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Ruthenium and Rhodium Complexes of Thioether-Alkynylborates

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Supporting Information

ABSTRACT: The species $((C_6F_5)_2BCH_2SPh)_2$ reacts with PhC \equiv CLi to give the thioether-alkynylborate $(C_6F_5)_2BCH_2SPh(C \equiv CPh)Li(THF)_2$ (1). Subsequent reaction with $(Ph_3P)_3RuHCl$, $(Ph_3P)_3RhCl$, and $[(COD)Rh(\mu-Cl)]_2$ gives $(C_6F_5)_2BCH_2SPh(C \equiv CPh)RuH(PPh_3)_2$ (2), $(C_6F_5)_2BCH_2SPh(C \equiv CPh)Rh(PPh_3)_2$ (4), and $(C_6F_5)_2BCH_2SPh(C \equiv CPh)Rh(COD)$ (5), respectively, dem-



onstrating a bidentate binding mode via the alkynyl and thioether donors of the borate. Subsequent reactions of **2** and **4** with H₂ gave $(C_6F_5)_2BCH_2SPh(CH_2CH_2Ph)RuH(PPh_3)_2$ (3) and $((C_6F_5)_2BCH_2SPh(CHCHPh))Rh(PPh_3)_2$ (6). In the former case, the borate remains bound to the metal via a π -interaction with the thioether-arene ring, while in the latter case, S and alkene binding is observed.

■ INTRODUCTION

Polydentate B-based ligands have garnered much attention over the past four decades. The quintessential example of such ligands are tris(pyrazolyl)borates. Such ligands have been popular for use in coordination chemistry, as a large range of modifications altering the steric and electronic properties of these ligands is conveniently achieved. Such chemistry has been widely explored and extensively reviewed.^{1–21} Other boratebased anionic ligands have garnered attention as well. For example, Peters and co-workers have exploited monodentate, bidentate, and tridentate borate-based ligands of the general forms $[R_3BC_6H_4PR'_2]^-$, $[RB(CH_2PR'_2)_3]^-$, and $[R_2B-(CH_2PR'_2)_2]^-$ (Scheme 1) in a variety of creative develop-

Scheme 1. Examples of Homoleptic and Heteroleptic Chelating Borate Ligands



ments.^{22–45} For example, these authors have developed unique approaches to Fe hydrazine, CO₂, and nitride chemistry,^{42,45,46} Cu aminyl radicals⁴⁴ as well as novel routes to stabilize unusual main-group species.^{23,32} Peters has also employed the heteroleptic bis(phosphino)pyrazolylborate ligand [PhB-(CH₂PtBu₂)₂(pz)] to prepare terminal Fe(IV) imides.⁴⁶

Related borate ligands with sulfur donors have been studied and reviewed by Riodan and co-workers.⁴⁷ In these cases, the coordination chemistry and subsequent reactivity of complexes derived from the related class of ligands polythioether borates, $[RB(CH_2SR')_3]^-$, $[RB(CH_2SR')_2(pz)]^-$, and $[R_2B(CH_2SR')_2]^-$ (Scheme 1), have been explored. On the other hand, borate ligands with alkyl, vinyl, or aryl borate ligands have been derived from reactions of donor-borane species with suitable metal precursors, resulting in abstraction of metal-bound fragments and the formation of chelating donor-borate systems.

In our own work, we have recently prepared the thioetherborane species $((C_6F_5)_2BCH_2SPh)_2$ and shown that it is capable of reacting with alkyne to generate B/S-based heterocycles via frustrated Lewis pair (FLP) addition reactions.⁵³ In this paper, we explore the utility of this species as a precursor to a thioether alkynyl-borate ligand. Herein, we demonstrate that this ligand forms dissymmetric chelating thioether alkynyl-borate complexes of Ru and Rh. Moreover, these products react with H₂ to give alkenyl and alkyl borates while remaining bound to the corresponding metal centers.

RESULTS AND DISCUSSION

A solution of $((C_6F_5)_2BCH_2SPh)_2$ was reacted with lithium phenylacetylide at -35 °C in THF. After the mixture was stirred overnight with gradual warming to 25 °C, workup afforded the white powder 1 in 85% yield (Scheme 2). The ¹¹B{¹H} NMR spectrum of 1 showed a sharp singlet at -18.32ppm, while the ¹⁹F{¹H} NMR spectrum showed multiplets at -134.20, -161.63, and -165.95 ppm. These data are consistent with the formation of a borate anion. ¹H NMR data were consistent with the presence of the thioether fragment as well as an additional arene moiety, presumably from the phenylacetylide. In addition, the NMR data support the inclusion of 2 equivalents of THF in 1. These data were consistent with the formulation of 1 as $(C_6F_5)_2BCH_2SPh(C\equiv$

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 $CPh)Li(THF)_2$. This was subsequently confirmed crystallographically (Figure 1). The Li ion of 1 is coordinated to two



Figure 1. POV-ray depiction of 1: C, black; O, red; S, yellow; F, pink; B, yellow-green; Li, blue-green. Hydrogen atoms are omitted for clarity. One conformation of the disordered thioether and alkynyl fragments is shown.

