Bis(amidinate) Complexes of Silicon and Germanium

Hans H. Karsch*, Peter A. Schlüter, and Manfred Reisky

Technische Universität München, Institut für Anorganische Chemie,
Lichtenbergstr. 4, D-85747 Garching, Germany
Fax: (internat.) +49 (0)89/ 28914421
E-mail: Hans.H.Karsch@lrz.tu-muenchen.de

Received January 17, 1998

Keywords: Silicon amidinates / Germanium amidinates / Bidentate coordination

The synthesis of novel bis(amidinate) silicon and germanium complexes is described. The reaction of two equiv. of $[MeC(N\textit{i}Pr)_2]Li\cdot THF$ (**1**) with $SiCl_4$, $GeCl_4$ or $GeCl_2$·dioxane affords $[MeC(N\textit{i}Pr)_2]_2SiCl_2$ (**2**), $[MeC(N\textit{i}Pr)_2]_2GeCl_2$ (**3**) and $[MeC(N\textit{i}Pr)_2]_2Ge$ (**4**), respectively. The complexes **2** and **4** have been structurally characterized. The crystallographic results confirm a bidentate coordination of the amidinate ligands at the Si/Ge center, as indicated by spectroscopic studies.

Introduction

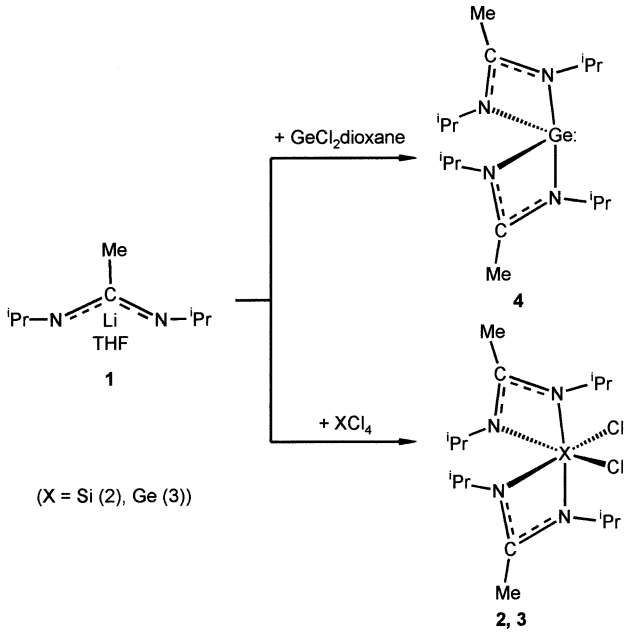
The coordination chemistry of amidinates is well established, not only for the transition metals[1][2] and the lanthanoides[3], but also for main group elements[4][5][6][7][8]. The main importance lies in the generation of element−nitrogen bonds as needed for CVD methods[9], and for the synthesis of new catalysts. However, the amidinate chemistry of Group 14 elements has hitherto only been investigated for tin and lead[10][11]. Amidinates of silicon and germanium are largely unknown, with only a few exceptions.

Thus, $PhC(NSiMe_3)[N(SiMe_3)_2]$[12] and $[PhC(NSiMe_3)_2]M\cdot(THF/Et_2O)_n$ (M = Li, Na, K, Rb)[11] are well known starting materials in amidinate chemistry. $PhC(NSiMe_3)[N(SiMe_3)_2]$ is the only compound of this type for which a crystal structure determination is available, and this confirms a monodentate amidinate coordination[11]. In contrast, a bidentate coordination was deduced from a $\delta^{29}Si$ value of −101.9 for the only other known amidinate silicon derivative, $PhC(NSiMe_3)_2SiCl_3$[14]. A report on structural investigations of two other silicon amidinate derivatives is currently in press[13]. With the aim of obtaining access to a new generation of molecular silicon−nitrogen compounds, which might easily be converted to polymeric materials of different but easily tunable structural units resembling silicate structures but with pseudochalcogenide bridges {i.e. $[N-C(R)-N(R')]^{2-}$ instead of O^{2-}}, and which further might be converted to Si/C/N/X materials, we have initiated a comprehensive study of silicon and germanium amidinate chemistry. We have found that modification of the organic substituents on the nitrogen as well as on the bridging carbon atom exerts a considerable effect on the coordination to the silicon or germanium center[15]. We report herein on preliminary results concerning the synthesis and characterization of novel bis(amidinate) complexes of Si^{IV}, Ge^{IV}, and Ge^{II}.

