

First X-Ray Structure of a Cationic Silicon Complex with Salen-Type Ligand: An Unusual Compound with Two Different Si-N Dative Bonds

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Z. Naturforsch. **59b**, 1348 – 1352 (2004); received August 12, 2004

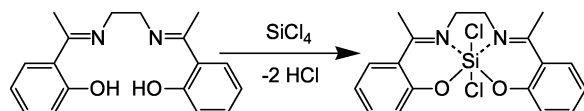
Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Two novel compounds containing pentacoordinate alkylsiliconium-cations with an $\langle O, N, N, O \rangle$ -chelating ligand of salen-type were prepared by reacting the trimethylsilyl derivatives of the ligand with alkyltrichlorosilanes. Pentacoordination of the silicon atom is found in solid state as well as in solution. Crystals of compound **2a**, ethylene- N, N' -bis(2-oxy-4-methoxybenzophenoneiminato)methylsiliconium chloride, were obtained from chloroform solution. This complex crystallizes in monoclinic space group $P2_1/n$. The chloride ion is surrounded by three chloroform molecules in the solid state. The siliconium cation has trigonal bipyramidal geometry in the solid state, although the signals of two chemically equal half-sides of the salen-type ligand were revealed in ^1H and ^{13}C NMR spectra of its chloroform solution. Therefrom two different Si-N dative bonds within the same molecule arise. The reaction of methyltrichlorosilane with two non-linked “half-ligands” of the salen-type leads also to a siliconium complex with similar cationic coordination sphere motif.

Key words: Chelates, Hypercoordination, Pentacoordinate, Schiff Base, Silicon

Introduction

Hypercoordinate silicon salen complexes result if various chlorosilanes are reacted with protonated salen-type ligands, *e.g.* ethylene- N, N' -bis(2-hydroxyacetophenoneimine) [1, 2] (Scheme 1). Its complexes with hexacoordinate silicon atoms were isolated and characterized by means of ^{29}Si NMR spectroscopy.

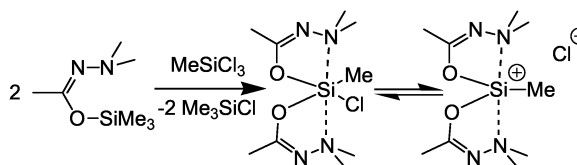


Scheme 1.

Starting from organotrichlorosilanes, those ligand precursors lead to products which show ^{29}Si NMR shift values typical for pentacoordinate silicon atoms in the solid state. Surprisingly, the solutions of these complexes in DMSO show chemical shifts in the characteristic region of hexacoordinate silicon atoms. Unfortunately, our attempts to crystallize these complexes failed. Unlike these results, we recently synthesized

pentacoordinate silicon complexes with enamine functionalized salen-type ligands. In these cases, the coordination spheres of these complexes are not significantly influenced by solvents like DMSO [3].

Kost *et al.* have proven the formation of pentacoordinate alkylsiliconium cations with bidentate $\langle N, O \rangle$ -donor ligands (Scheme 2) [4].



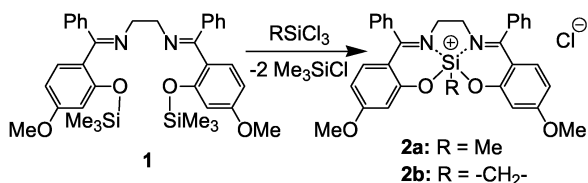
Scheme 2.

Such cationic complexes show interesting temperature-dependent dissociation characteristics in solution. Furthermore they reveal unexpected reactivities. Referring to these results, we suppose that our pentacoordinate silicon salen complexes should have a similar cationic structure. This hypothesis led to the question how a tetradentate chelating salen-type ligand could

dominate the coordination sphere of such a cationic complex.

Results and Discussion

The trimethylsilyl derivative **1** of the tetradentate ligand ethylene-*N,N'*-bis(2-hydroxy-4-methoxybenzophenoneimine) was reacted with methyltrichlorosilane and 1,2-bis(trichlorosilyl)ethane, respectively, in toluene (Scheme 3). Both reactions yielded products involving a pentacoordinate silicon atom, in the solid state as well as in chloroform solution. Fortunately, compound **2a** formed suitable crystals for X-ray structure analysis [5]. Its molecular structure, selected bond lengths and angles are given in Fig. 1.



Scheme 3.

