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Enyne and Butatriene Ligands from the Reaction of Diynes on the Square Face of the Hydrido Phosphinidene Cluster $(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PPh})$

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Summary: Diphenylbutadiyne reacts with the 62-electron cluster nido-$(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PPh})$ *(**1**) to afford* $\text{Ru}_4(\text{CO})_{12}[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-P(Ph)C\{C(H)Ph\}CC(H)Ph}]$ *(**2**),* $\text{Ru}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-PPh})[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-PhC(H)CCC(H)Ph}]$ *(**3**), and* $\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-PPh})(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-PhC(H)C(H)CCPh}]$ *(**4**), containing coordinated trans-diphenylbutatriene and trans-diphenylbut-3-en-1-yne ligands. These reactions proceed via P—C bond formation and 1,4- and 1,2-diinsertion reactions into the two Ru—H bonds. Cluster **4** reacts with excess diphenylbutadiyne to generate* $\text{Ru}_4(\text{CO})_{10}(\mu_4\text{-PPh})[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-PhCCC(H)C(H)PhC(Ph)CCCPh}]$ *(**5**) via an ene-yne coupling sequence on an* Ru_4 *square face.*

Metal-mediated alkyne dimerization to enynes and butatrienes[1,2] and the generation of unsaturated or partially unsaturated metallo-C_4 and -C_6 chains[3] from diynes are of considerable importance in the context of synthesizing new polyunsaturated organic materials and complexes from simple precursors. We describe herein the synthesis of the *trans*-butatriene Ph(H)C=C=C=C(H)Ph and the *trans*-but-3-en-1-yne PhC≡CCH=C(H)Ph ligands via the reaction of the readily available reagent 1,4-diphenylbutadiyne with the cluster $(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PPh})$ (**1**).[4] Although coordinated butatrienes and enynes are known in mononuclear[5] chemistry and binuclear compounds of the type $\text{Fe}_2(\text{CO})_6(\mu\text{-butatriene})$ have been reported,[6] the clusters $\text{Ru}_4(\text{CO})_{12}[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-P(Ph)C\{C(H)Ph\}CC(H)Ph}]$ (**2**), $\text{Ru}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-PPh})[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-PhC(H)CCC(H)Ph}]$ (**3**) and $\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-PPh})(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-PhC(H)C(H)CCPh}]$ (**4**) represent to our knowledge the first examples of polynuclear clusters bearing these organic ligands. The conversion of **1** to **2**–**4** is mediated by facile P—C bond formation on a square Ru_3P face followed respectively by 1,4- and 1,2-dihydrometalation and skeletal isomerization reactions. Finally, we demonstrate that addition of a diyne to the coordinated enyne in **4** generates, via ene-yne coupling, an eight-carbon hydrocarbyl chain in $\text{Ru}_4(\text{CO})_{10}(\mu_4\text{-PPh})[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-PhCCC(H)C(H)PhC(Ph)CCCPh}]$ (**5**).

Transition-metal clusters supported by main-group fragments offer a unique opportunity to examine the directing/mediating ability of the p-block elements when reacted with unsaturated organic molecules. Recent investigations have focused on binuclear and polynuclear cluster compounds with group 15 and 16 ligands.[7] In a recent communication[8] we described the coordination and trimerization of diynes on a square face of the *nido* cluster $\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-PPh})$ (**6**) and demonstrated that diynes coordinate readily to the Ru_3P square face of **6** via facile P—C bond formation and a typical μ_3-η^2-||-bonding mode. The main-group atom in this case functions in the same way as a skeletal metal atom. The presence of two potentially reactive hydride

