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Arylation of Hydrocarbyl Ligands Formed from *n*-Alkanes through C–H Bond Activation of Benzene Using a Triruthenium Cluster

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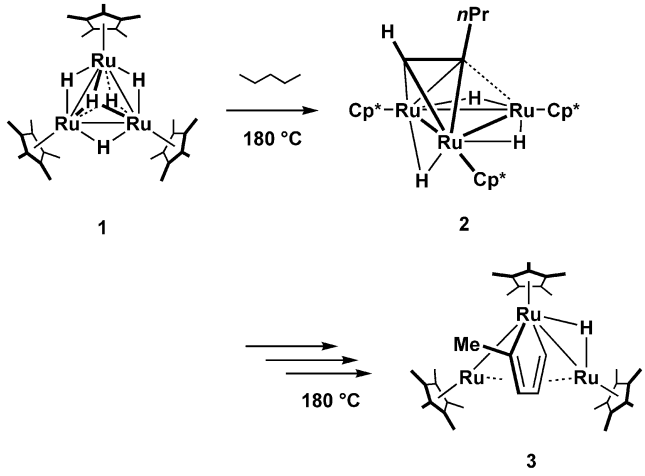
Keywords: C–H activation / C–C coupling / Cluster compounds / Ruthenium / Benzyne complexes

Triruthenium complex **2** containing a perpendicularly coordinated 1-pentyne ligand, which is one of the key intermediates of the reaction of triruthenium pentahydrido complex **1** with *n*-pentane, reacts with benzene to yield μ_3-benzyne–μ_3-pentylidyne complex **5** by C–H bond activation. β-H elimination form the μ_3-penytylidyne ligand occurred upon heating to yield μ_3-pentenylidene complex **6**, which was followed by the formation of *closo*-ruthenacyclopentadiene complex **8** by the connection of the two hydrocarbyl moieties placed on each face of the triruthenium plane with partial metal–metal bond breaking. Treatment of **8** with pressurized hydrogen resulted in exclusive liberation of *n*-pentylbenzene, which is difficult to synthesize by conventional Friedel–Crafts alkylation. These sequential transformations correspond to the formation of linear alkylbenzene by the reaction of pentane with benzene on a trimetallic plane.

Introduction

Functionalization of alkanes is of immense importance in organic chemistry owing to its potential applicability to organic synthesis. C–H bond activation, which is a crucial step in the functionalization of alkanes, has been studied intensively using transition-metal complexes as activators. However, there are very few examples of the successful transformation of the resulting metal–alkyl species into functionalized alkanes.[1] Thus far, we have carried out experiments on the reaction of triruthenium polyhydrido complex [{Cp*Ru(μ-H)}$_3$(μ_3-H)$_2$] (**1**) with alkanes in order to study the reaction chemistry of cluster complexes. Our results show that **1** reacts with an *n*-alkane to yield *closo*-ruthenacyclopentadiene **3** via the formation of perpendicularly coordinated alkyne complex **2** (Scheme 1).[2] Upon heating, H/D exchange occurs between C_6D_6 and the hydrido ligands of **2**, which can also be prepared by the reaction of **1** with 1-pentyne.[3] This shows that the C–H bond of benzene is able to be ruptured by **2**. We hence attempted to investigate the coupling between the hydrocarbyl ligands and the benzene moiety on the triruthenium cluster.

Herein, we report the formation of benzyne complex **5** by the reaction of **2** with benzene; in this reaction, two adjacent C–H bonds of benzene are cleaved. Subsequent coupling of the benzyne moiety with C_2 fragments results in the formation of a *closo*-ruthenacyclopentadiene complex. A linear alkylbenzene can then be liberated upon hydrogenation of this complex.



Scheme 1. Reaction of **1** with *n*-pentane.

Results and Discussion

Reaction of **2** with benzene proceeded slowly at 180 °C to afford a μ_3-benzyne complex **5** in 59% yield (Scheme 2). Complex **5** was identified by NMR spectroscopy, and its structure was confirmed by X-ray diffraction (XRD) studies (Figure 1).