The pentacoordinate silicon atom of the siliconium cation has a trigonal bipyramidal coordination sphere with one nitrogen and one oxygen atom in axial positions. The axial Si-N bond is significantly longer (1.937 Å) than the equatorial one (1.846 Å). This is a typical situation arising from axial and equatorial bonds to atoms of the same kind of donor within a trigonal bipyramidal coordination polyhedron. The different Si-N bond lengths remarkably influence the distances of the imine C=N bonds: the imine C=N bond at the axially situated nitrogen atom represents a typical CN double bond (N1-C7: 1.298 Å), but at the equatorially situated nitrogen atom, it is remarkably stretched (N2-C22: 1.327 Å). Owing to the tetradentate ligand's restricted flexibility, equal Si-O as well as Si-N bonds are not achieved within the trigonal bipyramidal coordination sphere in the solid state. However in CDCl₃ solution NMR spectra, we found only one set of ¹H and ¹³C NMR signals, respectively, corresponding to chemical identity of both half-sides of the salen-type ligand. Thus, we have to conclude that there is either only a small activation barrier regarding the configurational inversion process of the trigonal bipyramid or we have to take into account that a square planar coordination of the silicon atom is preferred in solution. Referring to the nearly identical ²⁹Si chemical shifts in the solid state of **2a**·3 CHCl₃ (−103.6 ppm) and in

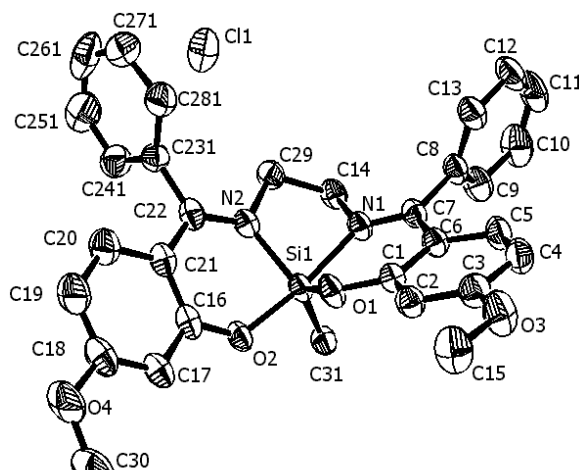


Fig. 1. Molecular structure of **2a** in the crystal (ORTEP plot with 50% probability ellipsoids, hydrogen atoms and chloroform molecules omitted for clarity). The phenyl group C23–C28 is disordered, only one position is shown in the figure. Selected bond lengths [Å] and angles [°]: Si1–N1 1.937(2), Si1–N2 1.846(2), Si1–O1 1.664(2), Si1–O2 1.730(2), Si1–C31 1.848(3), N1–C7 1.298(3), N2–C22 1.327(3), N1–Si1–O2 172.7(1), O1–Si1–N2 115.8(1), C31–Si1–N2 121.6(1), O1–Si1–C31 122.4(1).

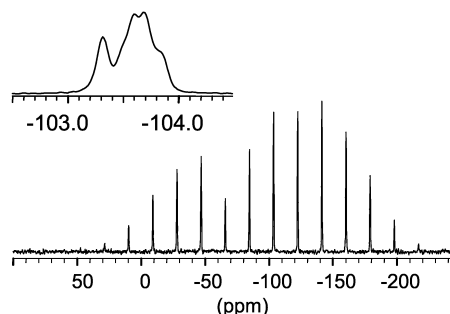
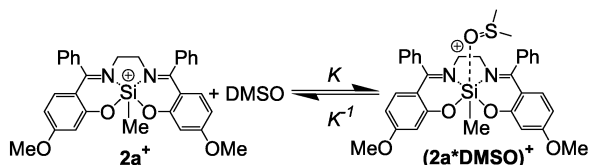


Fig. 2. ²⁹Si CP/MAS NMR spectrum (79.5 MHz) of **2a**·3 CHCl₃ at $\nu_{\text{spin}} = 1500$ Hz. The isotropic shift signal ($\delta_{\text{av}} = -103.6$ ppm, section top left) as well as the spinning side bands are subdivided due to different ²⁹Si chemical environments caused by disorder of solvent molecules and one phenyl group of molecule **2a**.