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(9) Selected data for **2**. Anal. Calcd for $C_{34}H_{17}O_{12}PRu_4$: C, 38.79; H, 1.63. Found: C, 38.58; H, 1.41. IR (ν(CO), cm^{-1}, C_6H_{12}): 2089 m, 2063 vs, 2035 m, 2029 m, 2016 w, 1990 w. $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, δ): 150.1 (s). ^1H NMR (200 MHz, $CDCl_3$, δ): 7.71–6.84 (mult, H_{phenyl}), 5.41 (s, PhC*H*=), 5.32 (s, PhC*H*=) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): 203.7 (s, *C*O), 199.9 (s, *C*O), 199.1 (d, J_{PC} = 16.6 Hz, *C*O), 195.0 (s, *C*O), 191.3 (s, *C*O), 189.9 (s, *C*O), 187.4 (d, J_{PC} = 6.0 Hz, *C*O), 186.9 (s, *C*O), 152.4 (d, J_{PC} = 10.6 Hz, =*C*=), 139.0 (s, C_{ipso}), 137.5 (d, J_{PC} = 6.5 Hz, =*C*H–), 137.3 (d, J_{PC} = 18.1 Hz, C_{ipso}), 134.5 (d, J_{PC} = 13.6 Hz, C_{ipso}), 132.3–128.5 (mult, C_{phenyl}), 72.1 (d, J_{PC} = 25.6 Hz, =*C*=), 71.1 (d, J_{PC} = 21.1 Hz, =*C*H–) ppm.

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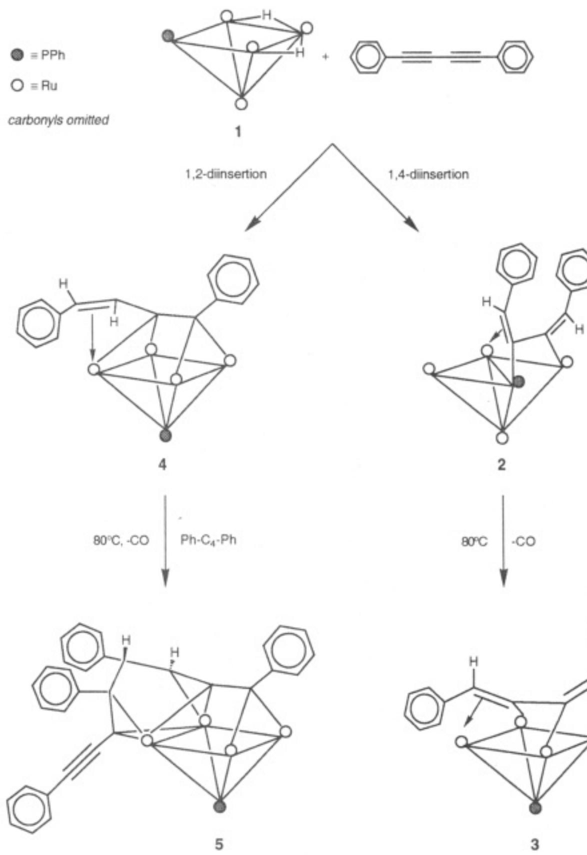
Scheme 1



