Fully Chlorinated *N*-Silyl Amides of Titanium and Tungsten – Crystal Structure of $Cl_3SiNW(Cl_3)N(SiCl_3)_2$

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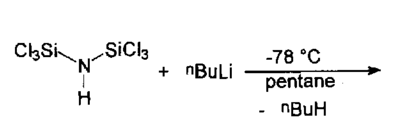
The reaction of hexachlorodisilazanyllithium $(Cl_3Si)_2NLi$ (**1**), with $TiCl_4$ leads selectively to the novel fully chlorinated amides $(Cl_3Si)_2NTiCl_3$ (**2**) or $[(Cl_3Si)_2N]_2TiCl_2$ (**3**), respectively, depending on the molar ratio of the starting materials. The analogous reaction of **1** with WCl_6 yielded the amide imide $Cl_3SiN{=}W(Cl_3)N(SiCl_3)_2$ (**5**) by elimination of $SiCl_4$. The relative amounts of the starting materials had no effect on the formation of **5**. $^{14/15}N$- and ^{29}Si-NMR data on the starting materials and products show significantly different effects, when compared with those of analogous *N*-trimethylsilyl derivatives, due to the lower energy of the electrons in the N–Si and N–M σ bonds. The crystal structure of **5** (triclinic, space group $P\bar{1}$) was determined by X-ray structure analysis.

Fully chlorinated *N*-silylamido or -imido compounds are promising candidates for molecular preorganization leading to novel polymer, and highly crosslinked, silicon-nitrogen networks. For example $SiPN_3$[1] has been synthesized via the molecular precursor $Cl_3Si{-}N{=}PCl_3$, which already contains the required structural element of two vertex-sharing tetrahedra centered by, respectively, a phosphorus or a silicon atom, which are connected through a common nitrogen atom. Ammonolysis of this precursor, followed by thermal condensation, preserves this structural element and directly yields the highly crosslinked crystalline ceramic compound $SiPN_3$, which contains a network structure of corner-sharing SiN_4 and PN_4 tetrahedra[1]. A similar approach has been used for the synthesis of the non-crystalline ceramic $Si_3B_3N_7$[2].

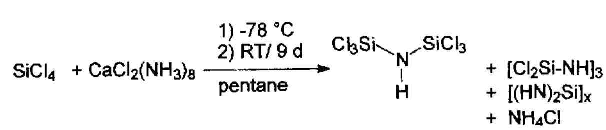
In the context of a systematic investigation of nitrido bridges between main-group elements and transition metals, we are now targeting molecular precursor compounds which might be valuable for the synthesis of ternary nitrides, or nanocomposites, in the system Ti–Si–N and W–Si–N. As in the synthesis of $SiPN_3$, fully chlorinated *N*-silylamido or -imido compounds of Ti and W seem to be appropriate candidates for this synthetic approach.

Several *N*-trimethylsilyl amides or imides with a large number of transition metals and main-group elements exist. Their synthesis by the reactions of metal halides with hexamethyldisilazane or with hexamethyldisilazanyllithium have been extensively studied in the literature[3–8]. In contrast there are only a few compounds reported with nitrogen-bearing trichlorosilyl groups instead of trimethylsilyl groups[9–11], and Zn is the only transition metal reported so far[11] in these systems.

Wannaget et al. have already investigated the preparation and the reactivity of hexachlorodisilazane and showed that *N*-lithiation is readily achieved by treatment with *n*BuLi in pentane to give hexachlorodisilazanyllithium (**1**; see Equation 1)[9]. Recently, Burgdorf et al. described an improved synthesis of chlorodisilazanes starting from $CaCl_2(NH_3)_8$[12] (see Equation 2). Reactions of **1** were carried out with boron and silicon halides and the possibility of substitution reactions was shown in principle[10].



(1)



(2)

Here we report on the synthesis and characterization of fully chlorinated *N*-silylamides obtained by the reaction of **1** with $TiCl_4$ and WCl_6.

Results and Discussion

The reactions of **1** with $TiCl_4$ are summarized in Scheme 1. The mono-substituted product **2** is obtained in high yield by the reaction of **1** with $TiCl_4$ in a molar ratio of 1:1 (Scheme 1a). It is a yellowish solid which gives bright yellow solutions in organic solvents. The treatment of **1** with $TiCl_4$ in a molar ratio of 2:1 (Scheme 1b) gives the corresponding diamide **3**. On heating, **3** decomposes to **2** and the well-characterized 4-membered ring **6**[9b,13] (Scheme 1c).

