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Direct Arylation of a Cluster-Bound Alkyne Ligand with Benzene†

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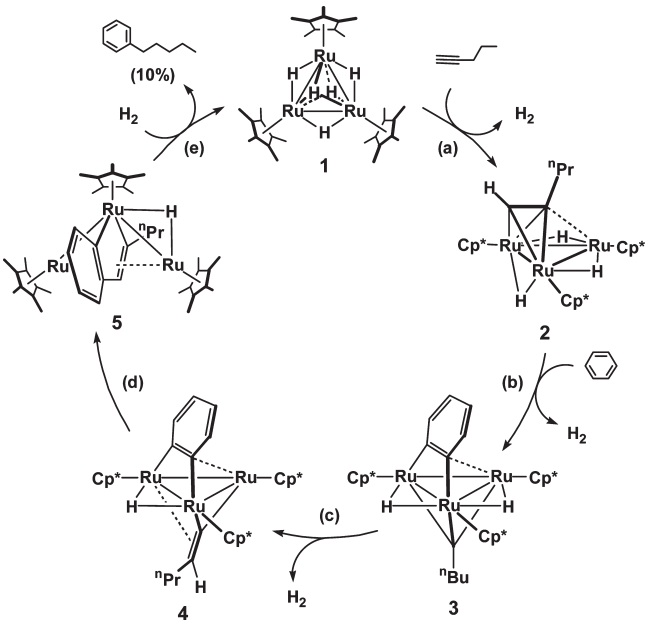
*Summary: Treatment of a triruthenium complex having μ_3-methylidyne and μ_3-propyne ligands, $(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^2\text{-}HCCMe)(\mu\text{-}H)_2$ (**6**), with benzene results in arylation of the propyne ligand via the C−H bond activation of benzene to yield the μ_3-phenylmethylacetylene complex $(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}PhCCMe)$ (**7**). An X-ray diffraction study of 7 clearly established that regiospecific arylation occurred at the terminal position of the propyne ligand.*

Arylation of olefins and alkynes by way of C−H bond activation of arenes has been one of the most intensely studied areas of organometallic chemistry in years,[1] emerging as an economically and environmentally useful alternative to cross-coupling reactions using aryl halides. Significant advances in catalytic metal-mediated Ar−H bond activation have been achieved in recent years, as exemplified by selective C−C bond formation at the ortho position by the directing effect of a heteroatom tether[2] and direct formation of styrene by Pd(II)-catalyzed oxidative arylation of ethylene.[3]

Recently, two excellent catalytic systems for the direct alkylation of benzene with linear preference were independently reported by two groups led by Matsumoto and Periana[4] and by Gunnoe.[5] Linear selectivity is determined by the direction of olefin insertion into the metal−phenyl bond formed by the C−H bond activation, whereas the orientation of the insertion is controlled by the steric environment around the metal center. However, selectivity for *n*-propylbenzene still remains around 60% when using propene. In this context, an alternative approach for the alkylation of benzene seems to be necessary.

We thus tried another route to access alkylbenzene using a polyhydrido cluster and reported the stoichiometric alkylation of benzene using triruthenium complex **2** having a (⊥)-alkyne ligand (Scheme 1).[6] This reaction was found to proceed via the formation of μ_3-benzyne complexes **3** and **4**; C−C bond formation took place between the μ_3-benzyne ligand and the C_5 fragment separated by the Ru_3 plane of **4**. Benzene was coordinated to the trimetallic site from the less hindered face of the Ru_3 plane of **2** and underwent C−H bond activation. In this paper, we report another type of arylation of an alkyne ligand using a trimetallic complex having alkyne and μ_3-methylidyne ligands on both faces of the Ru_3 plane. Occupation of both faces of the Ru_3 plane by hydrocarbyl groups prevents the approach of benzene in the same way as in **2** to form a μ_3-benzyne complex. Nevertheless, arylation occurred at the alkyne ligand in a manner different from that observed in **4**.

Scheme 1. Stoichiometric Arylation of an Alkyne Ligand on a Triruthenium Cluster[a]



[a] Legend: (a) 25 °C, 30 min; (b) 180 °C, 3 days; (c) 180 °C, 24 h; (d) 180 °C, 2 days; (e) 7 atm H_2, 180 °C, 3 days.

