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Preliminary communication

OPEN AND CLOSED RUTHENIUM AND OSMIUM CLUSTERS WITH μ_3-ACETYLIDE AND PHOSPHIDO BRIDGES

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Summary

The synthesis and structural characterisation of "open" $M_3(CO)_9$-$(C{\equiv}CR)(PPh_2)$ (M = Ru, Os; R = i-Pr, t-Bu) clusters with μ_3-acetylides and phosphido groups bridging an "open" edge of the M_3 triangle are described. Facile conversion of $Ru_3(CO)_9(C{\equiv}CR)(PPh_2)$ to "closed" $Ru_3(CO)_8(C{\equiv}CR)$-(PPh_2) occurs via loss of CO and metal—metal bond formation, a process which is reversible under one atmosphere of CO.

Facile opening of a strong metal—metal bond on addition of a substrate and subsequent M—M bond closure upon elimination of an elaborated molecule are likely to be key processes in homogeneous cluster catalysis. However, with the exception of metal—metal multiply bonded species [1] there are relatively few instances in which reversible M—M bond synthesis and cleavage in clusters have been conclusively demonstrated under mild conditions even for simple substrates [2]. In this regard phosphido (PR_2), arsenido (AsR_2) and phosphinidene (PR) complexes are of considerable current interest since these groups are capable of acting as stable yet flexible bridging ligands for the support of both bonding and non-bonding metal interactions. Thus Hüttner and coworkers [3] have recently demonstrated the reversible opening of a trinuclear heterometallic phosphinidene cluster and Vahrenkamp et al. [4] have described the dimerisation of norbornadiene catalysed by $AsMe_2$ bridged binuclear Fe_2 and FeCo complexes. In this communication we report what are, to our knowledge, the first examples of reversible M—M bond fission in a homonuclear triangular ruthenium cluster. The synthesis, spectroscopic and complete structural characterisation of "open" $M_3(CO)_9(C{\equiv}CR)(PPh_2)$ (M = Ru, Os; R = i-Pr, t-Bu) and "closed" $Ru_3(CO)_8(C{\equiv}CR)(PPh_2)$ (M = Ru; R = i-Pr, t-Bu) clusters with μ_3-acetylides and phosphido bridges are described.

Reaction of $M_3(CO)_{12}$ (M = Ru, Os) with $Ph_2PC{\equiv}CR$ (R = i-Pr, t-Bu) in heptane at 25°C for 12 h (M = Ru), or at 75°C for 4 h (M = Os) in the presence of two equivalents of Me_3NO gives good yields (~75%) of red (M = Ru) or yellow (M = Os) monosubstitution products $M_3(CO)_{11}(Ph_2PC{\equiv}CR)$ (I). (IR, ν(CO) (C_6H_{12}) (cm^{-1}); I (M = Ru, R = i-Pr) 2096w, 2046vs, 2029s, 2015vs, 1996m, 1985m, 1977w(sh), 1960vw(sh)); I (M = Os, R = t-Bu) 2107w, 2054vs, 2035s, 2019vs, 2000m, 1989m, 1980w(sh), 1974w).) X-ray analysis of $Ru_3(CO)_{11}Ph_2PC{\equiv}CPh$ (space group $P2_1/c$, a 9.280(1), b 27.042(2), c 13.451(1) Å, β 103.12(1)°, $Z = 4$, V 3287.95 Å^3, D_c 1.820 g cm^{-3}; 4314 reflections ($I \geqslant 3\sigma(I)$) (Syntex $P2_1$) were used in the structure solution and refinement to current $R = 0.035$ and $R_w = 0.040$) has shown that a phosphorus atom of the intact phosphinoacetylene occupies an equatorial site on one Ru atom, with all carbonyls terminal. Treatment of I (M = Ru, R = i-Pr, t-Bu) with Me_3NO at -10°C for 24 h afforded bright yellow $M_3(CO)_9(C{\equiv}CR)(PPh_2)$ (II). The osmium analogues were obtained on refluxing I (M = Os, R = i-Pr, t-Bu) in decalin for 5 h. (Yields: II, M = Ru, R = i-Pr, t-Bu, 55%; M = Os, R = i-Pr, t-Bu, 70%.) Infrared spectra (e.g. II, M = Ru, R = i-Pr, ν(CO) (C_6H_{12}) (cm^{-1}): 2084w, 2061vs, 2043s, 2014m, 2009m, 1999w, 1993w, 1987w, 1978w) are closely similar for all of these compounds. ^{31}P NMR spectra (δ (85% H_3PO_4): II, M = Ru, R = i-Pr, -51.79; II, M = Os, R = i-Pr, -65.42) consisted of a single high field resonance in each case.

