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Reactions of Ru-alkynyl Complexes with Electrophilic Boranes

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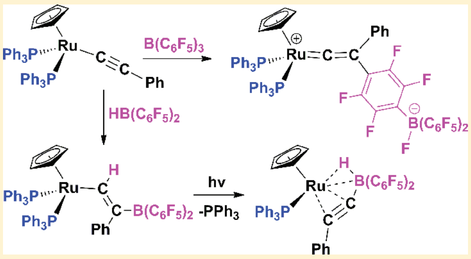
S Supporting Information

ABSTRACT: The species $CpRu(PPh_3)_2(C{\equiv}CPh)$ (**1**) reacts with $HB(C_6F_5)_2$ to effect the hydroboration of the metal-bound alkyne, giving the orange species $CpRu(PPh_3)_2CH{=}C(Ph)(B(C_6F_5)_2)$ (**2**) in 95% isolated yield. Subsequent photolysis of this species results in the rearrangement of the vinyl group to give the species $CpRu(PPh_3)[PhC{\equiv}C(B(H)(C_6F_5)_2)]$ (**3**) in 87% yield. The species exhibits a side-on alkyne donation to Ru as well as a bridging BH fragment. Intermediates in this conversion are discussed in relation to known species, and support for a transient zwitterionic intermediate is offered by the isolation of $CpRu(PPh_3)_2(C{=}CPh(C_6F_4)BF(C_6F_5)_2)$ (**4**) from the reaction of $CpRu(PPh_3)_2(C{\equiv}CPh)$ with $B(C_6F_5)_3$. The compounds **2**−**4** are crystallographically characterized.



INTRODUCTION

One of the important tools in the synthetic toolbox of the organic chemist is the activation of alkynes.[1] For example, transition-metal species can be employed to metalate terminal alkynes to give useful synthons, while transition-metal catalysts provide avenues to effect C−C coupling reactions, such as oxidative dimerizations,[2] alkyne−arene coupling reactions,[3] and alkynylations of aldehydes.[4] On the other hand, main group reagents, such as boranes, can be employed to derivatize alkynes to yield synthons, such as vinyl boranes, alkynyl boranes, or alkynyl borates.[5−7] Alternatively, boranes can be used to effect hydrostannation[8] or hydrogermylation[9] of alkynes, intramolecular additions of silyl enol ethers to alkynes,[10] and cyclization of dialkynylsilanes employing $B(C_6F_5)_3$.[11] Yamaguchi and co-workers[12] have demonstrated that intramolecular addition of phosphine and boron to alkyne fragments provides materials of interest for their electronic properties. In a related sense, we have previously shown that combinations of sterically demanding donors and electrophilic boranes, so-called “frustrated Lewis pairs”, react with terminal alkynes via two pathways.[13] Where the donor is Brønsted basic, such as tBu_3P, the reaction with $B(C_6F_5)_3$ and $PhC{\equiv}CH$ results in deprotonation of the alkyne, yielding the salt $[tBu_3PH][PhC{\equiv}CB(C_6F_5)_3]$ (Scheme 1). Conversely, using more nucleophilic donors, including phosphines, sulphides, amines, pyridines, and pyrroles, has been shown to add to the alkyne in the presence of boranes to give zwitterionic alkene derivatives of the form $(Donor)C(Ph){=}C(H)B(C_6F_5)_3$ (Scheme 1).[14,15] More recently, the research groups of Berke[16,17] and Erker[18−21] have discovered that both terminal and internal alkynes react with $B(C_6F_5)_3$ exclusively via 1,1-carboboration, affording novel, electrophilic vinyl borane products of the from $RR'C{=}C(C_6F_5)B(C_6F_5)_2$ (Scheme 1).

