J. Am. Chem. Soc. **1998,** *120,* 6401−6402 6401

Communications to the Editor

Synthesis and Characterization of a Terminal Borylene (Boranediyl) Complex

Alan H. Cowley,* Viviana Lomelí, and Andreas Voigt

Department of Chemistry and Biochemistry
The University of Texas at Austin
Austin, Texas 78712

Received February 25, 1998

The chemistry of terminal boryl (R_2B) complexes has blossomed into an area of considerable current interest because of the involvement of such species in the transition metal catalyzed diboration of alkenes and alkynes.[1] It is somewhat surprising, therefore, that structurally authenticated terminal borylene (RB) complexes have not been described in the literature,[2] particularly since analogous RE complexes of the remaining group 13 elements have been isolated and characterized by X-ray diffraction.[3] In planning a synthetic approach to a terminal borylene complex, we opted to employ the Me_5C_5 ligand on the basis that it would afford adequate steric shielding of and electron release to the boron center. As a further point of interest, we were aware that the cluster $[B(C_5Me_5)]_n$ is the only missing member of the series $[E(C_5Me_5)]_n$ (E = Al, Ga, In, Tl).[4,5]

Treatment of 1.69 g (7.8 mmol) of $(Me_5C_5)BCl_2$[6] with 1.92 g (7.8 mmol) of $K_2[Fe(CO)_4]$[7] in 60 mL of toluene at −78 °C, followed by slow warming to 25 °C and filtration, resulted in a dark brown colored solution from which 0.72 g (30% yield) of colorless crystals (mp 155 °C, dec.) deposited following concentration and storage at 0 °C for 1 week. Elemental analysis and HRMS data for the crystalline material (**1**) corresponded to the empirical composition $[(Me_5C_5)BFe(CO)_4]$, and the pattern of CO stretching frequencies in the IR spectrum (2018, 1938, 1908, and 1884 cm^{-1}) was indicative of an $Fe(CO)_4$ moiety of C_{3v} symmetry.[8] The ^{11}B NMR chemical shift of $\delta = -35.3$ was significantly different from those reported for bridged borylene complexes[9] (e.g., $[\{(\eta^5\text{-MeCp})Mn(CO)_2\}_2\mu\text{-BR}]$, R = NMe_2, $\delta = 103$; R = *t*-Bu, $\delta = 170$) and suggestive of terminal attachment of the Me_5C_5B fragment. The equivalence of the Me_5C_5 methyl groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra[8] down to −78 °C suggested an η^5-bonding mode to boron. However, since cyclopentadienyl-substituted boranes undergo facile sigmatropic shifts,[6] an X-ray crystal structure was desirable. The solid state of $(\eta^5\text{-}Me_5C_5)BFe(CO)_4$ (**1**) comprises isolated molecules with no short intermolecular contacts (Figure 1).[10] Each molecule is located on a crystallographic mirror plane which contains the iron atom, the axial carbonyl ligand, one of the equatorial carbonyl ligands, the boron atom, and one of the ring CMe moieties. Of primary importance is the fact that the Cp*−borylene unit is bonded to the 16-electron $Fe(CO)_4$ fragment in a terminal fashion. The iron atom adopts the traditional trigonal bipyramidal geometry, and the borylene fragment is located in an axial position. The B−Fe bond length of 2.010(3) Å falls between those reported for the boryl complexes $CpFe(CO)_2BCat$ (1.959(6) Å)[11] and $[Fe(CO)_4(BCat^*)_2]$ (2.028(7) Å; BCat* = $\text{-}BO_2C_6H_3\text{-}4\text{-}t\text{-}Bu$),[12] both of which feature a bond order of unity. The other salient structural facet relates to the observation that the C_5Me_5 group is η^5-bonded to boron. To our knowledge, the only other example of a crystallographically characterized compound with this bonding mode is the B(III) cation $[BBr(\eta^5\text{-}C_5Me_5)]^+$ for which the average B−C distance is 1.683 Å.[13] The observation of a longer average B−C distance in **1** (1.814(4) Å) is consistent with (a) the absence of a positive charge and (b) with the assignment of a formal oxidation state of +1 to boron. The ring centroid−B−Fe

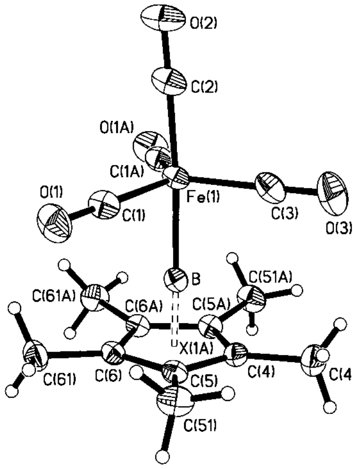

Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_5)BFe(CO)_4$ (**1**) showing the atom-numbering scheme. Important parameters: Fe−B 2.010(3) Å, Fe−C(1) 1.774(2) Å, Fe−C(2) 1.793(3) Å, Fe−C(3) 1.786(4) Å, B−X(1A) (ring centroid) 1.347 Å, B−C(4) 1.811(4) Å, B−C(5) 1.812(3) Å, B−C(6) 1.817(4) Å, C(4)−C(5) 1.428(3) Å, B−Fe−C(1) 85.52(8)°, B−Fe−C(3) 88.66(14)°.

---

[1] See, for example: Clegg, W.; Lawler, F. J.; Marder, T. B.; Nguyen, P.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Robins, E. G.; Scott, A. J.; Souza, F. E. S.; Stringer, G.; Whittel, G. R. *J. Chem. Soc., Dalton Trans.* **1998**, 301 and references therein.

