In solution, the ^{13}C NMR shifts of the ring atoms ($\delta = 120.56$, 113.76, 99.29, and 84.36) of 3 indicate the presence of η^5- and η^1-coordinated pyrroles. The hydrogen bonds are so stable that the η^1-pyrrole ligands cannot be exchanged at room temperature by addition of tetramethylpyrrole in excess.

The *anti* positions of the ring heteroatoms in 3 contrast to the structures of known 1,1'-diphospha- and 1,1'-diarsaferrocenes.[1b, 7] Apparently, the reduction of the charge density at the nitrogen atoms that accompanies formation of the hydrogen bonds contributes appreciably to the stability of the 1,1'-diazaferrocene system in 3[8] and points to a possible approach for the stabilization of nitrogen-richer metallocenes.

Experimental Procedure

1: Anhydrous FeCl$_2$ (1.57 g, 12.4 mmol) and C$_4$Me$_4$NLi (2.58 g, 20 mmol), prepared from C$_4$Me$_4$NH and *n*BuLi, were stirred in 30 mL of THF for 10 min. The residue remaining after removal of the solvent under vacuum was extracted at $-40\,^\circ$C with 20 mL of toluene. After addition of 20 mL of *n*-pentane, 1 crystallized at $-78\,^\circ$C as an ocher-colored solid. Yield: 2.13 g (48%).— ^{1}H NMR (60 MHz, [D$_8$]toluene, $-40\,^\circ$C, TMS int.): $\delta = 3.50$ (m, 8 H; OCH$_2$), 1.97 (s, 12 H; C(2,5)-CH$_3$), 1.93 (s, 12 H; C(3,4)-CH$_3$), 1.43 (m, 8 H; CCH$_2$).—^{13}C{^{1}H} NMR (75.43 MHz, [D$_8$]toluene, $-40\,^\circ$C, TMS int.): $\delta = 119.81$ (C2,5), 113.05 (C3,4), 68.42 (OCH$_2$), 26.26 (CCH$_2$), 11.33 (C2,5-CH$_3$), 9.73 (C3,4-CH$_3$).—MS (70 eV): *m/z* 300 ([$M^\oplus - 2$C$_4$H$_8$O], fragment of highest mass).

3: 1 (2.50 g, 5.60 mmol) was dissolved in dichloromethane (30 mL) and treated with 0.2 mL of water. Complex 3 precipitated from the filtrate after 10 min and was crystallized from dichloromethane at $-78\,^\circ$C as an orange-yellow, stable solid. Yield: 9.09 mg (59.4% based on C$_4$Me$_4$NH).— ^{1}H NMR (60 MHz, [D$_8$]toluene, TMS int.): $\delta = 2.05$ (s, 12 H; C2,5-CH$_3$), 1.95 (br. s, 24 H; C11,12,13,14-CH$_3$), 1.57 (s, 12 H; C3,4-CH$_3$), NH not observed.— ^{13}C{^{1}H} NMR (75.43 MHz, [D$_8$]toluene, TMS int.): $\delta = 120.56$ (C11,14), 113.76 (C12,13), 99.29 (C2,5), 84.36 (C3,4), 12.62 (C11,14-CH$_3$), 10.98 (C2,5-CH$_3$), 9.21 (C3,4-CH$_3$), 8.77 (C12,13-CH$_3$).—MS (70 eV): *m/z* 300 ([$M^\oplus - 2$C$_4$Me$_4$NH], fragment of highest mass).

[1] a) F. Mathey, A. Mitschler, R. Weiss, *J. Am. Chem. Soc. 99* (1977) 3537; b) G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey, A. Mitschler, *ibid. 102* (1980) 994; c) R. Bartsch, P. B. Hitchcock, J. F. Nixon, *J. Chem. Soc. Chem. Commun. 1987*, 1146; d) O. J. Scherer, T. Brück, *Angew. Chem. 99* (1987) 59; *Angew. Chem. Int. Ed. Engl. 26* (1987) 59; e) M. Baudler, S. Akpapoglou, D. Ouzounis, F. Wasgestian, B. Meinigke, H. Budzikiewicz, H. Münster, *ibid. 100* (1988) 288 and *27* (1988) 280.

