Reaction of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NH_2Pr^n)_2$ with Alkynes. Synthesis and Structural Characterization of Ruthenium Aminocarbene and Enamine Complexes

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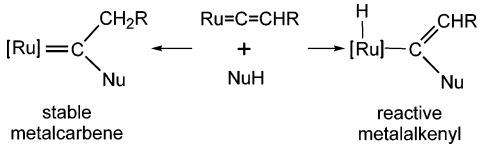
Syntheses of ruthenium aminocarbene and enamine complexes were achieved by tuning the electronic properties of alkynes. Reaction of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NH_2Pr^n)_2$ (**1**) with 2 equiv of phenylacetylene gave the aminocarbene $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[=C(NHPr^n)CH(Ph)\text{-}\eta^2\text{-}CH=CHPh]$ (**2a**) in 45% isolated yield in CH_2Cl_2 and the enamine complex $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]\text{-}Ru[\eta^4\text{-}CH(Ph)=C(NHPr^n)CH=CHPh]$ (**2b**) in 30% isolated yield in toluene. Treatment of **1** with the electron-rich alkynes 4-ethynyltoluene and 1-hexyne produced only the aminocarbene complexes $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[=C(NHPr^n)CH(p\text{-tolyl})\text{-}\eta^2\text{-}CH=CH(p\text{-tolyl})]$ (**3a**) and $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)\text{-}(C_2B_{10}H_{10})]Ru[=C(NHPr^n)CH(Bu^n)\text{-}\eta^2\text{-}CH=CH(Bu^n)]$ (**4a**), regardless of the solvents used. In contrast, the reaction of **1** with the electron-deficient alkynes 1-chloro-4-ethynylbenzene and 1-bromo-4-ethynylbenzene afforded only the enamine complexes $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[\eta^4\text{-}CH(XC_6H_4)=C(NHPr^n)CH=CH(XC_6H_4)]$ (X = Cl (**5b**), Br (**6b**)). All complexes were fully characterized by various spectroscopic techniques and elemental analyses. Their molecular structures (except for **4a)** were further confirmed by single-crystal X-ray analyses.

Introduction

The chemistry of Ru vinylidene complexes has become increasingly attractive over the past decades, because it has been disclosed that the catalytic organic transformation of terminal alkynes often proceeds via a vinylidene intermediate.[1] Typical examples of such catalytic reactions include the dimerization of alkynes[2] and the addition of nucleophiles to alkynes.[3] The reactivity of metal vinylidene complexes has been well studied in order to understand the reaction mechanism and to develop new catalytic reactions.[1−3] It has been documented that Ru=C_α=CHR contains an electrophilic α-carbon atom which readily reacts with nucleophiles to form either stable metal carbenes or reactive metal alkenyls (Scheme 1).[1g] These two types of metal complexes are very different in reactivity. Thus, the question arises as to what factor controls these nucleophilic reactions. In the course of our studies on the reaction of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NH_2Pr^n)_2$ with alkynes, we found that the electronic properties of the alkynes dominate the product of the reactions. Electron-rich alkynes favor the formation of Ru carbene complexes, whereas electron-deficient alkynes result in the formation of Ru alkenyl intermediates. These new findings are reported in this article.

Scheme 1



Results

Synthesis. Ruthenium vinylidene complexes can be directly prepared from the reactions of $LRu(COD)$ or $LRu(PPh_3)_2$ (L =

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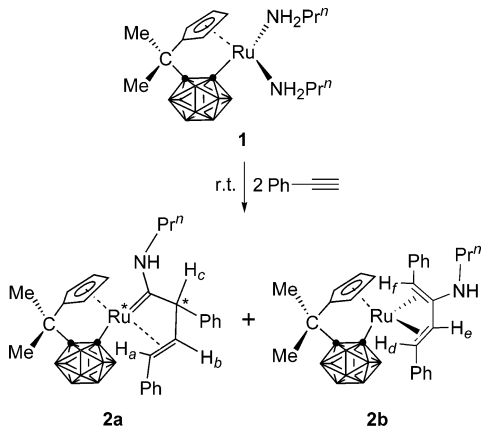
Scheme 2

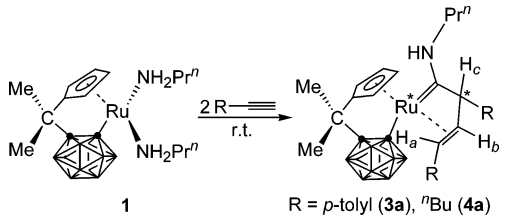


solvent	**2a** : **2b**
CH_2Cl_2	76 : 24
toluene	32 : 68

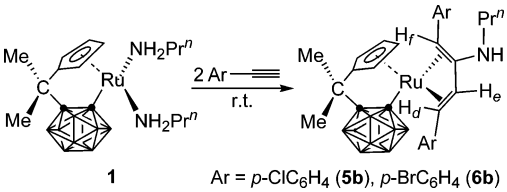
cyclopentadienyl and its derivatives) with alkynes.[4] Since [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru(COD) is inert to alkynes[5] and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$Ru(PPh_3)_2$ is not feasible,[6a] [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]$Ru(NH_2Pr^n)_2$ (**1**)[6b] was then chosen as the starting material. Treatment of **1** with 2 equiv of phenylacetylene in CH_2Cl_2 afforded both the ruthenium aminocarbene [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[=C(NHPr^n)CH(Ph)-$\eta^2$-CH=CHPh] (**2a**) and the ruthenium enamine [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$\eta^4$-CH(Ph)=C(NHPr^n)CH=CHPh] (**2b**) in a molar ratio of 76:24, as measured by the ^{1}H NMR spectrum (Scheme 2). Recrystallization from toluene gave **2a** as yellow crystals in 45% isolated yield. If the reaction solvent was switched from CH_2Cl_2 to toluene, the molar ratio of **2a** to **2b** was accordingly changed to 32:68. Recrystallization from toluene produced **2b** as yellow crystals in 30% isolated yield. Both **2a** and **2b** are reasonably stable in air in the solid state.

