DOI: 10.1002/anie.200901022

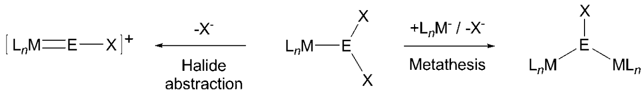
CO Analogues

Coordination and Activation of the BF Molecule**

*Dragoslav Vidovic and Simon Aldridge**

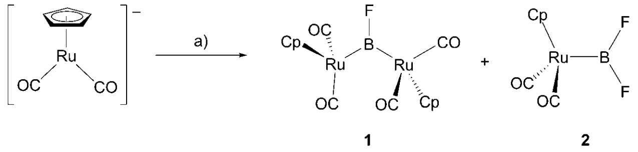
Coordination to a transition-metal center offers a convenient synthetic approach applicable both to the labilization of kinetically inert molecules and to the trapping of highly reactive species.[1–3] Thus, the activation of the dinitrogen molecule (N_2) at a metal center—mimicking the capabilities of complex biological systems—illustrates the significant changes in electronic structure which occur on coordination.[2,4] The isoelectronic molecule carbon monoxide (CO), while more reactive in the "free" state, is a much-utilized ligand in organometallic chemistry, primarily owing to its ability to stabilize low-valent transition-metal centers.[5] Among this family of simple diatomic molecules, fluoroborylene (BF) offers a stark contrast to both N_2 and CO, being an exotic species known only at extreme temperatures or in high vacuum, and as yet eluding structural characterization as a ligand in a simple metal complex.[6] In part, the steady increase in lability along the series of diatomic molecules N_2, CO, BF reflects the decreasing energy difference between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO gap) and increasing bond polarity.[7]

Notwithstanding this, quantum chemical studies have predicted BF to form stronger bonds to transition-metal centers than either N_2 or CO, principally owing to improved σ-donor capabilities.[7] Despite such thermodynamic advantages, the high B–F bond polarity, and consequent electrophilicity at boron, are likely to render such complexes very labile. The borylene ligand is therefore typically found in conjunction with more sterically bulky or π-electron-releasing substituents (such as amino groups).[8] However, recent synthetic studies have demonstrated the viability of complexes containing bridging BX or terminal GaX ligands (X = heavier Group 17 element),[9,10] together with transition-metal compounds containing the difluoroboryl (BF_2) unit, which might serve as precursors in the formation of BF-containing complexes by either fluoride abstraction or metathesis processes (Scheme 1).[11] With this in mind, we set out to synthesize BF-containing transition-metal complexes, focusing initially on systems featuring a bridging coordination mode, given the reduced lability typical of bridging borylene complexes compared to their terminally coordinated analogues.[12] Herein we report the synthesis and structural characterization of the first such system, together with a comparative study (vs. CO) of its reactivity towards electrophiles.



Scheme 1. Syntheses of transition-metal complexes containing Group 13 monohalide ligands in either terminal or bridging coordination modes.

The reaction of $BF_3{\cdot}OEt_2$ with Na[CpRu(CO)$_2$] (Cp = C_5H_5) in diethyl ether is shown by ^{11}B NMR spectroscopy to result in the formation of the fluoroborylene complex [{CpRu(CO)$_2$}$_2$(μ-BF)] (**1**) as the predominant boron-containing product in greater than 90% conversion (δ_B = 97.3 ppm, $^1J_{BF}$ = 247 Hz). The presence of a small amount (less than 10%) of a second product is also indicated by a triplet resonance ($^1J_{BF}$ = 169 Hz) at δ_B = 40.8 ppm; this species was subsequently shown to be the difluoroboryl complex [CpRu(CO)$_2$BF$_2$] (**2**).[13] Interestingly, this selectivity for boryl and borylene products is reversed when toluene is used as the reaction medium (for otherwise identical reaction stoichiometries and durations); under these conditions, only 10% of the product mixture is shown to be the desired fluoroborylene system **1**, with the remainder being the difluoroboryl complex **2** (Scheme 2).



	1	2
Diethyl ether	90 %	<10 %
Toluene	10 %	90 %

Scheme 2. Solvent-induced selectivity in the synthesis of fluoroborylene and difluoroboryl complexes **1** and **2**. Key reagents and conditions: a) $BF_3{\cdot}OEt_2$ (0.58 equiv), diethyl ether, −78 to 20°C, then a further 24 h at 20°C, 90% conversion to **1** as determined by ^{11}B NMR spectroscopy (32% yield of isolated product). The analogous reaction in toluene under otherwise identical conditions leads to 90% conversion to **2**.