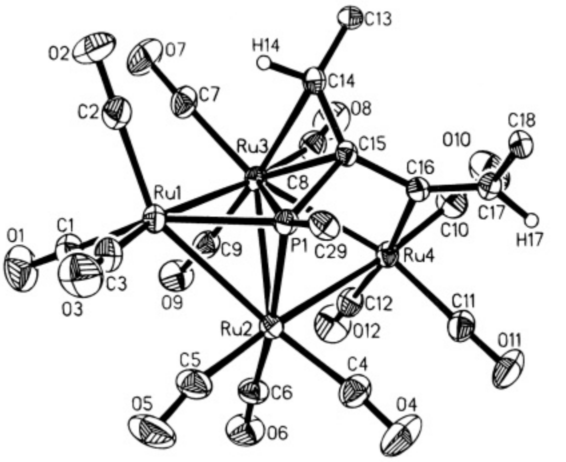


Figure 1. Molecular structure of $Ru_4(CO)_{12}[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-}P(Ph)C\{C(H)Ph\}CC(H)Ph]$ (**2**) illustrating the coordination mode of the diphenylbutatriene ligand. For clarity, only the *ipso* carbon atoms of the phenyl rings are illustrated. Important bond lengths (Å) and angles (deg): Ru(1)—Ru(2) = 2.857(1); Ru(1)—Ru(3) = 2.827(1); Ru(2)—Ru(3) = 2.891(1); Ru(2)—Ru(4) = 2.953(1); Ru(3)—Ru(4) = 2.813(1); Ru(1)—P(1) = 2.303(1); Ru(2)—P(1) = 2.317(1); Ru(3)—P(1) = 2.838(1); Ru(3)—C(14) = 2.420(4); Ru(3)—C(15) = 2.408(4); P(1)—C(15) = 1.818(5); Ru(4)—C(16) = 2.119(4); C(14)—C(15) = 1.396(6); C(15)—C(16) = 1.469(6); C(16)—C(17) = 1.340(6); C(13)—C(14)—C(15) = 128.5(4); C(14)—C(15)—P(1) = 117.5(3); C(14)—C(15)—C(16) = 129.8(4); C(15)—C(16)—C(17) = 127.0(3); C(16)—C(17)—C(18) = 130.6(4).

ligands in the isoelectronic cluster **1** prompted us to extend this fascinating chemistry.

Thermal treatment (*n*-heptane, 70 °C, 70 min) of **1** (0.100 g, 0.118 mmol) with excess diphenylbutadiyne (0.072 g, 0.354 mmol) results in a marked color change from orange to red-brown. Separation of the reaction products was achieved via thin-layer chromatography using silica gel plates (20 × 20 cm, Merck, TLC grade, Aldrich Chemical Co.) and a hexane/CH_2Cl_2 mixture (85:15) as the eluant. The first band eluted contained a mixture of **2** and **4**; however, cluster **2** could be fractionally crystallized from CH_2Cl_2/MeOH solutions at −10 °C. Four major products were recovered from the reaction mixture in varying yields (**2**, ~15%; **3**, ~10%; **4**, ~20%; **5**, ~5%) (Scheme 1). Clusters **2**−**5** have been fully characterized by IR and $^{31}P\{^1H\}$ and ^1H NMR spectroscopy and by single-crystal X-ray analyses.

The presence of a high-field signal in the $^{31}P\{^1H\}$ NMR spectrum of **2** (δ 150.1 ppm; $\Delta \approx 260$ ppm vs **1**) suggested substantial rearrangement of the coordination environment about phosphorus. Proton NMR spectra indicated the absence of hydride signals and the presence of uncoupled resonances (δ 5.41, 5.32 ppm) in the olefinic region. An X-ray analysis[10] provided full details of the molecular structure (Figure 1). The formation of **2** has occurred via a 1,4-diinsertion of the C_4 chain into the Ru—H bonds and the coordination of the generated 1,4-diphenylbutatriene ligand onto the distorted Ru_3P face. The phosphinidene ligand, originally capping the open Ru(1)—Ru(2)—Ru(4) face in **1**, is now coordinated to the two hinge atoms (Ru(2)—P(1) = 2.317(1) Å; Ru(3)—P(1) = 2.838(1) Å) and one wingtip atom (Ru(1)—P(1) = 2.303(1) Å) in **2**. The dihedral angle between the two Ru_3 planes in **2** (161°) is much greater than that found in **1** (104°), and the *trans*-diphenylbutatriene ligand lies exclusively to one side of the Ru_3P face. The C—C bond lengths (C(14)—C(15) = 1.396(6) Å; C(15)—C(16) = 1.469(6) Å; C(16)—C(17) = 1.340(6) Å) reflect the $2\sigma-\pi$ interactions of the unsaturated chain, which can be regarded as a 1,4-diphenylbuta-1,3-diene-2,3-diyl ligand. There was no evidence for the generation of the *cis*-butatriene.