In the case of the chemistry of alkynes and transition-metal reagents, metal alkyne complexes are well known to undergo the reversible interconversion of terminal alkyne and vinylidene species, a transformation that is important in a number of metal-mediated transformations.[22−31] In such conversions, the migrations of carbon-,[32−34] silyl-,[35−43] stannyl-,[44,45] sulfenyl-,[46] and iodo-substituents[47] have been reported and vinylidene complexes, such as $[CpRu\{C{=}C(Ph)Ar\}\text{-}(dppe)][B(C_6F_5)_4]$, have been reported to proceed via electrophilic 1,2-migration.[48] This observation suggests that boron-based electrophiles might also display interesting reactivity with metal alkyne complexes. Indeed, in the case of early transition-metal acetylide and metallocumulene complexes, the groups of Rosenthal[49−54] and Erker[55−61] have demonstrated a rich and unique reactivity (Scheme 2). With these precedents, we were prompted to explore reactions of the coordinatively saturated metal acetylide complex $CpRu(PPh_3)_2(C{\equiv}CPh)$ (**1**) with electrophilic boranes. Herein, we demonstrate the synthesis of a Ru-vinyl-borane and subsequent conversion to a borohydride-alkyne complex. In addition, we also isolate an unusual Ru-vinylidene-borate zwitterion.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an atmosphere of dry, O_2-free N_2 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 (hexane, toluene, and CH_2Cl_2) or were dried over the appropriate agents and distilled into the same kind of storage flasks (C_6H_6 and C_6H_{12}). All solvents were thoroughly degassed after purification (repeated freeze−pump−thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks, and degassed accordingly (CD_2Cl_2). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 25 °C on Bruker 400 MHz spectrometers, unless otherwise noted. Chemical shifts are

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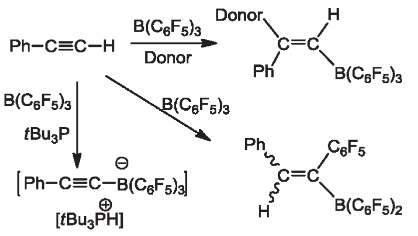
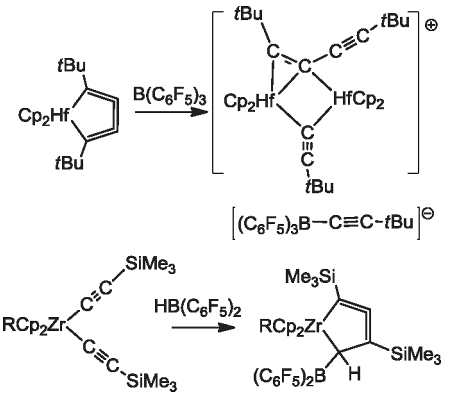
Scheme 1. Reactions of Alkynes with $B(C_6F_5)_3$



Scheme 2. Reactions of Early Metal Cumulenes with Electrophilic Boranes



given relative to $SiMe_4$ and referenced to the residue solvent signal (^1H, ^{13}C) or relative to an external standard (^{31}P: 85% H_3PO_4). Chemical shifts are reported in parts per million and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a PerkinElmer CHN Analyzer. $B(C_6F_5)_3$ was purchased from Boulder Scientific Company and used as received. $CpRu(PPh_3)_2(C{\equiv}CPh)$ (**1**) and $HB(C_6F_5)_2$ were prepared by literature methods.[62,63]

Synthesis of $CpRu(PPh_3)_2[CH{=}C(Ph)(B(C_6F_5)_2)]$ (2). Compound (**1**) (33 mg, 0.042 mmol) in CH_2Cl_2 (2 mL) was added to solid $HB(C_6F_5)_2$ (16 mg, 0.045 mmol) to yield an intense orange solution that was stirred for 4 h. The reaction was then pumped-dried in vacuo and the resulting residue dissolved in toluene (2 mL). To this was added hexanes (4 mL), and upon cooling to −35 °C, X-ray quality orange crystals were obtained (95%, 46 mg, 0.040 mmol). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 12.55 (t, 1H, vinyl H, $^3J_{PH} = 11.7$ Hz), 7.39−7.27 (m, 10H, Ph), 7.26−7.12 (m, 15H, Ph), 7.04−6.96 (m, 10H, Ph), 4.05 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ 51.62 (s, PPh_3). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ 46.1 (s (br)). ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K): δ −129.88 (s (br), 2F, *o*-C_6F_5), −131.89 (s (br), 2F, *o*-C_6F_5), −157.65 (s (br), 1F, *p*-C_6F_5), −158.17 (s (br), 1F, *p*-C_6F_5), −162.84 (s (br), 2F, *m*-C_6F_5), −164.54 (s (br), 2F, *m*-C_6F_5). ^{19}F NMR (376 MHz, CD_2Cl_2, 213 K): δ −129.96 to −130.21 (m, 2F, *o*-C_6F_5), −131.68 to −131.94 (m, 2F, *o*-C_6F_5), −156.83 (t, 1F, *p*-C_6F_5, $^3J_{FF} = 21.2$ Hz), −157.27 (t, 1F, *p*-C_6F_5, $^3J_{FF} = 21.2$ Hz), −161.97 to −162.21 (m, 2F, *m*-C_6F_5), −163.17 to −163.41 (m, 2F, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K, partial): δ 247.18 (t, vinyl C, $^2J_{CP} = 13.7$ Hz), 151.74 (s, Ph), 138.68−137.59 (m, Ph), 133.57 (t, *ipso*-C, Ph, $^1J_{CP} = 5.0$ Hz), 130.35 (s, Ph), 129.19 (s, Ph), 129.06 (s, Ph), 128.26 (s, Ph), 127.69 (t, *ipso*-C, Ph, $^1J_{CP} = 5.0$ Hz), 127.40 (s, Ph), 125.31 (s, Ph), 125.31 (s, Ph), 86.72 (s, Cp). The B−C and C−F carbons were not observed. Anal. Calcd for $C_{61}H_{41}BF_{10}P_2Ru$: C, 64.39; H, 3.63%. Found: C, 64.72; H, 4.10%.

