3160 *Organometallics* 1992, *11*, 3160–3163

hydrido–methylene-to-methyl transformation that was noted earlier for compound 8. These "RhIr" and "Ir_2" systems described offer a unique opportunity for the investigation of the stepwise transformations involved in the activation of an alkyl C–H bond by an adjacent metal. By varying the ancillary ligands, it should be possible to "fine tune" the electron density at the metals such that the transformation from terminal methyl to bridged methyl to hydrido–methylene species can be effected.

Binuclear complexes in which facile and reversible methyl-to-hydrido–methylene interconversions occur in the presence of unsaturated substrates, such as ethylene, are of obvious importance in studies involving the coupling of organic substrates. Such coupling may occur via alkyl migration to the olefin ligand,[25] by insertion of the olefin into a bridging methylene group,[26] or by olefin insertion into the metal–hydride bond to give a methylene-bridged alkyl complex,[19d] which may then undergo coupling of the alkyl and methylene moieties. It is hoped that future studies on these systems will yield information about these important processes.

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Registry No. **1**, 126501-61-9; **2**, 143171-99-7; **3**, 143172-00-3; **4**, 143172-02-5; **5**, 143172-04-7; **6**, 143172-06-9; **7**, 97487-41-7; **8**, 143172-08-1; **9**, 143172-10-5; **10**, 143172-11-6; **11**, 143172-13-8; **12**, 143172-15-0; **13a**, 143172-17-2; **13b**, 143172-19-4.

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Tailored Synthesis of Hydrocarbon Chains via C–C Coupling Reactions of Diynes and Alkynes on the Square Face of an Ru_4P Cluster

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Summary: The mixed transition-metal–main-group cluster $Ru_4(\mu_3\text{-}PPh)(CO)_{13}$ (1) trimerizes diynes and codimerizes alkynes and diynes to form novel 12- and 8-carbon-atom hydrocarbyls. The X-ray structures of $Ru_4(CO)_8(\mu_4\text{-}PPh)[\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}(Ph)CC(C{\equiv}CPh)C(Ph)C\text{-}\eta^4\text{-}CC(Ph)C(Ph)C\text{-}(C{\equiv}CPh)]$ (**2**) and $Ru_4(CO)_{10}(\mu\text{-}CO)_2[\mu_4\text{-}\eta^1(P){:}\eta^1(P){:}\eta^1\text{-}(P){:}\eta^1(C){:}\eta^2(C)\text{-}P(Ph)C(C{\equiv}CPh)C(Ph)]$ (**3**) are reported.

Carbon–carbon bond-forming reactions in di-[1] and polynuclear[2] clusters are of considerable current interest because of their potential for generating new and unusual types of linked hydrocarbon rings and chains. Such reactions may also serve as models for related processes occurring on metal surfaces.[3] Although there are many examples of novel reactivity patterns for alkynes coordinated in a multisite fashion at polynuclear metal centers, there are surprisingly few reports of diyne oligomerization at a cluster surface.[2a,4] An example of the synthesis of a diyne from an acetylide precursor has recently been described.[5] In this communication we report two new results: (i) the unprecedented coupling of three diynes to produce a 12-carbon hydrocarbyl fragment and (ii) the cocoupling of diynes and alkynes to afford novel co-oligomers with variable hydrocarbon chain lengths. While coupling of alkynes with μ_3 or μ_2 group 15 and 16 cluster stabilizing atoms to give novel M_nXC_2 (X = S, P, N) metallacycles is well established,[6] we are unaware of any examples of diyne or diyne–yne oligomerization via the intermediacy of $\mu_3\text{-}\eta^2\text{-}\|$ (M_2P) yne coordination and P–C bond making and breaking on a phosphinidene cluster.

