}Si NMR spectrum, **3** exhibits a singlet at δ −3.2 ppm with a ^{13}C

---

(11) Bai, G.; Roesky, H. W.; Hao, H.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2001**, *40*, 2424–2426.

(12) Evans, W. J.; Montalvo, E.; Champagne, T. M.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 16–17.

(13) Réau, R.; Veneziani, G.; Bertrand, G. *J. Am. Chem. Soc.* **1992**, *114*, 6059–6063.

(14) Fischer, S.; Wentrup, C. *J. Chem. Soc., Chem. Comm.* **1980**, 502–503.

(15) Granier, M.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. *Angew. Chem.* **1990**, *102*, 671–672. *Angew. Chem., Int. Ed.* **1990**, *29*, 659−661.

(16) Allan, R. E.; Beswick, M. A.; Edwards, A. J.; Paver, M. A.; Rennie, M.-A.; Raithby, P. R.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1995**, 1991–1994.

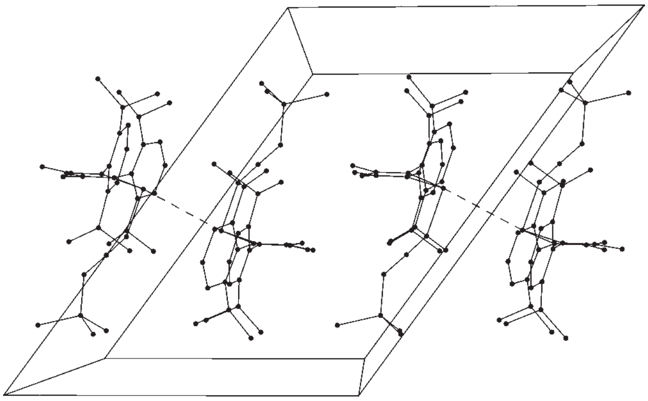
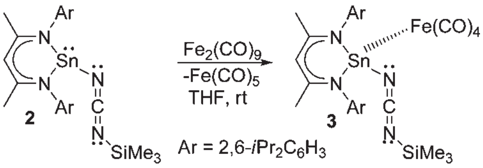


Figure 2. Unit cell of **2**, showing the weak Sn−Sn interactions (3.708 Å).

Scheme 3. Preparation of **3**



satellite ($^2J(^{29}Si-^{13}C)$ = 59.0 Hz). In the ^{119}Sn NMR spectrum, **3** displays a resonance at δ 11.45 ppm, which is downfield shifted when compared with that of **2** (δ −321.4 ppm). Moreover, in the ^{13}C NMR spectrum, the resonance arises at δ 212.9 ppm for the CO group, a value comparable to those of LGe(OH)Fe(CO)$_4$ (δ 214.8 ppm)[17] and LSn(OH)Fe(CO)$_4$ (δ 213.1),[18] and also matches with the other reported Sn(II)−Fe carbonyl complexes.[19]

Compound **3** crystallizes in the orthorhombic space group *Pnma* with one molecule in the asymmetric unit from a saturated toluene solution (Figure 3). The coordination polyhedron around the tin atom features a distorted tetrahedral geometry.

Summary and Conclusion

In this manuscript, we describe the facile synthesis of a carbodiimide with a tin(II) moiety. This reaction proceeds probably via a unique diazo-nitrilimine-isodiazirine-imidoylnitrene-carbodiimde rearrangement at ambient temperature. The high yield synthesis of a stable Sn(II) carbodiimide creates a potential precursor to generate a variety of compounds containing low valent group 14 elements.

Experimental Section

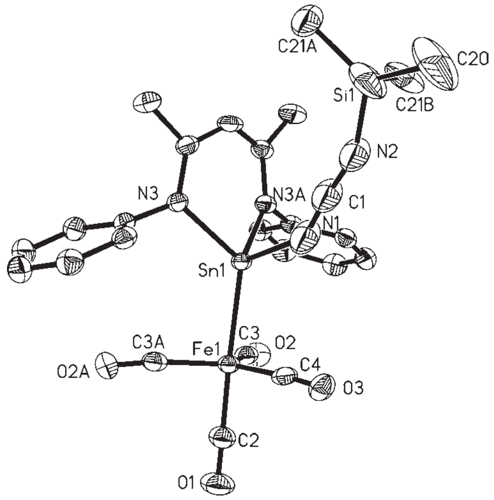


Figure 3. Molecular structure of **3**. Thermal ellipsoids are shown at 50% probability. H atoms and isopropyl groups are omitted for clarity reasons. Selected bond lengths [Å] and angles [deg]: Sn1−N1 2.081(6), N1−C1 1.136(9), C1−N2 1.198(9), N2−Si1 1.649(7), Sn1−N3 2.122(3), Sn1−Fe1 2.4777(9); Sn1−N1−C1 141.2(7), N1−C1−N2 172.9(10), N1−Sn1−N3 95.87(15), N3−Sn1−N3A 88.93(16).