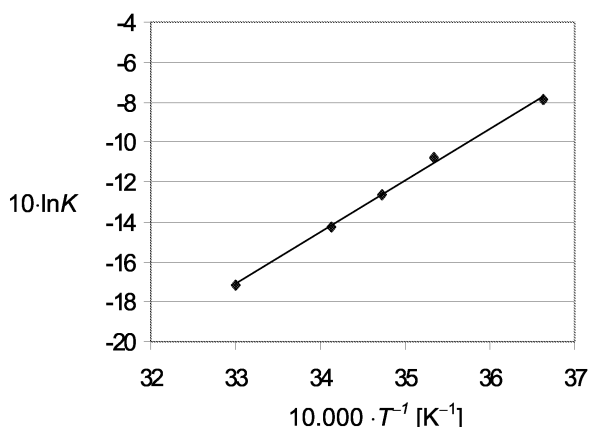
chloroform solution (−103.9 ppm), we assume that the trigonal bipyramidal coordination sphere is realized in solution, too. The complex should have an easily fluctuating configuration. In the solid state the chloride ion is surrounded by three chloroform molecules which are heavily rotationally disordered around the Cl[−]–H–C axes. This disorder influences the ²⁹Si NMR spectroscopic behavior of **2a**·3 CHCl₃ in solid state. The ²⁹Si CP/MAS NMR spectrum of the chloroform solvate is given in Fig. 2. The isotropic shift peak as well as the

Table 1. Results of the variable temperature ^{29}Si NMR study of the solvation of 2a^+ by DMSO.

T [K]	$\delta^{29}\text{Si}$ [ppm]	K
303	-114.0	0.1798
293	-116.6	0.2399
288	-118.3	0.2832
283	-120.3	0.3391
273	-123.9	0.4556



Scheme 4.

Fig. 3. Linearized plot of $\ln K$ versus T^{-1} for the solvation of 2a^+ by DMSO. $\ln K = 2592 \cdot T^{-1} - 10.265$ ($R^2 = 0.998$).

spinning side bands are subdivided into more signals and shoulders.

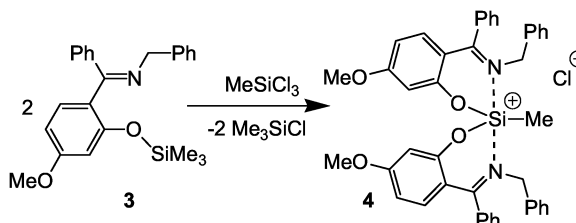
In DMSO solution the siliconium cation 2a^+ is solvated by one DMSO molecule. Hexacoordination of the silicon atom in $(2\text{a} \cdot \text{DMSO})^+$ is proven by ^{29}Si NMR spectroscopy ($\delta^{29}\text{Si} = -159.3$ ppm). But 2a^+ is only weakly solvated by DMSO in chloroform solution. The solvation equilibrium is temperature-dependent. It was analyzed by ^{29}Si NMR spectroscopy of a solution of $0.095 \text{ mol} \cdot \text{l}^{-1}$ 2a and $1.24 \text{ mol} \cdot \text{l}^{-1}$ DMSO in CDCl_3 (Table 1). Only one signal emerges in the ^{29}Si NMR spectrum. Its chemical shift value depends on the mole fractions ratio of the unsolvated ($\delta^{29}\text{Si} = -103.9$ ppm) to the solvated ($\delta^{29}\text{Si} = -159.3$ ppm) ion 2a^+ in the equilibrium (Scheme 4). (The concentration of free DMSO molecules remains nearly unchanged in the covered temperature interval.) Thus, the equilibrium constant was calculated for the temperatures listed in Table 1. The plot of $\ln K$ versus T^{-1}

gives the values of ΔH and ΔS of the solvation process (Fig. 3).

This NMR study is practicable only down to 0°C owing to crystallization of DMSO at lower temperatures. However, already in this small temperature interval our spectroscopic results clearly indicate that the solvation of the siliconium cation 2a^+ by DMSO represents an exothermic process ($\Delta H = -21.6 \text{ kJ} \cdot \text{mol}^{-1}$). The negative value of the solvation entropy ($\Delta S = -85.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) monitors that the hexacoordinate silicon complex $(2\text{a} \cdot \text{DMSO})^+$ undergoes a dissociation at higher temperature. Any competitive complexation of 2a^+ by the chloride ion may be excluded since Kost *et al.* have proven that the ionic dissociation of hypercoordinate siliconium chlorides in chloroform is promoted at lower temperatures [4].

