$[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}PhNNPh)]$: The First Example of an Azobenzene Molecule Coordinated on a Square Metal Face

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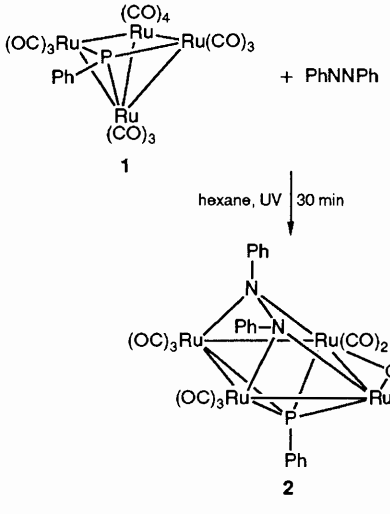
Reaction of azobenzene, under photolytic conditions, with the 62-electron butterfly cluster $[Ru_4(CO)_{13}(\mu_3\text{-}PPh)]$ **1** affords the first example of a 64-electron square-planar cluster containing a coordinated azobenzene ligand; a single crystal X-ray analysis of $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}PhNNPh)]$ **2** has revealed a novel capped trigonal prismatic Ru_4PN_2 skeleton.

The reactions of azoalkanes with transition metal carbonyls, first described many years ago by Pauson[1] and Knox,[2] have yielded a diverse array of complexes[3] including examples of symmetrical μ–η^2 coordination[2] at a binuclear centre, μ_3–η^2-bonding to a trinuclear fragment,[4] N=N bond cleavage leading to imido compounds[1,4,5] and orthometallation.[6] We report the first example of azobenzene bound in a symmetrical μ_4–η^2-fashion on a square metal face in the remarkable cluster $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}PhNNPh)]$ **2**. Several features of the synthesis and molecular structure of **2** are notable. (*i*) The quantitative conversion of $[Ru_4(CO)_{13}(\mu_3\text{-}PPh)]$ **1**,[7] a phosphinidene stabilised 62-electron butterfly cluster, to **2**, a 64-electron molecule with a square Ru_4 skeleton is to our knowledge unprecedented. Indeed with the exception of M_4 carbides[8] and nitrides[9] the chemical reactivity of butterfly clusters[10] has not been examined in detail because of a propensity for fragmentation. (*ii*) The overall Ru_4P skeletal framework of **1** closely approximates a square pyramid with the main group atom in the base. The transformation of **1** to **2**, where the phosphinidene caps a square Ru_4 face of an overall Ru_4PN_2 capped trigonal prism thus represents a novel example of a square-pyramidal skeletal rearrangement process.

Irradiation (UV, 450 W Hg lamp) of **1** (0.214 g, 0.24 mmol) in the presence of azobenzene (0.049 g, 0.26 mmol) in n-hexane (300 ml) for 30 minutes afforded **2** as the sole product after chromatographic work-up. Crystallisation of the complex from n-heptane–benzene afforded **2** in high yields (0.190 g, 0.18 mmol). The $^{31}P\{^1H\}$ shift† of **2** (+355.6 ppm) lies within the range expected for a μ_4-PPh ligand capping a 64-electron square-planar Ru_4 face, in contrast to the 62-electron related clusters $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}X)]$[11] [X=S, δ(P)=+238.9 ppm, X=Se δ(P)=+232.2 ppm] containing both group 15 and 16 atom vertices, the high field shifts of the latter clusters being attributed to electronic unsaturation. This notable difference in chemical shifts for the two types of compounds strongly suggests that the azobenzene cluster is electron-precise. Only recently has an example of an azoalkane coordinated to a tetranuclear framework been reported[12] in the butterfly cluster $[Ru_4(CO)_{12}(EtNNEt)]$[12] where the Ru_4N_2 framework, unlike that in **2**, is quite open. In contrast, the corresponding trinuclear systems have been studied extensively.[5a] Our work suggests that stabilised phosphinidene clusters such as **1** are convenient precursors of mixed main group–transition metal clusters with two or more main group atoms in the skeleton.[13]



Scheme 1 Formation of **2**

The structure of **2**‡ was determined by single-crystal X-ray diffraction. The molecule shown in Fig. 1 represents the first example of a square-planar array of Ru atoms capped symmetrically on one face by an azobenzene molecule. There is a distinct dihedral angle between the planes C(18)–N(1)–N(2) and C(24)–N(2)–N(1) of 23.8°. The μ_3-PPh ligand in **1**

