Inorganic Chemistry

Article

Structural Analysis of Five-Coordinate Transition Metal Boryl Complexes with Different d-Electron Configurations

King Chung Lam, Wai Han Lam, and Zhenyang Lin*

Department of Chemistry and Open Laboratory of Chirotechnology of Institute of Molecular Technology for Drug Discovery and Synthesis [The University Grant Committee Area of Excellence Scheme (Hong Kong)], The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Todd B. Marder*

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.

Nicholas C. Norman*

School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

The site preference of boryl ligands in five-coordinate transition metal boryl complexes has been investigated with the aid of density functional theory calculations. The preferred site for a boryl ligand depends on the electron count of the complex under consideration. Our studies show that the very strong σ-donating boryl ligands choose to occupy coordination sites such that those orbitals accommodating metal d electrons have minimal metal–boryl σ^*-antibonding character.

Introduction

Transition metal boryl complexes have attracted considerable interest because of their role in catalyzed hydroboration and diboration reactions of alkenes and alkynes[1–3] as well as catalyzed borylation of C–H bonds in alkanes and arenes.[4]

Among the numerous transition metal boryl complexes synthesized and structurally characterized since 1990,[5] several five-coordinate systems attracted our attention regarding their structural and bonding aspects. Chart 1 depicts the structural characteristics of these complexes.[6–12] Com-

* To whom correspondence should be addressed. E-mail: chzlin@ust.hk (Z.L.); todd.marder@durham.ac.uk (T.B.M.); n.c.norman@bristol.ac.uk (N.C.N.).

(1) (a) Männing, D.; Nöth, H. *Angew. Chem, Int. Ed. Engl.* **1985**, *24*, 878. For reviews see: (b) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179. (c) Burgess, K.; van der Donk, W. A. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: Chichester, 1994; Vol. 3, p 1420. (d) Fu, G. C.; Evans, D. A.; Muci, A. R. In *Advances in Catalytic Processes*; Doyle, M. P., Ed.; JAI: Greenwich, CT, 1995; p 95. (e) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957. (f) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695.

(2) For recent reviews, see: (a) Marder, T. B.; Norman, N. C. *Top. Catal.* **1998**, *5*, 63. (b) Ishiyama, T.; Miyaura, N. *Yuki Gosei Kagaku Kyokaishi* **1999**, *57*, 503. (c) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2000**, *611*, 392.

(3) (a) Musaev, D. G.; Mebel, A. M.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 10693. (b) Dorigo, A. E.; Schleyer, P. von R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 115. (c) Widauer, C.; Grützmacher, H.; Ziegler, T. *Organometallics* **2000**, *19*, 2097. For a review see: (d) Huang, X.; Lin, Z. Y. In *Computational Modeling of Homogeneous Catalysis*; Maseras, F., Lledós, A., Eds.; Kluwer Academic Publishers: Amsterdam, 2002; pp 189–212.

(4) (a) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (b) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III. *Science* **2002**, *295*, 305. (c) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995. (d) Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2168. (e) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3. (f) Lam, W. H.; Lin, Z. Y. *Organometallics* **2003**, *22*, 473. (g) Webster, C. E.; Fan, Y.; Hall, M. B.; Kunz, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 858. (h) Wan, X.; Wang, X.; Luo, Y.; Takami, S.; Kubo, M.; Miyamoto, A. *Organometallics* **2002**, *21*, 3703. (i) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2003**, *125*, 16114.

(5) For reviews, see: (a) Hartwig, J. F.; Waltz, K. M.; Muhoro, C. N.; He, X.; Eisenstein, O.; Bosque, R.; Maseras, F. In *Advances of Boron Chemistry*; Siebert, W., Ed.; Special Publication 201; The Royal Society of Chemistry: Cambridge, U.K., 1997; p 373. (b) Wadepohl, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2441. (c) Irvine, G. J.; Lesley M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685. (d) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786. (e) Smith, M. R., III. *Prog. Inorg. Chem.* **1999**, *48*, 505. (f) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1.