Cluster **2** undergoes a smooth and quantitative transformation to **3** (*n*-heptane, 80 °C, 4 h) via a decarbonylation/skeletal isomerization sequence. The $^{31}P\{^1H\}$ NMR signal for **3**[11] is in the region associated with μ_4-PR ligands capping an electron precise M_4 face[12] and full details were provided by an X-ray analysis.[13] The molecular structure of **3** is shown in Figure 2, emphasizing the coordination mode of the butatriene ligand

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[10] Dark red needle prisms of **2** were grown from CH_2Cl_2/*n*-hexane solutions at 263 K. Crystals of $Ru_4(CO)_{12}[P(Ph)C\{C(H)Ph\}CC(H)Ph]$ are monoclinic, space group $P2_1/c$, with $a = 19.162(2)$ Å, $b = 10.714(2)$ Å, $c = 17.955(3)$ Å, $\beta = 105.61(2)°$, $T = 295$ K, $V = 3550.5(9)$ Å^3, $d_{calc} = 1.969$ g cm^{-3}, and $Z = 4$. Data were collected via the ω-scan method on a Nicolet-Siemens R3m/V diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation in the 2θ range 4.0−50.0°. A total of 6293 independent reflections were collected, of which 4631 were observed ($F \geq 6.0\sigma(F)$). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to yield $R = 0.0240$ and $R_w = 0.0244$.

[11] Selected data for **3**. Anal. Calcd for $C_{33}H_{17}O_{11}PRu_4$: C, 38.68; H, 1.67. Found: C, 38.70; H, 1.60. IR (ν(CO), cm^{-1}, C_6H_{12}): 2080 m, 2046 s, 2037 vs, 2023 s, 2018 s, 1989 m, 1981 w, 1827 w. $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, δ): 366.2 (s). ^1H NMR (200 MHz, $CDCl_3$, δ): 7.39−7.03 (mult, H_{phenyl}), 5.18 (s, PhC*H*=) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): 149.6 (d, $J_{PC} = 3.0$ Hz, =*C*=), 141.6 (d, $J_{PC} = 24.6$ Hz, C_{ipso}), 136.6 (s, C_{ipso}), 133.3−128.1 (mult, C_{phenyl}), 95.8 (d, $J_{PC} = 5.0$ Hz, =*C*H) ppm.

[12] Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quinn, L. D., Eds.; VCH: New York, 1987, Chapter 16.

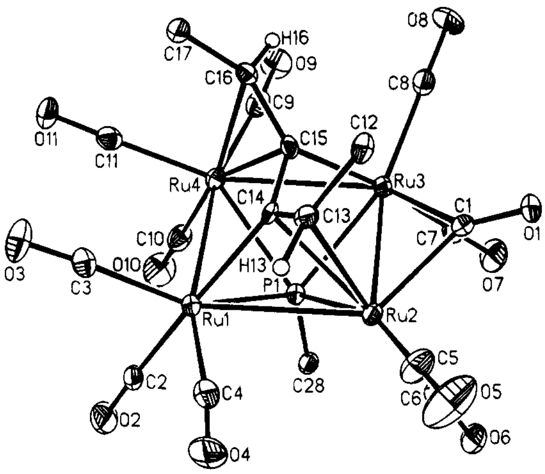

Figure 2. Molecular stucture of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}PhC(H)CCC(H)Ph]$ (**3**). For clarity, only the *ipso* carbon atoms of the phenyl rings are illustrated. Important bond lengths (Å) and angles (deg): Ru(1)—Ru(2) = 2.933(1); Ru(1)—Ru(4) = 2.915(1); Ru(2)—Ru(3) = 2.824(1); Ru(3)—Ru(4) = 2.912(1); Ru(1)—C(14) = 2.137(5); Ru(2)—C(13) = 2.462(5); Ru(2)—C(14) = 2.289(4); Ru(3)—C(15) = 2.121(5); Ru(4)—C(15) = 2.316(5); Ru(4)—C(16) = 2.479(5); C(13)—C(14) = 1.384(7); C(14)—C(15) = 1.479(7); C(15)—C(16) = 1.389(6); C(13)—Ru(2)—P(1) = 107.3(1); C(14)—Ru(1)—P(1) = 79.0(1); C(14)—Ru(2)—P(1) = 73.7(1); C(15)—Ru(3)—P(1) = 78.6(1); C(15)—Ru(4)—P(1) = 73.4(1); C(16)—Ru(4)—P(1) = 106.9(1); C(12)—C(13)—C(14) = 131.5(4); C(13)—C(14)—C(15) = 124.3(6); C(14)—C(15)—C(16) = 125.1(4); C(15)—C(16)—C(17) = 131.4(4).