[2] F. Seel, V. Sperber, *J. Organomet. Chem. 14* (1968) 405.

[3] N. Kuhn, E.-M. Horn, E. Zauder, D. Bläser, R. Boese, *Angew. Chem. 100* (1988) 572; *Angew. Chem. Int. Ed. Engl. 27* (1988) 579.

[4] The course of this reaction is still unclear; evidence against the involvement of 2 as an intermediate is provided by the fact that 3 cannot be detected after addition of tetramethylpyrrole to solutions of 1. Complex 3 is also not accessible by reaction of [Fe(H$_2$O)$_6$](BF$_4$)$_2$ with C$_4$Me$_4$NLi.

[5] 3: monoclinic, $P2_1/n$, $a = 8.1538(17)$, $b = 8.9063(19)$, $c = 21.817(5)$ Å, $\beta = 93.350(19)\,^\circ$, $V = 1581.7(6)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.49$ g cm^{-3}, Mo$_{K\alpha}$ radiation, scan range $3^\circ < 2\theta < 50^\circ$, 2780 unique reflections, 2309 observed ($F_0 > 4\sigma(F_0)$), $R = 0.039$, $R_w = 0.049$, $w^{-1} = (\sigma^2(F_0) + 0.00391 \times F_0^2)$. Number of refinement parameters 205, maximum residual electron density 0.23 e Å^{-3}. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-51183, the names of the authors, and the full journal citation.

[6] Cf. I. Olovsson, P.-G. Jönsson: *The Hydrogen Bond*, Schuster-Zundel-Sandorfy, Amsterdam 1976.

[7] P. L. Chiche, J. Galy, G. Thiollet, F. Mathey, *Acta Crystallogr. Sect. B36* (1980) 1344.

[8] This is in accordance with the argument presented in [2]. Additional stabilization in this case is provided by the blocking of the lone pair on the nitrogen atom; worthy of note, however, is the fact that a stability maximum is attained in the series of azaferrocenes [(C$_5$H$_5$)Fe(C$_4$Me$_4$N)] despite the highest nitrogen basicity: N. Kuhn, E. Zauder, unpublished.

[9] N. Kuhn, E.-M. Horn, E. Zauder, *Inorg. Chim. Acta 149* (1988) 163.

Tricyclo[3.1.0.0^{2,6}]hexanedione (the Valene of *o*-Benzoquinone), Bicyclo[2.1.1]hexane-2,3-dione, and Valenes of a Quinoxaline, of Phenazine, and of a Benzophenazine**

By *Manfred Christl* and *Arno Kraft*

α-Diketones are of interest to photochemists[1] and, along with triketones, to spectroscopists and theoretical chemists[2] as well. Further, their importance as precursors of hetero-[3] and carbocyclic[4] compounds is growing. The starting materials for the preparation of α-diketones include 1,2-diols, which can be oxidized by various reagents.[5] However, each case usually requires a search for a suitable oxidizing agent and the optimal conditions. Recently, the oxidations described by Corey and Kim,[6] Pfitzner and Moffatt,[7] and Swern[8] have been employed for this purpose.

