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Synthesis of [(η^5-C_5H_5)Fe(CO)$_2$BCl$_2$·NC$_5$H$_4$-4-Me] from [(η^5-C_5H_5)Fe(CO)$_2$BCl$_2$]: First Preparation of a Lewis Acid−Base Adduct from a Boryl Complex

Holger Braunschweig,* Krzysztof Radacki, Fabian Seeler, and George R. Whittell

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland,
D-97074 Würzburg, Germany

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Summary: The (dichloroboryl)iron complex [(η^5-C_5H_5)-Fe(CO)$_2$BCl$_2$] and its corresponding Lewis base adduct with 4-methylpyridine have been prepared; characterization by single-crystal X-ray diffraction has afforded a structural comparison between the two species.

The chemistry of transition-metal boryl complexes has been the subject of intense research for well over a decade.[1] Interest in this area has been driven by the role of these compounds in the hydro-[2] and diboration[3] of unsaturated organic substrates and selective C−H bond activation of hydrocarbons.[4] Crucial to the understanding of these novel processes is a knowledge of the nature of the metal−boron bond. To this aim, many fundamental studies have been conducted, in particular with a view to assessing the degree of π-bonding between the metal and the formally sp^2-hybridized boron center.[1] However, despite many advances, some elementary chemistry of these compounds, which might offer further insight into the character of this bond, still remains unexplored.

Given the propensity of boranes BR_3 to form adducts with Lewis bases, it must be considered surprising that only a few authentic Lewis base stabilized boryl complexes have been reported[5,6] and that none of these have been prepared from the corresponding free boryl compounds. Attempted syntheses may have been unsuccessful because only a few boryl complexes retain the metal−boron linkage through boron-centered reactivity.[7] Furthermore, as all examples of base-stabilized boryl complexes contain the parent $-BH_2$ ligand (which remains elusive when unstabilized)[5,6] and the vast majority of base-free boryl complexes contain π-donating substituents at boron,[1] it can be concluded that the latter may not be sufficiently Lewis acidic for such chemistry. As part of our studies on the synthesis and reactivity of dihaloboryl complexes, we herein report the synthesis and structure of the 4-methylpyridine adduct of [(η^5-C_5H_5)Fe(CO)$_2$BCl$_2$]. A comparison with the molecular structure of the starting dichloroboryl species provides strong experimental evidence for a π-interaction between the iron center and boron.

The dichloroboryl complex [(η^5-C_5H_5)Fe(CO)$_2$BCl$_2$] (**1**) was prepared by a procedure similar to that reported by Aldridge et al.[8] and was essentially identical spectroscopically. Subsequent recrystallization from heptane at −35 °C afforded orange plates suitable for single-crystal X-ray diffraction,[9] the first such study to be conducted on a dichloroboryl complex. The asymmetric unit contains one unique molecule which exhibits the expected three-legged piano-stool structure (Figure 1). The iron−boron bond distance (1.942(3) Å) is the shortest observed in any half-sandwich boryliron complex and is particularly noteworthy, given the angle of intersection (77.7°) between the planes defined by C_5H_5 ring centroid−Fe(1)−B(1) and Cl(1)−B(1)−Cl(2). The shortest such interaction previously reported was that in [(η^5-C_5H_5)Fe(CO)$_2$B(cat)][10] (cat = 1,2-$O_2C_6H_4$; 1.959(6) Å), which exhibited a corresponding interplanar angle of 7.9°. For the latter, these two features were interpreted concomitantly to conclude that the small bond distance was the consequence of a modest Fe−B π-interaction, facilitated by overlap between the vacant p orbital on boron and the HOMO of the [(η^5-C_5H_5)Fe(CO)$_2$]$^+$ fragment. Although the relative orientations of the transition-metal fragment and the boryl ligand preclude the same interaction in **1**, the possibility for π-overlap still exists, but in this instance with HOMO-2.[11] In a recent DFT study,[12] it was calculated for the model compound [(η^5-C_5H_5)Fe(CO)$_2$B($O_2C_2H_2$)] that the π-contribution to bonding is very similar for each orientation (12.2 and

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* To whom correspondence should be addressed. Fax: +49 931 888 4623. Tel: +49 931 888 5260. E-mail: h.braunschweig@mail.uni-wuerzburg.de.

