Reactions of Cp*RuCl(COD) with Alkynes: Isolation of Dinuclear Metallacyclopentatriene Complexes

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The reactions of Cp*RuCl(COD) with alkynes in different solvents were investigated. Treatment of Cp*RuCl(COD) with phenylacetylene in benzene or dichloromethane gives the ruthenacyclopentatriene complex Cp*RuCl(2,5-$Ph_2C_4H_2$) and free COD. In methanol, a formal [2+2+2] cycloaddition of the COD ligand with PhC≡CH occurred and the reaction produces a tricyclo[4.2.2.0^{2,5}]dec-7-ene (C_6H_5-$C_{10}H_{13}$) and its complex [Cp*Ru(η^6-C_6H_5-$C_{10}H_{13}$)]Cl along with the dinuclear ruthenacyclopentatriene complex [Cp*RuCl(η^2,η^4,μ-2,5-$Ph_2C_4H_2$)RuCp*]Cl. 3-Hexyne was found to be unreactive toward Cp*RuCl(COD) in benzene or dichloromethane at room temperature. In methanol, it reacts with Cp*RuCl(COD) to give a tricyclo[4.2.2.0^{2,5}]dec-7-ene (Et_2-$C_{10}H_{12}$) and the dinuclear ruthenacyclopentatriene complex [Cp*RuCl(η^2,η^4,μ-C_4Et_4)RuCp*]Cl. 1-Hexyne was found to react with Cp*RuCl(COD) in C_6D_6, CD_2Cl_2, and diethyl ether to give the neutral dinuclear ruthenacyclopentadiene complex Cp*$RuCl_2$(η^2,η^4,μ-$C_4H_2Bu_2$)RuCp* along with free COD, while in methanol it gives a tricyclo[4.2.2.0^{2,5}]dec-7-ene (Bu-$C_{10}H_{13}$) and Cp*$RuCl_2$(η^2,η^4,μ-$C_4H_2Bu_2$)RuCp*.

Introduction

Cp*RuCl(COD) has been widely used as a catalytic precursor for reactions involving alkynes,[1] for example, cyclotrimerization of alkynes to give benzene derivatives,[2] coupling of enynes with diazoalkanes to give alkenylbicyclo[3.1.0]hexanes,[3] dimerization of alkynes in the presence of carboxylic acids to give 1,3-dienes[4] or alkylidenecyclobutadienes,[5] [2+2+2] cocyclization of diene-yne to give cyclohexenes,[6] [2+2] cycloaddition reactions of alkynes with olefins to give cyclobutenes,[7] [2+2+2] cycloadditions of diynes with electron-deficient carbon−heteroatom multiple bonds to give heterocycles,[8] and cycloaddition of alkynes with azides to give triazoles,[9] to name a few. It is generally believed that the active species contains a Cp*RuCl or Cp*Ru^+ fragment, which can undergo oxidative coupling with unsaturated substrates to give reactive metallacycles. In agreement with the proposed mechanisms, complexes relevant to the proposed intermediates in some of the catalytic reactions have been successfully isolated from the reactions of alkynes with Cp*RuCl(COD), for example, ruthenacyclopentatrienes,[4,10,11] η^4-cyclobutadiene,[5,10d] and η^6-benzene complexes.[10a,e]

An interesting question is how COD is initially removed from Cp*RuCl(COD) to generate the catalytically active species. Since COD is a weakly coordinating ligand, it is reasonable to assume that COD is displaced by substrates under catalytic conditions. However, it may also be possible that the COD ligand may first react with an unsaturated substrate to give a less coordinating species, which then subsequently dissociates from the ruthenium center. In connection with our study on catalytic cycloaddition reactions of alkynes with azides mediated by Cp*RuCl(COD),[9] we have carefully studied the reactions of Cp*RuCl(COD) with alkynes in benzene, dichloromethane, and methanol. Our results show that the COD ligand is removed by simple dissociation when the reactions were carried out in

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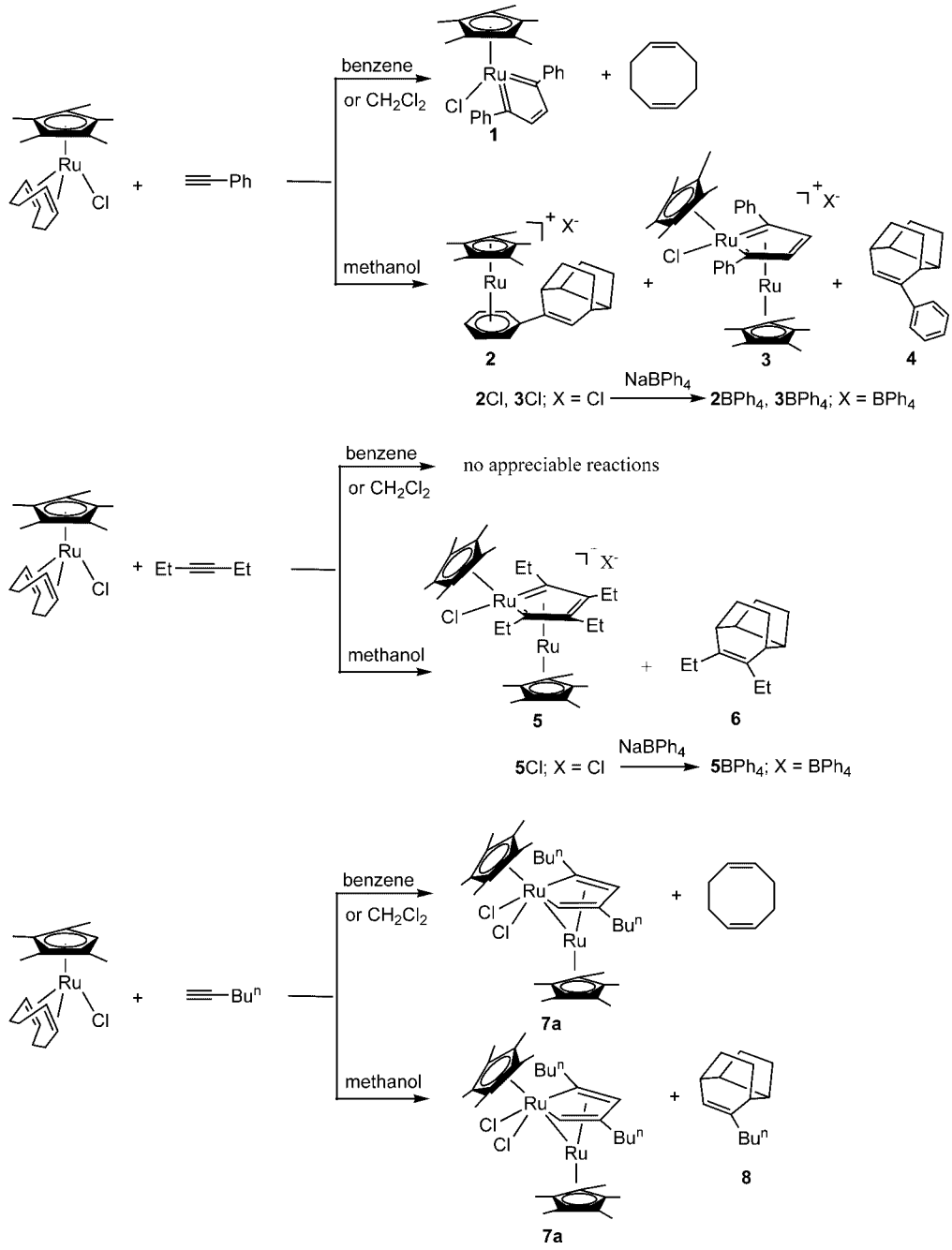
Scheme 1



benzene and dichloromethane, but is reactive toward alkynes when the reactions were carried out in methanol. During this study, we have isolated interesting dinuclear metallacyclopentatriene complexes. The details of the findings are reported in this paper.