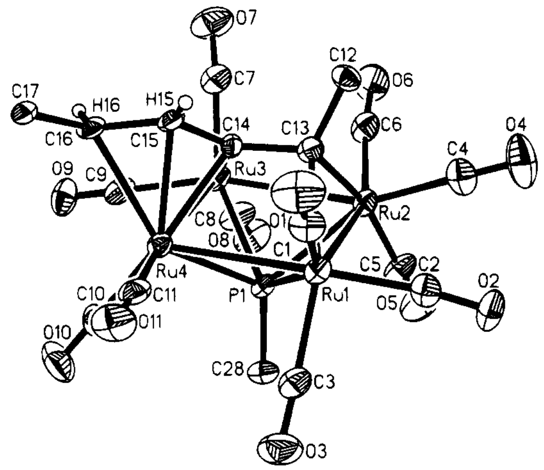

Figure 3. Projection of the molecular structure of $Ru_4(CO)_{11}(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^3\text{-}PhC(H)C(H)CCPh]$ (**4**) with phenyl rings omitted for clarity. Important bond lengths (Å) and angles (deg): Ru(1)—Ru(2) = 2.823(1); Ru(1)—Ru(4) = 2.889(1); Ru(2)—Ru(3) = 2.888(1); Ru(3)—Ru(4) = 2.806(1); Ru(1)—C(13) = 2.208(9); Ru(2)—C(13) = 2.155(10); Ru(3)—C(14) = 2.192(9); Ru(4)—C(14) = 2.166(9); Ru(4)—C(15) = 2.251(9); Ru(4)—C(16) = 2.352(9); C(13)—C(14) = 1.422(13); C(14)—C(15) = 1.418(13); C(15)—C(16) = 1.405(14); C(13)—Ru(1)—P(1) = 79.1(2); C(13)—Ru(2)—P(1) = 79.1(3); C(14)—Ru(3)—P(1) = 75.1(2); C(14)—Ru(4)—P(1) = 75.3(3); C(15)—Ru(4)—P(1) = 112.6(3); C(16)—Ru(4)—P(1) = 137.4(3); C(12)—C(13)—C(14) = 115.9(8); C(13)—C(14)—C(15) = 125.0(8); C(14)—C(15)—C(16) = 124.3(8); C(15)—C(16)—C(17) = 121.6(8).

on the Ru_4 face. The distances associated with the C_4 chain (C(13)—C(14) = 1.384(7) Å; C(14)—C(15) = 1.479(7) Å; C(15)—C(16) = 1.389(6) Å) reflect the additional π-interaction on going from **2** to **3**, required to satisfy the electronic requirements of the Ru_4 plane, resulting in a lengthening of the third C═C bond. The *trans* disposition of the olefinic protons is also retained on going from **2** to **3**.

The molecular structure of **4**, the final major product isolated from the reaction mixture, is shown in Figure 3.[14] The phosphinidene fragment caps a square Ru_4 face, and 1,2-diinsertion of diphenylbutadiyne has afforded 1,4-diphenylbut-3-en-1-yne, which is attached to the opposite side of the metal square. The coupling constants associated with the two olefinic protons ($^3J_{HH}$ = 7.9 Hz) reflect a relative pseudo *trans* relationship (dihedral angle ~141°) with H(16) also coupled to the phosphorus atom ($^3J_{PH}$ = 2.9 Hz).[15] The metal—carbon distances associated with the alkyne (Ru(1)—C(13) = 2.208(9) Å; Ru(2)—C(13) = 2.155(10) Å; Ru(3)—C(14) = 2.192(9) Å; Ru(4)—C(14) = 2.166(9) Å) and olefin moieties (Ru(4)—C(15) = 2.251(9) Å; Ru(4)—C(16) = 2.352(9) Å) lie within a narrow range. It is noteworthy that, including the Ru—olefin interaction, the C_4 hydrocarbyl acts as a six-electron donor to the metal framework which has a total of 64 cluster valence electrons. The related molecules $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}X)$ (X = four-electron donor)[7c,16] are electron deficient according to the EAN rule and exhibit marked upfield shifts in their $^{31}P\{^1H\}$ NMR spectra compared to **4**.

