Synthesis, characterization and C–H activation reactivity of bis(ethylene) boratabenzene rhodium complexes†

David H. Woodmansee, Xianhui Bu and Guillermo C. Bazan*

Departments of Chemistry and Materials, University of California, Santa Barbara, CA 93106, USA. E-mail: bazan@chem.ucsb.edu

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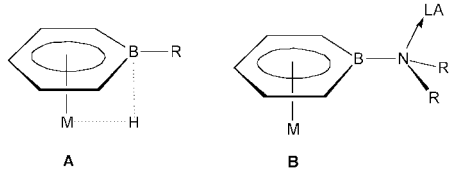
Reaction of Li[C_5H_5B–Ph] with [$RhCl(C_2H_4)_2]_2$ gives [C_5H_5B–Ph]$Rh(C_2H_4)_2$ 1 in 91% yield; similarly, Li[C_5H_5B–NMe_2] with [$RhCl(C_2H_4)_2]_2$ gives [C_5H_5B–NMe_2]$Rh(C_2H_4)_2$ 2 in 85% yield; single crystal X-ray analysis studies of 1 and 2 show a molecular geometry analogous to those of the Cp and Cp* complexes; the use of 1 and 2 in promoting alkane boration was evaluated against the activity of Cp*$Rh(C_2H_4)_2$ 3; the boratabenzene complexes 1 and 2 show faster initiation, but yield less thermally stable catalysts than 3.

Advances in the chemistry of homogeneous transition metal complexes containing boratabenzene (Bb) ligands[1] have shown that it is possible to control the catalytic activity at the metal by choice of the boron substituent.[2] The dependence of significant elementary reactions on the electron density at the metal and how these parameters change as a function of Bb structure have also been studied.[3] Dialkylaminoboratabenzene is a considerably stronger donor than phenylboratabenzene, and both are considerably weaker than the isoelectronic cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) ligands.[4] Given a Cp or Cp*-based catalyst, it is possible to obtain a nearly isostructural complex by Bb substitution, however these species will display slightly different catalytic cycles.[5]

Cp* complexes of Group 9 metals have been intensely studied in C–H activation reactions.[6] Recently, Iverson and Smith[7] and Hartwig and coworkers[8] have demonstrated that complexes such as Cp*$Ir(PMe_3)H(Cy)$ (Cy = *c*-C_6H_{11}), Cp*$Rh(C_2H_4)_2$[9] **3** and Cp*Rh(η^4-C_6Me_6) mediate the selective functionalization of unactivated alkanes. In particular, the rhodium complexes are highly effective in catalyzing the reaction of 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi-1,3,2-dioxaborolane (pinBBpin) to 2-(1-octyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[8] The importance of alkane functionalization is well appreciated and motivates considerable research.[10]

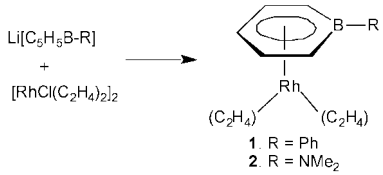
In view of the interest in these reactions, we decided to investigate whether boratabenzene complexes could participate in C–H activation processes. Three-center–two-electron interactions of type **A**[11] are known, which could weaken the M–H bond strength. It is also expected[12] that the nitrogen on aminoboratabenzene ligands will coordinate to Lewis acids, as in **B**. Precoordination of a diborane or a borane–hydride would



increase the local concentration of reactant near the vicinity of the metal center. Finally it is anticipated that in cycles that involve oxidative addition/reductive elimination sequences, the Bb counterparts will show more facile reductive elimination steps.[13]

In this contribution we report the synthesis and characterization of [C_5H_5B–Ph]$Rh(C_2H_4)_2$ **1** and [C_5H_5B–NMe_2]$Rh(C_2H_4)_2$ **2**. Phenyl and dimethylamino functionalities were chosen because they correspond to the weakest and strongest donors, respectively.[3] We also show that **1** and **2** can be used to catalyze C–H activation processes, that the boron substituent influences the reactivity of rhodium and that the relative stabilities of the resulting Bb catalysts are lower than that of the Cp* counterpart.