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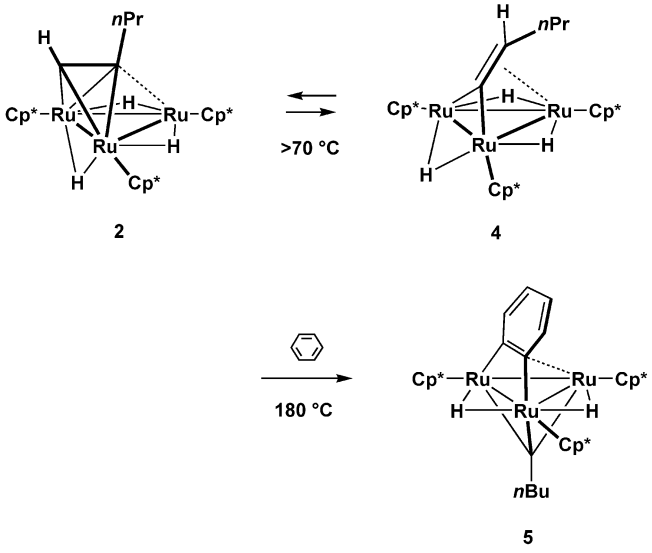


Scheme 2. Pre-equilibrium between **2** and **4**, and reaction with benzene.

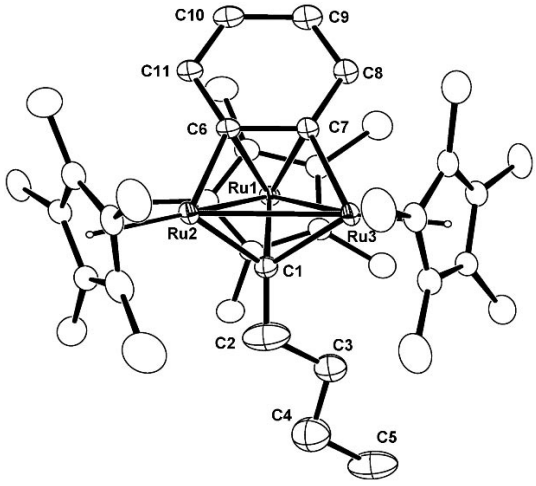


Figure 1. Molecular structure and labeling scheme of **5** with 30% thermal ellipsoid probability.

The XRD results unequivocally demonstrate the parallel orientation of the benzyne ligand with one of the Ru–Ru bonds. The benzyne ligand is σ bonded to Ru2 and Ru3 and π coordinated to Ru1. This π coordination of the benzyne moiety diminishes delocalization of π electrons, which in turn results in a notable bond alteration in the six-membered ring.

Two broad signals attributed to the hydrido ligands are observed at δ = –22.91 and –16.10 ppm in the ^{1}H NMR spectrum recorded at 23 °C. Broadening of these signals arises from site exchange of the hydrido ligands. As a consequence, two of the three Cp* signals become equivalent and appear as a single broad peak. These spectra reached a low-temperature limit at –40 °C. These phenomena are similar to those observed for triruthenium μ_3-alkylidyne–μ_3(‖)-alkyne complexes.[4]

The ^{13}C NMR signals corresponding to the benzyne ligand appear at δ = 119.0 (d), 119.5 (d), 124.7 (s), 142.6 (d), 145.8 (d), and 157.9 (s) ppm at –40 °C. The inequality between the two quaternary carbon atoms of the μ_3-benzyne ligand clearly implies that the two hydrido ligands are unsymmetrically located with respect to the plane that bisects the Ru2–Ru3 and C6–C7 vectors.

