B–H Agostic Interactions

DOI: 10.1002/anie.200806178

Phosphinoborane and Sulfidoborohydride as Chelating Ligands in Polyhydride Ruthenium Complexes: Agostic σ-Borane versus Dihydroborate Coordination**

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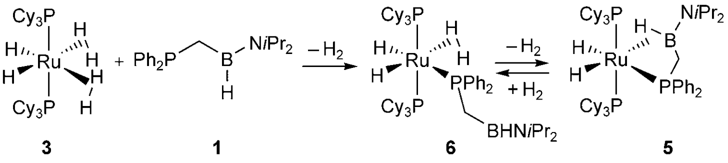
The chemistry of σ-borane complexes remains at an early stage of development by comparison to the analogous σ-dihydrogen and σ-silane families.[1–5] However, since the isolation of the first σ-borane metal complex in 1996,[6] important findings dealing with B–H bond activation have been regularly disclosed.[7–9] The σ-borane complexes are often invoked as intermediates in the formation of the corresponding hydridoboryl complexes and the microscopic reverse reductive elimination. More and more compelling evidence for σ-B–H coordination is found in catalyzed borylation processes,[10] which supports the recent metathesis mechanism termed σ-CAM for late-transition-metals (σ-complex-assisted metathesis, which involves metal-induced dynamic rearrangements of E–H bonds at constant oxidation state).[11] Moreover, σ-borane complexes and the related σ-amine–borane species are now found to be relevant to the catalytic dehydrogenation of amine–boranes.[12–16] As part of our research on B–H bond activation of less-common borane reagents,[17,18] we have decided to develop a new class of borane-attached ligands to study hydrogen-transfer reactions and compare the reactivity of true σ-borane complexes with agostic species.[19,20] The synthesis of bidentate and potentially hemilabile L~BHR (L = P, S and R = amino, alkyl) borane-containing ligands was challenging as this class of compounds remains unexplored in particular by comparison to the ambiphilic borane derivatives.[21,22] Braunschweig et al. very recently reported access to a vinylborane by insertion of a borylene chromium complex into an olefinic C–H bond.[23] The corresponding complex $[Cr\{HBN(SiMe_3)_2CH{=}CHCMe_3\}(CO)_4]$ was isolated and characterized as a formally chromium(0) olefin complex with a weak B–H coordination to the metal center. We now report the synthesis of two new boron-containing compounds, the phosphinomethyl(amino)borane $Ph_2PCH_2BHN\textit{i}Pr_2$ (**1**) and the lithium sulfido(methyl)borohydride $Li[MeSCH_2BH_2Me]$ (**2**), as well as their coordination to the two ruthenium precursors $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**3**) and $[RuHCl(\eta^2\text{-}H_2)(PCy_3)_2]$ (**4**). The strategy is based on the one we recently used to isolate the bis σ-borane complex $[RuH_2(\eta^2{:}\eta^2\text{-}H_2BMes)(PCy_3)_2]$ upon reaction of (**3**) with mesitylborane or the chloro complex (**4**) with lithium mesitylborohydride.[17] Our study includes the isolation of the first δ-agostic ruthenium complex containing an η^2-B–H bond that involves a trivalent boron atom and illustrates the competition between σ-coordination and dihydroborate ligation.

The addition of **1** to the bis(dihydrogen) complex **3** in toluene at room temperature led to the substitution of the two dihydrogen ligands by **1** (Scheme 1). The new complex $[RuH_2\{\eta^2\text{-}H\text{-}B(N\textit{i}Pr_2)CH_2PPh_2\}(PCy_3)_2]$ (**5**) was fully characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction. The $^{31}P\{^1H\}$ NMR spectrum of **5** displays an AM_2 pattern with a triplet at $\delta = 2.58$ ppm and a doublet at $\delta = 65.22$ ppm corresponding to the PPh_2 group *cis* to two PCy_3 ligands, as indicated by the small J_{PP} coupling constant of 15 Hz. The $^{11}B\{^1H\}$ NMR spectrum exhibits a broad signal centered at $\delta = 35.7$ ppm slightly more upfield than that of **1** ($\delta = 38.5$ ppm). The ^1H NMR spectrum of **5** in C_7D_8 at 258 K has, in the hydride region, a broad singlet, a multiplet (tdd), and a broad signal in a 1:1:1 integration ratio at $\delta = -7.29$, -11.52, and -18.38 ppm, respectively, in agreement with a ruthenium center surrounded by three hydrogen atoms. The singlet at $\delta = -7.29$ ppm was the only signal to sharpen upon boron decoupling, whereas the two other signals collapsed into doublets ($J_{HH} = 8.5$ Hz) upon phosphorus decoupling.