We have investigated the reactivity of the 62-electron butterfly or nido cluster $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$[7] (1) toward a variety of diyne ligands and observed facile P–C bond formation/cleavage reactions and framework rearrangements in which the phosphorus atom appears to adopt the role of a skeletal atom. Thus, a solution of 1 in *n*-hexane (maintained at 60 °C) reacts with 1,4-diphenylbutadiyne (5 mol equiv) to yield the novel clusters **2** (60%) and **3** (30%). Both **2**[8] and **3**[9] have been fully characterized by

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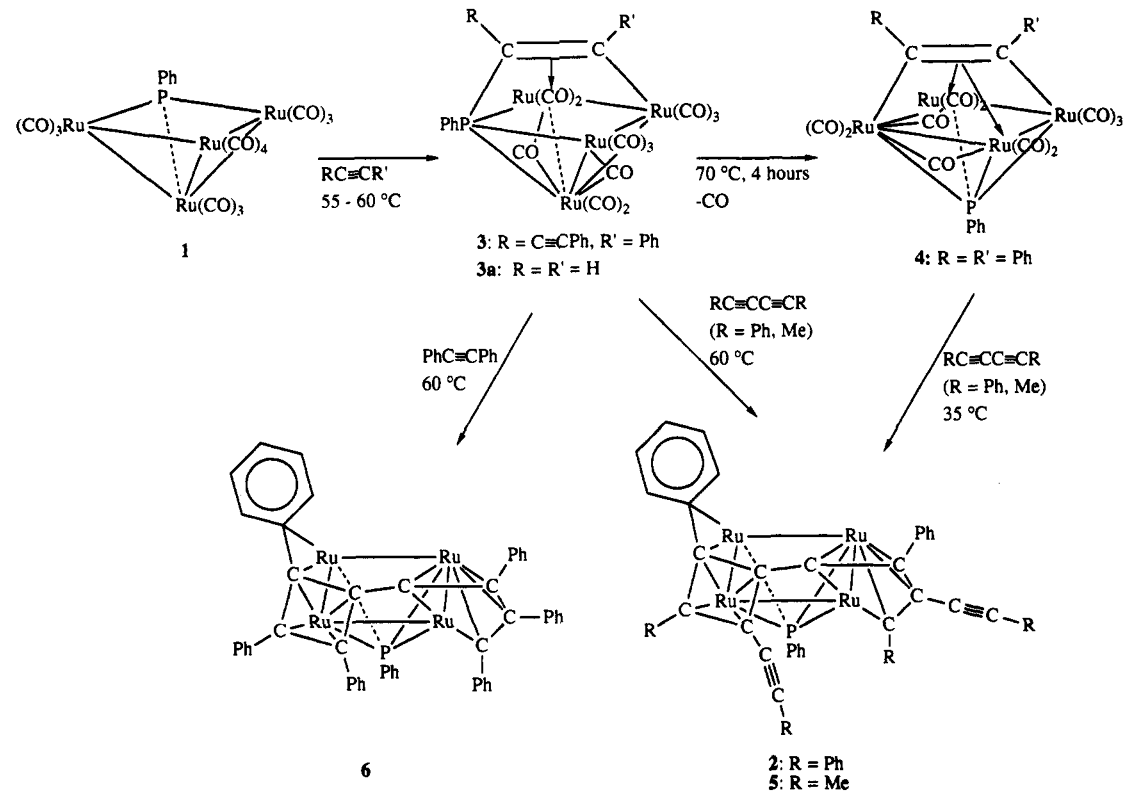
Scheme I[a]



1

3: R = C≡CPh, R' = Ph
3a: R = R' = H

4: R = R' = Ph

6

2: R = Ph
5: R = Me

[a] Carbonyl groups are omitted from 2, 5, and 6 for clarity.

