Coupling of Acetylide Ligands on an Electron-Rich Tetraruthenium Diphosphido Framework: Synthesis, Structure, and Reactivity Studies of $Ru_4(CO)_9(\mu\text{-}PPh_2)_2(C_2Bu^t)_2$ and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(C_4Bu^t{}_2)$

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*Summary: Thermolysis of $Ru_2(CO)_6(\mu\text{-}PPh_2)(C_2Bu^t)$ (**1**) in toluene afforded $Ru_4(CO)_9(\mu\text{-}PPh_2)_2(C_2Bu^t)_2$ (**2**) in which the acetylide ligands are coordinated to a novel 64-electron butterfly platform. Upon thermolysis, this complex underwent C−C bond coupling to give the diyne complexes $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(C_4Bu^t{}_2)$ (**3**) and $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(C_4Bu^t{}_2)$ (**4**) through sequential CO elimination and fragmentation, respectively.*

The coupling of terminal or functionalized metal acetylides via methodologies such as oxidative[1] or Cadiot−Chodkiewicz[2] coupling has been extensively exploited recently to generate polycarbon ligand complexes and new molecular materials possessing extended carbon unsaturation.[3] In principle, it should be possible to effect head-to-head or tail-to-tail linkage of acetylides or polyacetylides coordinated in a multisite fashion on a binuclear or cluster framework to synthesize new multimetallic polycarbon complexes in which the full potential of σ- and π-electrons of the alkynyl fragments are used in bonding. This strategy has as yet been little exploited in organometallic chemistry.[4] In this communication, we describe the stereospecific high-yield head-to-head intermolecular coupling of μ-η^1:η^2-alkynyl groups in $Ru_2(CO)_6(\mu\text{-}PPh_2)(C{\equiv}CBu^t)$[5] (**1**) molecules to produce an eight-electron-donor butadiyne ligand on an Ru_4 framework. Although the cleavage of diynes by transition-metal clusters has been reported,[6] the formation of diynes from intermolecular coupling of acetylides is, to our knowledge, rare.[7]

Thermolysis of **1** in toluene solution at reflux for 4 h afforded a 1:1 mixture of diacetylide complex $Ru_4(CO)_9(\mu\text{-}PPh_2)_2(C_2Bu^t)_2$ (**2**) and diyne metal complex $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(C_4Bu^t{}_2)$ (**3**) as a mixture of red crystalline materials in 57% yield after recrystallization from CH_2Cl_2 and methanol at room temperature. Attempts to separate these cluster complexes by chromatography proved fruitless because of the similar R_f values and the rapid decomposition of **3** on contact with silica gel. However, thermolysis of the mixture in toluene for 1 h led to the isolation of **3** with ≥95% purity and in nearly quantitative yield. This suggested that complex **2** is an intermediate prior to the formation of **3**. Accordingly, pure **2** was obtained by treatment of the mixture with carbon monoxide in toluene (1 atm, 80 °C) for 5 min. Under such conditions, complex **3** present in the mixture was found to convert into triruthenium cluster $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(C_4Bu^t{}_2)$ (**4**) in 90% yield, leaving **2** intact. The clusters **2** and **4** can then be separated using chromatographic workup followed by recrystallization. These stepwise transformations can be summarized:

$$\underset{\mathbf{1}}{2Ru_2(CO)_6(\mu\text{-}PPh_2)(C_2Bu^t)} \rightarrow$$
$$\underset{\mathbf{2}}{Ru_4(CO)_9(\mu\text{-}PPh_2)_2(C_2Bu^t)_2} \rightarrow$$
$$\underset{\mathbf{3}}{Ru_4(CO)_8(\mu\text{-}PPh_2)_2(C_4Bu^t{}_2)} \rightarrow$$
$$\underset{\mathbf{4}}{Ru_3(CO)_8(\mu\text{-}PPh_2)_2(C_4Bu^t{}_2)} + Ru_3(CO)_{12}$$

The reaction sequences **2** → **3** → **4** were further verified by conversion of a pure sample of **2** in toluene and by treatment of a pure sample of **3** with CO under identical conditions.