^1H and ^{13}C NMR spectroscopy and elemental microanalysis data for **1** are consistent with the proposed formulation, and the ^{11}B and ^{19}F NMR spectra show a doublet and a partially collapsed quartet, respectively ($^1J_{BF}$ = 284 Hz), consistent with an intact B–F bond.[11,14] The ^{11}B resonance (δ_B = 97.3 ppm) is shifted 50–60 ppm downfield from those of related difluoroboryl complexes (e.g. δ_B = 40.8, 47.1 ppm for **2** and [CpFe(CO)$_2$BF$_2$], respectively), consistent with previous

---

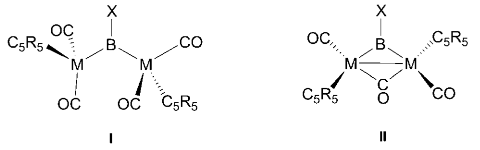
[*] Dr. D. Vidovic, Dr. S. Aldridge
Inorganic Chemistry, University of Oxford
South Parks Road, Oxford, OX1 3QR (UK)
Fax: (+44) 1865-272-690
E-mail: simon.aldridge@chem.ox.ac.uk
Homepage: http://users.ox.ac.uk/~quee1989/

[**] We thank the EPSRC for funding and for access to the National Mass Spectrometry facility and Dr. Amber L. Thompson for crystallographic assistance.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901022.

reports of the effects of increasing metalation at the boron center.[10,11] Moreover, the significant upfield shift of this signal compared to bridging borylene complexes featuring less strongly π-donating substituents (e.g. $\delta_B = 146.7$,[10] 158.1,[12a,b] 170.0 ppm[15] for related μ-BCl, μ-BMes, and μ-B*t*Bu systems) is as expected on the basis of ample precedent in tri(organo)borane chemistry (cf. $\delta_B = 119.1$ ppm for the more strongly π-stabilized μ-BN(SiMe$_3$)$_2$ ligand).[16]

Among bridging borylene complexes of the Group 8 metals, two structural types are precedented (types I and II, Scheme 3), that is, with or without a formal metal–metal bond (and associated bridging carbonyl ligand).[10,12,17] Although the mass spectrometric data for **1** cannot distinguish between a structure of type II and one of type I in which fragmentation has led to the loss of one carbonyl ligand under electron-impact conditions, the measured carbonyl stretching frequencies for **1** (2012, 1960 cm^{-1}) imply an exclusively terminally bound carbonyl ligand set.[10,12a,b] These spectroscopic inferences were subsequently confirmed crystallographically with single crystals of **1** obtained from a saturated hexane solution at −30 °C. The molecular structure (Figure 1) conforms to an unsupported type I geometry (d(Ru···Ru) = 3.844 Å) and features a planar tricoordinate boron center (sum of the angles = 360° within the standard 3σ limit). As far as we are aware, this mode of coordination of the BF ligand is unprecedented in carbonyl chemistry—there are no crystallographically authenticated examples of a single CO ligand bridging between two transition-metal centers without an attendant metal–metal bond or additional bridging ligand.[18]



Scheme 3. Unsupported (type I) and supported (type II) bridging modes of coordination of the borylene ligand BX.

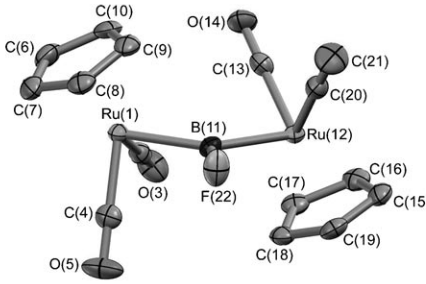
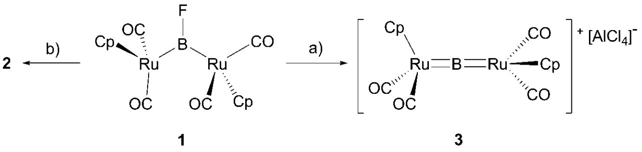


Figure 1. Molecular structure of fluoroborylene complex **1**. Hydrogen atoms are omitted for clarity, and thermal displacement ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ru(1)–B(11) 2.107(3), Ru(12)–B(11) 2.110(3), B(11)–F(22) 1.348(3); Ru(1)-B(11)-Ru(12) 131.4(1), Ru(1)-B(11)-F(22) 114.5(2), Ru(12)-B(11)-F(22) 114.0(2).

