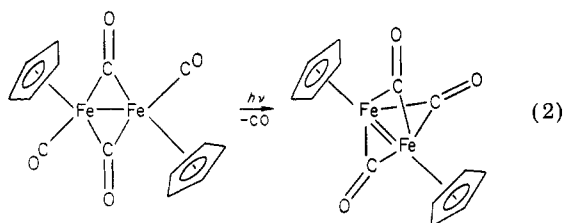


can form a symmetrical ( $\mu$ -CO)<sub>3</sub> complex without gross movement of the C<sub>5</sub> rings (eq 2), whereas reaction of the



cis isomer would require large movement of the C<sub>5</sub> rings. The inability to capture the tricarbonyl from photolysis of III with 2-MeTHF suggests that the loss of CO and rearrangement to form the ( $\mu$ -CO)<sub>3</sub> structure is concerted. The difference in photosensitivity of the cis and trans species and the role of the tricarbonyl photoproduct in solution photochemistry are presently under study in this laboratory.

**Acknowledgment.** We thank the National Science Foundation for support of this research.

**Registry No.** *cis*-I, 33221-55-5; *trans*-I, 32757-46-3; *cis*-II, 88080-00-6; *trans*-II, 87985-72-6; III, 12132-03-5; ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>, 87985-70-4; ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>, 87985-71-5; ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Bz)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>, 87985-73-7; Fe, 7439-89-6.

### Carbon Chain Growth via Methylene (CH<sub>2</sub>) Additions to Cluster-Bound Unsaturates: Conversion of $\mu_3$ - $\eta^2$ -Acetylides to $\mu_3$ - $\eta^3$ -Allenyl and $\mu_3$ - $\eta^4$ -2,3-Butadienyldene Complexes with Diazomethane

Donato Nucciarone, Nicholas J. Taylor, and Arthur J. Carty\*

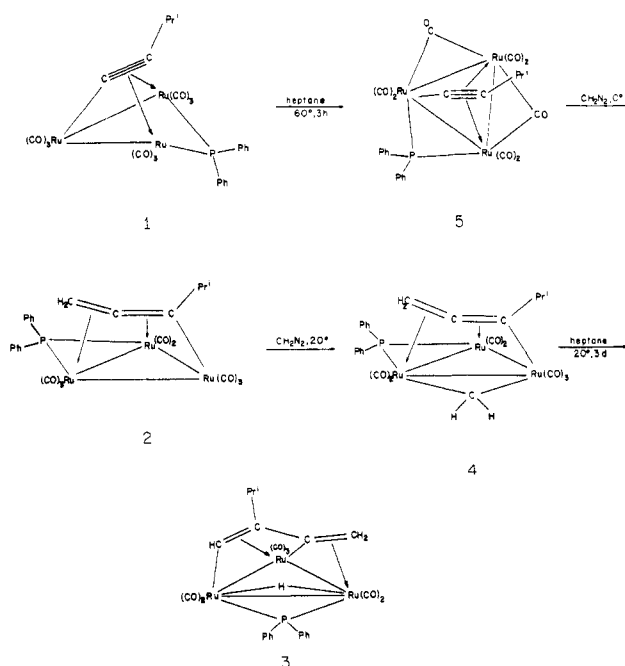
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Received September 2, 1983

**Summary:** The synthesis of a cluster-bound  $\mu_3$ - $\eta^3$ -allenyl ligand in Ru<sub>3</sub>(CO)<sub>8</sub>( $\mu_3$ - $\eta^2$ -CH<sub>2</sub>=C=C-*i*-Pr)( $\mu$ -PPh<sub>2</sub>) (**2**) from a  $\mu_3$ - $\eta^2$ -acetylide, Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -C≡C-*i*-Pr)( $\mu$ -PPh<sub>2</sub>) (**1**), via methylene (CH<sub>2</sub>) addition and the subsequent conversion of **2** to the 2,3-butadienyldene<sup>21</sup> cluster ( $\mu$ -H)-Ru<sub>3</sub>(CO)<sub>7</sub>( $\mu_3$ - $\eta^4$ -CH<sub>2</sub>=CC(*i*-Pr)=CH)( $\mu$ -PPh<sub>2</sub>) (**3**) by methylidyne (CH) transfer from the  $\mu$ -methylene intermediate Ru<sub>3</sub>(CO)<sub>7</sub>( $\mu_3$ - $\eta^3$ -CH<sub>2</sub>=C=C-*i*-Pr)( $\mu$ -CH<sub>2</sub>)( $\mu$ -PPh<sub>2</sub>) (**4**) are described. The structures of the new clusters **2**, **3**, and **4** have been determined by X-ray diffraction. Facile carbon-carbon bond formation between multisite-bound unsaturated ligands and diazomethane-derived methylene or methylidyne fragments may offer new opportunities for cluster-mediated ligand synthesis.