The ^{1}H NMR spectrum of **2a** showed that it existed in C_6D_6 solution as a 4:3 mixture of two diastereomerically related pairs of enantiomers, *RR*, *SS* and *RS*, *SR*, due to the presence of two chiral centers,[7] C* and Ru*, shown in Scheme 2. The characteristic PhCH_a=CH_bCH_cPh protons were observed as two doublets and one doublet of doublets at 4.87, 3.43, and 4.37 ppm for the major pair of diastereomers and at 4.45, 3.69, and 4.03 ppm for another pair, respectively. Two sets of Me_2C protons were also observed as singlets at 1.29 and 1.17 ppm for one pair and 1.29 and 1.07 ppm for the other pair. In the ^{13}C NMR spectrum, two sets of signals corresponding to the two pairs of diastereomers were again found. In particular, the unique Ru=*C* carbon chemical shift was observed at 250.6 and 241.7 ppm, respectively.[3e,8] These diastereomers did not show any significant differences in the ^{11}B NMR spectra, displaying a 1:1:2:6 pattern. It is noteworthy that the molar ratio of the two pairs of diastereomers (4:3) did not change upon heating the NMR solution close to the boiling point of C_6D_6, suggesting that epimerization did not proceed under these conditions.

Scheme 3



Scheme 4



In contrast, the ^{1}H NMR spectrum of **2b** was relatively simple. The characteristic resonances were two doublets at 5.54 and 1.73 ppm with ^3J = 8.1 Hz attributable to PhCH_d=CH_e protons, one singlet at 3.61 ppm assignable to the PhCH_f=C proton, and two singlets at 1.45 and 1.30 ppm corresponding to the Me_2C protons. The very high field chemical shift of the olefinic proton can be ascribed to the back-bonding effect of the Ru d electrons to the C=C bond, which was previously described in the literature.[9] The ^{13}C NMR spectrum of **2b** was consistent with its ^{1}H NMR data. No carbene carbon was observed.

The above results indicated that the solvent effect was important in the reaction of **1** with PhC≡CH. We wondered if this phenomenon would be observed in other terminal alkynes. Reaction of **1** with 2 equiv of the electron-rich alkynes 4-ethynyltoluene and 1-hexyne gave the ruthenium aminocarbene complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[=C(NHPr^n)-CH(*p*-tolyl)-η^2-CH=CH(*p*-tolyl)] (**3a**) and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[=C(NHPr^n)CH(Bu^n)-$\eta^2$-CH=CH(Bu^n)] (**4a**) in 63% and 71% isolated yields, respectively, regardless of the solvent used in the reaction, CH_2Cl_2 or toluene (Scheme 3). No ruthenium enamine complexes were detected by the ^{1}H NMR. On the other hand, interaction of **1** with 2 equiv of the electron-deficient alkynes 1-halo-4-ethynylbenzene produced exclusively the ruthenium enamine complexes [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[$\eta^4$-CH(X$C_6H_4$)=C(NHPr^n)-CH=CH(X$C_6H_4$)] (X = Cl (**5b**), Br (**6b**)) in good isolated yields (Scheme 4). No solvent effect was observed by the ^{1}H NMR experiments.

As for **2a**, the NMR spectra of **3a** and **4a** indicated that they existed in solution as 2:1 and 7:3 mixtures of two diastereomerically related pairs of enantiomers, respectively. The NMR spectra of **5b** and **6b** were very similar to that of **2b**.

Structure. Single-crystal X-ray analyses revealed that **2a** and **3a** have similar solid-state structures, although they crystallized in different space groups. The Ru atom is η^5 bound to the Cp, η^2 bound to the C=C double bond, and σ bound to one of the cage carbons and one carbene moiety in a three-legged piano-

(4) For example, see: (a) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105. (b) Yi, C. S.; Liu, N.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *Organometallics* **1997**, *16*, 3729.

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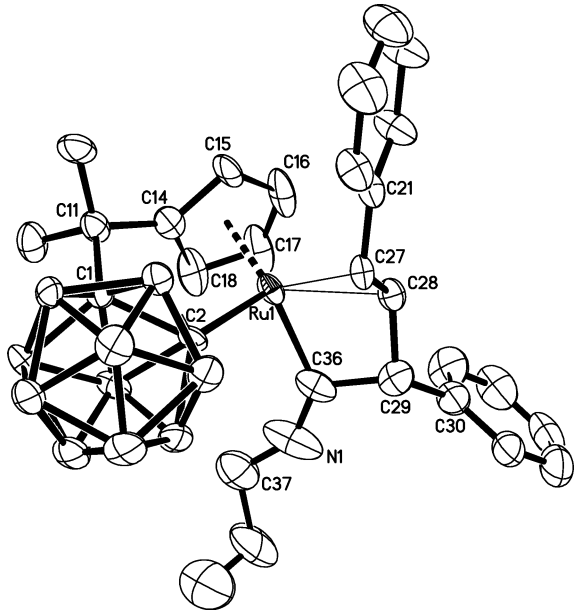


Figure 1. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-Ru[=C(NHPr^n)CH(Ph)-$\eta^2$-CH=CHPh] (**2a**).

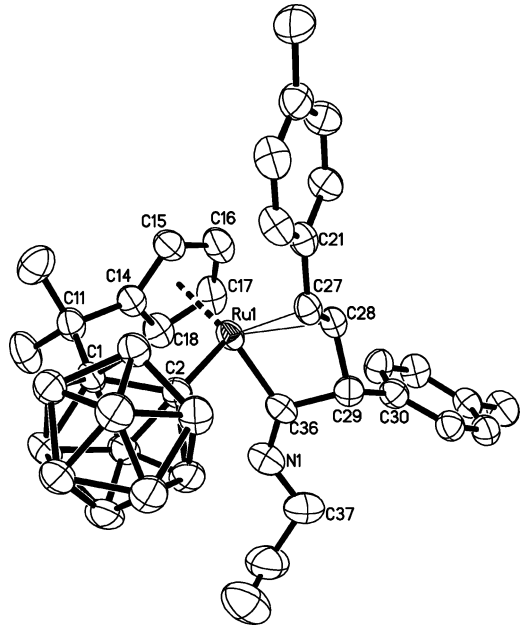


Figure 2. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-Ru[=C(NHPr^n)CH(*p*-tolyl)-η^2-CH=CH(*p*-tolyl)] (**3a**).