As described in our previous paper, the μ_3-methylidyne−μ_3-η^2(∥)-alkyne complex $(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^2(\parallel)\text{-}MeCCH)(\mu\text{-}H)_2$ (**6**) was prepared by the reaction of **1** with butadiene at 80 °C.[7] Thermolysis of **6** in benzene at 180 °C for 12 h resulted in the exclusive formation of the (⊥)-phenylmethylacetylene complex $(Cp^*Ru)_3(\mu_3\text{-}CH)(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-}PhCCMe)$ (**7**) in 92%

† Part of the Dietmar Seyferth Festschrift. Dedicated to Professor Dietmar Seyferth in honor of his outstanding service as Editor-in-Chief of Organometallics.

(1) (a) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633–639. (b) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826–834. (c) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731–1770.

(2) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529–531.

(3) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992–1995.

(4) (a) Matsumoto, T.; Taube, D. J.; Periana, R. A.; Taube, H.; Yoshida, H. *J. Am. Chem. Soc.* **2000**, *122*, 7414–7415. (b) Matsumoto, T.; Yoshida, H. *Catal. Lett.* **2001**, *72*, 107–109. (c) Periana, R. A.; Liu, X. Y.; Bhalla, G. *Chem. Commun.* **2002**, 3000–3001. (d) Matsumoto, T.; Periana, R. A.; Taube, D. J.; Yoshida, H. *J. Mol. Catal. A: Chem.* **2002**, *180*, 1–18. (e) Bhalla, G.; Oxgaard, J.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2005**, *24*, 3229–3232.

(5) (a) Lail, M.; Arrowood, B. N.; Gunnoe, T. B. *J. Am. Chem. Soc.* **2003**, *125*, 7506–7507. (b) Lail, M.; Bell, C. M.; Conner, D.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *Organometallics* **2004**, *23*, 5007–5020. (c) Feng, Y.; Lail, M.; Barakat, K. A.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 14174–14175.

(6) Moriya, M.; Tahara, A.; Takao, T.; Suzuki, H. *Eur. J. Inorg. Chem.* **2009**, 3393–3397.

(7) Takemori, T.; Inagaki, A.; Suzuki, H. *J. Am. Chem. Soc.* **2001**, *123*, 1762–1763.

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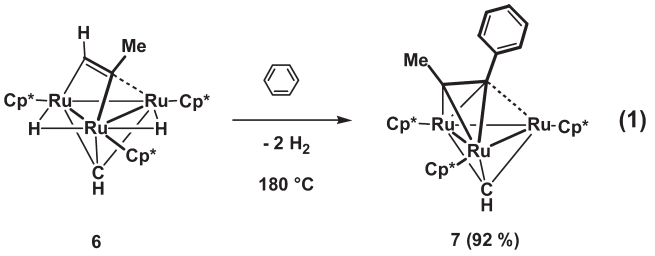
yield (eq 1).[8] The rate of this reaction was significantly faster than the transformation of **4** to **5**, which required 2 days at 180 °C. Reaction of **6** with benzene still proceeded at 120 °C, although it took more time (3 days).



6 7 (92 %)

It is noteworthy that the C−C bond between the methine carbon of the alkyne ligand and benzene is formed in an intermolecular fashion. Few examples of intramolecular reactions between alkyne and arene moieties on a trimetallic cluster are known,[9] but to the best of our knowledge, this type of direct arylation via the C−H bond activation of unactivated benzene by a cluster compound is unprecedented. Although Friedel−Crafts alkylation of benzene directly provides a C−C bond, it is a branched, not linear, alkylbenzene. It should also be noted that C−C bond formation occurred selectively at the terminal position of the alkyne ligand; C−C bond formation at the 2-position of the propyne ligand was completely suppressed on the Ru_3 plane.

