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Coordinatively and Electronically Unsaturated Tetraruthenium Clusters: Reversible Triple CO Addition to $Ru_4(CO)_9(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PCC(Ph)CC(Ph)]$

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*Summary: Two electronically unsaturated tetraruthenium clusters, $Ru_4(CO)_9(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PCC(Ph)CC(Ph)]$ (**2**) and $Ru_4(CO)_{10}(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PC(Ph)CCC(Ph)]$ (**3**), with spiked-triangular and open-chain structures have been synthesized via head-to-tail and head-to-head coupling of binuclear acetylides: cluster **2** contains a coordinatively unsaturated metal center and undergoes a fully reversible triple addition of carbon monoxide to afford $Ru_4(CO)_{11}(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PC(O)CC(Ph)CC(Ph)]$ (**4**).*

With the exception of molecules containing metals such as platinum and rhodium, which often favor a 16-electron configuration in polymetallic compounds, coordinatively and electronically unsaturated clusters of the later transition metals are still relatively rare.[1] This is particularly true for the iron triad. The few examples include $H_2Os_3(CO)_{10}$, which has a hydride-bridged Os=Os bond,[2] $HRu_3(CO)_9(\mu\text{-}PPh_2)$, where electronic unsaturation at a 16-electron metal site is partially compensated by a weak intramolecular interaction with a P−C(Ph) bond[3a] and 44-electron $[Ru_3H_2(CO)_6(PCy_3)_3]$.[3b] For these clusters, unsaturation leads to an extensive addition and small molecule activation chemistry. We describe herein two new electronically unsaturated clusters, $Ru_4(CO)_9(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PCC(Ph)CC(Ph)]$ (**2**) and $Ru_4(CO)_{10}(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PC(Ph)CCC(Ph)]$ (**3**), with spiked-triangular and open-chain Ru_4 frameworks, respectively. In **2** unsaturation is localized at a single 16e ruthenium site, whereas **3** is a 64 e cluster with only three Ru−Ru interactions, one of which is a short Ru−Ru bond. Cluster **2** undergoes a remarkable, unprecedented, and fully reversible triple addition of CO to afford $Ru_4(CO)_{11}(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PC(O)CC(Ph)CC(Ph)]$ (**4**).

An emerging strategy for the synthesis of polymetallic polycarbon ligand arrays is the *inter*molecular coupling of ynyl or polyynyl ligands coordinated in a multisite fashion on bi- or trinuclear frameworks.[4] We have applied this methodology to the condensation of $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)$ (**1**). Refluxing a toluene solution of **1**, and fractional crystallization from CH_2Cl_2/CH_3OH gave orange $Ru_4(CO)_9(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PCC(Ph)CC(Ph)]$ (**2**; 68%) and brown $Ru_4(CO)_{10}(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PC(Ph)CCC(Ph)]$ (**3**; 19%) (Scheme 1). Spectroscopic data[5] established the presence of phosphido and phosphine ligands, but X-ray analysis[6] was needed to determine the nature of the coupled organic fragments.

The structure of **2** (Figure 1) has three principal features. A spiked-triangular (4 Ru−Ru) Ru_4 framework has metal−metal bond lengths in the range 2.677(2) (Ru(3)−Ru(4)) to 3.015(1) Å (Ru(2)−Ru(3)). A PC_4 chain is bound to all four metal atoms, formed by head-to-tail coupling of two ynyl ligands and P−C bond formation between a phosphido bridge and C_α of one

