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Access to Unsaturated Ruthenium Complexes via Phosphine Complexation with Triphenylborane: Synthesis and Structure of a Zwitterionic Arene Complex, (η^6-Ph-BPh$_2$H)Ru(PMe$_3$)$_2$(SiMe$_3$)

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Triphenylborane, BPh$_3$, serves as a phosphine "sponge", scavenging free PMe$_3$ from alkane solutions of the $18e^-$ complex (PMe$_3$)$_4$Ru(SiMe$_3$)H to form sparingly soluble Ph$_3$B−PMe$_3$ and the $16e^-$ (PMe$_3$)$_3$Ru(SiMe$_3$)H. Under nitrogen atmosphere the $16e^-$ (PMe$_3$)$_3$Ru(SiMe$_3$)H forms a dimeric N$_2$ adduct, [(PMe$_3$)$_3$Ru(SiMe$_3$)H]$_2$N$_2$. Both the $16e^-$ complex and its N$_2$ adduct exist in equilibrium with the $18e^-$ silene complex, (PMe$_3$)$_3$Ru(CH$_2$=SiMe$_2$)H$_2$. However, long reaction times in the presence of excess borane leads to removal of another phosphine ligand as Ph$_3$B−PMe$_3$ and formation of a new zwitterionic complex, (η^6-PhBPh$_2$H)Ru(PMe$_3$)$_2$(SiMe$_3$) (**5**), in which a molecule of borane has abstracted a ruthenium hydride ligand and also coordinates as an η^6-arene. The merits and limitations of BPh$_3$ as a phosphine removal agent are discussed. Compound **5** has been characterized by single-crystal X-ray analysis and exhibits unusually long Ru−C$_{\text{arene}}$ bonds.

The reactivity of $18e^-$ phosphine complexes most commonly stems from initial reversible dissociation of a phosphine ligand, which generates sterically and electronically unsaturated $16e^-$ species. The ability to remove free phosphine from solution, hence shifting the equilibrium in favor of the reactive unsaturated species, is often a very desirable goal in the quest for more active catalysts, in synthetic chemistry, and in probing details of reaction mechanisms. Several reagents for capturing dissociated phosphine ligands have been reported, including MeI,[1−3] B(C$_6$F$_5$)$_3$,[4] (9-BBN)$_2$,[5] Me$_3$N=O,[6] CS$_2$,[7] sulfur,[2] CuI,[8] [Cu(MeCN)$_4$][PF$_6$],[9] Pd(PhCN)$_2$Cl$_2$,[2,10] PdCl$_2$(COD),[10] PdCl$_2$,[11] [Pd(OCMe$_2$)(bipy)(C$_6$F$_5$)][ClO$_4$],[7] (acac)Rh(C$_2$H$_4$)$_2$,[6,12−14] Ni(COD)$_2$,[4,6,14] [RhCl(C$_6$H$_{14}$)$_2$]$_2$,[15] and Au(PPh$_3$)(NO$_3$),[16] Unfortunately, many of these phosphine sponges also exhibit considerable activity in redox and ligand substitution reactions or greatly complicate isolation of the desired unsaturated metal species. We recently reported in a preliminary communication that treatment of (PMe$_3$)$_4$Ru(SiMe$_3$)H with BPh$_3$ yields the $16e^-$ (PMe$_3$)$_3$Ru(SiMe$_3$)H, **2**, and the sparingly soluble BPh$_3$−PMe$_3$.[17] In the present contribution we provide more detail regarding the use of triphenylborane as a convenient phosphine scavenger in the generation of **2** and a ruthenium silene complex derived from **2** and the isolation of an unusual ruthenium−borane complex resulting from subsequent reaction of BPh$_3$ with the products.

Results and Discussion

Compared with many of the potent Lewis acids (e.g., B(C$_6$F$_5$)$_3$) currently en vogue, BPh$_3$ is a distinctly mild reagent. Formation of **2** and PMe$_3$−BPh$_3$ is relatively fast (minutes at room temperature) and proceeds at a rate qualitatively consistent with phosphine dissociation from the starting complex. Complex **2** subsequently undergoes reversible β-hydride elimination from the silyl ligand, generating equilibrium concentrations of the silene complex **3**, (PMe$_3$)$_3$Ru(CH$_2$=SiMe$_2$)H$_2$ (Scheme 1).[17] Furthermore, in the presence of nitrogen, **2** exists in fast equilibrium with the bridging dinitrogen complex, [(PMe$_3$)$_3$Ru(SiMe$_3$)H]$_2$N$_2$, **4**, the structure of which has been previously reported.[17]

