DOI: 10.1002/ejic.200800844

Stable Trichlorosilane–Pyridine Adducts

Gerrit W. Fester,[a] Jörg Wagler,[a] Erica Brendler,[b] and Edwin Kroke*[a]

Keywords: Trichlorosilane / Hypercoordination / Solid-state NMR / Dismutation

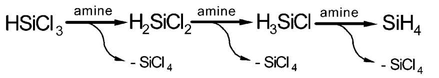
The prepapration, and first comprehensive spectroscopic and structural characterization of octahedral trichlorosilane adducts $HSiCl_3(Rpy)_2$ with R = H, 4-CH_3, 4-C_6H_5, 3-Br, 4-$CHCH_2$, 4-C_2H_5, 4-$C(CH_3)_3$ and 4-$N(CH_3)_2$ is reported. The products are surprisingly stable in the solid state and easily obtained in high yield. Single-crystal X-ray diffraction analysis of $HSiCl_3(3\text{-}Brpy)_2$ revealed relatively short Si–Cl bonds (218–223 pm) while the Si–N bonds (ca. 198 pm) are only slightly longer than in the corresponding $H_2SiCl_2(Rpy)_2$ adducts. Dismutation reactions were observed only in polar solvents at elevated temperatures.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

Trichlorosilane $HSiCl_3$ belongs to the most important industrial silicon compounds. It is the key intermediate in the so-called Siemens process used for the production of semiconductor-grade as well as solar-grade silicon. The production capacities are currently strongly increased by many companies due to the very fast growing demand for silicon solar cells. Furthermore, trichlorosilane may be transformed into numerous derivatives via hydrosilylation and/or chlorine substitution.

It is known that many halosilanes of the type H_nSiX_{4-n} – in particular the highly reactive trichlorosilane – tend to dismutate upon treatment with bases. These dismutation reactions are accompanied by the formation of Lewis acid-base adducts (as intermediates) and driven by the formation of silanes such as $SiCl_4$ and SiH_4 (Scheme 1).



Scheme 1. Dismutation of trichlorosilane to monosilane under base influence.

Whereas octahedral adducts of tetrachlorosilane with pyridines or related bases are easily formed, and many of them have been comprehensively characterized,[1] most attempts to synthesize and isolate a trichlorosilane–pyridine adduct or complexes with other Lewis bases failed.[2] Wannagat et al. synthesized $HSiCl_3(py)_2$ more than 40 years ago.[2d] However, the reported characterisation included a Si–H valence vibration at 2070 cm^{-1} and a powder diffractogram, which was not further analysed. Interestingly, the authors suggested that the pyridine molecules are in *cis*-position to each other.

In some cases extraordinarily facile disproportionation of hydridosilanes have been reported.[2f] Attempts to isolate chelate complexes of trichlorosilane with chelate ligands like 2,2′-dipyridine or 1,10-phenanthroline have been reported, again by Wannagat et al. in the 1960s.[3] Only one report describing the formation and structural characterization of a chelate complex between $HSiCl_3$ and tetramethylethylenediamine (tmeda) was published.[4]

Here we report the synthesis of octahedral trichlorosilane–pyridine 1:2 adducts via careful direct reactions of substituted pyridines with $HSiCl_3$. The experiments have to be performed at low temperatures in suitable solvents such as toluene or hexane. The colorless solid 1:2 adducts are obtained in good to excellent yields. They exhibit poor solubility in most organic solvents.

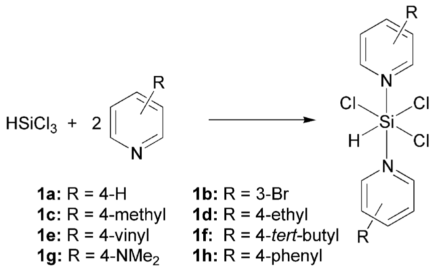
Results and Discussion

As a consequence of our work on octahedral adducts of dichlorosilane with substituted pyridines (Rpy)[5] we also investigated the formation of the hexacoordinate compounds $HSiCl_3(Rpy)_2$, which exhibit various substitution patterns (R) at the pyridine donor molecule (py). These solid adducts were found to be stable at room temperature (under inert atmosphere) and are directly accessible from trichlorosilane and the respective pyridine in various solvents.

In a representative reaction trichlorosilane (in aprotic solvents such as *n*-hexane, toluene or THF) is mixed with substituted pyridines to form compounds **1a**–**h** (Scheme 2).