Compounds **2**−**4** were initially characterized by spectral methods.[8] Single-crystal X-ray diffraction studies

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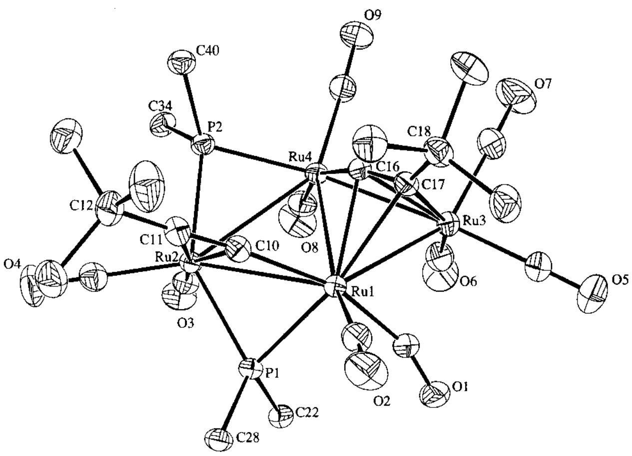

Figure 1. Molecular structure of **2** and the atomic numbering scheme. The phenyl groups of the phosphido ligands are omitted for clarity. Selected bond lengths (Å): Ru(1)−Ru(2) = 3.0207(4), Ru(1)−Ru(3) = 2.7815(4), Ru(1)−Ru(4) = 3.0437(4), Ru(2)−Ru(4) = 3.0974(4), Ru(3)−Ru(4) = 2.8575(4), Ru(1)−P(1) = 2.366(1), Ru(2)−P(1) = 2.344(1), Ru(2)−P(2) = 2.358(1), Ru(4)−P(2) = 2.302(1), Ru(1)−C(10) = 2.052(4), Ru(2)−C(10) = 2.293(4), C(10)−C(11) = 1.209(6), Ru(1)−C(16) = 2.222(4), Ru(3)−C(16) = 2.205(4), Ru(4)−C(16) = 1.968(4), Ru(1)−C(17) = 2.324(4), Ru(3)−C(17) = 2.214(4), C(16)−C(17) = 1.296(6).

on **2** and **3** were carried out to confirm their molecular structures. As indicated in Figure 1,[9] the cluster framework of **2** shows a flattened-butterfly geometry with the Ru−Ru distances adopting a pattern of two normal Ru−Ru bonds (2.7815(4)−2.8575(4) Å) and three elongated Ru−Ru bonds (3.0207(4)−3.0974(4) Å). This skeletal arrangement is similar to that of the 64e, electron-rich cluster compounds $Ru_4(CO)_{13}(\mu\text{-}PR_2)_2$ (R = Ph, Et, Cy, Pr^i).[10] In addition, the cluster contains two multisite-bound acetylide ligands. The acetylide C(16)-C(17), which possesses a μ_3-η^2-bonding mode,[11] lies on the Ru(1)−Ru(3)−Ru(4) triangle with its α-carbon connected to the Ru(4) atom via a σ-bond and with the C−C vector perpendicular to the Ru(1)−Ru(3) bond. The other, C(10)−C(11), which adopts the less common μ_2-η^2-mode,[12] resides on the Ru(1)−Ru(2) bond and pushes the phosphido bridge away from the triangular plane defined by Ru(1), Ru(2), and Ru(4) atoms. The lengths of the −C≡C− bonds in the acetylide ligands reflect the coordination mode[5,11,12] with the more highly coordinated μ_3-η^2-bond (C(16)−C(17) = 1.296(6) Å) being longer than the μ_2-η^2-bond (C(10)−C(11) = 1.209(6) Å). Interestingly, the acetylide ligands also align in a configuration with the sterically bulky *tert*-butyl substituents pointing away from each other.