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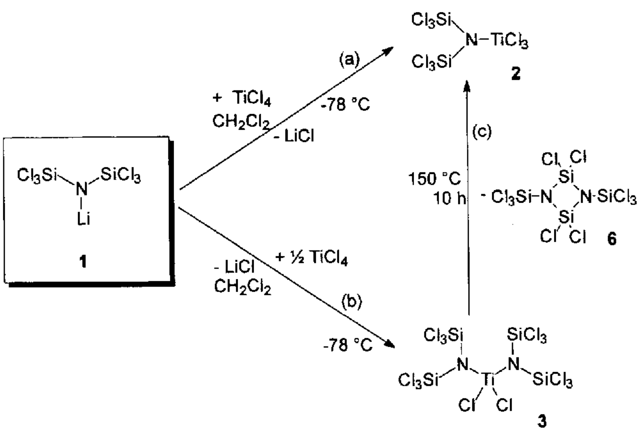
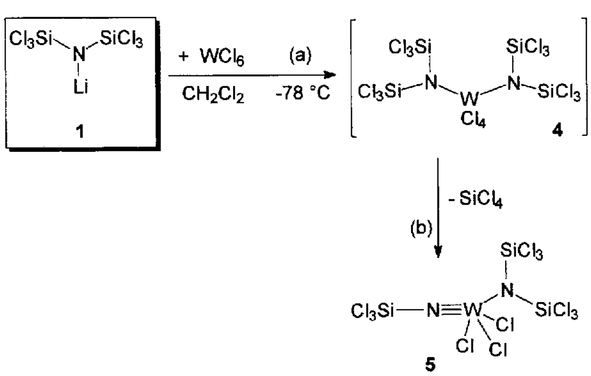
Scheme 1



The reaction of **1** with WCl_6 (Scheme 2) leads directly to the amide imide **5** which can be recrystallized from pentane to give yellow crystals (vide infra). Solutions of **5** in aromatic solvents exhibit a dark brown color. The formation of **5** can be explained by the elimination of $SiCl_4$ from the proposed intermediate **4**, resulting in a W≡N multiple bond (Scheme 2b). This type of reaction is well known for the analogous *N*-trimethylsilyl derivatives, e.g. with tantalum as the central atom[4a]. The relative amounts of the starting materials **1** and WCl_6 may be varied across a wide range without any effect on the formation of **5**. Obviously, a monosubstitution product analogous to **2** is much more reactive towards **1** than WCl_6 itself.

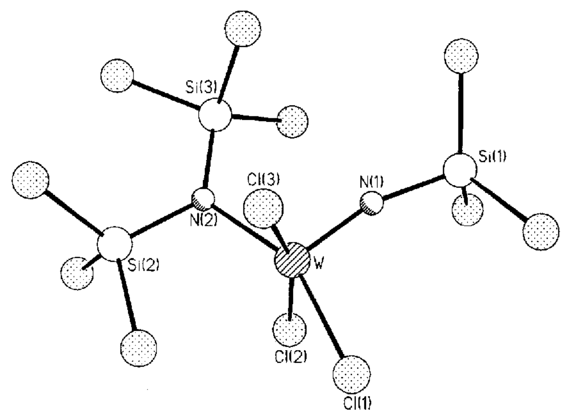
Scheme 2



Crystal Structure of 5[14]

Details of the X-ray structure analysis of **5** are summarized in Table 1. The tungsten amide imide $Cl_3SiN{\equiv}W(Cl_3)N(SiCl_3)_2$ is monomeric. There are no significantly short intermolecular atomic distances. The coordination sphere of the central atom of **5** is best described to be of pseudo-square-pyramidal geometry, with the imido group at the apex. The $SiCl_3$ groups [$Cl_3Si(3)$] and [$Cl_3Si(1)$] show rotational disorder. The imido group is nearly linear [angle W≡N−Si 165.4(6)°] and the imido nitrogen atom can be viewed as sp-hybridized. The coordination of the amido nitrogen atom is trigonal planar. The two bonds between W and N differ by nearly 30 pm [W≡N 171.8(9), W−N 200.7(8) pm] which is significantly larger than the value found for the comparable dimeric tantalum compound $[Me_3SiN{\equiv}Ta(Br_2)N(SiMe_3)_2]_2$[4a]. The bond lengths W−N are in the same range as those found for other tungsten amides and imides[15−17]. In contrast to the tantalum derivative $[Me_3SiN{\equiv}Ta(Br_2)N(SiMe_3)_2]_2$, the hybridization of the nitrogen atoms in **5** has no effect on the N−Si bond lengths (average value 171.5 pm) which correspond to those of a normal Si−N single bond[13] which also holds for the W−Cl bond lengths[18]. The bond lengths Si−Cl of the $Si(2)Cl_3$ group are as expected[13] (bond lengths in the rotationally disordered groups were fixed).