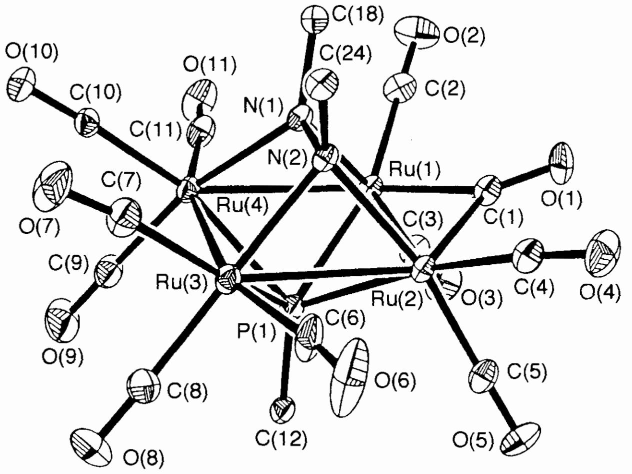


Fig. 1 A perspective view of the molecular structure of $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}PhNNPh)]$ illustrating the capped trigonal prismatic framework. For clarity, only the *ipso* carbon atoms of the phenyl rings are shown.

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† *Selected spectroscopic data* for **2**: IR ν(CO)/cm^{-1} (C_6H_{12}) 2082w, 2049m, 2040s, 2024m, 2018w, 2000w, 1988w, 1973w and 1811w; NMR $^{31}P\{^1H\}$ ($CDCl_3$) δ+355.6 ppm.

‡ *Crystal data* for **2**: red polyhedra from n-heptane–benzene; $C_{29}H_{15}N_2O_{11}PRu_4 \cdot 0.5C_6H_6$, M = 1041.7, monoclinic, space group $P2_1/n$, a = 11.187(1), b = 19.666(2), c = 16.700(2) Å, β = 107.72°, U = 3499.6(6) Å^3, Z = 4, D_c = 1.977 g cm^{-3}, $F(000)$ = 2012, μ(Mo-Kα) = 17.66 cm^{-1}. The structure was solved (Patterson, Fourier methods) and refined (full-matrix least-squares, all non-hydrogen atoms anisotropic) on the basis of 5028 observed [$F > 6.0\sigma(F)$] reflections measured at 200 K using Mo-Kα (λ = 0.71073 Å) radiation on a Siemens R3m/V diffractometer. The final R and R_w values were 0.028 and 0.042 respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

now caps the opposite Ru_4 face of **2** as a μ_4-fragment. Three of the Ru–Ru distances [Ru(1)–Ru(4) = 2.854(1), Ru(3)–Ru(4) = 2.839(1), Ru(2)–Ru(3) = 2.829(1) Å] are similar and within the range expected for Ru–Ru bonds in electron-precise Ru_4 structures, whilst the fourth [Ru(1)–Ru(2) = 2.788(1) Å], bridged by a μ-CO group, is significantly shorter. The bond shortening observed in **2** [*i.e.* the difference, Δ, between the carbonyl bridged bond distance and the average of the unbridged Ru–Ru lengths (Δ = 0.052 Å)] is not as large as that found in the 62-electron formally unsaturated clusters $[Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-PPh})(\mu_4\text{-X})]$ (X = S, Δ = 0.091 Å). These differences provide new evidence that the unique metal–metal bond in the square, seven-skeletal pair, 62-electron systems $[M_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-X})_2]$ (X = PR, S) is shortened by formal electron deficiency. The ν(CO) frequency of the bridging carbonyl absorption for **2** appears at lower energy [ν(CO) (C_6H_{12}) 1811 cm^{-1}] than that of the sulphur-capped cluster $[Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-PPh})(\mu_4\text{-S})]$[11] [ν(CO) ($C_6H_{12}$) 1845 cm^{-1}] and affords a measure of the electron-deficient nature of the cluster framework in the latter species.

The structure of **2** can be considered as a capped trigonal prism with the skeleton consisting of an Ru_4N_2 prism, face-capped by a μ_4-phosphinidene fragment. Molecules with two different group 15 atoms in the framework are rare[13] and the structure of **2** presents an interesting test of the applicability of skeletal electron-counting rules to mixed main group–transition metal systems.[14] Cluster **2** can be derived from the sharing of square-face polyhedra, an Ru_4N_2 prism and an Ru_4P square-based pyramid. The expected electron count in the corresponding M_7 condensed cluster is 102 but replacement of three transition metals by three main group atoms reduces the polyhedral count by 30. Thus cluster **2** is consistent with the predicted count as the two nitrogen and one phosphorus atoms, as part of the cluster framework, donate five electrons each and the three phenyl groups each contribute one electron to the valence electron count. Alternatively, the cluster can be considered as an electron-precise 64-electron square in which the phosphinidene ligand contributes four electrons and the azobenzene ligand acts as a six-electron donor.

Close examination of the coordinated azobenzene ligand reveals a significant elongation of the N–N bond [1.515(4) Å] relative to a formal N–N single bond (1.45 Å for N_2H_4).[15] This bond weakening, evident in the structure, should result in N–N bond activation. We are currently exploring the generation of other mixed group 15-16–transition metal clusters, their structural features and small molecule activation chemistry.

We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work and to the Government of Ontario for a scholarship (to J.F.C.).

Received, 10th July 1991; Com. 1/03474J

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