---

[a] Institut für Anorganische Chemie, TU Bergakademie Freiberg,
Leipziger Strasse 29, 09596 Freiberg, Germany
Fax: +49-3731-39-4058
E-mail: edwin.kroke@chemie.tu-freiberg.de
[b] Institut für Analytische Chemie, TU Bergakademie Freiberg,
Leipziger Strasse 29, 09596 Freiberg, Germany



Scheme 2. Reaction of trichlorosilane with substituted pyridines.

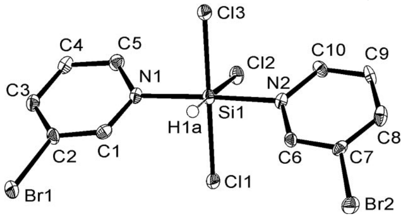


Figure 1. Molecular structure of **1b** (ORTEP plot with thermal ellipsoids at the 50 percent probability level, *C*-bound hydrogen atoms are omitted).

Because of the poor solubilities of the complexes characterization by solution NMR spectroscopy failed. Therefore, the hexacoordinate silicon complexes were characterized by ^{13}C and ^{29}Si CP/MAS NMR as well as Raman spectroscopy. As expected, compounds **1a**–**h** show a characteristic Si–H valence vibration band at 2061–2128 cm^{-1} in the Raman spectrum (see Table 1), which in comparison to $HSiCl_3$ is shifted to lower wavenumbers accompanied by broadening of the signal. The latter can be attributed to increasing ionic contributions to the Si–H bond. The ^{29}Si NMR shifts range between δ_{iso} = –165 and –172 ppm and confirm hexacoordination of the silicon atom.[6] In comparison with the previously reported dichlorosilane adducts $H_2SiCl_2(Rpy)_2$ the resonances of all compounds $HSiCl_3(Rpy)_2$ are significantly shifted to higher field (by about 20 ppm). This effect can be attributed to the substitution of one Si-bound hydrogen atom for a Cl substituent.

Table 1. ^{29}Si CP/MAS NMR spectroscopic data, selected bond lengths and ν(Si–H) Raman bands for compounds **1a**–**h** and $HSiCl_3$ (compounds in order of ^{29}Si NMR shift).

	R	δ_{iso} ^{29}Si [ppm]	ν(Si–H) [cm^{-1}]
$HSiCl_3$		–9.6[7]	2244[8]
1a	H	–164.8	2095
1c	4-CH_3	–165.0	2077
1h	4-C_6H_5	–165.6	2092
1b	3-Br	–165.7	2093
1e	4-$CHCH_2$	–168.2	2111
1d	4-CH_2CH_3	–168.5	2092
1f	4-$C(CH_3)_3$	–170.0	2128
1g	4-$N(CH_3)_2$	–172.0	2061

With increasing electron-releasing effects of the substituents at the pyridine moiety the Si atoms gain electron density which leads to a high field shift of the ^{29}Si NMR signal. This is most obvious for **1g** due to the strong mesomeric effect of the dimethylamino substituent.[5]

Under the synthesis conditions applied (–78 °C) the trichlorosilane–pyridine adducts precipitated immediately. In order to obtain single crystals of suitable for X-ray diffraction analyses diffusion experiments of trichlorosilane into solutions of the respective pyridine were performed. Fortunately, compound **1b** formed single crystals suitable for X-ray diffraction analysis. The molecular structure is depicted in Figure 1.

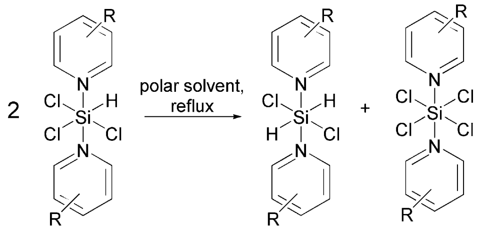
Unlike the dichlorosilane adducts $H_2SiCl_2(Rpy)_2$, which all exhibited the Si atom on a crystallographically imposed centre of symmetry,[5] compound **1b** bears one Si complex molecule per asymmetric unit. Furthermore, compound **1b** crystallized with 1/2 molecule of 3-bromopyridine in the asymmetric unit, which is located near a centre of inversion and, therefore, part of a symmetry-imposed disorder.