Reaction of Li[C_5H_5B–Ph][14] with [$RhCl(C_2H_4)_2]_2$, followed by standard workup, provides **1** in 85% yield as a red–orange powder [eqn. (1)].[15] A similar protocol, starting with Li[C_5H_5B–NMe_2], gives **2** in 91% yield.



(1)

Single crystal X-ray diffraction studies of **1** (Fig. 1) and **2** (Fig. 2)‡ confirm the isostructural relationship to **3**.[16] Three independent molecules are present in the unit cell of **2**, which differ slightly on the rotation of the Bb ring relative to the '$Rh(C_2H_4)_2$' base. The B–Rh distance is shorter for **1** (2.398 Å for **1**; av. = 2.516 Å for **2**) and the B–N distances in the three molecules of **2** are consistent with B–N π-bonding.[17] Interestingly, in both **1** and **2**, the Bb ring is rotated such that the boron atom sits above one of the ethylene ligands.

The ^{1}H NMR signals of the ethylene ligands in **1** and **2** show variable temperature behavior. Two doublets are observed at the

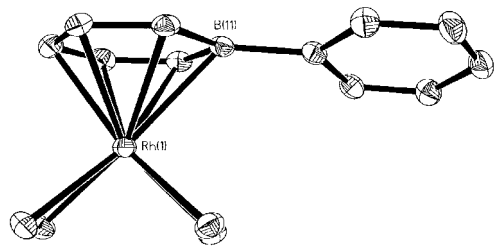


Fig. 1 ORTEP drawing of **1**; hydrogen atoms omitted for clarity.

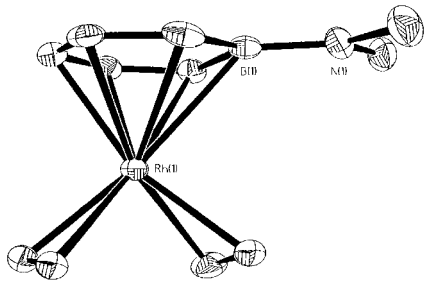


Fig. 2 ORTEP drawing of one of the three independent molecules in the crystal of **2**; hydrogen atoms omitted for clarity.

† Electronic supplementary information (ESI) available. Complete details for experimental procedures. See http://www.rsc.org/suppdata/cc/b0/b009246k/

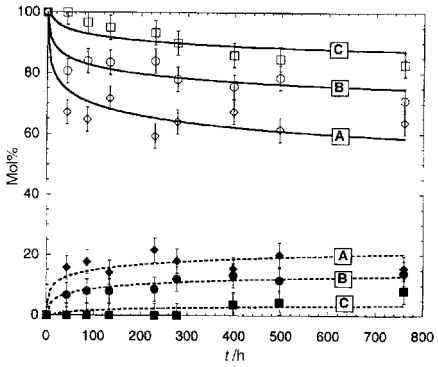
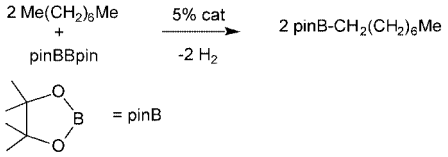


Fig. 3 Mol% of boron present as pinBBpin (——) and pinB–octyl (- - - -) as a function of time for reactions at 50 °C, containing (a) **1**, (b) **2** and (c) **3**; the lines are included to aid the eye.

low-temperature limit, which coalesce into a single resonance as the temperature increases. These data indicate facile ethylene rotation about the axis joining the metal to the center of the C=C bond. This propeller-like motion is well known in the cyclopentadienyl counterparts such as **3**[18] and its rate depends on the back-bonding ability of the metal.[19] From ^{1}H NMR coalescence experiments, $\Delta G^{\ddagger}$ = 60(3) kJ mol^{-1} (T_c = 311 K) for **1** and 50(3) kJ mol^{-1} (T_c = 265 K) for **2**. Both barriers are lower than that observed for **3** (71.5 kJ mol^{-1} at 340 K),[19] and are consistent with less efficient back bonding to ethylene in the Bb complexes.