Chart 1
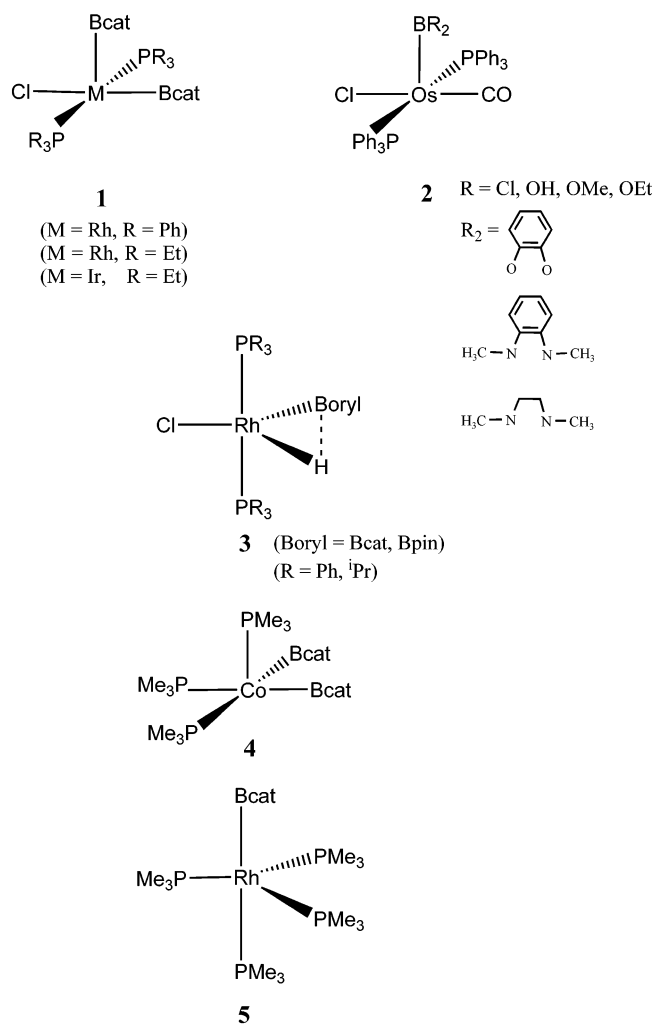
plexes **1**−**3** are 16-electron species, **4** is a 17-electron complex, and **5** has an 18-electron configuration.

It is well-known that, for a 16-electron ML_5 complex, both square-pyramidal (SQP) and Y-shape distorted trigonal-bipyramidal (DTBP) structures are possible.[13−15] For these complexes, having a very strong *trans*-influencing boryl

ligand, adoption of a square-pyramidal structure for complexes **1**−**2** is expected.[6−9] The structural description of complexes **1** requires some comments here. In a Communication published in 1993, [RhCl(PPh$_3$)$_2$(Bcat)$_2$] (cat = 1,2-O$_2$C$_6$H$_4$) was described as being distorted square-pyramidal.[6a] In the subsequent full paper, published in 1998, it was mentioned that the d^6 complexes can also be described as Y-shaped distorted TBP.[6b] In view of the fact that the two boryl groups in these complexes are in different environments, e.g., the two Cl−M−B (M = Rh, Ir) angles differ by 20−40° and the two M−B bond lengths differ by 0.02 Å, we feel that it is more appropriate to describe their structures as distorted SQP. Complexes **3**, due to the B···H attractive interaction, adopt structures ranging from SQP to an intermediate between SQP and DTBP depending on the nature of the R groups of the two phosphine ligands and the boryl ligand,[4d,10,16] a detailed discussion of which has been given very recently.[16] The 17-electron complex **4**[11] adopts an SQP structure as well, although both SQP and TBP structures exist for 17-electron complexes, e.g., [Co-(dppe)$_2$Cl]$^+$.[17] Interestingly, the two Bcat ligands in this complex occupy two of the basal positions in contrast to complexes **1**−**2**, wherein the apical site is occupied by one of the strong σ-donating boryl ligands.

For an 18-electron ML_5 complex, both SQP and TBP structures are possible, e.g., [Ni(CN)$_5$]$^{3-}$.[18] In the literature, the TBP structure is found to be more prevalent, and it is not unusual that complex **5** adopts a TBP structure. The interesting feature of this complex is that the Bcat ligand preferentially occupies one of the axial sites instead of an equatorial position.[12]

Clearly, the preferred site for a boryl ligand depends greatly on the electron count of the complex under consideration, and it is interesting to note that the very strong σ-donating boryl ligand switches coordination site in response to a change in the electron count. In this paper, we address briefly, with the aid of density functional theory calculations, the question of how different electron counts determine the ligand arrangement around the metal center.