The principal structural features of II (M = Ru, Os; R = i-Pr) were established by single crystal X-ray analysis*. An ORTEP plot for M = Ru is shown in Fig. 1. In each molecule the metal atoms form an isosceles triangle, with two strong metal—metal bonds (av. Ru—Ru 2.839 Å; av. Os—Os 2.879 Å) and one open edge (Ru(1)- - - -Ru(3) 3.466(1) Å; Os(1)- - - -Os(3) 3.508(1) Å). The open edge is bridged by a diphenyl-phosphido group (Ru(1)—P—Ru(3) 92.8(0)°; Os(1)—P—Os(3) 93.2(0)°) with the acetylide σ-bonded to M(2) and symmetrically η^2-bonded to both M(1) and M(3). The C(10)—C(11) distances of 1.284(8) Å in II (M = Ru, R = i-Pr) and 1.28(1) Å in II (M = Os, R = i-Pr) are appreciably longer than the carbon—carbon distance in acetylene (1.201(1) Å) [5] illustrating the bond weakening effects of the multi-site interaction. A comparison of the acetylide bond length in II with the μ_2-η^2 acetylides of $Ru_3(CO)_6(PPh_2)(\mu_2\text{-}C{\equiv}CBu\text{-}t)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu\text{-}t)(PPh_2C{\equiv}CBu\text{-}t)$ and $Ru_2(CO)_6(PPh_2)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu\text{-}t)$, having C≡C bond lengths of 1.239(13) [6] and 1.218(4) Å, [7] respectively, indicates significant bond lengthening on π-coordination to a second metal atom. The *trans*-bent geometry of the

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*X-ray data: $Ru_3(CO)_9(C{\equiv}CPr\text{-}i)(PPh_2)$, space group $P2_1/c$, a 13.189(1), b 9.674(1), c 22.481(2) Å, β 91.82(1)°; $Z = 4$, ρ_c 1.799, ρ_m 1.82 g cm^{-3}, μ 16.29 cm^{-1}; $F(000) = 1568$. Intensity date were collected on a Syntex $P2_1$ diffractometer with graphite monochromated Mo-K_α radiation. From 3785 measured reflections ($2\theta \leqslant 45°$), 2743 with $I \geqslant 3\sigma(I)$ were used in the structure solution and refinement. Final values of R and R_w are 0.025 and 0.028 respectively. $Os_3(CO)_9(C{\equiv}CPr\text{-}i)(PPh_2)$, space group $P2_1/c$, a 13.189(2), b 9.638(1), c 22.456(3) Å; β 92.20(1)°; $Z = 4$, ρ_c 2.431, ρ_m 2.45 g cm^{-3}, μ 142.84 cm^{-1}, $F(000) = 1952$. Final R and R_w values of 0.031 and 0.036 were obtained on refinement of 2485 observed (3761 measured) intensities corrected for absorption. Tables of atomic coordinates, thermal parameters and structure factors are available as supplementary data.

