

# Synthesis and Characterization of Triruthenium Complexes Containing a Perpendicularly Coordinated Alkyne Ligand

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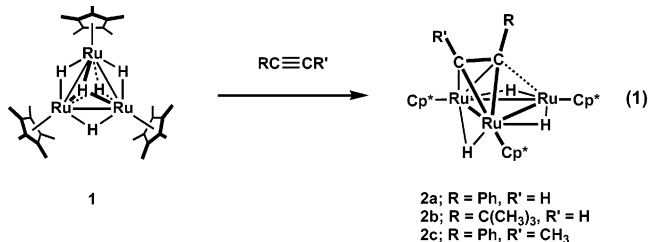
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**Summary:** Treatment of the triruthenium pentahydrido complex  $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu_3\text{-H})_2$  (**1**;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) with substituted alkynes results in the exclusive formation of the  $\mu_3$ -alkyne complex  $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu_3\text{-}\eta^2\text{-}\eta^2(\perp)\text{-RCCR}')_2$  (**2a**,  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{H}$ ; **2b**,  $\text{R} = \text{C}(\text{CH}_3)_3$ ,  $\text{R}' = \text{H}$ ; **2c**,  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{CH}_3$ ), in which the alkyne adopts a perpendicular coordination mode relative to one of the Ru–Ru edges, as revealed by an X-ray structure determination. The acetylenic carbon located inside the trinuclear core is shown to appear at particularly high magnetic field in the  $^{13}\text{C}$  NMR spectra.

Two distinct types of coordination geometry of an alkyne ligand are known for a trimetallic complex,<sup>1</sup> i.e., parallel ( $\mu_3\text{-}\eta^2(\parallel)\text{-alkyne}$ ) and perpendicular ( $\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-alkyne}$ ) with respect to one of the M–M bonds. The perpendicularly coordinated alkyne complex has been shown to be an intermediate of the C≡C bond scission<sup>2</sup> and cycloaddition of alkynes,<sup>3</sup> and its reactivity has been noted in relation to organic synthesis mediated by a transition-metal cluster, as well as elucidation of the reactivity of the chemisorbed species on a metal surface.

We have previously reported the reaction of the triruthenium pentahydrido complex  $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu_3\text{-H})_2$  (**1**) with acetylene; two acetylene molecules were incorporated into each face of the  $\text{Ru}_3$  plane.<sup>4</sup> The  $\text{C}_2$  moiety underwent transformation on the cluster to form  $\mu$ -vinyl,  $\mu$ -ethylidene,  $\mu_3$ -ethylidyne,  $\mu$ -vinylidene, and  $\mu_3(\parallel)\text{-ethyne}$  ligands sequentially. We report here the reaction of **1** with substituted alkynes. In contrast to the reaction of **1** with acetylene, only one molecule of alkyne is incorporated into the  $\text{Ru}_3$  core, where it adopts a perpendicular coordination mode.

Treatment of **1** with a slight excess of phenylacetylene at ambient temperature exclusively afforded the ( $\perp$ )-alkyne complex  $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-PhCCH})_2$  (**2a**) in a few minutes along with evolution of dihydrogen (eq 1).<sup>5</sup>



The reaction of **1** with phenylacetylene proceeds mainly via an associative reaction path;<sup>6</sup> a one-to-one adduct,  $(\text{Cp}^*\text{Ru})_3(\text{H})_5(\text{PhC}\equiv\text{CH})$ , is formed, and further releases dihydrogen to produce **2a**. During this reaction, formation of 0.2 equiv of styrene was observed. The reaction of **1** with 3,3-dimethyl-1-butyne also yielded **2b** with a small amount of a hydrogenated byproduct, 3,3-dimethyl-1-butene. These facts indicate that there is a minor reaction path to form **2** and alkene by the reaction of **1** with 2 equiv of phenylacetylene, which becomes the main path in the reaction of **1** with internal alkyne.