Synthesis of $CpRu(PPh_3)[PhCC(B(H)(C_6F_5)_2)]$ (3). Compound (**1**) (240 mg, 0.303 mmol) in CH_2Cl_2 (5 mL) was added to solid $HB(C_6F_5)_2$ (110 mg, 0.319 mmol) to yield an intense orange solution that was stirred for 1 h. The reaction was then irradiated with UV light while being stirred for 12 h. The reaction was pumped-dried in vacuo and washed with hexanes (2 × 5 mL), and the resulting orange solid was dissolved in dichloromethane (2 mL). To this, cyclohexane (18 mL) was added, and upon diffusion, X-ray quality orange crystals were obtained (87%, 242 mg, 0.276 mmol). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.49−7.45 (m, 2H, Ph), 7.37−7.21 (m, 12H, Ph), 7.00−6.91 (m, 6H, Ph), 4.63 (s, 5H, Cp), −8.02 (s (br), 1H, RuHB). $^1H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.49−7.45 (m, 2H, Ph), 7.37−7.21 (m, 12H, Ph), 7.00−6.91 (m, 6H, Ph), 4.63 (s, 5H, Cp), −8.02 (d, 1H, RuHB, $^2J_{PH} = 12.8$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ 40.29 (s, PPh_3). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −18.9 (s (br)). ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K): δ −128.55 to −128.78 (m, 2F, *o*-C_6F_5), −129.47 to −129.92 (m, 2F, *o*-C_6F_5), −159.92 (t, 1F, *p*-C_6F_5, $^3J_{FF} = 20.3$ Hz), −160.64 (t, 1F, *p*-C_6F_5, $^3J_{FF} = 20.3$ Hz), −164.01 to −164.42 (m, 2F, *m*-C_6F_5), −165.21 to −165.47 (m, 2F, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K, partial): δ 135.43 (s, Ph), 135.01 (s, Ph), 133.61 (d, *ipso*-Ph, $^1J_{CP} = 11.4$ Hz), 132.73 (s, Ph), 129.45 (s, Ph), 128.38 (s, Ph), 133.57 (d, *o*-Ph, $^2J_{CP} = 9.1$ Hz), 127.56 (s, Ph), 83.31 (s, alkyne), 83.03 (s, Cp). The B−C and C−F carbons were not observed. Anal. Calcd for $C_{43}H_{26}BF_{10}PRu \cdot C_6H_{12}$: C, 61.33; H, 3.99%. Found: C, 60.77; H, 4.02%.