General Considerations. All manipulations were performed under a dry and oxygen free atmosphere (N_2) using standard Schlenk techniques or inside an MBraun MB 150-GI glovebox maintained at or below 1 ppm of O_2 and H_2O. Solvents were purified with the MBraun solvent drying system. The starting material **1** was prepared using literature procedures.[6] Other chemicals were purchased and used as received. ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were recorded on a Bruker Avance DRX 500 MHz instrument and referenced to the deuterated solvent in the case of the ^1H and ^{13}C NMR spectra and $SiMe_4$ and $SnMe_4$ for the ^{29}Si and ^{119}Sn NMR spectra, respectively. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Infrared spectral data were recorded on a Perkin-Elmer PE-1430 instrument. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

Synthesis of LSnNCNSiMe$_3$ (L = HC{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$) (2). A solution of lithium trimethylsilyldiazomethane (4.0 mmol) prepared from a solution of trimethylsilyldiazomethane (2.0 mL, 2 M in *n*-hexane) and *n*BuLi (2.5 mL, 1.6 M in *n*-hexane) in THF (15 mL) was added drop by drop to the solution of **1** (2.20 g, 4.0 mmol) in THF (35 mL) at −78 °C. The resulting solution was allowed to warm slowly to room temperature and was stirred for another 30 min. Solvents were removed in a vacuum, and the residue was dissolved in *n*-hexane (80 mL). The solution was filtered, the solvent was partially removed, and **2** was obtained as a yellow crystalline solid after being stored for two days at −30 °C in a freezer. The crystals were suitable for X-ray structural analysis. Yield (1.76 g, 68%). Mp 177 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.02−7.15 (m, 6H, Ar-*H*), 4.96 (s, 1H, C*H*), 3.82 (sept, 2H, C*H*(CH$_3$)$_2$), 3.14 (sept, 2H, C*H*(CH$_3$)$_2$), 1.61 (s, 6H, C*H*$_3$), 1.51 (d, 6H, CH(C*H*$_3$)$_2$), 1.32 (d, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, 6H, CH(C*H*$_3$)$_2$), 0.27 (s, 9H, Si(C*H*$_3$)$_3$) ppm. ^{13}C NMR (75.46 MHz, C_6D_6, 25 °C): δ 165.4 (*C*N), 145.7, 142.8, 141.8, 125.3, 125.1, 124.0 (Ar*C*), 129.7 (N*C*N), 99.9 (*C*H), 29.2 (*C*H(CH$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 27.1 (*C*H$_3$), 24.7 (CH(*C*H$_3$)$_2$), 24.4 (CH-(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 2.0 (Si(*C*H$_3$)$_3$) ppm. $^{14}N\{^1H\}$ NMR (50.68 Hz, C_6D_6): δ −184 (*N*Sn), −291 (*N*C), −329 (*N*Si) ppm. $^{29}Si\{^1H\}$ NMR (125.77 Hz, C_6D_6): δ −6.0 (*Si*(CH$_3$)$_3$) ppm. $^{119}Sn\{^1H\}$ NMR (186.46 MHz, C_6D_6): δ −321.4 ppm. EI-MS (70 eV): *m*/*z* (%): 649 (100) [M]$^+$. Anal. Calcd for $C_{33}H_{50}N_4SiSn$ (649.55): C, 61.02; H, 7.76; N, 8.63. Found: C, 61.42; H, 8.04; N, 8.42.

Synthesis of LSnNCNSiMe$_3$Fe(CO)$_4$ (L = HC{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$) (3). A flask was charged with **2** (0.650 g, 1.00 mmol) and Fe$_2$(CO)$_9$ (0.370 g, 1.00 mmol) in THF (140 mL). The solution

---

(17) Pineda, L. W.; Jancik, V.; Colunga-Valladares, J. F.; Roesky, H. W.; Hofmeister, A.; Magull, J. *Organometallics* **2006**, *25*, 2381–2383.

(18) Jana, A.; Sarish, S. P.; Roesky, H. W.; Schulzke, C.; Samuel, P. P. *Chem. Commun.* **2010**, *46*, 707–709.