Some time ago we prepared the *cis*-diol 1 from benzvalene and converted it into the cyclobutyl thioether 2.[9a] The desulfurization of 2 to give bicyclo[2.1.1]hexane-*cis*-2,3-diol 3 has now been achieved in 70% yield.[9b]
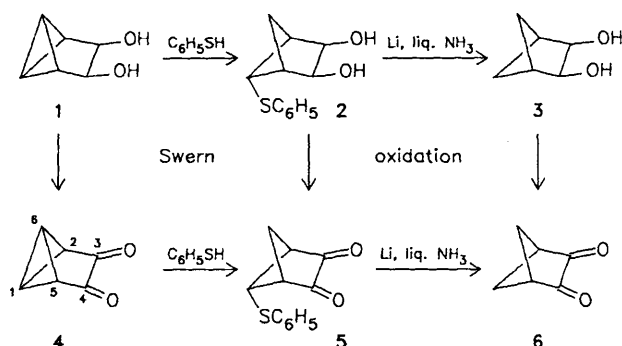
The successful application of the Corey-Kim oxidation to a substrate[6] structurally related to 1 encouraged us to subject 1 to these conditions. Although the desired product, tricyclo[3.1.0.0^{2,6}]hexanedione 4 (16%)[11] was indeed obtained, 4-(methylthiomethoxy)tricyclo[3.1.0.0^{2,6}]hexan-3-one[11] was also formed. Swern oxidation gave pure 4 in only 41% yield (see *Experimental Procedure*). Similarly, bicyclo[2.1.1]hexane-2,3-dione 6 (45%)[12] and its 5-phenylthio derivative 5 (59%)[11] were obtained from 3 and 2, respectively.
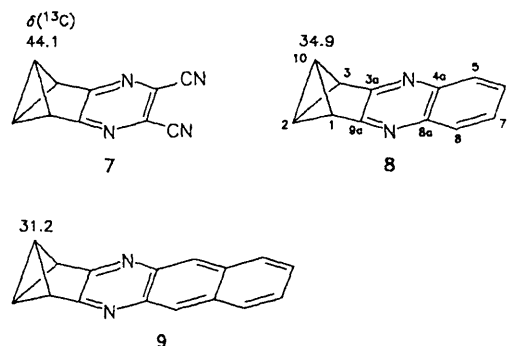
[*] Prof. Dr. M. Christl, Dipl.-Chem. A. Kraft
Institut für Organische Chemie der Universität
Am Hubland, D-8700 Würzburg (FRG)

As expected,[3] treatment of **4** with the primary 1,2-diamines diaminomaleodinitrile, o-phenylenediamine, and 2,3-diaminonaphthalene gave the valenes **7** (50%, m.p. 209-210°C),[11] **8** (95%, m.p. 122-125°C),[11, 13] and **9** (24%, m.p. 209-211°C)[11] of quinoxaline-2,3-dicarbonitrile, phenazine, and benzo[b]phenazine, respectively. We also prepared analogues of **8** from **5** and **6**.

Whereas the ^{13}C NMR chemical shift of the bicyclobutane bridgehead carbon atoms ($\delta = 10.0$) of **4** is found in the normal region, the annelation of the pyrazine ring in **7**, a quinoxaline unit in **8**, and a benzoquinoxaline system in **9** to the tricyclo[3.1.0.$0^{2,6}$]hexane framework leads, as expected,[14] to considerable deshielding. The chemical shift values written above the formulas of **7–9** show an interesting tendency—namely, the deshielding decreases with increasing size of the aromatic system; on going from **7** to **9**, $\Delta\delta = 12.9$ ppm.

Experimental Procedure

4: Dimethyl sulfoxide (910 mg, 11.7 mmol) was added under N_2 over 3 min to a mixture of oxalyl chloride (1.27 g, 10.0 mmol) and dichloromethane (36 mL) cooled to −70°C. The resulting, stirred solution was treated within 5 min with 1 (500 mg, 4.46 mmol) in dichloromethane (9 mL) and then stirred for 40 min at −70°C. Subsequently, triethylamine (2.70 g, 26.7 mmol) was added to the milky mixture at this temperature. The mixture was stirred for an additional 5 min and then allowed to warm to 20°C, affording a colorless precipitate in a yellow to dirty green solution. Silica gel (3.0 g, 0.063-0.2 mm) was added, the resulting suspension was stirred for 5 min, and the dichloromethane was then carefully removed at 20 torr. The brown residue was placed on a column already containing 5.0 g of silica gel. After elution with tert-butyl methyl ether (ca. 180 mL) until the column and the eluate were nearly colorless, the eluate was concentrated at 20 torr and dissolved in 3 mL of dry dichloromethane. Compound **4** was precipitated by addition of 4 mL of petroleum ether. Yield 179 mg (41%) yellow crystals, dec. 145-155°C (in a sealed tube). IR (KBr): $\tilde{v} = 3140, 3125, 3080, 1755$ cm^{-1}. UV (CH$_3$CN): $\lambda_{max}(\varepsilon) = 431$ nm (28). ^{1}H NMR (CDCl$_3$): $\delta = 3.13$ (t, $J_{1,2} = 2.2$ Hz; 2-H), 3.83 (t; 1-H), the assignments were made by means of the ^{13}C satellites: $J_{C-1,1-H} = 240$, $J_{1,6} = 4.5$, $J_{C-2,2-H} = 181$, $J_{2,5} = 3.7$ Hz. ^{13}C NMR (CDCl$_3$): $\delta = 10.0$ (dd, $J_{C-1,6-H} = 3$ Hz; C-1), 43.3 (dd, $J_{C-2,5-H} = 7$ Hz; C-2), 198.5 (t, $J_{C-3,1-H} = 5$ Hz; C-3).