Results and Discussion

The anionic amidinate compound $[MeC(N\textit{i}Pr)_2]Li\cdot THF$ (**1**) was obtained by reaction of *i*Pr−N=C=N*i*Pr with MeLi (THF, room temp.) and was isolated as a white, crystalline solid in good yield according to the published procedure[16]. Reactions of 2 equiv. of **1** with 1 equiv. of $SiCl_4$, $GeCl_4$ or $GeCl_2\cdot$dioxane resulted in the formation of the new complexes $[MeC(N\textit{i}Pr)_2]_2SiCl_2$ (**2**), $[MeC(N\textit{i}Pr)_2]_2GeCl_2$ (**3**), and $[MeC(N\textit{i}Pr)_2]_2Ge$ (**4**) (Scheme 1), which were obtained as colorless, crystalline solids.

Scheme 1. Reactions of $SiCl_4$, $GeCl_4$, and $GeCl_2\cdot$dioxane with $[CH_3C(N\textit{i}Pr)_2]Li\cdot THF$ (**1**)



The constitutions of the complexes were established on the basis of their ^1H-, ^{13}C-NMR and mass spectra, as well as by elemental analyses.

The room-temperature ^1H-NMR spectrum of **2** shows four doublets of equal intensity in the aliphatic region due to the methyl protons of the isopropyl groups, and two septets due to the CH protons of the isopropyl groups of the amidinate ligands. The CH_3 group of the bridging unit is

  1434−1948/98/0404−0433 $ 17.50+.50/0

observed as a singlet. Temperature-dependent NMR measurements establish a rigid molecular skeleton in the range −80 °C to +80 °C. In marked contrast, the analogous germanium compound **3** shows fluctional behavior. At room temp., four doublets are again observed for the isopropyl groups, but these broaden on heating and coalesce to one broad singlet at 80 °C.

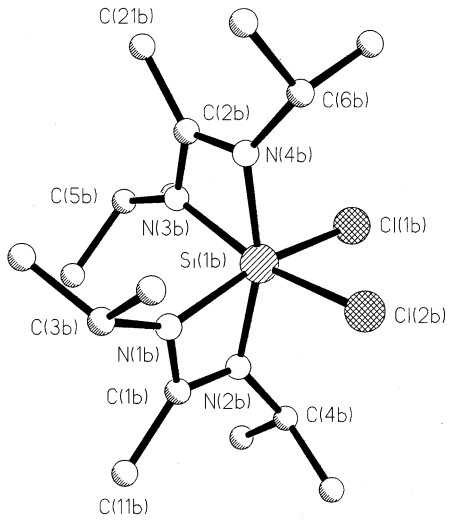
However, the germanium(II) compound **4** exhibits a single set of amidinate resonances over the whole temperature range, indicating equivalence of the two donor nitrogen atoms and symmetrical coordination to the germanium center on the NMR timescale.

The ^{29}Si-NMR resonance of **2** ($\delta = -169.33$) indicates hexacoordination at silicon. All three complexes show remarkable thermal stability. For example, **2** can be heated in toluene at 100 °C for several days without noticeable decomposition. No reaction was observed upon treatment with potassium or sodium metal (THF, room temp.).

Confirmation of the bidentate coordination mode of the amidinate ligands was obtained from X-ray structure determinations of **2** and **4**.

