Novel *ansa*-Ferrocenes with *o*-Phenylene-type Bridges by B–N Adduct Formation

Frieder Jäkle, Thomas Priermeier and Matthias Wagner*

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany

1,1′-Bis[bromo(methyl)boryl]ferrocene **1** reacts with 4-bromo-3,5-dimethylpyrazole to give a novel air-stable *ansa*-ferrocene where the self-assembly of B–N adducts provides an alternative to C-C coupling.

Stereorigid organometallic molecules are required for a wide range of important technical applications. *ansa*-Metallocene derivatives with suitably substituted covalently bridged ring ligands have proven to meet these conditions and their utilization in homogeneous Ziegler–Natta catalysis, for example, has enjoyed spectacular success. Therefore, great effort is still given to developing novel metallocenes with tailor-made interannular bridges. *o*-Phenylene-type bridges are of special interest because of their particular rigidity and the multiplicity of options for a precise design of their steric and electronic properties. However, very little is known about *ansa*-metallocenes with aromatic moieties spanning both cyclopentadienyl rings and only few examples have ever been structurally investigated by X-ray crystallography.[1,2]

This communication reports the synthesis, characterization and X-ray structure analysis of *ansa*-ferrocenes with novel *o*-phenylene-type bridges. The synthetic strategy is based on the close relationship between dative boron–nitrogen bonds and covalent carbon–carbon bonds, as deduced from the iso-electronic principle. Compound **2**-Br was prepared in a single step by adding dropwise a toluene solution of 1,1′-bis-[bromo(methyl)boryl]ferrocene, **1**,[3] to a toluene solution of 4-bromo-3,5-dimethylpyrazole (2 equiv.) at −78 °C (Scheme 1). After the addition of triethylamine (2 equiv.), the mixture was slowly warmed to room temp. The resulting orange suspension was filtered, all volatiles were removed from the filtrate *in vacuo* and the crude product was recrystallized from boiling dibutyl ether.

2-Br is stable towards air and moisture and can be kept at temperatures as high as 150 °C for several hours without decomposition.

The ^{11}B NMR spectrum of **2**-Br shows a single sharp resonance at δ 1.4, indicating four-coordinate boron centres.† The major feature of the ^1H and ^{13}C NMR spectra is the equivalence of positions 3 and 5 of the pyrazole rings. This can best be explained by the presence of two symmetrical pyrazole bridges spanning both cyclopentadienyl rings. In the ferrocene region of the ^1H NMR spectrum, a pronounced upfield shift of one of the two resonances is observed (δ = 3.26, 3.99). This remarkable shielding may be attributed to the magnetic anisotropy of the aromatic pyrazole rings. The exceptional stability of the *ansa*-metallocene structure of **2**-Br was confirmed by high temperature NMR spectra. Even at 100 °C ([$^2H_8$]toluene), no spectroscopically detectable concentration of an open-chain form of **2**-Br was present.

The X-ray structure analysis of **2**-Br proves the bridged nature of the molecule (Fig. 1) with the central B_2N_4 ring possessing an unsymmetrical boat conformation.‡ Bond distances and bond angles fall within the normally observed ranges.[4] The ferrocene moiety exhibits two almost parallel cyclopentadienyl rings. The bridging unit is slightly bent along the N–N bonds such that the pyrazole rings come closer to the ferrocene fragment.

Custom-tailored pyrazole derivatives, including chiral ones,[5] are an easily accessible class of compounds. This versatility makes them particularly valuable building blocks and offers a facile way of synthesizing a large variety of *ansa*-metallocenes using always the same key step for the formation of the interannular bridge. In case a particular substituent at the pyrazole ring is not compatible with the highly reactive boron precursor **1**, molecule **2**-Br offers the possibility to introduce this substituent after the formation of the *ansa*-metallocene