Scheme 1. Synthesis of the dihydride phosphinomethyl(amino)borane complex **5**.

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[**] We thank the CNRS and the ANR (programme blanc ANR-06-BLAN-0060-01) for support (Y.G., G.A., L.V., S.S.E.)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200806178.

Hydride disposition around the ruthenium was supported by selective phosphorus-decoupled ^{1}H NMR, NOESY and EXSY experiments. The X-ray structure of **5** was determined at 110 K (Figure 1 and Table 1). The Ru atom is in a distorted octahedral environment with the PCy_3 units in pseudo axial positions and bent away from the phosphinoborane ligand to reduce steric repulsion (P1-Ru-P3: 146.55(7)°). The coordination sites in the equatorial plane are occupied by three coplanar hydrogen atoms H1, H2, H3, and one phosphorus atom P2. The B−H3 bond length (1.23(7) Å) is in the range observed for ruthenium σ-borane complexes,[17,24,25] and comparable to that reported by Braunschweig et al. for the vinyl(amino)borane chromium complex.[23] As expected for an agostic species, the Ru···H3 distance is elongated compared to the two other ruthenium–hydride distances. The Ru−B distance (2.7574(80) Å), much longer than the sum of the covalent radii (2.09 Å), excludes a boryl formulation. It is also longer than those observed in ruthenium σ-B−H complexes,[24,25] but shorter than in the ruthenium complex $[RuH\{HBBNCH_2PMe_2\}(PMe_3)_3]$ resulting from HBBN (9-borabicyclo[3.3.1]nonane) insertion into a Ru−C bond of a metalated phosphine (2.994(1) Å).[26] The B-C1-P2 angle of 103.2(4)° in **5** is in agreement with a constrained δ-agostic coordination mode.[27] We noted that the substitution of the two dihydrogen ligands from **3** proceeds in a step-by-step manner as monitored by NMR spectroscopy. The ruthenium dihydrido(dihydrogen) intermediate **6** with a pendant borane ligand (Scheme 1) could be identified before evolution of the second dihydrogen and final formation of **5**. Interestingly, pressurization of a C_6D_6 solution of **5** with dihydrogen (3 bar) leads after 50 min to the complete disappearance of the agostic complex and formation of **6**, with traces of **3**.

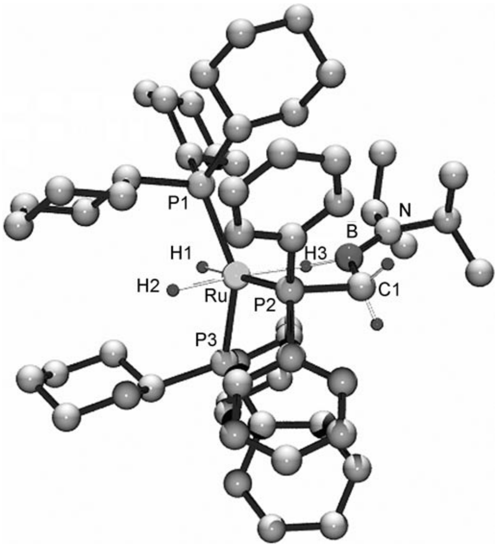
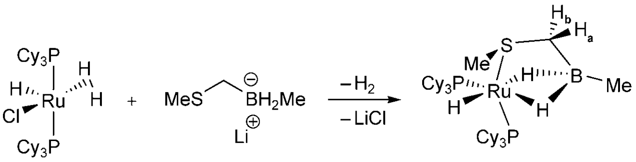


Figure 1. X-ray crystal structure of **5**.