Synthesis of $CpRu(PPh_3)_2[C{=}C(Ph)((C_6F_4)B(F)(C_6F_5)_2)]$ (4). Compound (**1**) (33 mg, 0.042 mmol) in toluene (2 mL) was added to solid $B(C_6F_5)_3$ (22 mg, 0.043 mmol). The reaction was heated at 120 °C for 12 h, resulting in a red oil to crash out. Solution was decanted off and oil taken up in dichloromethane (1 mL) and subsequently precipitated out with hexanes (10 mL). The precipitate was then dissolved in benzene (12 mL) and layered with hexanes (8 mL), resulting in X-ray quality red crystals upon diffusion (40%, 22 mg, 0.017 mmol). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.45−7.37 (m, 7H, Ph), 7.25−7.11 (m, 16H, Ph), 7.00−6.91 (m, 12H, Ph), 5.27 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ 40.29 (s, PPh_3). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −0.5 (d, $^1J_{BF} = 64$ Hz). ^{19}F NMR (376 MHz, CD_2Cl_2, 213 K): δ −134.64 to −134.38 (m, 2F, C_6F_4), −135.18 to −135.43 (m, 4F, *o*-C_6F_5), −142.16 to −142.41 (m, 2F, C_6F_4), −162.67 (t, 2F, *p*-C_6F_5, $^3J_{FF} = 20.8$ Hz), −166.87 to −167.08 (m, 4F, *m*-C_6F_5), −192.04 (s (br), 1F, BF). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K, partial): δ 133.42−133.21 (m, Ph), 131.17 (s, Ph), 129.37 (s, Ph), 129.05 (s, Ph), 128.77−128.54 (m, Ph), 128.37 (s, Ph), 128.13 (s, Ph), 95.24 (s, Cp). The Ru−C, B−C, and C−F carbons were not observed. Anal. Calcd for $C_{60}H_{40}BF_{15}P_2Ru$: C, 61.72; H, 3.09%. Found: C, 61.72; H, 3.10% (repeated analyses gave low carbon values, suggesting formation of metal or B carbides during combustion).

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 150(±2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

Structure Solution and Refinement. 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. 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. (see Table 1 and the Supporting Information).

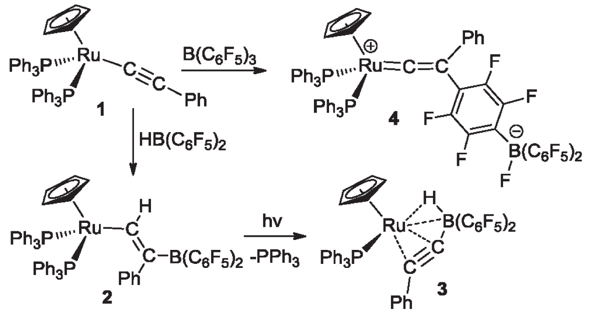
■ RESULTS AND DISCUSSSION

The species $CpRu(PPh_3)_2(C{\equiv}CPh)$[62] (**1**) was reacted with $HB(C_6F_5)_2$ to give an intense orange solution after 4 h.

Table 1. Crystallographic Data

	2·C_7H_8·$0.5C_6H_{14}$	**3**·C_6H_{12}	**4**·C_6H_6
formula	$C_{71}H_{56}BF_{10}P_2Ru$	$C_{73}H_{46}BF_{15}P_2Ruu$	$C_{49}H_{38}BF_{10}PRu$
wt	1272.98	1381.92	959.64
cryst syst	monoclinic	triclinic	triclinic
space grp	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	22.0269(9)	11.7355(17)	9.7474(10)
b (Å)	12.9666(5)	16.195(2)	18.4021(16)
c (Å)	21.5355(9)	17.148(3)	24.467(3)
α (deg)	90.00	94.811(9)	87.381(7)
β (deg)	107.048(2)	99.771(9)	81.646(7)
γ (deg)	90.00	106.499(9)	74.766(6)
V (Å^3)	5880.6(4)	3049.4(8)	4189.5(8)
Z	4	2	4
d (cal), g cm^{-1}	1.386	1.505	1.521
R(int)	0.0384	0.1599	0.1549
μ, cm^{-1}	0.394	0.401	0.493
total data	129 313	46 224	67 942
$>2\sigma(F_o{}^2)$	17 960	13 226	19 144
variables	766	829	1118
R ($>2\sigma$)	0.0406	0.0934	0.0827
R_w	0.1213	0.2611	0.1686
GOF	0.973	0.978	0.966