THF molecules, the thioether sulfur, and (in a π fashion) to the alkynyl unit on the borate. The Li–O distances were found to be 1.878(7) Å, while the Li–S and Li–C distances were 2.530(6), 2.405(12), and 2.368(13) Å; the B–C≡C angle of the alkynyl fragment was found to be 170.8(10)°. The corresponding C–C≡C angle was determined to be 178.1(11)°. These metric parameters should be viewed with

some caution, as 1 sits on a crystallographic 2-fold symmetry axis, resulting in crystallographic disorder of the methylenethioether and the alkyne fragments on the borate. Nonetheless, these data affirm the nature of 1.

Reaction of 1 with $(Ph_3P)_3RuHCl$ at room temperature gave rise to a dark green solution on stirring overnight. Isolation of the product 2 was achieved in 58% yield. The ¹¹B{¹H} and ¹⁹F{¹H} NMR spectra of 2 gave resonances at -14.4 ppm and -132.20, -162.18, and -165.87 ppm, respectively, consistent with the presence of the borate anion. The ³¹P{¹H} NMR spectrum shows a sharp resonance at 64.6 ppm, consistent with a single P environment. A ¹H NMR resonance was observed at -4.38 ppm, which is coupled to two P atoms with a coupling constant of 28 Hz. These data confirm the formulation of 2 as $(C_6F_5)_2BCH_2SPh(C\equiv CPh)RuH(PPh_3)_2$. The precise details of the geometry of 2 were determined unambiguously via X-ray diffraction (Figure 2). The Ru center of 2 adopts a pseudo-



Figure 2. POV-ray depiction of **2**: C, black; O, red; P, orange; S, yellow; F, pink; B, yellow-green; Ru, light blue. Hydrogen atoms, except for Ru–H, are omitted for clarity.

trigonal-bipyramidal geometry, with the hydride and thioether linkage of the borate fragment occupying the axial positions. The corresponding Ru-H and Ru-S distances were determined to be 1.61(1) and 2.5013(9) Å, respectively. Two phosphines complete the coordination sphere with Ru-P distances of 2.248(1) and 2.294(1) Å. The alkynyl fragment of the borate chelates to the metal in one of the equatorial plane positions with Ru-C distances of 2.107(3) and 2.151(3) Å with a C \equiv C bond length of 1.262(5) Å. The C \equiv C bond is elongated compared to free alkynes (1.190 Å) and is similar to that seen in the cation $[Ru(acac)_2(o-PhC \equiv C(C_6H_4)NMe_2)]^+$ (1.224(6) Å) and $[\operatorname{Ru}(\operatorname{acac})_2(\operatorname{o-PhC} \equiv C(C_6H_4)\operatorname{NMe}_2)]^+$ $(1.240(6) \text{ Å})^{.54}$ The corresponding C-C=C angle in 2 is 148.6(3)°, while the B-C \equiv C angle is 159.0(3)°. The former "bend-back" angle of 31° is slightly larger than that seen for the terminal phenyl ring on the alkyne of the Ru amine-alkyne species cited above $(25-26^{\circ})$.

The NMR data for 2 infer equivalent P atoms, while the structural data affirm their inequivalence as a result of the chirality at S. This suggests a fluxional process leads to equilibration of the two P sites. This could occur via alkyne dissociation or S inversion. Efforts to probe this fluxional process by variable-temperature ³¹P NMR spectroscopy showed broadening on cooling to -60 °C and the resolution of two broad resonances at 76.4 and 56.6 ppm at -80 °C. As a limiting

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spectrum is not observed, the energetics of this fluxional process could not be determined.

Exposure of **2** to 4 atm of H_2 was performed at 25 °C and the mixture stirred overnight. The solution changed color from dark green to pale yellow, allowing the subsequent isolation of pale yellow crystals of 3 in 96% yield. The presence of the borate anion was consistent with the ¹¹B{¹H} resonance at -11.5 ppm and the ¹⁹F{¹H} multiplets at -131.86, -163.00, and -165.68 ppm. ¹H NMR data reveal the presence of new methylene resonances at 3.05 and 2.28 ppm, while the corresponding ¹³C{¹H} resonances were observed at 34.7 and 29.4 ppm. In addition, the triplet resonance at 9.33 ppm in the ¹H NMR spectrum as well as the ³¹P{¹H} signal at 52.6 ppm were consistent with the presence of RuH and two phosphine ligands. These data suggest the formulation of 3 as a combination of the saturated borate ligand and a $RuH(PPh_3)_2$ fragment. The observation of resonances at 5.08, 4.59, and 4.19 ppm are consistent with the presence of a η^6 -C₆H₅ fragment. Xray crystallography was used to confirm the formulation of 3 as $(C_6F_5)_2BCH_2SPh(CH_2CH_2Ph)RuH(PPh_3)_2$ (Figure 3). These