Computational Methods

Geometry optimizations have been performed at the Becke3LYP (B3LYP) level of density functional theory.[19] The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis sets (LanL2DZ)[20] were used in describing metal centers, P, and Cl, whereas the 6-31G basis set was used for all other atoms.[21] Polarization functions were added for the transition metals, Co (ζ_f

(6) (a) Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Nguyen, P.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 4367. (b) Clegg, W.; Lawlor, 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.; Whittell, G. R. *J. Chem. Soc., Dalton Trans.* **1998**, *2*, 301.
(7) Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G. *Chem. Commun.* **1997**, *1*, 53.
(8) Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2003**, *680*, 81.
(9) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **1998**, *17*, 4869.
(10) (a) Kono, H.; Ito, K.; Nagai, Y. *Chem. Lett.* **1975**, 1095. (b) Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 304.
(11) (a) Dai, C.; Stringer, G.; Corrigan, J. F.; Taylor, N. J.; Marder, T. B.; Norman, N. C. *J. Organomet. Chem.* **1996**, *513*, 273. (b) The B···B interaction will be addressed further both experimentally and theoretically in a future paper on related Co boryl complexes.
(12) Dai, C.; Stringer, G.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Inorg. Chem.* **1997**, *36*, 272.
(13) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.
(14) Rachidi, I. E. I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671.
(15) Riehl, J. F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.

(16) Lam, W. H.; Shimada, S.; Batsanov, A. S.; Lin, Z.; Marder, T. B.; Cowan, J. A.; Howard, J. A. K.; Mason, S. A.; McIntyre, G. J. *Organometallics* **2003**, *22*, 4557.
(17) Stalick, J. K.; Corfield, P. W. R.; Meek, D. W. *Inorg. Chem.* **1973**, *12*, 1668.
(18) (a) Terzis, A.; Raymond, K. N.; Spiro, T. G. *Inorg. Chem.* **1970**, *9*, 2415. (b) Jurnak, F. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 2387.
(19) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, G. *Phys. Rev. B* **1988**, *37*, 785.
(20) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(21) (a) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Binning, R. C., Jr.; Curtiss, L. A. *J. Comput. Chem.* **1990**, *11*, 1206.

= 2.780), Rh (ζ_f = 1.350), and Os (ζ_f = 0.886),[22] and the atoms which are directly bonded to the metal center, P (ζ_d = 0.340), Cl (ζ_d = 0.514),[23] C (ζ_d = 0.800), and B (ζ_d = 0.600).[21] Frequency calculations have been performed for all fully optimized structures to confirm their characteristics as minima. All calculations were performed with the Gaussian 98 software package[24] on Pentium IV PC computers. Molecular orbitals obtained from the B3LYP calculations were plotted using the Molden 3.7 program written by Schaftenaar.[25]
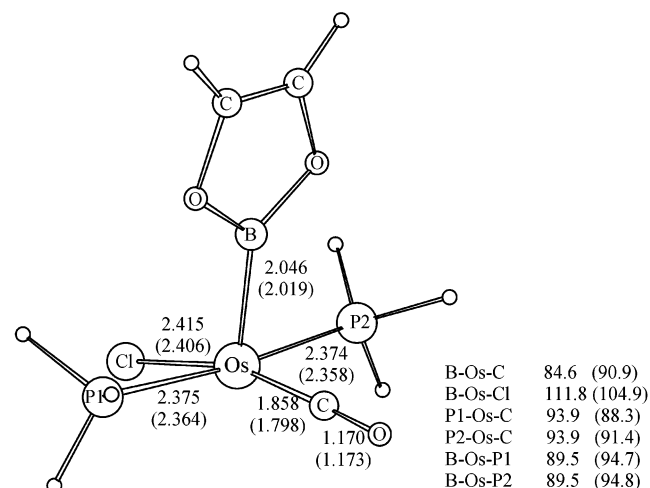
Results and Discussion

Structures of 16-Electron Boryl Complexes. Complexes **1**−**2** (Chart 1) are 16-electron species and adopt approximately SQP structures in which the apical position is occupied by one Bcat ligand.[6−9] We first optimized [RhCl-(PH₃)₂(BO₂C₂H₂)₂], a model for complex **1**. However, the relative orientation of the two boryl ligands in the experimental structures was not well reproduced with this model. In the experimental structures of **1**, the apical Bcat ligand is found to be coplanar with the P−Rh−P axis, and the basal Bcat ligand has its plane perpendicular to the basal plane of the SQP structure. In the calculated structure, while the orientation of the apical boryl ligand was accurately reproduced, the basal boryl ligand has its plane coplanar with the basal plane. When the model phosphine ligands (PH₃) were replaced by PH₂Ph, the calculated structure was found to be in good agreement with the experimental structures, not only in the relative orientation of the two boryl ligands but also in the bond distances and angles (see Figure 1). Apparently, the steric effect of the phosphine ligand is important. The plane of the basal Bcat ligand is sandwiched between the two phenyl rings from the two (PH₂Ph) phosphine ligands.

From Figure 1, we can see that the apical Rh−B bond is shorter than the basal Rh−B bond. This is expected because the *trans* position to the apical boryl ligand is vacant, enhancing the Rh−B interaction. We also tried to locate a structure in which both of the boryl ligands occupy basal sites. However, starting from such a structure, the geometry optimization leads to the final structure identical to the one discussed above.

