

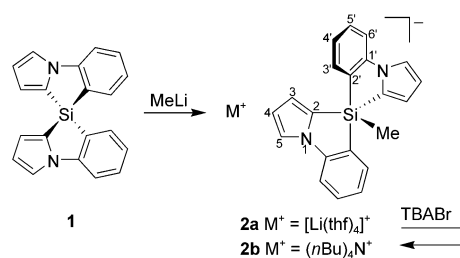
Pentaorganosilicate Pseudorotamers

Dynamic Configurational Isomerism of a Stable Pentaorganosilicate**

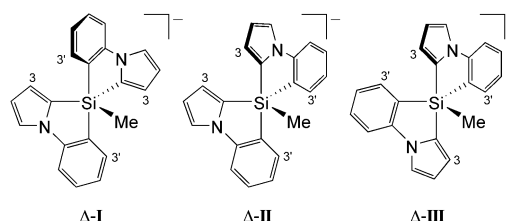
Erik P. A. Couzijn, Marius Schakel,
Frans J. J. de Kanter, Andreas W. Ehlers, Martin Lutz,
Anthony L. Spek, and Koop Lammertsma*

Stable silicates with five carbon substituents are extremely rare.^[1] These pentacoordinate anions often have a trigonal-bipyramidal geometry with three equatorial and two apical sites that should make them prone to configurational isomerism in which the substituent sites interchange. Such a process is known as the Berry pseudorotation mechanism.^[2] However, pseudorotamers other than the energetically preferred species have seldom been observed,^[3] even among the more accessible neutral phosphoranes.^[4] Insight into the thermodynamics of this type of isomerism is even more scarce,^[4c,d] and nonexistent for the silicates. Here we report a new, stable pentaorganosilicate of which different configurational isomers coexist in solution, and present thermodynamic and kinetic data on their interconversion.

The starting material bis(1-phenylpyrrole-2,2'-diyl)silane (**1**) was synthesized in 53% yield (white crystals from ethyl acetate; m.p. 276 °C (decomp)) from 2'-bromo-1-phenylpyrrole in diethyl ether by treatment with 2 equivalents of butyllithium (0 °C) and 0.5 equivalents SiCl₄ (reflux).^[5] Reaction of **1** with methyllithium in THF at –78 °C afforded a pale yellow solution of lithium silicate **2a** (Scheme 1), as indicated by the upfield shift of the ²⁹Si NMR signal from $\delta = -35$ to –131 ppm. The NMR spectra were recorded at –50 °C to minimize signal broadening (see below). Compound **2a** was fully characterized by ¹H NMR, ¹³C NMR, HMQC, and HMBC spectroscopic measurements. The silicate anion can potentially adopt three configurations **I–III**,^[6] which differ in the orientation of the bidentate substituents. The ¹H and ¹³C NMR spectra revealed twofold symmetry, while the 2D NOESY^[7] spectrum showed correlations between H3' and H3



Scheme 1. Synthetic route to silicate salts **2a** and **2b**.



as well as between H3' and the methyl group. Only geometry **I** is compatible with these observations (Table 1). Furthermore, the $J_{C_2, Si}$ value of 86 Hz is similar to that of a typical Si(sp²)–C(sp²) bond,^[8a] while the $J_{C_2, Si}$ value of 30 Hz is much smaller than that of a Si(sp³)–C(sp²) bond (64–70 Hz)^[8b] and reflects the small silicon s character of the apical bonds.

Table 1: H...H distances [Å] for the pseudorotamers of **2** calculated with B3LYP/6-31G(d).

	H3...H3'	H3...Me ^[b]	H3'...Me ^[b]
I	2.69	4.31–4.76	2.60–3.30
II ^[a]	6.05 eq–eq	4.41–4.79 eq	4.02–4.42 eq
	6.82 ap–ap	3.11–3.64 ap	2.51–3.07 ap
III	2.66	2.85–3.57	4.03–4.49

[a] Equatorial(eq) and apical (ap) H3 (H3') interactions are listed separately. [b] Minimum and maximum distances, depending on the rotation of the methyl group.

