> $C{=}NCH_3$ > PPh_3 > 3-hexyne > CH_3CN.

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Structural Versatility of Ru_4 Butterflies. The Molecular Structures of $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)\cdot{}^1/_2C_6H_{14}$. Clusters with Almost Planar Metal Frameworks

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Summary: The synthesis and structural characterization of two new 64-electron butterfly clusters of ruthenium $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)\cdot{}^1/_2C_6H_{14}$ are described. The former crystallizes in space groups $P2_1/n$ with $a = 8.941$ (1) Å, $b = 10.209$ (2) Å, $c = 39.753$ (6) Å, $\beta = 95.62°$ and $Z = 4$. The latter crystallizes in space group $P\bar{1}$ with $a = 11.954$ (1) Å, $b = 15.459$ (2) Å, $c = 19.830$ (4) Å, $\alpha = 97.19$ (1)° $\beta = 74.35$ (1)°, and $\gamma = 71.26$ (1)°, and $Z = 2$. These electron-rich clusters have almost planar Ru_4 frameworks with two or three elongated Ru–Ru bonds. The influence of electron count and ligand donation to the Ru_4 core on stereochemistry are discussed.

Although the most common skeletal stereochemistry for homotetranuclear metal clusters is tetrahedral, a substantial number of M_4 species have now been characterised in which the metal framework has a "butterfly" configuration derived from the tetrahedron by cleavage of one metal–metal bond.[1,2] Moreover, interest in the butterfly geometry has been greatly stimulated by the observation of enhanced reactivity for exposed carbidic carbon atoms bound in multisite fashion within the open nest-like frameworks of the butterfly clusters $[HFe_4(\mu_4\text{-}C)(CO)_{12}^-]$, $Fe_4(\mu_4\text{-}C)(CO)_{12}^{2-}]$,[3] and $[Fe_4(CO)_{13}C]$[4] and of highly coordinated carbon monoxide in $Fe_4(CO)_{13}^{2-}$.[5,6] It is possible that the butterfly configuration of tetrametal fragments may play a subtle role in facilitating reactions of ligands bound between the "wings" of the butterfly since in principle an exceedingly wide range of dihedral angles ϑ and M–M nonbonding distances c (Figure 1) can be tolerated for any particular M_4 fragment. For the known Fe_4 clusters[3-8] there are some indications that the dihedral angle may be sensitive to electronic structure but unfortunately the range of compounds, dihedral angles, and electron counts is relatively small. We have recently characterised by X-ray diffraction several tetranuclear ruthenium clusters including two new compounds $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$ with highly unusual, almost planar, Ru_4 frameworks which are described herein. These tetraruthenium clusters show unprecedented variations in butterfly geometry. Our results, together with other scattered data in the literature, suggest that electron donation from the ligands can play a major role in influencing butterfly geometry, with higher electron counts favoring larger dihedral angles, flattening of the Ru_4 butterfly, and Ru–Ru bond lengthening. These steps may be part of a logical sequence of stereochemical changes leading from a tetrahedral (60 electrons, six M–M bonds) geometry through a butterfly (62 electrons, five M–M bonds) core to a metal skeleton with only four M–M bonds. The results, which indicate the versatility of the butterfly structural unit, may have important ramifications for the modification and reactivity of clusters.

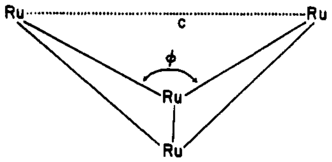

Figure 1. Definition of c, the nonbonding Ru···Ru distance and ϕ, the dihedral angle for an Ru_4 butterfly.

Structural data for the new butterfly structures,[9,13] together with a selection of other data for Ru_4 and mixed

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(9) $Ru_4(CO)_{13}$ $(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ was synthesized in ~10% yield as one product of the controlled decomposition of $Ru_3(CO)_{11}$ $(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$.[10] A dark blue band separated on Florisil (eluant benzene–heptane) afforded red-brown crystals when evaporated to dryness and recrystallized under a CO atmosphere [ν(CO) C_6H_{12}, 2076 (m), 2060 (m), 2041 (s), 2034 (vs), 2023 (vs), 2010 (m), 1998 (s), 1985 (m), 1972 (m), cm^{-1}]. $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$ was obtained as a minor product (~10%) from the pyrolysis of $Ru_3(CO)_9(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_3$[11] in toluene. The last red band eluted (3:1 benzene–heptane) from a Florisil column gave red crystals (ν(CO) 2034 (vs), 2014 (s), 1984 (m), 1973 (m), 1967 (s), 1950 (s), 1938 (w) cm^{-1}]. The phosphinidene derivative $Ru_4(CO)_{13}(PPh)$ (red crystals from heptane–benzene) is the major product (~50%) of thermolysis of the coordinately unsaturated cluster $Ru_3(CO)_9(\mu\text{-}PPh_2)(H)$.[12] Full details of the synthesis and spectroscopic properties of these clusters will be presented elsewhere.