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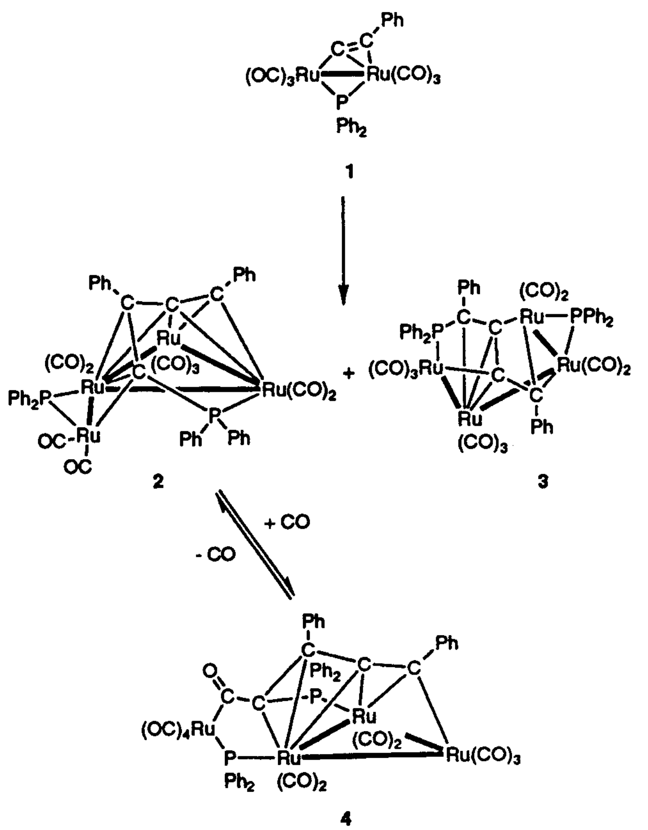
(5) Selected spectral data for **2**: MS (FAB, ^{102}Ru) m/z 1232 (M^+); IR (C_6H_{14}) ν(CO) 2061 (s), 2034 (m), 2028 (w), 2000 (vs), 1997 (s), 1983 (m), 1974 (vw), 1963 (m), 1930 (vw, br) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.24 (dd, 2H, $J_{H-H} = 7.2$ Hz and $J_{P-H} = 8.7$ Hz), 7.69 (t, 1H, $J_{H-H} = 7.2$ Hz), 7.59 (t, 2H, $J_{H-H} = 7.2$ Hz), 7.28 (m, 5H), 7.22−7.14 (m, 5H), 7.04−6.69 (m, 9H), 6.80−6.77 (m, 4H), 6.67 (t, 2H, $J_{H-H} = 7.5$ Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ 155.5 (s, 1P), 56.8 (s, 1P). Anal. Calcd for $C_{49}H_{30}O_9P_2Ru_4$: C, 47.89, H, 2.46. Found: C, 47.88, H, 2.38. Selected spectral data for **3**: MS (FAB) m/z 1260 (M^+). IR (C_6H_{14}) ν(CO), 2079 (s), 2045 (s), 2025 (m), 1990 (vs), 1966 (m), 1950 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75−7.63 (m, 5H), 7.49−7.38 (m, 8H), 7.26−7.17 (m, 7H), 7.15−7.03 (m, 3H), 6.97 (m, 3H), 6.90−6.85 (m, 4H); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 152.3 (s, 1P), 56.8 (s, 1P). Anal. Calcd for $C_{50}H_{30}O_{10}P_2Ru_4$: C, 47.77, H, 2.38. Found: C, 47.92, H, 2.20.

S0276-7333(98)00168-X CCC: $15.00

Scheme 1



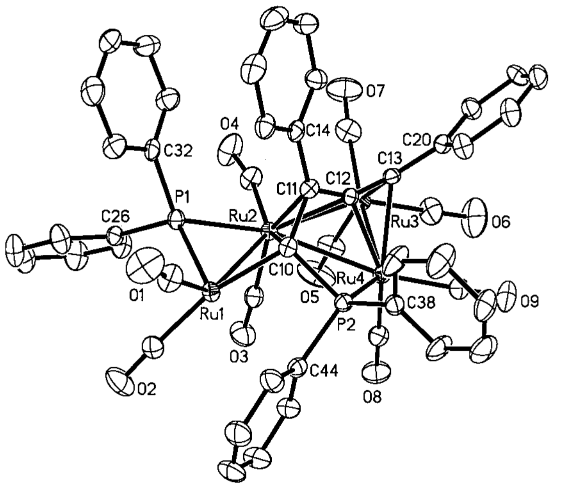


Figure 1. ORTEP plot of compound **2**. Selected bond lengths (Å) Ru(1)−Ru(2), 2.920(1); Ru(2)−Ru(4), 2.8319(8); Ru(1)−C(10), 2.021(6); Ru(2)−C(10), 2.274(5); Ru(2)−C(11), 2.240(6); Ru(2)−C(12), 2.184(6); Ru(3)−C(13), 2.063(6); Ru(4)−C(12), 2.086(6); Ru(4)−C(13), 2.318(6); P(2)−C(10), 1.796(6); C(10)−C(11), 1.474(8); C(11)−C(12), 1.430(8); C(12)−C(13), 1.362(8).