IR, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ spectroscopy and elemental analysis. Cluster 3 has two bridging CO ligands (ν(CO) 1858, 1828 cm^{-1}) and a high-field $^{31}P\{^1H\}$ NMR resonance (δ 40.5 ppm) more characteristic of a μ_3-phosphido group than a phosphinidene.[10] The conclusion that in 3 the μ_3-PPh group is coupled to the diyne was subsequently confirmed by X-ray diffraction (vide infra).[11]

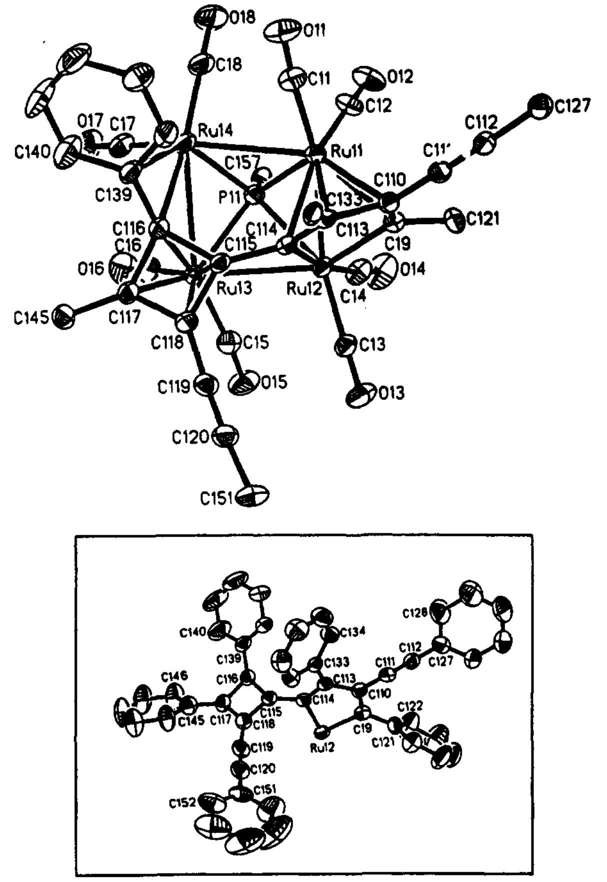


Figure 1. Perspective view of the molecular structure of Ru$_4$(CO)$_8$(μ_4-PPh)[η^1:η^1:η^2:η^2-(Ph)CC(C≡CPh)C(Ph)C-η^4-CC(Ph)C(Ph)C(C≡CPh)] (2), showing the atomic numbering scheme of molecule 1. For clarity only the ipso carbon atoms of the phenyl rings are illustrated. A view of the uncoordinated hydrocarbyl fragment is shown in the insert.

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(8) Data for 2: Anal. Calcd for $C_{62}H_{35}O_8PRu_4$: C, 55.44; H, 2.64. Found: C, 55.50; H, 2.54. IR (ν(CO), cm^{-1}; C_6H_{12}): 2036 (m), 2014 (s), 2011 (sh), 1975 (w), 1959 (w), 1945 (w). $^{31}P\{^1H\}$ NMR (101.3 MHz, CDCl$_3$; δ): +402.3. $^{13}C\{^1H\}$ NMR (62.8 MHz, CDCl$_3$; δ): 205.4 (d, CO, J_{PC} = 7.2 Hz), 204.2 (s, CO), 202.4 (d, CO, J_{PC} = 5.6 Hz), 201.6 (d, CO, J_{PC} = 4.0 Hz), 201.0 (s, C acetylene), 200.8 (s, C acetylene), 197.5 (d, CO, J_{PC} = 5.0 Hz), 197.3 (s, CO), 195.5 (s, CO), 192.9 (d, CO, J_{PC} = 33 Hz), 149.0 (s, C acetylene), 146.6 (d, C ipso, J_{PC} = 14.0 Hz), 145.0 (s, C ipso), 139.1 (s, C ipso), 139.0 (s, C ipso), 133.7 (s, C acetylene), 132.9 (s, C acetylene), 132.3–127.5 (phenyl region), 123.1 (s, C ipso), 122.1 (s, C ipso), 99.8 (s, C acetylene), 99.0 (C acetylene), 98.5 (s, C ipso), 93.6 (s, C acetylene), 88.2 (s, C acetylene), 87.8 (s, C acetylene), 78.2 (s, C acetylene), 75.7 (s, C acetylene).