(19) (a) Mehring, M.; Löw, C.; Schürmann, M.; Uhlig, F.; Jurkschat, K. *Organometallics* **2000**, *19*, 4613–4623. (b) Schneider, J. J.; Czap, N.; Bläser, D.; Boese, R.; Ensling, J.; Gütlich, P.; Janiak, C. *Chem.—Eur. J.* **2000**, *6*, 468–474. (c) Cardin, C. J.; Cardin, D. J.; Convery, M. A.; Dovereux, M. M.; Twamley, B.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1996**, 1145–1151.

Table 1. Crystallographic Data for the Structural Analyses of Compounds **2** and **3**

	2	**3**
empirical formula	$C_{33}H_{50}N_4SiSn$	$C_{37}H_{50}FeN_4O_4SiSn$
CCDC no.	745456	749249
T [K]	133(2) K	133(2) K
cryst syst	monoclinic	orthorhombic
space group	$C2/m$	$Pnma$
a [Å]	17.018(3) Å	23.764(5)
b [Å]	19.998(4)	16.231(3)
c [Å]	12.539(3) Å	10.373(2)
α [deg]	90	90
β [deg]	126.27(3)	90
γ [deg]	90	90
V [Å^3]	3440.5(12)	4001.3(14)
Z	4	4
D_{calcd} [g cm^{-3}]	1.254	1.357
μ [mm^{-1}]	0.803	1.057
F(000)	1360	1688
θ range [°]	1.94 to 25.86	1.71 to 25.82
data/restraints/params	3415/0/168	3837/3/237
reflns collected/unique	13525/3415 (R_{int} = 0.0419)	14172/3837 (R_{int} = 0.0288)
R1, wR2 [$I > 2\sigma(I)$]^a	0.0468, 0.1206	0.0472, 0.1220
R1, wR2 (all data)^a	0.0506, 0.1228	0.0554, 0.1269
GoF	1.026	1.021
$\Delta\rho$(max), $\Delta\rho$(min) [e Å^{-3}]	2.553, −1.638	2.739, −2.985

^{a}R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

was stirred for 24 h at ambient temperature. The byproduct was removed by filtration of the solution over Celite, resulting in a clear pale brown filtrate. From the resulting solution, the volatiles were removed, giving a pale brown solid. Crystallization of the crude product was attained from a saturated toluene solution of **3** and storing it at −30 °C in a freezer. Compound **3** deposited as light brown crystals. Yield: 0.60 g (73%). Mp 197 °C. ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C): δ 7.04−7.15 (m, 6H, ArH), 5.00 (s, 1H; CH), 3.71 (sept, 2H, CH(CH$_3$)$_2$), 3.06 (sept, 2H, CH(CH$_3$)$_2$), 1.56 (d, 6H, CH (CH_3)$_2$), 1.52 (s, 6H; CH_3), 1.32 (d, 6H, CH(CH_3)$_2$), 1.26 (d, 6H, CH(CH_3)$_2$), 1.02 (d, 6H, CH(CH_3)$_2$), 0.23 (s, 9H, Si(CH_3)$_3$) ppm. ^{13}C NMR (125.75 MHz, C_6D_6, 25 °C): δ 212.9 (CO), 169.9 (CN), 145.3, 143.2, 139.9, 128.8, 125.4, 124.8 (ArC), 129.1 (NCN), 101.6 (CH), 29.4 (CH(CH$_3$)$_2$), 28.6 (CH(CH$_3$)$_2$), 25.7 (CH$_3$), 24.5 (CH(CH$_3$)$_2$), 24.5 (CH(CH$_3$)$_2$), 24.3 (CH(CH$_3$)$_2$), 24.0 (CH(CH$_3$)$_2$), 1.5 (Si(CH$_3$)$_3$) ppm. ^{29}Si{^{1}H} NMR (125.77 Hz, C_6D_6): δ −3.2 (Si(CH$_3$)$_3$) ppm. ^{119}Sn NMR (111.92 MHz, C_6D_6, 25 °C): δ 11.4 ppm. EI-MS (70 eV; m/z (%)): 734 (15) [M − 3CO]$^+$, 706 (100) [M − 4CO]$^+$.

Crystallographic Details for Compounds 2 and 3. Suitable crystals of **2** and **3** were mounted on a glass fiber, and data were collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 133(2) K (Table 1). The data were integrated with X-Area. The structures were solved by direct methods (SHELXS-97)[20] 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.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: X-ray data for **2** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

---

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