A perpendicularly coordinated alkyne complex,  $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu_3\text{-}\eta^2\text{:}\eta^2(\perp)\text{-PhCCMe})_2$  (**2c**), was similarly synthesized by the reaction of **1** with 1-phenyl-1-propyne, but required twice the molar amount of alkyne to complete the reaction. During this reaction, an equimolar amount of 1-phenyl-1-propene to **2c** was formed. In contrast to the reaction of **1** with terminal

(5) NMR data for **2a**:  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_6$ ,  $-20^\circ\text{C}$ , TMS):  $\delta$  9.88 (s, 1H, CH), 6.72 (t,  $J_{\text{H-H}} = 7.6$  Hz, 2H, Ph-*meta*), 6.48 (t,  $J_{\text{H-H}} = 7.6$  Hz, 1H, Ph-*para*), 5.60 (d,  $J_{\text{H-H}} = 7.6$  Hz, 2H, Ph-*ortho*), 1.95 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 1.55 (s, 15H,  $\text{C}_5\text{Me}_5$ ),  $-6.78$  (d,  $J_{\text{H-H}} = 3.2$  Hz, 2H, RuH),  $-24.40$  (t,  $J_{\text{H-H}} = 3.2$  Hz, 1H, RuH).  $^{13}\text{C}$  NMR (100 MHz, toluene- $d_6$ ,  $-40.0^\circ\text{C}$ , TMS):  $\delta$  178.7 (d,  $J_{\text{C-H}} = 183.4$  Hz,  $-\text{CH}$ ), 148.1 (s, *Ph-*ipso**), 126.4 (d,  $J_{\text{C-H}} = 159.2$  Hz, *Ph*), 124.6 (d,  $J_{\text{C-H}} = 157.1$  Hz, *Ph*), 120.9 (d,  $J_{\text{C-H}} = 157.7$  Hz, *Ph*), 89.9 (s,  $\text{C}_5\text{Me}_5$ ), 84.7 (s,  $\text{C}_5\text{Me}_5$ ), 66.3 (s,  $-\text{CPh}$ ), 12.8 (q,  $J_{\text{C-H}} = 126.4$  Hz,  $\text{C}_5\text{Me}_5$ ), 11.9 (q,  $J_{\text{C-H}} = 126.1$  Hz,  $\text{C}_5\text{Me}_5$ ). **2b**:  $^1\text{H}$  NMR (400 MHz, toluene- $d_6$ ,  $-20^\circ\text{C}$ , TMS):  $\delta$  9.71 (s, 1H, CH), 2.03 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 1.92 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 0.38 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ),  $-0.61$  (s, 2H, RuH),  $-23.46$  (s, 1H, RuH).  $^{13}\text{C}$  NMR (100 MHz, benzene- $d_6$ ,  $23.0^\circ\text{C}$ , TMS):  $\delta$  160.5 (d,  $J_{\text{C-H}} = 181.7$  Hz, CH), 87.5 (s,  $\text{C}_5\text{Me}_5$ ), 84.5 (s,  $\text{C}_5\text{Me}_5$ ), 60.4 (s,  $\text{C}(\text{CH}_3)_3$ ), 34.4 (q,  $J_{\text{C-H}} = 124.5$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 30.3 (s,  $\text{C}(\text{CH}_3)_3$ ), 13.1 (q,  $J_{\text{C-H}} = 126.1$  Hz,  $\text{C}_5\text{Me}_5$ ), 12.7 (q,  $J_{\text{C-H}} = 126.1$  Hz,  $\text{C}_5\text{Me}_5$ ). **2c**:  $^1\text{H}$  NMR (500 MHz, benzene- $d_6$ ,  $23.0^\circ\text{C}$ , TMS):  $\delta$  7.07 (t,  $J_{\text{H-H}} = 7.6$  Hz, 2H, Ph-*meta*), 6.76 (t,  $J_{\text{H-H}} = 7.6$  Hz, 1H, Ph-*para*), 5.71 (d,  $J_{\text{H-H}} = 7.6$  Hz, 2H, Ph-*ortho*), 2.79 (s,  $-\text{CCH}_3$ ), 1.89 (s, 30H,  $\text{C}_5\text{Me}_5$ ), 1.70 (s, 15H,  $\text{C}_5\text{Me}_5$ ),  $-8.41$  (s, 2H, RuH),  $-24.78$  (s, 1H, RuH).  $^{13}\text{C}$  NMR (125 MHz, benzene- $d_6$ ,  $23.0^\circ\text{C}$ , TMS):  $\delta$  181.1 (s,  $-\text{CCH}_3$ ), 149.3 (s, *Ph-*ipso**), 126.9 (d,  $J_{\text{C-H}} = 156.0$  Hz, *Ph*), 124.0 (d,  $J_{\text{C-H}} = 155.6$  Hz, *Ph*), 120.9 (d,  $J_{\text{C-H}} = 157.6$  Hz, *Ph*), 90.8 (s,  $\text{C}_5\text{Me}_5$ ), 85.5 (s,  $\text{C}_5\text{Me}_5$ ), 73.7 (s,  $-\text{CPh}$ ), 25.8 (q,  $J_{\text{C-H}} = 125.8$  Hz,  $-\text{CCH}_3$ ), 12.2 (q,  $J_{\text{C-H}} = 125.6$  Hz,  $\text{C}_5\text{Me}_5$ ), 11.9 (q,  $J_{\text{C-H}} = 125.8$  Hz,  $\text{C}_5\text{Me}_5$ ).