The η^2-olefin interaction of the 1,4-diphenylbut-3-en-1-yne ligand in **4** is easily displaced and accounts for the formation of **5** during the reaction sequence. Once isolated, **4** is easily and quantitatively converted to **5** via the addition of excess PhC_4Ph (*n*-heptane, 80 °C).[17] The Ru(3)—Ru(4) bonding distance in **5** (2.714(1) Å) has contracted considerably on going from **4** to **5** and is unsymmetrically bridged by C(19) (Ru(3)—C(19) = 2.060(5) Å; Ru(4)—C(19) = 2.247(6) Å).[18] The eight-carbon atom chain has formed from the coupling of one of the alkyne units to the previously coordinated olefin. The second alkyne functionality of the incoming

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(13) Red needle plates of **3** were grown from the slow evaporation of n-hexane solutions at 295 K. Crystals of $Ru_4(CO)_{11}(PPh)[Ph(H)CCCC(H)Ph]$ are triclinic, space group $P\bar{1}$, with a = 9.256(2) Å, b = 12.198(3) Å, c = 15.700(3) Å, α = 95.54(2)°, β = 96.90(2)°, γ = 101.06(2)°, T = 200 K, V = 1714.0(6) Å^3, d_{calc} = 1.986 g cm^{-3}, and Z = 2. Data were collected as for **2** on an LT-2 equipped Nicolet-Siemens R3m/V diffractometer in the 2θ range 4.0−50.0°. The structure was solved (Patterson/Fourier) and refined using 4836 observed data (6061 independent data collected). Refinement converged at R = 0.0313 and R_w = 0.0365.

(14) Red-brown prisms of **4** were grown from the slow evaporation of CH_2Cl_2/*n*-hexane solutions at 295 K. Crystals of $Ru_4(CO)_{11}(PPh)[Ph(H)CCCC(H)Ph]$ are monoclinic, space group $P2_1/c$, with a = 9.952(2) Å, b = 16.189(3) Å, c = 20.888(4) Å, β = 94.17(2)°, T = 295 K, V = 3356.3(11) Å^3, d_{calc} = 2.028 g cm^{-3}, and Z = 4. Data were collected as for **2** in the 2θ range 4.0−50.0°. The structure was solved (Patterson/Fourier) and refined using 4333 observed reflections (5942 independent data collected) to yield R = 0.0491 and R_w = 0.0560.

(15) Selected data for **4**. Anal. Calcd for $C_{33}H_{17}O_{11}PRu_4$: C, 38.68; H, 1.67. Found: C, 38.46; H, 1.42. IR (ν(CO), cm^{-1}, C_6H_{12}): 2083 w, 2058 vs, 2049 s, 2024 s, 2019 s, 1984 m, 1966 w. $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, δ): 401.3 (s). ^1H NMR (200 MHz, $CDCl_3$, δ): 7.55−7.05 (mult, H_{phenyl}), 5.25 (d, $^3J_{HH}$ = 7.9 Hz, PhC*H*═), 3.86 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{PH}$ = 2.9 Hz, ═C*H*—) ppm. $^{13}C\{^1H\}$ NMR (63.0 MHz, $CDCl_3$): 203.2 (d, J_{PC} = 7.6 Hz, *C*O), 197.9 (s, *C*O), 195.6 (d, J_{PC} = 8.8 Hz, *C*O), 195.3 (d, J_{PC} = 10.1 Hz, *C*O), 193.7 (s, *C*O), 162.9 (d, J_{PC} = 6.9 Hz, C_{alkyne}), 154.3 (d, J_{PC} = 5.0 Hz, C_{alkyne}), 142.5 (d, J_{PC} = 20.2 Hz, C_{ipso}), 139.2−125.1 (mult, C_{phenyl}), 96.0 (d, J_{PC} = 3.0 Hz, C_{olefin}), 67.2 (d, J_{PC} = 7.6 Hz, C_{olefin}) ppm.

