Synthesis and Structure of the First η^1-Borazine Complexes

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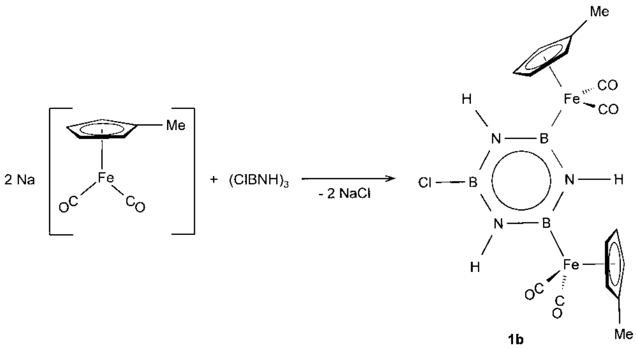
A series of η^1-borazine complexes were obtained by the reaction of trichloroborazine with Na[(η^5-C_5R_5)Fe(CO)$_2$]. The compounds [{(C_5R_5)(CO)$_2$Fe}$_n$Cl$_{3-n}$B$_3$N$_3$H$_3$] (**1a**, n = 1, R = Me; **1b**, n = 2, C_5R_5 = C_5H_4Me; **1c**, n = 3, R = H) have one to three iron–boron σ bonds and Fe–B π-interactions can be ruled out from the spectroscopic and structural results. All new borazine complexes were isolated as orange crystalline solids and characterized by multinuclear NMR methods and IR spectroscopy. The structure of **1b** in the crystalline state was also determined by a single-crystal X-ray study.

Introduction

The chemistry of borazine and its derivatives, in terms of their role as ligands in transition-metal complexes, is restricted to a few examples, such as [(EtBNEt)$_3$Cr(CO)$_3$][1a][1b]. In these compounds, which are mostly derived from peralkylated borazines, the (RBNR)$_3$ ligand always shows η^6 coordination similar to the corresponding benzene complexes[2][3]. η^1-Coordinated borazines with a boron–transition metal bond are believed to play an important role in the [RhH(CO)(PPh$_3$)$_3$]-catalyzed hydroboration of acetylenes with (HBNH)$_3$. This reaction yields a variety of alkenyl-substituted borazines which are suitable precursors for conversion into ceramic materials[4]. The similarity between this reaction and the rhodium-catalyzed hydroboration with boranes[5] suggests the oxidative addition of a borazine B–H bond to the metal center with formation of a boryl complex. However, there is no spectroscopic evidence for the formation of such a compound. Structurally characterized boryl complexes have, in most cases, been obtained from catecholborane and its derivatives[6a][6b][6c][6d][6e][6f][6g]. As a consequence of our investigations of alternative transition metal complexes of boron[7a][7b], we report here the synthesis and structure of the first η^1-coordinated borazine complexes having boron–transition metal σ bonds.

Results and Discussion

The reaction of (ClBNH)$_3$ with two equivalents of Na[(C_5H_4Me)Fe(CO)$_2$], as shown in Eq. 1, gives a borazine derivative with two boron–iron bonds, [{(C_5H_4Me)Fe(CO)$_2$}$_2$ClB$_3$N$_3$H$_3$] (**1b**) as orange needles in 29% yield. The structure of **1b** in solution can be elucidated from the NMR and IR spectra. The compound shows two broad resonances at δ = 5.53 and δ = 6.20 (2:1 ratio) in the ^{1}H-NMR spectrum, corresponding to the nitrogen-bound hydrogen atoms, along with characteristic ^{11}B-NMR signals in a 1:2 ratio for the Cl- and Fe-substituted boron atoms, respectively, at δ = 27.2 and δ = 53.1. The relative high field shift of 68 ppm for the second signal compared to that of [CpFe(CO)$_2$BPh$_2$][6c] is largely due to the B–N multiple bond character in the borazinyl ring. There is no evidence for an Fe–B π-interaction, which has been established for [CpFe(CO)$_2$BCat] (Cat = OC$_6$H$_4$O)[6c] in solution, and evidence for this is provided by the CO stretching frequencies of **1b** (1996 and 1937 cm^{-1}) that match the IR data of the methyl complex [(C_5H_4Me)Fe(CO)$_2$Me] (1995 and 1935 cm^{-1})[8].