Results and Discussion

In order to answer the question raised in the Introduction, we have carried out reactions of Cp*RuCl(COD) with phenylacetylene, 3-hexyne, and 1-hexyne in various solvents. Scheme 1 summarizes the reactions carried out and the results obtained. It is clear that the course of the reactions is affected by the solvents.

Reaction of Cp*RuCl(COD) with Phenylacetylene. The reactions of Cp*RuCl(COD) with phenylacetylene to give the ruthenacyclopentatriene complex Cp*RuCl(2,5-$Ph_2C_4H_2$) (**1**) (in THF or dichloromethane)[4,10] and the η^6-arene complex [Cp*Ru(η^6-1,2,4-$Ph_3C_6H_3$)]Cl (in dichloromethane)[10a,e] have been previously reported. However, the fate of COD in the reactions was not mentioned.

In this work, we have reinvestigated the reaction of Cp*RuCl(COD) with PhC≡CH in benzene, dichloromethane, and methanol. As indicated by an in situ NMR experiment, the reaction of Cp*RuCl(COD) with PhC≡CH (in 1:5 molar ratio) in C_6D_6 produced cleanly the ruthenacyclopentatriene complex Cp*RuCl(2,5-$Ph_2C_4H_2$) (**1**) and free COD (Scheme 1). The reaction is essentially completed in ca. 5.5 h at room temperature. A similar result was obtained when the reaction was carried out in dichloromethane. In the literature, reaction of Cp*RuCl(COD) with PhC≡CH in a molar ratio of ca. 1:50 in dichloromethane was reported to give the η^6-arene complex [Cp*Ru(η^6-1,2,4-$Ph_3C_6H_3$)]Cl.[10a] In our reaction conditions, the η^6-arene complex was not detectable by NMR. The formation

of **1** in the reaction is clearly indicated by the observations of the characteristic ^{1}H NMR (C_6D_6) signals at 1.18 (C_5Me_5) and 7.14 (Ru=C(Ph)C*H*) ppm and $^{13}C\{^1H\}$ NMR (C_6D_6) signals at 262.6 (Ru=*C*), 154.8 (Ru=C(Ph)*C*H), 105.9 (C_5Me_5), and 9.7 (C_5Me_5) ppm. The presence of free COD is indicated by the ^{1}H NMR spectrum (C_6D_6), which shows signals at 2.29 (s, CH_2) and 5.66 (s, C*H*) ppm, and by the $^{13}C\{^1H\}$ NMR spectrum (C_6D_6), which shows signals at 28.1(*C*H_2) and 77.6 (*C*H) ppm.

Different products were obtained when the reaction was carried out in methanol. When a mixture of Cp*RuCl(COD) and phenylacetylene (in 1:5 molar ratio) in methanol was stirred at room temperature for 0.5 h, a green solution was produced. The in situ ^{1}H NMR experiment (in CD_3OD) shows that the reaction produced the cationic complexes [Cp*Ru(η^6-C_6H_5-$C_{10}H_{13}$)]Cl (**2**Cl) and [Cp*RuCl(η^2,η^4,μ-2,5-$Ph_2C_4H_2$)RuCp*]Cl (**3**Cl) (in ca. 1:1.6 molar ratio) along with the organic compound C_6H_5-$C_{10}H_{13}$ (**4**) (Scheme 1). The ruthenacyclopentatriene complex Cp*RuCl(2,5-$Ph_2C_4H_2$) (**1**), the η^6-arene complex [Cp*Ru(η^6-1,2,4-$Ph_3C_6H_3$)]Cl,[10a] and free COD were not detectable by NMR. We also carried out the reaction with a molar ratio of 1:2 between Cp*RuCl(COD) and phenylacetylene in deuterated methanol. The in situ ^{1}H NMR shows that Cp*RuCl(COD) similarly reacted with phenylacetylene to give a mixture of **2**, **3**, and **4**, although the reaction is slower and some unreacted Cp*RuCl(COD) (ca. 16%) was detectable by NMR after 40 min. Again, no ruthenacyclopentatriene complex Cp*RuCl(2,5-$Ph_2C_4H_2$) (**1**) and free COD were detected.

A pure sample of compound **4** can be obtained from the reaction mixture by chromatography. However, complexes **2**Cl and **3**Cl can be isolated only as a mixture and attempts to separate complexes **2**Cl and **3**Cl by recrystallization and/or column chromatography failed. With a hope to separate complexes **2**Cl and **3**Cl, a mixture of **2**Cl and **3**Cl in methanol was treated with $NaBPh_4$; thereby complexes **2**Cl and **3**Cl were converted to [Cp*Ru(η^6-C_6H_5-$C_{10}H_{13}$)]BPh_4 (**2**BPh_4) and [Cp*RuCl(η^2,η^4,μ-2,5-$Ph_2C_4H_2$)RuCp*]BPh_4 (**3**BPh_4), respectively, which were precipitated out from methanol. However, it was still difficult to separate **2**BPh_4 from **3**BPh_4 by either recrystallization or chromatography. Fortunately, we were able to obtain single crystals of both **2**BPh_4 and **3**BPh_4, which allow us to determine their solid state structures (see below) and assign the corresponding ^{1}H NMR signals.

Compound **4** is a known compound and was previously obtained from the coupling reaction of phenylacetylene with COD mediated by (η^5-C_9H_7)RuCl(COD) (in neat COD).[12] The identity of **4** produced in our reaction can be readily assigned by comparing its ^{1}H and $^{13}C\{^1H\}$ NMR data with those of reported ones.

The structure of complex **2**BPh_4 has been determined by an X-ray diffraction study, and a view of cation **2** is shown in Figure 1. The X-ray diffraction study confirms that the complex contains a ligand derived from a formal [2+2+2] cycloaddition reaction between COD and phenylacetylene. The solid state structure is supported by the solution NMR data. For example, the ^{1}H NMR (in $CDCl_3$) spectrum of **2**BPh_4 shows a characteristic vinyl ^{1}H NMR signal at 6.58 ppm and those of the coordinated aryl group in the region 4.9−5.3 ppm.