However, addition of a single equivalent of BPh$_3$ to **1** (initial concentration = 0.035 M each) in C$_6$D$_{12}$ at room

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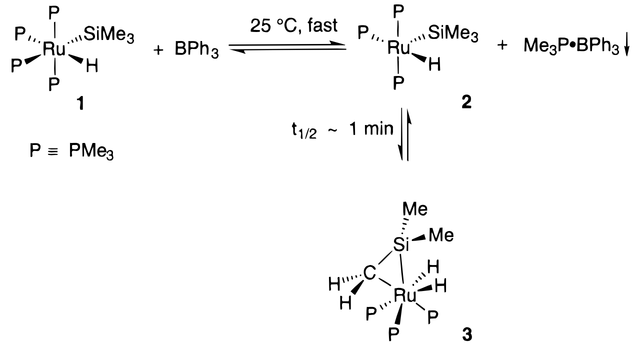
Scheme 1

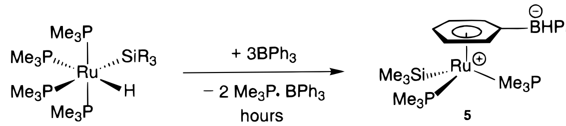


temperature under nitrogen does not consume all of the starting material, but after 2 h rather produces an equilibrium mixture containing **1** (42%), **2**/**4** (16%), **3** (34%), and ca. 8% total of (η^6-Ph-BPh$_2$H)Ru(PMe$_3$)$_2$-(SiMe$_3$) (vide infra) and (PMe$_3$)$_3$Ru(SiMe$_3$)H$_3$ (product of redistribution and dehydrocoupling of silyl ligands[18,19]). The equilibrium is less favorable in C$_6$D$_6$, leading to 53% **1**, 18% **2**/**4**, and 20% **3**. It is noteworthy how little the equilibrium is effected by the change of solvent, given that the borane–phosphine adduct is appreciably more soluble in C$_6$D$_6$ than in C$_6$D$_{12}$. Changes in the relative amounts of **3** and **2**/**4** may also reflect differences in the solubility of nitrogen gas. The effectiveness of BPh$_3$ in this case appears to rely more on the Lewis acidity of the borane than on the insolubility of the adduct. One obvious strategy to improve the stoichiometric trapping and removal of phosphines is to employ stronger Lewis acids such as B(C$_6$F$_5$)$_3$ and B(C$_6$H$_3$(CF$_3$)$_2$)$_3$, but these attempts led to extensive decomposition and neither **2**/**4** nor **3** was observed. It is likely these Lewis acids indiscriminately abstract hydride and/or silyl ligands, in addition to trapping dissociated PMe$_3$.

Alternatively, the equilibrium in Scheme 1 can be driven by the use of excess BPh$_3$, but this accelerates the slow (hours) formation of (η^6-Ph-BPh$_2$H)Ru(PMe$_3$)$_2$-(SiMe$_3$), **5**, at the expense of the desired **2**/**4** and **3**. The yield of **2**/**4** and **3** can be improved through the following procedure performed in aliphatic solvents such as pentane. An excess of BPh$_3$ is used to shift the equilibrium to the right; precipitation of Ph$_3$B–PMe$_3$ occurs within minutes, and most of the unreacted borane is removed by addition of polystyrene-supported triphenylphosphine.[17] Both solid Ph$_3$B–PMe$_3$ and the polymer-bound phosphine borane are removed by filtration. Some borane inevitably remains in solution and slowly reacts further to form **5** and Ph$_3$B–PMe$_3$, but these contaminants can be removed by crystallization from a large quantity of cold pentane. Prompt recrystallization of the concentrated mother liquors under nitrogen yields the bridging N$_2$ complex **4** (64%) as analytically pure material.

When compared to other phosphine sponges, one can expect BPh$_3$ to be preferred in instances where the products do not tolerate strong Lewis acids. Unfortunately, the mild acidity of BPh$_3$ limits its use to complexes with extremely labile phosphine ligands or to enhancing the equilibrium concentration of active unsaturated complexes during catalysis. In theory, one could devise improved phosphine sponges by employing triaryl- or trialkylboranes anchored on solid supports, e.g., analogous to polystyrene-supported PPh$_3$, which would allow phosphine removal without unduly complicating the separation of products from excess borane.