Perpendicular coordination of the phenylmethylacetylene ligand in **7** was clearly established by an X-ray diffraction study (Figure 1).[10] The phenylmethylacetylene ligand is coordinated to the Ru(1)−Ru(1#) edge in a perpendicular mode and bisects the Ru_3 triangle. On the basis of the orientation of the alkyne ligand, two regioisomers for **7** are possible. However, only one isomer, that with the phenyl group positioned inside the Ru_3 core, was obtained. This was attributed to thermodynamic factors, where steric repulsion between the Cp* groups and the phenyl group on the acetylenic carbon are minimized.[11]

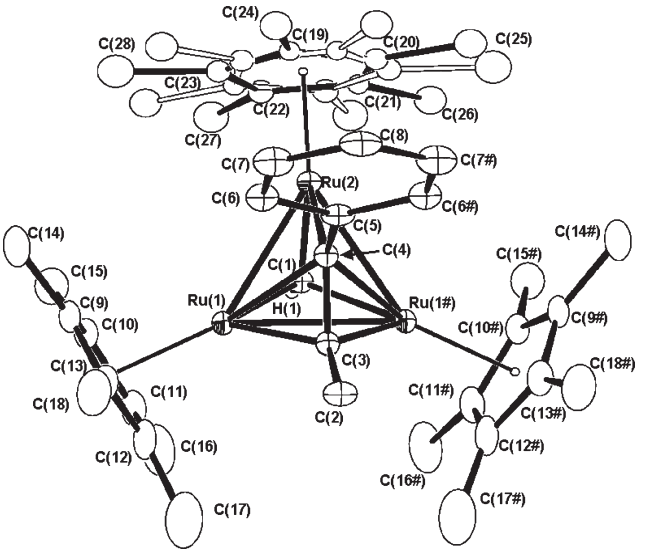


Figure 1. Molecular structure and labeling scheme of **7** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(1#), 2.6799(13); Ru(1)−Ru(2), 2.7024(13); Ru(1)−C(1), 2.020(6); Ru(1)−C(2), 1.980(5); Ru(1)−C(3), 2.213(6); Ru(2)−C(1), 1.960(7); Ru(2)−C(3), 2.064(8); C(2)−C(3), 1.466(10); C(2)−C(4), 1.514(11), C(3)−C(5), 1.480(10); Ru(2)−Ru(1)−Ru(1#), 60.28(2); Ru(1)−Ru(2)−Ru(1#), 59.46(2); C(2)−C(3)−C(4), 125.2(6); C(2)−C(3)−C(5), 115.0(6).

The size of the Ru_3 triangle of **7** is significantly smaller than that of the corresponding (⊥)-alkyne complex {Cp*Ru-(μ-H)}$_3$(μ_3-η^2:η^2(⊥)-PhCCMe) (**8**), which was obtained from the reaction of **1** and 1-phenyl-1-propyne.[11a,12] The Ru(1)−Ru(1#) length of 2.6799(13) Å, on which the phenylmethylacetylene ligand is perpendicularly coordinated, is shorter than that of **8** by 0.16 Å. The difference in the Ru−Ru bond lengths between **7** and **8** likely arises from the presence of the μ_3-methylidyne ligand, which, in comparison to the μ-hydrido ligands, seems to bind the ruthenium atoms more tightly.

The C(2)−C(3) bond distance (1.466(10) Å) is considerably longer than that of **8** (1.410(6) Å), while the Ru(2)−C(3) distance is significantly shorter: i.e. 2.064(8) Å in **7** compared to 2.139(5) Å in **8**. These structural features imply that back-donation from the metal centers to the π*(CC) orbital of the alkyne moiety was significantly enhanced by the replacement of the hydrido ligands with the μ_3-methylidyne ligand.

Similar to the case for other (⊥)-alkyne complexes derived from **1**, the alkyne ligand of **7** exhibits dynamic behavior, referred to as *switchback motion*.[13] The alkyne moiety of **7** slips over the Ru_3 core by alternating the position of the inner- and outer-carbon atoms in each step, causing the environments of all three Cp* groups to become equivalent within the NMR time scale. While the ^{1}H NMR spectrum of **7** revealed two well-separated signals assignable to the Cp* groups at δ 1.41 (15H) and 1.72 (30H) at 25 °C, these signals became broaden with increasing temperature.