The structure of complex **3**BPh_4 has also been determined by an X-ray diffraction study. As shown in Figure 2, the complex contains a five-membered metallacycle in which the two phenyl groups are on the two C_α atoms and the hydrogen atoms on the two C_β atoms. The metallacycle is η^5-coordinated

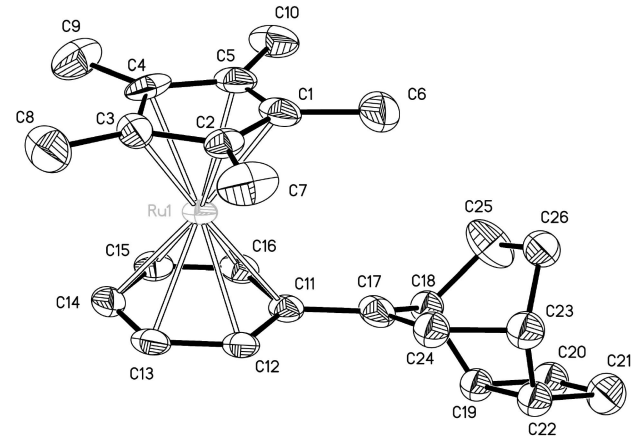


Figure 1. Crystal structure of cation **2**. The hydrogen atoms are omitted and the probability level used for the ellipsoids is 30%. Selected bond lengths (Å): Ru(1)−C(3), 2.154(3); Ru(1)−C(4), 2.157(3); Ru(1)−C(2), 2.178(3); Ru(1)−C(5), 2.189(3); Ru(1)−C(13), 2.209(3); Ru(1)−C(15), 2.209(3); Ru(1)−C(14), 2.212(3); Ru(1)−C(1), 2.214(4); Ru(1)−C(16), 2.215(3); Ru(1)−C(12), 2.218(3); Ru(1)−C(11), 2.267(3); C(11)−C(17), 1.470(5).

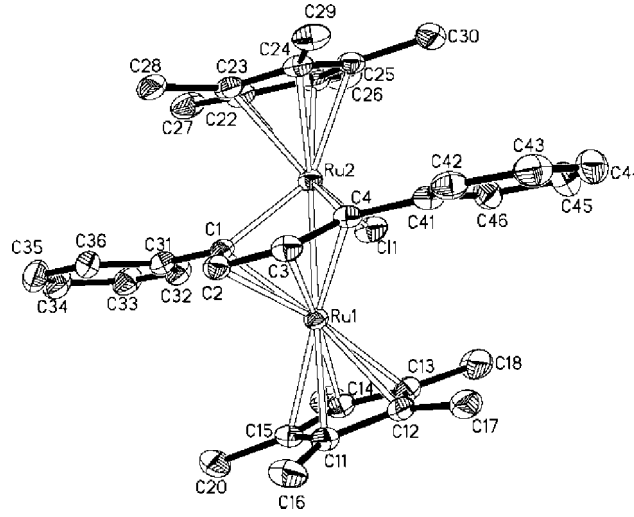


Figure 2. Crystal structure of cation **3**. The hydrogen atoms are omitted, and the probability level used for the ellipsoids is 30%. Selected bond lengths (Å): Ru(1)−Ru(2), 2.6691(2); Ru(2)−C(1), 2.102(2); Ru(2)−C(4), 2.090(2); Ru(2)−Cl(1), 2.3432(5); Ru(1)−C(1), 2.105(2); Ru(1)−C(2), 2.171(2); Ru(1)−C(3), 2.171(2); Ru(1)−C(4), 2.086(2); C(1)−C(2), 1.425(3); C(2)−C(3), 1.417(3); C(3)−C(4), 1.425(3).

to another ruthenium. The Ru(1)−Ru(2) distance (2.6691(2) Å) is expected for a Ru−Ru single bond. The distances between Ru(1) and carbons (C(1), C(4)) that are directly bonded to Ru(2) (2.105(2) and 2.086(2) Å) are shorter than those between Ru(1) and carbons (C(2), C(3)) that are not directly bonded to Ru(2) (2.171(2), 2.171(2) Å). The four C atoms (C(1), C(2), C(3), and C(4)) are almost coplanar, while the Ru(2)−C(1)−C(2)−C(3)−C(4) ring is puckered and the folding angle along the C(1)···C(4) line is 18.6°. The solid state structure is supported by the solution NMR data. For example, the ^{1}H NMR spectrum of **3**BPh_4 (in $CDCl_3$) shows a ^{1}H NMR signal at 6.40 ppm for the two CH's of the metallacycle. In the $^{13}C\{^1H\}$ NMR spectrum of **3**Cl (in CD_3OD), the signals of RuC_α and CH of the metallacycle were observed at 198.1 and 97.1 ppm, respectively.

The structure of cation **3** can be described as a ruthenacyclopentatriene being complexed through its five-membered

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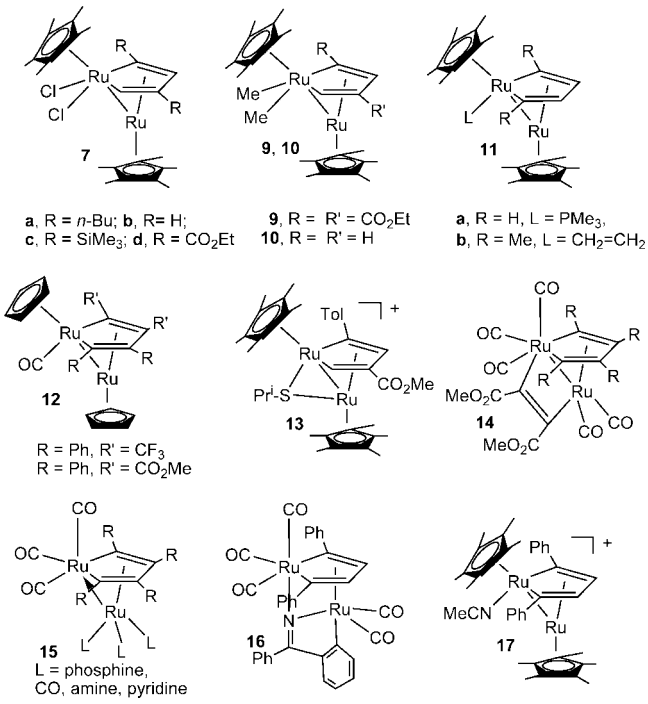
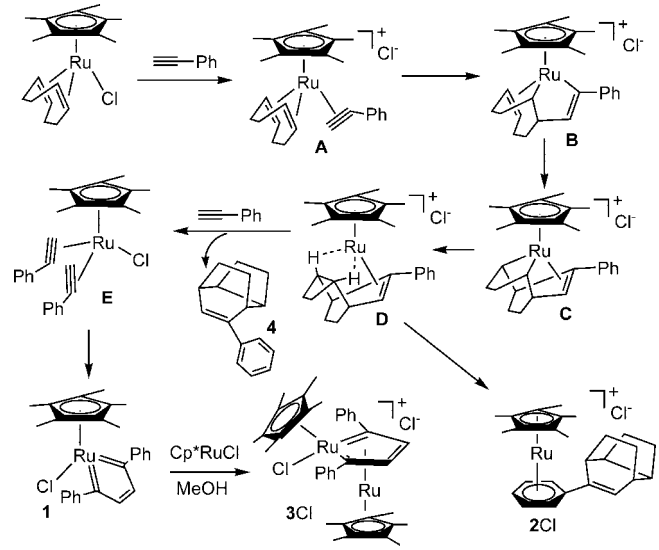
Chart 1