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alkyne, the reaction with internal alkyne took 20 h at ambient temperature. This prolonged reaction time is most likely due to the different mechanism for the removal of the hydrido ligands. While the hydride ligands were mainly removed as dihydrogen in the reaction with terminal alkyne, they were removed by hydrogenation of the coordinated alkyne in the reaction of internal alkyne.

The fact that a ( $\perp$ )-alkyne complex was obtained by the reaction of **1** with internal alkyne implies that formation of the ( $\perp$ )-1-alkyne complex proceeded without C–H bond cleavage at the acetylenic carbon atom; that is, complexes **2a** and **2b** are not formed via the formation of a  $\mu_3$ -acetylide intermediate. Most of the proton remained on the alkyne ligand during the reaction of pentadeuterido complex **1-d<sub>5</sub>** with phenylacetylene. The intensity ratio of the methine signal was estimated at ca. 0.82H based on the hydrido and Cp\* signals. The value of 0.82H strongly indicates the direct mechanism without C–H bond cleavage.

Incorporation of 0.18H amount of deuterium into the methine group from the deuteride ligands can be rationalized by the slow exchange between the hydrido ligands and the methine proton on the phenylacetylene due to equilibrium between **2a** and a  $\mu_3$ -vinylidene or a  $\mu_3$ -acetylide complex. The exchange between the hydrido ligands and the methine proton was confirmed by the SST experiment; irradiation at the hydrido signal at 100 °C resulted in decrease of the intensity of the methine signal by 14%.

There has thus far been no reported example of a trinuclear ( $\perp$ )-1-alkyne complex formed by the direct reaction of a trimetallic cluster with 1-alkyne. The reaction of a carbonyl cluster with 1-alkyne usually results in the cleavage of the C–H bond to yield a  $\mu_3$ -acetylide complex.<sup>1</sup> Although there were a few examples of the synthesis of  $\mu_3$ -( $\perp$ )-1-alkyne complex upon the protonation of the corresponding  $\mu_3$ -acetylide complex,<sup>2b,8c,f</sup> this is the first example of the direct synthesis of a  $\mu_3$ -( $\perp$ )-alkyne complex starting from 1-alkyne.

The X-ray structure analysis of **2a** was carried out using a dark green single crystal obtained from cold THF/pentane solution, and the ORTEP diagram is shown in Figure 1.<sup>7</sup> The most significant structural feature of **2a** is the conformation of the alkyne ligand, which adopts a perpendicular coordination to the Ru(2)–Ru(2#) edge. One of the acetylenic carbons, C(2), bridges three ruthenium atoms, and the other, C(1), is bonded to Ru(2) and Ru(2#). The relatively short Ru(1)–C(2) distance (2.157(6) Å) reflects the direct bonding interaction between these atoms, and this value is comparable with the corresponding metal–acetylenic carbon distances found in the ( $\perp$ )-alkyne complexes that have been

already reported (2.05–2.29 Å).<sup>1–3,8</sup> This suggests that there should exist a  $\sigma$ -bond between the two atoms. Elongation of the C(1)–C(2) distance in **2a** (1.392(7) Å), which lie in the range of the reported values for the ( $\perp$ )-alkyne complexes (1.391–1.441 Å),<sup>1–3,8</sup> indicates that the alkyne formally functions as a four-electron donor in the  $\mu_3$ - $\eta^2$ : $\eta^2$ ( $\perp$ )-alkyne complex. Thus, complex **2a** adopts a 46-electron configuration, which is characteristic of the ( $\perp$ )-alkyne complexes.

There would be two isomers for **2** in regard to the orientation of the alkyne ligand; one is **2-in**, in which the larger substituent attaches to the acetylenic carbon located inside the Ru<sub>3</sub> core, and the other is **2-out**, in which the larger substituent is located on the outer acetylenic carbon. It is noteworthy that only the “inner” isomer was observed for **2a** and **2b**. The other is probably disfavored due to steric repulsion between the Cp\* groups surrounding the Ru<sub>3</sub> triangle and the substituent on the acetylenic carbons. Morokuma and co-workers have estimated that **2b-in** is more stable than **2b-out** by 18 kcal/mol by using MM2 calculations.<sup>9</sup>