To compare how **1** and **2** catalyze C–H activation reactions relative to **3**, we examined the boration of octane[20] with pinBBpin [eqn. (2)], under the reagent ratios and conditions established by Hartwig and coworkers.[8] The progress of the reactions was monitored by ^{11}B NMR spectroscopy against an internal standard [B(C_6F_5)$_3$ inside a capillary]. Product identity was further confirmed by use of GC–MS analysis.



(2)

Fig. 3 shows the consumption of pinBBpin as a function of time using **1**, **2** or **3** with octane as the solvent at 50 °C, together with the molar percent of pinB–octyl. Mass balance is compensated by the formation of pinB–H (not shown). The reaction with **1** is most active at initial reaction times, followed by those of **2** and then **3**. As the reaction progresses, the activity quickly shuts down for the three cases. For **1**, the reaction yield of pinB–octyl is *ca*. 20% (assuming that one mole of pinBBpin yields two moles of pinB–octyl),[8] while for **3** the yield is only 7%. When the reaction temperature is 95 °C, the reactions mixtures containing **1** and **2** become inactive after 24 h and achieve only 15% conversion (Fig. 4). For the Cp* counterpart, the reaction continues until all starting material is consumed. The addition of mercury (300 and 3250 equiv. relative to Rh) does not affect the course of the reaction and suggests that the reactions are mediated by homogenous species.[21]

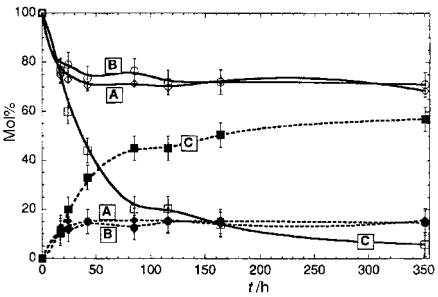


Fig. 4 Mol% of boron present as pinBBpin (——) and pinB-octyl (- - - -) as a function of time for reactions at 95 °C, containing (a) **1**, (b) **2** and (c) **3**; the lines are included to aid the eye.

In summary, we have shown that Bb complexes are capable of participating in catalytic C–H functionalization reactions. Under specific conditions these Bb complexes can initiate the reaction more quickly than their Cp* analogs. However, Bb compounds are less thermally stable and degrade before the reaction in eqn. (2) reaches completion. Compounds such as **1** and **2** may provide catalytic C–H activation possibilities for reactions that require milder conditions.

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Notes and references

‡ *Crystal data*: for **1**: $C_{15}H_{18}BRh$, M = 312.01, orthorhombic, $P2_12_12_1$, T = 293(2) K, λ = 0.71073 Å, a = 7.490(2), b = 8.566(2), c = 20.509(5) Å, V = 1315.8(5) Å^3, Z = 4, D_c = 1.575 Mg m^{-3}, μ = 1.271 mm^{-1}, reflections collected 7954, independent reflections 3001 [R(int) = 0.0459], final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0266, $wR2$ = 0.0505, largest diff. peak, hole: 0.816, −0.447 e Å^{-3}.

For **2**: $C_{11}H_{19}BNRh$, M = 278.99, monoclinic, $P2_1/c$, T = 293(2) K, λ = 0.71073 Å, a = 7.101(4), b = 17.021(8), c = 29.49(2) Å, β = 94.873(9)°, V = 3551(3) Å^3, Z = 12, D_c = 1.565 Mg m^{-3}, μ = 1.404 mm^{-1}, reflections collected 30927, independent reflections 6270 [R(int) = 0.1217], final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0374, $wR2$ = 0.0541, largest diff. peak, hole 0.529, 0.427 e Å^{-3}. CCDC 154632 and 154633.