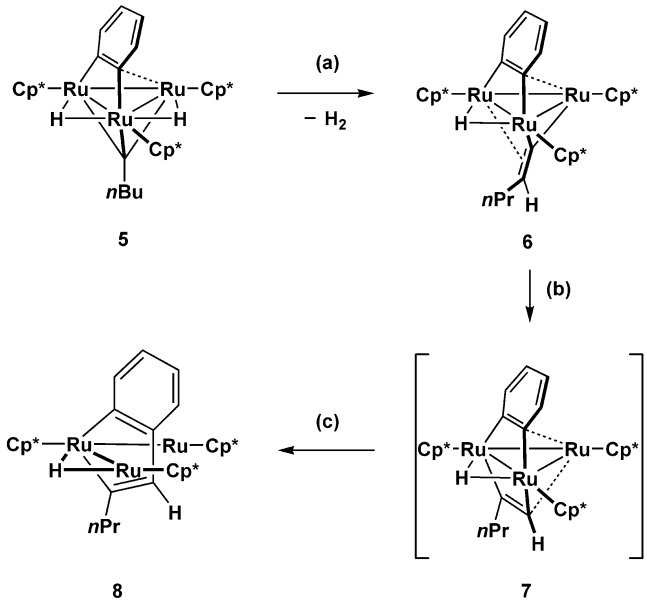
As shown in the previous paper, perpendicularly coordinated alkyne complex **2** is in equilibrium with the corresponding μ_3-alkenylidene complex **4** at temperatures above 70 °C; further, it is also shown that a μ_3-alkenylidene complex is more reactive than an alkyne complex.[5] Therefore, it can be reasonably proposed that the reaction proceeds via the formation of alkenylidene species. Benzene is expected to coordinate with **4** from the less-hindered face of the Ru_3 plane and undergo C–H bond activation. Subsequent insertion of the μ_3-pentenylidene group into an Ru–H bond affords a μ_3-pentylidyne ligand.

Cluster compounds containing a benzyne ligand have been intensively studied with regard to the active species formed on a metal surface.[6] Benzyne complexes are generally synthesized via E–Ph bond cleavage [E = P, As, Sb, NC, C(O), S];[7] however, very few attempts have been made for the direct synthesis of these complexes from unsubstituted benzene.[8] Lewis and co-workers reported the formation of a μ_3-benzyne complex by the reaction of a nitrile-substituted triosmium cluster with benzene.[8c] However, owing to degradation of the cluster skeleton, many byproducts were formed in this reaction. In contrast, because of its high thermal stability, the trimetallic skeleton of **2** remains unaffected during the reaction; this enables us to carry out a detailed investigation of the reactivity of the μ_3-benzyne complex.

Thermolysis of **5** at 180 °C yielded *closo*-ruthenacyclopentadiene complex **8** via μ_3-pentenylidene complex **6** (Scheme 3). The ratio of the concentrations of **6** and **8** depends on the reaction time. Upon heating at 180 °C for 24 h, 82% of **5** was consumed, and the concentration of **6** reached 63%. Prolonged heating of **6** at 180 °C resulted in the exclusive formation of **8**.[9] It is noteworthy that the two hydrocarbyl ligands separated by the Ru_3 plane are coupled together to form a C_{11} fragment. Both **6** and **8** were isolated and identified by NMR spectroscopy and XRD analysis (Figures 2 and 3).

The ^{13}C NMR spectrum of **6** shows signals characteristic of the μ_3-alkenylidene moiety at δ = 308.3 (s) and 91.4 [d, J(C,H) = 152 Hz] ppm, in addition to the signals due to the μ_3-benzyne ligand. The XRD results show that the μ_3-pentenylidene and μ_3-benzyne moieties are π coordinated to Ru2 and Ru3, respectively. The hydrido ligand is located between the Ru1 and Ru2 atoms, to which the benzyne moiety is σ bonded.

Because complex **8** adopts the same *closo*-ruthenacyclopentadiene structure as **3**, its NMR spectroscopic data are comparable to those of **3**.[2] The ^{13}C NMR signals corresponding to the two triply bridging carbon atoms (C2 and C7 in Figure 3) in the ruthenacycle moiety appear at δ = 146.8 (s) and 124.1 (s) ppm; signals corresponding to the



Scheme 3. Skeletal rearrangement of the hydrocarbyl ligands in the trimetallic plane. Conditions: (a) 180 °C, 24 h; (b, c) 180 °C, 2 d.