The Si–N distances are slightly longer than in the previously reported dichlorosilane adducts, i.e. 198.2(3) and 198.9(3) pm in **1b** and 196.9(1) pm in the analogous dichlorosilane adduct.[5] This Si–N bond lengthening can be seen as a result of the increased steric impact around the Si atom. Whereas in the dichlorosilane adducts the pyridine planes are tilted out of the Cl–Si–Cl axis by ca. 70–80° and the Si–H bonds were nearly in plane with the pyridine ligands, the third Si-bound chlorine atom of the $HSiCl_3$ adduct forces the other two Cl atoms closer to the pyridine 2,6-hydrogen atoms. Vice versa, well in accord with the Si–N bond lengthening, the Si–Cl bonds of the above trichlorosilane adduct [218.3(1) for Cl2, 221.9(1) for Cl1 and 222.7(1) pm for Cl3] are significantly shorter than in the analogous dichlorosilane complex [228.1(1) pm].

The shorter Si–Cl bonds support the following observation: contrary to the experiments described for dichlorosilane (formation of complexes $[H_2Si(Rpy)_4]^{2+}$ possible)[5,9] the cationic species of the type $[HClSi(Rpy)_4]^{2+}$ were not observed so far.[10] Both, the increased steric demand around the Si atom as well as the stronger (shorter) Si–Cl bonds vs. longer Si–N bonds render the addition of two further pyridine molecules less likely. Furthermore, the dissociation of the Si–X bonds depends on a variety of parameters, in particular temperature, solvent, the nature of the anion and further substituents at the Si atom.[11,12] Whereas electron releasing groups promote the formation of higher coordinate siliconium cations, electron withdrawing substituents (e.g. further chlorine atoms) inhibit ionic Si–Cl dissociation.

As mentioned in the introduction, dismutation of adducts of trichlorosilane and related silanes by the action of polar solvents has been documented.[2,4] Thus, the predominant decomposition reaction observed for the octahedral complexes was H vs. Cl redistribution. Pyridine adducts of $SiCl_4$ and H_2SiCl_2 formed upon treatment with polar solvents at elevated temperatures (Scheme 3).

This dismutation was monitored by ^{29}Si CP/MAS NMR spectroscopy. Whereas the complexes synthesized at lower



Scheme 3. Dismutation of $HSiCl_3(Rpy)_2$ in polar solvents at elevated temperatures.

temperatures delivered spectra with only one signal indicative of the $HSiCl_3(Rpy)_2$ complex, prolonged heating in polar solvents yielded solids which exhibit signals of the dichlorosilane complex $H_2SiCl_2(Rpy)_2$ and an additional signal at higher field, which can be attributed to the complex $SiCl_4(Rpy)_2$. Only small quantities of trichlorosilane–pyridine adducts remained (see Figures 2 and 3).

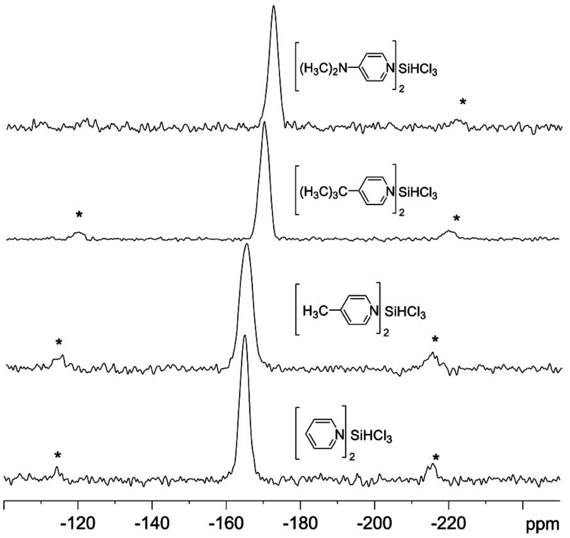


Figure 2. ^{29}Si CP/MAS NMR spectra of **1a**, **1c**, **1f** and **1g** (from bottom to top), asterisks mark spinning side bands.

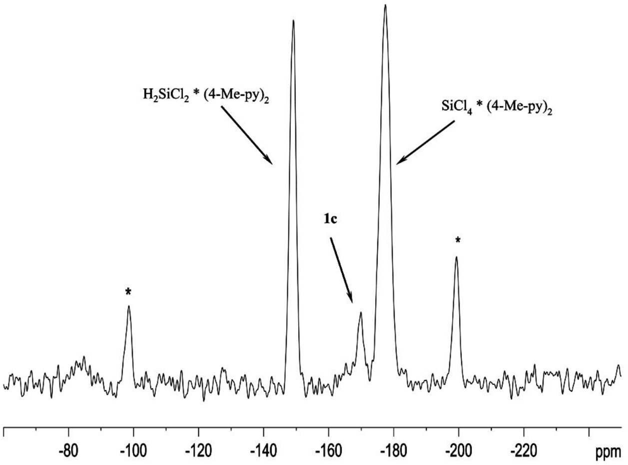


Figure 3. ^{29}Si CP/MAS spectrum of the product obtained by dismutation of **1c** in boiling acetonitrile after 6 hours (asterisks mark spinning side bands).