Figure 3. POV-ray depiction of 3: C, black; O, red; P, orange; S, yellow; F, pink; B, yellow-green; Ru, light blue. Hydrogen atoms are omitted for clarity.

data confirm the reduction of the alkyne fragment to the corresponding alkyl group. The Ru adopts a "piano-stool" type geometry with an η^6 interaction with the S-bound arene ring of the thioether-alkyl borate ligand. The Ru–C distances range from 2.264(4) to 2.323(4) Å. Two phosphines are bound to Ru at a distance of 2.308(1) and 2.313(1) Å. The third leg of the piano stool is presumably the hydride; however, this was not located in the electron density map. The geometry about B is, as expected, pseudo-tetrahedral and the B center is positioned 5.723 Å from Ru.

The thioether-alkynylborate 1 also reacts with $(Ph_3P)_3RhCl$ in THF at room temperature, resulting in a dark orange solution which on workup affords the yellow solid 4 in 94% yield. The borate anion in the complex 4 is evident from the ¹¹B{¹H} resonance at -15.27 ppm and the corresponding ¹⁹F{¹H} signals at -131.67, -161.80, and -165.46 ppm. At room temperature the ³¹P{¹H} NMR spectrum shows a broad resonance at 35.3 ppm with Rh–P coupling of 153 Hz. On cooling to -25 °C, the ³¹P{¹H} NMR spectrum broadens and splits into two doublets of doublets located at 42.4 and 29.2 ppm with P–P and Rh–P coupling constants of 41, 167, and 162 Hz (Figure 4). These data together with the ¹H NMR spectrum are consistent with the formulation of 4 as $(C_6F_5)_2BCH_2SPh(C\equiv CPh)Rh(PPh_3)_2$. This was confirmed



Figure 4. Variable-temperature ³¹P{¹H} NMR spectra of 4.

crystallographically (Figure 5). The pseudo-square-planar Rh center is coordinated to S and P at distances of 2.3918(7),



Figure 5. POV-ray depiction of 4: C, black; O, red; P, orange; S, yellow; F, pink; B, yellow-green; Rh, maroon. Hydrogen atoms are omitted for clarity.

2.2701(7), and 2.3133(7) Å. The alkynyl fragment is oriented approximately perpendicular to the coordination plane of Rh with Rh-C distances of 2.227(3) and 2.284(3) Å and a C-C distance of 1.226(4) Å. The C–C \equiv C angle for the PhC \equiv C fragment is $160.4(3)^\circ$, while the B-C=C angle was found to be $161.6(3)^{\circ}$. The corresponding bend-back angles are less than those seen in 2, consistent with a more electron-rich Rh center. A variable-temperature NMR study showed the coalescence temperature to be 44 °C, and analysis of the spectra revealed the activation energy for this fluxional process to be 13.3(1) kcal/mol. These data suggest that facile exchange of the phosphines occurs via dissociation of the alkyne, followed by rotation and recoordination of the alkyne. An alternative explanation could involve inversion at S. However, this notion is deemed less likely, as the analogous alkene-borate complex $(C_6F_5)_2BCH_2SPh(CHCHPh))Rh(PPh_3)_2$ (6) (vide infra) is not fluxional.

In a similar fashion, reaction of 1 with $[(COD)Rh(\mu-Cl)]_2$ affords the species $(C_6F_5)_2BCH_2SPh(C\equiv CPh)Rh(COD)$ (5) in 85% yield. The presence of the borate anion was consistent with the¹¹B{¹H} resonance at -16.41 ppm and the ¹⁹F{¹H} resonances at -132.27, -159.68, and -164.25 ppm. The ¹H NMR spectrum at room temperature shows a broad singlet at 4.11 ppm corresponding to the olefinic COD protons, a broad singlet at 1.57 ppm and a multiplet at 1.26 ppm arising from the methylene COD protons. Upon cooling to -15 °C, each of the two broad singlets split into two singlets at 4.19, 3.92, 1.64, and 1.45 ppm. These data suggest a fluxional process similar to that in **4**. The structure of **5** was confirmed crystallographically (Figure 6). The pseudo-square-planar coordination geometry



Figure 6. POV-ray depiction of 5: C, black; O, red; S, yellow; F, pink; B, yellow-green; Rh, maroon. Hydrogen atoms are omitted for clarity.

about the Rh cation is comprised of the two olefinic bonds of COD and the alkyne and S of 1. The Rh–C distances to the COD ligand range from 2.148(2) to 2.183(2) Å, while the Rh–C distances to the alkyne fragment are 2.269(2) and 2.306(2) Å. The corresponding C–C bond distance is 1.226(3) Å, while the C \equiv C–C and C \equiv C–B bend-back angles are 164.8(2) and 168.9(2)°, respectively. The Rh–S distance is 2.3833(6) Å, slightly shorter than that seen in 4, consistent with the cationic nature of **5**.