Currently favored mechanisms for carbon-carbon chain growth in Fischer-Tropsch synthesis<sup>1</sup> and C-C bond cleavage in hydrocarbon hydrogenolysis<sup>2</sup> involve the intermediacy of surface-bound  $\mu$ -methylenes. In the case of hydrocarbon synthesis, C-C bond formation may occur via

### Scheme I



CH<sub>2</sub> insertion into a metal-alkyl bond,<sup>1</sup> coupling with a surface olefin,<sup>3</sup> or migrations to other surface ligands including carbides or carbynes. Molecular models for some of these processes have recently been discovered in the chemistry of binuclear  $\mu$ -methylene complexes<sup>4,5</sup> and in the reactions of transition-metal compounds with methylene precursors.<sup>5,6</sup>

Somewhat surprisingly, in view of the metal cluster-metal surface analogy, few reports of C-C bond formation involving methylene groups and unsaturated fragments in polynuclear clusters have appeared<sup>8</sup> despite the obvious relevance of such reactions to cluster-mediated synthesis, ligand elaboration, and catalysis. As a continuation of our studies on reactivity patterns for multisite-bound unsaturates,<sup>7</sup> we have examined the behavior of the cluster acetylide Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -C≡C-*i*-Pr)( $\mu$ -PPh<sub>2</sub>), **1**, toward diazomethane. In this communication we report the facile transformation of **1** to the allenyl complex Ru<sub>3</sub>(CO)<sub>8</sub>( $\mu_3$ - $\eta^3$ -CH<sub>2</sub>=C=C-*i*-Pr)( $\mu$ -PPh<sub>2</sub>), **2**, and subsequently to the hydrido 2,3-butadienyldene cluster ( $\mu$ -H)Ru<sub>3</sub>(CO)<sub>7</sub>( $\mu_3$ - $\eta^4$ -CH<sub>2</sub>=CC(*i*-Pr)=CH)( $\mu$ -PPh<sub>2</sub>), **3**, via the intermediacy of a  $\mu$ -methylene compound, Ru<sub>3</sub>(CO)<sub>7</sub>( $\mu_3$ - $\eta^3$ -CH<sub>2</sub>=C=C-*i*-Pr)( $\mu$ -CH<sub>2</sub>)( $\mu$ -PPh<sub>2</sub>), **4**. These reactions support the

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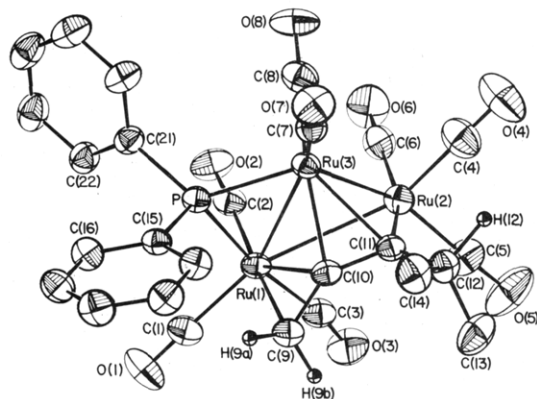
(5) For closely related reactions of other  $\mu$ -alkylidenes see, for example: (a) Colborn, R. E.; Dyke, A. F.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G. *J. Organomet. Chem.* 1982, 239, C15. (b) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* 1980, 803. (c) Cooke, M.; Davies, D. L.; Guerschais, J. E.; Knox, S. A. R.; Mead, K. A.; Rou e, J.; Woodward, P. *Ibid.* 1981, 862. (d) Herrmann, W. A. *Adv. Organomet. Chem.* 1982, 20, 159 and references therein.