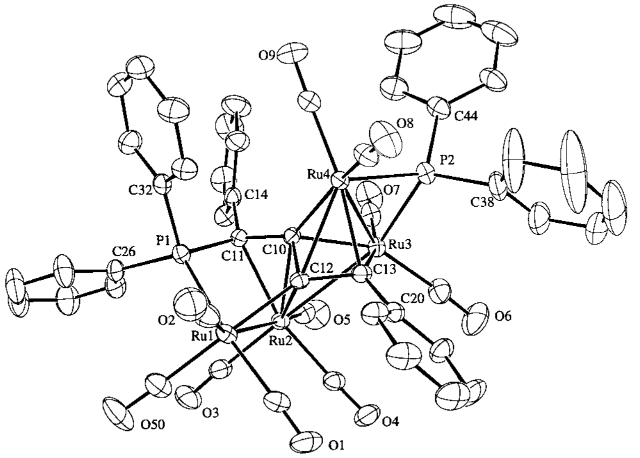


Figure 2. ORTEP plot of compound **3**. Selected bond lengths (Å) not given in the text: Ru(1)−P(1), 2.366(2); Ru(2)−C(11), 2.215(4); Ru(3)−C(13), 2.204(4); Ru(4)−C(12), 2.434(4); Ru(4)−C(13), 2.127(4); P(1)−C(11), 1.824(5).

acetylide. The $\mathrm{Ph_2PCC(Ph)CC(Ph)}$ chain functions as a 9e donor to the cluster and can be considered as a diphenylphosphino substituted ene-yne. In other examples of ynyl−ynyl coupling reported recently, only head-to-head linkage was observed.[4] The most unusual aspect of **2** is that the electron deficiency implied by its 62e (4 M−M) count is manifest in coordinative and electronic unsaturation at a single 16e Ru(1) site. This metal atom is coordinated to two CO groups and a phosphido bridge and has a σ-bond to C(10) and a contact with Ru(2) (Ru(1)−Ru(2) = 2.920(1) Å). The stereochemistry at Ru(1) is also highly unusual (Figure 1) with a vacant coordination position evident *trans* to P(1). The phenyl group C(44)−C(49) partially protects this site but is not coordinated.

Cluster **3** (Figure 2) consists of a twisted chain of four ruthenium atoms with one short (Ru(3)−Ru(4) = 2.7459(6) Å) and two normal (average 2.855 Å) bonds. This skeletal arrangement is rare for tetrametal clusters.[7] The hydrocarbyl chain in **3** differs from that in **2** in that head-to-head ynyl coupling has occurred, generating a C(10)−C(12) bond (1.498(6) Å), while P−C coupling has placed a phosphino group geminal to a phenyl substituent on C(11). The mode of attachment of the C_4 fragment (C(11)−C(10)−C(12)−C(13)) on the tetrametal framework poses an interesting challenge for conventional chemical bonding descriptions. The central carbon atoms C(10) and C(12) are pentacoordinate, each being attached to three metal atoms (C(10)−Ru(2), 2.233(4); C(10)−Ru(3), 2.115(4); C(10)−Ru(4), 2.208(5); C(12)−Ru(1), 2.091(4); C(12)−Ru(2), 2.309(4); C(12)−Ru(4) 2.434(4) Å), to a C(Ph) group (C(10)−C(11), 1.454-

