Stable Spirobis(radical cation)

# A Spiro-Fused Triarylaminium Radical Cation with a Triplet Ground State**

*Akihiro Ito, Masashi Urabe, and Kazuyoshi Tanaka**

The spiro structural motif has been occasionally revisited in the field of molecule-based materials science. For example, several spiro compounds were recently investigated for constructing metallic charge-transfer salts with unique three-dimensional structures[1,2] and molecular metals composed of a single molecular component.[3] With regard to molecule-based magnetism, Dougherty et al. elaborately examined the possibility of generating 1,4,6,9-spiro[4.4]nona-tetrayl.[4,5] Recently, Frank et al. reported the synthesis of a spiro-fused bis(nitronyl nitroxide) biradical and the magnetic interaction between the two radical centers.[6] From the viewpoint of magnetic interaction, the spin preference in spirobiradicals is determined by the balance between two contributions: 1) the two perpendicular π systems, which favor ferromagnetic interaction resulting from the degeneracy of the magnetic orbital derived from the two ring systems, and 2) so-called spiroconjugation,[7] which can lift the degeneracy of the two magnetic orbitals and thus lead to a singlet spin state. In fact, the biradical reported in ref. [3] exhibited a weak antiferromagnetic interaction, probably because of the second contribution. Two nitronyl nitroxide radicals incorporated in the two subunits of a spiro compound can be regarded as localized spin centers. The further apart the nitroxide centers are in the molecule, the weaker their ferromagnetic interaction becomes. In contrast, triarylaminium cations have more delocalized spin distributions than the nitroxide radical,[8] and this ensures stronger exchange interaction between two radical centers. Furthermore, it is well known that all-*para*-substituted triarylamines often give thermally and chemically robust radical cations.[8] Here we report the synthesis of the novel spiro-fused triarylamine **1** and the magnetic properties of its bis(radical cation) **1**[2+].


1
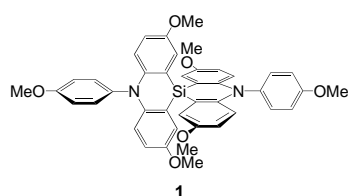
[*] Prof. K. Tanaka, Dr. A. Ito, M. Urabe
Department of Molecular Engineering
Graduate School of Engineering
Kyoto University
Sakyo-ku, Kyoto 606-8501 (Japan)
Fax: (+81) 75-771-0172
E-mail: a51053@sakura.kudpc.kyoto-u.ac.jp
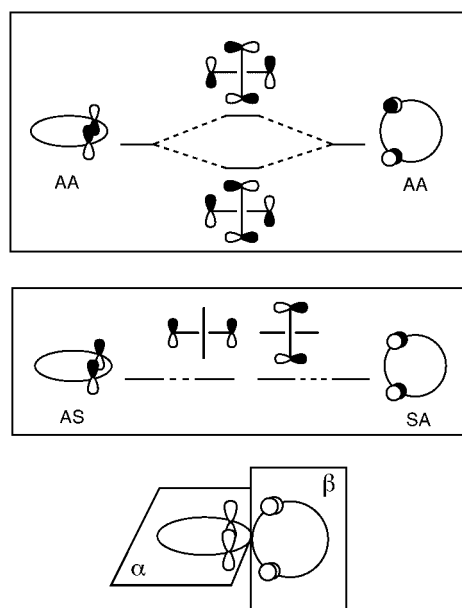
Figure 1. Schematic diagram of molecular interaction between two perpendicular subunits in a spiro compound. A and S denote antisymmetric and symmetric, respectively, with regard to the planes α and β.

