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Electron-Rich Cluster Chemistry. Stepwise Transformation of Rhomboidal 64-Electron $Ru_4(CO)_{13}\{\mu\text{-}P(N^iPr_2)_2\}_2$ to 62-Electron Butterfly and 60-Electron Tetrahedral Clusters via $\mu_4\text{-}\eta^2$-CO Coordination and Hydrogenolysis

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Summary: The electron-rich 64-electron rhombic cluster $Ru_4(CO)_{13}\{\mu\text{-}P(N^iPr_2)_2\}_2$ *(1) readily decarbonylates, undergoing an exceptionally facile transformation to the electron-precise butterfly* $Ru_4(CO)_9(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)\{\mu\text{-}P(N^iPr_2)_2\}_2$ *(2), which contains a* $\mu_4\text{-}\eta^2$*-carbonyl bound within the framework cavity. Cluster 2 reacts with dihydrogen under mild conditions to give the 60-electron tetrahedral molecule* $(\mu_3\text{-}H)Ru_4(CO)_9(\mu\text{-}CO)\{\mu\text{-}P(N^iPr_2)_2\}\{\mu_3\text{-}P(N^iPr_2)\}$ *(3) via hydrogenolysis of a phosphido bridge.*

Several classes of M_3, M_4, and M_5 clusters are now known in which the number of metal–metal interactions exceeds that predicted from a simple EAN rule count.[1] The expanded metal frameworks of these electron-rich clusters results from the presence of extra electron pairs antibonding with respect to the metal core.[2] The electronic structures of such molecules suggests a potential for novel chemistry based on 2-electron transformations. We have recently synthesized the extensive series of 64-electron rhomboidal or "flat butterfly" clusters $Ru_4(CO)_{13}(\mu\text{-}PR_2)_2$, with three elongated and two normal Ru–Ru bonds[3] which undergo facile two-electron loss accompanied by intramolecular ligand activation.[4] Herein we describe new patterns of chemical reactivity: the room-temperature decarbonylation of the electron-rich rhomboidal $Ru_4(CO)_{13}\{\mu\text{-}P(N^iPr_2)_2\}_2$ (1) to the electron-precise butterfly cluster $Ru_4(CO)_9(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)\{\mu\text{-}P(N^iPr_2)_2\}_2$ (2) bearing a $\mu_4\text{-}\eta^2$-carbonyl group and the hydrogenolysis of a phosphido bridge to the 60-electron, tetrahedral cluster $(\mu_3\text{-}H)Ru_4(CO)_9(\mu\text{-}CO)\{\mu\text{-}P(N^iPr_2)_2\}\{\mu_3\text{-}P(N^iPr_2)\}$ (3), rare examples of stepwise 64- to 60-electron cluster contractions.[5]

Treatment of $[K]_2[Ru_4(CO)_{13}]$[6] (1.95 g, 2.3 mmol) in THF with $ClP(N^iPr_2)_2$ (1.25 g, 4.7 mmol) at 298 K followed by filtration and chromatography gave cluster 1 as deep red crystals in 65% yield.[7] The X-ray structure of 1 bears a close resemblance to that of $Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2$, with a rhomboidal Ru_4 skeleton having one intratriangular set of three Ru–Ru bonds elongated with the two remaining bonds to the unique $Ru(CO)_4$ unit normal.[8]