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(13) X-ray crystal data: $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu_2\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$; mol wt 1034.7, $a = 8.941$ (1), $b = 10.209$ (2), $c = 39.753$ (6) Å; $\beta = 95.62$ (1)°; space group $P2_1/n$; $V = 3611$ (1) Å; $\rho_m = 1.90$, $\rho_c = 1.903$ g cm^{-3}, $Z = 4$; μ(Mo Kα) = 17.08 cm^{-1}; $R = 0.036$, $R_w = 0.042$ based on 3210 observed reflections (Syntex $P2_1$ diffractometer). $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)\cdot 1/2C_6H_{14}$: mol wt 1470.4, $a = 11.954$ (1), $b = 15.459$ (2), $c = 19.830$ (4) Å; $\alpha = 97.19$ (1)°, $\beta = 74.35$ (1°), $\gamma = 71.26$ (1)°; space group $P\bar{1}$; $V = 3250.0$ (7) Å^3; $\rho_m = 1.50$, $\rho_c = 1.502$ g cm^{-3}, $Z = 2$; μ(Mo Kα) = 10.16 cm^{-1}; R = 0.037, $R_w = 0.046$ based on 5298 observed diffractometer measurements. Listings of atomic coordinates and bond lengths and angles for both structures are available as supplementary data.

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Table I. Structural Parameters for Selected Ruthenium "Butterfly" Clusters

compd	av Ru-Ru, Å	ϕ, deg	C, Å	electron[19] count	ref
(PPN)($Ru_4(CO)_{13}Cl$)	2.819	91.0	3.452	62	14
$Ru_4(CO)_{13}(PPh)$	2.892	111.24	4.012	62	12
$Ru_4(CO)_8(PPh_2)_2$(C≡C-*t*-Bu)$_2$(PPh_2C≡C-*t*-Bu)	2.976	167.04	5.001	64	this work
$Ru_4(CO)_{13}(PPh_2)$(C≡C-*t*-Bu)	3.032	176.93	5.259	64	this work
$Ru_3Fe(CO)_{13}(PPh_2)_2$	3.128	177.85	5.163	64	17
$Ru_3Ni(CO)_9(C_5H_5)$(C=CH-*t*-Bu)	2.818	116.6	3.892	62	20
$Ru_4(CO)_{10}(OH)(PPh_2)$(C=CH-*i*-Pr)	2.766	141.49	4.124	64	18
$Ru_4(CO)_{10}(OEt)(PPh_2)$(C=CH-*i*-Pr)	2.758	143.69	4.150	64	18

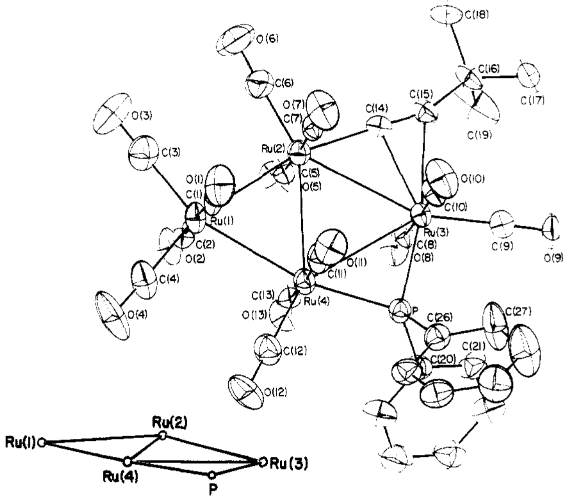

Figure 2. Molecular structure of $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ with Ru_4 skeleton inset.