Synthesis and Characterization of (η^6-PhBPh$_2$H)-Ru(PMe$_3$)$_2$(SiMe$_3$). Treatment of (PMe$_3$)$_4$Ru(SiMe$_3$)H with excess BPh$_3$ (3 equiv) initially produces a mixture of the unsaturated **2** and the silene complex **3**, but both of these species disappear within 4 h at room temperature. The principal new product is (η^6-PhBPh$_2$H)Ru-(PMe$_3$)$_2$(SiMe$_3$), **5**, in which a BPh$_3$H anion is coordinated to ruthenium as an η^6-arene (eq 1). Multinuclear NMR spectra are consistent with the structure indicated for **5**. Features in the ^{1}H NMR spectrum that are particularly diagnostic include three new signals between δ 5.88 and 4.49 ppm for the coordinated arene and a 1:1:1:1 pattern at δ 4.06 ppm for the hydride bound to four-coordinate boron. The latter is observed at −9.73 ppm in the ^{11}B NMR (d, J_{BH} = 82.5 Hz). A single-crystal X-ray diffraction study confirmed the proposed zwitterionic structure (vide infra).



(1)

Many examples of η^6-coordination of tetraphenylborate anions have been previously reported,[20–28] including several ruthenium complexes,[21–24,29] some of which were structurally characterized.[30–32] On the other hand, the BPh$_3$H fragment appears to be much less common, regardless of the coordination mode. A few alkali metal salts of [BPh$_3$H]$^-$ have been reported, generally prepared by treatment of BPh$_3$ with the corresponding alkali metal hydride.[33,34] It is surprising that such a weak acid as BPh$_3$ can abstract a hydride from a weak base, the neutral ruthenium–phosphine complex. Certainly, hydride-,[35–48] alkyl-,[35,45,49–52] and silyl-abstrac-

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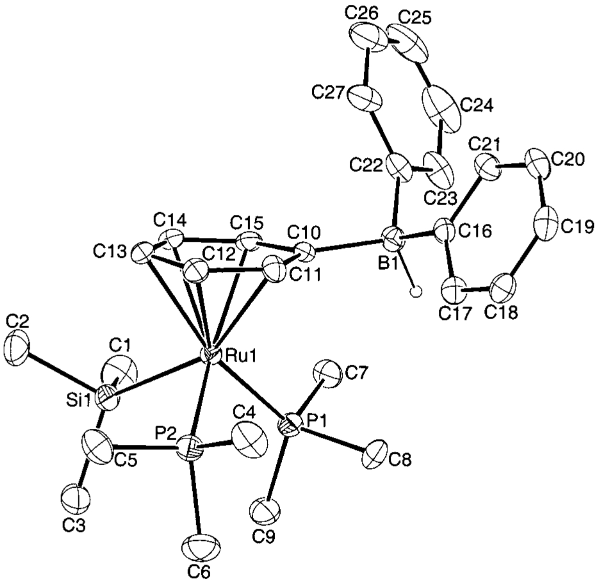

Figure 1. ORTEP drawing of $(PMe_3)_2Ru(SiMe_3)(\eta^6\text{-}Ph\text{-}BPh_2H)$, **5** (30% thermal ellipsoids). Hydrogen atoms other than the B−H are omitted for clarity.

tion[53] reactions by boranes are known, but these are generally associated with high Lewis acidity (e.g., fluorinated arylboranes,[35−46,49−52]) or chelating effects (e.g., 1,8-bis(dimethylboranyl)naphthalene, "hydride sponge"[47,48]). Compound **5** is most likely formed by reaction of the unsaturated **2** with BPh_3, although the order of the initial steps is not obvious. It is possible that η^2-arene coordination is assisted by concurrent borane−hydride association and formation of an η^1-borohydride. In any case, further substitution of PMe_3 by the increasing hapticity of the arene would be assisted by the presence of additional BPh_3 to scavenge free phosphine.