In Figure 1, the fragment MOs of the mutually perpendicular π systems are classified by symmetry with respect to two planes α and β. By consideration of symmetry it can be deduced that the two fragment MOs can interact with each other only when they are antisymmetric (AA) to both planes.[7] The fragment MOs of a triarylamine such as **1** indeed have AA symmetry, as illustrated in Figure 2. Hence, the resulting HOMO for **1** is expected to be doubly degenerate. In fact, CAS(2,2)/6-31G* MO calculations[9] on the dication of the unsubstituted model compound of **1** revealed degeneracy of two singly occupied MOs (SOMOs).
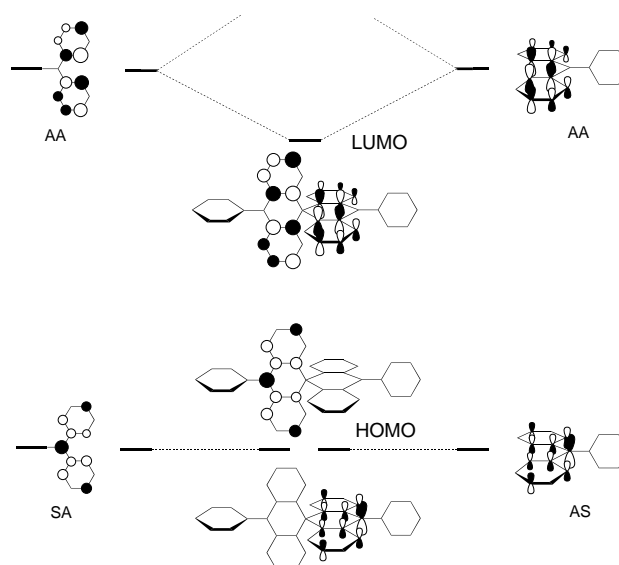

Figure 2. Schematic drawing of the frontier MOs for **1**. Methoxy groups are omitted for clarity.

In addition, the singlet state is 167 J mol^{-1} higher in energy than the corresponding triplet state. Although the calculated Mulliken spin density is mainly concentrated on the two N atoms, it is delocalized over the benzene rings to some extent. The distance between the two N atoms was estimated to be 6.4 Å from the optimized structure.

The synthesis of **1** (Scheme 1) started with diarylamine **2**. As a facile method to construct a spiro structure, we selected the method of Gilmann et al.,[10] in which treatment of silicon tetrachloride with N-alkyl-2,2′-dilithiodiphenylamine gives a spirobis(dihydrophenazasiline) in high yield. In terms of retrosynthetic strategy, the route starting from 2,2′-dibromotrianisylamine **4** is more convenient. However, dilithiated **4** and SiCl$_4$ did not react, probably owing to the buttressing effect[11] of the bulky N-aryl group. However, when N-benzyl-2,2′-dibromodianisylamine (**5**) was employed, the corresponding spiro compound **6** was obtained in 60% yield. Finally, after removal of benzyl protecting groups, a Pd^0-catalyzed amination reaction[12] afforded the target molecule **1** in high yield.[13]

The redox behavior of **1**, in which two oxidizable subunits are connected by a spiro atom, is of interest, as it will give information on the spiroconjugation between the two subunits and hence the intramolecular magnetic interaction in **1**$^{2+}$. The electrochemical properties of **1** were investigated by cyclic voltammetry (CV) at room temperature in acetonitrile (Figure 3). Compound **1** displayed two reversible one-electron oxidation waves at formal potentials of 0.30[14] and 0.46 V versus Fc/Fc$^+$, and this indicates that the first oxidation yields a monocation stabilized by spin delocalization over two trianisylamine units. The separation of the two oxidation potentials (160 mV) indicates that spiroconjugation between two subunits is weak but not negligible.
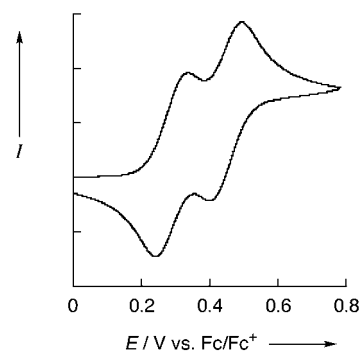
**Figure 3.** Cyclic voltammogram of **1** in MeCN at 25°C (scan rate 100 mV s^{-1}).