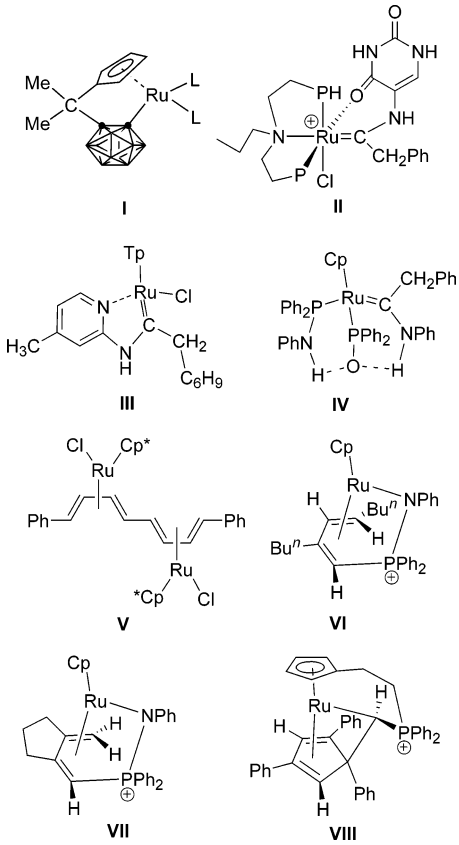
stool geometry, as shown in Figures 1 and 2, respectively. Selected bond distances and angles are given in Table 1. The average Ru−C_5 ring distances of 2.217(7) Å in **2a** and 2.243(5) Å in **3a** and Ru−C(cage) distances of 2.131(5) Å in **2a** and 2.156(4) Å in **3a** are very close to the corresponding values found in [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru($L_2$) ($L_2$ = amines, CH_3CN, phosphites, phosphines) (**I** in Chart 1) complexes.[5,6b] The Ru=C(36)/N(1)−C(36) distances of 1.953(8)/1.306(10) Å in **2a** and 1.952(5)/1.325(6) Å in **3a** are similar to those observed in other ruthenium aminocarbene complexes: for example, 1.956(6)/1.349(7) Å in *fac*,*cis*-[(PNP)RuCl{$C(NHC_4H_3N_2O_2)(CH_2$-Ph)}]Cl (PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$) (**II** in Chart 1),[10a] 1.915(1)/1.359(1) Å in TpRu(=$CCH_2C_6H_9$-apic)Cl (Tp = $[HB(pyrazolyl)_3]^-$, apic = 2-amino-4-picoline) (**III** in Chart 1),[10b] and 1.984(12)/1.352(14) Å in CpRu[=$C(CH_2Ph)$NHPh]-(PPh_2NHPh)[κ^1(*P*)-O=PPh_2] (**IV** in Chart 1).[10c] An observed

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a and 3a[a]

	2a	3a
Ru−C_{cage}	2.131(5)	2.156(4)
Ru−C_{ring} (av)	2.217(7)	2.243(5)
Ru−Cent	1.863y	1.886
Ru−C(36)	1.953(8)	1.952(5)
Ru−C(27)	2.275(5)	2.264(4)
Ru−C(28)	2.171(6)	2.184(4)
Ru−C_{vinyl} (av)	2.223(6)	2.224(4)
C(36)−N(1)	1.306(10)	1.325(6)
C(36)−C(29)	1.505(11)	1.504(6)
C(29)−C(28)	1.517(10)	1.543(6)
C(28)−C(27)	1.390(8)	1.398(6)
C(14)−C(11)−C(1)	108.4(5)	108.9(3)
Cent−Ru−C_{cage}	113.6	113.6
Ru−C(36)−N(1)	132.5(8)	131.1(4)
Ru−C(36)−C(29)	103.1(5)	105.2(3)
N(1)−C(36)−C(29)	123.6(9)	123.3(5)
C(36)−C(29)−C(28)	96.7(5)	95.1(3)
C(29)−C(28)−C(27)	118.8(5)	121.4(4)
C(28)−C(27)−C(21)	122.5(5)	124.5(4)

[a] In this table and in Table 2, Cent = the centroid of the five-membered ring.

Chart 1



substantial N(1)−C(36) double-bond character is a structural feature of Fischer-type aminocarbenes, which can be ascribed to the resonance Ru=C−NR_2 ↔ Ru^-−C=NR_2^+.

X-ray diffraction studies indicated that **2b**, **5b**, and **6b** are isostructural, in which the Ru atom is η^5 bound to the Cp, η^4 bound to the butadiene moiety, and σ bound to one of the cage

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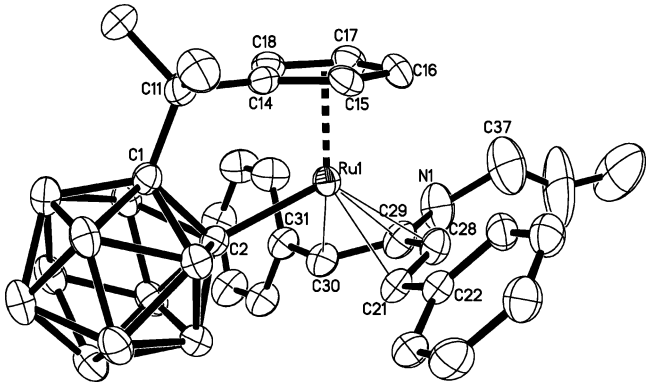


Figure 3. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-Ru[$\eta^4$-CH(Ph)═C(NHPr^n)CH═CHPh] (**2b**) (the solvated toluene molecule is not shown).

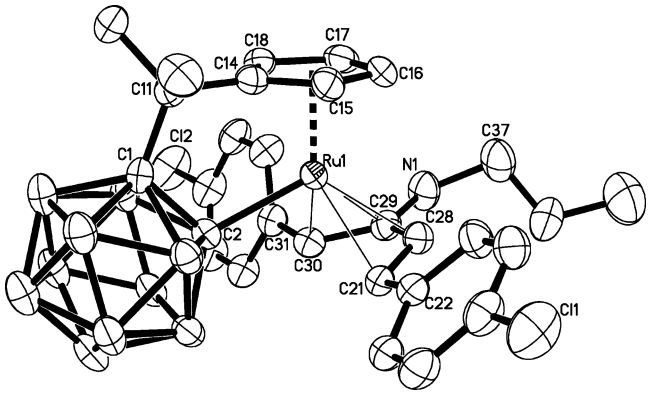


Figure 4. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-Ru[$\eta^4$-CH($ClC_6H_4$)═C(NHPr^n)CH═CH($ClC_6H_4$)] (**5b**).