Solutions of 1 readily lose CO over 24 h to afford $Ru_4(CO)_9(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)\{\mu\text{-}P(N^iPr_2)_2\}_2$ (2; Scheme I). The reaction proceeds quantitatively and more rapidly at elevated temperatures. Thus, heating 1 in THF at 60 °C for 3 h results in the rapid formation of deep red 2.[9] The same transformation can be induced photochemically: irradiation of a hexane solution of 1 (450 W, Hg lamp; 5 min) affords 2 quantitatively. The $^{31}P\{^1H\}$ NMR spectrum[9] of 2 contains a single resonance (δ 378.4 ppm) downfield of that of cluster 1 (δ 235.5 ppm) and indicative of a $\mu\text{-}P(N^iPr_2)_2$ group bridging a shorter Ru–Ru bond.[10] The $^{13}C\{^1H\}$ NMR spectrum revealed a static structure. A low-field ^{13}CO resonance[12c] (δ 246.0 ppm) prompted an X-ray analysis (Figure 1).[11] Cluster 2 is derived from 1 via loss of two CO ligands, the conversion of a terminal carbonyl to a $\mu_4\text{-}\eta^2$-CO group, and contraction of the metal framework from a rhombus to a butterfly. The structural change occurs with a net loss of two electrons. The metal–metal bond lengths (Ru–Ru = 2.755(1)–2.866(1) Å) and dihedral angle (115.4°) are typical for electron-precise Ru_4

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(1) Examples of such expanded M_3, M_4, and M_5 frameworks include the following. (i) Ru_3 clusters: (a) Lugan, N.; Lavigne, G.; Bonnet, J. J.; Rean, R.; Neibecker, D.; Tkatchenko, I. *J. Am. Chem. Soc.* **1988**, *110*, 5369. (b) Cabeza, J. A.; Lahoz, F. J.; Martin, A. *Organometallics* **1992**, *11*, 2754. (ii) Os_3 clusters: (c) Cherkas, A. A.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 385. (iii) Ru_4 clusters: (d) Carty, A. J.; MacLaughlin, S. A.; Wagner, J. V.; Taylor, N. J. *Organometallics* **1982**, *1*, 1013. (e) Churchill, M. R.; Bueno, C.; Young, D. A. *J. Organomet. Chem.* **1981**, *213*, 139. (f) Mul, W. P.; Elsevier, C. J.; van Leijen, M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 1877. (iv) Os_4 clusters: (g) Adams, R. D.; Yang, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 235. (v) Pt_3 clusters: (h) Pergola, D. R.; Garlaschelli, L.; Mealli, C.; Proserpio, D. M.; Zanello, P. *J. Cluster Sci.* **1990**, *1*, 93. (i) Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 448. (j) Bender, R.; Braunstein, P.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 861. (vi) Pd_3 clusters: (k) Bushnell, G. W.; Dixon, K. R.; Moroney, P. M.; Rattray, A. D.; Wan, C. *J. Chem. Soc., Chem. Commun.* **1977**, 709. (vii) Ru_5 clusters: (l) Adams, C. J.; Bruce, M. I.; Liddell, M. J.; Skeleton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1314. (m) Adams, C. J.; Bruce, M. I.; Skeleton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1992**, 3057.

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(7) Data for 1. Anal. Calcd for $C_{37}H_{56}N_4O_{13}P_2Ru_4$: C, 36.10; H, 4.59; N, 4.55. Found: C, 35.95; H, 4.71; N, 4.48. IR (ν(CO), cm^{-1}, C_6H_{12}): 2096 (w), 2061 (m), 2029 (s), 2025 (s), 1999 (w), 1987 (m), 1981 (m), 1971 (vw), 1963 (vw). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, δ): +235.0 (s). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, δ): 209.5 (s, CO), 201.8 (s, CO), 198.4 (s, CO), 197.0 (s, CO), 190.4 (t, CO, J_{PC} = 10.6 Hz), 53.9 (s, $\mathit{C}H(CH_3)_2$), 24.7 (s, $CH(\mathit{C}H_3)_2$). ^1H NMR (200 MHz, $CDCl_3$, δ): 4.38 (septet, $C\mathit{H}(CH_3)_2$, 1H, $^3J_{HH}$ = 6.4 Hz), 1.41 (t, $CH(C\mathit{H}_3)_2$, 6H, $^3J_{HH}$ = 6.4 Hz).