The <sup>1</sup>H NMR spectra of **2a** recorded at ambient temperature showed one broad signal of the Cp\* groups. This is due to fluxionality of the alkyne ligand, and we will mention the fluxionality of the ( $\perp$ )-alkyne ligand in the following communication.<sup>10</sup> This broad Cp\* resonance was split into 2:1 of two well-resolved signals observed at  $\delta$  1.95 and 1.55 at –20 °C. The shape and the chemical shift of the hydrido signals also depended on temperature. They appeared at  $\delta$  –6.78 (2H) and –24.40 (1H) as sharp signals at –20 °C, and they coalesced into one peak at elevated temperature. The intensity ratio of 2:1 for the signals of the Cp\* and the hydrides indicates that **2a** belongs to the C<sub>s</sub> symmetry group and clearly shows perpendicular coordination of the phenylacetylene ligand.

The signal of the methine proton located on the “outer” carbon was observed at  $\delta$  9.88, as well as that for Cp\*WRe<sub>2</sub>(CO)<sub>7</sub>( $\mu$ -SPh)( $\mu_3$ - $\eta^2$ : $\eta^2$ ( $\perp$ )-PhCCH),<sup>5d</sup> which is the only example of the structurally characterized ( $\perp$ )-1-alkyne complex containing a proton on the outer carbon. This downfield shift of the methine proton is characteristic of the bridging alkylidene proton, and it implies the carbenic character of the “outer” carbon. The <sup>13</sup>C signal of the methine carbon also showed a downfield shift ( $\delta$  178.7), and the J<sub>C–H</sub> value of 183.4 Hz also implied the carbenic character.

The signal of the *ortho*-proton of the phenyl group is observed in a considerably higher region ( $\delta$  5.60). This upfield shift is apparently due to the ring current shield effect of the three Cp\* groups.

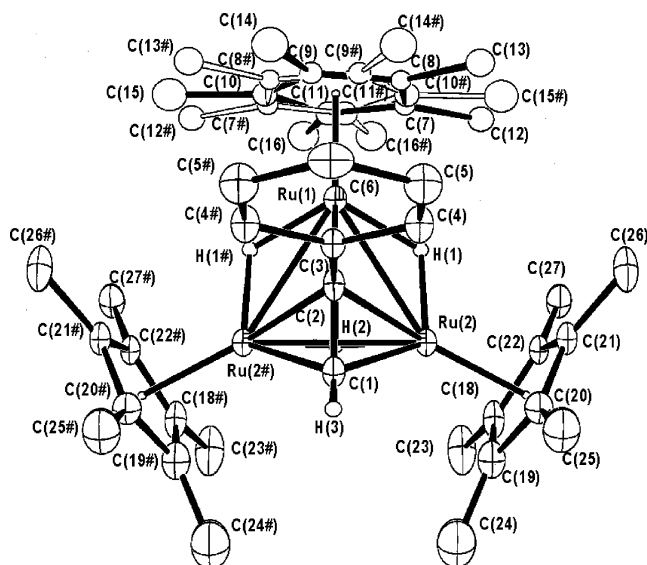
As shown in Figure 1, the inner carbon, C(2), is five-coordinate, and the magnetic property of the inner carbon should be quite different from that of the  $\mu_3$ -acetylide carbon in the  $\mu_3$ - $\eta^2$ : $\eta^2$ ( $\perp$ )-alkynyl complex, whose <sup>13</sup>C signal is observed in a lower magnetic field region. The <sup>13</sup>C signal of the “inner” carbon appeared as a singlet and showed significant upfield shift, as for the carbon atom triply bonded to the transition metals ( $\delta$  66.3). This is a quite similar value to the chemical

(7) Crystal data: empirical formula C<sub>38</sub>H<sub>54</sub>Ru<sub>3</sub>, *T* = 153 K,  $\lambda$  = 0.71069 Å, space group *C2/m* (#12), *a* = 17.083(6) Å, *b* = 18.356(6) Å, *c* = 11.473(4) Å,  $\beta$  = 105.732(15)°, and *V* = 3463(2) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.56 g/cm<sup>3</sup>. The final structure for **2a** was refined to *R*<sub>1</sub> = 0.0468 and *wR*<sub>2</sub> = 0.1166 for 4191 observed reflections (*I* > 2 $\sigma$ ) and 206 parameters.