Complexes **2** are interesting because each of them has two different strong *trans*-influencing ligands (Bcat and CO).[8,9]

B1-Rh-Cl	155.9° (162.1°)
P2-Rh-P1	170.8° (169.7°)
B2-Rh-B1	78.1° (78.8°)
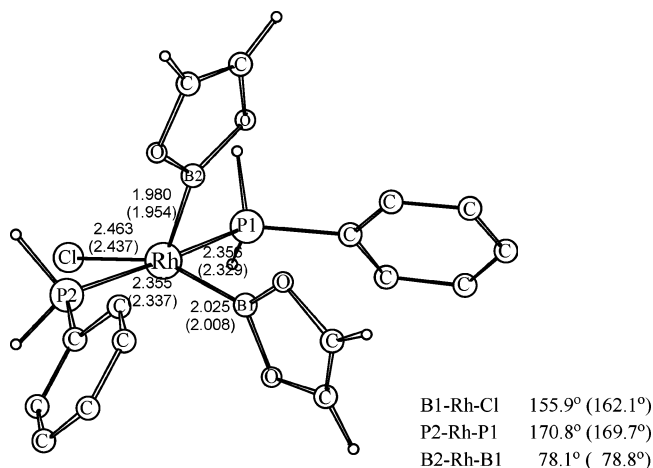
Figure 1. Selected calculated structural parameters (bond lengths in Å and bond angles in deg) for the model complex [RhCl(PH₂Ph)₂(BO₂C₂H₂)₂] together with the experimental structural parameters for [RhCl(PPh₃)₂-(Bcat)₂] shown in parentheses. For the purpose of clarity, hydrogen atoms on phenyl rings are omitted.

B-Os-C	84.6 (90.9)
B-Os-Cl	111.8 (104.9)
P1-Os-C	93.9 (88.3)
P2-Os-C	93.9 (91.4)
B-Os-P1	89.5 (94.7)
B-Os-P2	89.5 (94.8)

Figure 2. Selected calculated structural parameters (bond lengths in Å and bond angles in deg) for the model complex [Os(CO)Cl(PH₃)₂(BO₂C₂H₂)] together with the experimental structural parameters for [Os(CO)Cl(PPh₃)₂-(Bcat)] shown in parentheses.

The Bcat ligand occupies the apical site of the SQP structure, suggesting that as a result of its very strong σ-donating property, the boryl ligand exhibits an even stronger *trans* influence than the strong π-acceptor CO ligand. Figure 2 shows the calculated structural parameters of [OsCl(PH₃)₂-(CO)(BO₂C₂H₂)] together with experimental ones of [OsCl-(PPh₃)₂(CO)(Bcat)].[9] Again, the agreement between the calculated and experimental geometries is good. The rotational barrier of the boryl ligand around the Os−B bond was also estimated to be quite small (3.9 kcal/mol). The result is consistent with previous calculations on Os−B systems.[26] The presence of the *cis*-CO ligand in the complex in principle would give a higher rotational barrier if the boryl were a strong single-face π accepting ligand. In an earlier study,[27] metal complexes containing both single-face (e.g., η^2-olefin)

(22) Ehlers, A. W.; Bohme, M.; Dapprich, S.; Gobbi, A.; Hollwarth, A.; Jonas, V.; Kohler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.
(23) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier Science: Amsterdam, 1984.
(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(25) Schaftenaar, G. *Molden* v3.7; CAOS/CAMM Center Nijmegen: Toernooiveld, Nijmegen, Netherlands, 2001.