Table 1: Selected geometrical parameters (distances in Å, angles in °) for the experimental and calculated structures for **5** and **7**.

Parameter	**5** Exp	Calcd	Parameter	**7** Exp	Calcd
Ru-B	2.7574(80)	2.858	Ru-B	2.266(8)	2.250
Ru-P1	2.3397(17)	2.369	Ru-P1	2.3103(16)	2.370
Ru-P2	2.3016(18)	2.372	Ru-P2	2.3242(15)	2.378
Ru-P3	2.3234(17)	2.371	Ru-S	2.4071(16)	2.412
Ru-H1	1.77(7)	1.615	Ru-H1	1.85(5)	1.877
Ru-H2	1.69(6)	1.559	Ru-H2	1.70(7)	1.770
Ru···H3	1.92(7)	1.952	Ru-H3	1.65(8)	1.581
B-H3	1.23(7)	1.241	B-H1	1.15(6)	1.313
			B-H2	1.38(7)	1.366
P1-Ru-P2	105.46(6)	105.0	P1-Ru-P2	105.18(6)	106.7
P1-Ru-P3	146.55(7)	146.3	P1-Ru-S	90.29(6)	91.0
P2-Ru-P3	104.77(6)	105.0	P2-Ru-S	164.26(6)	161.0
P2-C1-B	103.2(4)	105.6	S-C1-B	101.4(4)	101.1
Ru-H3-B	120(5)	125.6	Ru-H2-B	94(4)	90.8
			Ru-H1-B	95(4)	87.8
Ru-P2-C1	100.1(2)	98.0	Ru-S-C1	89.00(19)	88.5
C1-B-H3	122(3)	121.1	C1-B-H1	114(3)	110.4
			C1-B-H2	100(3)	106.3

We have also designed a second type of L~BHR ligand which, compared to **1**, has marked electrophilic character at the boron center. The reaction of the new lithium borohydride salt **2** with the chloro complex **4** (Scheme 2) gave a complex formulated as a hydrido(dihydroborate) complex $[RuH\{(\mu\text{-}H)_2BMeCH_2SMe\}(PCy_3)_2]$ (**7**) which was isolated in 31 % yield and fully characterized by NMR spectroscopy and single-crystal X-ray diffraction.



4 **2** **7**

Scheme 2. Synthesis of the hydrido(dihydroborate) complex **7**.

The $^{31}P\{^{1}H\}$ NMR spectrum of **7** in C_7D_8 at 298 K consists of an AB pattern at $\delta = 67.79$ ppm and $\delta = 63.90$ ppm with a J_{PP} value of 17.2 Hz, typical of a *cis* arrangement of the phosphine groups. The $^{11}B\{^{1}H\}$ NMR spectrum exhibits a signal centered at $\delta = 19.6$ ppm which is upfield of that of **5**. The ^{1}H NMR spectrum of **7** displays at set of three hydride resonances in a 1:1:1 integration ratio: a broad signal at $\delta = -4.30$ ppm (H1), a broad doublet at $\delta = -8.99$ ppm (H2), and a doublet of doublet at $\delta = -14.36$ ppm (H3). The disposition of the hydrogen atoms around the ruthenium was ascertained by selective phosphorus and/or boron-decoupled ^{1}H NMR spectroscopy, TOCSY and NOE experiments at variable temperature. The X-ray structure of **7** was determined at 110 K (Figure 2 and Table 1).