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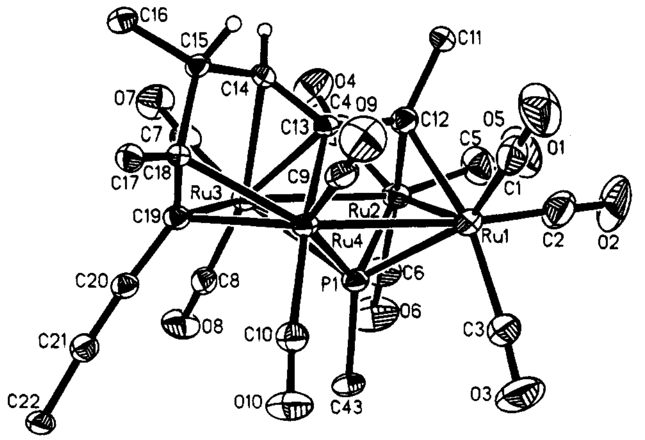

Figure 4. Molecular structure of $Ru_4(CO)_{10}(\mu_4\text{-PPh})[\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-PhCCC(H)C(H)PhC(Ph)CCCPh}]$ (**5**) illustrating the coordinated eight-carbon hydrocarbyl chain. Important bond lengths (Å) and angles (deg): Ru(1)—Ru(2) = 2.862(1); Ru(1)—Ru(4) = 2.908(1); Ru(2)—Ru(3) = 2.951(1); Ru(3)—Ru(4) = 2.714(1); Ru(1)—C(12) = 1.866(8); Ru(2)—C(12) = 2.172(6); Ru(3)—C(13) = 2.250(6); Ru(4)—C(13) = 2.084(5); Ru(3)—C(14) = 2.314(6); Ru(4)—C(18) = 2.329(5); Ru(3)—C(19) = 2.060(5); Ru(4)—C(19) = 2.247(6); C(12)—C(13) = 1.482(8); C(13)—C(14) = 1.349(7); C(14)—C(15) = 1.548(7); C(15)—C(18) = 1.520(7); C(18)—C(19) = 1.428(8); C(19)—C(20) = 1.423(8); C(20)—C(21) = 1.200(8); C(12)—Ru(1)—P(1) = 78.8(2); C(12)—Ru(2)—P(1) = 78.8(2); C(13)—Ru(3)—P(1) = 72.6(1); C(13)—Ru(4)—P(1) = 77.5(1); C(14)—Ru(3)—P(1) = 106.9(1); C(18)—Ru(4)—P(1) = 128.4(2); C(19)—Ru(3)—P(1) = 98.3(1); C(19)—Ru(4)—P(1) = 95.9(1); C(11)—C(12)—C(13) = 116.6(4); C(12)—C(13)—C(14) = 128.0(5); C(13)—C(14)—C(15) = 117.6(5); C(14)—C(15)—C(16) = 113.0(4); C(14)—C(15)—C(18) = 109.2(4); C(17)—C(18)—C(19) = 124.5(5); C(18)—C(19)—C(20) = 124.2(5); C(19)—C(20)—C(21) = 174.3(6); C(20)—C(21)—C(22) = 176.4(6).

butadiyne remains uncoordinated. The C—C distances of the 3,6-dimetalated 1,4,5,8-tetraphenylocta-1,7-diyn-3-ene ligand vary considerably, in accordance with the bonding nature of the generated hydrocarbyl (C(12)—C(13) = 1.482(8) Å; C(13)—C(14) = 1.349(7) Å; C(14)—C(15) = 1.548(7) Å; C(15)—C(18) = 1.520(7) Å; C(18)—C(19) = 1.428(8) Å; C(19)—C(20) = 1.423(8) Å; C(20)—C(21) = 1.200(8) Å) although the short distance between atoms C(13) and C(14) is unusual.