The Ru–B bond lengths in **1** (2.107(3), 2.110(3) Å) are very similar to the sum of the covalent radii for ruthenium and boron (2.12 Å)[19] and are comparable to those in related systems for which an essentially σ-only Ru–B linkage has been proposed (e.g. 2.115(2) Å for [CpRu(CO)$_2$B(Cl)N(SiMe$_3$)B(Cl)N(SiMe$_3$)$_2$]).[20] Furthermore, the B–F bond length (1.348(3) Å) is comparable to those found in fluoroboryl complexes (typically 1.32–1.35 Å);[11,14] while this value is somewhat smaller than the sum of the covalent radii for boron and fluorine (1.46 Å),[19] the shortening is much less significant than that observed for bridging carbonyl ligands (e.g. 1.166(3) Å for **4** (see below) vs. 1.43 Å for the sum of the covalent radii for carbon and oxygen),[19] consistent with a lower E–X (EX = BF, CO) bond order for BF. Furthermore, the more polar nature of the BF ligand is presumably responsible for intermolecular contacts in the solid-state structure of **1** (between the boron-bound fluorine atom F(22) and the hydrogen atom H(101) attached to C(10)), which fall within the sum of the respective van der Waals radii (2.67 Å).[19] Moreover, the H(101)···F(22) and C(10)···F(22) separations (2.56 and 3.161(3) Å) and the C(10)-H(101)···F(22) angle (120.3°) fall within the ranges expected for unconventional hydrogen bonds of the type C-H···X[21] and are reminiscent of the values reported for earlier examples of B-F···H-C interactions.[14d] Such interactions in solid **1** hint at an ability to interact with Lewis acids in a manner reminiscent of classical activation pathways for coordinated dinitrogen.[22] With this in mind, and as an additional comparison of the electronic structure of the coordinated diatomic molecules BF and CO, we examined the reactivity of **1** and of bridging carbonyl complexes towards a range of Lewis acids (Scheme 4).



Scheme 4. Reactivity of fluoroborylene complex **1**: heterolytic cleavage of the BF bond by reaction with the Lewis acid AlCl$_3$ and thermolysis to give difluoroboryl complex **2**. Key reagents and conditions: a) AlCl$_3$ (3.3 equiv), dichloromethane, 12 h, 20 °C, 50% yield of isolated product. The 1:1 reactions with AlCl$_3$ and B(C$_6$F$_5$)$_3$ also generate **3**, although less cleanly. b) Toluene, 80 °C, 14 days, quantitative yield as determined by ^{11}B NMR spectroscopy.

Tris(dimethylamino)borane does not appear to interact with **1** (as judged by ^{11}B NMR spectroscopy), while reaction with the much more Lewis acidic borane B(C$_6$F$_5$)$_3$ leads to the formation of two products. A broad peak at $\delta_B = 177$ ppm belongs to the cationic metallaborylene [{CpRu(CO)$_2$}$_2$(μ-B)]$^+$ (see below), while a triplet at $\delta_B = 41$ ppm ($J = 169$ Hz) arises from the difluoroboryl complex **2**. The same two products are also generated in the corresponding reaction with one equivalent AlCl$_3$.[23] The formation of [{CpRu(CO)$_2$}$_2$(μ-B)]$^+$ in both reactions is consistent with the ready heterolytic activation of the BF ligand; the presence of **2** as a side product in each case, however, points to additional modes of reactivity involving M−B bond cleavage. Complex **2** conceivably results from a competing reaction of the starting material **1** with abstracted fluoride (i.e. as $[FB(C_6F_5)_3]^-$ or $[AlCl_3F]^-$). Notwithstanding this, reaction of **1** with a greater than three-fold excess of $AlCl_3$ leads to the clean formation of $[\{CpRu(CO)_2\}_2(\mu\text{-}B)]^+$ as judged by ^{11}B NMR spectroscopy. The cationic metallaborylene can then be isolated as its $[AlCl_4]^-$ salt (**3**) in 50% yield by layering the dichloromethane reaction solution with hexanes.[24] The same cation can also be generated using $Na[B(C_6H_3(CF_3)_2\text{-}3,5)_4]$, although the reaction is much slower, presumably owing to the much lower solubility of the Lewis acid in dichloromethane (cf. $AlCl_3$). Interestingly, this fluoride abstraction reactivity for **1** with $AlCl_3$—the first reported example of such chemistry for substrates of this type—is the reverse of that reported by Braunschweig and co-workers for $[\{Mn(CO)_5\}_2(\mu\text{-}B)]^+$, which abstracts fluoride from borate anions.[25]