Ion exchange with tetrabutylammonium bromide (TBABr) in THF enabled near-quantitative isolation of silicate **2b** as a moisture-sensitive white solid (m.p. > 160 °C (decomp)). Studies by NMR spectroscopy in DMF gave results comparable to those of **2a**. X-ray crystal-structure determination of **2b** (from DMF) confirmed the geometry (Figure 1).^[9] The centrosymmetric crystal contained Δ -**I** and Λ -**I** in a 1:1 ratio.^[10] The trigonal-bipyramidal coordination environment around the pentacoordinate silicon atom is distorted by 16% towards square-pyramidal along the Berry pseudorotation coordinate.^[11] The observed bond lengths are in good accordance with those of previously reported pentaorganosilicates,^[1c,d,12] the apical Si–C bonds being distinctly longer than the equatorial bonds. There are no close contacts with the ammonium cation, which is disordered in one butyl chain.

We expected the apical-site preferences of the phenyl and pyrrole moieties to be very similar. This led us to the presumption that minor quantities of conformers **II** and **III**

[*] E. P. A. Couzijn, Dr. M. Schakel, Dr. F. J. J. de Kanter, Dr. A. W. Ehlers, Prof. Dr. K. Lammertsma
Department of Chemistry, Faculty of Sciences
Vrije Universiteit, De Boelelaan 1083
1081 HV Amsterdam (The Netherlands)
Fax: (+31) 20-44-47488
E-mail: lammert@chem.vu.nl

Dr. M. Lutz, Prof. Dr. A. L. Spek
Bijvoet Center for Biomolecular Research,
Crystal and Structural Chemistry
Utrecht University, Padualaan 8
3584 CH Utrecht (The Netherlands)

[**] This work was supported by the Netherlands Foundation for Chemical Sciences (CW) with financial aid from the Netherlands Organization for Scientific Research (NWO). We thank Prof. G. W. Klumpp for helpful discussions and J. W. H. Peeters of the University of Amsterdam for exact mass determinations.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

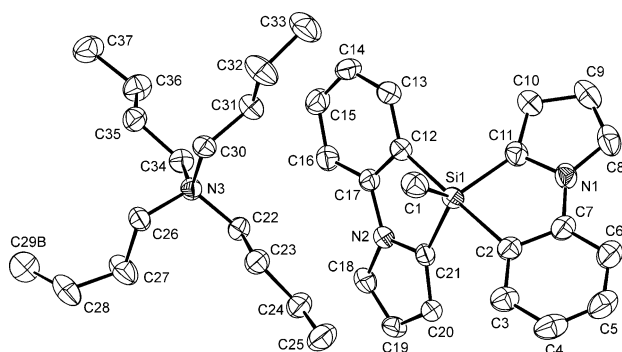


Figure 1. Displacement ellipsoid plot (50% probability) of **2b**. Hydrogen atoms are omitted for clarity. Only the major conformation of the disordered *n*-butyl group is shown. Selected bond lengths [Å] and angles [°]: Si-C1 1.903(2), Si-C2 2.024(2), Si-C11 1.909(2), Si-C12 2.026(2), Si-C21 1.9093(19); C1-Si-C2 93.95(9), C1-Si-C11 118.51(9), C1-Si-C12 93.31(9), C1-Si-C21 117.25(9), C2-Si-C11 82.97(9), C2-Si-C12 172.72(8), C2-Si-C21 92.92(8), C11-Si-C12 94.03(8), C11-Si-C21 124.23(8), C12-Si-C21 83.26(8)

might be present in solution. By using a concentrated solution of **2a**, an additional ^{13}C resonance was found in the NMR spectrum at $\delta = 9.3$ ppm, which was correlated to a methyl ^1H signal at $\delta = 0.36$ ppm with an intensity of 6% relative to the main silicate. The ^{29}Si INEPT spectrum also revealed a small but distinct extra signal at $\delta = -128$ ppm. We subsequently applied $^1\text{H}, ^{29}\text{Si}$ ge-HMQC as a very sensitive 2D NMR technique^[13] to detect and characterize the silicates. The spectra not only showed the methyl and pyrrole groups of the minor silicate (Figure 2), but even suggested a third pyrrole-