Conclusions

In summary, it is possible to deliberately prepare pyridine adducts of $HSiCl_3$ at low temperatures. These products can be obtained in yields >95% and are stable under inert atmosphere at room temperature. The octahedral complexes of $HSiCl_3$ are susceptible to dismutation reactions in polar solvents.

It is known that many reactions of (hydrido)-chlorosilanes are catalysed by pyridine bases. Therefore, the presented results provide a basis for a better control of these reactions, especially chlorine substitution and hydrosilylation. First results in the latter direction will be published soon.

Experimental Section

General Procedure for the Synthesis of 1a–h: Trichlorosilane (5 mmol) was dissolved in toluene (20 mL), stirred at –78 °C and the desired pyridine base (10 mmol) was added dropwise. The products precipitated as colorless solids. The suspension was stirred for one hour at –78 °C and than allowed to slowly adjust to ambient temperature. The white precipitate was filtered off, washed with toluene and dried under vacuum. Modifications to this procedure are outlined if applicable. All adducts **1a**–**h** slowly decompose upon heating above ca. 100 °C forming the corresponding chlorosilane, the pyridine and HCl. Therefore, melting or decomposition points cannot be determined.

Trichloro(hydrido)bis(pyridine)silicon (1a): Yield 1.45 g (4.94 mmol, 98.8%). ^{29}Si CP/MAS NMR: δ_{iso} = –164.8 ppm. IR (Raman): $\tilde{\nu}$ = 651 (m), 1021 (s), 1066 (w), 1151 (w), 1207 (m), 1261 (w), 1483 (w), 1573 (w), 1614 (m), 1947 (w), [ν(Si–H)] 2095 (m), 2514 (w), 2922 (w), 2960 (w), 3007 (w), 3063 (m), 3082 (s), 3090 (s), 3147 (m), 3226 cm^{-1} (w). $C_{10}H_{11}Cl_3N_2Si$ (293.65): calcd. Cl 36.2; found Cl 34.7.

Bis(3-bromopyridine)trichloro(hydrido)silicon (1b): Yield 1.26 g (2.79 mmol, 55.8%). ^{29}Si CP/MAS NMR: δ_{iso} = –165.7 ppm. IR (Raman): $\tilde{\nu}$ = 247 (w), 265 (m), 308 (m), 335 (m), 348 (m), 457 (w), 652 (w), 721 (m), 825 (w), 1035 (s), 1058 (m), 1094 (w), 1118 (w), 1199 (m), 1248 (w), 1320 (w) 1420 (w), 1468 (w), 1560 (m), 1605 (m), [ν(Si–H)] 2093 (m), 2491 (w), 2918 (w), 2968 (w), 3015 (w), 3056 (s), 3080 (s), 3096 (s), 3116 (w), 3205 cm^{-1} (w). Single crystals of **1b**·0.5(3-Brpy) were obtained by slow diffusion of trichlorosilane into 3-bromopyridine.

Trichloro(hydrido)bis(4-methylpyridine)silicon (1c): Yield 1.55 g (4.82 mmol, 96.3%). ^{29}Si CP/MAS NMR: δ_{iso} = –165.0 ppm. ^{13}C CP/MAS NMR: δ_{iso} = 23.4, 126.5, 142.4, 146.1 ppm. IR (Raman): $\tilde{\nu}$ = 235 (m), 289 (m), 299 (m), 359 (w), 471 (m), 505 (w), 559 (w), 669 (m), 796 (w), 824 (s), 972 (w), 1005 (w), 1040 (m), 1069 (m), 1214 (m), 1233 (m), 1261 (w), 1331 (w) 1388 (w), 1429 (w), 1564 (w), 1632 (m), 1930 (w), [ν(Si–H)] 2077 (w), 2512 (w), 2738 (w), 2926 (s), 2955 (m), 3005 (m), 3080 (s), 3106 cm^{-1} (s). $C_{12}H_{15}Cl_3N_2Si$ (321.71): calcd. Cl 33.1; found Cl 31.4.