While reactions of 4 and 5 with H_2 initially gave a complex mixture of uncharacterized products ultimately leading to the deposition of Rh black, reaction of 4 and Me₂NH·BH₃ proceeds at room temperature over 24 h to give dark orange crystals of 6 in 69% yield. The ${}^{11}B{}^{1}H{}$ signal at -13.5 ppm and the five ${}^{19}F{}^{1}H$ NMR signals at -131.45, -131.72, -163.63, -163.73, and -166.98 ppm are indicative of the presence of a borate anion with inequivalent C_6F_5 rings. The ³¹P{¹H} NMR spectrum of **6** shows two resonances at 48.1 and 24.9 ppm which exhibit Rh-P couplings of 161 and 152 Hz, respectively, and a P-P coupling of 36 Hz. This is consistent with inequivalent P environments. ¹H NMR data for 6 showed the expected resonances in addition to resonances at 6.15 and 4.83 ppm. These signals in addition to the ${}^{13}C{}^{1}H{}$ signals at 108.4 and 91.4 ppm were consistent with the presence of an olefinic fragment. These data lead to the formulation of 6 as $(C_6F_5)_2BCH_2SPh(CHCHPh))Rh(PPh_3)_2$.

An X-ray structure of **6** confirmed a geometry similar to that seen in **4**, with the alkyne fragment reduced to the corresponding alkene (Figure 7). It is noted that this reduction led to a cis substitution of the alkene. The Rh–S, Rh–P, and Rh–C distances in **6** were found to be 2.3648(5), 2.2737(6), 2.3700(6), 2.205(2), and 2.261(2) Å, respectively. The Rh–S and Rh–C distances are similar to those reported seen in the



Figure 7. POV-ray depiction of **6**: C, black; O, red; P, orange; S, yellow; F, pink; B, yellow-green; Rh, maroon. Hydrogen atoms are omitted for clarity.

chelated olefin-thioether complex $[(C_5H_7)_2SRh-(Ph_2PCH_2)_2CH_2]^+$ (Rh–S = 2.385(1) Å, Rh–C = 2.215(4), 2.230(4) Å) recently reported by Weller et al.⁵⁵ In addition, the Rh–S and Rh–C distances are somewhat shorter in **6** than in **4**, suggesting stronger binding of the thioether-alkenylborate ligand.

CONCLUSIONS

In this paper, we have demonstrated that the thioether alkynyl borate 1 serves as a facile precursor to mixed donor borate complexes of Ru and Rh. Moreover, these species are easily reduced to convert the alkynyl fragment to either the corresponding alkene or alkane moieties. Despite such reductions of the alkynylborates, these anions remain bound to the transition-metal center. We are continuing to study transition-metal chemistry involving main-group-based ligand systems.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an atmosphere of dry, O2-free N2 employing an Innovative Technology glovebox and a Schlenk vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentane, hexanes, toluene, THF, CH₂Cl₂) and stored over molecular sieves. Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks, and degassed accordingly (CD₂Cl₂, C₆D₆, Tol-d₈). ¹H, ¹³C, ¹¹B, ¹⁹F, and ³¹P NMR spectra were recorded at 25 °C on Varian 300 and 400 MHz and Bruker 400 MHz spectrometers. Chemical shifts are given relative to SiMe4 and referenced to the residual solvent signal $(^{1}H, ^{13}C)$ or relative to an external standard $(^{31}P, 85\% H_{3}PO_{4}; ^{11}B,$ (Et₂O)BF₃; ¹⁹F, CFCl₃). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments (HSQC). In the case of the ¹⁹F NMR data for the fluoroarylboron derivatives, the coupling constants given are only the apparent values as these spectra exhibit second-order effects. Chemical shifts are reported in ppm, and coupling constants as scalar values in Hz. Combustion analyses were performed in-house, employing a Perkin-Elmer CHN Analyzer.

Synthesis of $(C_6F_5)_2BCH_2SPh(C \equiv CPh)Li(THF)_2$ (1). A solution of lithium phenylacetylide (0.032 g, 0.296 mmol) in 3 mL of THF was added to a solution of $(PhSCH_2B(C_6F_5)_2)_2$ (0.137 g, 0.146 mmol) in 3 mL of THF at -35 °C, and the solution was left stirring overnight before the solvent was removed in vacuo and the white solid was