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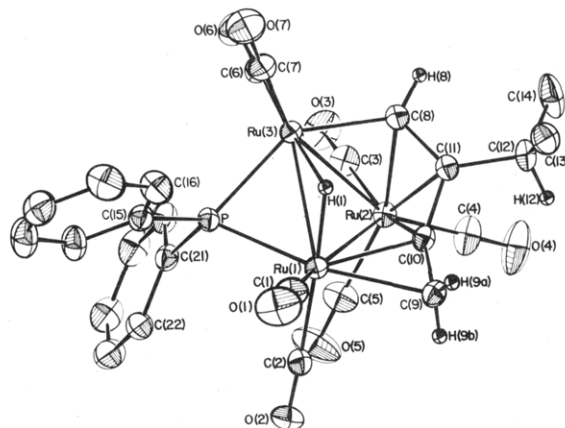
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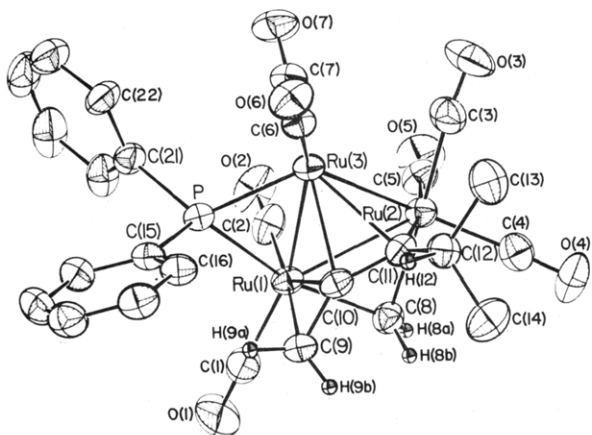
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**Figure 1.** A view of the structure of  $\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^3\text{-CH}_2\text{=C=C-}i\text{-Pr})(\mu\text{-PPPh}_2)$  (2) drawn to illustrate the interaction of the allenyl unit with the cluster.



**Figure 3.** The hydrido,2,3-butadienyldiene cluster  $(\mu\text{-H})\text{Ru}_3(\text{CO})_7(\mu_4\text{-}\eta^4\text{-CH}_2\text{=CC}(i\text{-Pr)=CH})(\mu\text{-PPPh}_2)$  (3).



**Figure 2.** An ORTEP plot of the structure of  $\text{Ru}_3(\text{CO})_7(\mu\text{-CH}_2)(\mu_3\text{-}\eta^2\text{-CH}_2\text{=C=C-}i\text{-Pr})(\mu\text{-PPPh}_2)$  (4) showing the stereochemical relationship to 2.

possibility of facile carbon chain growth involving methylene groups and unsaturated fragments in clusters and suggest that methylene additions to coordinated carbon ligands may provide new opportunities for novel ligand synthesis.

Addition of excess ethereal diazomethane<sup>8</sup> to an ether solution of  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C-}i\text{-Pr})(\mu\text{-PPPh}_2)$ , **1**<sup>9</sup> (200 mg, 0.25 mmol), at  $-5^\circ\text{C}$ , affords three new compounds separable by column chromatography on Florisil. Elution with heptane gives four bands:  $\text{Ru}_3(\text{CO})_7(\mu\text{-CH}_2)(\mu_3\text{-}\eta^3\text{-CH}_2\text{=C=C-}i\text{-Pr})(\mu\text{-PPPh}_2)$ , **4**,<sup>10</sup> first band, gray, 15%;  $(\mu\text{-H})\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^4\text{-CH}_2\text{=CC}(i\text{-Pr)=CH})(\mu\text{-PPPh}_2)$ , **3**,<sup>11</sup>

(8) Diazomethane was prepared according to standard procedures using Aldrich Chemical Co. *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide.

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(10) **4**: IR  $\nu(\text{CO})$  ( $\text{C}_6\text{H}_{12}$ ) 2064 m, 2025 m, 2011 s, 1973 w, 1953 m; <sup>31</sup>P NMR ( $\text{CD}_3\text{COCD}_3$ ,  $-65^\circ\text{C}$ )  $\delta$  +139.3 (wrt 85%  $\text{H}_3\text{PO}_4$ ); <sup>1</sup>H NMR ( $\text{CDCl}_3$ ,  $-60^\circ\text{C}$ )  $\delta$  0.99 (d, 3 H,  $J$  = 5.9 Hz), 1.02 (d, 3 H,  $J$  = 6.6 Hz), 2.46 (m, 1 H,  $J$  = 6.3 Hz), 2.76 (s, 1 H), 2.79 (s, 1 H), 6.19 (s, 2 H), 7.29–7.41 (m, 10 H).