(9) Data for 3: Anal. Calcd for $C_{34}H_{15}O_{12}PRu_4$: C, 38.88; H, 1.44. Found: C, 39.01; H, 1.53. IR (ν(CO), cm^{-1}; C_6H_{12}): 2087 (m), 2056 (s), 2045 (s), 2038 (s), 2024 (m), 2012 (sh), 2008 (w), 1987 (w), 1983 (w), 1979 (w), 1858 (w), 1828 (w). $^{31}P\{^1H\}$ NMR (CDCl$_3$, 101.3 MHz; δ): +40.5. $^{13}C\{^1H\}$ NMR (62.8 MHz, CDCl$_3$; δ): 207 (d, CO, $^2J_{PC}$ = 6.5 Hz), 198.4 (d, CO, $^2J_{PC}$ = 13 Hz), 192.7 (d, CO, $^2J_{PC}$ = 68 Hz), 186.7 (d, CO, $^2J_{PC}$ = 5 Hz), 185.2 (d, C acetylene, $^2J_{PC}$ = 30 Hz), 151.6 (d, C ipso, $^1J_{PC}$ = 18 Hz), 137.6 (d, C ipso, $^1J_{PC}$ = 35 Hz), 133.7 (d, C ortho, $^2J_{PC}$ = 11 Hz), 131.7 (s, C para), 128.1–129.4 (phenyl), 122.2 (s, C ipso), 92.0 (d, C acetylene, J_{PC} = 5 Hz), 91.5 (d, C acetylene, J_{PC} = 11 Hz), 89.0 (d, C acetylene, J_{PC} = 41 Hz).

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(11) Brown prisms of 3 were obtained by slow evaporation of a dichloroethane/*n*-heptane solution of the cluster at room temperature. Crystals of Ru$_4$(CO)$_{12}$(PPhC(C$_2$Ph)CPh) (3) are monoclinic, space group $P2_1/n$, with a = 9.606 (1) Å, b = 32.526 (3) Å, c = 11.825 (1) Å, and β = 101.25 (1)° at 294 K, V = 3523.67 Å^3, d_{calcd} = 1.926 g cm^{-3}, and Z = 4. Data were collected via ω scans on a Nicolet-Siemens R3m/V diffractometer with graphite-monchromated Mo Kα (λ = 0.71073 Å) radiation in the 2θ range 4.0–50.0°. A total of 6818 reflections were collected, of which 5121 were observed ($F \geq 6\sigma(F)$). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to yield R = 0.0246 and R_w = 0.0257.

The reaction of 1 with 1,4-diphenylbutadiyne to afford **3** (Scheme I) is highly regiospecific, only a single isomer being observed in the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra. The regiochemistry of addition was determined by identifying the ipso and acetylenic carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum[9] and by comparing the spectroscopic properties of **3** with those of the parent acetylenic cluster **3a**, $Ru_4(CO)_{12}[\mu_4\text{-}\eta^1(P)\text{:}\eta^1(P)\text{:}\eta^1(P)\text{:}\eta^1(C)\text{:}\eta^2(C)\text{-}P(Ph)\text{-}CHCH]$.[12] Compound **3a** was prepared similarly to **3** by heating an acetylene-saturated *n*-hexane solution of 1 at 60 °C for 3 h. Chromatographic separation using silica gel plates afforded **3a** (40%) as brown crystals from hexane (−20 °C). In **3** all four acetylenic carbon atoms couple to phosphorus (δ 185.2, $^2J_{PC}$ = 30 Hz; δ 92.0, $^2J_{PC}$ = 5 Hz; δ 91.5, J_{PC} = 11 Hz; δ 89, J_{PC} = 40 Hz), while only two of the three ipso carbons are coupled (δ 151, $^2J_{PC}$ = 18 Hz; δ 137, $^1J_{PC}$ = 35.2 Hz), the last two belonging to the phosphido phenyl ring and an alkyne phenyl ring. The shift to low field of the remaining ipso carbon signal (δ 123) is consistent with the deshielding effect of the alkyne triple bond.