The ^{13}C signal of the inner carbon of a (⊥)-alkyne ligand appears in the higher magnetic field region due to its five-coordinated nature as well as the ring current shielding effect caused by the three surrounding Cp* groups.[11] In the ^{13}C

(8) Benzene (10 mL) and **6** (50.6 mg, 0.066 mmol) were charged in a glass autoclave. The reaction vessel was heated to 180 °C for 12 h with vigorous stirring. After the solvent was removed under reduced pressure, the residual solid was washed with methanol (5 mL × 3). The residual solid was then dried under reduced pressure, and **7** was obtained as a red solid (51.2 mg, 0.061 mmol, 92% yield). ^{1}H NMR (400 MHz, 23 °C, THF-d_8): δ 1.41 (s, 15H, C_5Me_5), 1.72 (s, 30H, C_5Me_5), 2.28 (s, 3H, PhCC*Me*), 5.65 (dd, J_{H-H} = 7.6, 1.0 Hz, 2H, *o-Ph*), 6.63 (tt, J_{H-H} = 7.2, 1.0 Hz, 1H, *p-Ph*), 6.94 (dd, J_{H-H} = 7.6, 7.2 Hz, 2H, *m-Ph*), 17.28 (s, 1H, μ_3-C*H*). ^{13}C{^{1}H} NMR (100 MHz, 23 °C, THF-d_8): δ 11.6 (C_5Me_5), 27.5 (PhCC*Me*), 91.2 (C_5Me$_5$), 94.3 (C_5Me$_5$), 108.9 (Ph*C*CMe), 121.3 (*Ph*), 124.6 (*Ph*), 127.3 (*Ph*), 147.3 (*Ph*), 223.6 (PhC*C*Me), 348.8 (μ_3-*C*H). Anal. Calcd for $C_{40}H_{54}Ru_3$: C, 57.33; H, 6.49. Found: C, 57.62; H, 6.15.

(9) (a) Bruce, M. I.; Humphrey, P. A.; Skelton, B. W.; White, A. H.; Costuas, K.; Halet, J.-F. *Dalton* **1999**, 479–486. (b) Deng, M.; Leong, W. K. *Organometallics* **2002**, *21*, 1221–1226.

(10) Crystal data for **7**: $C_{40}H_{54}Ru_3$, fw = 838.04, monoclinic, space group *C*2/*m* (No. 12), *a* = 17.418(11) Å, *b* = 18.059(7) Å, *c* = 11.485(6) Å, β = 103.33(5)°, *V* = 3515(3) Å^3, *Z* = 4, D_{calcd} = 1.583 g/cm^3, temperature −120 °C, μ(Mo Kα) = 12.99 cm^{-1}, R1 = 0.0420, wR2 = 0.1106 for 2685 reflections with $I > 2\sigma(I)$.

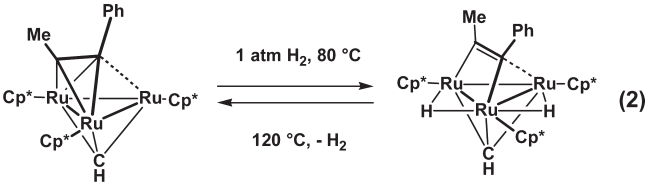
(11) (a) Takao, T.; Takaya, Y.; Murotani, E.; Tenjimbayashi, R.; Suzuki, H. *Organometallics* **2004**, *23*, 6094–6096. (b) Riehl, J.-F.; Koga, N.; Morokuma, K. *Organometallics* **1994**, *13*, 4765–4780.

(12) Results of the X-ray diffraction studies of **8** and molecular structure are given in the Supporting Information. Crystal data for **8**: $C_{39}H_{56}Ru_3$, fw = 828.05, monoclinic, space group *C*2/*m* (No. 12), *a* = 17.417(5) Å, *b* = 18.432(5) Å, *c* = 11.512(3) Å, β = 104.445(10)°, *V* = 3578.9(17) Å^3, *Z* = 4, D_{calcd} = 1.537 g/cm^3, temperature −50 °C, μ(Mo Kα) = 12.75 cm^{-1}, R1 = 0.0379, wR2 = 0.0925 for 4036 reflections with $I > 2\sigma(I)$. Hydrogen atoms attached to the ruthenium atoms were located by sequential difference Fourier synthesis and refined isotropically.

(13) Takao, T.; Kakuta, S.; Tenjimbayashi, R.; Takemori, T.; Murotani, E.; Suzuki, H. *Organometallics* **2004**, *23*, 6090–6093.