The reversibility of the two oxidation processes encouraged us to prepare a salt of the dication of **1**. Taking into account the observed potentials, we oxidized **1** with antimony pentachloride in CH$_2$Cl$_2$. Dry diethyl ether was added to the resulting blue solution at −78°C, and the hexachloroantimonate salt was isolated as a greenish blue powder.[15] In contrast to the comparatively high oxidation potentials of **1**, the isolated salt was quite stable in the solid state even at ambient temperature in air for days.[16] Although we have not yet obtained single crystals suitable for X-ray structural analysis, elemental analysis strongly suggested that the isolated salt has the composition **1**(SbCl$_6$)$_2$.[15,17]

To gain information on whether **1**$^{2+}$ has an open-shell electronic structure, we recorded the EPR spectrum of **1**(SbCl$_6$)$_2$ in a frozen CH$_2$Cl$_2$ matrix (Figure 4). The distinct fine structure attributed to spin-triplet species was detected together with the forbidden resonance resulting from $\Delta m_S =$
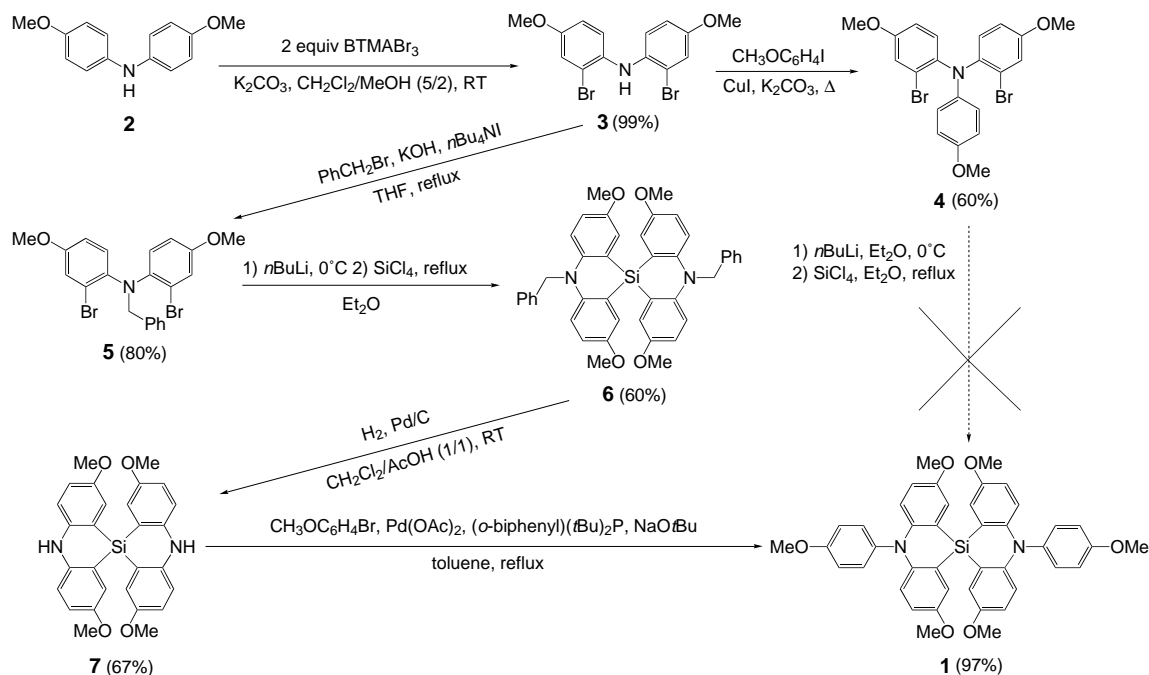
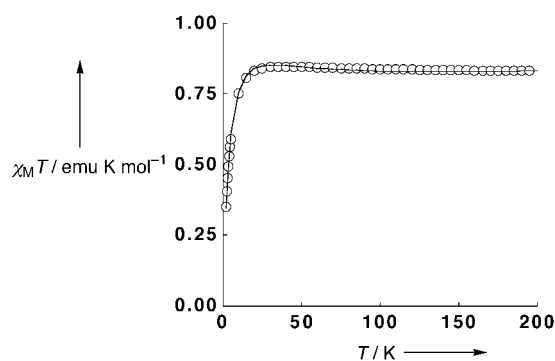**Scheme 1.** Synthetic route for **1**. BTMA = Benzyltrimethylammonium.
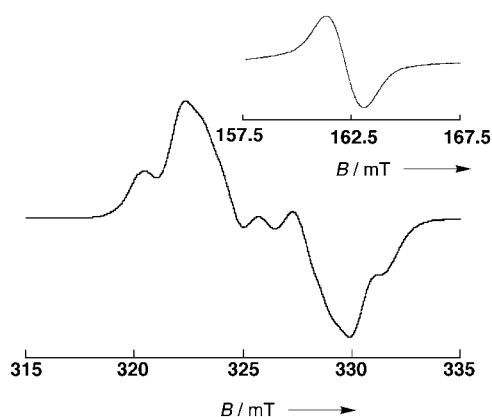
Figure 4. EPR spectra of **1**(SbCl$_6$)$_2$ in CH$_2$Cl$_2$ at 123 K. Inset: The forbidden $\Delta M_S = \pm 2$ resonance at 123 K.