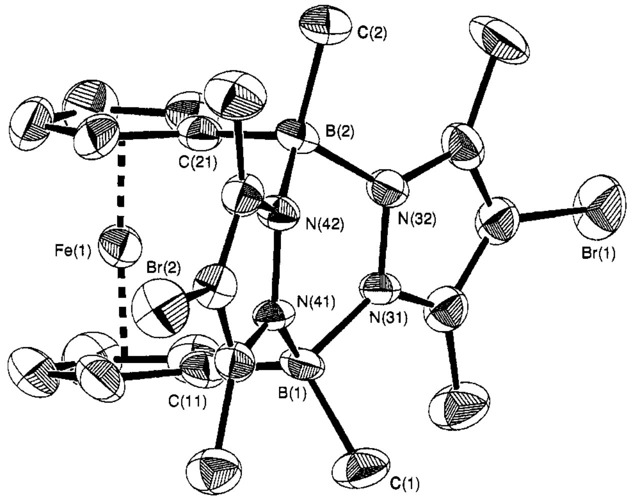
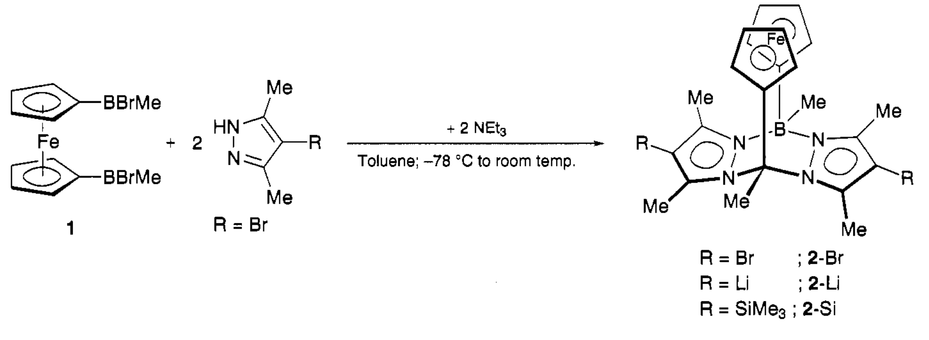


Fig. 1 PLATON[9] drawing of **2**-Br. Atoms are represented by thermal ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles and angles between best planes (°): B(1)–C(1) 1.600(6), B(1)–C(11) 1.603(6), B(1)–N(31) 1.610(4), B(1)–N(41) 1.589(4), B(2)–C(2) 1.591(5), B(2)–C(21) 1.582(5), B(2)–N(32) 1.602(5), B(2)–N(42) 1.594(4), N(41)–N(42) 1.380(4), N(31)–N(32) 1.378(4); C(1)–B(1)–C(11) 117.3(3), C(1)–B(1)–N(31) 107.5(3), C(1)–B(1)–N(41) 108.2(3), N(31)–B(1)–N(41) 106.6(3), C(2)–B(2)–C(21) 110.3(3), C(2)–B(2)–N(32) 111.7(3), C(2)–B(2)–N(42) 113.0(3), N(32)–B(2)–N(42) 103.4(3); C(11)–C(15)//C(21)–C(25) 4.5, N(31)–C(35)//N(41)–C(45) 24.0, B(1)N(31)N(32)B(2)//B(1)N(41)N(42)B(2) 42, B(1)N(31)N(41)//N(31)-N(32)N(41)N(42) 19, B(2)N(32)N(42)//N(31)N(32)N(41)N(42) 40.



Scheme 1

moiety, when the boron centres are already tamed. **2**-Br reacts quantitatively with *n*-butyllithium (2 equiv.) to give almost exclusively the 4,4′-dilithio derivative **2**-Li (the numbering refers to the parent pyrazole). The high site selectivity of this lithiation was confirmed by the reaction of crude **2**-Li with Me_3SiCl (2 equiv.). An NMR spectroscopic investigation of the product revealed the incorporation of trimethylsilyl groups in positions 4 and 4′ of the molecule only.§ Since carbodesilylation[6] is a well-known reaction for the modification of pyrazoles, **2**-Si may also serve as starting material for differently substituted *ansa*-ferrocenes.

Our findings suggest that dative B–N bonds can substitute covalent C–C links under certain circumstances, leading to equivalent structural motifs with similar chemical properties. The self-assembly of donor–acceptor bonds can therefore help to avoid synthetic problems, which would have been hard to overcome using conventional C–C coupling methods.

We are grateful to Professor Dr. W. A. Herrmann (Technical University of Munich) for his generous support. Financial funding by the 'Bayerisches Forschungsprogramm Katalyse' (FORKAT) is acknowledged.

Received, 1st June 1995; Com. 5/03484A

Footnotes

† Satisfactory elemental analysis for all compounds.