metallacycle with a Cp*Ru$^+$ cation in an η^5-coordination mode. The X-ray structures of related uncomplexed ruthenacyclopentatrienes including Cp*RuCl(2,5-$Ph_2C_4H_2$),[10a,e] CpRuBr(2,5-$Ph_2C_4H_2$),[11b] and Cp*RuCl(2,5-$Br_2C_4H_2$)[10b] have been reported. In comparison with those in these compounds, the Ru(2)−C(1) (2.102(2) Å) and Ru(2)−C(4) (2.090(2) Å) bonds of complex **3**BPh_4 are significantly lengthened (for example, being 1.969(4) Å for Cp*RuCl(2,5-$Ph_2C_4H_2$)). The C−C bond distances (C(1)−C(2), 1.425(3) Å; C(2)−C(3), 1.417(3) Å; C(3)−C(4), 1.425(3) Å) are also slightly longer than the corresponding ones in uncomplexed ruthenacyclopentatrienes. For example, the corresponding C−C bond distances are 1.40(2), 1.37(1), and 1.40(2) Å in Cp*RuCl(2,5-$Ph_2C_4H_2$).[10a] It is interesting to note that the C−C bond distances of the metallacycle in **3**BPh_4 are almost identical, whereas significant bond distance alternations were observed for uncomplexed ruthenacyclopentatrienes.

Complex **3**BPh_4 is structurally related to well-known dinuclear metallacyclopentadiene complexes.[13] A large number of such complexes are known. Complexes **7** and **9**−**16**[14−19] are the reported examples of such dinuclear ruthenium complexes (Chart 1). In complexes **7** and **9**−**14**, the ruthenacyclopentadiene ring formally donates five electrons to the other ruthenium based on a covalent bonding model. In complexes **15** and **16**, the ruthenacyclopentadiene ring formally donates four electrons to the other ruthenium. A simple electron-counting suggests that

Scheme 2



3BPh_4 has two less valence electrons when compared with complexes **7** and **9**−**16**. The metallacyclic ring of **3**BPh_4 formally donates six electrons to the other ruthenium. Thus it can be best described as a dinuclear metallacyclopentatriene complex. To the best of our knowledge, it is the first example of this type of complexes having such an electron count. It should be noted that the distinction between metallacyclopentadiene and metallacyclopentatriene is based on their different electron counts.

Despite the difference in electron count, the overall structural features associated with Ru(η^2,η^4,μ-C_4R_4) of **3**BPh_4 are very similar to those of dinuclear ruthenacyclopentadiene complexes such as **7b** and **10**. The only notable difference is the Ru−Ru distance: the Ru−Ru distance in **3**BPh_4 (2.6691(5) Å) is slightly shorter than those of **7b** (2.745(2) Å), **11a** (2.831(1) Å), and **11b** (2.867(1) Å).[16] Clearly, **3**BPh_4 shows a slightly more contracted Ru_2 moiety. Another reported complex closely related to **3**BPh_4 is the paramagnetic dinuclear complex [Cp*Ru(MeCN)-(η^2,η^4,μ-2,5-$Ph_2C_4H_2$)RuCp*](CF_3SO_3) (**17**).[20] The C−C distances (1.30(1)−1.37(1) Å) of the metallacycles as well as the Ru−Ru distance (2.6609(8) Å) in **17** are shorter than those of **3**BPh_4.

Scheme 2 shows a plausible mechanism for the formation of **2**−**4**. The chloride ligand in Cp*RuCl(COD) could initially be displaced by PhC≡CH to give the cationic alkyne complex **A**, which could undergo oxidative coupling to give intermediate **B**. An insertion reaction in **B** would give **C**, which could undergo reductive elimination to generate complex **D** containing **4** as a ligand. Complex **D** can rearrange to give the more stable η^6-arene complex **2**Cl, or dissociate **4** from the metal center to generate a reactive Cp*RuCl fragment. Further reaction of the Cp*RuCl fragment with PhC≡CH, presumably through intermediate **E** and **1**, could give complex **3**Cl. **E** could be formed from **D** via an intermediate, in which phenylacetylene and ligand **4** are both coordinated to the metal center. Although **1** was not detected in the reaction in methanol, its involvement in the formation of **3**Cl is consistent with the following observation. When a 1:1 mixture of Cp*RuCl(COD) and **1** in methanol was treated with phenylacetylene, **1** was completely consumed to give a 1:3 mixture of [Cp*Ru(η^6-C_6H_5-$C_{10}H_{13}$)]Cl (**2**Cl) and [Cp*RuCl(η^2,η^4,μ-2,5-$Ph_2C_4H_2$)RuCp*]Cl (**3**Cl).

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A sequence similar to the transformation of **A** to **D** has been proposed and studied computationally for the catalytic coupling reactions of COD with alkynes to give tricyco[4.2.2.0^{2,5}]dec-7-enes catalyzed by CpRuCl(COD) in methanol.[21] Formation of η^6-arene complex **2**Cl is not surprising, as arene complexes have also been isolated from the formal [2+2+2] coupling reactions of [Cp*Ru(H_2O)(NBD)]$^+$ with arylalkynes or arylallenes.[22] Stable mononuclear cyclopentatriene complexes have been isolated from the reactions of alkynes with complexes containing a (cyclopentadienyl)RuCl fragment, for example, CpRuBr(COD), Cp*RuCl(COD), and Cp*RuCl($Me_2NCH_2CH_2NMe_2$).[4,10,11] Reactive mononuclear ruthenacyclopentatrienes are formed in the reactions of alkynes with cationic complexes such as [CpRu(PR_3)(CH_3CN)$_2$]PF_6[23] and [CpRuL(CH_3CN)$_2$]PF_6 (L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).[24] The dinuclear complexes **7b**,**c** were obtained from the reactions of [Cp*RuCl]$_4$ with HC≡CR (R = H, $SiMe_3$) in toluene,[14] and **7a**,**d** from the reactions of Cp*RuCl($Me_2NCH_2CH_2NMe_2$) with HC≡CR (R = *n*-Bu, CO_2Et) in ether.[11c] Interestingly, the paramagnetic complex **17** was obtained from the reaction of PhC≡CH with [Cp*Ru(CH_3CN)$_3$](SO_3CF_3) in THF.[20]

Reaction of Cp*RuCl(COD) with 3-Hexyne. To further investigate the effect of solvent on the course of the reaction, we have also investigated the reaction of Cp*RuCl(COD) with 3-hexyne in benzene, dichloromethane, and methanol. As indicated by in situ NMR experiments, no appreciable reactions between Cp*RuCl(COD) and EtC≡CEt (in 1:5 molar ratio) in C_6D_6 or CD_2Cl_2 were observed after a mixture of Cp*RuCl(COD) and EtC≡CEt (in 1:5 molar ratio) was stood at room temperature for 4 h, suggesting that EtC≡CEt is much less reactive than PhC≡CH.