X-ray Analysis of $[CH_3C(NiPr)_2]_2SiCl_2$ (**2**) *and* $[CH_3C(NiPr)_2]_2Ge$ (**4**): The X-ray analysis of the colorless crystals of compound **2** (from toluene) shows two identical molecules in the asymmetric unit (see Table 2). The molecular geometry and atom numbering scheme are shown in Figure 1; selected bond distances [Å] and angles [°] are listed in Table 1.

Figure 1. Molecular structure of **2**

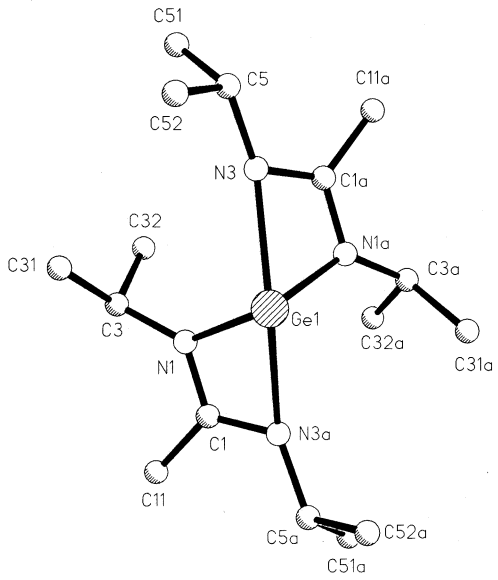


Both amidinate ligands are coordinated in a bidentate fashion, with one nitrogen in an axial and the other in an equatorial position of a distorted octahedron. Two chlorine atoms complete the *cis*-octahedral coordination sphere of the central silicon atom. As expected, the axial Si−N bond lengths [Si(1b)−N(2b): 1.837(2) Å, Si(1b)−N(4b): 1.841(2) Å] are slightly shorter than the equatorial distances [Si(1b)−N(1b): 1.915(2) Å, Si(1b)−N(3b): 1.914(2) Å]. This is accompanied by a slight shortening of the $C-N_{eq}$ bonds [N(1b)−C(1b): 1.312 Å, N(3b)−C(2b): 1.305(4) Å] compared to the $C-N_{ax}$ bonds [N(2b)−C(1b): 1.333(4) Å, N(4b)−C(2b): 1.341(4) Å] within the amidinate ligands, both being approximately intermediate between C−N double-bond and C−N(sp^2) single-bond distances. The four-membered Si−N−C−N rings are essentially planar, as are the arrangements about the nitrogen and carbon atoms. The overall structure of **2** resembles that of the structurally characterized tin compound $[MeC(NCy)_2]_2SnCl_2$[10a].

Table 1. Selected bond lengths [Å] and angles [°] of compounds **2** and **4**

	2		**4**
Cl(1b)−Si(1b)	2.185(1)	Ge(1)−N(1)	1.982(3)
Cl(2b)−Si(1b)	2.197(1)	Ge(1)−N(3)	2.300(2)
Si(1b)−N(4b)	1.841(2)	N(1)−C(1)	1.325(4)
Si(1b)−N(2b)	1.837(2)	N(3)−C(1a)	1.302(3)
Si(1b)−N(1b)	1.915(2)	N(1)−C(3)	1.459(4)
Si(1b)−N(3b)	1.914(2)	N(3)−C(5)	1.462(3)
N(1b)−C(1b)	1.312(4)		
N(2b)−C(1b)	1.333(4)		
N(3b)−C(2b)	1.305(4)		
N(4b)−C(2b)	1.341(4)		
N(2b)−Si(1b)−N(4b)	163.0(1)	N(1a)−Ge(1)−N(1)	100.7(1)
N(4b)−Si(1b)−N(1b)	98.0(1)	N(1)−Ge(1)−N(3)	96.20(9)
N(2b)−Si(1b)−N(1b)	69.0(1)	N(1)−Ge(1)−N(3a)	61.00(9)
N(4b)−Si(1b)−N(3b)	68.8(1)	C(1)−N(1)−C(3)	125.4(2)
N(2b)−Si(1b)−N(3b)	99.6(1)	C(3)−N(1)−Ge(1)	135.3(2)
N(3b)−Si(1b)−N(1b)	91.0(1)	C(1a)−N(3)−Ge(1)	85.5(2)
N(4b)−Si(1b)−Cl(1b)	96.8(8)	N(3a)−C(1)−N(1)	113.0(2)
N(2b)−Si(1b)−Cl(1b)	95.78(8)	N(3)−Ge(1)−N(3a)	145.7(1)
N(1b)−Si(1b)−Cl(1b)	164.75(8)	C(1)−N(1)−Ge(1)	99.2(2)
N(3b)−Si(1b)−Cl(1b)	90.81(8)	C(1a)−N(3)−C(5)	122.2(3)
N(3b)−Si(1b)−Cl(2b)	163.95(8)	C(5)−N(3)−Ge(1)	144.8(2)
N(1b)−C(1b)−N(2b)	107.0(2)		
N(3b)−C(2b)−N(4b)	106.7(2)		