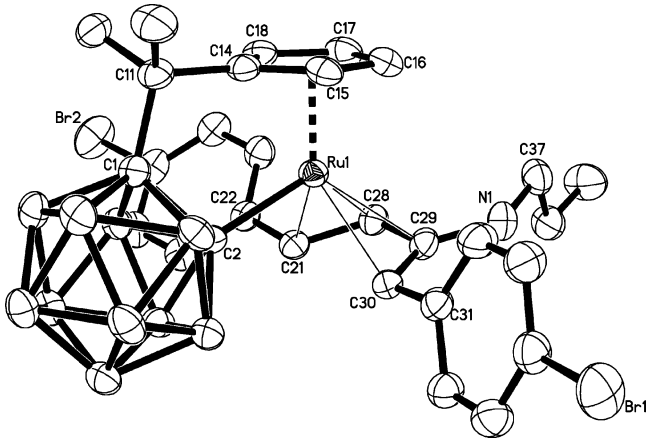


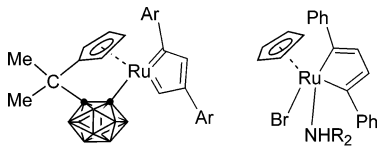
Figure 5. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-Ru[$\eta^4$-CH($BrC_6H_4$)═C(NHPr^n)CH═CH($BrC_6H_4$)] (**6b**) (the solvated toluene molecule is not shown).

carbons in a three-legged piano-stool geometry. Their structures are shown in Figures 3−5. As indicated in Table 2, the key structural parameters around the Ru atom in **2b**, **5b**, and **6b** are almost identical. The average Ru−C_5 ring and Ru−C(cage) distances are almost the same as those observed in **2a** and **3a**. The Ru−C(21,28,29,30) distances fall in a very narrow range with an average value of 2.222(7) Å in **2b**, 2.253(7) Å in **5b**, and 2.237(5) Å in **6b**, which are very close to those of 2.223(6) Å in **2a**, 2.224(4) Å in **3a**, 2.219(4) Å in μ-(*s-cis*-1,2,3,4-η:*s-cis*-5,6,7,8-η-PhCH═CHCH═CHCH═CHCH═CHPh)-$(RuClCp^*)_2$ (**V** in Chart 1),[11a] 2.218(3) Å in [CpRu(η^4-C_4H_3-(*n*-Bu)$_2$-PPh_2-κ^1*N*-NPh)][PF_6] (**VI** in Chart 1),[11b] 2.221(3) Å in

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2b, 5b, and 6b

	2b	5b	6b
Ru−C_{cage}	2.181(6)	2.179(6)	2.182(5)
Ru−C_{ring} (av)	2.210(7)	2.226(6)	2.228(6)
Ru−Cent	1.848	1.862	1.867
Ru−C(21)	2.206(6)	2.249(6)	2.229(5)
Ru−C(28)	2.160(7)	2.190(7)	2.186(5)
Ru−C(29)	2.296(7)	2.316(6)	2.290(5)
Ru−C(30)	2.225(6)	2.258(6)	2.228(5)
Ru−C_{vinyl} (av)	2.222(7)	2.253(7)	2.233(5)
C(21)−C(28)	1.428(10)	1.442(9)	1.449(8)
C(28)−C(29)	1.424(10)	1.412(10)	1.436(8)
C(29)−C(30)	1.414(10)	1.458(10)	1.440(8)
C(29)−N(1)	1.376(10)	1.381(9)	1.371(7)
C(14)−C(11)−C(1)	107.7(5)	108.4(5)	108.1(4)
Cent−Ru−C_{cage}	111.7	112.2	111.9
C(22)−C(21)−C(28)	119.4(7)	121.9(6)	120.8(5)
C(21)−C(28)−C(29)	122.5(7)	122.8(6)	120.4(5)
C(28)−C(29)−C(30)	116.5(6)	118.0(6)	117.5(5)
C(29)−C(30)−C(31)	119.6(6)	122.0(6)	121.4(5)
C(30)−C(29)−N(1)	122.4(7)	121.0(6)	122.2(5)
C(28)−C(29)-N(1)	120.6(8)	120.5(7)	119.8(6)

Chart 2



IX **X**

[CpRu(η^4-$C_4H_3(CH_2)_3$-PPh_2-κ^1*N*-NPh)][PF_6] (**VII** in Chart 1),[11b] and 2.195(2) Å in [Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1*C*-CH-η^4-$C_5Ph_3H_2$)][PF_6] (**VIII** in Chart 1).[11c] The bond distances of C(21)−C(28)/C(28)−C(29)/C(29)−C(30) are very similar and are between the typical single- and double-bond distances, suggestive of electron delocalization over four atoms. This phenomenon has often been observed in Ru butadiene complexes: for example, 1.399(5), 1.436(5), and 1.381(6) Å in μ-(*s-cis*-1,2,3,4-η:*s-cis*-5,6,7,8-η-PhCH═CHCH═CHCH═CHCH═CHPh)-$(RuClCp^*)_2$ (**V** in Chart 1),[11a] 1.416(4), 1.427(4), and 1.406(6) Å in [CpRu(η^4-C_4H_3(*n*-Bu)$_2$-PPh_2-κ^1*N*-NPh)][PF_6] (**VI** in Chart 1),[11b] 1.426(5), 1.436(6), and 1.408(6) Å in [CpRu(η^4-C_4H_3-$(CH_2)_3$-PPh_2-κ^1*N*-NPh)][PF_6] (**VII** in Chart 1),[11b] and 1.409(2), 1.434(3), and 1.416(2) Å in [Ru(η^5-$C_5H_4CH_2CH_2PPh_2$-κ^1*C*-CH-η^4-$C_5Ph_3H_2$)]PF_6 (**VIII** in Chart 1).[11c]

Discussion

The above experimental results indicated that a strong solvent effect was observed only in the reaction of **1** with PhC≡CH. Although no solvent effect was observed in the reaction of **1** with other alkynes, a significant electronic effect was found. Alkynes that are more electron rich than PhC≡CH gave ruthenium aminocarbene complexes, whereas those that are more electron deficient than PhC≡CH gave ruthenium enamine complexes. Subsequently, a question arises as to how these complexes were formed. One possible pathway may involve 1,3-disubstituted ruthenacyclopentatriene intermediates (**IX** in Chart 2), followed by nucleophilic attack of amine at the unsubstituted α-position to form ruthenium aminocarbene products, which is similar to the attack of phosphines at the