The ruthenium atom is also in a distorted octahedral environment but in contrast to **5**, the PCy_3 units are in a *cis* position with a P1-Ru-P2 angle of 105.18(6)°. The sulfur atom is *trans* to one PCy_3 ligand and occupies an apical position. The three hydrogen atoms H1–H3 are coplanar and located in the equatorial plane. The Ru−B distance of 2.266(8) Å is longer than those reported for σ-borane complexes, but

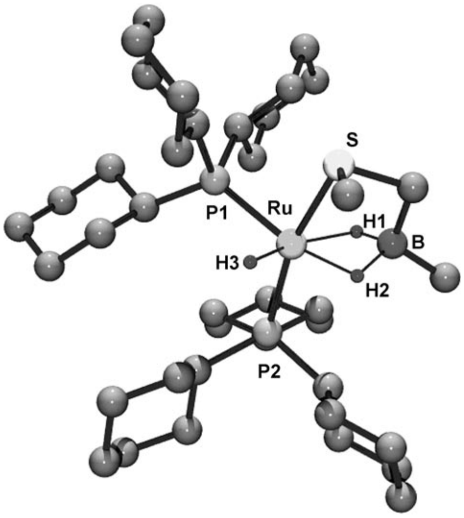
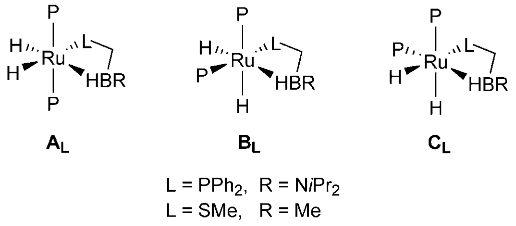


Figure 2. X-ray crystal structure of **7**.

similar to that of the dihydroborate metallacycle [Ru{(μ-H)$_2$BPhCMe$_2$ CHMeCH$_2$}(PMe$_3$)$_3$] (2.243(3) Å).[26]

Despite the different synthetic procedures, complexes **5** and **7** could be considered formally as adducts between the L~BHR ligand and the {RuH$_2$(PCy$_3$)$_2$} fragment. Thus, there are potentially three different isomers of general formulation [RuH$_2$(LCH$_2$BHR)(PCy$_3$)$_2$] as depicted in Scheme 3. To estimate the relative energies between these three isomers, ONIOM(B3PW91/HF) calculations have been performed. The geometries of the three complexes $\mathbf{A_L}$, $\mathbf{B_L}$, and $\mathbf{C_L}$ (**L** = **P** or **S**) are given in the Supporting Information.



Scheme 3. Different isomers resulting from the interaction of L~BHR with {RuH$_2$P$_2$} (P = PCy$_3$).

In the case of the phosphinoborane ligand (**L** = **P**) the most stable isomer is $\mathbf{A_P}$, in agreement with the X-ray structure of **5**. The two other isomers are less stable by 31.5 kJ mol^{-1} ($\mathbf{B_P}$) and 7.9 kJ mol^{-1} ($\mathbf{C_P}$). The calculated geometrical parameters for $\mathbf{A_P}$ are given in Table 1 and are in very good agreement with the X-ray data for **5**. The Ru–P bond distances are computed to be slightly longer than the experimental ones, but the P-Ru-P angles are faithfully reproduced. The interaction of B–H with Ru is best described as a δ-agostic interaction with an elongated B–H bond (1.241 Å in $\mathbf{A_P}$, 1.204 Å in free Ph$_2$PCH$_2$BHN*i*Pr$_2$) and a short Ru···H contact (1.952 Å). The HBN*i*Pr$_2$ moiety is almost planar with H-B-N-C dihedral angles of 0.1° and 175.6°. The interaction with Ru is essentially through the hydrogen atom bonded to B (Ru-H3-B = 125.6°). An NBO analysis confirmed the description of the system as a phosphinoborane ligand in interaction with a d^6 Ru^{II} center. The σ(B–H) bond, slightly more polarized toward H in the complex than in the free ligand (57 % vs. 54.4 %), interacts with the antibonding σ^*(Ru–H) orbital (143.8 kJ mol^{-1}) in a typical σ-donation process. However, no significant back-donation from Ru to B could be identified by the NBO procedure. The main contributor to the stabilization of the vacancy at boron is π donation from the nitrogen lone pair (367.0 kJ mol^{-1}), a second-order perturbation energy interaction approximately three-times larger than the σ donation from B–H to Ru. This stabilization from the nitrogen lone pair is already present in the free ligand (359 kJ mol^{-1}) and complexation has not significantly altered it.