(11) **3**: IR  $\nu(\text{CO})$  ( $\text{C}_6\text{H}_{12}$ ) 2066 m, 2033 s, 2014 s, 2004 m, 1983 m, 1950 m; <sup>31</sup>P NMR ( $\text{CD}_3\text{COCD}_3$ ,  $-65^\circ\text{C}$ )  $\delta$  +184.3; <sup>13</sup>C NMR ( $\text{CDCl}_3$ ,  $-60^\circ\text{C}$ , proton coupled)  $\delta$  199–193 (m, CO) 184.1 (s), 149.2 (dd, C(8)), <sup>2</sup> $J_{\text{PC}}$  = 38 Hz, <sup>1</sup> $J_{\text{CH}}$  = 150 Hz), 139.4 (d, ipso-CPh, <sup>1</sup> $J_{\text{PC}}$  = 25 Hz), 132.6 (d, ipso-CPh, <sup>1</sup> $J_{\text{CP}}$  = 10 Hz), 133–128 (m, phenyl rings), 120.0 (s), 41.8 (t, C(9)), <sup>1</sup> $J_{\text{CH}}$  = 164 Hz), 37.3 (d, C(12)), <sup>1</sup> $J_{\text{CH}}$  = 129 Hz), 22.7 (q, CMe, <sup>1</sup> $J_{\text{CH}}$  = 127 Hz), 22.0 (q, CMe, <sup>1</sup> $J_{\text{CH}}$  = 126 Hz); <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-70^\circ\text{C}$ )  $\delta$  -18.4 (d, 1 H,  $J_{\text{PH}}$  = 22 Hz), 1.3–1.4 (dd, 6 H), 2.7 (m, 1 H), 4.5 (s, 2 H), 7.0–8.0 (m, 6 H), 8.3 (s, 1 H).

second band, yellow, 5%;  $\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^3\text{-CH}_2\text{=C=C-}i\text{-Pr})(\mu\text{-PPPh}_2)$ , **2**,<sup>12</sup> third band, maroon, 35%;  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_2(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C-}i\text{-Pr})(\mu\text{-PPPh}_2)$ , **5**,<sup>9</sup> fourth band, orange, 10%. All yields are based on recovery by crystallization from heptane solutions except **5** which was precipitated as **1** by bubbling carbon monoxide through the eluted solution. The sequential nature of these reactions and the interrelationships between 2–4 have been thoroughly es-

(12) **2**: IR  $\nu(\text{CO})$  ( $\text{C}_6\text{H}_{12}$ ) 2075 m, 2047 s, 2018 m, 2007 m, 1996 w, 1989 w, 1975 w, 1946 m; <sup>31</sup>P NMR ( $\text{CDCl}_3$ ,  $40^\circ\text{C}$ )  $\delta$  +269.4 (wrt 85%  $\text{H}_3\text{PO}_4$ ); <sup>13</sup>C NMR ( $\text{CDCl}_3$ ,  $-60^\circ\text{C}$ , proton coupled)  $\delta$  210.9 (s, CO), 200.7 (s, CO), 197–195 (m, 4 CO), 194.8 (s, CO), 193.4 (d, CO, <sup>2</sup> $J_{\text{PC}}$  = 73 Hz), 172.0 (s), 142.7 (s), 140.6 (d, ipso-CPh, <sup>1</sup> $J_{\text{PC}}$  = 30 Hz), 134.6 (d, ipso-CPh, <sup>1</sup> $J_{\text{PC}}$  = 30 Hz), 133–128 (m, phenyl rings), 43.8 (d, C(12)), <sup>1</sup> $J_{\text{CH}}$  = 131 Hz), 24.8 (q, CMe, <sup>1</sup> $J_{\text{CH}}$  = 126 Hz), 23.6 (q, CMe, <sup>1</sup> $J_{\text{CH}}$  = 126 Hz), 20.1 (t, C(9)), <sup>1</sup> $J_{\text{CH}}$  = 161 Hz); <sup>1</sup>H NMR ( $\text{CDCl}_3$ ,  $-60^\circ\text{C}$ )  $\delta$  1.22 (d, 3 H,  $J$  = 7 Hz), 1.25 (d, 3 H,  $J$  = 7 Hz), 1.65 (d, 1 H,  $J_{\text{PH}}$  = 4 Hz), 1.67 (d, 1 H,  $J_{\text{PH}}$  = 4 Hz), 3.04 (m, 1 H,  $J$  = 7 Hz) 7.3–7.6 (10 H).