In contrast to the case for **3**, the $^{31}P\{^1H\}$ shift for **2** (δ 402.3 ppm)[8] indicates a face-capping μ_4-PPh fragment. The *J*-modulated $^{13}C\{^1H\}$ NMR spectrum shows the presence of 19 quaternary carbon atoms, suggesting the incorporation of at least three diyne units. A single-crystal X-ray diffraction study[13] revealed the structure illustrated in Figure 1.

Crystals of **2** contain two independent but structurally identical molecules in the asymmetric unit. Bond lengths and angles are given for molecule 1. The structure consists of a severely distorted square planar array of ruthenium atoms (Ru(11)–Ru(12) = 2.686 (1) Å, Ru(12)–Ru(13) = 2.892 (1) Å, Ru(13)–Ru(14) = 3.003 (1) Å, Ru(11)–Ru(14) = 2.952 (1) Å) capped asymmetrically on one face by a μ_4-PPh ligand with the opposite face coordinated to 8 of the 12 acetylenic carbon atoms of 3 diyne fragments. The most outstanding feature of **2** is the 12-carbon hydrocarbyl fragment illustrated in the insert of Figure 1. Both unsaturated units of a single diyne are coordinated to the square Ru_4 face (Ru(11)–C(113) = 2.351 (5) Å, Ru(11)–C(114) = 2.270 (5) Å, Ru(12)–C(114) = 2.092 (6) Å, Ru(13)–C(115) = 2.228 (5) Å, Ru(13)–C(116) = 2.275 (6) Å). The other diynes are linked to this central C_4 fragment C(116)–C(115)–C(114)–C(113). One is incorporated into a metallacyclopentadiene ring system with Ru(12);[2a] the other is involved in an η^4-cyclobutadiene interaction with Ru(13). The ruthenacyclopentadiene is π-coordinated to Ru(11) with carbon–carbon bond lengths within this C_4 fragment (C(113)–C(114) = 1.392 (7) Å, C(113)–C(110) = 1.465 (9) Å, C(19)–C(110) = 1.419 (8) Å) suggestive of limited delocalization over the C_4 unit.[2c,14] While the cyclobutadiene ring is coordinated to Ru(13) via atoms C(115), C(116), C(117), and C(118) in a normal η^4 fashion, a closer examination reveals a very unusual "agostic-like" interaction[15] of C(116)–C(139) with Ru(14). Such "agostic" η^2-X–C(Ph)–metal interactions are rare, the only examples known to us being in the electronically unsaturated clusters $(H)Ru_3(CO)_9(\mu\text{-}PPh_2)$,[7] $HFe_3(CO)_9(\mu\text{-}P(C_6H_4OMe)_2]$,[16] and most recently $Mo_2Co(CO)_2Cp_2[\mu_3\text{-}C(Ph)C(H)C(Ph)C(Ph)](\mu_3\text{-}CPh)$.[15] The analogous coordination in **2** is considered to be a weak η^2-interaction (Ru(114)–C(139) = 2.388 (7) Å, Ru(114)–C(116) = 2.405 (6) Å) to the sp^2–sp^2 single bond C(139)–C(116). This η^2 interaction is in part attributed to the intrinsic electronic unsaturation that would exist at Ru(114) in its absence. The bond length of 1.486 (8) Å associated with C(116)–C(139) is longer than the other C_{sp^2}–C_{ipso} bonds in the molecule but consistent with an sp^2–sp^2 carbon single bond.