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(6) Crystal data for **2**: $C_{49}H_{30}O_9P_2Ru_4$, $M_r = 1228.99$, monoclinic, space group $P2_1/c$, $a = 20.391(5)$ Å, $b = 12.858(2)$ Å, $c = 20.053(8)$ Å, $\beta = 118.95(4)°$, $V = 4600.6(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.744$ g cm^{-3}, $F(000) = 2387$, λ(Mo Kα) = 0.710 67 Å, $T = 298$ K, $\mu = 13.869$ cm^{-1}. The structure was solved and refined on the basis of 5020 ($I \geq 2\sigma(I)$) observed (8067 measured) reflections (Enraf-Nonius CAD-4 diffractometer) with a crystal of dimensions 0.10 × 0.15 × 0.50 mm. Final R and R_w values were 0.035 and 0.034. The NRCVAX computer program suite was used.[12] A final difference map showed residual electron density in the range ±0.54 e Å^{-3}. Crystal data for **3**: $C_{50}H_{30}O_{10}P_2Ru_4 \cdot 2CH_2Cl_2$, $M_r = 1422.83$, monoclinic, space group $P2_1/n$, $a = 12.8483(6)$ Å, $b = 25.2745(12)$ Å, $c = 16.5144(7)$ Å, $\beta = 93.16(1)°$, $V = 5354.6(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.752$ g cm^{-3}, $F(000) = 2745.9$, λ(Mo Kα) = 0.709 30 Å, $T = 298$ K, $\mu = 1.36$ mm^{-1}. The structure was solved and refined on the basis of 6584 ($I \geq 2.5\sigma(I)$) observed reflections (21 237 measured) (Siemens SMART CCD diffractometer) on a crystal of dimensions 0.10 × 0.10 × 0.10 mm. Final R and R_w values were 0.032 and 0.036. A final difference map showed residual electron density from −0.63 to +0.95 e Å^{-3}.

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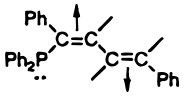
(6); C(12)−C(13), 1.438(6) Å), and to each other via a long C(10)−C(12) bond (1.498(6) Å). In the square cluster $Fe_4(CO)_8(\mu\text{-}PPh_2)_2(\mu_4\text{-}C_2Ph)_2$ a similar but even longer C−C bonding interaction "through the cluster" resulted from $C_\alpha-C_\alpha$ acetylide coupling.[4a] Clearly for **3**, C_4-Ru_4 bonding is multicentered, but the ligand can be simplistically described as a 9e donor, as represented by **A**. Cluster **3** has 64 cluster valence electrons and would be electron precise with a 66e (3 M−M) count. However, in contrast to **2**, its formal electron deficiency is not localized at one metal site.



A

Preliminary exploration of the chemical reactivity of coordinatively unsaturated **2** revealed novel and unexpected results. Bubbling CO through a $CDCl_3$ solution of **2** for 10 min resulted in the clean and quantitative disappearance of ^{31}P resonances at 155.5 and 56.8 ppm due to μ-PPh_2 and phosphine ligands of **2** and the concomitant growth of new peaks at 46.9 and 26.7 ppm from the new cluster **4**.[8] This facile carbonylation is fully reversible, the conversion back to **2** being rapid in air or under a stream of dinitrogen (Scheme 1). The cycle of CO addition and loss can be repeated many times with no noticeable decomposition. In the solid state this process is somewhat slower.

Crystals of **4** grown from CH_2Cl_2/CH_3OH saturated with CO were subjected to X-ray analysis.[8] As revealed in Figure 3, **4** is the tris-CO adduct of **2**, namely $Ru_4(CO)_{11}(\mu\text{-}PPh_2)[\mu_4\text{-}Ph_2PC(O)CC(Ph)CC(Ph)]$. The CO addition is centered on the unsaturated pendant ruthenium center (Ru(1) in **2**), which now carries four carbonyl ligands in **4** as opposed to two in **2**. Cleavage of a metal−metal bond (Ru(1)−Ru(2) in **2**) accompanies CO addition with the Ru(1)···Ru(2) distance in **4** (4.015(1) Å) clearly indicating the absence of any bonding interaction. The μ-PPh_2 bridge across this open Ru···Ru vector subtends a Ru(1)−P(1)−Ru(2) angle of 111.9(1)° and accounts for the high-field ^{31}P NMR shift. Perhaps the most unusual feature of **4** and the overall transformation of **2** to **4** is the insertion of CO into the Ru(1)−C(10) (alkylidene) bond to generate new metal−carbon (Ru(1)−C(52) = 2.143(9) Å) and carbon−carbon (C(10)−C(52) = 1.52(1) Å) bonds. Thus, the formally electronically and coordinatively unsaturated pendant ruthenium atom in cluster **2** achieves a full 18e count in **4**, albeit separated from the remaining Ru_3 cluster unit. The coordination geometry at Ru(1) in **4** is that of a slightly distorted octahedron. While major changes have occurred at the unsaturated 16e site in **2**, the remaining Ru_3 fragment and associated ligands remain relatively unchanged, in keeping with the view that unsaturation in **2** is localized at a single site.