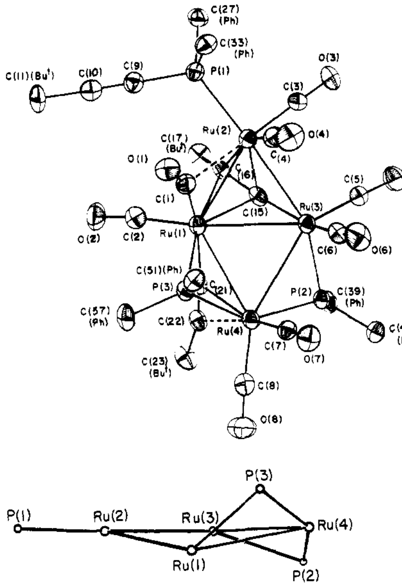

Figure 3. A perspective view of the molecule $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$. The almost flat Ru_4 skeleton is inset.

Ru/Fe or Ru/Ni clusters, are gathered in Table I. Figure 1 defines the various parameters. ORTEP plots of $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ and $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$ are shown in Figures 2 and 3, which also illustrate the skeletal geometry of each cluster. In $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ the phosphido group and the acetylide ligand bridge adjacent edges of one Ru_3 triangle. In the octacarbonyl cluster one acetylide is edge bridging and the other face bonded as a five-electron ligand.

It is immediately obvious from Table I and Figure 1 that there are dramatic differences in butterfly geometry for these Ru_4 species, with dihedral angles varying from 91.0° for PPN[$Ru_4(CO)_{13}Cl$][14] to 176.93° for $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ and nonbonding Ru···Ru distances ranging from 3.452 to 5.259 Å. The latter distances can be compared with the longest bonding Ru–Ru contact of 2.947 (6) Å in closed, tetrahedral $H_2Ru_4(CO)_{13}$.[15] Remarkably, a flattening of the M_4 butterfly as ϕ and c increase is accompanied by a gradual but emphatic lengthening of the average ruthenium–ruthenium distance. In the limit of an almost planar M_4 skeleton, exemplified by $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu^t)$ (ϕ = 176.93°), two of the Ru–Ru bond lengths (Ru(2)–Ru(3) = 3.157 (1) and Ru(3)–Ru(4) = 3.197 (1) Å), in one deltahedral fragment are exceptionally long when compared to the average Ru–Ru distance in $Ru_3(CO)_{12}$ (2.8555 Å).[16] Similar features are evident in the mixed-metal cluster[17] $Ru_3Fe(CO)_{13}(\mu_2\text{-}PPh_2)_2$, where the skeleton approaches planarity (Table I). In sharp contrast only four short Ru–Ru bonds (average 2.766 and 2.758 Å, respectively) are present in the vinylidene-based clusters[18] $Ru_4(CO)_{10}(\mu_3\text{-}OH)(\mu\text{-}PPh_2)(\mu_4\text{-}C{=}CH\text{-}i\text{-}Pr)$ and $Ru_4(CO)_{10}(\mu_3\text{-}OEt)$ $(\mu\text{-}PPh_2)(\mu_4\text{-}C{=}C\text{-}i\text{-}Pr)$, the "hinge" ruthenium–ruthenium distances of 3.455 (1) and 3.367 (1) Å being arguably nonbonding. It is interesting that while these compounds have four M–M bonds, the skeletal geometry does not correspond to the square or metal coordinated triangular array usually predicted for M_4 species with four M–M bonds.[1] Presumably the shallow butterfly configuration adopted represents a compromise between an idealized square framework and the stereochemical demands of the bridging ligands.

Closer inspection of the molecules in Table I reveals an unmistakable correlation of skeletal geometry with electronic structures.[19] The 62-electron Ru_4 clusters $Ru_4(CO)_{13}(PPh)$[12] and PPN[$Ru_4(CO)_{13}Cl$][14] as well as the mixed 62-electron species $Ru_3Ni(CO)_9(\eta^5\text{-}C_5H_5)(\mu_4\text{-}C{=}CH\text{-}t\text{-}Bu)$,[20] as predicted have butterfly structures derived from a 60-electron tetrahedron by rupture of one metal–metal bond. Here the butterfly is "steep" with dihedral angles between the wings of 91–116.6°. In the more

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(19) The donor characteristics of the ligands in these clusters are those normally associated with the particular bonding mode shown by X-ray crystallography. Thus: CO–2 e; μ-PPh_2–3 e; μ_3-PPh–4 e; μ-η^2-C≡C-*t*-Bu–3 e, μ_3-η^2-C≡C-*t*-Bu–5 e; μ_3-OH, OEt–5 e; μ-Cl–3 e; μ_4C=CH-*i*-Pr–4 e.