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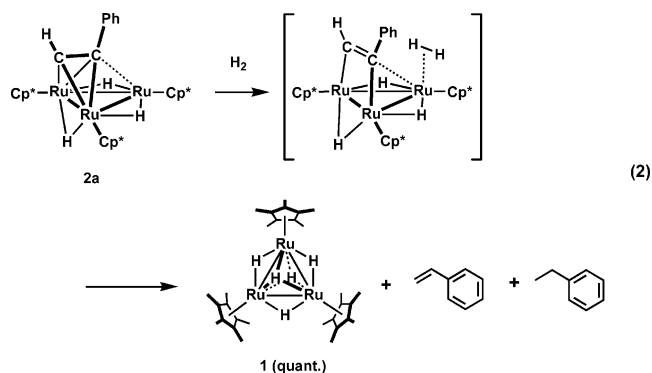


**Figure 1.** Molecular structure and labeling scheme of **2a** with thermal ellipsoids probability at the 30% level. Selected bond lengths (Å) and angles (deg): Ru(1)–Ru(2), 2.7919(8); Ru(2)–Ru(2#), 2.8531(10); Ru(1)–C(2), 2.157(6); Ru(2)–C(1), 2.006(5), Ru(2)–C(2), 2.242(4); C(1)–C(2), 1.392(7); C(2)–C(3), 1.485(8); Ru(2)–Ru(1)–Ru(2#), 61.457(13); Ru(2)–Ru(1)–C(2), 51.98(11); Ru(1)–Ru(2)–Ru(2#), 59.272(13); C(1)–Ru(2)–C(2), 37.7(2); Ru(2)–C(1)–Ru(2#), 90.6(3); Ru(2)–C(1)–C(2), 80.4(3); Ru(1)–C(2)–Ru(2), 78.76(18); Ru(2)–C(2)–Ru(2#), 79.01(18); Ru(1)–C(2)–C(1), 127.7(4); C(1)–C(2)–C(3), 118.6(5).

shifts observed for the “inner” carbon of  $(\text{CpM})\text{Fe}_2(\text{CO})_5(\mu\text{-CO})(\mu\text{-PPh}_2)(\mu_3\text{-}\eta^2\text{-}\eta^2(\text{L})\text{-HCCPh})$  ( $\text{M} = \text{W}$ ;  $\delta$  60.1,  $\text{M} = \text{Mo}$ ;  $\delta$  61.8).<sup>8f</sup> The five-coordinate property and the ring current shield effect should cause the upfield shift of the resonance for the “inner” carbon.

Most of the assignments of the  $^{13}\text{C}$  signal for the coordinated alkyne, reported thus far, were based on a preconception that the magnetic properties of the “inner” carbon are similar to those of the triply bridging acetylide carbon, and a resonance which appeared in a lower field ( $\delta$  210–270)<sup>2b,8b,11</sup> has been assigned to the signal for the “inner” carbon. Here, we have accomplished a valid assignment of the  $^{13}\text{C}$  signals, and the resonance signals for the “outer” carbon atom that has the  $\mu$ -carbenic character shift significantly downfield and those for the “inner” carbon atom are observed in the higher field.

Treatment of **2a** with 1 atm of dihydrogen resulted in quantitative formation of the starting pentahydrido complex **1** (eq 2). While the reaction of the 1-alkyne complexes, **2a** and **2b**, proceeded smoothly with atmo-



spheric dihydrogen at 70 °C, hydrogenation of **2c** required harsher conditions (170 °C, 5 atm of  $\text{H}_2$ ). When the hydrogenation of **2a** was monitored by NMR spectroscopy, both styrene and ethylbenzene were observed at the initial stage, and styrene was finally hydrogenated to ethylbenzene. Hydrogenation of the coordinated phenylacetylene likely proceeded via an intermediary ( $\perp$ )- $\text{PhCCH}$  complex that adopts a 48-electron configuration. Lavigne and co-workers elucidated transformation of a ( $\perp$ )-alkyne to a ( $\parallel$ )-alkyne ligand in the reaction with  $\text{H}_2$ .<sup>12</sup> Such transformation from a ( $\perp$ )- to a ( $\parallel$ )-alkyne complex has been usually observed for the ( $\perp$ )-alkyne complexes.<sup>5c,f,13</sup>

We have previously reported the reaction of **1** with linear alkane to yield a *closo*-ruthenacyclopentadiene complex as a result of multiple C–H bond cleavage.<sup>14</sup> During this reaction, a ( $\perp$ )-alkyne complex was observed as an intermediate. Investigation of the reactivity of the  $\mu_3$ -alkyne complex is now in progress in relation to the alkane activation.

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**Supporting Information Available:** Synthetic details and spectral data for compounds **2a**, **2b**, and **2c**, and X-ray crystallographic files of **2a**; the X-ray data are also given as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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