Complex 2b is easily soluble in chloroform, too. In spite of being a dication, there is no significant interaction with the counterions in solution, as indicated by ^{29}Si NMR chemical shift (-104.5 ppm) similar to that one of 2a . Even in this case of a more sterically encumbered coordination sphere due to the short Si-ethylene-Si bridge, only one set of ^1H and ^{13}C NMR signals is observed, which should be related to spectroscopically identical half-sides of the chelating ligand. The ^{13}C NMR spectra of 2a and 2b show 12 signals of aromatic carbon atoms. The rotation of the phenyl groups at the imine C-atom causes diastereotopic *ortho* and *meta* positions at these ring systems. Therefore, 16 instead of 14 ^{13}C NMR signals of these complexes are observed. The same effect was reported to occur in hexacoordinate silicon complexes with ligand **1** [6].

The donor strength of a chelating ligand applied to a silicon center is expected to be the key in the formation of such pentacoordinate siliconium cations [7]. Therefore, we checked the reaction of two non-linked “half-ligands” of the salen-type with methyltrichlorosilane (Scheme 5). The replacement of the tetradentate ligand’s ethylene bridge by two benzyl groups gives rise to a gain in flexibility of the ligand system. But this



Scheme 5.

does not suppress the ionic dissociation of the resulting complex **4**. Its ^{29}Si NMR shift value (-100.1 ppm) clearly indicates pentacoordination of the silicon atom.

Unfortunately, we did not succeed in growing suitable crystals of **4**. However, the comparison with similar complexes, which also contain two bidentate chelating ligands [4, 8] allows the conclusion that **4** should be featured with two similarly coordinating bidentate ligands having their Si-N bonds preferably situated in axial position of a trigonal bipyramidal coordination sphere. The ^{13}C NMR spectrum of **4** has 16 signals in the aromatic region. The rotation of the phenyl groups at the imine C-atom causes diastereotopic *ortho* and *meta* positions at these ring systems, too. Therefore, 20 instead of 18 ^{13}C NMR signals of **4** are observed.

Singh *et al.* [9] published a route to synthesize hypercoordinate methylsilicon complexes with salen-type ligands, *e.g.* (salen)SiMeCl with hexacoordinate silicon atoms, even in chloroform solution. But they did not give any X-ray structural evidence concerning the isolated products. Our results are in strong contrast to the structural proposals of these authors. Even the doubtful use of isopropanol for the handling of chlorosilanes by Singh *et al.* does not go along with our observations. The siliconium chlorides presented herein are very sensitive towards alcoholysis.

Conclusion

We presented the first example of a pentacoordinate siliconium cation with a tetradentate salen-type ligand, structurally confirmed by X-ray analysis. In spite of the NMR-spectroscopic identity of both half-sides of the ligand in solution different Si-N dative bonds are formed in the solid state to give a trigonal bipyramidal coordination sphere around the silicon atom. Starting from two bidentate $\langle O, N \rangle$ ligands plus methyltrichlorosilane, a siliconium complex with similar coordination sphere can be synthesized.

Experimental Section

All chemicals were commercially available. **1** and **3** were prepared according to a previously published method [10]. All following manipulations were carried out under an inert atmosphere of dry argon. Toluene and THF were distilled from sodium/benzophenone prior to use. Triethylamine was distilled from calcium hydride and stored over molecular sieve 3 Å. Chloroform (stabilized with amylene) was dried over molecular sieve 3 Å. NMR spectra were recorded on a BRUKER DPX 400 (CDCl_3 solution with TMS as inter-

nal standard) and a BRUKER Avance 400WB spectrometer (solid state). Elemental analyses were carried out on a Foss Heraeus CHN-O-Rapid.

2a: A Schlenk-flask was charged with THF (150 ml), ligand **1** (11.4 g, 23.8 mmol) and triethylamine (5.7 g, 56 mmol). The mixture was stirred at room temperature and trimethylchlorosilane (5.37 g, 49.5 mmol) was added dropwise. The resulting colorless suspension was stirred for further 15 minutes. The precipitated triethylamine hydrochloride was filtered off and washed with THF. Removal of the solvents from the filtrate under reduced pressure yielded a slightly yellowish colored oil, which was dissolved in toluene (150 ml) to give a clear solution. Methyltrichlorosilane (3.6 g, 24 mmol) was added at room temperature and the mixture was heated afterwards. Soon, a white solid precipitated. The suspension was refluxed for 2 h and stored at room temperature for 3 days. The precipitated product was filtered off, washed with toluene as well as pentane and dried in vacuum. Yield: 11.90 g (90%) white powder. It decomposes without melting. $\text{C}_{31}\text{H}_{29}\text{N}_2\text{O}_4\text{SiCl}$ (557.12): calcd. C 66.83, H 5.25, N 5.03; found C 66.51, H 5.51, N 4.98.