When a mixture of Cp*RuCl(COD) and EtC≡CEt (in 1:5 molar ratio) in methanol was stirred at room temperature for 0.5 h, a green solution was produced. The in situ ^{1}H NMR experiment showed that the reaction produced the cationic dinuclear complex [Cp*RuCl(η^2,η^4,μ-C_4Et_4)RuCp*]Cl (**5**Cl) and the organic compound **6**. On treatment with $NaBPh_4$, **5**Cl is converted to [Cp*RuCl(η^2,η^4,μ-C_4Et_4)RuCp*]BPh_4 (**5**BPh_4), which was isolated as a green solid in 78% yield (Scheme 1). Again no ruthenacyclopentatriene complex and free COD were detected by NMR.

A pure sample of the organic compound **6** can be obtained by chromatography. The compound has been characterized by NMR and MS spectroscopies. In particular, the MS spectrum shows the expected molecular ion peak at *m*/*z* 190. The $^{13}C\{^1H\}$ NMR (in $CDCl_3$) spectrum shows an olefinic signal at 138.3 ppm.

Complex **5**BPh_4 has been characterized by NMR, X-ray diffraction, and elemental analysis. A view of the complex cation

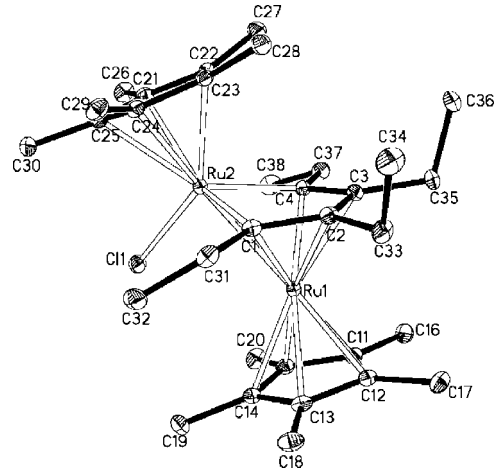

Figure 3. Structure of cation **5**. The hydrogen atoms are omitted and the probability level used for the ellipsoids is 30%. Selected bond lengths (Å): Ru(1)−Ru(2), 2.6650(3); Ru(2)−C(1), 2.073(2); Ru(1)−C(4), 2.087(3); Ru(2)−Cl(1), 2.3394(7); Ru(1)−C(1), 2.086 (2); Ru(1)−C(2), 2.186(3); Ru(1)−C(3), 2.197(3); Ru(1)−C(4), 2.091(3); C(1)−C(2), 1.416(4); C(2)−C(3), 1.435(4); C(3)−C(4), 1.424(4).

is shown in Figure 3. The X-ray diffraction study confirms that the complex is also a dinuclear ruthanacyclopentatriene complex, in which the 1,2,3,4-tetraethyl-1,3-butadiene fragment (C(1)−C(2)−C(3)−C(4)) is linked to Ru(2) to give rise to a five-memebered metallacycle, which is η^5-coordinated to Ru(1). Overall, the structural features associated with the metallacycle of **5**BPh_4 are very similar to those of **3**BPh_4. The Ru(1)−Ru(2) distance is 2.6650(3) Å. The distances between Ru(1) and carbons (C(1), C(4)) that are directly bonded to Ru(2) (2.086(2) and 2.091(3) Å) are also shorter than those between Ru(1) and carbons (C(2), C(3)) that are not directly bonded to Ru(2) (2.186(2), 2.197(3) Å). The four C atoms (C(1), C(2), C(3), and C(4)) are almost coplanar, while the Ru(2)−C(1)−C(2)−C(3)−C(4) ring is puckered and the folding angle along the C(1)···C(4) line is 18.5°. Consistent with the solid state structure, the ^{1}H NMR spectrum (in CD_2Cl_2) shows two sets of Cp* and ethyl signals. The $^{13}C\{^1H\}$ NMR (CD_2Cl_2) spectrum shows two $^{13}C\{^1H\}$ signals of the metallacycle at 215.2 (C_α) and 87.4 (C_β) ppm.

Reaction of Cp*RuCl(COD) with 1-Hexyne. In terms of chemical composition, complexes **3**Cl and **5**Cl are the same as **7** in that they all contain two Cp*Ru fragments, two chlorides, and one C_4R_4 chain. However, complexes **7** are neutral complexes with both chlorides coordinated to ruthenium, whereas complexes **3**Cl and **5**Cl are cationic complexes with only one chloride coordinated to ruthenium. Complexes **7** were previously obtained from the reactions of alkynes with [Cp*RuCl]$_4$, Cp*RuCl(P-*i*Pr_3), and Cp*RuCl($Me_2NCH_2CH_2NMe_2$) in toluene or ether.[11c,14] In the present study, **3**Cl and **5**Cl were obtained from the reactions of Cp*RuCl(COD) in methanol. The difference could be caused by either solvent effect or the reaction conditions or substrates.

If the difference is caused by solvent effects, one would expect that **5**Cl could be converted to the neutral complex Cp*RuCl$_2$(η^2,η^4,μ-C_4Et_4)RuCp* (**5′**) in nonpolar solvents such as benzene and dichloromethane, and the complex Cp*RuCl$_2$(η^2,η^4,μ-2,4-*n*-$Bu_2C_4H_2$)RuCp* (**7a**) could be converted to the cationic complex [Cp*RuCl(η^2,η^4,μ-2,4-*n*-$Bu_2C_4H_2$)RuCp*]Cl (**7a′**) in polar solvents. Experimentally, it is found that **5**Cl is almost insoluble in benzene and that no new NMR signals could be found in this solvent. In addition, there is no appreciable

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Table 1. Crystallographic Details for 2BPh$_4$ (2BPh$_4$·0.5CH$_2$Cl$_2$), 3BPh$_4$ (3BPh$_4$·0.5CH$_2$Cl$_2$·0.5hexane), and 5BPh$_4$ (5BPh$_4$·0.5CH$_2$Cl$_2$·0.25hexane)

	2BPh$_4$·0.5CH$_2$Cl$_2$	**3**BPh$_4$·0.5CH$_2$Cl$_2$·0.5hexane	**5**BPh$_4$·0.5CH$_2$Cl$_2$·0.25hexane
formula	$C_{50.5}H_{54}BClRu$	$C_{63.5}H_{70}BCl_2Ru_2$	$C_{58}H_{74.5}Cl_2BRu_2$
mol wt	808.27	1117.05	1055.53
symmetry	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/n$
a, Å	11.9964(3)	18.51220(10)	11.5277(8)
b, Å	17.8392(4)	11.58180(10)	12.1013(9)
c, Å	19.5444(5)	27.5397(2)	35.559(3)
α, deg	96.154(2)	90	90
β, deg	101.260(2)	106.6259(6)	95.1990(10)
γ, deg	94.707(2)	90	90
V, Å^3	4055.66(17)	5657.78(7)	4940.1(6)
Z	4	4	4
D_{cald}, g cm^{-3}	1.325	1.313	1.419
μ, mm^{-1}	3.980	5.463	0.758
2θ range, deg	9.30−135.00	8.34−142.96	3.62−52.00
no. of data collected	29 879	24 977	27 528
no. of unique data	14 006	10 402	9499
R(int)	0.0269	0.0235	0.0331
no. of params/restraints	945/6	637/10	587/0
goodness-of-fit on F^2	1.011	1.034	1.037
R1 [$I > 2\sigma(I)$]	0.0429	0.0294	0.0331
wR2 (all data)	0.1246	0.0754	0.0760
peak and hole, e Å^{-3}	0.800/−0.932	0.482/−0.594	0.770/−0.555

difference in the NMR data of **5**Cl in CD_2Cl_2 and CD_3OD. The observations suggest that **5**Cl was not converted to **5′** in benzene or dichloromethane.