(13) Crystals of **2** grown from a heptane solution at  $-20^\circ\text{C}$  are monoclinic of space group  $P2_1/c$  with  $a = 11.892$  (2) Å,  $b = 12.200$  (2) Å,  $c = 19.698$  (4) Å,  $\beta = 93.22$  (2)°,  $V = 2853$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $\rho(\text{measd}) = 1.85$  g·cm<sup>-3</sup>,  $\rho(\text{calcd}) = 1.847$  g·cm<sup>-3</sup>, and  $\mu(\text{Mo K}\alpha) = 16.32$  cm<sup>-1</sup>. Intensity data were collected on a crystal of dimensions 0.19 × 0.22 × 0.23 mm using the  $\theta$ - $2\theta$  scan technique ( $2\theta \leq 46.0^\circ$ ) on a Syntex P2<sub>1</sub> diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å), variable scan speeds (2.93–29.3° min<sup>-1</sup>), and a scan width from 0.8° below  $K\alpha_1$  to 0.8° above  $K\alpha_2$ . From a total of 3997 independent reflections, 3007 with  $I \geq 3\sigma(I)$  were used in the structure analysis. No decline in two standard reflections (308, 506) monitored every 100 measurements was noted. Data were corrected for Lorentz and polarization effects, but not for absorption. The three ruthenium atoms and the phosphorus atom were located from a Patterson map and light atoms via Fourier syntheses. Refinement with isotropic parameters for all non-hydrogen atoms gave an  $R$  ( $R = \sum |F_o| - |F_c| / \sum |F_o|$ ) of 0.075 while with anisotropic coefficients  $R$  was 0.041. All hydrogen atoms were located in a difference map, and these were included in subsequent refinement cycles. Final  $R$  and  $R_w$  values ( $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ ) were 0.029 and 0.031, the final weighting scheme being of the form  $w^{-1} = 1.9 - 0.0185|F| + 0.00015|F|^2$ . The highest electron density in a final difference map was 0.5 e Å<sup>-3</sup>. Scattering factors including corrections for anomalous dispersion for Ru were taken from ref 16. Computer programs used have been described elsewhere.<sup>17</sup> Atomic positions, thermal parameters, and bond lengths and angles are listed in supplementary Tables I–III, respectively. Structure factors are also available as supplementary data.

(14) Crystals of **3** grown from heptane solution at ambient temperature are triclinic of space group  $P1$  with  $a = 9.333$  (2) Å,  $b = 10.200$  (1) Å,  $c = 16.297$  (2) Å,  $\alpha = 87.25$  (1)°,  $\beta = 83.26$  (1)°,  $\gamma = 64.29$  (1)°,  $V = 1388.2$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $\rho(\text{measd}) = 1.86$  g·cm<sup>-3</sup>,  $\rho(\text{calcd}) = 1.865$  g·cm<sup>-3</sup>,  $F(000) = 760$ , and  $\mu(\text{Mo K}\alpha) = 16.72$  cm<sup>-1</sup>. Intensity data were collected on a crystal of dimensions 0.25 × 0.29 × 0.29 mm as outlined above for **2**. The structure was solved and refined by using 5899 observed (6760 measured) data to final  $R$  and  $R_w$  values of 0.025 and 0.029, respectively. All hydrogen atoms were located and refined. A final difference map had no peaks >0.5 e Å<sup>-3</sup>. Atomic coordinates, thermal parameters, bond lengths and angles are listed in supplementary Tables IV–VI. Structure factors have been deposited.

established by converting each of the intermediates as indicated in Scheme I.