All attempts to locate an isomer with two hydrides and a σ(B–H) coordination, as formally depicted for $\mathbf{B_S}$ in Scheme 3 (**L** = **S**), failed: the hydride *cis* to B always formed the second B–H bond of a borohydride ligand. The lowest minimum, $\mathbf{B'_S}$ (Figure S2 in Supporting Information), displays calculated geometrical parameters for the heavy atoms in excellent agreement with the X-ray data for **7**. The two other isomers are respectively at 50.3 kJ mol^{-1} ($\mathbf{A_S}$) and 17.0 kJ mol^{-1} ($\mathbf{C_S}$). Moreover, the calculations allowed more secure location of the hydrogen atoms in $\mathbf{B'_S}$, and, in particular, the hydride and the H atoms bonded to B. The calculated geometry around the boron is indicative of a borohydride character with two B–H bond lengths of similar magnitudes (1.313 Å and 1.366 Å). The NBO analysis confirmed the geometrical analysis with the formation of a borohydride species. The dissymmetry in the B–H bond lengths originates from the different nature of the ligand *trans* to the coordinated B–H bonds.[28]

The relative energies obtained for the complexes $\mathbf{A_L}$, $\mathbf{B_L}$, and $\mathbf{C_L}$ and the NBO analysis illustrate the subtle influence of the substituent on B to trigger the mode of coordination. For L = PPh$_2$, the amino group on B is a strong π-base that provides enough stabilization to boron. The preferred isomer is thus the one that puts the weakest ligands (PPh$_2$ and σ(BH)) *trans* to the strongest ones, the hydrides as in **5**. For L = SMe, the boron atom is strongly electrophilic and seeks electron density upon coordination. This is best achieved with the isomer $\mathbf{B'_S}$, where hydride transfer to boron affords the borohydride complex **7**.

In conclusion, we report herein the first example of an agostic ruthenium complex containing a η^2-B–H bond involving a trivalent boron. The hemilability of the ligand is illustrated by the reversible loss of dihydrogen from the complex. When using a more electrophilic boron reagent, a dihydroborate complex is stabilized. Further work is in progress to design new L~BHR as potentially hemilabile ligands and to study their impact in stoichiometric and catalytic reactions.

Experimental Section

1: Ph$_2$PCH$_2$Li (0.849 g, 4.118 mmol) was added to an ethereal solution (40 mL) of *i*Pr$_2$NBHCl (0.730 g, 4.951 mmol) at −78 °C. The suspension was stirred for 30 min at this temperature and for 17 h at room temperature. After filtration over celite, removal of the solvent and trap-to-trap distillation, $Ph_2PCH_2BHN\mathit{i}PR_2$ (**1**) was isolated as a colorless oil (1.012 g) contaminated by 10% of Ph_2PMe. Selected NMR data ($CDCl_3$, 298 K): $^{31}P\{^1H\}$ NMR (121.494 MHz): $\delta = -16.96$ ppm. $^{11}B\{^1H\}$ NMR (128.377 MHz): $\delta = 38.5$ ppm. ^1H NMR (400.132 MHz): $\delta = 0.95$ and 1.04 (d, 2×6H, $^3J_{HH} = 6.70$ Hz, CH_3 *i*Pr), 1.73 (m, 2H, BCH_2P), 3.17 and 3.90 (h, 2×1H, $^3J_{HH} = 6.70$ Hz, CH *i*Pr), 4.60 (br, BH), 7.20–7.50 ppm (m, 10H, CH Ph). $^{13}C\{^1H\}$ NMR (100.613 MHz): $\delta = 17.82$ (br, BCH_2P), 22.15 (s, CH_3 *i*Pr), 26.80 (s, CH_3 *i*Pr), 45.15 (s, CH *i*Pr), 49.08 ppm (s, CH *i*Pr).

