

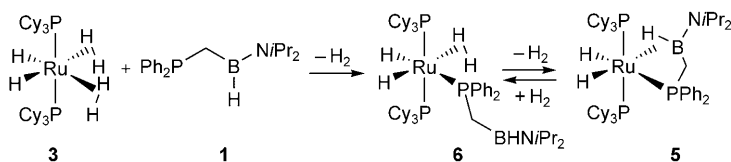
Phosphinoborane and Sulfidoborohydride as Chelating Ligands in Polyhydride Ruthenium Complexes: Agostic σ -Borane versus Dihydroborate Coordination**

Yann Gloaguen, Gilles Alcaraz,* Anne-Frédérique Pécharman, Eric Clot, Laure Vendier, and Sylviane Sabo-Etienne*

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 $L \sim BHR$ ($L = P, S$ and $R = \text{amino, alkyl}$) 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 $Ph_2PCH_2BHNiPr_2$ (**1**) and the lithium sulfido(methyl)borohydride $Li[MeSCH_2BH_2Me]$ (**2**), as well as their coordination to the two ruthenium precursors $[RuH_2(\eta^2-H_2)_2(PCy_3)_2]$ (**3**) and $[RuHCl(\eta^2-H_2)(PCy_3)_2]$ (**4**). The strategy is based on the one we recently used to isolate the bis σ -borane complex $[RuH_2(\eta^2:\eta^2-H_2BMes)(PCy_3)_2]$ 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



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

dihydrogen ligands by **1** (Scheme 1). The new complex $[RuH_2\{\eta^2-H-B(NiPr_2)CH_2PPh_2\}(PCy_3)_2]$ (**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.

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Hydride disposition around the ruthenium was supported by selective phosphorus-decoupled ^1H 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 : $146.55(7)^\circ$). 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

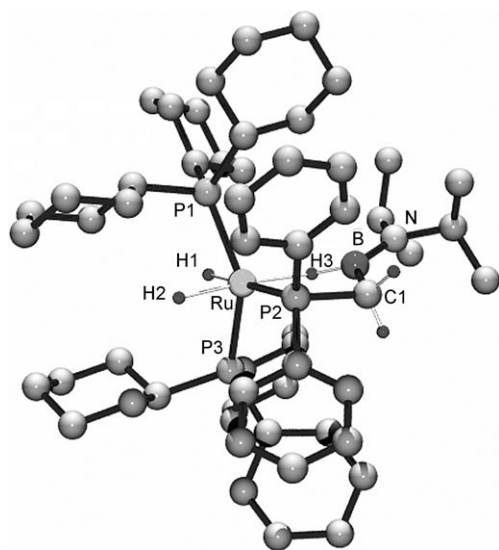


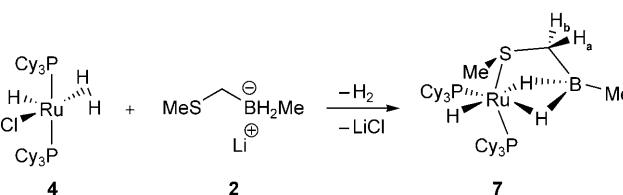
Figure 1. X-ray crystal structure of **5**.

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

Parameter	5		Parameter	7	
	Exp	Calcd		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

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 $[\text{RuH}(\text{HBBNCH}_2\text{PMe}_2)(\text{PMe}_3)_3]$ 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 $103.2(4)^\circ$ 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**.

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 $[\text{RuH}(\mu\text{-H})_2\text{BMeCH}_2\text{SMe}](\text{PCy}_3)_2$ (**7**) which was isolated in 31 % yield and fully characterized by NMR spectroscopy and single-crystal X-ray diffraction.



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

The $^{31}\text{P}\{^1\text{H}\}$ 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 $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum exhibits a signal centered at $\delta = 19.6$ ppm which is upfield of that of **5**. The ^1H NMR spectrum of **7** displays a 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 ^1H 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 $105.18(6)^\circ$. 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

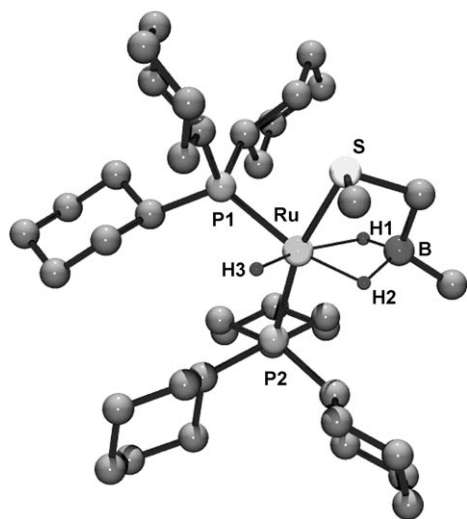
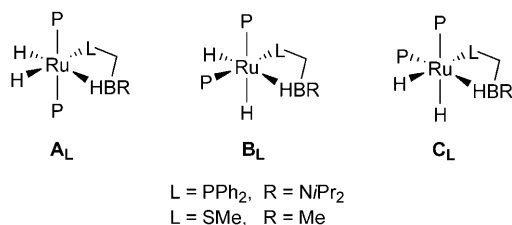