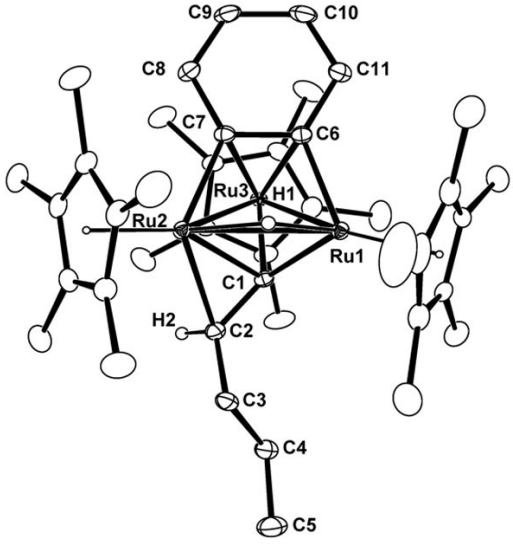


Figure 2. Molecular structure and labeling scheme of **6** with 30% thermal ellipsoid probability. A solvent molecule (pentane) in the unit cell is omitted for clarity.

doubly bridging carbon atoms (C1 and C6) are observed in the upfield region of the spectrum, that is, at δ = 64.2 [d, J(C,H) = 169 Hz] and 73.1 (s) ppm.

The open-structure of **8** and the formation of the C_{11} fragment are clearly demonstrated in the ORTEP diagram. Structural features of **8** resemble those of previously reported *closo*-metallacyclopentadiene complexes.[10] Although **8** has a hydrido ligand attached to one of the Ru–Ru bonds, the difference in the Ru–Ru distances in this complex is only 0.02 Å. This is probably due to the disordered structure about the position of the hydrido ligand. Hence, the exact position of the hydrido ligand cannot be determined.

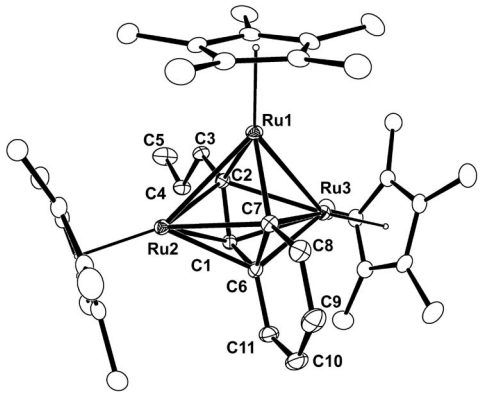
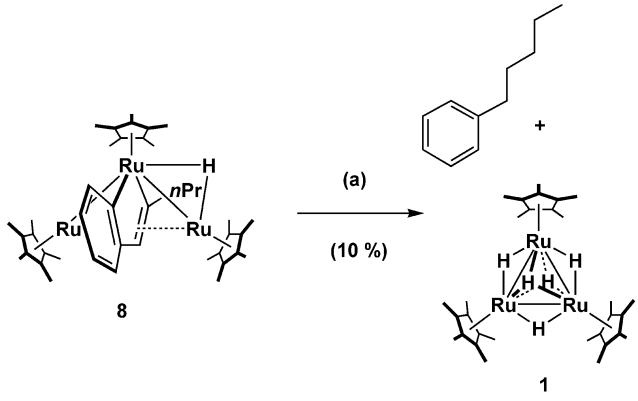


Figure 3. Molecular structure and labeling scheme of **8** with 30% thermal ellipsoid probability.