Scheme 3. Synthesis of 2−4



Subsequent isolation afforded an orange crystalline product **2** in 95% yield (Scheme 3). The ^{1}H NMR spectrum of **2** revealed a triplet at 12.55 ppm that showed a P−H coupling of 11.7 Hz, suggesting a vinylic proton coupling to two equivalent P atoms. In addition to the aromatic signals, a singlet resonance was observed at 4.05 ppm corresponding to the Cp group. The ^{31}P{^{1}H} NMR spectrum of **2** showed a single peak at 51.62 ppm, whereas the ^{11}B NMR spectrum gave rise to a resonance at 46.1 ppm. The corresponding ^{19}F NMR spectrum showed two sets of broad resonances attributable to inequivalent C_6F_5 rings. These signals sharpened at −60 °C. These data appeared to suggest the formulation of **2** as a Ru-vinyl species; the precise geometry of product **2** was confirmed crystallographically (Figure 1). Species **2** was confirmed as $CpRu(PPh_3)_2CH{=}C(Ph)(B(C_6F_5)_2)$, in which the borane has undergone hydroboration of the alkynyl fragment on Ru to give the cis-addition product. This reaction is regioselective with the B adding exclusively to the *beta*-carbon, presumably a result of steric demands and the electron-rich character of the *beta*-carbon of metal acetylides. The steric congestion about the pseudotrigonal planar B results in restricted rotation about the B−C(vinyl) bond accounting for the inequivalence of the C_6F_5 rings. The Ru−P, Ru−C, and C=C bond lengths in **2** were found to be 2.3059(5), 2.3116(5), 2.0272(19), and 1.403(3) Å, respectively. The remaining metric parameters were unexceptional.

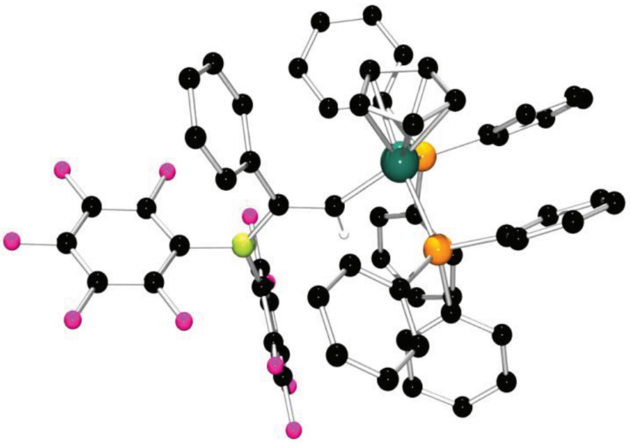


Figure 1. POV-ray depiction of **2**: C, black; H, gray; P, orange; Ru, deep-green; B, yellow-green; F, pink.

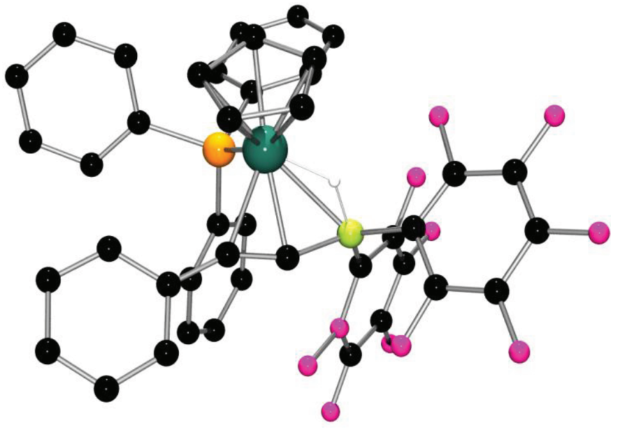
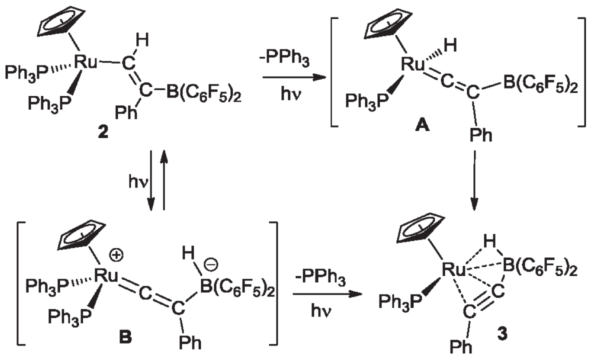


Figure 2. POV-ray depiction of **3**: C, black; H, gray; P, orange; Ru, deep-green; B, yellow-green; F, pink.