(26) Giju, K. T.; Bickelhaupt, F. M.; Frenking, G. *Inorg. Chem.* **2000**, *39*, 4776.
(27) (a) Choi, S. H.; Bytheway, I.; Lin, Z.; Jia, G. *Organometallics* **1998**, *17*, 3974. (b) Lam, W. H.; Lin, Z. *J. Organomet. Chem.* **2001**, *635*, 84.
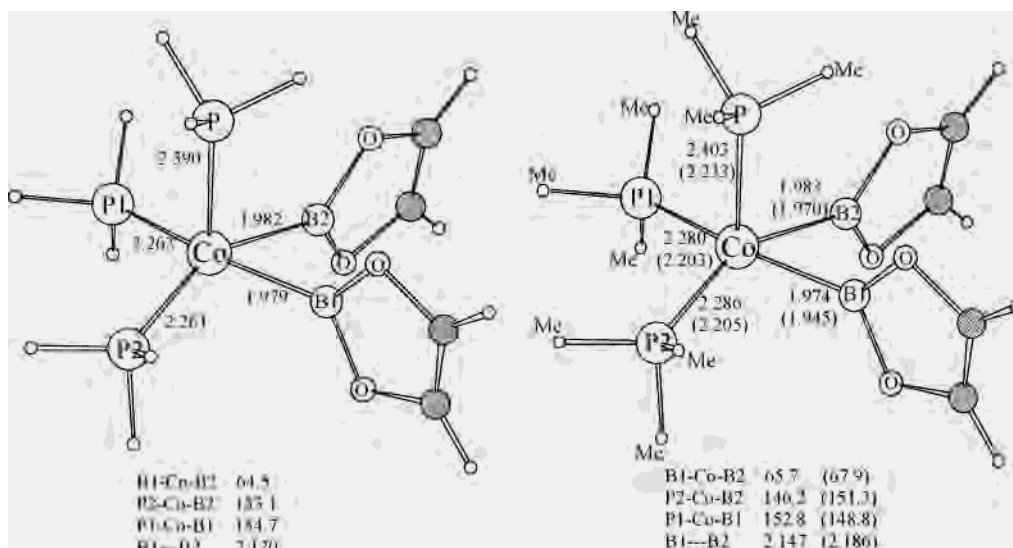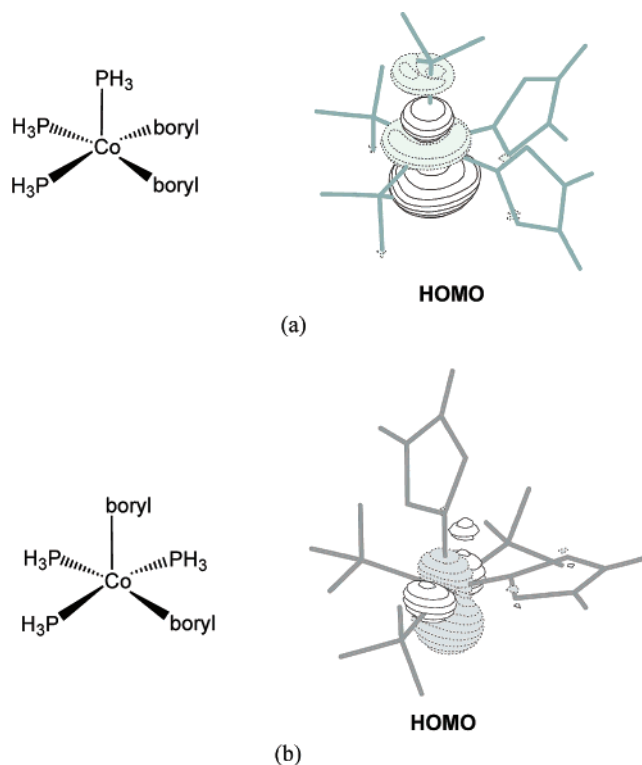
Figure 3. Selected calculated structural parameters (bond lengths in Å and bond angles in deg) for the model complexes [Co(PH₃)₃(BO₂C₂H₂)₂] and [Co(PMe₃)₃(BO₂C₂H₂)₂] together with the experimental structural parameters for [Co(PMe₃)₃(Bcat)₂] shown in parentheses.

and double-face (e.g., CO) π-accepting ligands were shown to exhibit unique structural preferences. The rotational barriers of the single-face π-accepting ligands are in the range 7−8 kcal/mol.[27] Therefore, the small rotational barrier calculated for [OsCl(PH₃)₂(CO)(BO₂C₂H₂)] indicates that the Os−B π bonding through the "empty" p orbital of the boryl ligand is weak. The results may also indicate that the B−O σ^* orbital, in addition to the "empty" p orbital, of the boryl ligand also plays a role in the Os−B π interaction, as pointed out earlier.[16]

Structures of 17-Electron Boryl Complexes. The 17-electron metal boryl complex, [Co(PMe₃)₃(Bcat)₂], **4**, adopts an approximately square pyramidal structure with the two boryl ligands *cis* to each other,[11] quite different from the site preference in the 16-electron complexes.

For an ideal C_{4v} ML₅ (SQP) complex, the frontier orbitals consist of "t₂g" orbitals and a higher energy a₁ orbital.[28] The electron configurations of 16- and 17-electron SQP complexes are ("t₂g")⁶(a₁)⁰ and ("t₂g")⁶(a₁)¹, respectively. Apparently, whether the a₁ orbital is occupied or not plays an important role in determining the arrangement of ligands.