The structures of clusters **2**, **3**, and **4** have been determined by single crystal X-ray diffraction.<sup>13-15</sup> ORTEP plots and structural formulas are depicted in Figures 1-3. In **2** the hydrocarbon moiety bonded to the face of the metal triangle is present as a 3-isopropyl-3-allenyl ligand formed by addition of a methylene fragment (C(9)H<sub>2</sub>) to the  $\alpha$ -carbon atom C(10) of the acetylide. The three-carbon allenyl unit<sup>18</sup> is coordinated to Ru(2) via a  $\sigma$  bond to C(11) and to Ru(3) and Ru(1) via  $\eta^2$  interactions with C(10)-C(11) and C(9)-C(10). Although allene clusters have been characterized as products of reactions between metal carbonyls and dienes,<sup>19</sup> this represents the first synthesis of such a ligand on a cluster framework from the combination of a methylene group and a two-carbon fragment. Shapley and co-workers<sup>6</sup> have recently reported the synthesis of a face-bonded allyl group via thermally induced coupling of diphenylacetylene and methylene ligands. Similar diphenylacetylene-methylene coupling at a binuclear center yielding a vinyl carbene has been described.<sup>5a</sup>

Spectroscopic data<sup>10,11</sup> suggested that **3** and **4** were derived from the allenyl compound **2** via further addition of methylene units. Although the skeletal framework of **4** (Figure 2) resembles that of **2** with an edge-bridging PPh<sub>2</sub> group and an allenyl moiety across the Ru<sub>3</sub> face, a semi-bridging carbonyl in **2** (C(3)-O(3)) has been replaced by a methylene group bridging the Ru(1)---Ru(2) bond (Ru(1)-C(8)-Ru(2) = 81.6 (1)°). Stereochemically, the methylene carbon atom C(8) is *cis* related to both allenyl carbon atoms (C(10) on Ru(1) and C(11) on Ru(2)), thus providing a ready rationale for conversion to the more highly coupled product **3**. It is significant, however, that coupling of  $\mu$ -methylene and allenyl groups in **4** yields mainly **3** whose structure (Figure 3) confirms bond formation between C(11), the original  $\beta$ -carbon atom of the acetylide bearing an isopropyl group, and C(8), the  $\mu$ -methylene carbon atom of **4**. Furthermore, the conversion **4**  $\rightarrow$  **3** occurs with hydrogen transfer from the methylene group onto the cluster leading to a hydrido-bridged  $\mu_3$ - $\eta^4$ -2,3-butadienylidene molecule. Thus the  $\mu$ -methylene group provides a methylidyne (CH) unit for transfer to the hydrocarbyl ligand. The hydride is located along the

shortest of the three Ru-Ru bonds (Ru(1)-Ru(3) = 2.7534 (2) Å) and on the same side of the cluster as the methylene-derived carbon atom C(8). That the bridging hydride in **3** is derived from the bridging methylene group of **4** was conclusively established by deuterium labeling experiments.<sup>20</sup> The hydrocarbyl unit in **3** is conveniently described as  $\sigma$  bonded to Ru(3) via C(8),  $\eta^2$  coordinated to Ru(2) through C(8) and C(11),  $\sigma$  bonded to Ru(2) via C(10), and  $\eta^2$  coordinated to Ru(1) through the double bond C(9)-C(10). To our knowledge this synthesis of the 2,3-butadienylidene ligand<sup>21</sup> of **3** on the face of a cluster from a multisite-bound unsaturated ligand and two molecules of diazomethane is unprecedented. It is interesting to note that the carbon atoms derived from diazomethane in **3** end up at *opposite* ends of the hydrocarbon chain. In the only other example of a two-carbon transfer reported to date,<sup>5a</sup> the methylene-derived atoms were coupled, affording a methyl vinyl carbene ligand in the binuclear compound Ru<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(Ph)C(Ph)C(H)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>.