There are several notable and distinctive features of the synthesis of butatriene, enyne, and enediyne ligands from **1** and diynes. Formation of *trans*-1,4-diphenylbutatriene and *trans*-1,4-diphenylbut-3-en-1-yne (PhC≡CCH=C(H)Ph) occurs via 1,4- and 1,2-dihydrometalation reactions from the cluster $(\mu\text{-H})_2Ru_4(CO)_{12}(\mu_3\text{-PPh})$. This reaction sequence may have potential for the synthesis of less accessible butatrienes and enynes. Moreover, the synthesis of **5** from a coordinated enyne and free diyne shows that ene−yne coupling can be mediated at a polynuclear site. Finally, it has become evident from this and previous work[8] that alkyne−alkyne and alkyne−ene couplings on Ru_4 clusters with square M_3P or M_4 faces yield *noncyclic* unsaturated hydrocarbon products. We are currently examining the potential of this cluster-mediated chemistry for the generation of other saturated and unsaturated hydrocarbon chains via ene−ene, ene−yne, and related coupling sequences.

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Supplementary Material Available: For complexes **2**−**5**, details of the structure determination (Tables S1, S7, S13, and S19, non-hydrogen atomic positional parameters (Tables S2, S8, S14, and S20), bond distances (Tables S3, S9, S15, and S21), bond angles (Tables S4, S10, S16, and S22), anisotropic thermal parameters (Tables S5, S11, S17, and S23), and hydrogen atom positions (Tables S6, S12, S18, and S24) (38 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors are available from the authors upon request.

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(17) Selected data for **5**. Anal. Calcd for $C_{48}H_{27}O_{10}PRu_4$: C, 48.08; H, 2.27. Found: C, 48.34; H, 2.22. IR (ν(CO), cm^{-1}, C_6H_{12}): 2075 m, 2051 vs, 2032 s, 2022 s, 2015 m, 2005 w, 1989 w. $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, δ): 473.3 (s). ^1H NMR (200 MHz, $CDCl_3$, δ): 8.21−7.00 (mult, H_{phenyl}), 5.19 (s, −C*H*−), 4.98 (s, −C*H*−) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): 197.9 (d, J_{PC} = 4.2 Hz, *C*O), 198.6 (d, J_{PC} = 15.6 Hz, *C*O), 198.2 (d, J_{PC} = 30.2 Hz, *C*O), 196.2 (d, J_{PC} = 7.5 Hz, *C*O), 195.9 (d, J_{PC} = 11.6 Hz, *C*O), 194.9 (d, J_{PC} = 10.6 Hz, *C*O), 183.1 (s, C_{alkyne}), 175.5 (d, J_{PC} = 4.5 Hz, C_{alkyne}), 154.9 (d, J_{PC} = 3.0 Hz, C_{alkyne}), 144.4 (d, J_{PC} = 19.6 Hz, C_{ipso}), 141.1 (s, C_{ipso}), 140.9 (s, C_{ipso}), 133.7−124.8 (mult, C_{phenyl}), 123.4 (s, C_{ipso}), 122.0 (d, J_{PC} = 4.0 Hz, C_{alkyne}), 118.1 (s, C_{ipso}), 113.4 (d, J_{PC} = 6.0 Hz, C_{alkyne}), 107.4 (s, −*C*H−=), 98.3 (s, C_{alkyne}), 62.0 (s, −*C*H−) ppm.

(18) Red-brown prisms of **5** were grown from the slow evaporation of CH_2Cl_2/*n*-hexane solutions at 295 K. Crystals of $Ru_4(CO)_{10}(\mu_4\text{-PPh})$-[PhCCC(H)C(H)PhC(Ph)CCCPh] are monoclinic, space group $P2_1/n$, with a = 11.491(2) Å, b = 31.812(7) Å, c = 12.465(4) Å, β = 102.68(2)°, T = 295 K, V = 4445.3(14) Å^3, d_{calc} = 1.791 g cm^{-3}, and Z = 4. Data were collected as for **2** on in the 2θ range 4.0−50.0°. The structure was solved (Patterson/Fourier) and refined using 5033 observed reflections (7868 independent data collected) to yield R = 0.0329 and R_w = 0.0316.