The neutral complex Cp*RuCl$_2$(η^2,η^4,μ-2,4-*n*-Bu$_2$C$_4$H$_2$)RuCp* (**7a**) was previously prepared from the reaction of Cp*RuCl(Me$_2$NCH$_2$CH$_2$NMe$_2$) with HC≡C-*n*-Bu.[11c] In the present work, we prepared complex **7a** (Cp*RuCl$_2$(η^2,η^4,μ-2,4-*n*-Bu$_2$C$_4$H$_2$)RuCp*) from the reaction of [Cp*RuCl]$_4$ with HC≡C-*n*-Bu in benzene. Again, no appreciable difference in the NMR data of **7a** in benzene and methanol was observed. Thus it appears that solvent effects may not be the major cause for the adoption of the neutral or cationic forms.

Further experiment shows that complex **7a** was produced along with organic compound **8** from the reaction of Cp*RuCl(COD) with HC≡C-*n*-Bu (1:3 molar ratio) in methanol (Scheme 1). We also noted that **7a** was also produced (along with free COD) from the reactions of Cp*RuCl(COD) with HC≡C-*n*-Bu in C_6D_6, CD_2Cl_2, and diethyl ether. We therefore believe that the substrates play a major role in determining the relative stability of the neutral and cationic forms.

A possible explanation for the relative stability of the cationic and neutral forms of **7**, **3**Cl, and **5**Cl is as follows. In complexes **3**Cl and **5**Cl, both C_α carbon atoms are attached with a substitutent, while only one C_α carbon atom of **7** has a substituent. Apparently the additional substituent in **3**Cl or **5**Cl pushes one of the chloride ligands out of the coordination sphere due to steric effects.

In summary, we have carefully studied the reactions of Cp*RuCl(COD) with alkynes in different solvents. In nonpolar solvents, EtC≡CEt was found to be unreactive toward Cp*RuCl(COD), but PhC≡CH reacts with Cp*RuCl(COD) to give the ruthenacyclopentatriene complex Cp*RuCl(2,5-Ph$_2$C$_4$H$_2$) and free COD. HC≡C-*n*-Bu reacts with Cp*RuCl(COD) to give the neutral dinuclear ruthenacyclopentadiene complex Cp*RuCl$_2$(η^2,η^4,μ-C$_4$H$_2$Bu$_2$)RuCp* along with free COD. In methanol, a formal [2+2+2] cycloaddition of the COD ligand with alkynes followed by oxidative coupling of the alkyne occurred to give either cationic dinuclear ruthenacyclopentatriene complexes or neutral dinuclear ruthenacyclopentadiene complexes, depending on the alkynes.

Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenck techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether, THF), sodium (benzene), or calcium hydride (CH_2Cl_2). The starting materials [Cp*RuCl$_2$]$_2$ and Cp*RuCl(COD)[25] were prepared following the procedures described in the literature. All other reagents were used as purchased from Aldrich Chemical Co. USA. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^{1}H and ^{13}C{^{1}H} spectra were collected on a Bruker ARX 300 MHz spectrometer or a Bruker AV 400 MHz spectrometer.

Reactions of Cp*RuCl(COD) with PhC≡CH in Benzene and Dichloromethane. To an NMR tube were added CD_2Cl_2 or C_6D_6 (0.5 mL), Cp*RuCl(COD) (10 mg, 0.026 mmol), and phenylacetylene (0.015 mL, 0.13 mmol). The mixture was stood at room temperature for 5.5 h. A ^{1}H NMR experiment showed that all Cp*RuCl(COD) was consumed to give free COD and Cp*RuCl(2,5-Ph$_2$C$_4$H$_2$) (**1**). Characteristic NMR data for **1** are as follows. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.33 (s, 15 H, C$_5$*Me*$_5$), 7.46 (s, 2 H, RuC(Ph)C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 262.2 (s, Ru*C*), 154.7 (s, RuC(Ph)*C*H), 106.3 (*C*$_5$Me$_5$), 9.7 (C$_5$*Me*$_5$). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.18 (s, 15 H, C$_5$*Me*$_5$), 7.14 (s, 2 H, RuC(Ph)C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 262.6 (Ru=*C*), 154.8 (RuC(Ph)*C*H), 105.9 (*C*$_5$Me$_5$), 9.7 (C$_5$*Me*$_5$). Characteristic NMR data for COD: ^{1}H NMR (C_6D_6, 300 MHz): δ 2.29 (s, 8 H, C*H*$_2$), 5.66 (s, 4 H, C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 28.1 (*C*H$_2$) and 77.6 (*C*H). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 2.49 (s, 8 H, C*H*$_2$), 5.69 (s, 4 H, C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 28.1 (*C*H$_2$) and 77.1 (*C*H).

Reactions of Cp*RuCl(COD) with PhC≡CH in Methanol. Preparation of Complexes 2Cl and 3Cl. A mixture of Cp*RuCl(COD) (0.300 g, 0.789 mmol) and phenylacetylene (0.435 mL, 3.95 mmol) in methanol (10 mL) was stirred at room temperature for 0.5 h to give a green solution. An in situ ^{1}H NMR showed that all Cp*RuCl(COD) was consumed to give a mixture of **4**, [Cp*Ru(η^6-C$_6$H$_5$-C$_{10}$H$_{13}$)]Cl (**2**Cl), and [Cp*RuCl(2,5-Ph$_2$C$_4$H$_2$)RuCp*]Cl (**3**Cl). The mixture was concentrated to dryness and the residue was washed with diethyl ether (10 mL × 5) and benzene (5 mL) to give 270 mg of a green powder, which was identified to be a