Figure 2. Molecular structure of **4**



The X-ray structure determination of the colorless crystals of **4** (from pentane) reveals the presence of one-half of the molecule in the asymmetric unit (see Table 2). The whole molecule can be generated by symmetric transformations. The molecular geometry and atom numbering

scheme are shown in Figure 2; selected bond distances [Å] and angles [°] are listed in Table 1.

In the monomeric molecule, the germanium atom is surrounded by four nitrogen atoms originating from two amidinate ligands, each spanning an axial and an equatorial site of a heavily distorted Ψ-trigonal bipyramid, with the "lone pair" of germanium(II) occupying the third equatorial position. Although, as in the case of **2**, the four-membered rings are almost planar, only the equatorial nitrogen atoms N(1)/(1a) are planar [sum of angles at N(1)/(1a): 359.9°]. The respective Ge(1)−N(1)/(1a) bonds [1.982(3) Å] are significantly shorter than the axial Ge(1)−N(3)/(3a) bonds [2.300(1) Å], which coincides with a considerable deviation from planarity of the N(3)/(3a) atoms [sum of angles at N(3)/(3a): 352.5°]. The axial N(3)−Ge(1)−N(3a) bond angle [145.7(1)°] is very small compared the ideal tbp value of 180° and highlights the considerable ring strain in **4**. The angle N(1)−Ge(1)−N(1a) is also rather small (100.7°). Instead of a Ψ-tbp structure, the geometry might be classified as a distorted tetragonal pyramid − in fact, an intermediate state is the best compromise for an adequate description. In this regard, the structure resembles those of other Ge^{II} compounds bearing four-membered chelate rings[17]. As a consequence of this structural dilemma, fluctional behavior may be anticipated and is indeed observed (see above). Again, small element to nitrogen distances [Ge−N(1)/(1b): 1.982(3) Å] coincide with slightly longer C−N distances in the ligand [C(1)−N(1)/C(1a)−N(1a): 1.325(4) Å] and vice versa: the long Ge(1)−N(3)/(3a) bond [2.300(2) Å] corresponds to a short C(1)−N(3)/(3a) bond [1.302(3) Å]. The amidinate bite angle [N(1a)−Ge(1)−N(3)] is rather acute (61.0°), which is compensated by a concomitant widening of the N−C−N bond angle (125.4°).

Conclusions

Monoanionic, bidentate four-electron donor amidinates are highly suitable ligands for stabilizing low oxidation states and/or high coordination numbers at group 14 element centers (Si, Ge). The newly synthesized *cis*-dichlorosilicon bis(amidinate) complex **2** may be a potentially useful precursor for novel stable Si^{II} compounds. Work in this area is currently in progress.

We thank the *Deutschen Forschungsgesellschaft* for financial support.