The formation of **6** was rationalized by β-H elimination from the μ_3-pentylidyne moiety along with liberation of dihydrogen. Then, a C–C bond was formed between the two hydrocarbyl moieties present on each face of the Ru_3 plane; this was accompanied by the rupture of a Ru–Ru bond. This type of C–C bond formation was similar to that observed in the coupling of two alkyne moieties on the well-known trimetallic cluster $M_3(CO)_8(PhCCPh)_2$ (M = Fe, Ru).[11] On the basis of this information, the μ_3-pentenylidene moiety would be converted into a pentyne ligand to form alkyne–benzyne intermediate **7**. The C–C bond formation that results in the formation of **8** occurs only at the methine carbon. Formation of a possible branched-type regioisomer is not observed.

When **8** is treated with pressurized dihydrogen, the formed hydrocarbyl ligand is liberated as *n*-pentylbenzene, and pentahydrido complex **1** is regenerated (Scheme 4). Although the reaction proceeds very slowly (10% completion in 3 d) and is not catalytic, the series of reactions mentioned in this paper correspond to the formation of a linear alkylbenzene by the reaction of an alkane with benzene.



Scheme 4. Hydrogenation of **8**. Conditions: (a) 7 atm H_2, 180 °C, 3 d.

Recently, two research groups independently reported excellent catalytic reactions for the direct alkylation of benzene.[12] In the reaction with propene, *n*-propylbenzene is preferentially produced rather than cumene; a selectivity of

up to 60% is generally achieved. The mechanism of alkylation of benzene by the trimetallic cluster differs completely from that observed for the alkylation of benzene using monometallic complexes. Linear selectivity would result from the cooperative interaction of multiple metal centers with the substrate. Therefore, the results of this study are expected to be useful in designing an alternative method for the synthesis of linear alkylbenzenes by a cluster catalyst.

Conclusions

In summary, we successfully carried out the activation of two adjacent C–H bonds in benzene to obtain a μ_3-benzyne complex; we also succeeded in forming a C–C bond between the two hydrocarbyl fragments present on each face of the trimetallic plane by partial metal–metal bond cleavage. Although these reactions are stoichiometric, *n*-pentylbenzene, which is difficult to synthesize by conventional Friedel–Crafts alkylation, is exclusively formed by the reaction of benzene. Our results also correspond to the functionalization of an alkane on a trimetallic cluster. The selective formation of linear alkylbenzene in this study shows the potential usefulness of polyhydrido clusters in synthetic reactions.

Experimental Section

General Procedures: All air- and moisture-sensitive compounds were manipulated using standard Schlenk and high-vacuum line techniques under an argon atmosphere. Dehydrated benzene, toluene, and pentane used in this study were purchased from Kanto Chemicals and stored under an argon atmosphere. C_6D_6 and [D_8]-thf were distilled from sodium benzophenone ketyl and stored under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded with a Varian INOVA–400 spectrometer. ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard. ^{13}C NMR spectra were referenced to the natural-abundance carbon signal of the solvent employed. Elemental analysis was performed with a Perkin–Elmer 2400II series CHN analyzer. Complex **2**was prepared according to a previously published method.[4]