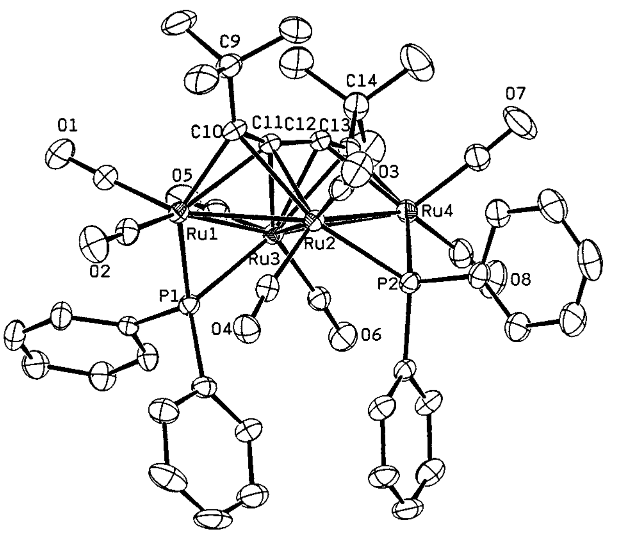

Figure 2. Molecular structure of **3** and the atomic numbering scheme. Selected bond lengths (Å): Ru(1)−Ru(2) = 2.814(1), Ru(1)−Ru(3) = 2.875(1), Ru(2)−Ru(3) = 2.924(1), Ru(2)−Ru(4) = 2.844(1), Ru(3)−Ru(4) = 2.821(1), Ru(1)−P(1) = 2.319(1), Ru(3)−P(1) = 2.352(2), Ru(2)−P(2) = 2.331(1), Ru(4)−P(2) = 2.313(2), Ru(1)−C(10) = 2.053(5), Ru(2)−C(10) = 2.430(5), Ru(1)−C(11) = 2.361(5), Ru(2)−C(11) = 2.183(5), Ru(3)−C(11) = 2.363(5), Ru(2)···C(12) = 2.700(5), Ru(3)−C(12) = 2.186(5), Ru(4)−C(12) = 2.247(5), Ru(3)−C(13) = 2.371(5), Ru(4)−C(13) = 2.106(5), C(10)−C(11) = 1.332(7), C(11)−C(12) = 1.366(7), C(12)−C(13) = 1.321(7).

The molecular structure of the diyne complex **3** is shown in Figure 2.[13] The cluster, with 62 valence electrons, adopts a butterfly geometry similar to that of **2**. The four peripheral Ru−Ru bonds span the narrow range 2.814(1)−2.875(1) Å and are shorter than the hinge Ru(2)−Ru(3) bond (2.924(1) Å). Although the basic cluster framework is retained, one phosphido ligand has migrated to the Ru−Ru edge parallel to the

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[8] Spectral data for **2**: MS (FAB, ^{102}Ru), m/z 1192 (M$^+$); IR (C_6H_{14}) ν(CO) 2068 (vs), 2031 (vs), 2014 (s), 1999 (s), 1993 (m), 1962 (m), 1952 (m), 1936 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (m, 2H), 7.96 (m, 2H), 7.58−7.44 (m, 6H), 7.30 (m, 2H), 7.10−7.06 (m, 6H), 6.58 (m, 2H), 1.53 (s, 9H, Bu^t), 0.31 (s, 9H, Bu^t); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 138.3 (d, J_{P-P} = 177 Hz, 1P), 135.8 (d, J_{P-P} = 177 Hz, 1P). Anal. Calcd for $C_{45}H_{38}O_9P_2Ru_4$: C, 45.46; H, 3.22. Found: C, 45.43; H, 3.22. Spectral data for **3**: MS (FAB, ^{102}Ru), *m/z* 1164 (M$^+$); IR (C_6H_{14}): ν(CO), 2032 (vw), 2009 (vs), 1997 (m), 1971 (s), 1961 (w), 1949 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28−7.11 (m, 16H), 7.01−6.93 (m, 4H), 1.63 (s, 18H, 2Bu^t); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 194.8 (s, 2P). Anal. Calcd for $C_{44}H_{38}O_8P_2Ru_4$: C, 45.52, H, 3.30. Found: C, 45.30; H, 3.17. Spectral data for **4**: MS (FAB, ^{102}Ru), *m/z* 1034 (M$^+$); IR (C_6H_{14}) ν(CO) 2056 (s), 2028 (s), 2013 (vs), 1993 (s), 1987 (m), 1973 (m), 1948 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ 7.92−7.88 (m, 4H), 7.72−7.67 (m, 4H), 7.42−7.40 (m, 6H), 7.33−7.29 (m, 6H), 1.13 (s, 9H, Bu^t), 0.69 (s, ^{9}H, Bu^t); ^{31}P NMR (121.5 MHz, $CDCl_3$, 203 K) δ 275.8 (d, J_{P-P} = 152 Hz, 1P), 188.3 (J_{P-P} = 152 Hz, 1P). Anal. Calcd for $C_{43}H_{38}O_7P_2Ru_3$: C, 50.05; H, 3.71. Found: C, 49.99, H, 3.75.