Subsequent irradiation of **2** with ultraviolet light for 12 h resulted in the isolation of a new orange product **3**, which was isolated as orange crystals in 87% yield (Scheme 3). Most notably, the resonance attributable to the vinyl proton in **2** was not observed, while the signal attributable to the Cp protons was shifted to 4.63 ppm. In addition, and interestingly, a new broad signal was observed at −8.02 ppm. This latter signal became a simple doublet upon ^{11}B decoupling and exhibited a P−H coupling of 12.8 Hz. The ^{31}P{^{1}H} NMR spectrum of **3** showed a singlet at 40.29 ppm, whereas the ^{11}B NMR spectrum gave a broad signal at −18.9 ppm. The ^{19}F NMR spectrum of **3** showed inequivalent C_6F_5 rings. As these data were not conclusive, the nature of **3** was determined unambiguously to be $CpRu(PPh_3)[PhC{\equiv}C(B(H)(C_6F_5)_2)]$ (Figure 2). The photoinduced rearrangement results in a CpRu fragment that is coordinated to a single PPh_3 as well as the alkynyl moiety and B−H fragment of the alkynyl-borate ligand. The Ru−P distances in the two molecules in the asymmetric unit were found to average 2.307(2) Å, whereas the Ru−C distances to the alkynyl unit were 2.207(7)

Scheme 4. Proposed Pathways from **2** to **3**



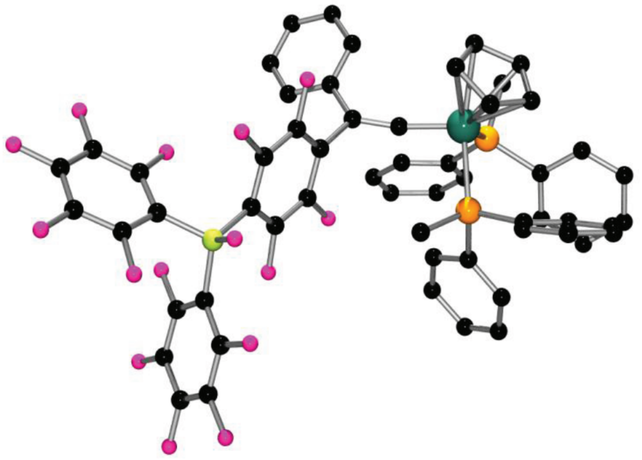


Figure 3. POV-ray depiction of **4**: C, black; H, gray; P, orange; Ru, deep-green; B, yellow-green; F, pink. Two of the Ph's from PPh3 groups are omitted for clarity.

and 2.256(6) Å, for the α and β carbons, respectively. The corresponding C−C bond length was 1.236(10) Å. The Ru−H approaches on average 1.51 Å, with a B−H bond length of 1.22 Å and a Ru−B bond length of 2.470(11) Å. This is significantly shorter than typical Ru−B bond distances of η^1 B−H complexes that range from 2.586 to 2.797 Å.[63−65] It is also noteworthy that the Ph and borate groups on the alkynyl-borate ligand adopt a pseudo-transoid disposition as the angle between the C−C−C and C−C−B planes is 16.6° with the BH unit disposed toward the Ru center. This is in contrast to traditional binding modes of alkynes to metal centers and may result from the BH binding to Ru. Similar transoid binding geometries have been previously reported for alkynyl-borane complexes of Ni.[64]

The mechanism of this rearrangement from **2** to **3** is a subject of some speculation; related literature precedent suggests two possibilities. One possibility involves photoinduced rearrangement of the Ru-vinyl species **2** to a vinylidene hydride species with loss of phosphine generating species **A**. Subsequent rearrangement of this vinylidene species to the corresponding alkyne complex with formation of the bridging B−H−Ru fragment yields the observed product **3**. A second possibility would involve hydride abstraction by the Lewis acidic B center, generating a transient zwitterionic Ru-cation/hydroborate species **B**, which could also undergo vinylidene to alkyne rearrangement, affording the product **3** (Scheme 4). These two pathways differ only in the initial step. It is noteworthy that, in the first pathway, the intermediate **A** is analogous to the Os hydride-vinylidene species $Cp(iPr_3P)Os(H)(C{=}CHPh)$ isolated and characterized by Baya and Esteruelas.[66] Related ruthenium vinylidene hydride species have also been investigated by Caulton and co-workers[67,68] and more recently by Goosen's group.[69] On the other hand, the intermediate **B** in the second pathway is analogous to the cationic Ru-vinylidenes $[CpRu\{C{=}C(Ph)Ar\}(dppe)][BArf_4]$ described by Mutoh et al. In either pathway, the latter steps are reasonable to propose given the established and recent work of Mutoh et al.,[48] where the reversible interconversion of vinylidene and alkyne complexes was demonstrated. Presumably, in the present case, the interaction with the hydride stabilizes product **3** and precludes the reverse reaction.

