A single-bonded cationic terminal borylene complex

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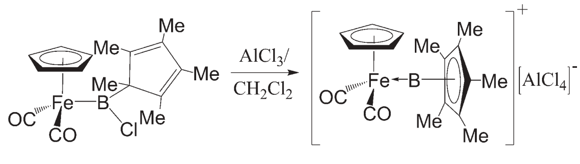
The cationic terminal borylene complex [(η^5-C_5H_5)(CO)$_2$-FeB(η^5-C_5Me_5)][$AlCl_4$] has been isolated from the reaction of [(η^5-C_5H_5)(CO)$_2$FeB(Cl)(η^1-C_5Me_5)] with $AlCl_3$ and on the basis of X-ray crystallographic data, spectroscopic data and a DFT calculation it is concluded that the B→Fe bond order is one.

Following the disclosure of the first structurally characterized terminal borylene complexes in 1998,[1] this field has grown rapidly, both in terms of the number of new compounds and also from the standpoint of reactivity studies.[2] The early examples of such complexes are neutral species of general formula L_nMBR that are typically prepared by metathetical routes.[2] More recently, halide ion abstraction chemistry has been successfully employed[3] for the generation of cationic terminal borylene complexes, one of which proved to be suitable for a single-crystal X-ray diffraction study, namely [(η^5-C_5Me_5)Fe(CO)$_2$(BMes)]$^+$[BAr′$_4$]$^-$ (**1**, Mes = 2,4,6-$Me_3C_6H_2$; Ar′ = 3,5-$(CF_3)_2C_6H_3$). An intriguing aspect of the structure of the cation of **1** is the fact that it features the shortest transition metal–boron distance reported to date (1.792(8) Å). The implication of the presence of an iron–boron double bond was confirmed on the basis of DFT calculations[4] which also revealed that the Fe=B bond comprises B→Fe σ-donor and Fe→B π back-bonding components.

We now report the first structurally authenticated example of a cationic terminal borylene complex with a single B→metal bond, thereby demonstrating that such complexes can range in bond order from 1 to 2 depending upon the nature of the boron substituent.

The salt [(C_5H_5)Fe(CO)$_2$]K was added to an equimolar quantity of (η^1-C_5Me_5)BCl_2[5] in hexane solution at 25 °C and the reaction mixture was stirred overnight. Removal of the KCl by filtration, followed by solvent stripping, resulted in a 67% yield of red, solid [(C_5H_5)Fe(CO)$_2${B(η^1-C_5Me_5)Cl}] (**2**). Compound **2** was characterized on the basis of NMR, IR and HRMS data.[6] When **2** was allowed to react with an equimolar amount of $AlCl_3$ in CH_2Cl_2 solution at 25 °C, the ^{11}B signal for **2** at δ 111.34 ppm was replaced by a new resonance at δ −37.85 ppm and a sharp peak at δ 103.4 ppm diagnostic of $[AlCl_4]^-$ was evident in the ^{27}Al NMR spectrum, thus suggesting that the chloride abstraction reaction shown in Scheme 1 had taken place. A crystalline sample of **3** was obtained in 73% yield by recrystallization of the reaction mixture following removal of the solvent and other volatiles. The ^{13}C and ^1H NMR data[6] were in accord with the proposed structure and the parent peaks for the cation and anion were detected by HRMS.[6] Structural confirmation was provided by a single-crystal X-ray diffraction study.[7]



2 **3**

Scheme 1

The crystalline state of **3** consists of an assembly of discrete cations and anions (Fig. 1) and there are no unusually short interionic contacts. The C_5Me_5 group is bonded to boron in an η^5-fashion with an average B–C distance of 1.799(4) Å and the X–B–Fe vector (X = C_5Me_5 ring centroid) is essentially linear (177.86°). The most significant feature of the structure of the cation is that the B–Fe bond distance (1.977(3) Å) is 10.3% longer than that reported for the cation of **1**, thus suggesting single bond character. Moreover, the B–Fe bond distance in cationic **3** is very close to that in the neutral terminal borylene complex (η^5-C_5Me_5)BFe(CO)$_4$ (2.010(3) Å)[1a] which has been shown to possess a B→Fe donor–acceptor bond of order 1.

Significant differences are also evident in the IR spectra of **1** and **3** in the CO stretching region. Thus, the CO stretching vibrations for **3** (2020 and 1962 cm^{-1}) appear at lower energy than those for

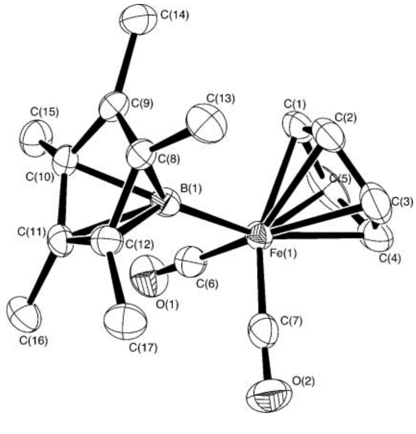


Fig. 1 ORTEP view of the structure of [(η^5-C_5H_5)(CO)$_2$FeB(η^5-C_5Me_5)]$^+$ showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are set at the 50% probability level. Important bond distances (Å) and angles (°): Fe(1)–B(1) 1.977(3), B(1)–C(8) 1.794(4), B(1)–C(9) 1.792(4), B(1)–C(10) 1.803(4), B(1)–C(11) 1.803(4), B(1)–C(12) 1.801(4), B(1)–X 1.326, Fe(1)–C(6) 1.754(3), C(6)–O(1) 1.149(3), Fe(1)–C(7) 1.760(4), C(7)–O(2) 1.145(4), Fe(1)–X 1.719, Fe(1)–B(1)–X 177.86, B(1)–Fe(1)–X 123.63, C(6)–Fe(1)–C(7) 96.25(13).