Experimental Section

General: All reactions were carried out under dry nitrogen. The solvents used were distilled under nitrogen from Na/K alloy. MeLi (1.6 M in Et_2O) and *i*PrNCN*i*Pr were used as purchased. $SiCl_4$ and $GeCl_4$ were freshly distilled from K_2CO_3 prior to use. *$GeCl_2 \cdot dioxane$*[18] and *[MeC(NiPr)$_2$]Li·THF* (**1**)[16] were prepared according to literature procedures. Elemental analyses were obtained on a Vario EL CHN Automat Analyzer at the microanalytical laboratory of the TU München. − NMR: Jeol GX 270 and 400 FT-NMR spectrometers. All chemical shifts are reported in parts per million and coupling constants *J* in Hz. Spectra were recorded at 25 °C unless otherwise stated. − MS: Varian MAT 311A, CI.

Preparation of [MeC(NiPr)$_2$]$_2$SiCl$_2$ (**2**): To a suspension of 13.85 mmol (3.05 g) of **1** in 50 ml of Et_20, 6.58 mmol (0.83 ml) of $SiCl_4$ was added at −78 °C. The reaction mixture was allowed to warm to room temp. with stirring. After 18 h, the solvent was replaced by 40 ml of toluene and the resulting suspension was filtered. Evaporation of the solvent from the filtrate afforded 2.4 g (95%) of colorless crystals. − ^{1}H NMR (C_6D_6): δ = 0.96 (d, $^3J_{HH}$ = 8.0, 6 H, CH_3CH), 1.28 (d, $^3J_{HH}$ = 8.0, 6 H, CH_3CH), 1.37 (d, $^3J_{HH}$ = 8.0, 6 H, CH_3CH), 1.41 (s, 6 H, CH_3C), 1.48 (d, $^3J_{HH}$ = 8.0, 6 H, CH_3CH), 3.33 (sept, 2 H, $^3J_{HH}$ = 8.0, CH$_3$C*H*), 4.30 (sept, 2 H, $^3J_{HH}$ = 8.0, CH$_3$C*H*). − ^{13}C NMR (C_6D_6): δ = 12.37 (*C*H$_3$C), 21.76 (*C*H$_3$CH), 23.24 (*C*H$_3$CH), 23.32 (*C*H$_3$CH), 23.59 (*C*H$_3$CH), 45.19 (CH$_3$*C*H), 46.37 (CH$_3$*C*H), 166.77 (N*C*N). − ^{29}Si NMR (C_6D_6): δ = −169.33. − MS (CI, 150 eV): *m/z* (%) = 380 (2) [M$^+$], 345 (100) [M − Cl], 262 (11) [M − Cl − CN*i*Pr], 239 (50) [M − *i*PrNC(Me)N*i*Pr]. − $C_{16}H_{24}Cl_2N_4Si$ (381.46): calcd. C 50.38, H 8.98, N 14.69; found C 48.15, H 8.75, N 12.90.

Preparation of [MeC(NiPr)$_2$]$_2$GeCl$_2$ (**3**): To a suspension of 8.42 mmol (1.85 g) of **1** in 50 ml of THF, 4.00 mmol (0.46 ml) of $GeCl_4$ was added at −78 °C and the reaction mixture was allowed to warm to room temp. After stirring for 18 h at room temp., the solvent was replaced by 40 ml of pentane. The residue was extracted several times. The combined extracts were slowly concentrated in vacuo to afford 1.41 g (83%) of colorless crystals. − ^{1}H NMR (20 °C, [D$_8$]toluene): δ = 1.11 (d, $^3J_{HH}$ = 6.4, 6 H, CH_3CH), 1.46 (d, $^3J_{HH}$ = 6.4, 6 H, CH_3CH), 1.63 (d, $^3J_{HH}$ = 6.4, 6 H, CH_3CH), 1.65 (d, $^3J_{HH}$ = 6.4, 6 H, CH_3CH), 1.55 (s, 6 H, CH_3C), 3.49 (sept, $^3J_{HH}$ = 6.4, 2 H, CH$_3$C*H*), 4.22 (sept, $^3J_{HH}$ = 6.4, 2 H, CH$_3$C*H*). − ^{1}H NMR (80 °C, [D$_8$]toluene): δ = 1.51 (br, 24 H, CH_3CH), 1.62 (s, 6 H, CH_3C), 3.6−4.2 (br, 4 H, CH$_3$C*H*). − ^{13}C NMR (C_6D_6): δ = 11.06 (*C*H$_3$C), 21.68, 23.23, 23.46, 23.73 (*C*H$_3$CH), 46.34 (CH$_3$*C*H), 47.36 (CH$_3$*C*H), 162.46 (N=*C*N). − MS (CI, 150 eV): *m/z* (%) = 391 (58) [M − Cl], 285 (39) [M − MeC(N*i*Pr)$_2$], 141 (100) [MeC(N*i*Pr)$_2$]. − $C_{16}H_{34}Cl_2GeN_4$ (425.99): calcd. C 45.11, H 8.04, N 13.15; found C 45.28, H 8.00, N 12.61.