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[9] Crystal data for **1**: $C_7H_5BCl_2FeO_2$, M_r = 258.67, triclinic, a = 7.6434(17) Å, b = 8.4881(19) Å, c = 8.843(2) Å, α = 89.656(4)°, β = 70.731(4)°, γ = 63.761(4)°, U = 0.47912(19) Å^3, T = 173(2) K, space group $P\bar{1}$ (No. 2), Z = 2, μ(Mo Kα) = 2.088 mm^{-1}, 10 279 reflections measured, 1914 unique (R_{int} = 0.0312), which were used in all calculations. The final R1 and wR2 values (all data) were 0.0330 and 0.0764, respectively.

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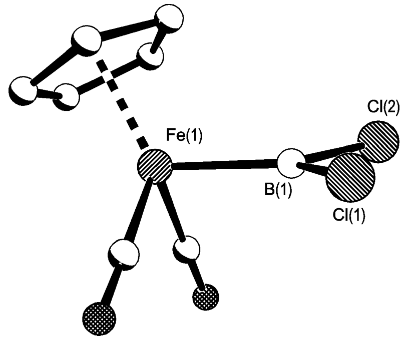

Figure 1. Molecular structure of [(η^5-C_5H_5)Fe(CO)$_2$BCl$_2$] (**1**). Selected bond lengths (Å) and angles (deg): Fe(1)−B(1) = 1.942(3), B(1)−Cl(1) = 1.781(3), B(1)−Cl(2) = 1.783(3); Cl(1)−B(1)−Cl(2) = 110.83(15).

13.8% for the broadly coplanar and orthogonal alignments, respectively) and results in only a small energy difference (0.025 kcal mol^{-1}) between the two conformers. It was also noted that due to the relatively small π-component to the Fe−B bond and the associated low barrier to rotation (ca. 1 kcal mol^{-1}), the adoption of either conformation in the solid state could well be dominated by crystal-packing forces. Indeed, the compound [(η^5-C_5H_5)Fe(CO)$_2$B{Si(SiMe$_3$)$_3$}Cl] exhibits a relatively small Fe−B bond distance (1.964(8) Å), in addition to an almost orthogonal orientation of the symmetry planes of both the boryl ligand and transition-metal fragment.[13] In this case, however, such an orientation is likely to be also favored on steric grounds, an argument that cannot be invoked when discussing the dichloro- and catecholatoboryl complexes. Consistent with the structural data, the DFT calculations on [(η^5-C_5H_5)Fe(CO)$_2$B(cat)] and **1** reveal the latter to contain a significantly larger π-component (10.7 and 17.8%, respectively) of the orbital contribution to bonding. Although the calculated bond length for the dichloroboryl complex (2.008 Å) is longer than that determined by X-ray diffraction, the overestimation (3.3%) is of an order similar to that found when comparing calculated structural parameters with those observed experimentally. However, the larger calculated π-component to covalent bonding in the dichloroboryl complex, relative to that containing the catecholate substituent, does not appear to be reflected spectroscopically. The carbonyl stretching frequencies of **1** are only slightly blue-shifted with respect to those of [(η^5-C_5H_5)Fe(CO)$_2$B(cat)][10] (2026, 1974 and 2024, 1971 cm^{-1}, respectively), and this is especially surprising, as the catecholatoboryl group would be expected to be the weaker σ-donor, on account of the more electronegative substituents at boron.

The reaction of **1** with 4-methylpyridine in toluene at 0 °C afforded the boryl complex Lewis base adduct [(η^5-C_5H_5)Fe(CO)$_2$BCl$_2$·NC$_5$H$_4$-4-Me] (**2**), in almost quantitative yield. Compound **2** exhibits carbonyl stretching bands which appear at frequencies (1976 and 1916 cm^{-1}) significantly lower than those observed for **1**, and this is consistent with an increase in electron density at the metal center, arising from collapse of the Fe−B π-interaction through rehybridization at boron. These, however, are still noticeably higher in frequency than those reported for [(η^5-C_5Me_5)Fe(CO)$_2$BH$_2$·PMe$_3$] (1932 and 1896 cm^{-1}): the only half-sandwich, base-stabilized boryliron complex previously reported.[14] This, presumably, is a feature of the greater electron-releasing nature of both C_5Me_5 and BH$_2$·PMe$_3$ relative to C_5H_5 and BCl$_2$·NC$_5$H$_4$-4-Me, respectively. The ^{11}B{^{1}H} NMR spectrum of **2** exhibits the expected sharp singlet resonance (δ 18.8) at high field compared to that observed for **1** (δ 90.0), which is characteristic of an increase in coordination number at boron from 3 to 4. The phosphine-stabilized parent boryl complex [(η^5-C_5Me_5)Fe(CO)$_2$BH$_2$·PMe$_3$] exhibits a resonance at considerably higher field (δ −25.9), presumably due to the less electronegative substituents. Consistent with our findings is the observation that the ^{11}B{^{1}H} NMR resonance of [(CO)$_4$CoBH$_2$·L] also shifts to low field on increasing the σ-donor strength of L (e.g. δ −10.0 and 3.6 for L = Me$_2$S and NEt$_3$, respectively).[5]