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(9) Selected data for 2. Anal. Calcd for $C_{35}H_{56}N_4O_{11}P_2Ru_4\cdot CH_2Cl_2$: C, 34.32; H, 4.64; N, 4.45. Found: C, 34.21; H, 4.74; N, 4.34. IR (ν(CO), cm^{-1}, C_6H_{12}): 2058 (s), 2023 (s), 2003 (m), 1995 (vs), 1974 (w), 1988 (w), 1945 (w), 1877 (w). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, δ): +378.4 (s). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, δ): 246.8 (s, $\mu^4\text{-}\eta^2$-CO), 214.0 (t, μ-CO, $^2J_{PC}$ = 55.3 Hz), 204.0 (t, CO, J_{PC} = 4.1 Hz), 202.6 (s, CO), 201.3 (t, CO, $^2J_{PC}$ = 7.0 Hz), 1991 (s, CO), 198.7 (t, CO, $^2J_{PC}$ = 4.16 Hz), 51.5 (s, $\mathit{C}H(CH_3)_2$), 50.6 (s, $\mathit{C}H(CH_3)_2$), 23.8 (d, $CH(\mathit{C}H_3)_2$, $^3J_{PC}$ = 19.9 Hz), 22.7 (d, $CH(\mathit{C}H_3)_2$, $^3J_{PC}$ = 20.9 Hz).

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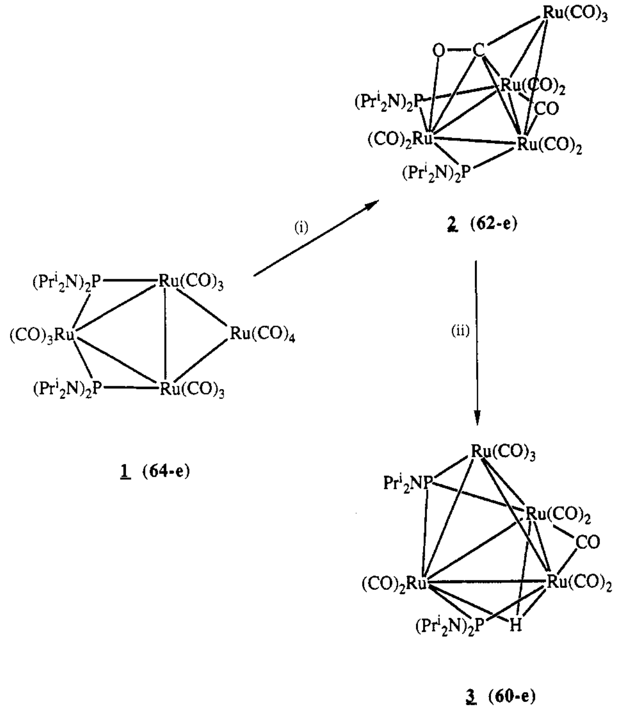
Scheme I[a]



[a] Reagents: (i) $h\nu$, *n*-hexane, 5 min or 60 °C, THF, 3 h; (ii) *n*-heptane, H_2, 65 °C, 45 min.

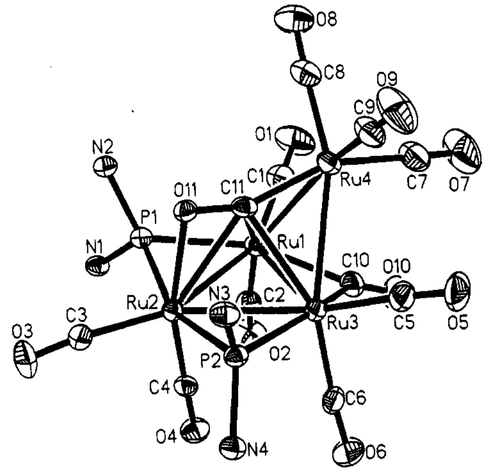


Figure 1. Perspective view of the molecular structure of $Ru_4(CO)_9(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}P\{N^iPr_2\}_2)_2$ (**2**) showing the atomic numbering scheme. Isopropyl substituents are omitted for clarity. Ru(1)–Ru(2) = 2.806(1) Å, Ru(1)–Ru(3) = 2.755(1) Å, Ru(1)–Ru(4) = 2.886(1) Å, Ru(2)–Ru(3) = 2.803(1) Å, Ru(3)–Ru(4) = 2.879(1) Å, Ru(1)–P(1) = 2.362(1) Å, Ru(2)–P(1) = 2.429(1) Å, Ru(2)–P(2) = 2.416(1) Å, Ru(3)–P(2) = 2.369(1) Å, P(1)–N(1) = 1.674(4) Å, P(1)–N(2) = 1.669(4) Å, P(2)–N(3) = 1.681(4) Å, P(2)–N(4) = 1.682(4) Å; Ru(4)–C(11)–O(11) = 153.0(4)°.