Trichlorobis(4-ethylpyridine)(hydrido)silicon (1d): Yield 1.66 g (4.75 mmol, 95%). ^{29}Si CP/MAS NMR: δ_{iso} = –168.5 ppm. ^{13}C CP/MAS NMR: δ_{iso} = 11.5, 14.7, 27.6, 30.4, 121.2, 125.6, 141.8, 145.2, 146.5, 159.8, 162.2 ppm. IR (Raman): $\tilde{\nu}$ = 427 (w), 459 (w), 559 (w), 668 (m), 793 (m), 842 (w), 972 (m), 983 (m), 1004 (s), 1038 (m), 1066 (m), 1131 (w), 1200 (m), 1209 (m), 1267 (w), 1314 (w), 1383 (w), 1423 (m), 1459 (m), 1506 (w), 1556 (w), 1626 (s), 1932 (w), [ν(Si–H)] 2092 (m), 2511 (w), 2733 (w), 2829 (m), 2883 (s), 2901 (s), 2923 (s), 2937 (s), 2972 (s), 2990 (m), 3066 (s), 3086 (s), 3104 (m), 3247 cm^{-1} (w).

Trichloro(hydrido)bis(4-vinylpyridine)silicon (1e): Yield 1.72 g (4.98 mmol, 99.5%). ^{29}Si CP/MAS NMR: δ_{iso} = –168.2 ppm. ^{13}C CP/MAS NMR: δ_{iso} = 119.5, 126.5, 129.1, 131.5, 145.5, 149.7 ppm. IR (Raman): $\tilde{\nu}$ = 222 (w), 248 (m), 290 (w), 318 (m), 398 (w), 444 (w), 473 (w), 640 (w), 666 (m), 757 (w), 811 (m), 848 (w), 947 (w), 984 (w), 1003 (w), 1025 (m), 1040 (m), 1069 (m), 1127 (w), 1211 (s), 1232 (w), 1259 (w), 1299 (w), 1338 (w), 1419 (m), 1437 (w), 1507 (w), 1548 (w), 1626 (s), [ν(Si–H)] 2111 (w), 2510 (w), 2919 (w), 2994 (w), 3015 (m), 3055 (m), 3084 (m), 3101 cm^{-1} (m).

Bis(4-*tert*-butylpyridine)trichloro(hydrido)silicon (1f): Yield 1.95 g (4.8 mmol, 96.1%). ^{29}Si CP/MAS NMR: δ_{iso} = –170.0 ppm. ^{13}C CP/MAS NMR: δ_{iso} = 29.9, 31.5, 37.0, 120.4, 123.0, 124.7, 145.2, 147.8, 167.1 ppm. IR (Raman): $\tilde{\nu}$ = 443 (m), 478 (w), 550 (w), 574 (w), 666 (m), 735 (m), 845 (w), 930 (w), 987 (w), 1035 (m), 1070 (m), 1129 (m), 1204 (m), 1234 (m), 1254 (w), 1276 (w), 1334 (w), 1370 (w), 1398 (w), 1447 (m), 1467 (m), 1505 (w), 1548 (w), 1625 (s), 1944 (w), [ν(Si–H)] 2128 (m), 2468 (w), 2718 (w), 2786 (w), 2866 (m), 2906 (s), 2935 (s), 2969 (m), 2978 (s), 3050 (m), 3079 (s), 3110 cm^{-1} (m).

Trichlorobis[4-(dimethylamino)pyridine](hydrido)silicon (1g): THF was used instead of toluene. To a solution of 4-(dimethylamino) pyridine in 20 mL of THF trichlorosilane was added dropwise. Yield 1.85 g (4.87 mmol, 97.4%). ^{29}Si CP/MAS NMR: δ_{iso} = –172.0 ppm. ^{13}C CP/MAS NMR: δ_{iso} = 39.2, 105.2, 143.8, 146.2, 155.2 ppm. IR (Raman): $\tilde{\nu}$ = 236 (m), 316 (m), 425 (m), 496 (w), 524 (w), 558 (w), 644 (w), 663 (m), 745 (w), 768 (s), 812 (w), 951 (m), 1018 (m), 1072 (s), 1134 (w), 1195 (w), 1237 (m), 1309 (m), 1348 (w), 1425 (m), 1445 (m), 1480 (m), 1554 (m), 1632 (m), 1927 (w), [ν(Si–H)] 2061 (m), 2094 (w), 2309 (m), 2543 (w), 2612 (w), 2824 (m), 2869 (m), 2929 (s), 3012 (m), 3094 cm^{-1} (s).