Figure 5. Plot of $\chi_M T$ versus T for **1**(SbCl$_6$)$_2$ at 500 G. The solid line represents the best theoretical fit [Eq. (2)] to the data.

$$\chi_M = \frac{1}{k_B (T-\theta)} \frac{2 N g^2 \mu_B}{3 + \exp\left(-\frac{2J}{k_B T}\right)} \tag{2}$$

± 2. This clearly indicates that **1**$^{2+}$ is a bis(radical cation). The zero-field splitting constants were determined from the $\Delta m_S = \pm 1$ transitions to be $D = 5.5$ mT and $E = 0.7$ mT by spectral simulation. The midpoints of three pairs of resonances did not coincide, and this indicates anisotropy of the g factor: $g_{xx} \approx g_{yy} = 2.0022$, $g_{zz} = 2.0034$ (the z axis is in the direction connecting the two nitrogen atoms). The average spin–spin distance was estimated to be 8.0 Å within the point-dipole approximation.[18] The discrepancy between the value of 8.0 Å and the distance between the two N atoms estimated from the aforementioned MO calculations on the unsubstituted model compound (6.4 Å) clearly shows deviation from the simple dipole approximation for **1**$^{2+}$. For spin-delocalized diradical molecules, Equation (1) can be adopted[19] where r_{ij}

$$D = \frac{3}{4} g^2 \beta^2 \sum_{ij} \frac{r_{ij}^2 - 3 z_{ij}^2}{r_{ij}^5} \rho_i \rho_j \tag{1}$$

is the distance between atoms i and j, r_i and r_j are the spin densities on atom i in one dianisylaminium moiety and on atom j on the other, and the z axis is in the direction connecting the two N atoms. On the basis of the B3LYP/6-31G* calculations on the dication of the unsubstituted model compound of **1**, the D value is estimated to be 6.0 mT. This indicates that the spin densities are to some extent delocalized over each dianisylaminium moiety. Furthermore, the temperature dependence of the signal intensity corresponding to the $\Delta m_S = \pm 2$ transition exhibited Curie-like behavior, which suggests that **1**$^{2+}$ has a triplet ground state.

Corroboration for ferromagnetic interaction between two trianisylaminium radical cations was provided by magnetic susceptibility measurements in the range between 4 and 300 K (Figure 5). The $\chi_M T$ value was almost constant at 0.83 emu K mol^{-1} between room temperature and 100 K. This value is larger than that expected for two uncoupled spins of 1/2 (0.75 emu K mol^{-1}) and suggests high-spin correlation even at higher temperature. Furthermore, the $\chi_M T$ value increased gradually with decreasing temperature, reached a maximum value of 0.85 emu mol^{-1} K at 18 K, and finally decreased. The measured data best fit to Equation (2)

corresponding to the modified Bleany–Bowers singlet–triplet model for a diradical[20] under a weak Weiss mean field (Weiss constant θ). The exchange coupling J is defined by a Heisenberg Hamiltonian for a diradical [Eq. (3)] where

$$\mathscr{H} = -2J \mathbf{S}_1 \mathbf{S}_2 \quad (S_1 = S_2 = 1/2) \tag{3}$$

positive J indicates ferromagnetic interaction between two radical centers. The optimized values were estimated to be $J = 1.12$ cm^{-1} (1.6 K) and $\theta = -4.3$ K. The ferromagnetic J for **1**$^{2+}$ is in contrast to the antiferromagnetic J (-4.00 cm^{-1} ($= -5.8$ K)) for the spirobis(nitronyl nitroxide) in ref. [3]

In summary, we have prepared a spiro compound with high-spin correlation. To the best of our knowledge, this is the first example of a stable organic spirobis(radical cation). It is of great interest to extend **1** to polymeric systems, and further work is in progress in this direction.