[(Cp*Ru)$_3$\{μ_3-η^2($\|$)-C_6H_4\}(μ_3-C*n*Bu)(μ-H)$_2$] (5): A glass autoclave was charged with benzene (20 mL) and **2** (0.215 g, 0.28 mmol). The solution was heated at 180 °C for 3 d. The solvent was then removed under reduced pressure. The resulting solid was extracted with pentane (5 mL) and purified by column chromatography on neutral alumina. After the first purple band was removed with pentane, the second dark-brown fraction was collected with toluene. Removal of the solvent under reduced pressure afforded **5** (0.140 g, 59% yield) as a brown solid. ^{1}H NMR (400 MHz, [D_8]thf, –40 °C): δ = –22.99 [d, ^3J(H,H) = 2.0 Hz, 1 H, Ru-*H*], –16.16 [d, ^3J(H,H) = 2.0 Hz, 1 H, Ru-*H*], 1.13 [t, ^3J(H,H) = 7.2 Hz, 3 H, μ_3-CCH$_2$CH$_2$CH$_2$C*H*$_3$], 1.40 (s, 15 H, C$_5$*Me*$_5$), 1.63 (by HMQC; μ_3-CCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.77 (s, 15 H, C$_5$*Me*$_5$), 1.78 (s, 15 H, C$_5$*Me*$_5$), 1.91 (by HMQC; μ_3-CCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.48 (m, 1 H, μ_3-CC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.57 (m, 1 H, μ_3-CC*H*$_2$CH$_2$CH$_2$CH$_3$) 6.41 [dd, ^3J(H,H) = 8.0, 7.6 Hz, 1 H, μ_3-C$_6$*H*$_4$], 6.73 [dd, ^3J(H,H) = 8.0, 8.0 Hz, 1 H, μ_3-C$_6$*H*$_4$], 7.03 [d, ^3J(H,H) = 7.6 Hz, 1 H, μ_3-C$_6$*H*$_4$], 7.48 [d, ^3J(H,H) = 8.0 Hz, 1 H, μ_3-C$_6$*H*$_4$] ppm. ^{13}C NMR (100 MHz, [D_8]thf, –40 °C): δ = 10.4 [q, ^1J(C,H) = 126 Hz, C$_5$*Me*$_5$], 11.9 [q, ^1J(C,H) = 126 Hz, C$_5$*Me*$_5$], 12.0 [q, ^1J(C,H) = 126 Hz, C$_5$*Me*$_5$], 14.9 [q, ^1J(C,H) = 124 Hz, μ_3-CCH$_2$CH$_2$CH$_2$*C*H$_3$], 24.4 [q, ^1J(C,H) = 122 Hz, μ_3-CCH$_2$CH$_2$*C*H$_2$CH$_3$], 36.0 [t, ^1J(C,H) = 124 Hz, μ_3-CCH$_2$*C*H$_2$CH$_2$CH$_3$], 58.8 [dd, ^1J(C,H) = 126, 123 Hz, μ_3-C*C*H$_2$CH$_2$CH$_2$CH$_3$], 91.2 (s, *C*$_5$Me$_5$), 95.3 (s, *C*$_5$Me$_5$), 95.6 (s, *C*$_5$Me$_5$), 119.0 [d, ^1J(C,H) = 154 Hz, μ_3-*C*$_6$H$_4$], 119.5 [d, ^1J(C,H) = 154 Hz, μ_3-*C*$_6$H$_4$], 124.7 (s, μ_3-*C*$_6$H$_4$), 142.6 [d, ^1J(C,H) = 155 Hz, μ_3-*C*$_6$H$_4$], 145.8 [d, ^1J(C,H) = 154 Hz, μ_3-*C*$_6$H$_4$], 157.9 (s, μ_3-*C*$_6$H$_4$), 334.1 (s, μ_3-*C*CH$_2$CH$_2$CH$_2$CH$_3$) ppm. $C_{41}H_{60}Ru_3$ (856.13): calcd. C 57.52, H 7.06; found C 57.61, H 7.06.