5: The oxidation of **2** was effected according to the procedure described for **4** but with tetrahydrofuran instead of dichloromethane as solvent. The workup was not carried out by adsorption on silica gel but rather by hydrolysis with 2 N HCl and subsequent extraction with ether. Yield after dissolution in dichloromethane and precipitation with petroleum ether: 59%, m.p. 98-101°C.

6: The oxidation of **3** was effected according to the procedure described for **4**. The workup was not carried out by adsorption on silica gel but rather by concentration of the reaction mixture in vacuo followed by treatment of the residue with ether, filtration of the ether suspension to remove the precipitate (HEt$_3$N$^\oplus$Cl$^\ominus$), concentration of the filtrate in vacuo until the onset of crystallization, and driving the crystallization to completion by addition of petroleum ether. Strict exclusion of moisture is necessary. Yield: 45%. For physical data, see [12].

[1] M. B. Rubin, *Top. Curr. Chem.* **129** (1985) 1.
[2] H.-D. Martin, M. Kummer, G. Martin, J. Bartsch, D. Brück, A. Heinrichs, B. Mayer, S. Röver, A. Steigel, D. Mootz, B. Middelhauve, D. Scheutzow, *Chem. Ber.* **120** (1987) 1133.
[3] For example, pyrazine: A. E. A. Porter in A. R. Katritzky, C. W. Rees, A. J. Boulton, A. McKillop (Eds.): *Comprehensive Heterocyclic Chemistry, Vol. 3*, Pergamon, Oxford 1984, p. 157.
[4] For example, the Weiss reaction: H.-U. Reissig, *Nachr. Chem. Tech. Lab.* **34** (1986) 162.
[5] E. Schaumann in *Houben-Weyl, Methoden der organischen Chemie, 4. Aufl., Bd. VI/1b*, Thieme, Stuttgart 1984, p. 892.
[6] R. A. Russell, P. A. Harrison, R. N. Warrener, *Aust. J. Chem.* **37** (1984) 1035.
[7] R. Schobert, *Synthesis 1987*, 741.
[8] R. E. Ireland, D. W. Norbeck, *J. Org. Chem.* **50** (1985) 2198; C. M. Amon, M. G. Banwell, G. L. Gravatt, *ibid.* **52** (1987) 4851.
[9] a) M. Christl, H. Leininger, P. Kemmer, *Chem. Ber.* **117** (1984) 2963. In procedure b) for the synthesis of 1, (C$_2$H$_5$)$_4$N$^\oplus$Cl$^\ominus$ should be replaced by (C$_2$H$_5$)$_4$N$^\oplus$OH$^\ominus$. b) Thus, **3** is accessible in 10% overall yield in four steps from cyclopentadiene; in the earlier synthesis from acrolein and allyl chloride,[10] the product was obtained in only 3% overall yield in a