[9] Crystal data for **2**: $C_{45}H_{38}O_9P_2Ru_4$, M = 1189.01, monoclinic, space group $P2_1/n$, a = 14.201(1) Å, b = 18.009(1) Å, c = 18.218(1) Å, β = 98.698(4)°, V = 4605.6(3) Å^3, Z = 4, ρ_{calcd} = 1.715 g cm^{-3}, F(000) = 2344, λ(Cu K$_\alpha$) = 1.541 Å, T = 298 K, μ = 11.79 mm^{-1}. The intensities were measured on a Nonius CAD4 diffractometer on a crystal with dimensions 0.30 × 0.25 × 0.13 mm. Of the 8742 unique reflections collected, 7427 reflections with $I > 2.5\sigma(I)$ were used for the refinement. The structure was solved by using the NRCC-SDP-VAX package and refined to R_F = 0.032, R_w = 0.044, and GOF = 1.46 for 98 atoms and 542 parameters, weighting scheme $\omega^{-1} = \sigma^2(F_o) + 0.0005F_o^2$, and highest Δ/σ ratio 0.14. A difference map following convergence showed residual electron density within the range −0.61/1.33 e/Å^3 (min/max).

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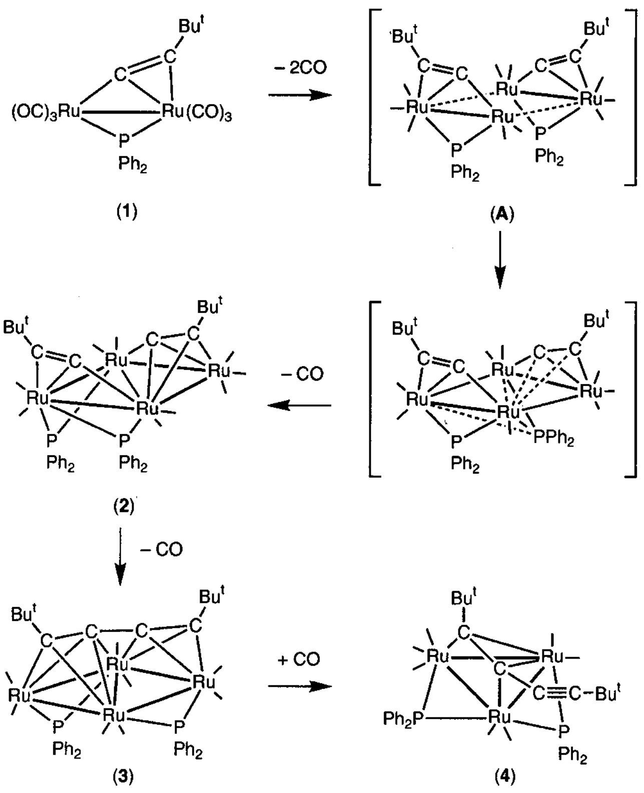
[13] Crystal data for **3**: $C_{44}H_{38}O_8P_2Ru_4$, M = 1161.00, triclinic, space group $P\bar{1}$, a = 12.022(3) Å, b = 12.768(4) Å, c = 16.218(3) Å, α = 85.42(2)°, β = 86.11(2)°, γ = 63.56(2)°, V = 2220.6(10) Å^3, Z = 2, ρ_{calcd} = 1.736 g cm^{-3}, F(000) = 1133, λ(Mo Kα) = 0.7107 Å, T = 298 K, μ = 14.33 cm^{-1}. The intensities were measured on a crystal with dimensions 0.20 × 0.25 × 0.25 mm. Of the 7806 unique reflections collected, 5690 reflections with $I > 2\sigma(I)$ were used for the refinement. The structure was refined to R_F = 0.029, R_w = 0.030, and GOF = 1.20 for 96 atoms and 524 parameters, weighting scheme $\omega^{-1} = \sigma^2(F_o) + 0.0001\,F_o^2$, and highest Δ/σ ratio 0.009. A difference map following convergence showed residual electron density within the range −0.36/0.34 e/Å^3 (min/max).