Figure 1. Molecular structure of **5**[a]



[a] Selected bond lengths [pm] and angles [°]: W−Cl1 229.8(3), W−Cl2 231.4(3), W−Cl3 230.5(3), N1−Si1 171.1(9), N2−Si2 171.4(8), N2−Si3 172.5(10); N1−W−N2 104.0(4), N1−W−Cl1 102.5(3), N2−W−Cl1 153.5(3), N1−W−Cl2 98.5(3), Cl2−W−Cl3 162.1(1), W−N1−Si1 165.4(6).

Table 1. Crystallographic data of **5**

Empirical formula	$Cl_{12}N_2Si_3W$
Crystal system, space group	triclinic, $P\bar{1}$
Unit-cell dimensions [pm] [°]	a = 879.8(2)
	b = 888.5(2)
	c = 1318.4(2)
	α = 99.14(2)
	β = 98.10(2)
	γ = 100.55(2)
Unit-cell volume V [10^6 pm^3]	985.0(3)
Z	2
Density (calcd.) [g/cm^3]	2.433
Diffractometer, radiation	Siemens P4, Mo-K_α, λ = 71.073 pm
Temperature [K]	296
2θ range [°]	2.0–55.0
Reflections collected	5391, ω scan
Independent reflections	4509 (R_{int} = 0.0423)
Observed reflections	4181 with $F_o \geq 2.0\ \sigma(F_o)$
Absorption correction	semi-empirical (ψ scans)
Min./max. transmission factors	0.0282/0.0575
Solution	direct methods
Number of parameters refined	162
Program	Siemens SHELXTL PLUS (VMS)
R/wR [$w^{-1} = \sigma^2(F_o)$]	0.0583/0.0571

Crystalline **5** shows a reversible phase transition between room temperature and −100°C, associated with an enlargement of the unit cell without destruction of the single crystal.

NMR Spectroscopic Results

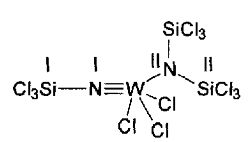
The measured NMR data of hexachlorodisilazane and of the compounds **1**−**6** are listed in Tables 2 and 3. All NMR data of the compounds **2** and **3** are consistent with the proposed structures. Because of the absence of any protons which could be used for polarization transfer only direct ^{29}Si-NMR measurements were possible. The ^{29}Si nuclei of the transition-metal derivatives are shielded by 4−8 ppm when compared with hexachlorodisilazane; this is caused by the replacement of the proton by a transition-metal halide group. In contrast, the ^{29}Si nuclei of $(Me_3Si)_2N-TiCl_3$, the methyl analogue of **2**, are deshielded with respect to hexamethyldisilazane[19]. The replacement of a second chlorine atom at the titanium center against a bis(trichlorosilyl)amido group leads to further ^{29}Si shielding by 1.8 ppm. The trichlorosilyl groups at the imido nitrogen atoms of **5** give signals with a high shielding at $\delta = -59.8$. This significantly high shielding of the ring Si nuclei in **6** to a value of $\delta = -39.8$ is typical of 4-membered rings, and is probably a result of the short transannular Si···Si distance of 246.3 pm[13] which is comparable to a covalent Si−Si single bond length of 234 pm[20].

Table 2. ^{14}N- and ^{29}Si-NMR data[a] of hexachlorodisilazane, compounds **1**−**3**, and **6**

Compound	Hexachloro-disilazane[b]	1	2	3	6
$\delta^{14}N$ ($\nu_{1/2}$)	−313 (430)	−283 (250)	−117 (160)	−140 (510)	−283 (220)
$\delta^{29}Si$	−25.5	−43.5	−29.6	−31.4	−30.2 ($SiCl_3$) −39.8 ($SiCl_2$)

[a] C_6D_6, 25°C. − [b] δ^1H = 2.82; $^1J[^{15}N,^1H]$ = 71.9 Hz; $^1J[^{29}Si,^{15}N]$ = 28.8 Hz.