We have investigated the electronic structure of the 17-electron metal boryl complex, **4**, via calculations on the model complexes [Co(PH₃)₃(BO₂C₂H₂)₂] and [Co(PMe₃)₃-(BO₂C₂H₂)₂]. Selected structural parameters for the calculated model complexes are shown in Figure 3 together with the experimental values. The theoretical calculations reproduced reasonably well the basal Co−P and Co−B bond lengths as well as the B−Co−B and P−Co−B angles. However, the apical Co−P distance was poorly reproduced. Use of different phosphine ligands (PMe₃ and PH₃) did not improve the result. In the case where PMe₃ is used, the Co−B bond lengths calculated are almost the same as those calculated for the PH₃ model complex. However, the Co−P bond lengths calculated are even longer, by 0.013−0.025 Å, than those calculated for the PH₃ model complex. The steric effect

(28) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.
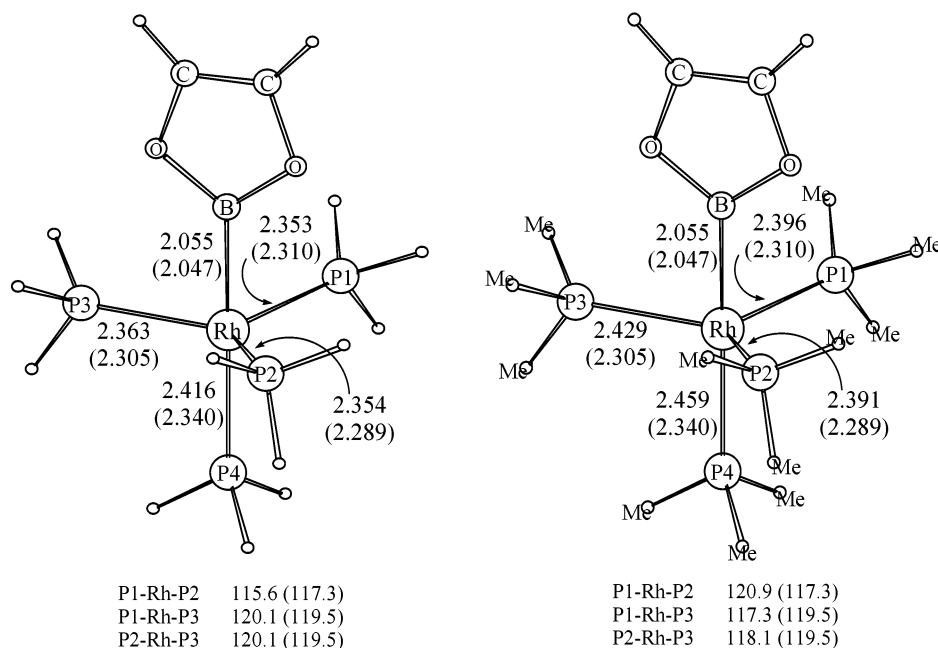
HOMO

(a)

HOMO

(b)

Figure 4. Spatial plots of the highest occupied MO accommodating the unpaired d electron of the d⁷ cobalt bis-boryl complex at the fully optimized structure when the apical site is occupied by one of the three phosphine ligands (a) and at the partially optimized structure when the apical site is occupied by one boryl ligand (b).

of the bulkier PMe₃ ligands might have been overestimated. At this moment, it is not clear what causes the significant error, as the theoretical method does well for the M−P bonds in the 16-electron complexes discussed above. Despite the poor reproduction of the Co−P bonds, the trend that the apical Co−P bond is longer than the basal Co−P bonds was correctly predicted.

The HOMO of the 17-electron model complex was plotted (Figure 4a), from which it can be seen that it corresponds to the "a₁" orbital of a SQP ML₅ complex, having maximal

Figure 5. Selected calculated structural parameters (bond lengths in Å and bond angles in deg) for the model complexes, [Rh(PH$_3$)$_4$(BO$_2$C$_2$H$_2$)] and [Rh(PMe$_3$)$_4$(BO$_2$C$_2$H$_2$)], together with the experimental structural parameters for [Rh(PMe$_3$)$_4$(Bcat)] shown in parentheses.

amplitude in the vacant site opposite the apical position. In addition, the HOMO, which can also be called the SOMO (singly occupied molecular orbital), has significant σ^* antibonding character between the metal center and the apical ligand i.e., Co−P σ^*. If the very strong σ-donating boryl ligand occupies the apical site, it is expected that the "a$_1$" orbital, which accommodates the unpaired d electron, would be very high in energy because of its strong σ^*-antibonding character. Such a structural arrangement would make the complex very unstable. In complex **4**, occupation of the apical site by a weaker σ-donating PMe$_3$ ligand instead of a very strong σ-donating boryl ligand makes the "a$_1$" orbital less antibonding, and the complex more stable.