1 G. E. Herberich and H. Ohst, *Adv. Organomet. Chem.*, 1986, **25**, 199; A. J. Ashe III, S. Al-Ahmad and X. G. Fang, *J. Organomet. Chem.*, 1999, **581**, 92.
2 G. C. Bazan, G. Rodriguez, A. J. Ashe III, S. Al-Ahmad and C. Müller, *J. Am. Chem. Soc.*, 1996, **118**, 2291; G. C. Bazan, G. Rodriguez, A. J. Ashe III, S. Al-Ahmad and J. W. Kampf, *Organometallics*, 1997, **16**, 2492; J. S. Rogers, G. C. Bazan and C. K. Sperry, *J. Am. Chem. Soc.*, 1997, **119**, 9305; R. W. Barnhart, G. C. Bazan and T. Mourey, *J. Am. Chem. Soc.*, 1998, **120**, 1082.
3 R. A. Lee, R. J. Lachicotte and G. C. Bazan, *J. Am. Chem. Soc.*, 1998, **120**, 6037; G. C. Bazan, W. D. Cotter, Z. J. A. Komon, R. A. Lee and R. J. Lachicotte, *J. Am. Chem. Soc.*, 2000, **122**, 1371.
4 G. E. Herberich, C. Engelke and W. Pahlmann, *Chem. Ber.*, 1979, **112**, 607.
5 H. Bönnemann, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 248.
6 B. A. Arndtsen, R. G. Bergmann, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154; R. H. Crabtree, *Chem. Rev.*, 1995, **95**, 2599.
7 C. N. Iverson and M. R. Smith III, *J. Am. Chem. Soc.*, 1999, **121**, 7696.
8 H. Chen, S. Schlecht, T. C. Semple and J. F. Hartwig, *Science*, 2000, **287**, 1995.
9 K. Moseley, J. W. Kang and P. M. Maitlis, *J. Chem. Soc.*, 1970, 2875.
10 W. D. Jones, *Science*, 2000, **287**, 1942; K. M. Waltz, C. N. Muhoro and J. F. Hartwig, *Organometallics*, 1999, **18**, 3383; R. H. Carbtree, *Chem. Rev.*, 1985, **85**, 245; in *Activation and Functionalization of Alkane*, ed. C. L. Hill, Wiley, New York, 1989; A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, 1997, **97**, 2879; R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, *Science*, 1998, **280**, 560; S. S. Stahl, J. A. Labinger and J. E. Bercaw, *Angew. Chem., Int. Ed.*, 1998, **37**, 2180.
11 G. E. Herberich, B. D. Hessner and D. P. J. Köffer, *J. Organomet. Chem.*, 1989, **362**, 243; C. K. Sperry, W. D. Cotter, R. A. Lee, R. J. Lachicotte and G. C. Bazan, *J. Am. Chem. Soc.*, 1998, **120**, 7791.
12 J. S. Rogers, R. J. Lachicotte and G. C. Bazan, *J. Am. Chem. Soc.*, 1999, **121**, 1288.
13 A. J. Ashe III, S. Al-Ahmad, J. W. Kampf and V. G. Young, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2014; C. K. Sperry, G. C. Bazan and W. D. Cotter, *J. Am. Chem. Soc.*, 1999, **121**, 1513.
14 A. J. Ashe III and P. Shu, *J. Am. Chem. Soc.*, 1971, **93**, 1804.
15 For the synthesis of boratabenzene–rhodium(cyclooctadiene) complexes see: G. E. Herberich, H. J. Becker, K. Carsten, C. Engelke and W. Koch, *Chem. Ber.*, 1976, **109**, 2382.
16 R. Blom, D. W. H. Rankin, H. E. Robertson and R. N. Perutz, *J. Chem. Soc. Dalton Trans.*, 1993, 1983; M. Arthurs, C. Piper, D. A. Morton-Blake and M. G. B. Drew, *J. Organomet. Chem.*, 1992, **429**, 257.
17 P. Paetzold, *Adv. Inorg. Chem.*, 1987, **31**, 123.
18 R. Cramer, *J. Am. Chem. Soc.*, 1964, **86**, 217.
19 R. Cramer and J. Mrowca, *Inorg. Chim. Acta*, 1971, **5**, 528.
20 Purified according to: D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1988.
21 D. R. Anton and R. H. Crabtree, *Organometallics*, 1983, **2**, 855; K. S. Weddle, J. D. Aiken III and R. G. Finke, *J. Am. Chem. Soc.*, 1998, **120**, 5653.