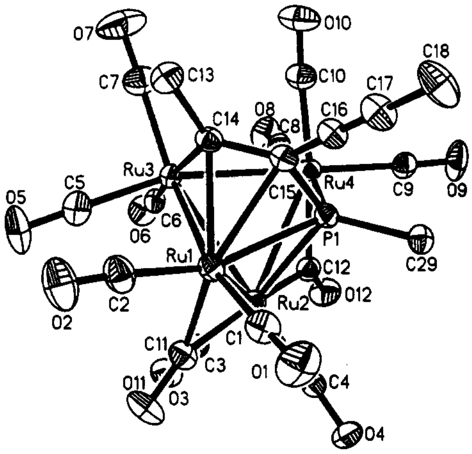

Figure 2. Perspective view of the molecular structure of $Ru_4(CO)_{12}[\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}P(Ph)C(C_2Ph)C(Ph)]$ (**3**) showing the atomic numbering scheme. For clarity only the ipso carbon atoms of the phenyl rings are shown.

Heating a solution of **3** in *n*-hexane (60 °C) with 2 equiv of 1,4-diphenylbutadiyne results in a remarkably facile transformation to **2** in yields of up to 70% (Scheme I). We were unable to isolate any intermediate resulting from the addition of a single diyne unit to **3** even in the presence of a deficiency of ligand, the major product under these conditions being **4**, identified as *closo*-$Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)$ from its characteristic IR and $^{31}P\{^1H\}$ spectroscopic data.[6c] The isolation of intermediates **3** and **4** offered the unique opportunity to utilize this coupling reaction to prepare mixed diyne-containing oligomers in a manner similar to the formation of **2**. The structure of intermediate **3** was determined by single-crystal X-ray diffraction. The structure (Figure 2)

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[12] Data for **3a**: Anal. Calcd for $C_{20}H_7O_{12}PRu_4$: C, 27.48; H, 0.81. Found: C, 27.72; H, 0.68. IR (ν(CO), cm^{-1}; C_6H_{12}): 2088 (w), 2057 (s), 2042 (s, sh), 2039 (s), 2024 (m), 2016 (sh), 2004 (w), 1992 (sh, w), 1982 (w), 1856 (w), 1830 (w). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.3 MHz; δ): 45.2. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.32 MHz, 298 K; δ): 207.2 (s, broad, CO), 205.3 (s, broad, CO), 201.5 (d, J_{PC} = 13.0 Hz, CO), 201.0 (d, J_{PC} = 13.0 Hz, CO), 193.3 (s, CO), 192.1 (s, CO), 187.0 (d, J_{PC} = 5.0 Hz, CO), 165.6 (d, J_{PC} + 20.0 Hz, C acetylene), 136.24 (d, J_{PC} = 30.0 Hz, C ipso), 131.1 (d, J_{PC} = 2.2 Hz, C para), 130.5 (d, J_{PC} = 12.0 Hz, C ortho), 128.7 (d, J_{PC} = 10.0 Hz, C meta), 89.8 (d, J_{PC} = 38.0 Hz, C acetylene).

[13] Deep red prisms of **2** were obtained by slow evaporation of a methanol/diethyl ether solution of the cluster at room temperature. Crystals of $Ru_4(CO)_8(PPh)(PhC{\equiv}CC{\equiv}CPh)_3$ are triclinic, space group $P\bar{1}$, with a = 10.748 (2) Å, b = 21.528 (3) Å, c = 24.519 (5) Å, α = 110.63 (1)°, β = 91.39 (2)°, and γ = 91.69 (1)° at 295 K, V = 5303.5 (16) Å^3, d_{calcd} = 1.682 g cm^{-3}, and Z = 4. Data were collected via ω scans on a Nicolet-Siemens R3m/V diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation in the 2θ range 4.0–46.0°. A total of 14838 reflections were collected, of which 10835 were observed ($F \geq 6\sigma(F)$). The structure was solved by direct methods and Fourier techniques and refined by blocked-matrix least-squares techniques to yield R = 0.0338 and R_w = 0.0431.

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[16] Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 739. (b) Knoll, K.; Huttner, G.; Zsolnai, L.; Orama, O.; Wasiucionek, M. *J. Organomet. Chem.* **1986**, *310*, 225.