Table 1. Selected Bond Distances (Å) and Angles (deg) in $(PMe_3)_2Ru(SiMe_3)(\eta^6\text{-}Ph\text{-}BPh_2H)$

Ru1−Si1	2.418(2)	Ru1−P1	2.307(2)	Ru1−P2	2.282(2)
Ru1−C10	2.467(6)	C10−C11	1.419(9)	C10−B1	1.636(9)
Ru1−C11	2.376(7)	C10−C15	1.441(9)	C16−B1	1.620(10)
Ru1−C12	2.264(6)	C11−C12	1.415(9)	C22−B1	1.614(10)
Ru1−C13	2.284(6)	C12−C13	1.412(10)	B1−H1	1.22(5)
Ru1−C14	2.255(6)	C13−C14	1.429(10)		
Ru1−C15	2.280(7)	C14−C15	1.405(9)		

P2−Ru1−P1	94.19(7)	C16−B1−C10	113.7(5)
P1−Ru1−Si1	88.66(7)	C22−B1−H1	104(3)
P2−Ru1−Si1	90.44(7)	C16−B1−H1	109(3)
C22−B1−C16	113.4(6)	C10−B1−H1	109(3)
C22−B1−C10	107.0(6)		

The solid state structure of complex **5** (Figure 1) adopts a three-legged piano-stool geometry with all bonds and angles in normal ranges, except for the Ru−C_{arene} bond lengths (Table 1).[54] There appears to be no ambiguity regarding the location of PMe_3 and $SiMe_3$ ligands, as attempts to refine the structure with these groups interchanged or disordered were unsuccessful. The boron hydride was located and refined isotropically. The B−H distance (1.22(5) Å) is unexceptional, and there is no indication of any significant interaction with the metal center (D(Ru···HB) = 3.91(5) Å.) As previously found for other η^6-borates, the phenyl is coordinated asymmetrically, with the longest distance between Ru and the *ipso*-C (2.467(6) Å), and the B(1)−C(11) vector nearly eclipsed with that of Ru−P(1). The Ru−C_{ipso} distance is the longest among all η^6-arene complexes of ruthenium reported in the Cambridge Database,[55] except perhaps for one structure containing an η^6-arene indole ligand. The longest Ru−C bond in the latter case is 2.44(4) Å,[56] but the high value of the standard deviation precludes meaningful comparison to the structure of **5**. Longer Ru−C_{arene} contacts have been observed in metal clusters.[55] However, arenes in these clusters are not coordinated η^6 to any single ruthenium; hence the Ru−C distances cannot be compared directly to **5**. The elongation of Ru−C bonds in **5** is especially surprising in light of the formal positive charge on Ru, which is expected to result in tighter binding of electron-rich ligands.

In conclusion, BPh_3 can be utilized as a phosphine sponge in the synthesis of coordinatively and electronically unsaturated organometallic complexes. The mild reactivity of BPh_3 offers distinct advantages over many other phosphine-trapping reagents in some circumstances. However, it is also clear that BPh_3 can undergo secondary reactions with the unsaturated products, although this can be minimized by prompt removal of excess borane. Overall, this method of phosphine removal is a potentially useful addition to the methodologies available to organometallic chemists.

Experimental Section

All manipulations were performed in Schlenk-type glassware on a dual-manifold Schlenk line or in a nitrogen-filled Vacuum Atmospheres glovebox. NMR spectra were obtained at 200 and 500 MHz (for ^1H) on Bruker AF-200 and AM-500

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FT NMR spectrometers, respectively. All NMR spectra were recorded at 303 K unless stated otherwise. Chemical shifts for ^{1}H and ^{13}C spectra are reported relative to tetramethylsilane; for ^{11}B and ^{31}P experiments external samples of $BF_3 \cdot OEt_2$ and 85% H_3PO_4 were used as references. ^{11}B, ^{13}C, and ^{31}P NMR spectra were recorded with broadband ^{1}H decoupling, unless stated otherwise. Infrared spectra were recorded on a Perkin-Elmer model 1430 spectrometer. Elemental analyses were performed by Robertson Microlit Laboratory, Inc. (Madison, NJ).

Hydrocarbon solvents were dried over Na/K alloy−benzophenone. Benzene-d_6 and cyclohexane-d_{12} were dried over Na/K alloy. Trimethylsilane was prepared by the reaction of Me_3SiCl and $LiAlH_4$ in $^nBu_2O$ and purified by trap-to-trap vacuum fractionation. $(PMe_3)_4Ru(H)SiMe_3$[57] and PMe_3[58] were synthesized according to the literature procedures. Triphenylborane (Aldrich) was recrystallized from hexanes/toluene before use.