The chloroform solvate **2a**·3 CHCl_3 (colorless crystals) was obtained by recrystallization from chloroform.

^1H NMR (400 MHz, CDCl_3): δ = 0.86 (s, 3, Si- CH_3), 3.58, 4.37 (2 \times m, 4, N- CH_2CH_2 -N), 3.91 (s, 6, - OCH_3), 6.48 (dd, 2, ar, 3J = 9.2 Hz, 4J = 2.4 Hz), 6.64 (d, 2, ar, 4J = 2.4 Hz), 6.84 (d, 2, ar, 3J = 9.2 Hz), 7.35–7.75 (m, 10, phenyl). – ^{13}C NMR (101 MHz, CDCl_3): δ = 4.3 (Si- CH_3), 48.1 (N- CH_2CH_2 -N), 56.2 (- OCH_3), 103.9, 111.0, 112.5, 127.2, 127.5, 129.2, 129.6, 130.9, 132.4, 135.2 (ar), 162.9, 168.3 (ar O-C), 177.4 (C=N). – ^{29}Si NMR (79.5 MHz, CDCl_3): δ = -103.9 ; (79.5 MHz, DMSO- d_6): δ = -159.3 ; (79.5 MHz, solid state) δ_{iso} = -103.6 . – $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_4\text{SiCl}_{10}$ (915.25): calcd. C 44.62, H 3.52, N 3.06; found C 45.28, H 3.69, N 3.17.

2b: Analogous procedure as for the synthesis of **2a**. Yield: 86%, pale yellow powder. It decomposes without melting.

^1H NMR (400 MHz, CDCl_3): δ = 1.53 (s, 4, Si- CH_2 -), 3.32, 4.57 (2 \times m, 8, N- CH_2CH_2 -N), 3.90 (s, 12, - OCH_3), 6.48 (dd, 4, ar, 3J = 9.2 Hz, 4J = 2.4 Hz), 6.64 (d, 4, ar, 4J = 2.4 Hz), 6.77 (d, 4, ar, 3J = 9.2 Hz), 7.15–7.60 (m, 20, phenyl). – ^{13}C NMR (101 MHz, CDCl_3): δ = 14.5 (Si- CH_2 -), 49.0 (N- CH_2CH_2 -N), 56.4 (- OCH_3), 103.8, 111.0, 112.5, 127.0, 127.8, 129.1, 129.5, 131.0, 132.5, 135.1 (ar), 163.1, 168.4 (ar O-C), 177.8 (C=N). – ^{29}Si NMR (79.5 MHz, CDCl_3): δ = -104.5 . – $\text{C}_{62}\text{H}_{56}\text{N}_4\text{O}_8\text{Si}_2\text{Cl}_2$ (1112.22): calcd. C 66.95, H 5.07, N 5.04; found C 66.92, H 5.21, N 4.82.

4: A Schlenk flask was charged with THF (100 ml), **3** (3.0 g, 16 mmol) and triethylamine (2.0 g, 17 mmol). Chlorotrimethylsilane (1.8 g, 17 mmol) was added dropwise to the stirred mixture at room temperature. After 2 h, the precipitated hydrochloride was filtered off and washed with

THF (30 ml). The solvent of the filtrate was removed under reduced pressure to give an oily liquid. This was dissolved in toluene (100 ml), methyltrichlorosilane (1.20 g, 8.03 mmol) was added and the mixture was refluxed for 1 h. The resulting suspension was stored at room temperature overnight. The precipitated product was filtered off, washed with toluene (20 ml) and dried in vacuum. Yield: 2.50 g (45%) white powder. M.p. 177 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.00 (s, 3, Si-CH₃), 4.82, 5.09 (2 × d, 4, N-CH₂-Ph, $^2J_{\text{HH}}$ = 15.6 Hz), 3.49 (s, 6, -OCH₃), 5.49 (d, 2, ar, 4J = 2.4 Hz), 6.45 (dd, 2, ar, 3J = 9.2 Hz, 4J = 2.4 Hz), 6.71 (d, 2, ar, 3J = 9.2 Hz), 6.70–7.65 (m, 20, phenyl). ^{13}C NMR (101 MHz, CDCl_3): δ = 4.6 (Si-CH₃), 54.6 (N-CH₂-Ph), 56.1 (-OCH₃), 103.6,

111.5, 113.1, 125.9, 126.7, 126.9, 127.3, 128.4, 128.5, 129.2, 130.3, 132.2, 135.4, 137.6 (ar), 158.8, 167.3 (ar O-C), 178.4 (C=N). – ^{29}Si NMR (79.5 MHz, CDCl_3): δ = –100.1. – $\text{C}_{43}\text{H}_{39}\text{N}_2\text{O}_4\text{SiCl}$ (711.33): calcd. C 72.61, H 5.53, N 3.94; found C 72.20, H 5.77, N 3.78.