[1] P. Maslak, M. P. Augustine, J. D. Burkey, *J. Am. Chem. Soc.* **1990**, *112*, 5339–5360.

[2] K. Ueda, M. Yamanoha, T. Sugimoto, H. Fujita, A. Ugawa, K. Yakushi, K. Kano, *Chem. Lett.* **1997**, 461–462.

[3] X. Chi, M. E. Itkis, B. D. Patrick, T. M. Barclay, R. W. Reed, R. T. Oakley, A. W. Cordes, R. C. Haddon, *J. Am. Chem. Soc.* **1999**, *121*, 10395–10402.

[4] L. McElwee-White, W. A. Goddard III, D. A. Dougherty, *J. Am. Chem. Soc.* **1984**, *106*, 3461–3466.

[5] L. McElwee-White, D. A. Dougherty, *J. Am. Chem. Soc.* **1984**, *106*, 3466–3474.

[6] N. L. Frank, R. Clérac, J.-P. Sutter, N. Daro, O. Kahn, C. Coulon, M. T. Green, S. Golhen, L. Ouahab, *J. Am. Chem. Soc.* **2000**, *122*, 2053–2061.

[7] H. Dürr, R. Gleiter, *Angew. Chem.* **1978**, *90*, 591–601; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 559–569.

[8] A. R. Forrester, J. M. Hay, R. H. Thomson, *Organic Chemistry of Stable Free Radicals*, Academic Press, New York, **1968**.

[9] 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**.

[10] D. Wittenberg, H. A. McNince, H. Gilman, *J. Am. Chem. Soc.* **1958**, *80*, 5418–5422.

[11] For examples, see M. S. Newman, *Effects in Organic Chemistry*, Wiley, New York, **1956**; L. N. Ferguson, *The Modern Structural Theory of Organic Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, **1963**.

[12] a) M. Beller, *Angew. Chem.* **1995**, *107*, 1436–1437; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1316; b) J. F. Hartwig, *Synlett* **1997**, 329; c) J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154–2177; *Angew. Chem. Int. Ed.* **1998**, *37*, 2046–2067; d) J. P. Wolfe, S. Wagaw, J.-F. Marcoux, S. L. Buchwald, *Acc. Chem. Res.* **1998**, *31*, 805; e) J. F. Hartwig, *Acc. Chem. Res.* **1998**, *31*, 852.

[13] Physical data for **1**: White solid; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.30$ (d, 4H), 7.17 (d, 4H), 6.90 (d, 4H), 6.75 (dd, 4H), 6.47 (d, 4H), 3.94 (s, 6H), 3.64 ppm (s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 158.9$, 152.5, 145.2, 136.83, 132.30, 119.5, 118.0, 117.3, 116.8, 116.1, 55.5 ppm; ^{13}C NMR (75 MHz, C$_6$D$_6$): $\delta = 159.4$, 153.7, 146.0, 137.5, 132.8, 119.3, 119.0, 118.7, 117.6, 116.4, 55.0, 54.9 ppm; elemental analysis (%): calcd for C$_{42}$H$_{38}$N$_2$O$_6$Si: C 72.60, H 5.51, N 4.03; found: C 72.41, H 5.44, N 3.97.

[14] The oxidation potential of trianisylamine was 0.16 V vs Fc/Fc$^+$ under the same conditions. This discrepancy of the first oxidation potential between **1** and trianisylamine probably results from a difference in conformation of the trianisylamine moieties. In **1**, the propellerlike conformation can be hardly adopted because of its spiro structure.