Reactions of 1 with BPh_3 in C_6D_6 and C_6D_{12}. Aliquots of 4 mL of stock solutions of BPh_3 and $(PMe_3)_4Ru(H)SiMe_3$ in pentane were added to two NMR tubes, and the solvent was stripped in vacuo before addition of 0.57 mL of C_6D_6 or C_6D_{12}. The calculated initial concentrations of **1** and BPh_3 were 0.035 M each. A substantial amount of white solid ($PMe_3{-}BPPh_3$) precipitated within minutes from the cyclohexane tube. ^{1}H NMR spectra measured after 2 h at room temperature revealed the following product distributions: C_6D_{12}: 42% **1**, 16% **2**/**4**, 34% **3**, 6% **5**, and 2% $(PMe_3)_3Ru(H)_3SiMe_3$. C_6D_6: 53% **1**, 18% **2**/**4**, 20% **3**, 9% **5**, and small and poorly resolved signal for $(PMe_3)_3Ru(H)_3SiMe_3$.

Synthesis of $[(PMe_3)_3Ru(H)SiMe_3]_2N_2$ (4). BPh_3 (290 mg, 1.2 mmol) and $(PMe_3)_4Ru(H)SiMe_3$ (479 mg, 1.0 mmol) were suspended in 3 mL of cold (ca. −20 °C) pentane. A color change from yellow to dark red and formation of a white precipitate started within seconds. The mixture was stirred for 5 min warming from −20 °C to room temperature and was kept at −40 °C for 30 min. The dark red mother liquor was filtered through a frit, and the precipitate was washed with additional 2 × 1 mL of pentane. The combined extracts were chilled (ca. −20 °C) and stirred with 200 mg of polymer-supported PPh_3 (cross-linked polystyrene beads, 3 mmol of PPh_3 per 1 g of polymer) for 10 min, decanted, treated again with 200 mg of PPh_3-polystyrene beads, and decanted again. The beads were washed with 2 × 1 mL of cold pentane. The combined extracts were left overnight at −40 °C to form a fine precipitate of **5** and $Ph_3B{-}PMe_3$. The mother liquor was decanted, reduced in volume to 2 mL, and left to crystallize under nitrogen at −40 °C. A color change from dark red to light yellow occurred upon cooling. $[(PMe_3)_3Ru(H)SiMe_3]_2N_2$ formed large colorless plates on the walls and in the bulk of the solution. Exposure of the crystals to solvents at room temperature leads to formation of small amounts of the dark red **3**. The crystals of **4** were mechanically separated from the small amount of microcrystalline **1** on the bottom of the vial. Yield: 267 mg (64%). Anal. Calcd for $C_{24}H_{74}N_2Si_2P_6Ru_2$: C 34.52, H 8.93, N 3.35. Found: 34.64, H 8.76, N 3.06.

$[(PMe_3)_3(H)(SiR_3)Ru]_2N_2$: ^{1}H NMR ($C_6D_{12}$) δ 1.41 (br t, $J_{PH} = 2.2$ Hz, 18H, P*Me*$_3$), 1.32 (d, $J_{PH} = 5.6$ Hz, 9H, P*Me*$_3$), 0.061 (s, 9H, Si*Me*$_3$), −8.1 (dt, 1H, $J_{PH} = 72$ and 32 Hz, Ru*H*); ^{13}C NMR (C_6D_{12}) δ 27.32 (m, *mer*-P*Me*$_3$), 23.49 (virtual t, $J_{PC} = 12.8$ Hz, *fac*-P*Me*$_3$), 12.77 (s, Si*Me*$_3$); ^{31}P NMR (C_6D_{12}) δ −2.82 (d, $J_{PP} = 22.6$ Hz, 2P, *fac*-*P*Me$_3$), −11.61 (t, $J_{PP} = 22.6$ Hz, 1P, *mer*-*P*Me$_3$); IR (powder) $\nu(N_2)$ 2150, 2070 cm^{-1}, ν(RuH) 1820 cm^{-1}; (solution in C_5H_{12}) $\nu(N_2)$ 2155 cm^{-1}, ν(RuH) 1835 cm^{-1}.