2: Methyllithium 1.6 M in diethyl ether (1.28 mL, 2.048 mmol) was added to a cooled (−78 °C) ethereal solution (20 mL) of $MeSCH_2B(O\mathit{i}Pr)_2$ (0.390 g, 2.051 mmol). The resulting solution was stirred for 2.5 h at this temperature before warming to room temperature. It was then transferred to a cooled (−78 °C) ethereal suspension (20 mL) of $LiEtOAlH_3$ (2.051 mmol) and stirred for 2 h before warming to room temperature. After workup, $MeSCH_2BH_2MeLi$ (**2**) was isolated as a white powder (0.200 g) contaminated by traces of $LiBH_4$ and $LiMeBH_3$. **2** was used without any further purification. ^{11}B NMR ($[D_8]$THF, 298 K, 128.377 MHz): $\delta = -23.6$ ppm (t, $^1J_{BH} = 72$ Hz, BH_2). ^1H NMR ($[D_8]$THF, 298 K, 400.132 MHz): $\delta = -0.43$ (s, 3H, BCH_3), 0.55 (q, 2H, $^1J_{BH} = 72$ Hz, BH_2), 1.56 (br, 2H, CH_2), 1.90 ppm (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR ($[D_8]$THF, 298 K, 100.623 MHz): $\delta = 3.35$ (q, $^1J_{CB} = 44.0$ Hz, BCH_3), 19.39 (m, 3H, SCH_3), 32.73 ppm (q, $^1J_{BC} = 41.9$ Hz, CH_2).

5: A toluene (10 mL) solution of **1** (93.7 mg) was added to a toluene (10 mL) solution of $[RuH_2(H_2)_2(PCy_3)_2]$ (**3**; 200.5 mg, 0.300 mmol) and stirred for 48 h at room temperature. After workup, **5** was isolated as a white solid (54.8 mg, 18%). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.50 MHz): $\delta = 65.22$ (d, $^2J_{PP} = 15$ Hz, Cy_3P), 2.58 ppm (t, $^2J_{PP} = 15$ Hz, Ph_2P). $^{11}B\{^1H\}$ NMR (C_7D_8, 298 K, 160.52 MHz): $\delta = 35.7$ ppm (s). ^1H NMR (C_7D_8, 258 K, 500.33 MHz): $\delta = -18.38$ (br, 1H, $^2J_{P1,3-H2} = 25.10$ Hz, $^2J_{P2H2} = 9.8$ Hz, $J_{H1H2} = 8.5$ Hz, H2), −11.52 (tdd, 1H, $^2J_{P1,3-H1} = 30.9$ Hz, $^2J_{P2H1} = 70.6$ Hz, $^2J_{H1H2} = 8.5$ Hz, H1), −7.29 (s, br, 1H, BH), 1.18 and 1.38 (d, 2×6H, $^3J_{HH} = 6.65$ Hz, CH_3 *i*Pr), 3.14 (d, 2H, $^2J_{PH} = 9.70$ Hz, CH_2P), 3.20 and 4.21 ppm (h, 2×1H, $^3J_{HH} = 6.65$ Hz, CH *i*Pr). $^{13}C\{^1H\}$ NMR (C_7D_8, 278 K, 125.808 MHz): $\delta = 56.63$ (s, CH *i*Pr), 45.12 (s, CH *i*Pr), 33.88 (br, BCH_2P), 24.39 (s, CH_3 *i*Pr), 21.78 ppm (s, CH_3 *i*Pr).