[(Cp*Ru)$_3$\{μ_3-η^2($\|$)-C_6H_4\}\{μ_3-η^2-C=C(H)*n*Pr\}(μ-H)] (6): A glass-tube equipped with a Teflon-valve was charged with benzene (3 mL) and **5** (20.4 mg, 0.024 mmol). The solution was heated at 180 °C for 1 d. The solvent was then removed under reduced pressure. The resulting solid was extracted with pentane (5 mL) and purified by column chromatography on neutral alumina. After the first purple band was removed with pentane, the second dark-brown band was collected with pentane/toluene (12:1). Product **6** (5.8 mg, 28% yield) was obtained as a brownish yellow solid upon removal of the solvent under reduced pressure. ^{1}H NMR (400 MHz, [D_8]thf, 23 °C): δ = –28.08 (s, 1 H, Ru-*H*), 1.22 [t, ^3J(H,H) = 7.6 Hz, 3 H, –CH$_2$CH$_2$C*H*$_3$], 1.40 (s, 15 H, C$_5$*Me*$_5$), 1.42 (m, 2 H, –CH$_2$C*H*$_2$CH$_3$), 1.56 (br., 15 H, C$_5$*Me*$_5$), 1.84 (br., 15 H, C$_5$*Me*$_5$), 2.11 (m, 2 H, –C*H*$_2$CH$_2$CH$_3$), 5.95 [dd, ^3J(H,H) = 7.2, 6.8 Hz, 1 H, μ_3-C=C(*H*)*n*Pr], 6.34 (br., 1 H, μ_3-C$_6$*H*$_4$), 6.55 (br., 1 H, 1 H, μ_3-C$_6$*H*$_4$), 7.44 (br., 1 H, μ_3-C$_6$*H*$_4$), 7.90 (br., 1 H, μ_3-C$_6$*H*$_4$) ppm. ^{13}C NMR (100 MHz, [D_8]thf, 23 °C): δ = 10.4 [q, ^1J(C,H) = 126 Hz, C$_5$*Me*$_5$], 11.2 [q, ^1J(C,H) = 126 Hz, C$_5$*Me*$_5$], 12.5 [q, ^1J(C,H) = 124 Hz, C$_5$*Me*$_5$], 14.9 [q, ^1J(C,H) = 124 Hz, –CH$_2$CH$_2$*C*H$_3$], 30.1 [t, ^1J(C,H) = 123 Hz, –CH$_2$*C*H$_2$CH$_3$], 40.0 [t, ^1J(C,H) = 126 Hz, –*C*H$_2$CH$_2$CH$_3$], 89.3 (s, *C*$_5$Me$_5$), 91.4 [d, ^1J(C,H) = 152 Hz, μ_3-C=*C*(H)*n*Pr], 93.3 (s, *C*$_5$Me$_5$), 94.3 (s, *C*$_5$Me$_5$), 115.0 [d, ^1J(C,H) = 155 Hz, μ_3-*C*$_6$H$_4$], 117.1 [d, ^1J(C,H) = 155 Hz, μ_3-*C*$_6$H$_4$], 147.0 [d, ^1J(C,H) = 149 Hz, μ_3-*C*$_6$H$_4$], 147.9 [d, ^1J(C,H) = 148 Hz, μ_3-*C*$_6$H$_4$], 155.2 (s, μ_3-*C*$_6$H$_4$), 156.2 (s, μ_3-C$_6$H$_4$), 308.3 [s, μ_3-*C*=C(H)*n*Pr] ppm. $C_{41}H_{58}Ru_3$ (854.11): calcd. C 57.66, H 6.84; found C 57.44, H 6.89.