Preparation of [MeC(NiPr)$_2$]$_2$Ge (**4**): To a mixture of 8.12 mmol (1.79 g) of **1** and 3.45 mmol (0.8 g) of $GeCl_2 \cdot$dioxane, 40 ml of Et_2O was added at −78 °C. The reaction mixture was slowly allowed to warm to room temp. and stirred for a further 18 h. The solvent was then removed and the product was extracted with 50 ml of pentane. The pentane extract was concentrated and **4** was isolated as colorless crystals (1.02 g, 81%). − m.p. 41 °C. − ^{1}H NMR (C_6D_6): δ = 1.31 (d, $^3J_{HH}$ = 6.5, 24 H, CH_3CH), 1.53 (s, 6 H, CH_3C), 3.63 (sept, $^3J_{HH}$ = 6.5, 4 H, CH$_3$C*H*). − ^{13}C NMR (C_6D_6): δ = 11.91 (*C*H$_3$C), 24.89 (*C*H$_3$CH), 47.16 (CH$_3$*C*H), 162.53 (N*C*=N). − MS (CI, 150 eV): *m/z* (%) = 357 (15) [M], 183 (3) [M − 4 *i*Pr], 143 (100) [MeC(N*i*Pr)$_2$]. − $C_{16}H_{34}GeN_4$ (355.08): calcd. C 54.12, H 9.65, N 15.77; found C 51.93, H 9.50, N 14.77.

Crystal Structure Determination: Suitable crystals of **2** and **4** were sealed into glass capillaries. The structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2 (SHELXL-93)[19]. Crystal data and numerical data of the structure determinations are given in Table 2. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in ideal positions. Further information may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-408153 (**2**) and CSD-408152 (**4**).

Table 2. Crystal data of the X-ray structural analyses of compounds **2** and **4**

	$[CH_3C(NiPr)_2]_2SiCl_2$ (**2**)	$[CH_3C(NiPr)_2]_2Ge$ (**4**)
Empirical formula	$C_{16}H_{34}N_4Cl_2Si$	$C_{16}H_{34}GeN_4$
Molecular mass [g/mol]	381.46	355.06
Temperature [K]	199(2)	185(2)
Crystal system	orthorhombic	tetragonal
Space group	*Pbca*	$P4_12_12_1$
a [Å]	15.089(2)	7.185(6)
b [Å]	17.224(2)	7.185(6)
c [Å]	32.622(3)	36.886(6)
α, β, γ [°]	90	90
Diffractometer	Enraf-Nonius CAD4-Turbo	Enraf-Nonius CAD4-Turbo
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
Density (calculated) [Mg/m^3]	1.195	1.175
Absorption coefficient [mm^{-1}]	0.368	1.527
F (000)	3296	760
θ range for data collection [°]	3−26	3−27
Limiting indices	$0 \le h \le 18$, $0 \le k \le 21$, $0 \le l \le 40$	$-9 \le h \le -1$, $0 \le k \le 9$, $-49 \le l \le 48$
Reflections collected	8290	4237
Independent reflections	8238 (R_{int} = 0.000)	2168 (R_{int} = 0.0271)
Data/ restrained/ parameters	5910/ 0/ 415	1843/ 0/ 96
Goodness-of-fit on F^2	1.023	1.070
Final *R* indices [F_0>4σ(F_0)]	*R1* = 0.0400; *wR2* = 0.0976	*R1* = 0.0293; *wR2* = 0.0704
R indices (all data)	*R1* = 0.0785; *wR2* = 0.1392	*R1* = 0.0436; *wR2* = 0.0769
Largest diff. peak and hole	0.427; −0.330 e/Å^3	0.445; −0.376 e/Å^3
Scan modes	ω/θ	ω