six-step synthesis. This comparison highlights the importance of the bicyclobutane route for the preparation of cyclobutanes.
[10] W. Trautmann, H. Musso, *Chem. Ber.* **114** (1981) 982.
[11] Elemental analyses, NMR, IR, UV, and MS data are in agreement with the structures of the new compounds.
[12] The transformation of cyclopentadiene to **6** is thus possible in five steps in 5% overall yield. In the only earlier route to **6**, a nine-step synthesis from pentaerythritol gave the product in 11% overall yield: P. Hofmann, E. Beck, unpublished work, presented at the Chemiedozenten-Tagung 1987 in Göttingen; E. Beck, *Dissertation*, Technische Universität München 1985. We thank Prof. P. Hofmann for providing us with these results.
[13] **8**, ^{1}H NMR (CDCl$_3$): $\delta = 2.98$ (t, $J_{1,2} = 1.8$ Hz; 1-H), 4.38 (t; 2-H), 1-H and 2-H were assigned on by means of the ^{13}C satellites: $J_{C-1,1-H} = 177$, $J_{1,3} = 4.8$, $J_{C-2,2-H} = 226$, $J_{2,10} = 7.0$ Hz; 7.53 and 7.84 (AA'XX' spectrum, 5-H, 6-H). ^{13}C NMR (CDCl$_3$): $\delta = 34.9$ (dd, $J_{C-2,10-H} = 5$ Hz; C-2), 36.7 (ddt, $J_{C-1,3-H} = 9$, $J_{C-1,2-H} = 3$ Hz; C-1), 127.8 and 128.0 (each dm, $^1J_{C,H} = 161$ Hz; C-5, C-6), 139.3 ($\approx$t, $J = 7$ Hz; C-4a), 163.7 (t, $J = 5$ Hz; C-3a).
[14] M. Christl, S. Freund, *Chem. Ber.* **118** (1985) 979.

## A Monomeric Diboryldilithiomethane with a 1,3-Diborataallene Structure**

By *Monika Pilz, Jürgen Allwohn, Ralf Hunold, Werner Massa,* and *Armin Berndt**

Dedicated to Professor Heinrich Nöth on the occasion of his 60th birthday

Boryllithioalkenes[1] are boron-stabilized[2] carbanions having the borataalkene structure **1**.[3] We have now prepared the first diboryldilithiomethane **2b** and present here data establishing its 1,3-diborataallene structure **2**.[4]
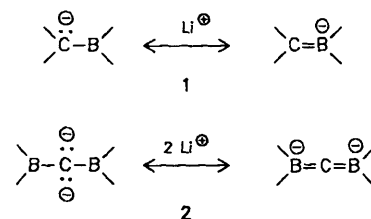
When we attempted to prepare the 1,3-diborataallene **2a** by addition of tert-butyllithium to **3**,[5] we obtained instead the 1,3-diborataallene **2b**, which contains a second tert-butyl group in place of the CH(SiMe$_3$)$_2$ group. The dilithium

2a: R = CH(SiMe$_3$)$_2$
2b. R = tBu

Mes = 2,4,6-Me$_3$C$_6$H$_2$
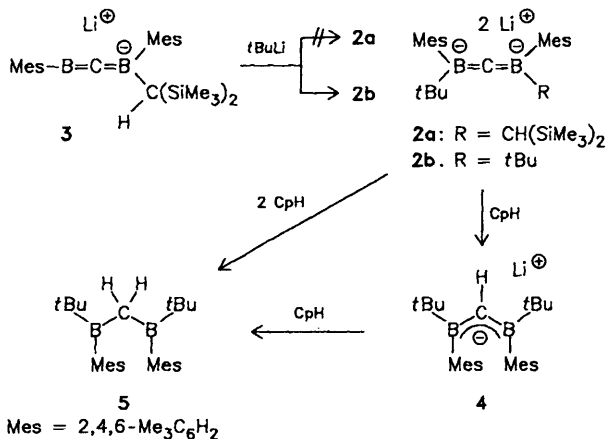
[*] Prof. Dr. A. Berndt, Priv.-Doz. Dr. W. Massa, M. Pilz, J. Allwohn, Dr. R. Hunold
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-3550 Marburg (FRG)