Table 3. ^{14}N- and ^{29}Si-NMR data[a] of compound **5**



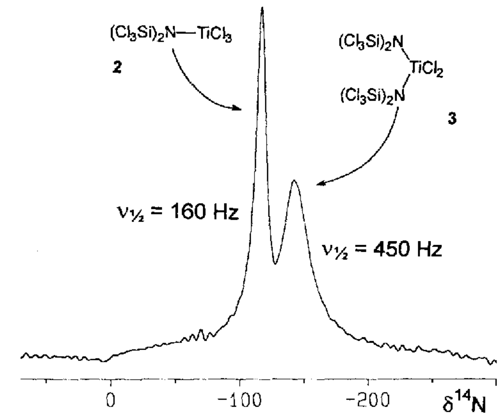
5

$\delta^{14}N$ ($\nu_{1/2}$) (N-I)	$\delta^{14}N$ ($\nu_{1/2}$) (N-II)	$\delta^{29}Si$ (Si-I)	$\delta^{29}Si$ (Si-II)
93 (110)	−167 (310)	−59.8	−33.1

[a] C_6D_6, 25°C.

The most instructive information on the product distribution, and on the progress of the reactions, is obtained by ^{14}N-NMR spectroscopy. Previously, only a few $^{14/15}$N chemicals shifts of transition-metal amides and imides were measured[17], most of them by ^{15}N-NMR spectroscopy of samples enriched with ^{15}N[17,21]. Our investigations on ^{14}N-NMR spectroscopy show that the resonances of transition-metal amides and imides are surprisingly easy to observe (see Figure 2).

Figure 2. 18.1-MHz ^{14}N-NMR spectrum of a 1:1 mixture of the compounds **2** and **3**



The substitution of the proton of hexachlorodisilazane against lithium in **1** leads to a ^{14}N deshielding of 30 ppm and to a sharpening of the ^{14}N-NMR signal. The $\delta^{14}N$ values of the compounds **2** ($\delta^{14}N = -117$) and **3** ($\delta^{14}N = -140$) can be explained by the lower acidity of the $TiCl_2$ group when compared with that of the $TiCl_3$ group. In a mixture, the increase of the line width of the ^{14}N-NMR signal due to the higher molecular weight of **3** (Figure 2) is also indicative. The low ^{14}N shielding, together with a sharp ^{14}N-resonance signal for the imido-nitrogen atom of **5**, is typical of sp-hybridized ^{14}N atoms[17,21,22].

The marked ^{14}N deshielding in metal amides or imides, if the metal is an early transition element in a high oxidation state, may be explained by the contribution to the paramagnetic shielding term σ_p of B_0-induced mixing of ground and electronic excited states. This concerns in particular the electrons in the M−N σ bond, the nitrogen lone pair of electrons, and the presence of unoccupied metal d-orbitals. The comparison between $\delta^{14}N$ of **2** ($\delta^{14}N = -117$) and $(Me_3Si)_2NTiCl_3$ ($\delta^{14}N = +30$[19]) indicates the influence of the electronegative chloro substituents. The energy of electrons in the N−Si and also in the M−N σ bonds, as well as that of the lone pairs of electrons, is lower in **2** than in $(Me_3Si)_2NTiCl_3$. Therefore, the mean ΔE is larger in **2** and paramagnetic contributions become smaller[23] i.e. ^{14}N-nuclear shielding increases. The same arguments explain the high shielding of the ^{29}Si nuclei. However, in comparison with amines, the effect of the neighboring metal center still dominates the ^{14}N deshielding but not the ^{29}Si shielding in **2**, **3**, and **5**.

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Experimental Section

All preparative work and handling of the samples was carried out under pure N_2 using dry glassware and dry solvents.

$CaCl_2(NH_3)_8$[12] and hexachlorodisilazanyllithium (1)[9b] were prepared as described. The preparation of hexachlorodisilazane is analogous to literature procedures[12]. $SiCl_4$, $TiCl_4$, WCl_6, and *n*BuLi in hexane (1.6 M) were commercial products and used without further purification. – IR spectra: Bruker IFS 66v/; KBr pellets. – NMR spectra: Bruker ARX 250 (^1H, ^{14}N, ^{15}N, ^{29}Si); chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_6) = 7.15; $\delta^{29}Si$: $\Xi(^{29}Si)$ = 19.867184 MHz] and neat $MeNO_2$ [$\delta^{14}N$: $\Xi(^{14}N)$ = 7.223656 MHz; $\delta^{15}N$: $\Xi(^{15}N)$ = 10.136767 MHz].