While the formulation of **3** is strongly implied by its ^{11}B NMR chemical shift ($\delta_B = 177$ ppm; cf. 191.2 ppm for an analogous iron complex)[25] and its blue-shifted carbonyl stretching frequencies (2062, 2027 cm^{-1} vs. 2012, 1960 cm^{-1} for **1**), its unambiguous structural characterization is afforded by single crystal X-ray diffraction (Figure 2). An approximately linear environment is revealed for the boron center ($\measuredangle$(Ru-B-Ru) = 175.5(2)°), consistent with a two-coordinate geometry. Moreover, the Ru−B bonds (1.963(3) and 1.931(3) Å) are significantly shorter (7.7%) than those measured for **1**[26] and are very similar to those measured for the aminoborylene complexes $[CpRu(CO)(L)(BNCy_2)]^+$ (L = CO 1.960(6) Å, L = PMe_3 1.928(4) Å; Cy = cyclohexyl), consistent with an enhanced π component to the Ru−B bond.[27]

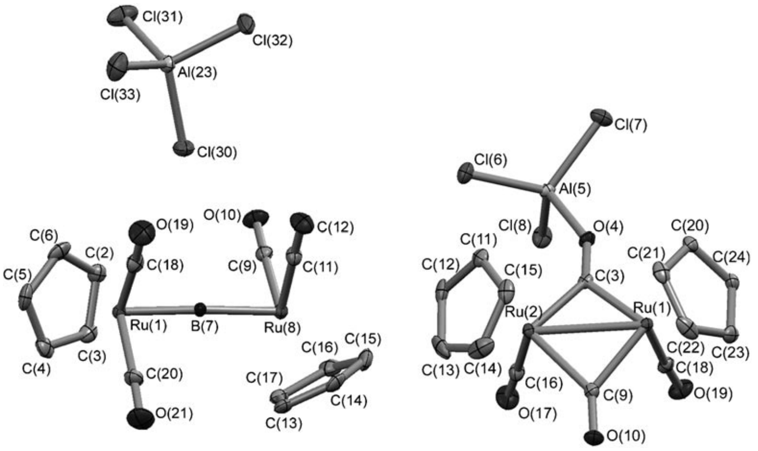


Figure 2. Molecular structures of $[\{CpRu(CO)_2\}_2(\mu\text{-}B)]^+[AlCl_4]^-$ (**3**, left) and $[\{Cp(CO)Ru\}_2(\mu\text{-}COAlCl_3)(\mu\text{-}CO)]$ (**4**, right). Hydrogen atoms are omitted for clarity, and thermal displacement ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: **3**: Ru(1)–B(7) 1.931(3), Ru(8)–B(7) 1.963(3); Ru(1)-B(7)-Ru(8) 175.5(2), Cp centroid-Ru(1)-Ru(8)-Cp centroid 95.8. **4**: Ru(1)–Ru(2) 2.7159(3), Ru(1)–C(3) 1.986(2), Ru(1)–C(9) 2.045(3), Ru(2)–C(3) 1.978(2), Ru(2)–C(9) 2.066(3), C(3)–O(4) 1.235(3), O(4)–Al(5) 1.812(2), C(9)–O(10) 1.166(3).

Finally, in an attempt to compare the reactivities of bridging CO and BF ligands, we also examined the reactivity of $[\{CpRu(CO)(\mu\text{-}CO)\}_2]$ towards $AlCl_3$.[28] In this case, crystallographic studies (Figure 2) are consistent with the formation of a simple $CO \rightarrow AlCl_3$ donor–acceptor adduct (*cis*-$[\{Cp(CO)Ru\}_2(\mu\text{-}COAlCl_3)(\mu\text{-}CO)]$, **4**) rather than complete EX bond cleavage.[29] Significant weakening of the CO bond is effected on coordination of the Lewis acid, as implied by CO bond lengths of 1.235(3) and 1.166(3) Å for the bridging $COAlCl_3$ and CO ligands. However, the greater multiple-bond character and less polar nature of the CO linkage are presumably responsible for the markedly reduced degree of bond activation compared to BF-containing complex **1**.