Synthesis of $(PMe_3)_3Ru(H)SiMe_3$ (2) and $(PMe_3)_3Ru(CH_2{=}SiMe_2)(H)_2$ (3). Crystalline $[(PMe_3)_3Ru(H)SiMe_3]_2N_2$ was dissolved in C_6D_{12} and thoroughly degassed by four freeze−thaw cycles to furnish a dark red equilibrium mixture of nitrogen-free $(PMe_3)_3Ru(H)SiMe_3$ and $(PMe_3)_3Ru(CH_2{=}SiMe_2)(H)_2$.

$(PMe_3)_3Ru(H)SiMe_3$: ^{1}H NMR (C_6D_{12}) δ 1.42 (t, $J_{HH} = 2.2$ Hz, 18H, P*Me*$_3$), 1.31 (d, $J_{HH} = 6.0$ Hz, 9H, P*Me*$_3$), 0.048 (s, 9H, Si*Me*$_3$), −5.94 (∼dt, 1H, $J_{PH} = 34$ Hz, Ru*H*); ^{13}C NMR (C_6D_{12}) δ 27.32 (m, *mer*-P*Me*$_3$), 22.33 (tm, $J_{PC} = 13.4$ Hz, *fac*-P*Me*$_3$), 12.61 (s, Si*Me*$_3$); ^{29}Si NMR (C_6D_{12}) δ 0.62 (br s, *Si*Me$_3$); ^{31}P NMR (C_6D_{12}) δ 5.58 (d, $J_{PP} = 22.7$ Hz, 2P, *fac*-*P*Me$_3$), −3.31 (t, $J_{PP} = 22.9$ Hz, 1P, *mer*-*P*Me$_3$). There is no indication in the NMR spectra (between +30 and −100 °C in C_7D_{14}) that **2** contains any other NMR active ligands, but weak coordination of hydrocarbon solvent or a C−H bond of a phosphine or silyl methyl group cannot be rigorously excluded.

$(PMe_3)_3Ru(H)_2(SiMe_2{=}CH_2)$: ^{1}H NMR ($C_6D_{12}$) δ 1.37 (d, $J_{PH} = 6.7$ Hz, 9H, P*Me*$_3$), 1.28 (d, $J_{PH} = 6.1$ Hz, 18H, P*Me*$_3$), 0.28 (s, 6H, Si*Me*$_2$), −0.84 (m, 2H, RuC*H*$_2$), −10.6 (m, $J_{PH} =$ 45.6 and 20.5 Hz, 2H, Ru*H*); ^{13}C NMR (C_6D_{12}) δ 29.29 (dt, $J_{PC} = 21.68$ and 2.22 Hz, 1P*Me*$_3$), 24.36 (m, 2P*Me*$_3$), 2.73 (s, Si*Me*$_2$), −20.75 (dt, $J_{PC} = 21.7$ and 6.5 Hz, *C*H$_2$); ^{29}Si NMR (C_6D_{12}) δ −12.93 (∼dt, $J_{PSi} = 4.4$ and 2.2 Hz, *Si*Me$_2$); ^{31}P NMR (C_6D_{12}) δ 0.37 (d, $J_{PP} = 22.5$ Hz, 2P, *P*Me$_3$), −1.41 (t, $J_{PP} =$ 22.5 Hz, 1P, *P*Me$_3$)

Synthesis of $(\eta^6$-Ph-$BPh_2H)Ru(PMe_3)_2(SiMe_3)$ (5). A toluene solution (5 mL) of BPh_3 (72.6 mg, 0.3 mmol) and $(PMe_3)_4Ru(H)SiMe_3$ (47.9 mg, 0.1 mmol) was stirred at room temperature for 4 h. The solvent was evaporated in a vacuum, and $PMe_3{-}BPh_3$ was removed by sublimation at 120 °C/4 h. The Ru-containing residue was recrystallized from THF/toluene at −20 °C to yield 22 mg of colorless crystals (39%). Anal. Calcd for $C_{27}H_{43}B_1P_2Si_1Ru_1$: C 56.94, H 7.6. Found: C 57.08, H 7.83. ^{1}H NMR (C_6D_6): δ 7.90 (d, $J_{HH} = 7.1$ Hz, 4H, *o-Ph*), 7.45 (t, $J_{HH} = 7.4$ Hz, 4H, *m-Ph*), 7.29 (t, $J_{HH} = 7.5$ Hz, 2H, *p-Ph*), 5.88 (d, $J_{HH} = 5.6$ Hz, 2H, η^6-*o-Ph*), 4.96 (t, $J_{HH} =$ 5.9 Hz, 1H, η^6-*p-Ph*), 4.49 (t, $J_{HH} = 5.9$ Hz, 2H, η^6-*m-Ph*), 4.06 (4 lines, $J_{BH} = 82.5$ Hz, 1H, *BH*), 0.86 (m, 18H, P*Me*$_3$), 0.07 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 136.0 (*o-Ph*), 127.3 (*p-Ph*), 123.8 (*m-Ph*), 103.9 (η^6-*o-Ph*), 94.7 (η^6-*p-Ph*), 90.1 (η^6-*m-Ph*), 23.1 (dd, $J_{PC} = 17.0$ and 15.1 Hz, P*Me*$_3$), 10.2 (s, Si*Me*$_3$). ^{11}B NMR (C_6D_6): δ −9.73 (d, $J_{BH} = 82.5$ Hz). ^{11}B{^{1}H} NMR: δ −9.73 (s). ^{31}P{^{1}H} NMR (C_6D_6): δ 4.48. IR (Nujol): ν(BH) 2270 cm^{-1}.