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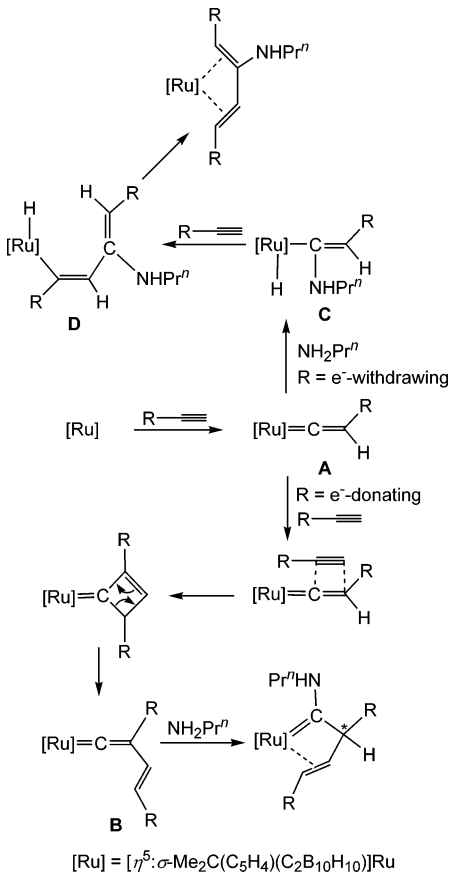
α-position of the 1,3-disubstituted ruthenacyclopentatriene, as documented in the literature.[12] However, the formation of ruthenium enamine complexes in which the two aryl substituents are in 1,4-positions is very unlikely via ruthenacyclopentatriene intermediates, since the α,α′-diaryl-substituted ruthenacyclopentatriene complex does not undergo a nucleophilic reaction with amine but, rather, gives the amine-coordinated ruthenacyclopentadiene (**X** in Chart 2).[13] Given this, the formation of ruthenium enamine complexes should undergo another pathway.

We have very recently isolated and fully characterized the ruthenium vinylvinylidene complex [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]-Ru[=C=C($SiMe_3$)CH=CH($SiMe_3$)], stabilized by another [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru moiety from the reaction of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru$(NCCH_3)_2$ with excess $Me_3SiC{\equiv}CH$.[14] The formation of this complex is suggested to involve the (vinylidene)ruthenium intermediate [η^5:σ-$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})$]Ru[=C=CH($SiMe_3$)], followed by [2 + 2] cycloaddition and a ring-opening reaction. The sterically demanding σ-ligand carboranyl may prevent the formation of a disubstituted ruthenacyclopentatriene intermediate and makes the coupling products different from those obtained via the reaction of CpRuX(L) (L = COD, $(CH_3CN)_2$; X = Cl, Br, BF_4) with $RC{\equiv}CH$.[15] In this connection and with respect to the formation of **2a**,**b** in the same reaction, it is reasonable to suggest that the formation of ruthenium aminocarbene and enamine complexes is unlikely via ruthenacyclopentatriene intermediates. A stepwise mechanism is then proposed, as shown in Scheme 5.

Reaction of $RC{\equiv}CH$ with **1** generates the common (vinylidene)ruthenium intermediate **A**. In the presence of electron-rich alkynes, it reacts with **A** via [2 + 2] cycloaddition followed by ring-opening reactions to afford the (vinylvinylidene)-ruthenium intermediate **B**, similar to [η^5:σ-$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})$]Ru[=C=C($SiMe_3$)CH=CH($SiMe_3$)].[14] Nucleophilic attack of the primary amine on the electrophilic α-C of **B** produces the final products, ruthenium aminocarbene complexes. On the other hand, in the presence of electron-deficient alkynes, nucleophilic attack of the primary amine at Ru=C of **A** gives the alkenylruthenium intermediate **C**.[9b,16] Addition of alkynes into the Ru−C bond yields the intermediate **D**, followed by reductive elimination to afford the final ruthenium enamine complexes. Electronic effects on the reaction pathway are not clear.

Scheme 5



Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. Toluene and *n*-hexane were freshly distilled from sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 was freshly distilled from CaH_2 and P_2O_5, respectively, immediately prior to use. [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru$(NH_2Pr^n)_2$ was prepared according to literature methods.[6b] All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with reference to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.0 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd., Egham, Surrey, U.K., or the Shanghai Institute of Organic Chemistry, CAS, Shanghai, People's Republic of China. Melting points were determined on an Electrothermal M-IA9100 digital melting point apparatus and were uncorrected.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru[=C($NHPr^n$)-CH(Ph)-$\eta^2$-CH=CHPh] (2a). Phenylacetylene (44 μL, 0.40 mmol) was added via microsyringe to a CH_2Cl_2 solution (5 mL) of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ru$(NH_2Pr^n)_2$ (**1**; 88 mg, 0.20 mmol) at 0 °C; the mixture was then warmed to room temperature and stirred for 2 days to give a brown solution. After removal of CH_2Cl_2, the resulting solid was washed with *n*-hexane. The ^1H NMR spectrum indicated that this solid was a mixture of **2a** and **2b** in a molar ratio of 76:24. Recrystallization from toluene gave **2a** as yellow crystals (56 mg, 45%), mp 172.5 °C. IR (KBr, cm^{-1}): ν 3420 (m)

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(16) Addition of phosphines into Ru=C of (vinylidene)ruthenium complexes were reported; see ref 9b and: Jérôme, F.; Monnier, F.; Lawicka, H.; Dérien, S.; Dixneuf, P. H. *Chem. Commun.* **2003**, 696.