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mixture of **2**Cl and **3**Cl (4:3 molar ratio). The washings were concentrated to dryness to give a brown oil, from which a pure sample of compound **4** was obtained via chromatography using hexane as the eluting solvent and silica gel as the adsorbent. Characterization data of complex **2**Cl: ^{1}H NMR (CD_3OD, 400 MHz): δ 1.23 −1.30 (m, 2 H), 1.96 (s, 15 H, C_5Me_5), 2.10−2.15 (m, 4 H), 2.28−2.35 (m, 4 H), 2.73 (br, 1 H), 2.95 (br, 1 H), 5.85−5.92 (m, 3 H, η^5-Ph), 6.13−6.14 (m, 2 H, η^5-Ph), 6.95 (d, 1 H, J(HH) = 6.8 Hz, C*H*═C). ^{13}C{^{1}H} NMR (CD_3OD, 100.6 MHz): δ 10.9 (C_5Me_5), 18.7 (CH_2), 18.8 (CH_2), 21.1 (CH_2), 21.4 (CH_2), 35.9 (*C*H), 36.20 (*C*H), 36.26 (*C*H), 36.5 (*C*H), 84.7 (η^5-Ph), 84.8 (η^5-Ph), 88.5 (η^5-Ph), 88.7 (η^5-Ph), 97.5 (C_5Me_5), 103.5 (η^5-Ph), 139.5 (*C*H═C), 140.0 (CH═*C*). MS: *m*/*z* 446 (M + 1 − Cl^-). Characterization data of complex **3**Cl: ^{1}H NMR (CD_3OD, 400 MHz): δ 0.97 (s, 15 H, C_5Me_5), 1.27 (s, 15 H, C_5Me_5), 6.62 (d, 2 H, J(HH) = 8.0 Hz, Ph), 6.99 (s, 2 H, C(Ph)═C*H*), 7.24−7.27 (m, 2 H, Ph), 7.36−7.39 (m, 2 H, Ph), 7.45−7.49 (m, 2 H, Ph), 7.90 (d, 2 H, J(HH) = 7.6 Hz, Ph). ^{13}C{^{1}H} NMR (CD_3OD, 100.6 MHz): δ 9.1 (C_5Me_5), 10.7 (C_5Me_5), 97.1 (RuC(Ph)*C*H), 101.1 (C_5Me_5), 108.9 (C_5Me_5), 123.6 (Ph), 129.5 (Ph), 130.6 (Ph), 131.6 (Ph), 137.6 (Ph), 148.6 (Ph), 198.1 (Ru*C*(Ph)). MS: *m*/*z* 713 (M − Cl^-). Characterization data of **4**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.21−1.27 (m, 3 H), 1.94−2.03 (m, 4 H), 2.19−2.27 (m, 3 H), 2.57−2.60 (m, 1 H), 3.00 (br, 1 H), 6.59 (dd, J(HH) = 6.8, 1.4 Hz, 1 H, C*H*═C), 7.18−7.21 (m, 1 H, Ph), 7.23−7.34 (m, 2 H, Ph), 7.40−7.43 (m, 2 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 17.9, 18.2, 20.5, 20.5, 33.9, 35.2, 35.8, 124.9, 126.7, 128.6, 129.6, 139.7, 145.2. MS: *m*/*z* 210.

Preparation of Complexes 2BPh$_4$ and 3BPh$_4$. A mixture of Cp*RuCl(COD) (0.500 g, 1.32 mmol) and phenylacetylene (0.726 mL, 6.58 mmol) in methanol (10 mL) was stirred at room temperature for 0.5 h to give a green solution. The reaction mixture was concentrated to dryness, and then was added a methanol (2 mL) solution of $NaBPh_4$ (0.384 g, 1.12 mmol). The mixture was stirred at room temperature for several minutes to give a green precipitate, which was collected by filtration, washed with methanol (3 mL × 3) and diethyl ether (10 mL × 3), and then dried under vacuum to give a green solid composed of [Cp*Ru(η^6-C_6H_5-$C_{10}H_{13}$)]BPh_4 (**2**BPh_4) and [Cp*RuCl(η^2,η^4,μ-2,5-$Ph_2C_4H_2$)-RuCp*]BPh_4 (**3**BPh_4) (in 1:1.6 molar ratio). The filtrate was concentrated to dryness, to give a brown oil. A pure sample of compound **4** was obtained from the brown oil via chromatography using hexane as the eluting solvent and silica gel as the adsorbent. Characterization data of **2**BPh_4: ^{1}H NMR ($CDCl_3$. 400 MHz): δ 0.95 (br, 2 H), 1.74 (s, 15 H, C_5Me_5), 1.97−2.03 (m, 2 H), 2.11−2.25 (m, 6 H), 2.64 (br, 1 H), 2.70 (br, 1 H), 4.89−4.94 (m, 3 H, η^5-Ph), 5.30−5.32 (m, 2 H, η^5-Ph), 6.58 (d, 1 H, J(HH) = 6.8 Hz, C*H*═C), 6.92−6.95 (m, BPh_4), 7.06−7.09 (m, BPh_4), 7.49 (br, BPh_4). MS: *m*/*z* 446 (M + 1 − BPh_4^-). Characterization data of **3**BPh_4: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77 (s, 15 H, C_5Me_5), 1.19 (s, 15 H, C_5Me_5), 6.40 (s, 2 H, C(Ph)═C*H*), 6.45 (m, 2 H, Ph), 6.92−6.95 (m, BPh_4), 7.06−7.09 (m, BPh_4), 7.15−7.18 (m, 4 H, Ph), 7.27−7.31 (m, 4 H, Ph), 7.38−7.42 (m, 2 H, Ph), 7.49 (br, BPh_4), 7.52 (m, 2 H, Ph). MS: *m*/*z* 678 (M − BPh_4^- − Cl^-).

Reactions of Cp*RuCl(COD) with EtC≡CEt in Methanol. Formation of Complexes 5Cl and 6. A mixture of Cp*RuCl(COD) (0.300 g, 0.790 mmol) and 3-hexyne (0.449 mL, 3.95 mmol) in methanol (10 mL) was stirred at room temperature for 0.5 h. The solution turned green and was concentrated to dryness to give a brown oil. The residue was washed with hexane (10 mL × 5) and dried under vacuum to give a green powder. Yield: 0.157 g (56%). The washings were concentrated to dryness to give a brown oil. Pure samples of compound **6** could be obtained from the brown oil via chromatography using hexane as the eluting solvent and silica gel as the adsorbent. Characterization data of complex **5**Cl: ^{1}H NMR (CD_3OD, 300 MHz): δ 0.52 (t, J(HH) = 7.4 Hz, 6 H, CH_2CH_3), 1.39 (s, 15 H, C_5Me_5), 1.69 (s, 15 H, C_5Me_5), 1.84 (t, J(HH) = 7.6 Hz, 6 H, CH_2CH_3), 1.97−2.06 (m, 2 H, CH_2CH_3), 2.21−2.34 (m, 4 H, CH_2CH_3), 2.82−2.89 (m, 2 H, CH_2CH_3). ^{13}C{^{1}H} NMR (CD_3OD, 75.5 MHz): δ 8.3 (C_5Me_5), 9.4 (C_5Me_5), 14.3 (CH_2CH_3), 21.8 (CH_2CH_3), 33.8 (CH_2CH_3), 99.7 (Ru*C*C), 106.6 (C_5Me_5), 114.8 (C_5Me_5), 214.5 (Ru*C*C). FAB-MS: *m*/*z* 637 (M + 1 − 2Cl^-). Characterization data of **6**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.96 (t, J(HH) = 7.5 Hz, 6 H, CH_2CH_3), 1.10 (m, 2 H), 1.82−1.98 (m, 4 H), 2.03−2.18 (m, 8 H), 2.21−2.25 (m, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 14.0 (CH_2CH_3), 18.4, 21.3, 23.6, 36.0 (*C*H), 37.5 (*C*H), 138.3 (*C*═*C*). MS: *m*/*z* 190.