washed with pentane, yielding a white powder (0.178 g, 85%). ¹H NMR (400 MHz, C₆D₆): δ 7.29 (m, 2H, C₆H₅), 7.23 (t, ⁴J_{H-H} = 2 Hz, 1H, C₆H₅), 7.21 (t, ⁴J_{H-H} = 1 Hz, 1H, C₆H₅), 6.99 (t, ³J_{H-H} = 8 Hz, 2H, C₆H₅), 6.91 (m, 3H, C₆H₅), 6.88 (t, ⁴J_{H-H} = 2 Hz, 1H, C₆H₅), 3.33 (s, 2H, BCH₂S), 3.21 (m, 8H, THF-CH₂(2,5)), 1.13 (m, 8H, THF-CH₂(3,4)). ¹⁹F{¹H} NMR (178 MHz, C₆D₆): δ -134.20 (dd, ⁴J_{F-F} = 7 Hz, ³J_{F-F} = 18 Hz, 4F, *o*-C₆F₅), -161.63 (t, ³J_{F-F} = 21 Hz, 2F, *p*-C₆F₅), -165.95 (dt, ⁴J_{F-F} = 7 Hz, ³J_{F-F} = 22 Hz, 4F, *m*-C₆F₅). ¹³C{¹H} NMR (101 MHz, C₆D₆, partial): δ 131.6 (C₆H₅), 128.9 (C₆H₅), 128.3 (C₆H₅), 127.3 (C₆H₅), 127.0 (C₆H₅), 126.1 (C₆H₅), 125.1 (C₆H₅), 68.3 (THF-CH₂(2,5)), 27.8 (BCH₂S), 25.05 (THF-CH₂(3,4)). ¹¹B{¹H} NMR (96 MHz, C₆D₆): δ -18.32 (sharp s). IR (KBr) ν : 2155 cm⁻¹ (C≡C). Anal. Calcd for C₃₅H₂₈BF₁₀LiO₂S: C, 58.35; H, 3.92. Found: C, 58.08; H, 4.02.

Synthesis of $(C_6F_5)_2BCH_2SPh(C \equiv CPh)RuH(PPh_3)_2$ (2). A solution of 1 (0.050 g, 0.069 mmol) in 3 mL of THF was added to a suspension of (PPh₃)₃RuHCl (0.064 g, 0.069 mmol) in 5 mL of THF at room temperature, and the mixture was stirred overnight. The solvent was then removed in vacuo and the product extracted into 10 mL of CH₂Cl₂ and filtered over Celite, resulting in a dark green solution. The filtrate was concentrated to 1 mL, and pentane was added, resulting in a green-brown solid that was then collected on a frit and dried under vacuum. The pentane layer was put in the freezer to collect more of the product (0.048 g, 58%). X-ray-quality crystals were grown from benzene/pentane at 25 °C. ¹H NMR (400 MHz, CD_2Cl_2): δ 7.72 (d, ${}^{3}J_{H-H}$ = 7 Hz, 2H, C_6H_5), 7.40 (m, 3H, C_6H_5), 7.28 (t, ${}^{3}J_{H-H} = 7$ Hz, 6H, PPh₃), 7.16 (t, ${}^{3}J_{H-H} = 7$ Hz, 1H, C₆H₅), 7.01 (t, ${}^{3}J_{H-H} = 7$ Hz, 12H, PPh₃), 6.82 (m, 14H, C₆H₅ + PPh₃), 6.12 $(d_{1}^{3}J_{H-H} = 8 \text{ Hz}, 2H, C_{6}H_{5}), 3.34 (s, 2H, BCH_{2}S), -4.38 (t, {}^{2}J_{H-P} =$ 28 Hz, 1H, Ru-H). ¹⁹F{¹H} NMR (178 MHz, CD_2Cl_2): δ -132.20 (dd, ${}^{4}J_{F-F} = 9$ Hz, ${}^{3}J_{F-F} = 24$ Hz, 4F, $o - C_{6}F_{5}$), -162.18 (t, ${}^{3}J_{F-F} = 21$ Hz, 2F, p-C₆F₅), -165.87 (dt, ${}^{4}J_{F-F} = 8$ Hz, ${}^{3}J_{F-F} = 21$ Hz, 4F, m- C_6F_5). ³¹P{¹H} NMR (161 MHz, CD_2Cl_2): δ 64.6 (s, PPh₃). ³¹P{¹H} NMR (161 MHz, CD_2Cl_2 , -80 °C): $\overline{\delta}$ 76.4 (br s), 56.6 (br s). ¹³C{¹H} NMR partial (101 MHz, CD₂Cl₂): δ 149.1 (m, Ar-F), 146.8 (m, Ar-F), 137.4 (m, Ar-F), 135.4 (C_6H_5), 134.9 (C_6H_5), 135.3 (d, ${}^{1}J_{C-P} = 43 \text{ Hz}, C_{ipso'} \text{ PPh}_{3}$, 133.2 (t, ${}^{2}J_{C-P} = 5 \text{ Hz}, o-C, \text{ PPh}_{3}$), 131.9 (C₆H₅), 131.3 (C₆H₅), 129.7 (p-C, PPh₃), 128.2 (C₆H₅), 127.9 (t, ${}^{2}J_{C-P} = 5$ Hz, m-C, PPh₃), 127.6 (C₆H₅), 34.07 (BCH₂S). {}^{11}B{}^{1}H{} NMR (96 MHz, CD₂Cl₂): δ -14.4 (sharp s). IR (KBr) ν: 2088 cm⁻¹ $(C \equiv C)$. Anal. Calcd for $C_{63}H_{43}BF_{10}P_2RuS$: C, 63.27; H, 3.62. Found: C, 63.34; H, 4.08.