[17] Data for **5**: Anal. Calcd for $C_{42}H_{27}O_8PRu_4$: C, 46.08; H, 2.49. Found: C, 45.98; H, 2.36. IR (ν(CO), cm^{-1}; C_6H_{12}): 2033 (m), 2009 (s), 2003 (sh), 1966 (w), 1956 (w), 1941 (w). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.3 MHz, 298 K; δ): 406. ^1H NMR (CD_2Cl_2, 250 MHz; δ): 8.1–6.9 (phenyl region, 15 H), 3.1 (s, CH_3, 3 H), 2.1 (d, J_{CH} = 1.6 Hz, CH_3, 3 H), 2.03 (s, CH_3, 3 H), 2.01 (s, CH_3, 3 H).

[18] Data for **6**: Anal. Calcd for $C_{58}H_{35}O_8PRu_4$: C, 53.79; H, 2.72. Found: C, 53.39; H, 3.10. IR (ν(CO), cm^{-1}; C_6H_{12}): 2033 (m), 2010 (s), 2003 (sh), 1972 (w), 1953 (w), 1943 (w). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.3 MHz, 298 K; δ): 409.

consists of a butterfly arrangement of metal atoms or, alternatively, a square-pyramidal Ru_4P arrangement, the phosphorus acting as a basal skeletal atom. If we assume the latter structural description, the diyne is μ_3-η^2-bonded to Ru(1)Ru(3)P(1) in a fashion commonly encountered for alkynes at a trimetal center with a C(14)–C(15) bond length of 1.394 (5) Å. The longest Ru–Ru bond (Ru(3)–Ru(4) = 2.915 (1) Å) is the hinge to wingtip vector void of any bridging ligands. Of particular interest is the bonding mode of the acetylene. Atoms Ru(3) and P(1) are σ-bound to the acetylenic carbons C(14) and C(15) (Ru(3)–C(14) = 2.188 (4) Å, P(1)–C(15) = 1.827 (4) Å), and Ru(1) is involved in a π-interaction with the same fragment (Ru(1)–C(14) = 2.282 (4) Å, Ru(1)–C(15) = 2.309 (4) Å). While the overall Ru_4PC_2 skeleton of **3** is nido with Ru(1) capping a distorted-pentagonal Ru(2)–Ru(3)–P(1)–C(14)–C(15) face as observed in the trimetal cluster $Fe_3(CO)_9[P(p\text{-}CH_3O\text{-}C_6H_4)C(Ph)C(Ph)]$,[6a,f] the original square Ru(1)–Ru(3)–Ru(4)–P(1) face of **1** is retained, with the four-coordinate P(1) atom in **1** becoming five-coordinate in **3**. The diphenylbutadiyne in **3** is coordinated in a manner similar to that found in $Ru_5(CO)_{12}(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(\mu\text{-}PPh_2)$[19] with a pendant acetylenic fragment (C(16)–C(17) = 1.187 (6) Å). Ten of the twelve carbonyl ligands in **3** are terminally bound to the ruthenium atoms, the remaining two, C(12)O(12) and C(11)O(11), bridging Ru(2)–Ru(4) and Ru(1)–Ru(2), respectively (Ru(1)–C(11) = 1.997 (4) Å, Ru(2)–C(11) = 2.173 (5) Å and Ru(4)–Ru(12) = 2.144 (4) Å, Ru(2)–C(12) = 2.086 Å).