Figure 2. X-ray crystal structure of **7**.

similar to that of the dihydroborate metallacycle $[\text{Ru}\{\mu\text{-H}\}_2\text{BPhCMe}_2\text{CHMeCH}_2\text{CH}_2(\text{PCy}_3)_2]$ (2.243(3) Å).^[26]

Despite the different synthetic procedures, complexes **5** and **7** could be considered formally as adducts between the $\text{L} \sim \text{BHR}$ ligand and the $[\text{RuH}_2(\text{PCy}_3)_2]$ fragment. Thus, there are potentially three different isomers of general formulation $[\text{RuH}_2(\text{LCH}_2\text{BHR})(\text{PCy}_3)_2]$ 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 **A_L**, **B_L**, and **C_L** ($\text{L} = \text{P}$ or S) are given in the Supporting Information.



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

In the case of the phosphinoborane ligand ($\text{L} = \text{P}$) the most stable isomer is **A_P** in agreement with the X-ray structure of **5**. The two other isomers are less stable by 31.5 kJ mol⁻¹ (**B_P**) and 7.9 kJ mol⁻¹ (**C_P**). The calculated geometrical parameters for **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 **A_P**, 1.204 Å in free $\text{Ph}_2\text{PCH}_2\text{BHNiPr}_2$) and a short Ru...H contact (1.952 Å). The HBNiPr_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 con-

firmed the description of the system as a phosphinoborane ligand in interaction with a d⁶ Ru^{II} center. The $\sigma(\text{B} \sim \text{H})$ bond, slightly more polarized toward H in the complex than in the free ligand (57% vs. 54.4%), interacts with the antibonding $\sigma^*(\text{Ru} \sim \text{H})$ 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 $\sigma(\text{B} \sim \text{H})$ coordination, as formally depicted for **B_S** in Scheme 3 ($\text{L} = \text{S}$), failed: the hydride *cis* to B always formed the second B–H bond of a borohydride ligand. The lowest minimum, **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 (**A_S**) and 17.0 kJ mol⁻¹ (**C_S**). Moreover, the calculations allowed more secure location of the hydrogen atoms in **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 **A_L**, **B_L**, and **C_L** and the NBO analysis illustrate the subtle influence of the substituent on B to trigger the mode of coordination. For $\text{L} = \text{PPh}_2$, 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 $\sigma(\text{BH})$) *trans* to the strongest ones, the hydrides as in **5**. For $\text{L} = \text{SMe}$, the boron atom is strongly electrophilic and seeks electron density upon coordination. This is best achieved with the isomer **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 $\eta^2\text{-B} \sim \text{H}$ 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 $\text{L} \sim \text{BHR}$ as potentially hemilabile ligands and to study their impact in stoichiometric and catalytic reactions.

Experimental Section

1: $\text{Ph}_2\text{PCH}_2\text{Li}$ (0.849 g, 4.118 mmol) was added to an ethereal solution (40 mL) of $i\text{Pr}_2\text{NBHCl}$ (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, $\text{Ph}_2\text{PCH}_2\text{BHNiPr}_2$ (**1**) was isolated as a colorless oil (1.012 g) contaminated by 10% of Ph_2PMe . Selected NMR data (CDCl_3 , 298 K): $^{31}\text{P}\{^1\text{H}\}$ NMR (121.494 MHz): $\delta = -16.96$ ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128.377 MHz): $\delta = 38.5$ ppm. ^1H NMR (400.132 MHz): $\delta = 0.95$ and 1.04 (d, $2 \times 6\text{H}$, $^3J_{\text{HH}} = 6.70$ Hz, CH_3 iPr), 1.73 (m, 2H , BCH_2P), 3.17 and 3.90 (h, $2 \times 1\text{H}$, $^3J_{\text{HH}} = 6.70$ Hz, CH iPr), 4.60 (br, BH), 7.20 – 7.50 ppm (m, 10H , CH Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.613 MHz): $\delta = 17.82$ (br, BCH_2P), 22.15 (s, CH_3 iPr), 26.80 (s, CH_3 iPr), 45.15 (s, CH iPr), 49.08 ppm (s, CH iPr).