(NH), 2562 (vs) (BH). $^{11}B\{^1H\}$ NMR (C_6D_6): δ −2.6 (1B), −4.4 (1B), −6.2 (2B), −8.3 (6B). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 250.6 241.7 (Ru=*C*), 144.8, 144.1, 140.6, 139.6, 136.8, 134.2, 129.4, 127.3, 125.7, 125.5, 125.3, 125.0 (aryl *C*), 88.6, 87.9, 87.1, 83.5, 82.5, 80.2, 78.5, 76.4, 74.8, 74.5, 71.9, 62.9 ($CH_{a/b}$ and C_5H_4), 52.3, 51.3 ($NHCH_2$), 44.9, 42.1 (CH_c), 41.2, 40.8 ($C(CH_3)_2$), 32.3, 31.2 30.2 ($C(CH_3)_2$), 22.6, 22.2 (CH_2CH_3), 11.3, 10.9 (CH_2CH_3); cage carbons were not observed. For the major pair of diastereomers: ^1H NMR (C_6D_6) δ 7.99 (br s, 1H, N*H*), 7.33−6.81 (m, 10H, C_6H_5), 4.87 (d, ^3J = 9.9 Hz, 1H, PhCH_a=CH_b), 4.83 (m, 1H, C_5H_4), 4.70 (m, 1H, C_5H_4), 4.37 (dd, ^3J = 4.8 and 9.9 Hz, PhCH_a=CH_b), 3.87 (m, 1H, C_5H_4), 3.43 (d, ^3J = 4.8 Hz, 1H, PhCH_a=CH_bCH_c), 3.07 (m, 1H, C_5H_4), 2.49 (m, 2H, NHCH_2), 1.29 (s, 3H, C(CH_3)$_2$), 1.17 (s, 3H, C(CH_3)$_2$), 0.97 (m, 2H, NHCH$_2$CH_2), 0.57 (t, ^3J = 7.5 Hz, 3H, CH$_2$CH_3). For the other pair of diastereomers: ^1H NMR (C_6D_6) δ 7.99 (br s, 1H, N*H*), 7.33−6.81 (m, 10H, C_6H_5), 4.51 (m, 1H, C_5H_4), 4.45 (d, ^3J = 9.6 Hz, 1H, PhCH_a=CH_b), 4.43 (m, 1H, C_5H_4), 4.03 (dd, ^3J = 3.3 and 9.6 Hz, PhCH_a=CH_b), 3.97 (m, 1H, C_5H_4), 3.69 (d, ^3J = 3.3 Hz, 1H, PhCH_a=CH_bCH_c), 3.23 (m, 1H, C_5H_4), 2.45 (m, 2H, NHCH_2), 1.29 (s, 3H, C(CH_3)$_2$), 1.07 (s, 3H, C(CH_3)$_2$), 0.87 (m, 2H, CH_2CH$_3$), 0.46 (t, ^3J = 7.5 Hz, 3H, CH$_2$CH_3). Anal. Calcd for $C_{29}H_{41}B_{10}NRu$: C, 56.84; H, 6.74; N, 2.29. Found: C, 56.91; H, 6.93; N, 2.38.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru[η^4-CH(Ph)=C(NHPr^n)CH=CHPh]·C$_7$H$_8$ (2b·C$_7$H$_8$). This complex was prepared as yellow crystals from [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru(NH$_2$Pr^n)$_2$ (**1**; 88 mg, 0.20 mmol) and phenylacetylene (44 μL, 0.40 mmol) in toluene (5 mL) using procedures identical with those reported for **2a**. The initial product was a mixture of **2a** and **2b** in a molar ratio of 32:68, as measured by the ^1H NMR spectrum. Recrystallization from toluene gave **2b** as yellow crystals (37 mg, 30%), mp 167 °C. IR (KBr, cm^{-1}): ν 3451 (m) (NH), 2584 (vs) (BH). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −2.6 (1B), −3.6 (1B), −5.9 (2B), −7.1 (2B), −8.0 (2B), −9.4 (2B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 143.5, 138.3, 130.1, 128.6, 128.4, 127.8, 126.9, 126.2, 126.1, 125.2 (aryl *C*), 83.7, 82.6, 81.9, 76.4, 65.7, 59.5, 58.0 ($CH_{d/e/f}$ and C_5H_4), 44.2 ($NHCH_2$), 40.1 ($C(CH_3)_2$), 31.8, 30.5 ($C(CH_3)_2$), 22.1 (CH_2CH_3), 20.8 (CH_3 of toluene), 11.0 (CH_2CH_3); cage carbons were not observed. ^1H NMR (CD_2Cl_2): δ 7.39−7.24 (m, 15H, C_6H_5), 5.54 (d, ^3J = 8.1 Hz, PhCH_d=CH_e), 5.14 (m, 1H, C_5H_4), 5.08 (m, 1H, C_5H_4), 4.39 (m, 1H, C_5H_4), 3.99 (m, 1H, C_5H_4), 3.61 (s, 1H, PhCH_f=C), 3.22 (m, 1H, NHCH_2), 2.83 (m, 1H, NHCH_2), 2.34 (s, 3H, CH_3 of toluene), 1.73 (d, ^3J = 8.1 Hz, PhCH_d=CH_e), 1.50 (m, 2H, CH_2CH$_3$), 1.45 (s, 3H, C(CH_3)$_2$), 1.30 (s, 3H, C(CH_3)$_2$), 0.91 (t, ^3J = 7.5 Hz, 3H, CH$_2$CH_3). Anal. Calcd for $C_{29}H_{41}B_{10}NRu$ (**2b**): C, 56.84; H, 6.74; N, 2.29. Found: C, 57.01; H, 6.73; N, 2.14.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru[=C(NHPr^n)-CH(*p*-tolyl)-η^2-CH=CH(*p*-tolyl)] (3a). This complex was prepared as yellow crystals from [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru(NH$_2$Pr^n)$_2$ (**1**; 88 mg, 0.20 mmol) and 4-ethynyltoluene (51 μL, 0.40 mmol) in toluene (5 mL) using procedures identical with those reported for **2a**: yield 81 mg (63%); mp 181 °C. IR (KBr, cm^{-1}): ν 3429 (m) (NH), 2582 (vs) (BH). $^{11}B\{^1H\}$ NMR (C_6D_6): δ −2.1 (1B), −3.8 (1B), −5.5 (2B), −7.9 (6B). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 251.1, 242.1 (Ru=*C*), 141.8, 141.2, 137.8, 137.6, 137.3, 136.7, 136.5, 135.0, 134.5, 134.1, 130.1, 129.1, 127.2, 126.9, 125.5, 125.0 (aryl *C*), 88.6, 88.0, 83.5, 82.3, 80.1, 78.2, 77.0, 74.6, 74.3, 72.4, 62.6, 62.4 ($CH_{a/b}$ and C_5H_4), 52.2, 51.2 ($NHCH_2$), 45.2, 42.3 (CH_c), 41.1, 40.8 ($C(CH_3)_2$), 32.4, 32.0, 30.2 ($C(CH_3)_2$), 23.1, 22.6 (CH_2CH_3), 21.2, 21.1 (CH_3 of tolyl), 11.3, 11.0 (CH_2CH_3); cage carbons were not observed. For the major pair of diastereomers: ^1H NMR (C_6D_6) δ 7.97 (br s, 1H, N*H*), 7.33−6.76 (m, 8H, C_6H_4), 4.95 (d, ^3J = 10.2 Hz, 1H, tolyl CH_a=CH_b), 4.84 (m, 1H, C_5H_4), 4.70 (m, 1H, C_5H_4), 4.44 (dd, ^3J = 4.8 and 10.2 Hz, 1H, tolyl CH$_a$=CH_b), 3.91 (m, 1H, C_5H_4), 3.43 (d, ^3J = 4.8 Hz, 1H, tolyl CH$_a$=CH$_b$CH_c), 3.12 (m, 1H, C_5H_4), 2.51 (m, 2H, NHCH_2), 2.14 (s, 3H, CH_3 of tolyl), 2.13 (s, 