NMR spectra of **7**, a singlet assignable to the inner acetylenic carbon was observed at δ 108.9, while the signal of the outer carbon atom appeared in the lower magnetic field region characteristic of a bridging alkylidene ligand (δ 223.6). Both signals underwent a downfield shift of ca. 30−40 ppm in comparison to those of **8** (C^{in}, δ 73.7: C^{out}, δ 181.1).[11a]

When the reaction was carried out at 100 °C for 3 days, slow formation of a trace amount of an intermediate, $(Cp^*Ru)_3(\mu\text{-}H)_2(\mu_3\text{-}CH)(\mu_3\text{-}\eta^2(\parallel)\text{-}PhCCMe)$ (**9**), containing a (∥)-phenylmethylacetylene ligand was observed. Alternatively, **9** was synthesized in 89% yield by treatment of **7** with 1 atm of H_2 at 80 °C (eq 2).[14] Complex **9** was stable below 80 °C; however, it was quantitatively converted to **7** upon heating at 120 °C. Although there have been a few examples of reversible transformation between the two alkyne bridging modes via the addition of CO,[15] this is the first example of the reversible transformation between them via the oxidative addition of dihydrogen.



7 **9 (89%)** (2)

The parallel coordination mode of the phenylmethylacetylene ligand in **9** was unambiguously confirmed by an X-ray diffraction study (Figure 2).[16] Although a pair of enantiomeric isomers having similar geometrical features was present in the unit cell, only one enantiomer is depicted in Figure 2. The alkyne moiety is σ-bonded to Ru(1) and Ru(3) and π-bonded to Ru(2) in a $\mu_3\text{-}\eta^2(\parallel)$ fashion. The C(2)−C(3) distance of 1.395(5) Å lies within reported values for (∥)-alkyne ligands on triruthenium complexes (1.31−1.42 Å).[17] The hydrido ligands are coordinated to the Ru_3 core in an unsymmetrical manner with respect to the alkyne ligand; one of the hydrido ligands is located on the Ru(1)−Ru(3) edge, while the other is on the Ru(2)−Ru(3) edge below the phenyl group.

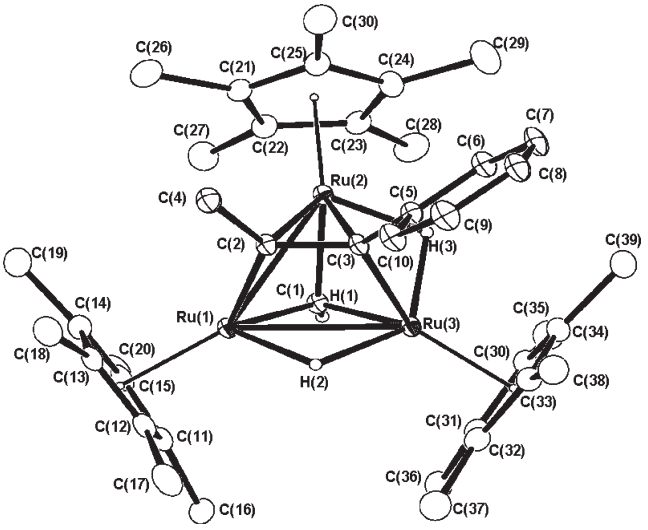


Figure 2. Molecular structure and labeling scheme of **9** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)−Ru(2), 2.7521(5); Ru(1)−Ru(3), 2.7724(5); Ru(2)−Ru(3), 2.6765(5); Ru(1)−C(1), 1.951(4); Ru(1)−C(2), 2.028(4); Ru(2)−C(1), 2.047(4); Ru(2)−C(2), 2.173(4); Ru(2)−C(3), 2.147(4); Ru(3)−C(1), 2.014(4); Ru(3)−C(3), 2.104(4); C(2)−C(3), 1.395(5); C(2)−C(4), 1.507(6); C(3)−C(5), 1.478(5); Ru(2)−Ru(1)−Ru(3), 57.955(3); Ru(1)−Ru(2)−Ru(3), 61.402(12); Ru(1)−Ru(3)−Ru(2), 60.643(12); C(2)−C(3)−C(4), 122.5(4); C(2)−C(3)−C(5), 126.5(4).