We also attempted to calculate a structure for the 17-electron complex [Co(PH$_3$)$_3$(BO$_2$C$_2$H$_2$)$_2$] having a boryl ligand in the apical site. However, the calculation suggests that such a structure does not correspond to a local minimum on the potential energy (PE) surface. In order to obtain such a structure, we fixed the three phosphine ligands in a plane in order to perform a partial geometry optimization. The partially optimized structure was found to be 15.6 kcal/mol higher in energy than the fully optimized one. The HOMO (Figure 4b), which again has the maximal amplitude in the vacant site opposite the apical position, was raised by 0.435 eV in energy in comparison with the one from the fully optimized structure. These additional calculations further demonstrate the importance of reducing the σ^* antibonding character of the "a$_1$" orbital for the stability of such a 17-electron complex.

One of the reviewers wondered whether the presence of a second boryl ligand has a significant influence on the site preference as a direct interaction between the two *cis* boryl ligands may exist.[11] To examine this possibility, we performed calculations on the model complex [Co(PH$_3$)$_3$-(BO$_2$C$_2$H$_2$)Cl], obtained by replacing one boryl ligand of the

bis-boryl complex with Cl. The results of calculations show that the boryl ligand still prefers the basal site in the mono-boryl complex. The structure with the boryl ligand occupying the apical site does not correspond to a local minimum on the potential energy surface. In the calculated mono-boryl complex, the boryl ligand plane is perpendicular to the basal plane of the distorted SQP structure. The orientation of the boryl ligand plane again suggests that the Co−B π bonding through the "empty" p orbital is not particularly strong. The reason is as follows. If the Co−B π-bonding were strong and important, we would anticipate that the boryl ligand plane would be coplanar with the basal plane as this would allow overlap of the "empty" p-orbital on B with the SOMO orbital which would be expected to stabilize the SOMO.

Structures of 18-electron boryl complexes. The 18-electron metal boryl complex, [Rh(PMe$_3$)$_4$(Bcat)], **5**,[12] adopts a trigonal bipyramidal structure with the boryl ligand occupying one of the two axial sites. For 18-electron TBP ML$_5$ complexes, it is well-known that π-acceptor ligands preferentially occupy the equatorial sites while σ-donor ligands tend to choose the axial sites.[13] The axial site occupation of the Bcat ligand in **5** implies that the σ-donating property of the Bcat ligand is predominant over its π-accepting character.[12,26,29]

The calculated structures of the model complexes [Rh-(PH$_3$)$_4$(BO$_2$C$_2$H$_2$)] and [Rh(PMe$_3$)$_4$(BO$_2$C$_2$H$_2$)], which reproduced reasonably well the experimental structure of **5**, are shown in Figure 5. We do not see any significant differences in the structural parameters between the two model complexes. Similar to the situation of the 17-electron cobalt complexes discussed above, there is a systematic overestimation of the Rh−P bond lengths by about 0.1 Å

(29) Dickinson, A. A.; Willock, D. J.; Calder, R. J.; Aldridge, S. *Organometallics* **2002**, *21*, 1146.
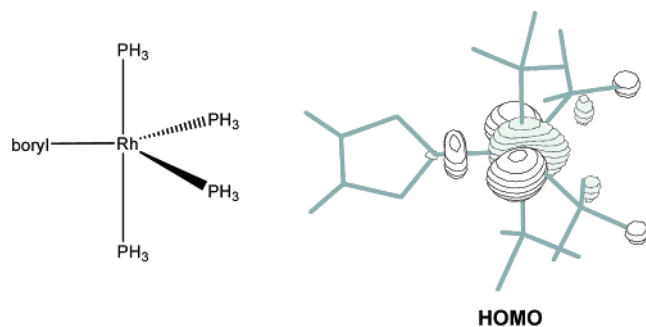
Figure 6. Spatial plots of the highest occupied MO for a hypothetical TBP complex in which the boryl ligand is forced to be in an equatorial site.

compared with the crystal structure when PMe_3 is used. PMe_3 is not well modeled for some reason. Again, the trend that the axial Rh−P bond is longer than the equatorial Rh−P bonds is well predicted.

To understand the preference of the boryl ligand for an axial site in the TBP structure, we attempted to calculate a structure of $[Rh(PH_3)_4(BO_2C_2H_2)]$ in which the boryl ligand occupies one of the equatorial sites. The result of this additional calculation indicated that such a structure does not correspond to a local minimum on the PE surface. In order to determine how unstable such a structure is, we partially optimized a structure in which the boryl ligand was forced to be in the equatorial plane by fixing all of the ligand−metal−ligand angles at either 90° or 120° of a perfect TBP structure. The partially optimized structure is highly unstable and lies 14.2 kcal/mol higher in energy than the fully optimized one. We also partially optimized a perfect TBP by applying the same angle constraints in which the boryl ligand occupies the preferred site, one of the two axial positions. This structure is calculated to be only slightly higher in energy, by 2.3 kcal/mol, than the fully optimized one. These results further indicate that there is a strong preference for the boryl ligand to occupy one of the axial sites.