In conclusion, fluoroborylene (BF) has been trapped in the coordination sphere of a transition metal and structurally characterized for the first time. The dinuclear complex $[\{CpRu(CO)_2\}_2(\mu\text{-}BF)]$ (**1**) has been shown crystallographically to contain an unsupported bridging BF ligand—a mode of coordination unprecedented in the chemistry of CO. Moreover, further differences in the electronic structures of the EX bonds (EX = CO, BF) have been revealed by the contrasting extents of their reactivity towards Lewis acids. Thus, in the presence of $AlCl_3$, simple coordination at oxygen (without bond rupture) is observed for CO, while heterolytic cleavage is observed for the more polar and less significantly π-bonded BF ligand. Further studies of structure and reactivity of BF-containing complexes are ongoing and will be reported in due course.

Experimental Section

Included here are the preparative and spectroscopic data for **1**; crystallographic data for **1** and complete data for **2**–**4** are included in the Supporting Information.

Synthesis of **1**: $BF_3{\cdot}OEt_2$ (0.09 mL, 0.710 mmol) was added to $Na[CpRu(CO)_2]$ (0.300 g, 1.223 mmol) in diethyl ether (20 mL) at −78°C, and the reaction mixture was warmed to 20°C. After 24 h the reaction was judged incomplete by ^{11}B NMR spectroscopy, and additional $BF_3{\cdot}OEt_2$ (0.05 mL) was added, again at −78°C. After stirring for a further 24 h at 20°C, volatile reaction components were removed in vacuo, and the resulting solid was extracted with pentane (2 × 20 mL). The resulting yellow solution was concentrated to approximately 10 mL and stored at −30°C. A yellow solid formed, which was isolated by filtration and dried in vacuo. Single crystals suitable for X-ray diffraction were obtained by cooling a concentrated hexane solution to −30°C. Yield of isolated product: 0.93 g (32%). ^1H NMR (300 MHz, $[D_6]$benzene): $\delta = 4.67$ ppm (s, 10H, Cp). ^{13}C NMR (126 MHz, $[D_6]$benzene): $\delta = 87.6$ (Cp), 201.8 ppm (CO). ^{11}B NMR (96 MHz, $[D_6]$benzene): $\delta = 97.3$ ppm (d, $^1J_{BF} = 247$ Hz). ^{19}F NMR (282 MHz, $[D_6]$benzene): $\delta = -185.0$ ppm (broad partially collapsed quartet, $^1J_{BF} \approx 250$ Hz). IR (hexane solution, cm^{-1}): $\tilde{\nu} = 2012$, 1960 (CO). EI-MS, *m*/*z* (%) 446.9 (70) $[M-CO]^+$; correct isotope pattern for two Ru, one B atom. Exact mass calcd for $[M-CO]^+$, ^{10}B and ^{96}Ru isotopomer: *m*/*z* 435.8854, found 435.8848. Elemental analysis (%) calcd for **1** ($C_{14}H_{10}BFO_4Ru_2$): C 35.43, H 2.13; found: C 35.37, H 2.00.

Received: February 22, 2009
Published online: April 16, 2009

Keywords: boron · borylene ligands · halide abstraction · Lewis acids · ruthenium

---

[1] See, for example: H. H. Thorp, *Science* **2000**, *289*, 882 – 883.

[2] C. E. Laplaza, C. C. Cummins, *Science* **1995**, *268*, 861 – 863.

[3] For important examples of transition-metal complexes containing the diatomic molecules CX (X = S, Se, Te) as terminally bound ligands see, for example: a) M. C. Baird, G. Wilkinson, *J. Chem. Soc Chem. Commun.* **1966**, 267 – 268; b) G. R. Clark, S. M. James, *J. Organomet. Chem.* **1977**, *134*, 229 – 236; c) G. R. Clark, K. Marsden, W. R. Roper, L. J. Wright, *J. Am. Chem. Soc.* **1980**, *102*, 1206 – 1207; d) G. R. Clark, K. Marsden, C. E. F. Rickard, W. R. Roper, L. J. Wright, *J. Organomet. Chem.* **1988**, *338*, 393 – 410.