[(Cp*Ru)$_2$\{Cp*Ru[–C(*n*Pr)C=C(H)–C$_6$H$_4$–]\}(μ-H)] (8): A glass-tube equipped with a Teflon-valve was charged with benzene (10 mL) and **5** (33.6 mg, 0.039 mmol). The solution was heated at 180 °C for 3 d. The solvent was then removed under reduced pressure. The resulting solid was extracted with pentane (5 mL) and purified by column chromatography on neutral alumina with pentane. After the first purple band was removed, the second dark-brown band was collected. Product **8** (11.2 mg, 34% yield) was obtained as a brownish yellow solid upon removal of the solvent under reduced pressure. ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ = –10.24 (s, 1 H, Ru-*H*), 1.02 [t, ^3J(H,H) = 6.8 Hz, 3 H, –CH$_2$CH$_2$C*H*$_3$], 1.40 (by COSY; –CH$_2$C*H*$_2$CH$_3$), 1.41 (s, 15 H, C$_5$*Me*$_5$), 1.54 (s, 15 H, C$_5$*Me*$_5$), 1.80 (by COSY; –C*H*$_2$CH$_2$CH$_3$), 2.21 (s, 15 H, C$_5$*Me*$_5$), 4.94 [s, Ru\{–C(*n*Pr)=C*H*–C$_6$H$_4$–\}], 6.21 [dd, ^3J(H,H) = 8.8, 6.8 Hz, 1 H, Ru\{–C(*n*Pr)=C(H)–C$_6$*H*$_4$–\}], 6.57 [dd, ^3J(H,H) = 8.8, 6.8 Hz, 1 H, Ru\{–C(*n*Pr)=C(H)–C$_6$*H*$_4$–\}], 6.80 [d, ^3J(H,H) = 8.8 Hz, 1 H, Ru\{–C(*n*Pr)=C(H)–C$_6$*H*$_4$–\}], 7.58 [d, ^3J(H,H) = 8.8 Hz, 1 H, Ru\{–C(*n*Pr)=C(H)–C$_6$H$_4$–\}] ppm. ^{13}C NMR (100 MHz, C_6D_6, 23 °C): δ = 10.5 [q, ^1J(C,H) = 126 Hz, C$_5$*Me*$_5$], 11.1 [q, ^1J(C,H) = 125 Hz, C$_5$*Me*$_5$], 12.8 [q, ^1J(C,H) = 125 Hz, C$_5$*Me*$_5$], 14.7 [q, ^1J(C,H) = 129 Hz, –CH$_2$CH$_2$*C*H$_3$], 26.5 [t, ^1J(C,H) = 125 Hz, – CH$_2$*C*H$_2$CH$_3$], 47.7 [t, ^1J(C,H) = 129 Hz, –*C*H$_2$CH$_2$CH$_3$], 64.2 [d, ^1J(C,H) = 169 Hz, Ru\{–C(*n*Pr)=*C*(H)–C$_6$H$_4$–\}], 73.1 [s, Ru\{–C(*n*Pr)=C(H)–*C*$_6$H$_4$–\}], 80.6 (s, *C*$_5$Me$_5$), 81.0 (s, *C*$_5$Me$_5$), 90.5 (s, *C*$_5$Me$_5$), 114.7 [d, ^1J(C,H) = 141 Hz, Ru-

{–C(*n*Pr)=C(H)–C_6H_4–}], 121.6 [d, ^1J(C,H) = 162 Hz, Ru{–*C*(*n*Pr)=CH–C_6H_4–}], 124.1 [s, Ru{–C(*n*Pr)=C(H)–C_6H_4–}], 129.6 [d, ^1J(C,H) = 157 Hz, Ru{–C(*n*Pr)=C(H)–C_6H_4–}], 146.8 [s, Ru{–*C*(*n*Pr)=C(H)–C_6H_4–}], 147.7 [d, ^1J(C,H) = 157 Hz, Ru{–C(*n*Pr)=C(H)–*C*$_6H_4$–}] ppm. $C_{41}H_{58}Ru_3$ (854.11): calcd. C 57.66, H 6.84; found C 57.58, H 6.69.

CCDC-728587 (for **5**), -728588 (for **6**), and -728589 (for **8**) contain supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental and crystallographic details for **5**, **6**, and **8**.

Acknowledgments

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[9] During formation of **8**, a byproduct characterized as a triruthenium complex containing a perpendicularly coordinated 1-phenyl-1-butyne ligand, [(Cp*Ru)$_3$(μ_3-CH){μ_3-η^2:η^2($\perp$)-EtC=CPh}], was also obtained in 12% yield (by NMR). This complex was presumably formed by the reaction of one of the intermediates to **3** with benzene. Experimental details will be published elsewhere in near future. ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ = 1.70 (s, 30 H, C_5Me_5), 1.57 (s, 15 H, C_5Me_5), 1.05 [t, ^3J(H,H) = 7.5 Hz, 3 H, –CH_2CH_3], 3.07 [q, ^3J(H,H) = 7.5 Hz, 2 H, –CH_2CH_3], 5.98 [d, ^3J(H,H) = 8.0 Hz, 2 H, *o*-C_6H_5], 6.82 [t, ^3J(H,H) = 8.0 Hz, 1 H, *p*-C_6H_5], 7.10 [t, ^3J(H,H) = 8.0 Hz, 2 H, *m*-C_6H_5], 17.14 (s, 1 H, μ_3-C*H*) ppm.

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