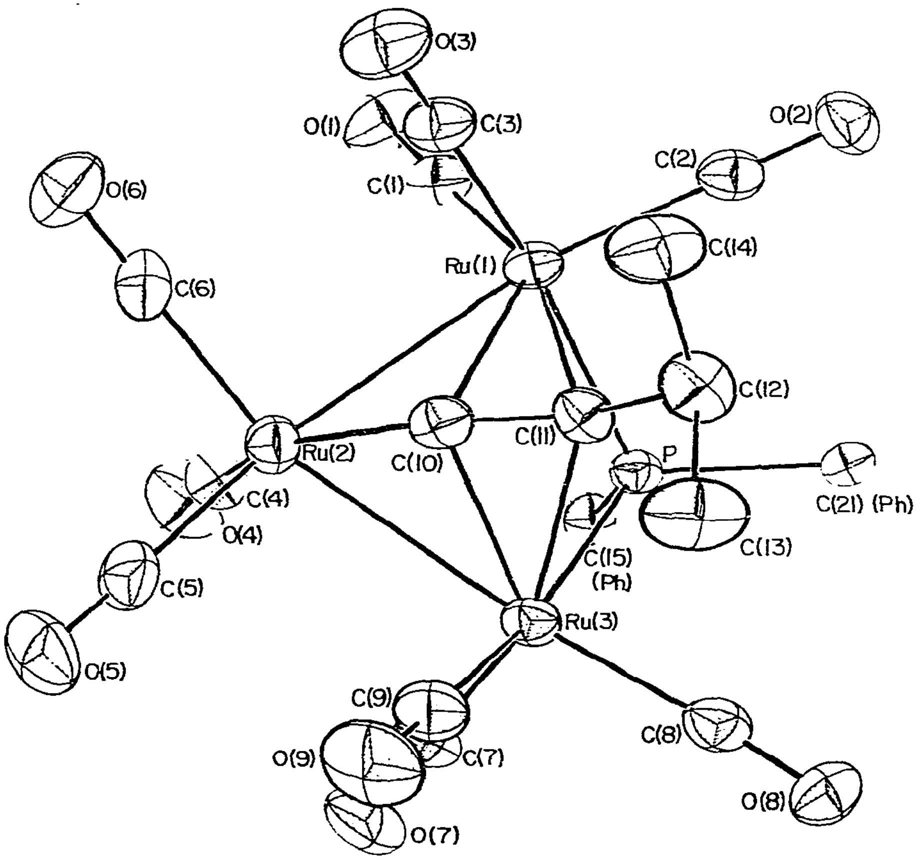

Fig. 1. The molecular structure of $Ru_3(CO)_9(C_2Pr\text{-}i)(PPh_2)$ (II, M = Ru, R = i-Pr) showing the atomic numbering. Ellipsoids are drawn at the 30% level.

acetylide, the large bend back angles at the acetylenic carbon atoms and the unhindered nature of C(10) are notable. The open environment at C(10) may have particular relevance to chemical reactivity, specifically nucleophilic addition at that site.

The molecules II are 50 electron species in the absence of a third metal—metal bond if the acetylide is considered to be a 5-electron donor. There is an interesting contrast with $M_3(CO)_9(H)(C_2Bu\text{-}t)$ [8] M = Ru, Os, where a strong metal—metal bond and a bridging hydride replace the PPh_2 group in II. Thus the electronic characteristics of the bridging ligand exert a dramatic influence on cluster structure, even to the extent of opening an otherwise stable M_3 triangle.

Not unexpectedly, in view of structural considerations, complex II (M = Ru, R = i-Pr) appears to be metastable in solution, converting to $Ru_3(CO)_6(\mu_2\text{-}CO)_2$-($PPh_2$)(C≡CPr-i) (III) on standing (III, M = Ru, R = i-Pr, IR, $\nu(CO)$ (C_6H_{12}) (cm^{-1}): 2061m, 2030s, 2020s, 1997s, 1983m, 1969m, 1848m; ^{31}P NMR, δ