butterfly clusters.[12] The hinge of the butterfly framework in **2** is associated with the shortest metal–metal bond (Ru(1)–Ru(3) = 2.755(1) Å).

The most notable feature of **2** is the μ_4-η^2-coordinated carbonyl ligand bound within the butterfly cavity. This carbonyl (C(11)–O(11)) is involved in three Ru–C σ interactions and an η^2 interaction to Ru(2). The wingtip metal atom Ru(4) is bound most strongly to the μ_4-η^2-CO ligand (Ru(4)–C(11) = 1.897(5) Å), with the remaining two σ bonds being substantially longer (Ru(1)–C(11) = 2.413(5) Å, Ru(3)–C(11) = 2.419(4) Å). Carbon monoxide coordinated in this manner is typically characterized by a substantial elongation of the C–O bond (C(11)–O(11) = 1.246(6) Å) although very few neutral μ_4-η^2-CO complexes are known.[13-15]

Shriver and co-workers have described an extensive chemistry for the quadruply bridging ligand in the anion $[HFe_4(CO)_{13}]^-$.[16] In contrast, Dahl observed that the μ_4-η^2-CO group in $(\eta^5\text{-}C_5Me_5)_2Mo_2Fe_2(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{10}$ was unreactive toward a variety of reagents.[15] Preliminary studies of **2** reveal unusual reactivity, resulting in skeletal transformation.

Heating **2** (C_7H_{16}, 45 min) under a purge of H_2 results in a smooth conversion to the single orange-red product **3** (80%) (Scheme I).[17] The $^{31}P\{^1H\}$ NMR spectrum consists of two resonances, one at low field (δ 467.0 ppm, $^2J_{PP}$ = 141.0 Hz) and the other essentially unchanged (δ 383.0 ppm, $^2J_{PP}$ = 141.0 Hz) relative to that of the precursor **2** (δ 378.4 ppm). An X-ray structural analysis (Figure 2)[18] revealed **3** to be the 60-electron, tetrahedral, phosphido–phosphinidene cluster $(\mu_3\text{-}H)Ru_4(CO)_9(\mu\text{-}CO)\{\mu\text{-}P(N^iPr_2)_2\}\{\mu_3\text{-}P(N^iPr_2)\}$. The molecule can also be described as a closo trigonal bipyramid with P(1) and Ru(3) occupying apical positions and Ru(1), Ru(2), and Ru(4) comprising the trigonal plane. The molecule has a face-capping phosphinidene ligand, μ_3-P(N^{i}Pr$_2$), and a μ_3-ligated hydride and is electronically and structurally related to $[H_2Ru_4(CO)_9(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$ (**4**).[19] The shortest Ru–Ru bond in **3** (Ru(1)–Ru(3) = 2.733(1) Å) is that asymmetrically bridged by a carbonyl ligand (Ru(3)–C(10)

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[11] Red polyhedra of **2**·CH_2Cl_2 were grown by slow evaporation of a CH_2Cl_2/CH_3OH solution at 298 K. Crystals of $Ru_4(CO)_{11}\{\mu\text{-}P(N^iPr_2)_2\}_2\cdot CH_2Cl_2$ are monoclinic, space group $P2_1/n$, with a = 11.426(2) Å, b = 21.082(4) Å, c = 21.160(3) Å, β = 101.07(2)°, T = 295 K, V = 5002(1) Å^3, d_{calcd} = 1.673 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 (λ = 0.710 73 Å) radiation in the 2θ range 4.0–45.0°. A total of 6579 independent reflections were collected, of which 4934 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. Refinement converged at R = 0.0245 and R_w = 0.0246.