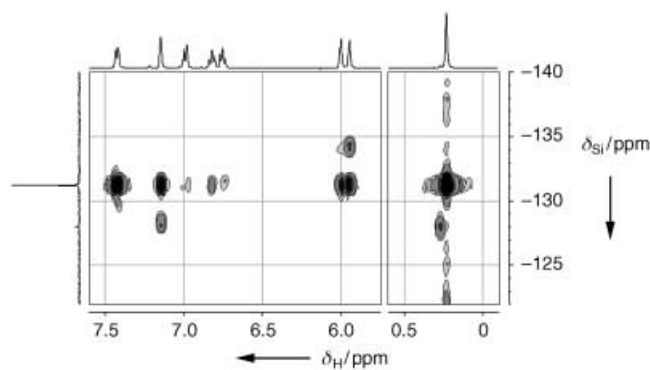


Figure 2. $^1\text{H}, ^{29}\text{Si}$ ge-HMQC spectrum of 0.33 M **2a** (THF/ C_6D_6 , -50°C ; optimized for $J = 2.25$ Hz; ^1H and ^{29}Si INEPT spectra are displayed along the axes)

containing silicate at $\delta = -134$ ppm in an even smaller amount. Unfortunately, no distinctly resolved proton signals could be associated with the latter compound.^[15]

If the minor silicate at $\delta = -128$ ppm is indeed **II** or **III**, it should be able to interchange with **I** by Berry pseudorotation. Barriers for such processes are generally about 9–14 kcal mol $^{-1}$,^[14,1a] which can be readily overcome at room temperature and thus lead to line broadening and coalescence phenomena. Indeed, the extra ^{29}Si correlations vanished at 25°C and reappeared upon cooling again to -50°C . Similar

behavior was observed for a solution of **2b** in DMF. Exchange was also indicated by broadening of various ^{13}C resonances at 25°C , particularly that for the methyl carbon atom; the aromatic signals narrowed again at 90°C . The extra ^1H signal also disappeared at room temperature, but the main resonance of the methyl protons resonance of pseudorotamer **I** did not broaden significantly. This is a consequence of its abundance, as confirmed by dynamic NMR simulations. Hence, we carried out ^1H magnetization-transfer experiments^[16] at -25°C , at which temperature both methyl signals are still separated, thus indicating that exchange is slow on the NMR timescale. Substantial magnetization transfer indeed occurred from the major ($\delta_{\text{H}} = 0.32$ ppm, **I**) to the minor ($\delta_{\text{H}} = 0.36$ ppm) resonance on increasing the mixing time from 10 ms to 0.5 s. This unequivocally demonstrates interchange between **I** ($\delta_{\text{Si}} = -131$ ppm) and the minor silicate ($\delta_{\text{Si}} = -128$ ppm).

Thermodynamic and kinetic parameters for the exchange process were determined by lineshape analysis for the methyl regions of ^{13}H NMR spectra in the temperature range from -36 to 0°C . A plot of $\ln K$ versus temperature displayed excellent linear behavior and gave an energy difference between the pseudorotamers of $\Delta G_{258} = 1.66(6)$ kcal mol $^{-1}$. The Eyring plot gave an activation barrier of $\Delta G_{258}^\ddagger = 15.5(5)$ kcal mol $^{-1}$ for pseudorotation of the major to the minor isomer. These values are in very good agreement with B3LYP/6-31G(d) calculations,^[17] which indicated that **I** is more stable than **II** (+1.8 kcal mol $^{-1}$), with an overall barrier of 15.0 kcal mol $^{-1}$ (**I** \rightarrow **III** \rightarrow **II**). On this basis we assign configuration **II** to the silicate with a ^{29}Si NMR resonance at $\delta = -128$ ppm. The similar temperature behavior of the $^1\text{H}, ^{29}\text{Si}$ correlation at $\delta = -134$ ppm makes us speculate that it might originate from the third pseudorotamer. The calculated relative energy of **III** (+2.6 kcal mol $^{-1}$) would be consistent with a rather low abundance, since its pseudorotation barrier is also modest (12.1 kcal mol $^{-1}$).