1b

In the crystal (Figure 1) **1b** adopts C_1 symmetry. Fe-B π-interactions in the solid state can be excluded because of the orthogonal arrangement of the N–B–N planes with respect to the Cp centroid–Fe–B planes (90.6° and 94.5°)[6c][9]. The Fe–B distances of 2.041(1) and 2.045(1) Å, respectively, can be compared with the value of 2.034(3) Å found for [CpFe(CO)$_2$BPh$_2$], which shows a similar geometry in the crystal in terms of the dihedral angle between the Cp centroid–Fe–B and C–B–C planes (75°)[6c]. The replacement of two Cl atoms by the more bulky [(C_5H_4Me)Fe(CO)$_2$] moieties has no significant influence on the geometry of the central six-membered B–N core, as shown

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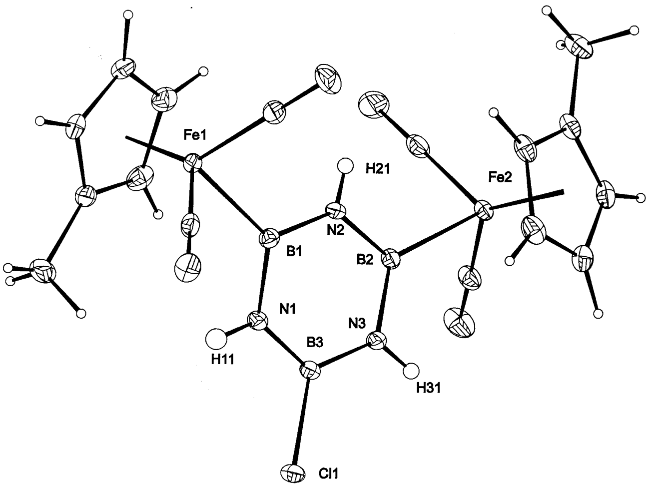
by the B−N bond distances [1.414(2)−1.442(2) Å] and N−B−N angles [115.3(1)−120.5(1)°] which resemble the corresponding values in the parent compound $(ClBNH)_3$; the planarity of the $(B-N)_3$ ring of **1b** is also preserved[10].

Figure 1. Structure of **1b** in the crystal (ellipsoids at 50% probability, drawing package CAMERON[14]).



Selected distances (Å) and angles (°): Fe1−B1 2.041(1); Fe2−B2 2.045(1); B1−N1 1.441(2); B3−N1 1.410(2); Fe1−centroid 1 1.721; Fe2−centroid 2 1.716; Fe1−B1−N1 123.10(9); Fe2−B2−N2 120.64(9); N1−B1−N2 115.3(1), N2−B2−N3 115.4(1)

Apart from **1b**, the corresponding borazine complexes containing one or three boron−iron bonds, respectively, were obtained by similar methods. In the case of the monosubstituted derivative $[\{(C_5Me_5)Fe(CO)_2\}Cl_2B_3N_3H_3]$ (**1a**) the best results were obtained from the reaction of $(ClBNH)_3$ with one equivalent $Na[(C_5Me_5)Fe(CO)_2]$, while $[\{CpFe(CO)_2\}_3B_3N_3H_3]$ (**1c**) is obtained with three equivalents of $Na[CpFe(CO)_2]$. In order to obtain the crystalline compounds **1a,b** it was necessary to employ the alkylated Cp derivatives, whereas the parent compound, $Na[CpFe(CO)_2]$, always led to oily products containing impurities. The structures of **1a,c** in solution can be deduced from the similarity between the IR- and NMR-spectroscopic data and the results obtained for **1b**. All compounds proved to be extremely air-sensitive and showed signs of decomposition after storage at room temperature under a nitrogen atmosphere for a few days.

Conclusion

The first η^1-borazine complexes have been obtained by the reaction of trichloroborazine with $Na[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$, extending the scope of borazine in transition-metal chemistry. Depending on the borazine-to-iron ratio employed, the mono-, di- and trisubstituted compounds $[\{(C_5R_5)(CO)_2Fe\}_nCl_{3-n}BNH_3]$ (**1a**, $n = 1$, R = Me; **1b**, $n = 2$, $C_5R_5 = C_5H_4Me$; **1c**, $n = 3$, R = H) were obtained as crystalline solids. These complexes show, both in solution and in the crystal, iron−boron σ bonds with no further π stabilization, which was proved by NMR and IR spectroscopy as well as by X-ray studies.

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Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere in Schlenk glassware. Solvents and reagents were dried by standard procedures, distilled, and stored under nitrogen and over molecular sieves. $Na[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$[11] and $(ClBNH)_3$[12] were synthesized according to the literature procedures. − NMR: Varian Unity 500 at 499.843 (^1H, internal standard TMS), 150.364 (^{11}B, external standard $BF_3\cdot OEt_2$ in C_6D_6), 125.639 MHz ($^{13}C\{^1H\}$, APT, internal standard TMS); all NMR spectra were recorded in C_6D_6 as solvent. − Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, model 1106. − IR: Perkin-Elmer FT-IR 1720x.