3H, CH_3 of tolyl), 1.29 (s, 3H, C(CH_3)$_2$), 1.16 (s, 3H, C(CH_3)$_2$), 0.97 (m, 2H, CH_2CH$_3$), 0.59 (t, ^3J = 7.5 Hz, 3H, CH$_2$CH_3). For the other pair of diastereomers: ^1H NMR (C_6D_6) δ 7.97 (br s, 1H, N*H*), 7.33−6.76 (m, 8H, C_6H_4), 4.52 (m, 1H, C_5H_4), 4.42 (d, ^3J = 9.6 Hz, 1H, tolyl CH_a=CH$_b$), 4.41 (m, 1H, C_5H_4), 4.09 (dd, ^3J = 3.0 and 9.6 Hz, 1H, tolyl CH$_a$=CH_b), 4.04 (m, 1H, C_5H_4), 3.70 (d, ^3J = 3.0 Hz, 1H, tolyl CH$_a$=CH$_b$CH_c), 3.28 (m, 1H, C_5H_4), 2.51 (m, 2H, NHCH_2), 2.17 (s, 3H, CH_3 of tolyl), 2.15 (s, 3H, CH_3 of tolyl), 1.29 (s, 3H, C(CH_3)$_2$), 1.08 (s, 3H, C(CH_3)$_2$), 0.87 (m, 2H, CH_2CH$_3$), 0.47 (t, ^3J = 7.5 Hz, 3H, CH$_2$CH_3). Anal. Calcd for $C_{31}H_{45}B_{10}NRu$: C, 58.10; H, 7.08; N, 2.19. Found: C, 58.12; H, 7.19; N, 2.45.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru[=C(NHPr^n)-CH(Bu^n)-η^2-CH=CH(Bu^n)] (4a). This complex was prepared as yellow crystals from [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru(NH$_2$Pr^n)$_2$ (**1**; 88 mg, 0.20 mmol) and 1-hexyne (46 μL, 0.40 mmol) in toluene (5 mL) using procedures identical with those reported for **2a**: yield 81 mg (71%); mp 153 °C. IR (KBr, cm^{-1}): ν 3448 (m) (NH), 2568 (vs) (BH). $^{11}B\{^1H\}$ NMR (C_6D_6): δ −2.9 (1B), −5.0 (1B), −6.4 (2B), −8.9 (6B). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 254.6, 245.4 (Ru=*C*), 90.1, 88.8, 85.5, 82.6, 80.3, 80.1, 78.1, 75.8, 74.3, 70.9, 56.8, 54.3 ($CH_{a/b}$ and C_5H_4), 51.2, 50.4 ($NHCH_2$), 47.9, 45.7 (CH_c), 41.1, 40.8 ($C(CH_3)_2$), 38.5, 37.0, 36.8, 36.5 ($CH_2CH_2CH_2CH_3$), 32.5, 31.9, 31.6, 30.4 ($C(CH_3)_2$), 28.9, 28.6, 28.5, 27.2, 22.9, 22.8, 22.7, 22.6, 22.4, 22.1 (Bu^n and CH_2CH_3 of NHPr^n), 14.5, 14.4, 14.3, 14.2 (CH_3 of Bu^n), 11.4, 11.1 (CH_3 of NHPr^n); cage carbons were not observed. For the major pair of diastereomers: ^1H NMR (C_6D_6) δ 7.92 (br s, 1H, N*H*), 4.45 (m, 1H, C_5H_4), 4.18 (m, 2H, C_5H_4), 3.88 (m, 1H, C_5H_4), 3.33 (dd, ^3J = 2.4 and 9.6 Hz, 1H, ^{n}BuCH$_a$=CH_b), 3.11 (dt, ^3J = 2.7 and 9.6 Hz, 1H, ^{n}BuCH_a=CH$_b$), 2.77 (dt, ^3J = 2.4 and 8.7 Hz, 1H, ^{n}BuCH$_a$=CH$_b$CH_c), 2.58 (m, 2H, NHCH_2), 1.53−0.90 (m, 20H, CH_2 and CH_3 of ^{n}Bu, ^{n}Pr and Me$_2$C), 0.67 (t, ^3J = 7.5 Hz, 3H, CH$_2$CH_3 of NHPr^n). For the other pair of diastereomers: ^1H NMR (C_6D_6) δ 7.92 (br s, 1H, N*H*), 4.65 (m, 2H, C_5H_4), 3.84 (m, 1H, C_5H_4), 3.70 (dd, ^3J = 2.4 and 9.9 Hz, 1H, ^{n}BuCH$_a$=CH_b), 3.69 (m, 1H, C_5H_4), 3.22 (dt, ^3J = 4.8 and 9.9 Hz, 1H, ^{n}BuCH_a=CH$_b$), 2.75 (dt, ^3J = 2.4 and 8.7 Hz, 1H, ^{n}BuCH$_a$=CH$_b$CH_c), 2.58 (m, 2H, NHCH_2), 1.53−0.90 (m, 20H, CH_2 and CH_3 of ^{n}Bu, ^{n}Pr, and Me$_2$C), 0.73 (t, ^3J = 7.5 Hz, 3H, CH$_2$CH_3 of NHPr^n). Anal. Calcd for $C_{25}H_{48}B_{10}NRu$: C, 52.51; H, 8.46; N, 2.45. Found: C, 52.25; H, 8.06; N, 2.45.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru[η^4-CH-(ClC$_6$H$_4$)=C(NHPr^n)CH=CH(ClC$_6$H$_4$)] (5b). This complex was prepared as yellow crystals from [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]-Ru(NH$_2$Pr^n)$_2$ (**1**; 88 mg, 0.20 mmol) and 1-chloro-4-ethynylbenzene (55 mg, 0.40 mmol) in toluene (5 mL) using procedures identical with those reported for **2a**: yield 98 mg (73%); mp 176 °C. IR (KBr, cm^{-1}): ν 3422 (m) (NH), 2562 (vs) (BH). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −2.5 (1B), −3.4 (1B), −5.8 (2B), −7.9 (4B), −9.5 (2B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 143.3, 138.0, 134.9, 132.7, 132.4, 131.6, 129.6, 128.8, 128.1, 125.9, 109.9 (aryl *C*), 84.9, 83.7, 83.1, 77.5, 65.3, 59.8, 58.1 ($CH_{d/e/f}$ and C_5H_4), 45.3 ($NHCH_2$), 41.2 ($C(CH_3)_2$), 32.9, 31.6 ($C(CH_3)_2$), 23.1 (CH_2CH_3), 12.0 (CH_2CH_3); cage carbons were not observed. ^1H NMR (CD_2Cl_2): δ 7.37−7.18 (m, 8H, C_6H_4), 5.50 (d, ^3J = 7.8 Hz, PhCH_d=CH_e), 5.12 (m, 1H, C_5H_4), 5.06 (m, 1H, C_5H_4), 4.37 (m, 1H, C_5H_4), 3.96 (m, 1H, C_5H_4), 3.52 (s, 1H, PhCH_f=C), 3.21 (m, 1H, NHCH_2), 2.84 (m, 1H, NHCH_2), 1.67 (d, ^3J = 7.8 Hz, PhCH_d=CH_e), 1.54 (m, 2H, CH_2-CH$_3$), 1.46 (s, 3H, C(CH_3)$_2$), 1.31 (s, 3H, C(CH_3)$_2$), 0.92 (t, ^3J = 7.5 Hz, 3H, CH$_2$CH_3). Anal. Calcd for $C_{29}H_{39}B_{10}Cl_2NRu$: C, 51.09; H, 5.77; N, 2.05. Found: C, 50.83; H, 6.10; N, 1.65.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ru[η^4-CH-(BrC$_6$H$_4$)=C(NHPr^n)CH=CH(BrC$_6$H$_4$)]·C$_7$H$_8$ (6b·C$_7$H$_8$). This complex was prepared as yellow crystals from [η^5:σ-Me$_2$C(C$_5$H$_4$)-(C$_2$B$_{10}$H$_{10}$)]Ru(NH$_2$Pr^n)$_2$ (**1**; 88 mg, 0.20 mmol) and 1-bromo-4-ethynylbenzene (73 mg, 0.40 mmol) in toluene (5 mL) using procedures identical with those reported for **2a**: yield 140 g (81%);