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[17] Selected data for **3**. Anal. Calcd for $C_{28}H_{43}N_3O_{10}P_2Ru_4$: C, 32.09; H, 4.14; N, 4.01. Found: C, 32.15; H, 4.06; N, 4.14. IR (ν(CO), cm^{-1}, C_6H_{12}): 2055 (m), 2018 (vs), 2010 (vs), 1977 (s), 1968 (w), 1956 (w), 1948 (w), 1986 (broad, w). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, δ): +467.0 (d, μ_3-*P*{N^{i}Pr$_2$}, $^2J_{PP}$ = 143.0 Hz), +383.0 (d, μ-*P*{N^{i}Pr$_2$}$_2$, $^2J_{PP}$ = 143.0 Hz). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, 233 K, δ): 231.7 (t, μ-CO, J_{PC} = 35.2 Hz), 206.0 (br, CO), 198.0 (br, CO), 197.5 (s, CO), 196.5 (s, CO), 192.2 (s, CO), 189.7 (s, CO), 187.8 (d, CO, J_{PC} = 4.0 Hz), 56.5 (br, μ_3-P{N*C*H(CH$_3$)$_2$}), 51.0 (s, μ_2-P{N*C*H(CH$_3$)$_2$}$_2$), 48.3 (d, μ_2-P{N*C*H(CH$_3$)$_2$}$_2$, $^2J_{PC}$ = 9.0 Hz), 23.5 (d, μ_2-P{NCH(*C*H$_3$)$_2$}, $^3J_{PC}$ = 48.3 Hz), 22.4 (d, μ_2-P{NCH(*C*H$_3$)$_2$}$_2$, $^3J_{PC}$ = 48.7 Hz), 22.5 (broad, μ_3-P{NCH(*C*H$_3$)$_2$}).

[18] Orange-red platelets of **3** were grown by slow evaporation of a CH_2Cl_2/C_2H_5OH solution at 298 K. Crystals of $HRu_4(CO)_{10}\{P(N^iPr_2)_2\}\{P(N^iPr_2)\}$ are monoclinic, space group $P2_1/n$, with unit cell constants a = 13.279(2) Å, b = 18.956(2) Å, c = 15.740(2) Å, β = 101.98(2)°, T = 200 K, V = 3875.8(8)Å^3, d_{calcd} = 1.796 g cm^{-3}, and Z = 4. Data were collected as for **2** via the ω-scan method on an LT2-equipped Nicolet-Siemens R3m/V diffractometer in the 2θ range 4.0–50.0°. The structure was solved (Patterson/Fourier) and refined using 5455 observed ($F \geq 6\sigma(F)$) (7178 measured) reflections to give final R and R_w values of 0.0231 and 0.0252, respectively. The hydride ligand was located in the final difference Fourier map using the low-angle data only ($2\theta \leq 36°$).

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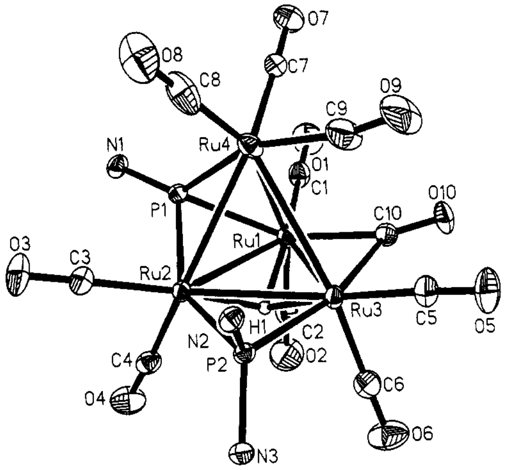