Acknowledgements

This work was financially supported by The German Science Foundation (DFG) and the German Chemical Industry Fund. We kindly acknowledge the X-ray structure analysis of **2a** by Prof. Dr. Joachim Sieler, Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig (Germany).

- [1] F. Mucha, J. Haberecht, U. Böhme, G. Roewer, *Monatsh. Chem.* **130**, 117 (1999).
- [2] F. Mucha, U. Böhme, G. Roewer, *Chem. Commun.* 1289 (1998).
- [3] a) J. Wagler, U. Böhme, G. Roewer, *Angew. Chem.* **114**, 1825 (2002); *Angew. Chem. Int. Ed.* **41**, 1732 (2002); b) J. Wagler, U. Böhme, G. Roewer, in N. Auner, J. Weis (eds): *Organosilicon Chemistry V – From Molecules to Materials*, p. 317–320, VCH, Weinheim (2003).
- [4] a) D. Kost, B. Gostevskii, N. Kocher, D. Stalke, I. Kalikhman, *Angew. Chem.* **115**, 1053 (2003); *Angew. Chem. Int. Ed.* **42**, 1023 (2003); b) D. Kost, V. Kingston, B. Gostevskii, A. Ellern, D. Stalke, B. Walfort, I. Kalikhman, *Organometallics* **21**, 2293 (2002); c) I. Kalikhman, O. Girshberg, L. Lameyer, D. Stalke, D. Kost, *J. Am. Chem. Soc.* **123**, 4709 (2001).
- [5] X-ray data of **2a** were recorded on a Siemens SMART CCD-diffractometer with Mo-K α -radiation. Structure was solved with direct methods, refined with least squares method, all non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in idealized positions and isotropically refined. Structure solution and refinement of F^2 against all reflections with the software SHELXS-97 and SHELXL-97, G. M. Sheldrick, Universität Göttingen, Germany (1986–1997).
Compound **2a**·3 CHCl_3 : $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_4\text{SiCl}_{10}$, M_r = 915.21, colorless crystal, $0.3 \times 0.3 \times 0.2$ mm, a = 13.068(2), b = 18.649(3), c = 16.987(3) Å, β = 90.000(3)°, V = 4139.6(13) Å³, $\rho_{\text{calcd.}}$ = 1.468 g cm^{–3}, $2\theta_{\text{max}}$ = 50°, $F(000)$ = 1864, μ = 0.741 mm^{–1}, absorption correction: multi-scan (SAD-ABS), Z = 4, monoclinic space group $P2_1/n$, λ = 0.71073 Å, T = 213(2) K, 21334 recorded reflections ($-15 \leq h \leq 15$, $-14 \leq k \leq 22$, $-18 \leq l \leq 20$), 7267 independent and 5324 observed reflections with $F_0 > 2\sigma(F_0)$, 647 parameters, R = 0.0531, wR_2 = 0.1127 [$I > 2\sigma(I)$], R = 0.0791, wR_2 = 0.1250 (all data), residual electron density (highest peak and deepest hole) 0.420 and –0.487 e Å^{–3}.
Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC-238013. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
- [6] J. Wagler, T. Doert, G. Roewer, *Angew. Chem.* **116**, 2495 (2004); *Angew. Chem. Int. Ed.* **43**, 2441 (2004).
- [7] I. Kalikhman, B. Gostvskii, O. Girshberg, S. Krivonos, D. Kost, *Organometallics* **21**, 2551 (2002).
- [8] a) J. Belzner, D. Schär, B. O. Kneisel, R. Herbst-Irmer, *Organometallics* **14**, 1840 (1995); b) C. Brelière, F. Carré, R. J. P. Corriu, M. Wong Chi Man, *Chem. Commun.* 2333 (1994); c) J. M. Anglada, C. Bo, J. M. Bofill, R. Crehuet, J. M. Poblet, *Organometallics* **18**, 5584 (1999).
- [9] M. S. Singh, P. K. Singh, *Main Group Met. Chem.* **23**, 183 (2000).
- [10] U. Dinjus, H. Stahl, E. Uhlig, *Z. Anorg. Allg. Chem.* **464**, 37 (1980).