second phosphido ligand, and the phosphido-bridged Ru–Ru bonds (2.875(1) and 2.844(1) Å) are noticeably shorter than those of **2**, consistent with an increase of bond order through alleviation of excess electrons from the metal–metal antibonding orbital.[14] The butadiyne ligand, generated from the end-to-end coupling of acetylide ligands, now acts as a μ_4-bridge across the Ru_4 surface. The diyne C_4 backbone is slightly nonlinear with angles C(10)–C(11)–C(12) = 158.9(5)° and C(11)–C(12)–C(13) = 156.2(5)°. The C–C bond lengths within this C_4 unit are consistent with the parameters observed for other coordinated diynes,[15] where the net effect of coordination is to elongate the outer formal triple bonds (C(10)–C(11) = 1.332(7) Å and C(12)–C(13) = 1.321(7) Å in **3**) and shorten the inner C_{sp}–C_{sp} single bond (C(11)–C(12) = 1.366(7) Å). In fact, C(10)–C(11) and C(12)–C(13) in **3** are both longer than the acetylenic triple bonds in **2** from which they are derived. It is of interest to note that the Ru(2)–C(12) bond (2.700(5) Å) is significantly longer than the rest of the Ru–C distances (2.053(5)–2.430(5) Å), indicating the absence of direct bonding. However, if we ignore this nonbonding interaction, the cluster core skeleton can be considered to possess a C_2 axis passing through the center of the diyne ligand and the middle of the hinge Ru(2)–Ru(3) bond. In fact, the observation of only one ^{1}H NMR signal at δ 1.63 due to the Bu^t groups and one ^{31}P NMR signal at δ 194.8 even at 190 K indicates the formation of such dynamic C_2 symmetry in solution.

The isolation and characterization of complexes **2** and **3** provide an opportunity to explore the reactions taking place at the Ru_2 metal centers. We propose that dimerization with CO loss leads to the formation of an intermediate (**A**) via a side-by-side and head-to-head alignment of **1** and the formation of two Ru-Ru interactions (Scheme 1). Upon further removal of a CO ligand the intermediate **A** would strengthen the bonding between each $Ru_2(\mu\text{-}PPh_2)(CCBu^t)$ unit through the simultaneous generation of a third Ru–Ru bond at the hinge position. Phosphido ligand migration, and formation of one μ_3-η^2-acetylide ligand, eventually leads to the formation of **2**. With loss of CO from **2** the acetylide ligands then undergo head-to-head coupling to afford the diyne ligand on cluster **3**. This diyne ligand is considered as an eight-electron donor and is bonded to all four ruthenium atoms, but in an almost linear fashion, quite different from that observed in other diyne clusters such as $Ru_4(CO)_{10}(\mu_4\text{-}PR)(C_4R'_2)$ (R = C_2-Bu^t, Ph; R′ = Bu^t, Ph, $SiMe_3$),[15] which contains a square-planar metal framework with a highly distorted C_4 skeleton.

The degradation of **3** and formation of **4** is somewhat unexpected but may involve the conversion of the butterfly metal framework to a 64-electron spiked-triangular geometry via addition of CO, followed by removal of the pendant "$Ru(CO)_4$" unit as $Ru_3(CO)_{12}$. The assignment of **4** follows directly from the similarity of spectroscopic data with those of the related, structurally characterized derivatives $Ru_3(CO)_7(\mu\text{-}PPh_2)_2(RC_4R')$ (R = R′ = Ph and R = H, R′ = Ph, Bu^t, and Pr^i).[16] The dynamic process of the diyne ligand of **4**, which is similar to the windshield wiper motion of the μ_3-η^2-alkynes,[17] was revealed by the observation of only two doublets at δ 275.8 and 188.3 with a coupling constant $^2J_{P-P}$ of 152 Hz at the limiting temperature of 203 K and one broad ^{31}P NMR resonance at δ 230 at room temperature.

Scheme 1



The high-yield head-to-head intermolecular coupling of μ-η-alkynyl groups in converting dinuclear **1** to tetranuclear diyne cluster **3** may be applicable to the generation of other polyyne ligands on a polymetallic framework from μ-η^2-butadiynyl or higher polyynyl complexes.[18] We are currently exploring the synthesis of clusters bearing polyunsaturated $R(C{\equiv}C)_nR$ hydrocarbyls via such reactions.

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Supporting Information Available: Text describing the experimental details for complexes **2** and **3** and ^{13}C NMR data for **2** and full details of crystal structure analyses, including tables of bond distances, atomic coordinates, and anisotropic thermal parameters (14 pages). Ordering information is given on any current masthead page.

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