Trichloro(hydrido)bis(4-phenylpyridine)silicon (1h): Yield 2.21 g (4.95 mmol, 99%). ^{29}Si CP/MAS NMR: δ_{iso} = –165.6 ppm. ^{13}C CP/MAS NMR: δ_{iso} = 123.1, 129.4, 135.5, 143.6, 148.4, 154.9 ppm. IR (Raman): $\tilde{\nu}$ = 240 (m), 285 (w), 303 (w), 322 (w), 359 (w), 396 (w), 448 (w), 558 (w), 619 (w), 666 (w), 765 (m), 850 (w), 1000 (m), 1016 (m), 1035 (m), 1076 (m), 1160 (w), 1181 (w), 1231 (m), 1599 (s), 1625 (s), [ν(Si–H)] 2092 (w), 2496 (w), 2572 (w), 2918 (w), 3063 cm^{-1} (s).

CCDC-689839 (for **1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

---

[1] a) O. Bechstein, B. Ziemer, D. Hass, S. I. Troyanov, V. B. Rybakov, G. N. Maso, *Z. Anorg. Allg. Chem.* **1990**, *582*, 211–216; b) K. Hensen, R. Mayr-Stein, B. Spangenberg, M. Bolte, S. Ruhl, *Z. Naturforsch., Teil B* **2000**, *55*, 248–252; c) K. Hensen, R. Mayr-Stein, B. Spangenberg, M. Bolte, *Acta Crystallogr., Sect. C* **2000**, *56*, 610–613; d) S. E. Denmark, B. M. Eklov, *Chem. Eur. J.* **2008**, *14*, 234–239.

[2] a) A. B. Burg, *J. Am. Chem. Soc.* **1954**, *76*, 2674–2675; b) H. J. Campell-Fergusson, E. A. V. Ebsworth, *J. Chem. Soc. A* **1966**, 1508–1514; c) H. J. Campell-Fergusson, E. A. V. Ebsworth, *J. Chem. Soc. A* **1967**, 705–712; d) U. Wannagat, K. Hensen, P. Petesch, *Monatsh. Chem.* **1967**, *98*, 1407–1414; e) E. A. Batyaev, N. P. Kharitonov, *Zh. Obshch. Khim.* **1973**, *43*, 444–445; f) W. Wolfsberger, *Chem.-Ztg.* **1985**, *109*, 227–228; g) S.-B. Choi, B.-K. Kim, P. Boudjouk, D. G. Grier, *J. Am. Chem. Soc.* **2001**, *123*, 8117–8118.

[3] U. Wannagat, K. Hensen, P. Petesch, F. Vielberg, *Monatsh. Chem.* **1967**, *98*, 1415–1422.

[4] P. Boudjouk, S. D. Kloos, B. K. Kim, M. Page, D. Thweatt, *J. Chem. Soc., Dalton Trans.* **1998**, 877–879.

[5] G. W. Fester, J. Wagler, E. Brendler, U. Böhme, G. Roewer, E. Kroke, *Chem. Eur. J.* **2008**, *14*, 3164–3176.

[6] J. P. Kintzinger, C. Marsmann, *NMR-Basic Principles and Progress*, vol. 17, Springer Verlag, Berlin, Heidelberg, New York, **1981**.

[7] R. Löwer, M. Vongehr, H. C. Marsmann, *Chem.-Ztg.* **1975**, *99*, 33.

[8] M. Brehm, B. S. Ault, *J. Mol. Struct.* **2003**, *649*, 95–103.

[9] K. Hensen, T. Stumpf, M. Bolte, C. Näther, H. Fleischer, *J. Am. Chem. Soc.* **1998**, *120*, 10402–10408.

[10] K. Hensen, M. Kettner, T. Stumpf, M. Bolte, *Z. Naturforsch., Teil B* **2000**, *55*, 901–906.

[11] B. Gostevskii, G. Silbert, K. Adear, A. Sivaramakrishna, D. Stalke, S. Deuerlein, N. Kocher, M. Voronkov, I. Kalikhman, D. Kost, *Organometallics* **2005**, *24*, 2913–2920.

[12] D. Kost, V. Kingston, B. Gostevskii, A. Ellern, D. Stalke, B. Walfort, I. Kalikhman, *Organometallics* **2002**, *21*, 2293–2305.

Received: August 22, 2008
Published Online: September 30, 2008