To probe a related reaction further, we reacted (**1**) with $B(C_6F_5)_3$ at 120 °C for 12 h. This resulted in the separation of a red oil. Subsequent isolation and crystallization afforded a red crystalline product **4** in 40% yield (Scheme 3). The ^1H NMR signal attributable to the Cp protons was observed at 5.27 ppm, whereas the $^{31}P\{^1H\}$ and ^{11}B NMR spectra gave resonances at 40.29 and −0.5 ppm, respectively. The latter signal exhibited a B−F coupling of 64 Hz consistent with the presence of a direct B−F bond. The corresponding ^{19}F NMR resonance was observed at 192.04 ppm, whereas the resonances arising from the fluoroaryl groups showed multiplets at −134.5 and −142.3 ppm attributable to a C_6F_4 fragment, in addition to the signals arising from the C_6F_5 rings. Efforts to observe the vinylidene carbons by ^{13}C NMR or HMBC spectroscopy were unsuccessful despite prolonged data acquisition. Nonetheless, these spectral data suggest the substitution of one of the *para*-fluorine atoms of $B(C_6F_5)$ with concurrent transfer of the fluorine to B. The precise nature of **4** was unambiguously determined by X-ray crystallography (Figure 3). This confirmed the formulation of **4** as the zwitterionic species $CpRu(PPh_3)_2(C{=}C(Ph)((C_6F_4)BF(C_6F_5)_2)$ in which the formerly β-alkyne carbon of **1** is now linked to the para position of one of the fluoroarene rings of $B(C_6F_5)_3$ with concurrent fluoride transfer to B. This generates a zwitterionic species with an anionic borate center and a cationic Ru-vinylidene unit. The Ru=C=C fragment gives rise to Ru−C and C=C bond lengths of 1.835(6) and 1.346(9) Å, with a Ru−C−C angle of 167.8(6)°. This differs slightly from those seen in $[Cp(Ph_3P)_2Ru{=}C{=}C(Me)Ph][I]$, where the Ru−C distance is 1.863(10) Å and the C=C distance is 1.293(15) Å.[70] The Ru−C distance in the cation $[CpRu(PPh_3)_2(C{=}C(Me)Ph]^+$ is similar to that in **4**, while the shorter C=C bond likely results from the electron-withdrawing fluorinated aryl ring. It is also noteworthy that the Ru−C distance is longer than that reported in $Cl_2(iPr_3P)_2Ru{=}C{=}C(Me)SiMe_3$ (1.787(5) Å).[71] This may reflect diminished π-back-bonding to C as a result of the formal cationic charge at Ru in **4**.

The formation of **4** is an interesting observation and provides a structural analog of the intermediate **B** in the latter proposed mechanism for the formation of **3**. Although this cannot be regarded as conclusive, the characterization of **4** lends support to this postulate. It is also important to note that the formation of **4** indicated the nucleophilic nature of the *beta*-carbon of the acetylide species (**1**), consistent with alkylations and protonations of metal acetylides to give vinylidene species. In this regard, one can also image species **B** as the intermediate en route to the hydroboration of the alkyne, giving **2**. It is presumably the photolabilization of phosphine as well as the stabilization of

Ru−H via an additional B−H interaction that drives the conversion of **2** to **3**.

It is also interesting to note that the proposed intermediate **B** is derived from the reaction of the nucleophilic *beta*-acetylide carbon interaction with a Lewis acid. However, the steric encumbrance about this C atom presumable precludes such an interaction at the B center of $B(C_6F_5)_3$. Instead, attack at the *para*-C of a C_6F_5 ring generates **4**. This is highly reminiscent of the reaction of bulky phosphines with $B(C_6F_5)_3$ that yields zwitterionic phosphonium borates.[72] It is also noteworthy that the present results stand in contrast to the thermolysis reactions of sterically hindered alkynes with $B(C_6F_5)_3$, where 1,1-carboboration reactions afford species of the general formula $RR'C{=}C(C_6F_5)B(C_6F_5)_2$.[19,43]

In summary, the present work has demonstrated some interesting reactions of Ru-alkyne complexes with electrophilic boranes. We are continuing to explore reactivity at the interface of transition-metal and main group chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic details are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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