Synthesis of $(C_6F_5)_2BCH_2SPh(CH_2CH_2Ph)RuH(PPh_3)_2$ (3). A flask containing a solution of 2 (0.050 g, 0.042 mmol) in 5 mL of C_6H_6 was cooled to 77 K, evacuated, and filled with 1 atm of H₂ and sealed. Upon warming to 298 K, a pressure of ca. 4 atm was generated. The reaction mixture was stirred at 25 °C overnight. A color change from dark green to pale yellow was observed as pale yellow crystals precipitated on standing overnight. The crystals were collected by filtration, washed with pentane, and dried under vacuum (0.048 g, 96%). X-ray-quality crystals were grown from CH₂Cl₂/pentane at 25 °C. ¹H NMR (400 MHz, C_6D_6): δ 7.57 (d, ³ J_{H-H} = 7 Hz, 2H, C_6H_5), 7.20 (t, ${}^{3}J_{H-H}$ = 7 Hz, 2H, C₆H₅), 7.13–7.18 (m, 15H, PPh₃), 7.09 (m, 1H, C_6H_5), 6.88 (m, 15H, PPh₃), 5.08 (t, ${}^{3}J_{H-H} = 6$ Hz, 1H, $\eta^{6}-C_6H_5$), 4.59 (d, ${}^{3}J_{H-H} = 6$ Hz, 2H, η^{6} -C₆H₅), 4.19 (t, ${}^{3}J_{H-H} = 6$ Hz, 2H, η^{6} -C₆H₅), 3.35 (s, 2H, BCH₂S), 3.05 (m, 2H, CH₂CH₂), 2.28 (m, 2H, CH_2CH_2 , -9.33 (t, ${}^2J_{H-P}$ = 28 Hz, 1H, Ru-H). ${}^{-19}F{}^{1}H$ NMR (178) MHz, C_6D_6): $\delta - 131.86$ (dd, ${}^4J_{F-F} = 9$ Hz, ${}^3J_{F-F} = 23$ Hz, 4F, $o - C_6F_5$), -163.00 (t, ${}^{3}J_{F-F} = 21$ Hz, 2F, $p-C_{6}F_{5}$), -165.68 (dt, ${}^{4}J_{F-F} = 7$ Hz, ${}^{3}J_{F-F} = 18$ Hz, 4F, $m-C_{6}F_{5}$). ${}^{31}P{}^{1}H$ NMR (161 MHz, $C_{6}D_{6}$): δ 52.6 (s, PPh₃). ${}^{13}C{}^{1}H$ NMR partial (101 MHz, CD₂Cl₂): δ 149.2 (m, Ar-F), 147.8 (m, Ar-F), 133.9 (PPh₃), 132.4 (C₆H₅), 132.3 (C₆H₅), 130.5 (PPh₃), 128.6 (C_6H_5), 128.4 (PPh₃), 128.2 (C_6H_5), 98.9 (η^6 - C_6H_5), 90.8 $(\eta^6 - C_6H_5)$, 87.8 $(\eta^6 - C_6H_5)$, 34.7 (CH_2CH_2) , 29.4 (BCH_2S) , (CH_2CH_2) . ¹¹B $\{^{1}H\}$ NMR (96 MHz, C_6D_6): δ –11.5 (sharp s). Anal. Calcd for C₆₃H₄₇BF₁₀P₂RuS: C, 63.06; H, 3.95. Found: C,62.62; H,4.08

Synthesis of $(C_6F_5)_2BCH_2SPh(C \equiv CPh)Rh(PPh_3)_2$ (4). A solution of 1 (0.075 g, 0.103 mmol) in 3 mL of THF was added to a stirred