Although the intermediacy of an edge-bridged  $\mu$ -methylene complex was evident in the conversion of **2** to **3**, no such species was detected in the sequence **1**  $\rightarrow$  **2**. However, since the 50-electron cluster Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu_3$ - $\eta^2$ -C $\equiv$ C-*i*-Pr)( $\mu$ -PPh<sub>2</sub>) reversibly loses CO in solution giving the reactive 48-electron species Ru<sub>3</sub>(CO)<sub>8</sub>( $\mu$ -CO)<sub>2</sub>( $\mu_3$ - $\eta^2$ -C $\equiv$ C-*i*-Pr)( $\mu$ -PPh<sub>2</sub>), **5**,<sup>9</sup> it is likely that a short-lived  $\mu$ -methylene adduct of the latter is involved in the formation of **2**. Consistent with this, the rate of formation of **2** is greatly improved by prior synthesis of **5**.

In summary, our results confirm that methylene migration to cluster-bound unsaturated ligands is a rational strategy for C-C bond formation and hydrocarbon chain extension in cluster chemistry. Moreover, when considered in the light of related studies on trinuclear systems by Shapley,<sup>6</sup> and binuclear complexes by Knox,<sup>5a</sup> it is apparent that methylene-hydrocarbon reactions on polynuclear clusters may well provide useful models for certain aspects of catalytic hydrocarbon synthesis.

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**Registry No.** 1, 77681-75-5; 2, 87829-51-4; 3, 87829-52-5; 3-*d*<sub>1</sub>, 87829-53-6; 4, 87829-54-7; 4-*d*<sub>2</sub>, 87829-55-8; 5, 77681-78-8; diazomethane, 334-88-3.

**Supplementary Material Available:** Tables of atomic positions, thermal parameters, bond lengths and angles, and structure factor amplitudes for **2**, **3**, and **4** (84 pages). Ordering information is given on any current masthead page.

(15) Crystals of **4** grown from heptane at -20 °C are monoclinic of space group P2<sub>1</sub>/c with  $a = 11.890$  (2) Å,  $b = 11.973$  (1) Å,  $c = 19.675$  (2) Å,  $\beta = 90.10$  (1)°,  $V = 2800.9$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $\rho(\text{measd}) = 1.85$  g·cm<sup>-3</sup>,  $\rho(\text{calcd}) = 1.849$  g·cm<sup>-3</sup>,  $F(000) = 1520$ ,  $\mu(\text{Mo K}\alpha) = 16.58$  cm<sup>-1</sup>. The crystal used for data collection had dimensions 0.17  $\times$  0.17  $\times$  0.27 mm. Data were collected out to  $2\theta \leq 50^\circ$  giving 4957 independent reflections of which 3339 were considered observed ( $I \geq 3\sigma(I)$ ). Refinement using anisotropic coefficients converged to  $R = 0.035$  and  $R_w = 0.039$  (including hydrogen atoms) using a final weighting scheme of  $w^{-1} = 1.89 - 0.0173|F| + 0.00017|F|^2$ . Monitoring of the selected standard reflections having indices 304 and 322 showed a variation of 6% over the course of data collection. Atomic coordinates, thermal parameters, and bond lengths and angles are listed in supplementary Tables VII-IX. Structure factors are also available.

(16) (a) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(17) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

(18) Consideration of the geometry of the allenyl fragment C(9)-C(10)-C(11) and the Ru-C distances (Ru(1)-C(9) = 2.274 (6), Ru(1)-C(10) = 2.301 (5), Ru(2)-C(11) = 2.033 (6), Ru(3)-C(10) = 2.127 (5), Ru(3)-C(11) = 2.299 (5) Å) indicates coordination of the allenyl unit as a  $\sigma_2\pi$  five-electron donor, the  $\sigma$  interaction being that between C(11) and Ru(2).

(19) Gervasio, G.; Osella, D.; Valle, M. *Inorg. Chem.* **1976**, *15*, 1221.

(20) The dideuteriomethylene derivative **4** was synthesized from **2** and dideuteriodiazomethane and then converted to deuterated **3**. The hydride resonance at  $\delta -18.4$  in nondeuterated **3** was absent in the labeled complex. Moreover the resonance attributed to the methine hydrogen (C(8)-H(8) of Figure 3) at  $\delta 8.3$  was also absent.

(21) Chemical Abstracts Service names the organic fragment in **3** on the basis of the most preferred form. **3** might be described as an allenylcarbene or as a butadienediyl ligand. Chemical Abstracts has indicated that the preferred nomenclature is 2-(1-methylethyl)-2,3-butadienylidene. We are grateful to B. R. Cook for this advice.