[2] For NMR and IR assays of species of empirical composition $R_2NBFe(CO)_4$, see, for example: Schmid, G.; Petz, W.; Nöth, H. *Inorg. Chim. Acta* **1970**, *4*, 423.

[3] Of particular relevance are the following: (a) (M = Al) Weiss, J. W.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70. (b) (M = Ga) Su, J.; Li, X.-W.; Crittendon, C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511.

[4] Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129.

[5] Alkali metal reduction of sterically encumbered arylboron dihalides leads to a range of 9-borafluorenyl derivatives via an intermediate borylene (boranediyl) species. Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981.

[6] Jutzi, P.; Krato, B.; Hursthouse, M.; Howes, A. J. *Chem. Ber.* **1987**, *120*, 565.

[7] Gladysz, J. A.; Tam, W. *J. Org. Chem.* **1978**, *43*, 2279.

[8] HRMS (CI, CH_4): calcd for $[M + H]^+$ ($C_{14}H_{16}{}^{11}B^{56}FeO_4$), 315.0491; found 315.0497. IR (Nujol mull): $\nu_{CO} = 2018, 1938, 1908, 1884\ cm^{-1}$. ^1H NMR (300.00 MHz, 295 K, C_6D_6): δ 1.49 (s) CH_3. $^{13}C\{^1H\}$ NMR (75.48 MHz, 295 K, C_6D_6): δ 114.52 (ring C), 8.94 (ring Me). ^{11}B NMR (96.28 MHz, 295 K, C_6D_6): δ −35.3 (s).

[9] Braunschweig, H.; Wagner, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 825.

[10] Crystal data for **1**: $C_{14}H_{15}BFeO_4$, orthorhombic, *Pnnm*, $a = 13.095(4)$, $b = 9.663(2)$, and $c = 11.294(1)$ Å, $V = 1429.2(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.459$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 1.063\ mm^{-1}$. A suitable single crystal of **1** was covered with mineral oil and mounted on a Siemens P4 diffractometer at 178(2) K. A total of 1904 unique reflections were collected in the range of $4.76 < 2\theta < 57.0$ using Mo Kα radiation ($\lambda = 0.710\,73$ Å). Of these, 1555 reflections were considered observed ($I > 2.0\sigma(I)$) and were used to solve (direct methods) and refine (full matrix, least squares) the structure of **1**; wR2 = 0.1170, R = 0.0465.

[11] Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908.

[12] He, X.; Hartwig, J. F. *Organometallics* **1996**, *15*, 400.

[13] Dohmeier, C.; Köppe, R.; Robl, C.; Schnöckel, H. *J. Organomet. Chem.* **1995**, *487*, 127.

S0002-7863(98)00643-X CCC: $15.00

arrangement is close to linear (178.6°), and the equatorial CO ligands are bent slightly toward the boron atom.[14]

The nature of the transition metal−group 13 element bonding in REML$_n$ complexes is a subject of current dispute, particularly in the case of E = Ga. Basically, two bonding models have been proposed for covalent interaction between group 13 (RE) and transition metal (ML$_n$) fragments, namely (i) a triple-bonded model, **A** (E = Ga),[3b] and (ii) a single, dative-bonded model, **B** (E = Ga).[15]

$\mathrm{RE{\equiv}ML}_n$	$\mathrm{RE{\rightarrow}ML}_n$	$\mathrm{RE{=}ML}_n$
A	**B**	**C**

A double-bonded model, **C**, is also conceivable; however, this would require the RE fragment to adopt a triplet state[16] and, in turn, demand a high oxidation state ML$_n$ moiety. As pointed out above, the B−Fe distance in **1** corresponds to that of a single bond. Moreover, the CO stretching frequencies (vide supra) are similar to those of typical two-electron donor $\mathrm{L{\rightarrow}Fe(CO)_4}$ complexes;[17] hence, on experimental grounds we believe that, as in the case of the aluminum analogue, $(\eta^5\text{-}C_5Me_5)AlFe(CO)_4$,[3a] **B** is the most appropriate bonding model.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for support.

Supporting Information Available: X-ray experimental details with positional parameters and full bond distances and angles for **1** (6 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available via the Web only. See any current masthead page for ordering information and Web access instructions.

JA9806433

---

[14] This weak “umbrella effect” has been observed previously: Crabtree, R. H.; Lavin, M. *Inorg. Chem.*, **1986**, *25*, 805. Simpson, C. Q., II.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 1641. Fischer, R. A.; Miehr, A.; Priermeier, T. *Chem. Ber.* **1995**, *128*, 831.

[15] Cotton, F. A.; Feng, X. *Organometallics* **1998**, *17*, 128.

[16] The parent borylene, BH, is known to possess a singlet ground state ($^1\Sigma^+$). The triplet state, ($^3\Pi$) is computed to lie 31.9 kcal/mol above the ground state. See: Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1986**, *129*, 279 and references therein.

[17] The CO stretching frequencies (in cm^{-1}) for, e.g., $Ph_3PFe(CO)_4$ appear at 2052, 1979, and 1947.[15] The ν_{CO} values (in cm^{-1}) for $(\eta^5\text{-}C_5Me_5)AlFe(CO)_4$ are 2024, 1948, and 1903,[3a] while those for Ar*GaFe(CO)$_4$ (Ar* = 2,6-bis(2,4,6-triisopropylphenyl)phenyl) are 2032, 1959, 1941, and 1929.[3b]