Since complex **6** is coordinatively saturated (48e configuration), elimination of dihydrogen is required to generate a coordination site for benzene. Elimination of dihydrogen from **6** yields the intermediate **A**, in which the alkyne ligand adopts a perpendicular coordination mode due to the 46e configuration nature of the complex[18] (Scheme 2). The (⊥)-alkyne ligand in **A** is then transformed into a μ_3-propenylidene ligand in **B** via a 1,2-shift of the methine proton. We have reported facile interconversion between a perpendicularly coordinated phenylacetylene complex and a μ_3-styrylidene complex, where the μ_3-styrylidene isomer was shown to be more reactive than the (⊥)-alkyne complex.[19] Thus, we propose that benzene coordinates to the μ_3-propenylidene intermediate **B** and undergoes C−H bond scission to form the phenyl intermediate **D**. For the formation of the phenylmethylacetylene ligand, a *Z* isomer is required to form for the intermediate **E**. Therefore, it is reasonable to assume that C−H bond activation occurs at the ruthenium center beneath the methyl group on the μ_3-propenylidene ligand. Subsequent reductive C−C bond coupling followed by C−H bond cleavage at the μ-vinyl group in **E** affords the parallel alkyne complex **9**, and finally the (⊥)-alkyne complex **7** was obtained after elimination of dihydrogen.

(14) Heptane (20 mL) and **7** (222.4 mg, 0.265 mmol) were charged in a glass autoclave. The reaction vessel was degassed and then charged with 1 atm of dihydrogen. The solution was heated at 80 °C for 12 h with vigorous stirring, after which the solvent was removed under reduced pressure. The residual solid was dissolved in 10 mL of pentane and purified by column chromatography on alumina (Merck, Art. No. 1097) using toluene as eluent. The first red band, containing **9**, was collected. Drying under reduced pressure afforded **9** as an orange solid (196.5 mg, 0.235 mmol, 89% yield). ^{1}H NMR (400 MHz, 23 °C, THF-d_8): δ −21.81 (s, 1H, Ru*H*), −16.17 (s, 1H, Ru*H*), 1.50 (s, 15H, C_5Me_5), 1.76 (s, 15H, C_5Me_5), 1.89 (s, 15H, C_5Me_5), 2.17 (s, 3H, PhCC*Me*), 6.37 (br, 1H, *o*-*Ph*), 6.83 (m, 1H, *p*-*Ph*), 7.04 (br, 2H, *m*-*Ph*), 7.10 (br, 1H, *o*-*Ph*), 14.39 (s, 1H, μ_3-C*H*). ^{13}C{^{1}H} NMR (100 MHz, 23 °C, THF-d_8): δ 11.0 (C_5Me_5), 11.4 (C_5Me_5), 12.3 (C_5Me_5), 28.2 (PhC*C*Me), 94.7 (C_5Me_5), 95.1 (C_5Me_5), 95.3 (C_5Me_5), 123.0 (*Ph*), 127.2 (Ph*C*CMe), 127.3 (*Ph*), 129.5 (*Ph*), 147.8 (*Ph*), 157.8 (Ph*C*CMe), 312.9 (μ_3-*C*H).

(15) (a) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Inorg. Chem.* **1991**, *30*, 4110–4112. (b) Peng, J.-J.; Peng, S.-M.; Lee, G.-H.; Chi, Y. *Organometallics* **1995**, *14*, 626–633. (c) Smith, A. K.; Harding, R. A. *J. Chem. Soc., Dalton Trans.* **1996**, 117–123. (d) Rivomanana, S.; Mongin, C.; Lavigne, G. *Organometallics* **1996**, *15*, 1195–1207. (e) Mays, M. J.; Raithby, P. R.; Sarveswaran, K.; Solan, G. A. *Dalton Trans.* **2002**, 1671–1677.