suspension of (PPh₃)₃RhCl (0.095 g, 0.103 mmol) in 5 mL of THF at room temperature, and the mixture was stirred overnight. A dark orange solution was obtained. The solvent was then removed in vacuo, and the product was extracted into 10 mL of C₆H₆ and filtered over Celite, resulting in an orange solution. The filtrate was concentrated to 1 mL, and pentane was added, resulting in a yellow solid which was then collected on a frit and dried under vacuum (0.116 g, 94%). X-rayquality crystals were grown from benzene/pentane at 25 °C. ¹H NMR (400 MHz, C_6D_6): δ 7.62 (d, ${}^{3}J_{H-H} = 7$ Hz, 2H, C_6H_5), 7.52 (br t, ${}^{3}J_{H-H} = 7$ Hz, 1H, C_6H_5), 7.29 (t, ${}^{3}J_{H-H} = 8$ Hz, 12H, PPh₃), 6.98 (m, 4H, C_6H_5), 6.86–6.78 (overlapping t, ${}^{3}J_{H-H} = 7$ Hz, 18H, PPh₃), 6.69 (t, ${}^{3}J_{H-H} = 7$ Hz, 1H, C_6H_5), 6.54 (t, ${}^{3}J_{H-H} = 7$ Hz, 2H, C_6H_5), 3.37 (br s, 2H, BCH₂S). ¹⁹F{¹H} NMR (178 MHz, C₆D₆): δ -131.67 (d, (b) 3) 2H, BCH_{2}). (c) (1) Mink (1/8 Min2, $C_{6}D_{6}$). (c) (3) $^{3}J_{F-F} = 23$ Hz, 4F, $o-C_{6}F_{5}$), -161.80 (t, $^{3}J_{F-F} = 21$ Hz, 2F, $p-C_{6}F_{5}$), -165.46 (dt, $^{4}J_{F-F} = 9$ Hz, $^{3}J_{F-F} = 21$ Hz, 4F, $m-C_{6}F_{5}$). $^{31}P\{^{1}H\}$ NMR (161 MHz, $C_{6}D_{6}$): δ 35.3 (broad d, $^{1}J_{P-Rh} = 153$ Hz). $^{31}P\{^{1}H\}$ NMR (161 MHz, Tol- d_{8} , -25 °C): δ 42.4 (dd, $^{1}J_{P-Rh} = 167$ Hz, $^{2}J_{P-P} = 41$ Hz, PPh_{3}), $^{23}P\{^{1}H\}$ NMR (161 MHz, Tol- d_{8} , -450 °C): δ 42.4 (dd, $^{1}J_{P-Rh} = 167$ Hz, $^{2}J_{P-P} = 41$ Hz, PPh_{3}). $^{31}P\{^{1}H\}$ NMR (161 MHz, Tol- d_{87} +50 °C): δ 35.1 (d, ${}^{1}J_{P-Rh}$ = 164 Hz, PPh₃).¹³C{¹H} NMR partial (101 MHz, C₆D₆): δ 149.4 (m, Ar-F), 147.0 (m, Ar-F), 138.6, 137.9 (m, Ar-F), 134.7 (d, ${}^{3}J_{C-P} = 11$ Hz, PPh₃), 133.7 (C_6H_5), 133.3 (C_6H_5), 133.08 (C_6H_5), 131.9 (d, ${}^{3}J_{C-P}$ = 9 Hz, PPh₃), 131.1 (PPh₃), 129.4 (PPh₃), 128.2 (C₆H₅), 127.0 (C₆H₅), 34.1 (BCH₂S). ¹¹B{¹H} NMR (96 MHz, C₆D₆): δ -15.27 (sharp s). IR (KBr) ν : 1961 cm⁻¹ (C=C). Anal. Calcd for C₆₃H₄₂BF₁₀P₂RhS: C, 63.23; H, 3.54. Found: C, 63.17; H, 3.73.

Synthesis of (C₆F₅)₂BCH₂SPh(C=CPh)Rh(COD) (5). A solution of 1 (0.050 g, 0.070 mmol) in 3 mL of THF was added to a solution of [RhCl(COD)]₂ (0.017 g, 0.035 mmol) in 5 mL of THF at room temperature and the mixture was stirred overnight. A pale orange solution was obtained. The solvent was then removed in vacuo and the product extracted into 6 mL of C₆H₆ and filtered over Celite, resulting in a pale orange solution. The filtrate was concentrated to 1 mL, and pentane was added, resulting in a yellow solid ,which was then collected on a frit and dried under vacuum (0.046 g, 85%). X-rayquality crystals were grown from benzene/pentane at 25 °C. ¹H NMR (400 MHz, C_6D_6): δ 7.56 (m, 2H, C_6H_5), 7.49 (m, 2H, C_6H_5), 7.00 (m, 3H, C₆H₅), 6.95 (m, 3H, C₆H₅), 4.11 (br s, 4H, COD-CH), 3.11 (s, 2H, BCH₂S), 1.57 (br s, 4H, COD-CH₂), 1.26 (m, 4H, COD-CH₂). ¹H NMR partial (400 MHz, Tol- d_8 , -15 °C): δ 4.19 (br s, 2H, COD-CH), 3.92 (br s, 2H, COD-CH), 3.10 (s, 2H, BCH₂S), 1.64 (br s, 2H, COD-CH₂), 1.45 (br s, 2H, COD-CH₂), 1.22 (br s, 4H, COD-CH₂). ¹⁹F{¹H} NMR (178 MHz, C₆D₆): δ –132.27 (d, ³J_{F-F} = 22 Hz, 4F, $o-C_6F_5$, -159.68 (t, ${}^{3}J_{F-F}$ = 21 Hz, 2F, $p-C_6F_5$), -164.25 (dt, ${}^{4}J_{F-F}$ = 9 Hz, ${}^{3}J_{F-F}$ = 21 Hz, 4F, m-C₆F₅). ${}^{13}C{}^{1}H{}$ NMR partial (101 MHz, C₆D₆): δ 150.1 (m, Ar-F), 147.8 (m, Ar-F), 139.3, 137.7 (m, Ar-F), 133.3 (C₆H₅), 131.9 (C₆H₅), 129.9 (C₆H₅), 129.7 (C₆H₅), 129.3 (C₆H₅), 126.7 (C₆H₅), 93.6 (br s, COD-CH), 88.4 (br s, COD-CH), 34.8 (BCH₂S), 31.2 (br s, COD-CH₂), 29.9 (br s, COD-CH₂). ¹¹B{¹H} NMR (96 MHz, C_6D_6): δ –16.41 (sharp s). Anal. Calcd. for C35H24BF10RhS·Et2O: C, 54.82; H, 4.01. Found: C, 54.51; H, 3.69.