$(Cl_3Si)_2NH$: To a cooled (−78°C) solution of 400 g of $SiCl_4$ (2.4 mol) in 500 ml of pentane, 40 g of $CaCl_2(NH_3)_8$ (0.16 mol ≈ 1.28 mol of NH_3) was added in one portion. Then the mixture was stirred at room temp. for 8 d. After that, the reaction mixture was filtered, and pentane and $SiCl_4$ were removed from the filtrate by distillation. Distillation of the residue at reduced pressure gave 60 g (18%) of hexachlorodisilazane as a colorless, extremely moisture-sensitive liquid (b.p. 81°C/40 Torr).

$(Cl_3Si)_2N-TiCl_3$ (**2**) and *$[(Cl_3Si)_2N]_2TiCl_2$* (**3**): To a solution of 0.7 g of **1** (2.4 mmol) in 20 ml of CH_2Cl_2 at −78°C, 0.5 g (2.4 mmol) or 0.25 g (1.2 mmol) of $TiCl_4$, respectively, were added in one portion. After the mixture was warmed to room temp., it was stirred for 4 h. Then the mixture was filtered. Removal of the solvent from the filtrate gave 1.0 g of **2** (95%; m.p. 190°C) or 0.8 g of **3** (97%; m.p. 140°C under decomposition), as yellowish solids. – **3**: IR: $\tilde{\nu}$ [cm^{-1}] = 1405, 985, 815, 746, several vibrations between 400 and 630.

$Cl_3SiN{\equiv}W(Cl_3)N(SiCl_3)_2$ (**5**): A solution of 0.7 g of **1** (2.4 mmol) in 10 ml of CH_2Cl_2 was added carefully to a stirred solution of 0.5 g of WCl_6 (1.3 mmol) in 20 ml of CH_2Cl_2 at −78°C. The mixture was allowed to warm up. At a temperature of 0°C the color changed from dark brown to yellow and LiCl began to precipitate. After stirring for 1 h at room temp., the reaction mixture was filtered. Removal of the solvent in vacuo from the filtrate gave an orange oil. Recrystallization from pentane gave 0.5 g of **5** (58%) as yellow platelets (m.p. 115°C). – IR: $\tilde{\nu}$ [cm^{-1}] = 1403, 1178 [νW≡N)], 1083, 964, 772, 624, several vibrations between 400 and 600.