[4] A. D.; Allen, C. V. Senoff, *J. Chem. Soc. Chem. Commun.* **1965**, 621 – 622.

[5] See, for example: J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Sausalito, California, **1987**.

[6] a) P. L. Timms, *J. Am. Chem. Soc.* **1967**, *89*, 1629 – 1632; b) P. L. Timms, *J. Am. Chem. Soc.* **1968**, *90*, 4585 – 4589. A highly labile compound postulated as $[Fe(PF_3)_4BF]$ has also been identified spectroscopically: c) P. L. Timms, *Acc. Chem. Res.* **1973**, *6*, 118 – 123.

[7] a) A. W. Ehlers, E. J. Baerends, F. M. Bickelhaupt, U. Radius, *Chem. Eur. J.* **1998**, *4*, 210 – 221; b) U. Radius, F. M. Bickelhaupt, A. W. Ehlers, N. Goldberg, R. Hoffmann, *Inorg. Chem.* **1998**, *37*, 1080 – 1090; c) G. Frenking, N. Fröhlich, *Chem. Rev.* **2000**, *100*, 717 – 774.

[8] For recent reviews of transition-metal borylene chemistry see, for example: a) H. Braunschweig, D. Rais, *Heteroat. Chem.* **2005**, *16*, 566 – 571; b) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380 – 5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254 – 5274; c) S. Aldridge, D. L. Kays, *Main Group Chem.* **2006**, *5*, 223 – 249; d) H. Braunschweig, C. Kollann, F. Seeler, *Struct. Bonding (Berlin)* **2008**, *130*, 1 – 27; e) D. Vidovic, G. A. Pierce, S. Aldridge, *Chem. Commun.* **2009**, 1157 – 1171.

[9] a) N. D. Coombs, W. Clegg, A. L. Thompson, D. J. Willock, S. Aldridge, *J. Am. Chem. Soc.* **2008**, *130*, 5449 – 5451; b) H.-J. Himmel, G. Linti, *Angew. Chem.* **2008**, *120*, 6425 – 6427; *Angew. Chem. Int. Ed.* **2008**, *47*, 6326 – 6328; c) N. D. Coombs, D. Vidovic, J. K. Day, A. L. Thompson, D. D. LePevelen, A. Stasch, W. Clegg, L. Russo, L. Male, M. B. Hursthouse, D. J. Willock, S. Aldridge, *J. Am. Chem. Soc.* **2008**, *130*, 16111 – 16124.

[10] P. Bissinger, H. Braunschweig, F. Seeler, *Organometallics* **2007**, *26*, 4700 – 4702.

[11] a) A. Kerr, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, P. L. Timms, G. R. Whittell, *Chem. Commun.* **1998**, 319 – 320; b) N. Lu, N. C. Norman, A. G. Orpen, M. J. Quayle, P. L. Timms, G. R. Whittell, *J. Chem. Soc. Dalton Trans.* **2000**, 4032 – 4037; c) H. Braunschweig, K. Radacki, F. Seeler, G. R. Whittell, *Organometallics* **2006**, *25*, 4605 – 4610.

[12] See, for example: a) S. Aldridge, D. L. Coombs, C. Jones, *Chem. Commun.* **2002**, 856 – 857; b) D. L. Coombs, S. Aldridge, C. Jones, *J. Chem. Soc. Dalton Trans.* **2002**, 3851 – 3858; c) D. L. Coombs, S. Aldridge, C. Jones, D. J. Willock, *J. Am. Chem. Soc.* **2003**, *125*, 6356 – 6357.

[13] See the Supporting Information for synthetic and spectroscopic details, and reference [10] for comparative data for a related iron complex.

[14] a) Z. Lu, C.-H. Jun, S. R. de Gala, M. Sigalas, O. Eisenstein, R. H. Crabtree, *J. Chem. Soc. Chem. Commun.* **1993**, 1877 – 1880; b) Z. Lu, C.-H. Jun, S. R. de Gala, M. P. Sigalas, O. Eisenstein, R. H. Crabtree, *Organometallics* **1995**, *14*, 1168 – 1175; c) H. Braunschweig, M. Colling, C. Kollann, U. Englert, *J. Chem. Soc. Dalton Trans.* **2002**, 2289 – 2296; d) D. L. Coombs, S. Aldridge, A. Rossin, C. Jones, D. J. Willock, *Organometallics* **2004**, *23*, 2911 – 2926.