[2,4-Dichloro-6-{(η⁵-pentamethylcyclopentadienyl)dicarbonyliron}borazine] (**1a**): 0.86 g (3.18 mmol) of $Na[(C_5Me_5)Fe(CO)_2]$ was suspended in 20 ml of benzene and a solution of 0.58 g (3.18 mmol) of $(ClBNH)_3$ in 15 ml of benzene was added dropwise at ambient temperature. After stirring for 45 min all volatile materials were removed under high vacuum (25°C/0.001 torr) and the solid residue was treated with 40 ml of hexane and filtered. 0.25 g (20%) of **1a** was recovered from the filtrate at −30°C as yellow needles. − ^1H NMR δ = 1.33 (s, 15 H, Me), 4.68 (s, 1 H, ClBNHBCl), 5.52 (s, 2 H, ClBNHBFe). − ^{11}B NMR: δ = 28.44 (s, 2 B, BCl), 58.99 (s, 1 B, BFe). − ^{13}C NMR: δ = 9.55 (Me), 94.66 (C1−C5, C_5Me_5), 217.55 (CO). − IR (hexane): $\tilde{\nu}$ = 1995, 1935 cm^{-1} (CO). − $C_{16}H_{17}B_3ClFe_2N_3O_4$ (494.91): calcd. C 38.83, H 3.46, N 8.49; found C 38.48, H 3.51, N 8.53.

[Chloro-4,6-bis{(η⁵-methylcyclopentadienyl)dicarbonyliron}borazine] (**1b**): As described for **1a**, $Na[(C_5H_4Me)Fe(CO)_2]$ (0.90 g, 4.20 mmol) was reacted with $(ClBNH)_3$ (0.39 g, 2.10 mmol) and 0.30 g (29%) of $[\{(C_5H_4Me)Fe(CO)_2\}_2ClB_3N_3H_3]$ (**1b**) was recovered from the filtrate at −30°C as orange crystals. − ^1H NMR: δ = 1.51 (s, 6 H, Me), 3.92−4.05 (broad, 8 H, C_5H_4), 5.53 (s, 2 H, ClBNHBFe), 6.20 (s, 1 H, FeBNHBFe). − ^{11}B NMR: δ = 27.15 (s, 1 B, BCl), 53.05 (s, 2 B, BFe). − ^{13}C NMR: δ = 12.97 (Me), 81.50, 84.31 (C2−C4, C_5H_4), 99.86 (C1, C_5H_4), 217.19 (CO). − IR (hexane): $\tilde{\nu}$ = 1996, 1937 cm^{-1} (CO). − $C_{12}H_{18}B_3Cl_2FeN_3O_2$ (395.48): calcd. C 36.45, H 4.59, N 10.56; found C 36.33, H 4.60, N 10.56.

[2,4,6-Tris{(η⁵-cyclopentadienyl)dicarbonyliron}borazine] (**1c**): As described for **1a**, 1.29 g (6.45 mmol) of $Na[CpFe(CO)_2]$ suspended in 30 ml of benzene was reacted with 0.40 g (2.15 mmol) of $(ClBNH)_3$ and 0.37 g (28%) of **1c** was obtained as orange needles. − ^1H NMR: δ = 4.28 (s, 15 H, C_5H_5), 6.03 (s, 3 H, NH). − ^{11}B NMR: δ = 49.69 (s). − ^{13}C NMR: δ = 83.10 (C_5H_5), 217.46 (CO). − IR (hexane): $\tilde{\nu}$ = 1988, 1928 cm^{-1} (CO). − $C_{21}H_{18}B_3Fe_2N_3O_6$ (606.36): calcd. C 41.46, H 2.98, N 6.91; found C 41.08, H 3.02, N 6.86.

Crystal Data for **1b**: $C_{16}H_{17}B_3ClFe_2N_3O_4$, M = 494.91 g mol^{-1}, unit cell dimensions: a = 13.682(1) Å, b = 7.163(1) Å, c = 20.504 Å, V = 2009.3 Å^3, β = 90.864(1)°, $P2_1/n$, Z = 4, D_{calcd} = 1.636 cm^{-3}, μ = 16.05 cm^{-1}. The data were collected using an Enraf-Nonius DIP2020 image plate diffractometer at 150 K with Mo-K_α radiation, λ = 0.71069 Å. 26825 reflections were measured giving 3954 reflections with $I > 3\ \sigma(I)$. The images were processed with DENZO and SCALEPACK programs[14]. All non-hydrogen atoms were refined in anisotropic and all nitrogen-bound hydrogen atoms in isotropic approximation. The carbon-bound hydrogen atoms were placed geometrically and included in the final refinement with fixed positional and thermal parameters. A correction for secondary extinction was applied and refinement completed using a Chebyshev weighting scheme with parameters 4.09, 3.54, and 3.18[15]. Refinement on F converged at $R = 0.032$, $R_w = 0.048$, and GOF = 0.86. A final difference Fourier synthesis showed minimum and maximum residual electron densities of -0.71 and 0.63 e Å^{-3}. Further details of the crystal-structure investigations can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, GB-Cambridge CB2 1EZ; Tel.: Int. +7247/808-205, Telefax: Int. +44(0)1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk; World Wide Web: http://www.ccdc.cam.ac.uk) on quoting the depository number 100374.

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