[15] Compound **1** (69 mg, 0.1 mmol) was dissolved in dry dichloromethane and stirred at -78°C under argon. SbCl$_5$ (0.5 ml, 1M in CH$_2$Cl$_2$) was added to the solution. After 10 min, the resulting blue solution was poured into dry diethyl ether. The precipitate was washed with dry diethyl ether to provide **1**(SbCl$_6$)$_2$ (110 mg, 81%) as a greenish blue solid. **1**(SbCl$_6$)$_2$: elemental analysis (%): calcd for C$_{42}$H$_{38}$Cl$_{12}$N$_2$O$_6$Sb$_2$Si: C 36.99, H 2.81, N 2.05, Cl 31.19; found: C 36.99, H 2.71, N 2.05, Cl 29.61.

[16] The isolated solid sample was dissolved in CH$_2$Cl$_2$, and the ESR signal intensity was compared to that of a sample oxidized in situ at the same concentration. The two signals gave the same fine structure with almost the same intensity.

[17] Example of oxidation with SbCl$_5$ in CH$_2$Cl$_2$: H. Bock, A. Rauschenbach, K. Ruppert, Z. Havlas, *Angew. Chem.* **1991**, *103*, 706–708; *Angew. Chem. Int. Ed.* **1998**, *37*, 714–716.

[18] N. Hirota, *J. Am. Chem. Soc.* **1967**, *89*, 32–41.

[19] K. Mukai, A. Sogabe, *J. Chem. Phys.* **1980**, *72*, 598–601.

[20] B. Bleaney, K. D. Bowers, *Proc. R. Soc. London Ser. A* **1952**, *214*, 451–456.

[1.1]Diborataferrocenophane: A Highly Efficient Li$^+$ Scavenger**

Matthias Scheibitz, Rainer F. Winter, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner*

In various cases, electrophilic substitution reactions of ferrocene are known to proceed via precomplexation of the iron atom by the electrophile.[1] Moreover, direct iron-to-metal bonding appears to influence the complexation behavior of certain ferrocene-based redox-switchable cryptands,[2] as well as the properties of catalytically active 2-metalla[3]-ferrocenophanes (metal = Ti^{IV}, Pd^{II}, Pt^{II}).[3] The interaction of ferrocene with Li$^+$ was studied theoretically by Ugalde et al.,[4] who located two minima on the energy surface. In the lower energy structure, the lithium cation is η^5-coordinated on top of one of the cyclopentadienyl rings (**I**; Scheme 1). The second minimum structure **II** is 8 kcal mol^{-1} higher in energy and has the Li$^+$ ion bonded laterally to the iron atom. We recently reported the synthesis and structural characterization of a ferrocene/gallium(I) cation complex with essentially the same structural motif as **I**.[5] Here we report on the isolation of a ferrocene/lithium complex that provides experimental evidence for the existence of structure **II**.

When a slurry of 1,1′-dilithioferrocene (**1**)[6] in hexane is treated with a solution of 1,1′-bis(dimethylboryl)ferrocene (**2**) in THF,[7] the cyclic dinuclear aggregate **3**$^{2-}$ is formed in good yield (Scheme 1). X-ray quality crystals of [**3**-Li]Li([12]crown-4)$_2$ were grown by gas-phase diffusion of diethyl ether into a solution of the crude material in THF after addition of [12]crown-4.

The ^{11}B NMR spectrum of [**3**-Li]Li([12]crown-4)$_2$ reveals one signal at $\delta(^{11}$B, [D$_8$]THF) $= -21.8$ ppm, which testifies to

[*] Prof. Dr. M. Wagner, Dipl.-Chem. M. Scheibitz, Dr. H.-W. Lerner
Institut für Anorganische Chemie
Johann Wolfgang Goethe-Universität Frankfurt
Marie-Curie-Strasse 11, 60439 Frankfurt/Main (Germany)
Fax: (+49) 69-798-29260
E-mail: matthias.wagner@chemie.uni-frankfurt.de

Dr. R. F. Winter
Institut für Anorganische Chemie
Universität Stuttgart
Pfaffenwaldring 55, 70569 Stuttgart (Germany)

Dr. M. Bolte$^+$
Institut für Organische Chemie
Johann Wolfgang Goethe-Universität Frankfurt
Marie-Curie-Strasse 11, 60439 Frankfurt/Main (Germany)

[$^+$] X-ray crystallography

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