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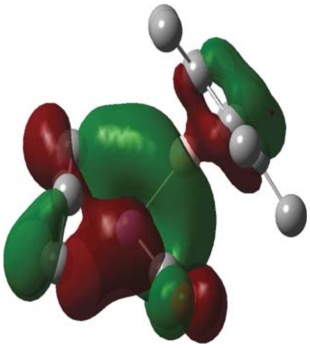

Fig. 2 View of the HOMO-4 MO of $[(\eta^5\text{-}C_5H_5)(CO)_2FeB(\eta^5\text{-}C_5Me_5)]^+$ as calculated by DFT (B3LYP) showing the B→Fe σ-bond.

1 (2055 and 2013 cm^{-1}), a trend which is consistent with less (or the absence of) Fe→B π back-bonding in the cation of **3**. Moreover, it is interesting to note that, while the CO stretching frequencies for cation **1** are blue shifted with respect to those of the precursor chloride $[(C_5Me_5)Fe(CO)_2\{BMesCl\}]$ (ν_{CO} = 2006, 1961 cm^{-1}), those of cation **3** are red shifted *vis-à-vis* those of **1** (ν_{CO} = 2052, 2000 cm^{-1}).

In order to gain additional insight into the electronic structure of the cation of **3**, a DFT calculation was carried out at the B3LYP level of theory[8] using the Gaussian 03 suite of programs.[9] The fractional coordinates from the X-ray crystal structure were used as input data. The LANL2DZ basis set was used for the boron atom and the 6-31+G* basis set was employed for the remaining elements. In general, there is a very good agreement between the theoretical and experimental values. For example, the computed B–Fe bond distance of 2.009 Å compares well with the experimental value of 1.978 Å. Likewise, there is a satisfactory accord between the computed X–B–Fe angle (178.16°) and that determined by experiment (177.86°). Based on a population analysis of the MO's, most of the covalent boron–iron bonding interaction is found in the HOMO-4 MO (Fig. 2) and is best described as a B→Fe donor–acceptor bond, the primary contributions to which arise from overlap of boron 2s and $2p_z$ AO's with the iron $3d_{z^2}$ AO (40.20, 16.38 and 26.1%, respectively). An NBO analysis[10] indicates that the overall B–Fe bond order is one.

In summary, the first example of a cationic terminal borylene complex with a metal–boron single bond has been prepared and structurally characterized thus demonstrating the metal–boron bond order in such complexes is sensitive to the electronic properties of the boron substituent.[11] Current effort is focused on the potential of **3** to serve as a source of $(Me_5C_5)B$ units.

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6 Spectroscopic data for **2**: ^{1}H NMR (300 MHz, C_6D_6): δ 1.80 (s, 15H, C_5Me_5), 4.10 (s, 5H, C_5H_5); ^{13}C NMR (75 MHz, C_6D_6): δ 13.50 (s, C_5Me_5), 84.70 (s, C_5H_5), 126.25 (s, C_5Me_5), 214.04 (s, CO); ^{11}B NMR (96 MHz, C_6D_6): 111.34 (s). HRMS (CI, CH_4) calc. for $[M - H]^-$, 357.0516; found 357.0519. IR (KBr disc) ν_{CO} = 2000, 2052 cm^{-1}. Spectroscopic data for **3**: ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.21 (s, 15H, C_5Me_5), 5.04 (s, 5H, C_5H_5); ^{13}C NMR (75 MHz, CD_2Cl_2): 9.90 (s, C_5Me_5), 83.59 (s, C_5H_5), 115.5 (C_5Me_5), 211.78 (s, CO); ^{11}B NMR (96 MHz, CD_2Cl_2): −37.85 (s); ^{27}Al NMR (78 MHz, CD_2Cl_2) 103.4 (s). HRMS (CI, CH_4) calc. for $[M]^+$ 323.0906; found 323.0912. IR (KBr disc) ν_{CO} 1962, 2020 cm^{-1}.

7 *Crystal data* for **3**: $C_{17}H_{20}AlBCl_4FeO_2$ (491.77), monoclinic, space group $P2_1/n$, $a = 11.227(2)$, $b = 15.692(3)$, $c = 12.337(3)$ Å, $\beta = 91.24(3)°$, $V = 2173.0(8)$ Å^3, $Z = 4$, $D_c = 1.503$ g cm^{-3}, μ(Mo-Kα) = 1.235 mm^{-1}, T = 153(2) K, 4966 independent reflections [R_{int} = 0.0595], final R indices (240 parameters) for 4966 independent reflections [$I < 2\sigma(I)$] are $R1$ = 0.0435, w$R2$ = 0.0843, GOF = 1.024. Crystals of **3** were covered with mineral oil prior to mounting on the goniometer of a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream liquid nitrogen cooling system. The data set was corrected for absorption. CCDC 612715. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609475a.

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