Table 3. Crystal Data and Summary of Data Collection and Refinement for 2a,b, 3a, 5b, and 6b

	2a	**2b**·C_7H_8	**3a**	**5b**	**6b**·C_7H_8
formula	$C_{29}H_{41}B_{10}NRu$	$C_{36}H_{49}B_{10}NRu$	$C_{31}H_{45}B_{10}NRu$	$C_{29}H_{39}B_{10}Cl_2NRu$	$C_{36}H_{47}B_{10}Br_2NRu$
cryst size (mm)	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.40
fw	612.8	704.9	640.9	681.7	862.7
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	10.591(1)	10.541(2)	10.743(2)	10.486(2)	10.520(2)
b, Å	13.194(1)	20.906(4)	12.860(3)	14.769(3)	12.986(3)
c, Å	22.471(2)	16.959(3)	24.952(5)	14.983(3)	15.644(3)
α, deg	90	90	90	67.50(3)	112.14(3)
β, deg	90	104.12(3)	99.85(3)	86.25(3)	95.12(3)
γ, deg	90	90	90	75.30(3)	92.37(3)
V, Å^3	3140.1(2)	3624.5(13)	3396.5(12)	2072.4(7)	1965.2(7)
Z	4	4	4	2	2
D_{calcd}, Mg/m^3	1.296	1.292	1.253	1.092	1.458
radiation (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
$2\theta_{max}$, deg	50.0	50.0	50.0	50.0	51.0
μ, mm^{-1}	0.520	0.460	0.484	0.525	2.460
F(000)	1264	1464	1328	696	868
no. of obsd rflns	5515	5287	5462	6349	6258
no. of params refined	381	392	389	388	452
goodness of fit	1.062	1.164	1.124	1.160	1.051
R1	0.049	0.071	0.057	0.078	0.065
*w*R2	0.119	0.190	0.159	0.246	0.177

mp 188 °C. IR (KBr, cm^{-1}): *ν* 3406 (m) (NH), 2542 (vs) (BH). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): *δ* −2.5 (1B), −3.4 (1B), −5.8 (2B), −7.9 (4B), −9.5 (2B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 143.3, 138.0, 134.9, 132.7, 132.4, 131.6, 129.6, 128.8, 128.1, 125.9, 109.9 (aryl *C*), 84.9, 83.7, 83.1, 77.5, 65.3, 59.8, 58.1 (*C*H$_{d/e/f}$ and *C*$_5$H$_4$), 45.3 (NH*C*H$_2$), 41.2 (*C*(CH$_3$)$_2$), 32.9, 31.6 (C(*C*H$_3$)$_2$), 23.1 (*C*H$_2$CH$_3$), 20.8 (*C*H$_3$ of toluene), 12.0 (CH$_2$*C*H$_3$); cage carbons were not observed. ^1H NMR (CD_2Cl_2): *δ* 7.52−7.14 (m, 13H, C_6H_4 + C_6H_5), 5.50 (d, ^3J = 7.8 Hz, PhCH$_d$=C*H*$_e$), 5.12 (m, 1H, C$_5$*H*$_4$), 5.06 (m, 1H, C$_5$*H*$_4$), 4.37 (m, 1H, C$_5$*H*$_4$), 3.96 (m, 1H, C$_5$*H*$_4$), 3.52 (s, 1H, PhC*H*$_f$=C), 3.21 (m, 1H, NHC*H*$_2$), 2.84 (m, 1H, NHC*H*$_2$), 2.34 (s, 3H, C*H*$_3$ of toluene), 1.67 (d, ^3J = 7.8 Hz, PhC*H*$_d$=CH$_e$), 1.54 (m, 2H, C*H*$_2$-CH$_3$), 1.46 (s, 3H, C(C*H*$_3$)$_2$), 1.31 (s, 3H, C(C*H*$_3$)$_2$), 0.92 (t, ^3J = 7.5 Hz, 3H, CH$_2$C*H*$_3$). Anal. Calcd for $C_{36}H_{47}B_{10}Br_2NRu$ (**6b** + C_7H_8): C, 50.12; H, 5.49; N, 1.62. Found: C, 49.98; H, 5.69; N, 1.59.

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS-II imaging plate using Mo Kα radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An empirical absorption correction was applied using the SADABS program.[17] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[18] For the noncentrosymmetrical structure of **2a**, the appropriate enantiomorph was chosen by refining the Flack parameter *χ* toward zero.[19] All hydrogen atoms were geometrically fixed using the riding model. Complexes **2b** and **6b** showed one toluene of solvation. Crystal data and details of data collection and structure refinements are given in Table 3.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **2a**, **2b**·C_7H_8, **3a**, **5b**, and **6b**·C_7H_8. This material is available free of charge via the Internet at http://pubs.acs.org.

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