Single-Crystal X-ray Diffraction Analysis. Compound $(PMe_3)_2Ru(SiMe_3)(\eta^6$-PhBPh$_2$H), $RuC_{27}BH_{43}SiP_2$, crystallizes in the monoclinic space group $P2_1/c$ (No. 14) (systematic absences $0k0$: $k =$ odd and $h0l$: $l =$ odd) with $a = 12.3927(2)$ Å, $b = 9.7566(1)$ Å, $c = 24.2436(5)$ Å, $\beta = 99.541(1)°$, $V =$ 2890.76(8) Å^3, $Z = 4$, and $d_{calc} = 1.309$ g/cm^3. X-ray intensity data were collected on an Rigaku R-AXIS IIc area detector employing graphite-monochromated Mo Kα radiation ($\lambda =$ 0.71069 Å) at a temperature of 210 K. Indexing was performed from a series of 1° oscillation images with exposures of 400 s per frame. A hemisphere of data was collected using 4° oscillation angles with exposures of 1500 s per frame and a crystal-to-detector distance of 82 mm. Oscillation images were processed using bioteX,[59] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the teXsan[60] program package for further processing and structure solution on a Silicon Graphics Indigo R4000 computer. A total of 18 351 reflections were measured over the ranges $5.14° \leq 2\theta \leq 50.68°$, $-14 \leq h \leq 14$, $-11 \leq k \leq 11$, $-29 \leq l \leq 28$, yielding 5123 unique, nonzero reflections ($R_{int} = 0.0674$). The intensity data were corrected for Lorentz and polarization effects but not for absorption.

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(57) Procopio, L. J. Ph.D. Thesis, University of Pennsylvania, 1991.

(58) Luetkens, M. L.; Sattelberger, A. P.; Murray, H. H.; Basil, J. D.; Fackler, J. P. *Inorg. Synth.* **1989**, *26*, 7.

(59) *bioteX: A Suite of Programs for the Collection, Reduction and Interpretation of Imaging Plate Data*; Molecular Structure Corporation: 1995.

(60) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation: 1985 and 1992.

The structure was solved by direct methods (SIR92[61]). Refinement was by full-matrix least-squares based on F^2 using SHELXL-93.[62] All reflections were used during refinement (F^2's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + 0.0189P^2 + 14.5619P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. The boron hydride was located and refined isotropically. Refinement converged to $R_1 = 0.0760$ and $wR_2 = 0.1248$ for 4457 reflections for which $F > 4\sigma(F)$ and $R_1 = 0.0929$, $wR_2 = 0.1320$, and GOF = 1.229 for all 5123 unique, nonzero reflections and 461 variables.[63] The maximum Δ/σ in the final cycle of least squares was −0.034, and the two most prominent peaks in the final difference Fourier were +0.511 and −0.680 e/Å^3.

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Supporting Information Available: Details of the X-ray structure determination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[61] SIR92: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giocovazzo, C.; Guagliardi, A.; Polidoro, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[62] Sheldrick, G. M. *SHELXL-93: Program for the Refinement of Crystal Structures*; Göttingen University: Göttingen, Germany, 1993.

[63] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. GOF = $\{\sum w(F_o^2 - F_c^2)^2/(n - p)\}^{1/2}$ where n = the number of reflections and p = the number of parameters refined.