[1] H. P. Baldus W. Schnick, J. Lücke, U. Wannagat, G. Bogedain, *Chem. Mater.* **1993**, *5*, 845–850.
[2] H. P. Baldus, O. Wagner, M. Jansen, *Mat. Res. Soc. Symp. Proc.* **1992**, *271*, 821–826.
[3] [3a] R. A. Andersen, *Inorg. Chem.* **1979**, *18*, 1724–1725. – [3b] C. Airoldi, D. C. Bradley, H. Chudzynska, M. B. Hursthouse, K. M. Abdul Malik, P. R. Raithby, *J. Chem. Soc., Dalton Trans.* **1980**, 2010–2015. – [3c] R. Schichtenmaier, J. Strähle, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1526–1529. – [3d] M. A. Putzer, J. Magull, H. Goesmann, B. Neumüller, K. Dehnicke, *Chem. Ber.* **1996**, *129*, 1401–1405.
[4] [4a] D. C. Bradley, M. B. Hursthouse, K. M. Abdul Malik, G. B. Chota Vuru, *Inorg. Chim. Acta* **1980**, *44*, L5–L6. – [4b] D. C. Bradley, M. B. Hursthouse, K. M. Abdul Malik, A. J. Nielson, G. B. Chota Vuru, *J. Chem. Soc., Dalton Trans.* **1984**, 1069–1072. – [4c] K. D. Scherfise, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1985**, *528*, 117–124. – [4d] D. M. Hoffman, S. Suh, *J. Chem. Soc., Chem. Commun.* **1993**, 714–715.
[5] R. D. Köhn, G. Kociac-Köhn, M. Haufe, *Chem. Ber.* **1996**, *129*, 25–27.
[6] M. A. Putzer, B. Neumüller, K. Dehnicke, J. Magull, *Chem. Ber.* **1996**, *129*, 715–719.
[7] P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, *J. Chem. Soc., Chem. Commun.* **1996**, 1189–1190.
[8] [8a] M. Allen, H. C. Aspinall, R. S. Moore, M. B. Hursthouse, A. I. Karvalov, *Polyhedron* **1992**, *11*, 409–413. – [8b] H. W. Turner, R. A. Andersen, A. Zalkin, D. H. Templeton, *Inorg. Chem.* **1979**, *18*, 1221–1224. – [8c] L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin, B. D. Zwick, *Inorg. Chem.* **1994**, *33*, 2248–2256. – [8d] M. Westerhausen, J. Greul, H.-D. Hauser, W. Schwarz, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1295–1305.
[9] [9a] U. Wannagat, P. Schmidt, *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 355–359. – [9b] U. Wannagat, P. Schmidt, M. Schulze, *Angew. Chem.* **1967**, *79*, 409–410; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 446. – [9c] U. Wannagat, H. Moretto, P. Schmidt, *Z. Anorg. Allg. Chem.* **1971**, *385*, 164–176. – [9d] U. Wannagat, *Fortschr. Chem. Forsch.* **1967**, *9*, 102–144. – [9e] U. Wannagat, *Pure Appl. Chem.* **1969**, *19*, 325–338.
[10] [10a] U. Wannagat, M. Schulze, H. Bürger, *Z. Anorg. Allg. Chem.* **1970**, *375*, 157–165. – [10b] U. Wannagat, H. Moretto, P. Schmidt, M. Schulze, *Z. Anorg. Allg. Chem.* **1971**, *381*, 288–311.
[11] U. Wannagat, P. Schmidt, *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 331–334.
[12] H. Fleischer, K. Hensen, D. Burgdorf, E. Flindt, U. Wannagat, H. Bürger, G. Pawelke, *Z. Anorg. Allg. Chem.* **1995**, *621*, 239–248.
[13] U. Wannagat, E. Flindt, D. J. Brauer, H. Bürger, F. Dörrenbach, *Z. Anorg. Allg. Chem.* **1989**, *572*, 33–46.
[14] Further details of the crystal-structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406413, the names of the authors, and the journal citation.
[15] [15a] M. G. B. Drew, G. W. A. Fowles, D. A. Rice, N. Rolfe, *J. Chem. Soc., Chem. Commun.* **1971**, 231–232. – [15b] M. G. B. Drew, K. C. Moss, N. Rolfe, *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1219–1222.
[16] [16a] D. M. Berg, P. R. Sharp, *Inorg. Chem.* **1987**, *26*, 2959–2962. – [16b] K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1981**, 2088–2097.
[17] W. A. Nugent, J. M. Mayer, *Metal-Ligand Multiple Bonds*, John Wiley & Sons, New York **1988**, pp. 129–219, and refs. cited therein.
[18] [18a] T. Godemeyer, A. Berg, H.-D. Groß, U. Müller, K. Dehnicke, *Z. Naturforsch., B* **1985**, *40*, 999–1004. – [18b] T. Godemeyer, K. Dehnicke, D. Fenske, *Z. Naturforsch., B* **1985**, *40*, 1005–1009.
[19] B. Wrackmeyer, J. Weidinger, in preparation.
[20] *Gmelin Handbook of Inorganic and Organometallic Chemistry*, 8th ed., 4 th suppl., vol. B1, H. Keller-Radek, D. Koschel, U. Krüerke; P. Merlet (Eds.), Springer, Berlin **1982**, pp. 182–183.
[21] [21a] Donovan-Mtunzi, R. L. Richards, J. Mason, *J. Chem. Soc., Dalton Trans.* **1984**, 1329–1332. – [21b] T. Godemeyer, K. Dehnicke, E. Fluck, *Z. Anorg. Allg. Chem.* **1988**, *565*, 41–46.
[22] [22a] M. Witanowsky, G. A. Webb, *Annu. Rep. NMR Spectroscopy* **1972**, *5B*, 395–464. – [22b] M. Witanowsky, L. Stefaniak, G. A. Webb, *Annu. Rep. NMR Spectroscopy* **1986**, *18*.
[23] [23a] V. Jones, G. Frenking, M. T. Reetz, *J. Comput. Chem.* **1992**, *13*, 919–934. – [23b] S. Berger, W. Bock, G. Frenking, F. Mueller, *J. Am. Chem. Soc.* **1995**, *117*, 3820–3829.

[97006]