Spectroscopic data: **2**-Br: ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 1.4 ($h_{\frac{1}{2}}$ 250 Hz); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (6H, s, BCH_3), 2.63 (12H, s, CH_3), 3.26 (4H, vtr, J_{HH} 2 Hz, C_5H_4), 3.99 (4H, vtr, J_{HH} 2 Hz, C_5H_4); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 11.6 (broad, BCH_3), 15.7 (CH_3), 69.2 (C_5H_4), 69.3 (C_5H_4), 85.0 (C_5H_4-*ipso*), 101.1 (CBr), 144.3 (CCH_3); CI-MS: *m/z* 582 [(M^+); 100%], 567 [($M^+ - CH_3$); 7%].

‡ *Crystal data* for **2**-Br: An air-stable, yellow crystal of **2**-Br ([$C_{22}H_{26}B_2Br_2FeN_4$]; M = 583.75) was mounted on top of a glass filament on an Image Plate Diffraction System (IPDS, STOE). Final lattice parameters were obtained by least-squares refinement of 1404 reflections (graphite monochromator, λ = 71.073 pm (Mo-K$\bar{\alpha}$). Triclinic system, space group $P\bar{1}$ (No. 2), a = 882.4(1), b = 1103.6(2), c = 1241.5(1) pm, α = 78.47(1)°, β = 85.45(1)°, γ = 72.51(1)°, $V = 1130 \times 10^6$ pm^3, D_c = 1.716 g cm^{-3}, Z = 2. Data were collected at room temp., distance from crystal to image plate 80 mm ($5.8 < 2\theta < 48.4°$), 360 images collected $0 < \phi < 360°$, $\Delta\phi$ = 1°, exposure time 7 min. Data were corrected for Lorentz and polarization terms. 13003 Data measured, 150 overflows, 0 overlaps, 13003 data merged (R = 0.044), 3317 independent reflections, 82 with negative intensity, 3235 reflections with $I > 0.01\sigma(I)$ used for refinement. The structure was solved by direct methods[7] and refined with standard difference Fourier techniques.[8] All hydrogen positions were located in difference Fourier maps and refined isotropically. 384 Parameters refined, 8.42 data per parameter, $w = 1/\sigma^2$, shift/error < 0.0001 in the last cycle of refinement, residual electron density +0.53 e Å^{-3} 91 pm near Br(1), −0.69 e Å^{-3}, R = 0.038, R_w = 0.022, minimized function was $\Sigma w(|F_o| - |F_c|)^2$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ **2**-Si: ^{11}B NMR (128.3 MHz, C_6D_6) δ 1.3 ($h_{\frac{1}{2}}$ 250 Hz); ^{1}H NMR (400 MHz, C_6D_6) δ 0.32 (18H, s, $SiCH_3$), 0.95 (6H, s, BCH_3), 2.52 (12H, s, CH_3), 3.61 (4H, vtr, J_{HH} 2 Hz, C_5H_4), 4.27 (4H, vtr, J_{HH} 2 Hz, C_5H_4); ^{13}C NMR (100.5 MHz, C_6D_6) δ 1.2 ($SiCH_3$), 13.3 (broad, BCH_3), 17.6 (CH_3), 69.7 (C_5H_4), 70.3 (C_5H_4), n.o. (C_5H_4-*ipso*), 113.7 (CSi), 151.1 (CCH_3); CI-MS: *m/z* 570 [(M^+); 100%].

References

1 K. Yasufuku and H. Yamazaki, *J. Organomet. Chem.*, 1977, **127**, 197.
2 K. Yasufuku, K. Aoki and H. Yamazaki, *Inorg. Chem.*, 1977, **16**, 624.
3 W. Ruf, T. Renk and W. Siebert, *Z. Naturforsch. Teil B*, 1976, **31**, 1028.
4 K. Niedenzu and H. Nöth, *Chem. Ber.*, 1983, **116**, 1132.
5 H. Brunner, U. P. Singh, T. Boeck, S. Altmann, T. Scheck and B. Wrackmeyer, *J. Organomet. Chem.*, 1993, **443**, C16.
6 F. Effenberger, M. Roos, R. Ahmad and A. Krebs, *Chem. Ber.*, 1991, **124**, 1639.
7 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *Sir-92*, University of Bari, Italy, 1992.
8 D. J. Watkin, P. W. Betteridge and J. R. Carruthers, *CRYSTALS, User Manual*, Oxford University Computing Laboratory, Oxford, England, 1986.
9 A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, C34.