[1] D. Walther, R. Fischer, M. Friedrich, P. Gebhardt, H. Görls, *Chem. Ber.* **1996**, *129*, 1389.
[2] W. Hiller, J. Stähle, A. Zinn, K. Dehnicke, *Z. Naturforsch.* **1989**, *44b*, 999.
[3] M. Wedler, M. Noltemeyer, U. Pieper, H. G. Schmidt, D. Stahlke, F. T. Edelmann, *Angew. Chem.* **1990**, *102*, 941; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 894.
[4] Y. Zhou, D. S. Richeson, *Inorg. Chem.* **1996**, *35*, 1423.
[5] Y. Zhou, D. S. Richeson, *Inorg. Chem.* **1996**, *35*, 2448.
[6] M. P. Coles, D. C. Swenson, R. F. Jordan, *Organometallics* **1997**, *16*, 5183.
[7] U. Patt-Siebel, U. Müller, C. Ergezinger, B. Borgsen, K. Dehnicke, D. Fenske, G. Baum, *Z. Anorg. Allg. Chem.* **1990**, *582,* 30.
[8] J. Barker, N. C. Blacker, P. R. Phillips, N. W. Alcock, W. Errington, M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.* **1996**, 431.
[9] R. Riedel, A. Greiner, G. Miehe, W. Dreßler, H. Fueß, J. Bill, F. Aldinger, *Angew. Chem.* **1997**, *109*, 657; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 603.
[10] [10a] Y. Zhou, D. S. Richeson, *Inorg. Chem.* **1997**, *36*, 501. − [10b] S. Appel, F. Weller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1990**, *583*, 7. − [10c] J. D. Kildea, W. Hiller, B. Borgsen, K. Dehnicke, *Z. Naturforsch.* **1989**, *44b*, 889. − [10d] C. Ergezinger, F. Weller, K. Dehnicke, *Z. Naturforsch.* **1988**, *43b*, 1621.
[11] K. Dehnicke, *Chemiker Zeitung* **1990**, *114*, 295.
[12] A. R. Sanger, *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 351.
[13] H. H. Karsch, P. A. Schlüter, F. Bienlein, M. Heckel, M. Herker, A. Sladek, E. Witt, *Z. Anorg. Allg. Chem.* **1998**, in press.
[14] H. Roesky, B. Miller, M. Noltemeyer, H. G. Schmidt, U. Scholz, G. M. Sheldrick, *Chem. Ber.* **1988**, *121,* 1403.
[15] H. H. Karsch, P. A. Schlüter, M. Reisky, **1998**, to be published.
[16] S. Hao, S. Gambarotta, C. Bensimon, J. J. H. Edema, *Inorg. Chim. Act*. **1993**, *213*, 65.
[17] [17a] H. H. Karsch, B. Deubelly, G. Hanika, J. Riede, G. Müller, *J. Organomet. Chem.* **1988**, *344*, 153. − [17b] H. H. Karsch, M. Hollstein, G. Müller, *Z. Naturforsch.* **1990**, *45b*, 775.
[18] W. A. Herrmann, M. Denk, *Deutsches Patent* DE 4214281.
[19] [19a] G. M. Sheldrick, C. Krüger, R. Goddard, *Oxford Univ. Press*, **1985**, 175. − [19b] G. M. Sheldrick, *Program for the refinement of structures*, **1993**, University of Göttingen. − [19c] J. Kopf, H. C. Rübcke, *Progr. CADHKL4*, **1993**, Universität Hamburg.

[98009]