Coordinately and Electronically Unsatuated Tetraruthenium Clusters: Reversible Triple CO Addition to Ru4(CO)9(µ-PPh2)[µ4-PhP(C)CC(Ph)CC(Ph)]

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Summary: Two electronically unsaturated tetraruthenium clusters, Ru4(CO)9(µ-PPh2)[µ4-PhP(C)CC(Ph)CC(Ph)] (2) and Ru4(CO)10(µ-PPh2)[µ4-PhP(C)CC(Ph)CC(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 coordinately unsaturated metal center and undergoes a fully reversible triple addition of carbon monoxide to afford Ru4(CO)11(µ-PPh2)[µ4-PhP(C)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 polymeric 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 H2Os(CO)10, which has a hydride-bridged Os=Os bond,2 HRu3(CO)9(µ-PPh2), where electronic unsaturation at a 16-electron metal site is partially compensated by a weak intramolecular interaction with a P−C(Ph) bond3a and 44-electron [Ru6H2(CO)6(PCy3)3].3b For these clusters, unsaturation leads to an extensive addition and small molecule activation chemistry. We describe herein two new electronically unsaturated clusters, Ru4(CO)9(µ-PPh2)[µ4-PhP(C)CC(Ph)CC(Ph)] (2) and Ru4(CO)10(µ-PPh2)[µ4-PhP(C)CC(Ph)CC(Ph)] (3), with spiked-triangular and open-chain Ru4 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 Ru4(CO)11(µ-PPh2)[µ4-PhP(C)CC(Ph)CC(Ph)] (4).

An emerging strategy for the synthesis of polynuclear polycarbon ligand arrays is the intermolecular 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 Ru3(CO)12(µ-PPh2)(µ-η1:η2-Ph) [1]. Refluxing a toluene solution of 3, and fractional crystallization from CH2Cl2/C6H6 gave orange Ru4(CO)9(µ-PPh2)[µ4-PhP(C)CC(Ph)CC(Ph)] (2) (68%) and brown Ru4(CO)10(µ-PPh2)[µ4-PhP(C)CC(Ph)CC(Ph)] (3) (19%) (Scheme 1). Spectroscopic data5 established the presence of phosphino and phosphine ligands, but X-ray analysis6 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) Ru4 framework has metal–metal bond lengths in the range 2.677–2.738 (2) (Ru3–Ru4)) to 3.015 Å (Ru2–Ru3)). A PC4 chain is bound to all four metal atoms, formed by head-to-tail coupling of two ynyl ligands and –P bond formation between a phosphino bridge and C4 of one


(5) Selected spectral data for 2: MS (FAB, 102Ru) m/z 1232 (M+) IR (CH2Cl2) 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, CDCl3) δ 8.24 (dd, 2H, J = 7.2 Hz and J = 8.7 Hz), 7.69 (t, 1H, J = 7.2 Hz), 7.28 (m, 5H), 7.22–7.14 (m, 9H), 7.04–6.69 (m, 9H), 6.80–6.77 (m, 4H), 6.67 (t, 2H, J = 7.2 Hz), –PPh2); 13C NMR (121.5 MHz, CDCl3) δ 155.5 (s, 1H), 156.8 (s, 1P). Anal. Calcd for C49H30O9P2Ru4: C, 47.88, H, 2.46. Found: C, 47.88, H, 2.45.

(6) Selected spectral data for 3: MS (FAB) m/z 1260 (M+) IR (CH2Cl2) ν(CO) 2079 (s), 2045 (s), 2025 (m), 1990 (vs), 1966 (m), 1950 (m), 1934 (w), 1930 (w), 1922 (w), 1845 (w), 1830 (w); 1H NMR (300 MHz, CDCl3) δ 7.75–7.63 (m, 3H), 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); 31P (1H) NMR (121.5 MHz, CDCl3) δ 152.3 (s, 1P), 56.8 (s, 1P). Anal. Calcd for C49H30O9P2Ru4: C, 47.77, H, 2.38. Found: C, 47.92, H, 2.20.

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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), 2.183(4); Ru(3)–C(13), 2.063(6); Ru(4)–C(12), 2.086(6); Ru(4)–C(13), 2.318(6); P(2)–C(12), 1.362(8); P(2)–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), 2.2153(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).

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. The head-to-head ynyl coupling has occurred, generating a C(10)–C(12) bond (1.4986(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)–C(14)) 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–

(6) Crystal data for 2: C₉H₉O₅P₂Ru₂, Mᵣ = 1228.99, monoclinic, space group P2₁/c, a = 20.391(5) Å, b = 12.858(2) Å, c = 20.053(3) Å, \( \beta = 118.95(4)^\circ \), \( V = 4600.0(2) \text{ Å}^3 \), \( Z = 4, \rho_{\text{calc}} = 1.744 \text{ g cm}^{-3} \), \( F(000) = 2387, \lambda(\text{Mo K}α) = 0.7107 \text{ Å}, \ T = 298 \text{ K}, \mu = 13.869 \text{ cm}^{-1} \). The structure was solved and refined on the basis of 5020 (\( \bar{l} \geq 2\sigma(l) \)) observed reflections (Enraf-Nonius CAD-4 diffractometer) with a crystal of dimensions 0.10 \( \times \) 0.20 \( \times \) 0.40 mm. Final \( R \) and \( R_w \) values were 0.035 and 0.034. The NRCVAX computer program suite was used. A final difference map showed residual electron density in the range 0.709 30 Å\(^{-3}\) and 0.036. A final difference map showed residual electron density from 0.63 to +0.95 Å\(^{-3}\).

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.

Preliminary exploration of the chemical reactivity of coordinatively unsaturated 2 revealed novel and unexpected results. Bubbling CO through a CDC13 solution of 2 for 10 min resulted in the clean and quantitative disappearance of 31P resonances at 155.5 and 56.8 ppm due to μ-PPh2 and phosphine ligands of 2 and the concomitant growth of new peaks at 46.9 and 26.7 ppm from the new cluster 4. Clearly 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 CH2Cl2/CH3OH saturated with CO were subjected to X-ray analysis. As revealed in Figure 3, 4 is the tris-CO adduct of 2, namely Ru4(CO)11(μ-PPh2)(μ3-PPh3(PC(O)(OCC)(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 μ3-PPh2 bridge across this open Ru...Ru vector subtends a Ru(1)...Ru(2) angle of 111.9(1)° and accounts for the high-field 31P 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) (alkylidyne) bond to generate new metal carbons (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 Ru3 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 Ru3 fragment and associated ligands remain relatively unchanged, in keeping with the view that unsaturation in 2 is localized at a single site.

The sequence and mechanism of addition of three CO molecules to 2 is as yet unclear, since no intermediates could be detected by 31P 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 pseudo-octahedral Ru(II) site from which CO insertion into the Ru(1)–C(10) bond would be favored. 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.