6: Selected NMR data (C_7D_8, 298 K): $^{31}P\{^1H\}$ NMR (202.547 MHz): $\delta = 67.22$ (d, $^2J_{PP} = 16.3$ Hz, Cy_3P), 39.52 ppm (t, $^2J_{PP} = 16.3$ Hz, Ph_2P). $^{11}B\{^1H\}$ NMR (160.526 MHz): $\delta = 40.2$ ppm (br). ^1H NMR (400.130 MHz): $\delta = -8.53$ (td, 4H, $^2J_{HP1,2} = 13.91$ Hz, $^2J_{HP3} = 13.51$ Hz , $RuH_2(H_2)$), 0.93 and 1.10 (d, 2×6H, $^3J_{HH} = 6.71$ Hz, CH_3 *i*Pr), 1.10–2.30 (m, CH_2P + Cy), 3.05 and 3.93 (h, 2×1H, $^3J_{HH} = 6.71$ Hz, CH *i*Pr), 4.92 ppm (br, BH). T_{1min} (258 K, 500.33 MHz): $\delta = -8.46$ (57 ms).

7: A diethyl ether solution (6 mL) of **2** (70.6 mg, 0.736 mmol) was added to a diethyl ether solution (8 mL) of $[RuH(H_2)Cl(PCy_3)_2]$ (**4**; 386.9 mg, 0.552 mmol) and stirred for 15 min at room temperature. After workup, **7** was isolated as a beige solid in 31% yield. $^{31}P\{^1H\}$ NMR (C_7D_8, 298 K, 202.537 MHz): $\delta = 67.79$ (d, $^2J_{P\text{-}P} = 17.2$ Hz, Cy_3P1) , 63.90 ppm (d, $^2J_{P\text{-}P} = 17.2$ Hz, Cy_3P2). $^{11}B\{^1H\}$ NMR (C_7D_8, 298 K, 160.526 MHz): $\delta = 19.6$ ppm (br). ^1H NMR (C_7D_8, 298 K, 500.330 MHz): $\delta = -14.36$ (dd, 1H, $^2J_{P\text{-}H1} = 25$ and 30 Hz, H3), −8.99 (br d, 1H, $J_{P1\text{-}H2} = 40.6$ Hz, H2), −4.30 (br s, 1H, H1), 0.65 (s, 3H, B CH_3), 2.42 (br s, 3H, SCH_3), 2.69 (dd, 1H, , $^2J_{Ha\text{-}Hb} = 13.76$ Hz, , $^3J_{Ha\text{-}H3} = 9.11$ Hz, H_a), 3.50 ppm (dd, 1H, $^2J_{Hb\text{-}Ha} = 13.76$ Hz, $^3J_{Hb\text{-}H2} = 6.71$ Hz, H_b). $^{13}C\{^1H\}$ NMR (C_7D_8, 298 K, 125.808 MHz): $\delta = 9.74$ (br s, BCH_3), 31.29 (s, SCH_3), 52.77 ppm (br s, BCH_2S). Elemental analysis (%) calcd for $C_{39}H_{77}BP_2RuS$: C 62.30; H 10.32; found: C 62.26; H 10.41.

CCDC 713433 (**5**) and CCDC 713434 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The calculations have been performed with the Gaussian03 package (see Supporting Information). ONIOM(B3PW9/HF) calculations have been carried out on the experimental systems.[29] In the high-level layer, treated with the hybrid functional B3PW91,[30,31] the PCy_3 ligands were modeled as PMe_3, the PPh_2 ligand as PH_2, the *i*Pr groups as H. These groups were explicitly incorporated in the low-level layer and were treated at the HF level. All the other groups on the complex were explicitly incorporated in the high-level layer. For the calculations at the B3PW91 level, the Ru and P atoms were described with the pseudo-potentials from Dolg et al. and the associated basis sets,[32,33] augmented by a polarization function.[34,35] The other atoms were treated with a 6-31G(d,p) basis set.[36] For the calculations at the HF level, the Ru and P atoms were described by the pseudo-potentials from Hay and Wadt and the associated basis sets.[37,38] The other atoms were treated with a 4–31G basis set.[39] The NBO analysis[40] was performed on the B3PW91 electronic density obtained on the ONIOM geometry with the basis set described for the high-level layer.

Received: December 18, 2008

Keywords: agostic interactions · bifunctional ligands · boron · hydrides · ruthenium

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