Figure 2. Perspective view of the molecular structure of $(\mu_3\text{-H})Ru_4(CO)_9(\mu\text{-CO})(\mu\text{-P}\{N^iPr_2\}_2)(\mu_3\text{-P}\{N^iPr_2\})$ (3) showing the atomic numbering scheme. Isopropyl substituents are omitted for clarity. Ru(1)–Ru(2) = 2.937(1) Å, Ru(1)–Ru(3) = 2.733(1) Å, Ru(2)–Ru(3) = 2.787(1) Å, Ru(2)–Ru(4) = 2.941(1) Å, Ru(3)–Ru(4) = 3.118(1) Å, Ru(1)–Ru(4) = 2.823(1) Å, Ru(1)–P(1) = 2.293(1) Å, Ru(2)–P(1) = 2.298 (1) Å, Ru(4)–P(1) = 2.296(1) Å, Ru(2)–P(2) = 2.395(1) Å, Ru(3)–P(2) = 2.329(1) Å, P(1)–N(1) = 1.642(3) Å, P(2)–N(2) = 1.680(3) Å, P(2)–N(3) = 1.684(3) Å.

= 2.301(4) Å, Ru(1)–C(10) = 2.006(4) Å), while the longest metal–metal bond (Ru(3)–Ru(4) = 3.118(1) Å) is associated with the only unbridged vector. The triangular face comprised of Ru(1), Ru(2), and Ru(4) is symmetrically capped by the phosphinidene ligand μ_3-P(N^{i}Pr$_2$), presumably formed via elimination of HN^{i}Pr$_2$ upon hydrogenolysis of a μ-P(N^{i}Pr$_2$)$_2$ group. The P–N bond length in the phosphinidene fragment (P(1)–N(1) = 1.642(3) Å) is considerably shorter than those in the μ-P(N^{i}Pr$_2$)$_2$ ligands of **3** (P–N$_{av}$ = 1.682(4) Å) and **2** (P–N$_{av}$ = 1.677(4) Å). During the early development of the chemistry of aminophosphine ligands King et al. isolated trinuclear $Co_3(CO)_9(\mu_3\text{-P}\{N^iPr_2\})$ from the reaction of $Co_2(CO)_8$ and HP(N^{i}Pr$_2$)$_2$.[20] The μ_3-hydride in **3**, located in a final difference Fourier map using the low-angle data only ($2\theta \leq 36.0°$), lies over an Ru$_3$ face (Ru(1), Ru(2), Ru(3)).[18] A limited number of triply bridging hydride ligands have been structurally characterized in clusters.[21] With a closo-trigonal-bipyramidal Ru$_4$P structure, **3** is closely related to the elusive closo molecule $Ru_4(CO)_{12}(\mu_3\text{-PR})$. The corresponding nido clusters $M_4(CO)_{13}(\mu_4\text{-PR})$ (M = Fe, Ru, Os) have been predicted to be stable by Hoffmann and co-workers.[22]

The series of clusters **1**–**3** are electronically related by stepwise 2-electron transformations from 64 to 60 electrons. There are few reported examples where a systematic reduction in the electron count has resulted in a rhomboidal–butterfly–tetrahedral conversion. Pomeroy has demonstrated the conversion of a 64-electron spiked triangular cluster into a 60-electron tetrahedron.[5b] Kyba has recently described a reverse transformation in which M–M bond cleavage in tetrahedral $Cp_2Mo_2Co_2(CO)_7(\mu\text{-}^tBuP\{C_6H_4\}P^tBu)$ was induced by NO$^+$, forming a μ_4-η^2-NO-coordinated butterfly.[23] Our studies suggest that the rhomboidal clusters $Ru_4(CO)_{13}(\mu\text{-PR}_2)_2$ have a diverse chemistry based on a 2-electron loss and intramolecular ligand activation. We are currently exploring the chemistry of other members of this class of electron-rich clusters.

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Supplementary Material Available: Details of the structure determination of complexes 2 and 3 (Tables S1 and S7), atomic positional parameters (Tables S2 and S8), bond distances (Tables S3 and S9), bond angles (Tables S4 and S10), anisotropic thermal parameters (Tables S5 and S11), and hydrogen atom positions (Tables S6 and S12) (21 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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