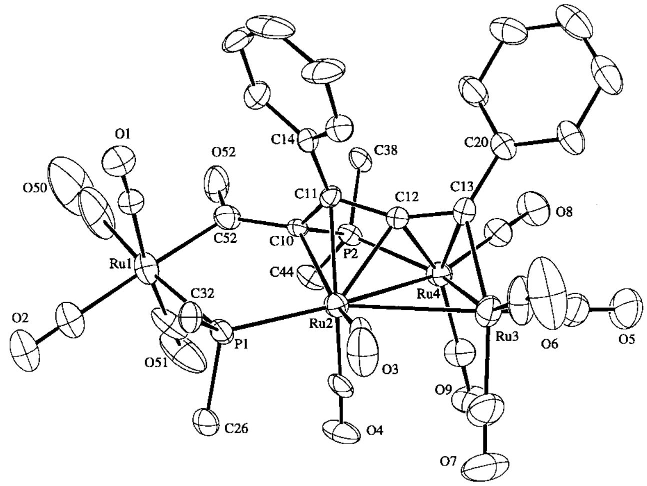


Figure 3. ORTEP plot of compound **4**. Only the *ipso* carbons of the phenylphosphido groups are shown for clarity. Selected bond lengths (Å) not given in the text: Ru(1)−P(1), 2.437(3); Ru(2)−P(1), 2.406(2); Ru(2)−Ru(3), 3.037(1); Ru(2)−Ru(4), 2.8352(9); Ru(3)−Ru(4), 2.669(1); P(2)−C(10), 1.824(8); Ru(4)−P(2), 2.307(3); Ru(2)−C(10), 2.233(8); C(10)−C(11), 1.46(1); C(11)−C(12), 1.42(1); C(12)−C(13), 1.36(1); Ru(2)−C(11), 2.191(8); Ru(2)−C(12), 2.151(8); Ru(3)−C(13), 2.083(9); Ru(4)−C(13), 2.293(9); Ru(4)−C(12), 2.096(8).

The sequence and mechanism of addition of three CO molecules to **2** is as yet unclear, since no intermediates could be detected by ^{31}P NMR spectroscopy. We note, however, that initial CO addition at Ru(1) in **2**, followed by a second addition with M−M bond cleavage, would afford a pseudooctahedral Ru(II) site from which CO insertion into the Ru(1)−C(10) bond would be favored.[9] However, while CO insertion into metal−alkyl and −aryl bonds is common,[10] insertion into metal−alkylidenes is rare.[11] We are currently investigating related additions to **2**.

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Supporting Information Available: Tables giving details of the X-ray structure determinations, atomic coordinates and anisotropic displacement parameters, bond lengths, and bond angles for **2**−**4** (27 pages). Ordering information is given on any current masthead page.

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[8] Selected spectroscopic data for **4**: IR (KBr) ν(CO) 2145 (m), 2103 (w), 2075 (s), 2053 (s), 2028 (m), 1992 (vs), 1971 (s), 1957 (m), 1946 (m), 1931 (m), 1918 (w), 1900 (m), 1638 (m), 1617 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05−6.45 (m, Ph); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ 46.9 (s, 1P), 26.7 (s, 1P). The facile loss of CO from **4** precluded satisfactory microanalysis. Crystal data for **4**: $C_{52}H_{30}O_{12}P_2Ru_4\cdot 0.88CH_2Cl_2$, $M_r = 1385.98$, monoclinic, space group $P2_1/n$, $a = 14.2417(2)$ Å, $b = 20.8937(5)$ Å, $c = 17.9378(1)$ Å, $\beta = 95.975(1)°$, $V = 5308.6(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.734$ g cm^{-3}, $F(000) = 2696.7$, λ(Mo Kα) = 0.709 30 Å, $T = 298$ K, $\mu = 1.30$ mm^{-1}. The structure was solved and refined on the basis of 4339 ($I \geq 2.5\sigma(I)$) observed reflections (21 910 measured) (Siemens SMART CCD diffractometer) using a crystal of dimensions 0.20 × 0.20 × 0.20 mm. Final R and R_w values were 0.048 and 0.031. A final difference map showed residual electron density from −0.67 to +0.87 e Å^{-3}. A disordered solvent molecule was modeled as CH_2Cl_2, occupancy 0.88, following trial refinement.

[9] See for example: Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 961.

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[12] Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.