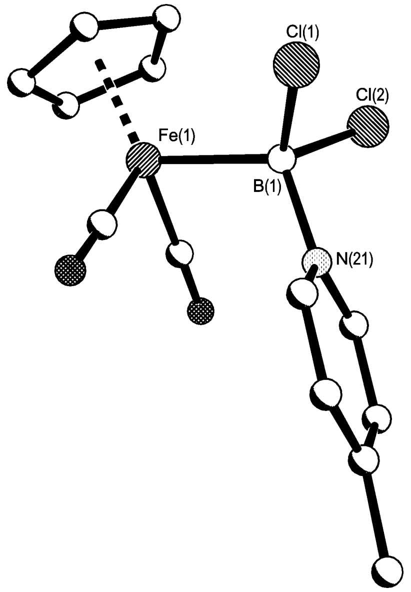

Figure 2. Molecular structure of [(η^5-C_5H_5)Fe(CO)$_2$BCl$_2$·NC$_5$H$_4$-4-Me] (**2**). Selected bond lengths (Å) and angles (deg): Fe(1)−B(1) = 2.1326(14), B(1)−Cl(1) 1.8853(14), B(1)−Cl(2) = 1.8774(14), B(1)−N(1) = 1.6103(17); Cl(1)−B(1)−Cl(2) = 107.18(7).

Crystals suitable for a single-crystal X-ray diffraction study were grown by slow diffusion of heptane into a solution of **2** in toluene.[15] These contain one molecule per asymmetric unit with no short intermolecular contacts. The boron center exhibits the expected tetrahedral geometry while the [(η^5-C_5H_5)Fe(CO)$_2$]$^+$ fragment is essentially unchanged from that in **1** (Figure 2). The most striking structural features are the Fe−B (2.1326(14) Å) and B−Cl (average 1.8814(14) Å) bond distances, which are elongated by 10 and 5.6%, respectively, upon coordination of 4-methylpyridine. These afford compelling evidence for the existence of an Fe−B π-interaction in **1** when structural data for B$_2$Cl$_4$[16] and B$_2$Cl$_4$·

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$2NHMe_2$[17] are considered. In the absence of a π-component to the B−B bond, there is negligible lengthening upon rehybridization, whereas the B−Cl bonds extend to an extent (7.7%) similar to that observed in this study. Although the former appears surprising and could be attributed to the relatively low precision to which the molecular structure of B_2Cl_4 was determined, a similarly small lengthening (2%) was reported for the conversion of $B_2(cat)_2$ to the corresponding bis(4-methylpyridine) adduct.[18] The absence of an appropriate π-acceptor orbital on boron is also manifested in the relative orientations of the iron fragment and the boryl ligand in **2**. Here steric interactions dominate, resulting in an anti conformation, as evidenced by the C_5H_5 centroid−Fe−B−N dihedral angle (177.3°). A similar conformation is also observed for $[(\eta^5\text{-}C_5Me_4Et)Fe(CO)_2BH_2\cdot PMe_3]$ which exhibits a significantly longer Fe−B distance (2.195(14) Å).

In conclusion, the reaction of **1** with 4-methylpyridine yields **2**, in the first demonstration of Lewis acid−base adduct formation involving a transition-metal boryl complex. A comparison of the spectroscopic and structural data for **1**, **2**, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2B(cat)]$ reflects the relative π-accepting properties of the respective boryl ligands, as predicted by theory, if not necessarily the size of the differences between them.

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Supporting Information Available: Text detailing the synthetic procedures, spectroscopic data and structural determinations for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-237191 (**1**) and CCDC-237192 (**2**). Copies of these data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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