In conclusion, silicate pseudorotamers have been observed in dynamic equilibrium for the first time. This allowed the determination of the thermodynamics and kinetics of the Berry pseudorotation mechanism involved. The reported pentaorganosilicate also gives more insight into the stabilizing factors of these very rare anions.

Experimental Section

1: *n*-Butyllithium (16 mmol) was added slowly to a solution of 1-(2'-bromophenyl)pyrrole (8 mmol) in diethyl ether (15 mL) at 0°C . The yellow solution was treated with tetrachlorosilane (4 mmol), and the resulting suspension was heated at reflux for 4 h. Acidic aqueous workup, extraction, and evaporation of the solvent afforded crude **1**, which was recrystallized from ethyl acetate in 52% yield. M.p. 275.7 – 279.6°C (minor decomp); ^1H NMR (CDCl_3): $\delta = 7.54$ (dd, 2H, $^3J_{\text{H,H}} = 2.6$, $^4J_{\text{H,H}} = 0.9$ Hz, H5), 7.47 (td, 2H, $^3J_{\text{H,H}} = 7.6$, $^4J_{\text{H,H}} = 1.3$ Hz, H5'), 7.41–7.40 (m, 4H, H6/H3'), 7.07 (td, 2H, $^3J_{\text{H,H}} = 7.2$, $^2J_{\text{H,H}} = 0.9$ Hz, H4'), 6.58 (dd, 2H, $^3J_{\text{H,H}} = 3.3$, $^4J_{\text{H,H}} = 0.9$ Hz, H3), 6.46 ppm (t, 2H, $^3J_{\text{H,H}} = 3.0$ Hz, H4); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 148.8$ (C1'), 135.2 (C3'), 132.2 (C5'), 124.8 (C4'), 124.4 (C2'), 123.8 (C2), 120.7 (C3), 119.2 (C5), 114.5 (C4), 111.8 ppm (C6); $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (CDCl_3 , $^3J_{\text{H,Si}} = 4.5$ Hz, 4H): $\delta = -35$ ppm; HR FAB-MS: found: 311.1009; calcd for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{Si}$ [$M+H$] $^+$: 311.1005.

2a: Methyllithium (0.144 mmol) was added to a solution of **1** (0.138 mmol) in THF (1.0 mL) at -78°C . After stirring the mixture for 30 min, the pale yellow solution of **2a** was warmed to room temperature. $^1\text{H NMR}$ (THF/[D₈]THF, -50°C): $\delta = 7.51$ (d, 2H, $^3J_{\text{H,H}} = 6.4$ Hz, H3'), 7.25 (s, 2H, H5), 7.10 (d, 2H, $^3J_{\text{H,H}} = 7.6$ Hz, H6'), 6.92 (t, 2H, $^3J_{\text{H,H}} = 7.0$ Hz, H5'), 6.85 (t, 2H, $^3J_{\text{H,H}} = 6.9$ Hz, H4'), 6.08 (d, 2H, $^3J_{\text{H,H}} = 2.4$ Hz, H3), 6.04 (t, 2H, $^3J_{\text{H,H}} = 2.6$ Hz, H4), 0.32 ppm (s, 3H, $^2J_{\text{H,Me}} = 7$ Hz, Me); $^{13}\text{C}\{^1\text{H}\}$ NMR (THF/[D₈]THF, -50°C): $\delta = 155.6$ (C2'), $^{13}\text{C}_{\text{Si}} = 30$ Hz), 144.8 (C1'), 139.2 (C2, $^1J_{\text{C,Si}} = 86$ Hz), 132.7 (C3'), 123.9 (C5'), 121.6 (C4'), 118.7 (C3), 113.1 (C5), 110.1 (C4), 108.7 (C6'), 6.1 ppm (Me, $^1J_{\text{C,Si}} = 64$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR ($^2J_{\text{H,Si}} = 7.0$ Hz, 3H, THF/[D₈]THF, -50°C): $\delta = -131$ ppm ($^1J_{\text{Si,C2}} = 86$ Hz, $^1J_{\text{SiMe}} = 64$ Hz, $^1J_{\text{Si,C2}'} = 30$ Hz).