(20) Sappa, E.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Inorg. Chim. Acta* **1980**, *41*, 11. See also ref 25.

electron-rich, formally 64-electron compounds $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu^t)(PPh_2C{\equiv}C\text{-}t\text{-}Bu)$ and $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ as well as $Ru_3Fe(CO)_{13}(\mu\text{-}PPh_2)_2$ the metal polyhedra are almost planar with values of ϕ close to 180°. However the expected cleavage of a second M–M bond on progressing from a 62-electron to 64-electron count is not evident. Instead a marked lengthening of specific M–M bonds, compared to the 62-electron species, is apparent. We see the interesting feature that for these M_4 butterflies the "shallowness" of the butterfly and the degree of distortion from a 60-electron tetrahedron increases with increasng ligand donation to the core.[21] Moreover, opening of the butterfly is accompanied by Ru–Ru bond weakening in one specific fragment of the polyhedron. A similar preference for two weaker M–M bonds rather than one strong interaction has been noted by Adams in the osmium cluster $Os_4(CO)_{12}(\mu\text{-}S_2)$.[22] It is significant, however, that in the electron precise 64 electron vinylidene clusters $Ru_4(CO)_{10}(\mu_3\text{-}OR)(\mu\text{-}PPh_2)(\mu_4\text{-}C{=}CH\text{-}i\text{-}Pr)$ (R = H, Et) where rupture of a second metal-metal bond has indeed occurred, the four remaining Ru–Ru distances are short.

The above results prompt several observations. Clearly Ru_4 butterfly stereochemistry is quite sensitive to changes in electron density resulting from ligand donation.[23] In principle therefore modification of a butterfly geometry should be possible via a change in ligand donor characteristics. Modification of cluster geometry in this way could have important ramifications for cluster reactivity. In addition, it seems apparent that within the regime of 62–64 electrons, for four atom clusters there is considerable scope for structural change prior to M–M bond rupture. "Opening" of the butterfly and M–M bond lengthening may precede M–M cleavage. The implications of this for the detailed electronic structure of M_4 butterflies are under active investigation.

Acknowledgment. We are grateful to NSERC and Imperiall Oil for financial support of this work.

Registry No. $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$, 81956-22-1; $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$, 81939-71-1.

Supplementary Material Available: Tables of final fractional coordinates, interatomic bond distances and angles, final thermal parameters, and structure factors for the title compounds (55 pages). Ordering information is given on any current masthead page.

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[21] The smaller dihedral angle in $Ru_4(CO)_8(\mu\text{-}PPh_2)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)_2(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$(167.04°) than in $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ is consistent with somewhat reduced ligand donation to the Ru_4 core. Examination of the structure (Figure 3) shows that the Ru(4)–C(22) bond (2.620 (8) Å) in the former is extremely long when compared to Ru(4)–C(21) (2.292 (7) Å), indicating that while the stereochemistry of the acetylide is appropriate for a 2-electron η interaction with Ru(4), this bond is weak. Accordingly donation of the full formal complement of three electrons for this acetylide seems unlikely. For the latter the Ru(3)–acetylide interaction (Ru(3)–C(14) = 2.285 (8) Å, Ru(3)–C(15) = 2.509 (8) Å) is stronger although still asymmetric.

[22] Adams, R. D.; Yang, L. W., personal communication.

[23] A reviewer has suggested that the large dihedral angles for the electron-rich 64-electron Ru_4 clusters described herein may be a consequence of the lack of ligand bridging between the wing tips of the butterfies. However, the absence of wing tip bridging ligands does not *preclude* much smaller dihedral angles. Thus in $Ru_4(CO)_8$[glyoxal bis(isopropylimine)]$_2$, formally a 64-electron cluster, there are four strong and one weaker Ru–Ru bonds, with no ligand bridging the wing tip atoms. The dihedral angle is 142.2°.[24]

[24] Staal, L. H.; Polm, L. H.; Vrieze, K.; Ploeger, F.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 3590.

[25] Note added in proof. We have recently shown that this molecule is actually a hydride, $(\mu\text{-}H)Ru_3Ni(CO)_9(\mu\text{-}C{=}CH\text{-}t\text{-}Bu)$: Carty, A. J.; Taylor, N. J.; Sappa, E.; Tiripicchio, A., submitted for publication.