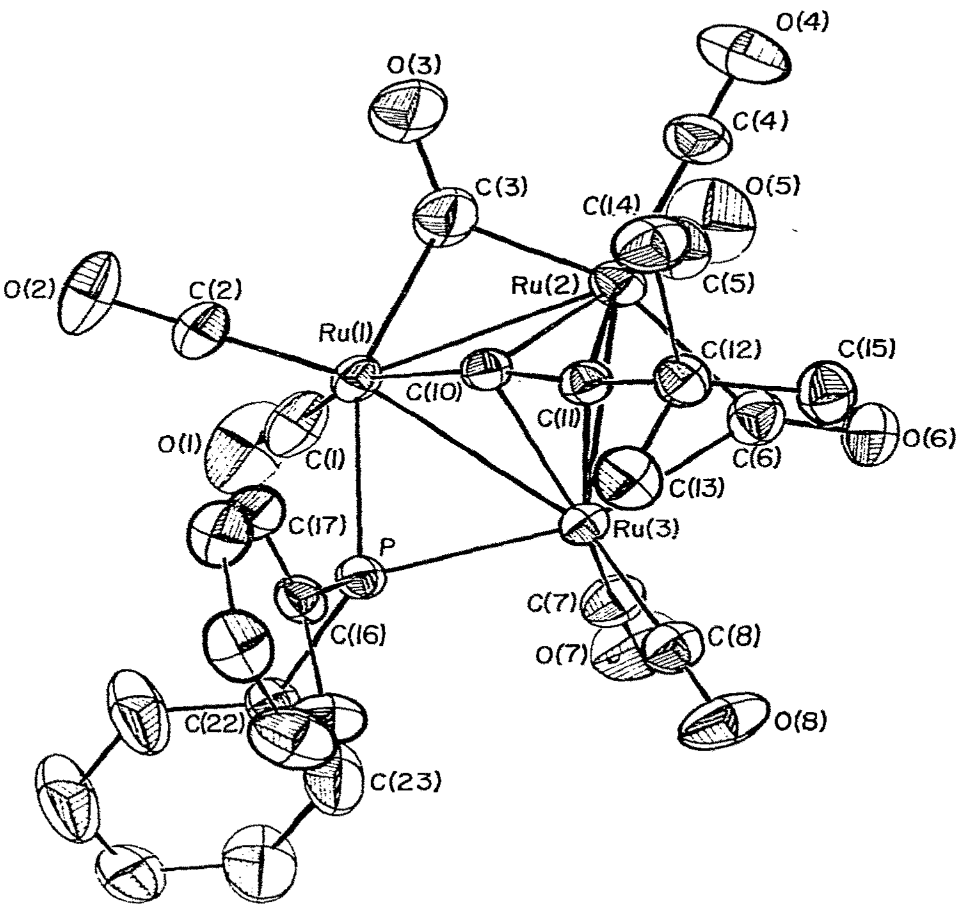

Fig. 2. A persoective view of the structure of $Ru_3(CO)_8(C_2Bu\text{-}t)(PPh_2)$ (III, M = Ru, R = t-Bu). Solvent of crystallisation is not illustrated. Important bond distances not mentioned in the text are Ru(1)—C(3) 2.060(6), Ru(2)—C(3) 2.292(6), Ru(2)—C(6) 2.079(5), Ru(3)—C(6) 2.1614(4), Ru(1)—P 2.337(1), Ru(3)—P 2.337(1) Å.

113.30). An X-ray analysis of III (M = Ru, R = i-Pr) revealed the structure shown in Fig. 2*.

Within the "closed" triangle of metal atoms, there are three strong metal—metal bonds (Ru(1)—Ru(2) 2.8151(4) Å, Ru(1)—Ru(3) 2.7084(4) Å and Ru(2)—Ru(3) 2.8257(4) Å). The hydrocarbyl unit is still bound in μ_3-η^2-fashion, with the σ-bond to Ru(1)- and η-interactions to Ru(2) and Ru(3).

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*X-ray data: $Ru_3(CO)_8(C_2Bu\text{-}t)(PPh_2)$ 0.5 C_6H_6, space group $P\bar{1}$, a 9.674(1), b 13.373(1), c 13.654(1) Å; α 108.97(1), β 72.64(1), γ 93.79(1)°; Z = 2, d_c 1.735, d_m 1.74 g cm^{-3}, μ = 14.70 cm^{-1}, $F(000)$ = 814. Final R and R_w values of 0.028 and 0.034 were obtained on refinement using 4911 observed data. Tables of atomic coordinates, thermal parameters and structure factors are available as supplementary data. (Supplementary data available. Lists of atomic coordinates, anisotropic thermal parameters, observed and calculated structure factors will be deposited as a NAPS document (55 pages). Order from ASIS/NAPS, c/o Microfile Publications, P.O. Box 3513 Grand Central Station, New York, N.Y. 10017.

Whereas in II, the phosphido group bridged the open side of the triangle, linking the two ruthenium atoms involved in η-interactions with the acetylide, in III the phosphido bridge links Ru(1) and Ru(3) which are respectively σ- and π-coordinated by the acetylide. The remaining two edges are bridged by asymmetric carbonyl bridges. Thus, although overall in the conversion of II to III loss of a carbonyl ligand is compensated for by Ru—Ru bond formation, a rearrangement of the peripheral ligands occurs, presumably to redistribute the remaining electron density. There are marked differences between the phosphido bridges in II and III. In II (M = Ru, R = i-Pr) an Ru(2)—P—Ru(3) angle of 92.8(0)° contrasts sharply with the acute angle Ru(1)—P—Ru(2) of 74.4(0)° in III. Moreover the Ru—P distances (av. 2.398 Å, M = Ru, R = i-Pr) in II are considerably longer than the corresponding average bond length (2.341 Å) in III (M = Ru, R = t-Bu). Also, in II (M = Ru, R = i-Pr) the phosphido bridge is axially coordinated to Ru(2) and Ru(3) whereas in III the phosphido bridge occupies equatorial sites on Ru(1) and Ru(2). These changes, indicative of the versatility of the PPh_2 group as a bridging ligand, result in characteristically different ^{31}P chemical shifts in ^{31}P NMR spectra. The larger M—P—M angle has a correspondingly higher field ^{31}P chemical shift, indicative of a phosphido bridge across a nonbonded pair of metal atoms.

Certain features of the structures and chemistry of II and III are of interest in the wider context of processes involved in cluster catalysis. Treatment of III (M = Ru, R = i-Pr) with 1 atmosphere of CO results in rapid (~5 sec) regeneration of II via Ru—Ru bond scission. In turn II reverts to III slowly on standing or more quickly (~12 h) when a stream of nitrogen is passed through the solution. The opening of the closed metal triangle in III presumably reflects the electron deficiency of this cluster and the reversibility of the reaction with CO is facilitated by the availability of a strong bridging ligand (PPh_2) capable of supporting two non-bonded ruthenium atoms. Preliminary work has confirmed that III is extremely sensitive to the addition of unsaturated Lewis bases other than CO. Finally, we note that the multisite bound acetylides in II should, by virtue of the electron deficiency of the cluster and by analogy with the extensive chemistry of the μ_2-acetylide in $Fe_2(CO)_6(C{\equiv}CR)(PPh_2)$ [9] be extremely carbocationic. A rich chemistry for the clusters II and III can therefore be confidently predicted.

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