2b: A slightly warmed solution of tetrabutylammonium bromide (0.138 mmol) in THF (1.0 mL) was added to a solution of **2a** in THF at -78°C . The resulting white suspension was warmed to room temperature, precipitated by centrifugation, washed with THF, and dried under vacuum. This afforded **2b** as a white powder in 94% yield, which could be recrystallized from DMF; m.p. $>160^{\circ}\text{C}$ (decomp); $^1\text{H NMR}$ (DMF/[D₇]DMF, -50°C): $\delta = 7.51$ (s, 2H, H5), 7.49 (d, 2H, $^3J_{\text{H,H}} = 6.8$ Hz, H3'), 7.28 (d, 2H, $^3J_{\text{H,H}} = 7.6$ Hz, H6'), 6.95 (t, 2H, $^3J_{\text{H,H}} = 6.8$ Hz, H5'), 6.88 (t, 2H, $^3J_{\text{H,H}} = 6.9$ Hz, H4'), 6.08 (s, 4H, H3/H4), 1.66 (brs, 8H, NCH₂CH₂), 1.29 (m, 8H, CH₂CH₃), 0.89 (t, 12H, $^3J_{\text{H,H}} = 7.3$ Hz, CH₂CH₃), 0.29 ppm (s, 3H, Me). NCH₂ is buried under the solvent peak; $^{13}\text{C}\{^1\text{H}\}$ NMR (DMF/[D₇]DMF, -50°C): $\delta = 156.0$ (C2'), 145.6 (C1'), 139.6 (C2), 133.4 (C3'), 125.3 (C5'), 122.9 (C4'), 119.8 (C3), 115.3 (C5), 111.5 (C4), 110.3 (C6'), 58.4 (NCH₂), 24.1 (NCH₂CH₂), 20.3 (CH₂CH₃), 14.2 (CH₂CH₃), 7.3 ppm (Me); $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR ($^2J_{\text{H,Si}} = 7.0$ Hz, 3H, DMF/[D₇]DMF, -50°C): $\delta = -131$ ppm; HR FAB-MS: found 326.1240; calcd for C₂₁H₁₈N₂Si [M+H]⁺: 326.1239.

Received: October 2, 2003

Revised: March 18, 2004 [Z53006]

Keywords: density functional calculations · hypervalent compounds · isomers · NMR spectroscopy · silicon

- [1] a) A. H. J. F. de Keijzer, F. J. J. de Kanter, M. Schakel, R. F. Schmitz, G. W. Klumpp, *Angew. Chem.* **1996**, *108*, 1183–1184; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1127–1128; b) A. H. J. F. de Keijzer, F. J. J. de Kanter, M. Schakel, V. P. Osinga, G. W. Klumpp, *J. Organomet. Chem.* **1997**, *548*, 1, 29–32; c) S. Deerenberg, M. Schakel, A. H. J. F. de Keijzer, M. Kranenburg, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Commun.* **2002**, 348–349; d) D. Ballweg, X. Liu, I. A. Guzei, R. West, *Silicon Chem.* **2002**, *1*, 57–60.
- [2] R. S. Berry, *J. Chem. Phys.* **1960**, *32*, 933–938.
- [3] a) M. Pülm, R. Willeke, R. Tacke in *Organosilicon Chemistry IV—From Molecules to Materials* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **2000**, pp. 478–488; b) D. Kost, I. Kalikhman, S. Krivonos, R. Bertermann, C. Burschka, R. E. Neugebauer, M. Pülm, R. Willeke, R. Tacke, *Organometallics* **2000**, *19*, 1083–1095.
- [4] a) D. Hellwinkel, W. Krapp, *Chem. Ber.* **1979**, *112*, 292–297; b) S. Kojima, K. Kajiyama, M. Nakamoto, K. Akiba, *J. Am. Chem. Soc.* **1996**, *118*, 12866–12867; c) O. Lösking, H. Willner, H. Oberhammer, J. Grobe, D. L. Van, *Inorg. Chem.* **1992**, *31*, 3423–3427; d) S. Matsukawa, K. Kajiyama, S. Kojima, S. Furuta, Y. Yamamoto, K. Akiba, *Angew. Chem.* **2002**, *114*, 4912–4916; *Angew. Chem. Int. Ed.* **2002**, *41*, 4718–4722, and references therein.
- [5] Analogous to: G. W. H. Cheeseman, S. G. Greenberg, *J. Organomet. Chem.* **1979**, *166*, 139–152.
- [6] Only pseudorotamers **I**, **II**, and **III** are identified as minima in calculations with B3LYP/6-31G(d).