Addition of 2,4-hexadiyne to an *n*-hexane solution of either **3** (at 60 °C) or **4** (at 35 °C) results in the formation (60%) of the cluster $Ru_4(CO)_8(\mu_4\text{-}PPh)(PhC{\equiv}CC{\equiv}CPh)(MeC{\equiv}CC{\equiv}CMe)_2$ (**5**; Scheme I). Compound **5** exhibited IR and ^{31}P NMR spectroscopic properties similar to those of **2**.[17] The formation of **5** from **3** identifies the source of the η^2 interaction to Ru(14) as originating from the μ_3-η^2-bound acetylene in the intermediate. The two uncoordinated acetylenic fragments in **2** therefore result from the additional diyne units added to **3**, the original μ_3-η^2-Ru_2P bound diyne interacting with all four ruthenium atoms in **2**. Overall, the unsaturated hydrocarbon ligand donates 12 electrons and in terms of cluster electron counting compound **2** is a 64-electron cluster, consistent with its square-planar arrangement of ruthenium atoms. The formation of clusters **2** and **5** proceeds with remarkable regiospecificity, a single isomeric form being observed for both compounds. In each case there are four potential isomers, differing in their regiochemistry of addition during the formation of the metallacyclopentadiene and cyclobutadiene rings. We found no spectroscopic evidence supporting the formation of other possible isomers.

The generation of **5** from **3** or **4** and 2,4-hexadiyne suggests a strategy for the designed synthesis of unsymmetrically substituted hydrocarbon fragments via cooligomerization of variously functionalized diynes and monoynes. Moreover, in **3** both the pendant triple bond and the μ_3-η^2-alkyne are sites of unsaturation. Accordingly, reaction of **3** (1 equiv) with $PhC{\equiv}CPh$ (2 equiv) affords $Ru_4(CO)_8(\mu_4\text{-}PPh)[\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}(Ph)CC(Ph)C(Ph)C\text{-}\eta^4\text{-}CC(Ph)C(Ph)C(Ph)]$ (**6**), which is spectroscopically similar to **2**[18] but lacks two uncoordinated $-C{\equiv}CPh$ moieties.

These studies suggest that mixed transition-metal–main-group clusters may direct new and unusual oligomerization reactions. We are currently exploring the potential of ruthenium–phosphinidene clusters to effect novel coupling sequences.

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Supplementary Material Available: For complexes **2** and **3**, details of the structure determination (Tables S1 and S8), atomic positional parameters (Tables S2 and S9), bond distances (Tables S3 and S10), bond angles (Tables S4 and S11), anisotropic thermal parameters (Tables S5 and S12), and hydrogen atom positions (Tables S6 and S13) (27 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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Transition Metal Stannyl Complexes. 6.[1] Chelate-Assisted Oxidative Addition of Sn–C Bonds to an Iron Center

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Summary: The phenyl stannyl complex $(CO)_3(Ph)FePPh_2CH_2CH_2SnPh_2$ (**3**) is prepared by oxidative addition of a Sn–Ph group of $Ph_2PCH_2CH_2SnPh_3$ (**1**) by two different routes: reaction of $Fe_2(CO)_9$ with **1** via $(CO)_4FePPh_2CH_2CH_2SnPh_3$ or reaction of $(CO)_4Fe(H)SiMePh_2$ with **1** via $(CO)_3(H)(MePh_2Si)FePPh_2CH_2CH_2SnPh_3$.

While oxidative addition of E–H bonds (E = C, Si, Sn) to transition metal centers is well understood, there are hardly any systematic investigations on the oxidative addition (reductive elimination) of Si–Si, Sn–Sn, Si–C, or Sn–C bonds. A better understanding on how these bonds can be activated by transition metals is necessary to develop catalytic processes involving these bonds.

We recently reported that reaction of $(Ph_3P)_4Pd$ with $Ph_2PCH_2CH_2SnR_3$ (R = Ph, Me) readily gave *trans*-$Pd(PPh_2CH_2CH_2SnR_2)_2$ by oxidative addition of two Sn–R groups and elimination of R–R. Products corresponding to earlier steps of the reaction, $(Ph_3P)(Ph)PtPPh_2(CH_2)_nSnPh_2$ (n = 2, 3) and *cis,cis,cis*-$(Me)_2Pt(PPh_2CH_2CH_2SnMe_2)_2$, were obtained by reaction of

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[1] Part 5: Schubert, U.; Schubert, J. *J. Organomet. Chem.*, in press.