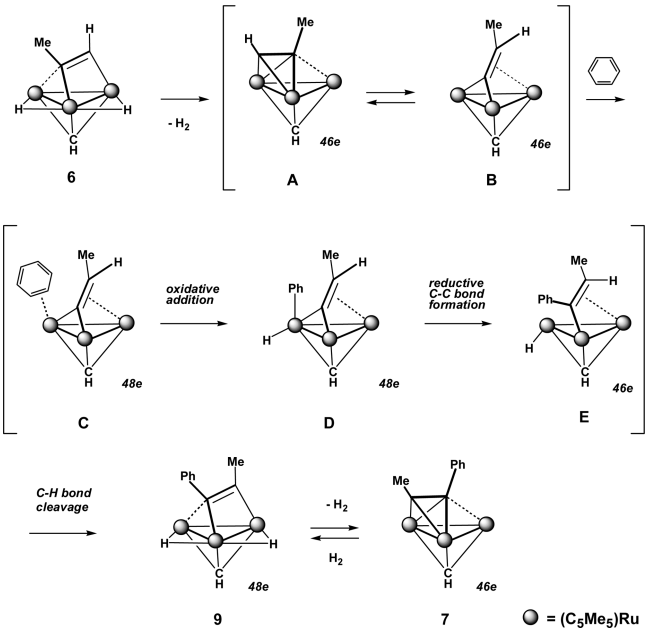
(16) Crystal data for **9**: $C_{40}H_{56}Ru_3$, fw = 840.06, monoclinic, space group $P2_1/n$ (No. 14), a = 25.106(4) Å, b = 11.6225(14) Å, c = 25.482(4) Å, β = 102.892(6)°, V = 7248.0(18) Å^3, Z = 8, D_{calcd} = 1.540 g/cm^3, temperature −160 °C, μ(Mo Kα) = 12.60 cm^{-1}, R1 = 0.0498, wR2 = 0.1010 for 15 589 reflections with $I > 2\sigma(I)$. Hydrogen atoms attached to the ruthenium atoms were located by sequential difference Fourier synthesis and refined isotropically.

(17) Structural data for 78 triruthenium complexes having a $\mu_3\text{-}\eta^2(\parallel)$-alkyne ligand were obtained from Cambridge Structural Database System Version 5.31 (November 2009 + 2 updates): Allen, F. H. *Acta Crystallogr.* **2002**, *B52*, 380–388.

(18) (a) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456–3467. (b) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858–3875. (c) Granozzi, G.; Tondello, E.; Casarin, M.; Aime, S.; Osella, D. *Organometallics* **1983**, *2*, 430–434. (d) Halet, J.-F.; Saillard, J.-Y.; Lissillour, R.; McGlinchey, M. J.; Jaoen, G. *Inorg. Chem.* **1985**, *24*, 218–224. (e) Osella, D.; Pospisil, L.; Fieldler, J. *Organometallics* **1993**, *12*, 3140–3144. (f) Deabate, S.; Giordano, R.; Sappa, E. *J. Cluster Sci.* **1997**, *8*, 407–459.

(19) Tenjimbayashi, R.; Murotani, E.; Takemori, T.; Takao, T.; Suzuki, H. *J. Organomet. Chem.* **2007**, *692*, 442–454.

Scheme 2. Plausible Mechanism for the Arylation of the Propyne Ligand in 6



Although more information is necessary for complete elucidation, this mechanism is quite consistent with the initial formation of **9** during the reaction carried out at 100 °C.

In summary, direct arylation of the terminal alkyne ligand in **6** by way of C−H bond activation of benzene was achieved. This arylation performed on a trimetallic cluster demonstrates the high regioselectivity for the C−C bond formation at the terminal position of the alkyne ligand, which likely arises from the formation of a μ_3-vinylidene intermediate. Facile transformations of a hydrocarbyl ligand on the cluster appear to be crucial in demonstrating reactivities different from those observed in a monometallic complex. In addition, this type of reaction has never been seen in the common carbonyl cluster chemistry. This is probably due to the nature of the Ru_3 plane surrounded by the three Cp* groups, which can stabilize the coordinatively unsaturated species without deactivation by a coordinating ligand such as CO. Since the reaction discussed here is stoichiometric, these results imply the potential usefulness of the polyhydrido cluster in synthetic reactions. We are now concentrating our efforts on detailed mechanistic arylation studies using substituted arene molecules.

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Supporting Information Available: Text, tables, and figures providing synthetic details for compounds **7** and **9** and CIF files giving X-ray crystallographic data for **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.