- [7] R. Wagner, S. Berger, *J. Magn. Reson. Ser. A* **1996**, *123*, 119–121.
- [8] a) A. G. Brook, M. A. Brook in *Advances in Organometallic Chemistry*, Vol. 39 (Eds.: F. G. A. Stone, R. West), Academic Press, New York, **1996**, pp. 71–158; b) G. C. Levy, D. M. White, J. D. Cargioli, *J. Magn. Reson.* **1972**, *8*, 280–283.
- [9] Crystal data for **2b**: [C₁₆H₃₆N]₂[C₂₁H₁₇N₂Si], *M_r* = 567.91, colorless block, 0.24 × 0.15 × 0.15 mm, monoclinic, space group *P2₁/c* (no. 14), *a* = 11.0900(2), *b* = 18.5217(3), *c* = 19.5505(3) Å, $\beta = 122.1753(12)^{\circ}$, *V* = 3399.05(10) Å³, *Z* = 4, $\rho_{\text{exptl}} = 1.110$ g cm⁻³, $\mu = 0.097$ mm⁻¹. 35804 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at 150(2) K up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.60$ Å⁻¹; 5991 reflections were unique (*R_{int}* = 0.067); an absorption correction was not considered necessary. The structure was solved with direct methods (SHELXS-97)^[18] and refined with SHELXL-97^[19] against *F²* of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters; H atoms were refined as rigid groups. One *n*-butyl group was refined with a disorder model. 381 refined parameters, 14 restraints. *R* values [*I* > 2σ(*I*): *R*1 = 0.0504, *wR*2 = 0.1231. *R* values (all data): *R*1 = 0.0726, *wR*2 = 0.1357. GOF = 1.029. Residual electron density between -0.25 and 0.37 e Å⁻³. Molecular illustration, structure checking, and calculations were performed with the PLATON package.^[20]
- [10] Δ (Λ) denotes a positive (negative) helicity of the spirocyclic system.
- [11] Assuming a *trans* basal angle of 150° ; see R. R. Holmes, *Prog. Inorg. Chem.* **1984**, *32*, 119–235.
- [12] A. Kolomeitsev, G. Bissky, E. Lork, V. Movchun, E. Rusanov, P. Kirsch, G.-V. Rösenthaller, *Chem. Commun.* **1999**, 1017–1018.
- [13] S. Provera, S. Davalli, G. H. Raza, S. Contini, C. Marchioro, *Magn. Reson. Chem.* **2001**, *39*, 38–42.
- [14] C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371–1448, and references therein.
- [15] Identification of the third silicate is hampered by its low abundance, the absence of resolved ^1H signals, and the inherent NMR insensitivity of C and Si nuclei.
- [16] a) S. Forsen, R. A. Hoffman, *J. Chem. Phys.* **1963**, *39*, 2892–2901; b) J. Stonehouse, P. Adell, J. Keeler, A. J. Shaka, *J. Am. Chem. Soc.* **1994**, *116*, 6037–6038; c) K. Stott, J. Stonehouse, J. Keeler, T. L. Hwang, A. J. Shaka, *J. Am. Chem. Soc.* **1995**, *117*, 4199–4200.
- [17] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [18] G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, **1997**.
- [19] G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**.
- [20] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.