Formation of Complexes 5BPh$_4$ and 6. A mixture of Cp*RuCl(COD) (0.426 g, 1.12 mmol) and 3-hexyne (0.637 mL, 5.61 mmol) in methanol (10 mL) was stirred at room temperature for 0.5 h to give a green solution. The solution was concentrated to dryness to give a brown oil. To the residue was added a methanol (2 mL) solution of $NaBPh_4$ (0.384 g, 1.12 mmol). The mixture was stirred at room temperature for several minutes to give a green precipitate, which was collected by filtration, washed with methanol (3 mL × 3) and diethyl ether (10 mL × 3), and then dried under vacuum. Yield: 0.417 g (78%). The filtrate was concentrated to dryness to give a brown oil. Pure samples of compound **6** could be obtained from the brown oil via chromatography using hexane as the eluting solvent and silica gel as the adsorbent. Characterization data of complex **5**BPh_4: Anal. Calcd for $C_{56}H_{70}BClRu_2$: C, 67.83; H, 7.12. Found: C, 68.00; H, 7.12. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 0.33 (t, J(HH) = 7.2 Hz, 6 H, CH_2CH_3), 1.12 (s, 15 H, C_5Me_5), 1.51 (s, 15 H, C_5Me_5), 1.66 (t, J(HH) = 7.8 Hz, 6 H, CH_2CH_3), 1.75−1.79 (m, 2 H, CH_2CH_3), 1.94−2.04 (m, 4 H, CH_2CH_3), 2.57−2.62 (m, 2H, CH_2CH_3), 6.85 (t, J(HH) = 7.0 Hz 4 H, BPh_4), 6.99 (t, J(HH) = 7.4 Hz, 8 H, BPh_4), 7.30 (br, 8 H, BPh_4). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz): δ 10.0 (C_5Me_5), 11.1 (C_5Me_5), 15.4 (CH_2CH_3), 15.8 (CH_2CH_3), 22.8 (CH_2CH_3), 34.8 (CH_2CH_3), 87.4 (Ru*C*C), 99.9 (C_5Me_5), 106.9 (C_5Me_5), 115.4 (BPh_4), 122.4 (BPh_4), 126.3 (BPh_4), 136.6 (BPh_4), 215.2 (Ru*C*C). FAB-MS: 638 (M − BPh_4 − Cl^-).

Preparation of Complex 7a. Complex **7a** has been reported by K. Kirchner et al.[11c] We synthesized **7a** by the reaction of [Cp*RuCl]$_4$ and 1-hexyne in benzene at 0 °C. The detailed procedure is as follows. A mixture of [Cp*$RuCl_2$]$_2$ (0.500 g, 1.63 mmol) and zinc dust (1.06 g, 16.3 mmol) in ethanol (30 mL) was stirred at room temperature overnight to give a yellow precipitate of [Cp*RuCl]$_4$. The ethanol was removed by filtration. The reaction flask containing the residue, including [Cp*RuCl]$_4$, $ZnCl_2$, and unreacted Zn dust, was immersed in an ice−water bath. After that, benzene (10 mL) and 1-hexyne (0.375 mL, 3.26 mmol) were added, and the reaction mixture was stirred for 3 h around 0 °C to give a brownish-red solution. After removal of $ZnCl_2$ and the unreacted Zn dust by filtration, the filtrate was concentrated to dryness to give a dark red powder, which was then washed with Et_2O and dried under vacuum. Yield: 100 mg (16%). Characteristic data for **7a** are as follows. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.18 (s, C_5Me_5), 1.93 (s, C_5Me_5), 5.23 (d, J(HH) = 1.50 Hz, RuC(Bu)═C*H*), 8.77 (d, J(HH) = 1.65 Hz, Ru*CH*═C(Bu)). ^{1}H NMR (CD_3OD, 400 MHz): δ 1.44 (s, C_5Me_5), 1.81 (s, C_5Me_5), 5.51 (d, J(HH) = 1.38 Hz, RuC(Bu)═C*H*) and 8.71 (d, J(HH) = 1.68 Hz, Ru*CH*═C(Bu)). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): δ 8.7 (C_5Me_5), 10.4 (C_5Me_5), 13.8 (Bu), 14.2 (Bu), 23.17 (Bu), 23.23 (Bu), 31.3 (Bu), 32.2 (Bu), 33.4 (Bu), 42.0 (Bu), 91.9. 93.0, 102.5, 108.2, 164.9 (Ru*C*H═C(Bu), 183.7 (Ru*C*(Bu)═CH).

Reactions of Cp*RuCl(COD) with 1-Hexyne in Methanol. Observation of 7a and 8. To an NMR tube was added Cp*RuCl(COD) (16.5 mg, 0.0435 mmol) and CD_3OD (0.5 mL). The reaction mixture changed to dark red immediately upon the addition of 1-hexyne (0.015 mL, 0.130 mmol). An in situ ^{1}H NMR (CD_3OD) spectrum showed that Cp*RuCl(COD) was completely consumed and mainly converted to **7a** and **8**. Characteristic proton signals of **7a** in ^{1}H NMR (CD_3OD, 300 MHz): δ 8.71 (d, J(HH) =

1.68 Hz, RuC*H*═C(Bu)), 5.51 (d, J = 1.38 Hz, RuC(Bu)═C*H*), 1.81 (s, C_5Me_5), and 1.44 (s, C_5Me_5). After the reaction mixture was concentrate to dryness under vacuum, **8** could be obtained by extraction of the residue with hexane. ^{1}H NMR ($CDCl_3$, 300 MHz) of **8**: δ 0.89 (t, J(HH) = 7.1 Hz, 3 H), 1.07−1.09 (m, 2 H), 1.33−1.38 (m, 4 H), 1.86−2.11 (m, 10 H), 2.25 (br, 1 H), 2.32 (br, 1 H), 5.84 (dd, J(HH) = 6.6, 1.3 Hz, 1 H, C*H*═C(Bu)). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of **8**: δ 13.8, 17.5, 17.9, 20.0, 20.7, 22.2, 29.7, 32.8, 34.5, 34.7, 35.4, 36.7, 125.6 (*C*H═C(Bu)), 146.8 (*C*(Bu)═CH).

Crystal Structure Analyses. Crystals of **2**BPh_4, **3**BPh_4, and **5**BPh_4 were grown from their CH_2Cl_2 solutions layered with hexane. **2**BPh_4 is cocrystallized with CH_2Cl_2 to give **2**$BPh_4 \cdot 0.5CH_2Cl_2$, and **3**BPh_4 and **5**BPh_4 are cocrystallized with CH_2Cl_2 and hexane to give **3**$BPh_4 \cdot 0.5CH_2Cl_2 \cdot$0.5hexane and **5**$BPh_4 \cdot 0.5CH_2Cl_2 \cdot$0.25-hexane, respectively. The intensity data of **5**BPh_4 were collected with a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K. Lattice determination and data collection were carried out using SMART v.5.625 software.[26] Data reduction and absorption correction by empirical methods were performed using SAINT v 6.26[27] and SADABS v 2.03,[28] respectively. Structure solution and refinement were performed using the SHELXTL v.6.10 software package.[29] The data of **2**BPh_4 and **3**BPh_4 were collected on an Oxford Diffraction XcaliburS Ultra with CCD area detector and Enhance Ultra Cu Kα radiation (λ = 1.54178Å) at 173 K. Lattice determination, data collection, and reduction were carried out using CrysAlisPro 171.32.5. Absorption corrections were performed using the built-in SADABS program of the CrysAlisPro program suite. Structure solutions and refinements were performed using the SHELXTL v.6.10 software package. All the structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms. Further details on crystal data, data collection, and refinements are summarized in Table 1.

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Supporting Information Available: X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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