Synthesis of (C₆F₅)₂BCH₂SPh(CHCHPh)Rh(PPh₃)₂ (6). To a solution of 4 (0.045 g, 0.038 mmol) in 3 mL of THF was added Me₂NH·BH₃ (0.0023 g, 0.038 mmol), and the mixture was stirred at room temperature for 24 h before the solvent was removed in vacuo; the resulting residue was dissolved in 3 mL of Et₂O and was left overnight at 25 °C, upon which dark orange crystals formed. The solvent was decanted, and the crystals were dried under vacuum (0.031 g, 69%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.85 (d, ³J_{H-H} = 6 Hz, 2H, C₆H₅), 7.44 (m, 9H, PPh₃), 7.35 (t, ³J_{H-H} = 7 Hz, 3H, C₆H₅), 7.16 (m, 9H, PPh₃), 6.94 (m, 12H, PPh₃), 6.77 (t, ³J_{H-H} = 11 Hz, 1H, Cf=CH), 5.21 (d, ³J_{H-H} = 7 Hz, 2H, C₆H₅), 4.83 (d, ²J_{H-Rh} = 11 Hz, 1H, CH=CH), 3.21 (br s, 1H, BCH₂S), 2.75 (d, ²J_{H-Rh} = 11 Hz, 1H, BCH₂S). ¹⁹F^{{1}H} NMR (178 MHz, CD₂Cl₂): δ -131.45 (d, ³J_{F-F} = 21 Hz, 1F, *p*-C₆F₅), -163.73 (t, ³J_{F-F} = 21 Hz, 1F, *p*-C₆F₅), -163.73 (t, ³J_{F-F} = 21 Hz, 1F, *p*-C₆F₅), -163.73 (t, ³J_{F-F} = 161 Hz, ²J_{P-P} = 36 Hz, PPh₃), 24.9 (dd, ¹J_{P-Rh} = 152 Hz, ²J_{P-P} = 36 Hz, PPh₃). ¹³C^{{1}H} NMR partial (101 MHz, CD₂Cl₂): δ 135.6 (d,

 ${}^{3}J_{C-P} = 12 \text{ Hz}, \text{PPh}_{3}$), 134.7 (d, ${}^{3}J_{C-P} = 12 \text{ Hz}, \text{PPh}_{3}$), 133.2 (d, ${}^{2}J_{C-P} = 42 \text{ Hz}, \text{PPh}_{3}$), 132.0 (PPh₃), 131.9 (d, ${}^{2}J_{C-P} = 38 \text{ Hz}, \text{PPh}_{3}$), 131.0 (PPh₃), 130.6 ($C_{6}\text{H}_{5}$), 129.9 ($C_{6}\text{H}_{5}$), 128.4 (PPh₃), 128.3 (PPh₃), 128.1 (PPh₃), 128.0 (PPh₃), 127.7 ($C_{6}\text{H}_{5}$), 127.6 ($C_{6}\text{H}_{5}$), 127.2 ($C_{6}\text{H}_{5}$), 108.4 (CH=CH), 91.4 (CH=CH), 34.7 (BCH₂S). ¹¹B{¹H} NMR (96 MHz, CD₂Cl₂): δ -13.5 (sharp s). Anal. Calcd for $C_{63}\text{H}_{44}\text{BF}_{10}\text{P}_2\text{RhS}\cdot\text{C}_5\text{H}_{12}$: C, 64.26; H, 4.44. Found: C, 63.84; H, 4.58.

X-ray Data Collection, Reduction, Solution, and Refinement. Single crystals were coated in Paratone-N oil in the glove-box, mounted on a MiTegen Micromount and placed under an N₂ stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(\pm 2) K for all crystals. Data reduction was performed using the SAINT software package, and an absorption correction was applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least squares on F^2 using XL as implemented in the SHELXTL suite of programs.^{56–58} All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

ASSOCIATED CONTENT

Supporting Information

CIF files and a table giving crystallographic data for the structures given in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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