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 $\text{MeSCH}_2\text{B}(\text{OiPr})_2$ (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, $\text{MeSCH}_2\text{BH}_2\text{MeLi}$ (**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 ($[\text{D}_8]\text{THF}$, 298 K, 128.377 MHz): $\delta = -23.6$ ppm (t, $^1J_{\text{BH}} = 72$ Hz, BH_2). ^1H NMR ($[\text{D}_8]\text{THF}$, 298 K, 400.132 MHz): $\delta = -0.43$ (s, 3H , BCH_3), 0.55 (q, 2H , $^1J_{\text{BH}} = 72$ Hz, BH_2), 1.56 (br, 2H , CH_2), 1.90 ppm (s, 3H , SCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$, 298 K, 100.623 MHz): $\delta = 3.35$ (q, $^1J_{\text{CB}} = 44.0$ Hz, BCH_3), 19.39 (m, 3H , SCH_3), 32.73 ppm (q, $^1J_{\text{BC}} = 41.9$ Hz, CH_2).

5: A toluene (10 mL) solution of **1** (93.7 mg) was added to a toluene (10 mL) solution of $[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$ (**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%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 121.50 MHz): $\delta = 65.22$ (d, $^2J_{\text{PP}} = 15$ Hz, Cy_3P), 2.58 ppm (t, $^2J_{\text{PP}} = 15$ Hz, Ph_2P). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_7D_8 , 298 K, 160.526 MHz): $\delta = 35.7$ ppm (s). ^1H NMR (C_7D_8 , 258 K, 500.33 MHz): $\delta = -18.38$ (br, 1H , $^2J_{\text{P1-3-H2}} = 25.10$ Hz, $^2J_{\text{P2H2}} = 9.8$ Hz, $J_{\text{H1H2}} = 8.5$ Hz, H_2), -11.52 (tdd, 1H , $^2J_{\text{P1-3-H1}} = 30.9$ Hz, $^2J_{\text{P2H1}} = 70.6$ Hz, $^2J_{\text{H1H2}} = 8.5$ Hz, H_1), -7.29 (s, br, 1H , BH), 1.18 and 1.38 (d, $2 \times 6\text{H}$, $^3J_{\text{HH}} = 6.65$ Hz, CH_3 iPr), 3.14 (d, 2H , $^2J_{\text{PH}} = 9.70$ Hz, CH_2P), 3.20 and 4.21 ppm (h, $2 \times 1\text{H}$, $^3J_{\text{HH}} = 6.65$ Hz, CH iPr). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 278 K, 125.808 MHz): $\delta = 56.63$ (s, CH iPr), 45.12 (s, CH iPr), 33.88 (br, BCH_2P), 24.39 (s, CH_3 iPr), 21.78 ppm (s, CH_3 iPr).

6: Selected NMR data (C_7D_8 , 298 K): $^{31}\text{P}\{^1\text{H}\}$ NMR (202.547 MHz): $\delta = 67.22$ (d, $^2J_{\text{PP}} = 16.3$ Hz, Cy_3P), 39.52 ppm (t, $^2J_{\text{PP}} = 16.3$ Hz, Ph_2P). $^{11}\text{B}\{^1\text{H}\}$ NMR (160.526 MHz): $\delta = 40.2$ ppm (br). ^1H NMR (400.130 MHz): $\delta = -8.53$ (td, 4H , $^2J_{\text{HP1,2}} = 13.91$ Hz, $^2J_{\text{HP3}} = 13.51$ Hz, $\text{RuH}_2(\text{H}_2)$), 0.93 and 1.10 (d, $2 \times 6\text{H}$, $^3J_{\text{HH}} = 6.71$ Hz, CH_3 iPr), 1.10 – 2.30 (m, $\text{CH}_2\text{P} + \text{Cy}$), 3.05 and 3.93 (h, $2 \times 1\text{H}$, $^3J_{\text{HH}} = 6.71$ Hz, CH iPr), 4.92 ppm (br, BH). $T_{1\text{min}}$ (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 $[\text{RuH}(\text{H}_2)\text{Cl}(\text{PCy}_3)_2]$ (**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. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8 , 298 K, 202.537 MHz): $\delta = 67.79$ (d, $^2J_{\text{P-P}} = 17.2$ Hz, $\text{Cy}_3\text{P1}$), 63.90 ppm (d, $^2J_{\text{P-P}} = 17.2$ Hz, $\text{Cy}_3\text{P2}$). $^{11}\text{B}\{^1\text{H}\}$ 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 , $^2J_{\text{P-H1}} = 25$ and 30 Hz, H_3), -8.99 (br d, 1H , $J_{\text{P1-H2}} = 40.6$ Hz, H_2), -4.30 (br s, 1H , H_1), 0.65 (s, 3H , BCH_3), 2.42 (br s, 3H , SCH_3), 2.69 (dd, 1H , $^2J_{\text{Ha-Hb}} = 13.76$ Hz, $^3J_{\text{Ha-H3}} = 9.11$ Hz, H_a), 3.50 ppm (dd, 1H , $^2J_{\text{Hb-Ha}} = 13.76$ Hz, $^3J_{\text{Hb-H2}} = 6.71$ Hz, H_b). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{39}\text{H}_{77}\text{BP}_2\text{RuS}$: 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 iPr 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.

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