Examining the bonding characteristics of the HOMO (Figure 6) for the highly unstable structure, we again found that there exists significant antibonding character between the metal center and the boryl ligand in such a highly unstable structure. For an idealized (D_{3h}) 18-electron ML_5 complex, the HOMOs correspond to the metal's $d_{x^2-y^2}$ and d_{xy} (e′) orbitals when the z axis coincides with the C_3 rotation axis. These two d orbitals have σ^*-antibonding character between the metal center and the equatorial ligands.[28] When the very strong σ-donating boryl ligand occupies one of the equatorial sites, the HOMO is destabilized significantly. The energy gap between the HOMO and the HOMO − 1 (2nd HOMO) is 0.335 eV. The instability of such a structure, in which the boryl ligand occupies one of the equatorial sites, is apparently a result of the unfavorable, high orbital energy of the HOMO.

Examining the orientation of the highly unstable structure, we found that the boryl ligand plane is perpendicular to the equatorial plane of the TBP structure (Figure 6). The preference for the perpendicular orientation suggests there is a certain degree of Rh−B π bonding in this structure

through the "empty" p orbital of the boryl ligand. However, the rotational barrier of the boryl ligand around the Rh−B bond was estimated to be only 3.8 kcal/mol. Again, the barrier is relatively small, indicating that the B−O σ^* orbital, in addition to the "empty" p orbital, of the boryl ligand may also play a role in the Rh−B π interaction, as pointed out earlier.[16]

Summary

The site preference of boryl ligands in ML_5 metal−boryl complexes has been discussed. In the absence of hydride−boryl attractive interactions, 16-electron complexes normally adopt SQP structures in which the apical site is occupied by a boryl ligand. By adopting such a structure, the metal−boryl σ-bonding interaction can be maximized because the *trans* position of the apical boryl ligand is vacant.

For 17-electron SQP complexes, the *trans* position of the apical ligand is no longer exactly "vacant". The unpaired metal d electron occupies the "vacant" site; i.e., the molecular orbital accommodating the unpaired electron has the maximum amplitude in the direction of the vacant site. The singly occupied orbital also has significant M−L σ^*-antibonding character between the metal center and the apical ligand preventing the very strong σ-donating boryl ligand from occupying the apical site. An interesting way of seeing the site preference is as follows. The unpaired electron is in an orbital that becomes the strongest *trans*-influencing "ligand", stronger than the boryl ligand, forcing the boryl ligand to go to one of the basal sites so that the position *trans* to the strongest *trans*-influencing "ligand" is a weaker ligand. In other words, it is significantly destabilizing when the unpaired metal d electron "ligand" and the very strong σ-donating ligand are mutually *trans*.

It has been shown that 18-electron ML_5 metal−boryl complexes adopt the prevalent TBP structure. The boryl ligand avoids occupation of the equatorial sites in order to stabilize orbitals that accommodate metal d electrons. For an 18-electron ML_5 complex, there are two pairs of metal d electrons residing in two d orbitals having maximum amplitudes on the equatorial plane. These two metal d orbitals also contain significant M−L σ^*-antibonding character between the metal center and the equatorial ligands. If the very strong σ-donating boryl ligand occupies one of the equatorial sites, one pair of the metal d electrons would have to reside in an orbital that is even more strongly antibonding. Similarly, one can envision the site preference as follows. To alleviate the significantly M−L σ^*-antibonding interactions, the "ligands" of the metal d electrons force the boryl ligand to go to one of the axial sites so that the *trans* position of the boryl ligand is a normal weaker ligand instead of the "ligands" of the metal d electrons.

It should be pointed out that this paper deals mainly with the site preferences of boryl ligands in various five-coordinate complexes having different electron counts. The satisfactory explanations given in the text suggest that the strong σ-donating properties of boryl ligands determine the site preferences in the five coordinate complexes discussed here. The π-electronic properties of different boryl ligands are

clearly less important. Discussion regarding the importance of σ- and π-electronic properties in other complexes can be found in the literature.[26,29−31] Our calculations also suggest that different aryl or alkyl phosphine ligands should not change the qualitative conclusions regarding the site preferences discussed in this paper.

(30) Sivignon, G.; Fleurat-Lessard, P.; Onno, J.-M.; Volatron, F. *Inorg. Chem*. **2002**, *41*, 6656.
(31) Cundari, T. R.; Zhao, Y. *Inorg. Chim. Acta* **2003**, *345*, 70.