[15] H. Braunschweig, T. Wagner, *Angew. Chem.* **1995**, *107*, 904 – 905; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 825 – 826.

[16] H. Braunschweig, C. Kollann, U. Englert, *Eur. J. Inorg. Chem.* **1998**, 465 – 468.

[17] See, for example: H. Braunschweig, M. Colling, *J. Organomet. Chem.* **2000**, *614–615*, 18 – 26.

[18] As determined by a survey of the Cambridge Structural Database, February 11, 2009.

[19] J. Emsley, *The Elements*, Clarendon Press, Oxford, **1989**.

[20] See, for example: H. Braunschweig, C. Kollann, K. W. Klinkhammer, *Eur. J. Inorg. Chem.* **1999**, 1523 – 1529.

[21] See, for example: a) G. R. Desiraju, *Acc. Chem. Res.* **1991**, *24*, 290 – 296; b) G. A. Jeffrey, *J. Mol. Struct.* **1999**, *485–486*, 293 – 298; c) R. Vargas, J. Garza, D. A. Dixon, B. P. Hay, *J. Am. Chem. Soc.* **2000**, *122*, 4750 – 4755.

[22] See, for example: G. J. Leigh, *Nitrogen Fixation at the Millenium*, Elsevier, Amsterdam, **2002**, chap. 11.

[23] Reaction of **1** with one equivalent $AlCl_3$ also gives rise to a small amount of a third product ($\delta_B = 128$ ppm), thought to be the chloroborylene complex $[\{CpRu(CO)_2\}_2(\mu\text{-}BCl)]$,[10] which is presumably generated by the abstraction of chloride from $[AlCl_3F]^-$ by the strong electrophile $[\{CpRu(CO)_2\}_2(\mu\text{-}B)]^+$.

[24] Presumably the presence of the $[AlCl_4]^-$ counterion (rather than $[AlCl_3F]^-$ as implied by the reaction stoichiometry) reflects ready halide exchange in aluminate anions of this type and the insolubility of species containing aluminium and fluorine (such as AlF_3) in the dichloromethane reaction solvent.

[25] For a previous report of an ^{11}B resonance ascribed to a putative fluoroborylene complex ($\delta_B = 123.9$ ppm, $^1J_{BF} = 265$ Hz), see H. Braunschweig, K. Kraft, T. Kupfer, K. Radacki, F. Seeler, *Angew. Chem.* **2008**, *120*, 5009 – 5011; *Angew. Chem. Int. Ed.* **2008**, *47*, 4931 – 4933.

[26] A similar M–B bond shortening is observed for the corresponding iron complex $[\{(C_5H_4Me)Fe(CO)_2\}_2(\mu\text{-}B)]^+$ with respect to related chloroborylene precursors (8.5 %).[25]

[27] G. A. Pierce, D. Vidovic, D. L. Kays, N. D. Coombs, A. L. Thompson, E. D. Jemmis, S. De, S. Aldridge, *Organometallics*, DOI: 10.1021/om801215b.

[28] Although not completely structurally analogous with **1** (which has a type I structure; Scheme 3), $[\{CpRu(CO)(\mu\text{-}CO)\}_2]$ (type II) was chosen for comparative reactivity studies towards $AlCl_3$, as neither $[\{CpRu(CO)_2\}_2(\mu\text{-}CO)]$ (type I) nor $[\{CpRu(CO)\}_2(\mu\text{-}CO)(\mu\text{-}BF)]$ (type II) is known. Attempts to access $[\{CpRu(CO)\}_2(\mu\text{-}CO)(\mu\text{-}BF)]$ from **1** via thermally, photolytically, or chemically initiated CO loss have, to date, met with no success. Thus, while photolysis or reactions with amine oxides do not lead to the isolation of any tractable compounds containing Ru and B, thermolysis of **1** (at 80 °C for ca. 16 days in toluene) rather surprisingly leads to clean generation of difluoroboryl complex **2**, as judged by both ^{11}B and ^{19}F NMR spectroscopy (see the Supporting Information). Although the nature of accompanying organometallic product(s) could not be definitively established, **2** appears to be the only ^{11}B-containing species present in the final reaction solution.

[29] For other reports of the coordination of Lewis acids to the oxygen atom of a carbonyl ligand see, for example: N. E. Kim, N. J. Nelson, D. F. Shriver, *Inorg. Chim. Acta* **1973**, *7*, 393 – 396.