Preliminary communication

Co-ordinatively unsaturated metal cluster compounds: facile reactivity of the phosphinidene-capped phosphido-bridged triruthenium cluster [Ru₃(μ₃-PPh)(μ₂-PPh₂)₂(CO)₇]

John S. Field, Raymond J. Haines and Faizel Mulla

Unit of Metal Cluster Chemistry, Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg 3200 (South Africa)

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Abstract

The purple, phosphinidene-capped, phosphido-bridged triruthenium cluster [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_7$] reacts readily with carbon monoxide, trimethylphosphite, sodium borohydride and diphenylacetylene under mild conditions to afford product mixtures from which [Ru$_3$(μ-PPh)(μ_2-PPh$_2$)$_2$(CO)$_{7+n}$] (n = 1, 2 or 3), [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_6${P(OMe)$_3$}], [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(μ_2-H)(CO)$_6$]$^-$ and [Ru$_3$(μ_3-η^3-PhPCPhCPh)(μ_2-PPh$_2$)$_2$(CO)$_6$], respectively, can be isolated. The structure of [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_6${P(OMe)$_3$}] has been established X-ray crystallographically.

One of the accepted requirements for a low valent mononuclear complex to function as a homogeneous catalyst is that it is either formally coordinatively unsaturated, *i.e.* the metal atom or ion does not obey the E.A.N. rule or that it contains weakly bound and readily replaceable ligands. A similar requirement will apply to closed metal clusters *i.e.* the number of valence electrons or the polyhedral electron count should be less than that predicted by the E.A.N. or the Wade–Mingos Rules respectively. However, a limited number of metal cluster compounds have been reported which according to these rules are co-ordinatively saturated but which readily participate in associative-type reactions, *e.g.* [Fe$_2$Mn(μ_3-PPh)(η^5-C$_5$H$_5$)(CO)$_8$] [1], [Fe$_4$(μ_4-PPh)$_2$(μ_2-CO)(CO)$_{10}$] [2] and [Ru$_4$(μ_4-PPh)$_2$(μ_2-CO)(CO)$_{10}$] [3]. We thus prefer to apply a more general definition for co-ordination unsaturation in metal clusters namely that the energy separation between the filled and unfilled frontier orbitals is small; in this situation the LUMO or LUMO's will be readily accessible to nucleophilic attack by incoming ligands. The LUMO's of a metal cluster derivative are essentially

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Correspondence to: Professor R.J. Haines.

metal-based and antibonding with respect to the skeletal framework. This property is an unfavourable feature of metal clusters in terms of their functioning as homogeneous catalysts as it can lead to their fragmenting during a chemical reaction particularly in those reactions involving an associative-type mechanism. The fragmentation can be curtailed to a considerable extent, however, by the introduction of non-labile bridging and/or capping ligands to the metal cluster framework; in fact the introduction of a capping atom such as the phosphorus of a phenylphosphinidene into the framework can lead to the stabilization of the LUMO and to it becoming overall weakly bonding in character [4].

As part of a programme involving the synthesis of formally coordinatively unsaturated metal cluster compounds containing capping phenylphosphinidene and/or bridging diphenylphosphido ligands we have synthesized the triruthenium species $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ (1) * in which, as established X-ray crys-


(1)
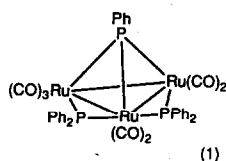
tallographically, the ruthenium atoms adopt a closed triangular structure [5]. This compound contains the correct number of electrons (48) for a closed triangular structure in terms of the E.A.N. Rule or alternatively the correct number of skeletal electron pairs (6) for a nido-trigonal bipyramidal structure in terms of the Wade–Mingos Rules and thus according to both Rules is formally co-ordinatively saturated. However its colour (purple) can be interpreted in terms of a low-lying LUMO. Its reactivity towards small molecule nucleophiles was thus investigated. Some of the results of this study are reported here.

Passage of carbon monoxide through a solution of compound 1 at room temperature was found to lead to a rapid colour change from purple to yellow; prolonged passage of the CO effected the evaporation of the solvent and the separation of a yellow crystalline product. This compound was found to undergo decarbonylation very readily to give compound 1, and thus it could not be characterized fully, but it is undoubtedly an adduct of 1 and of formula $[Ru_3(\mu\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_{7+n}]$ (2) where n = 1, 2 or 3 **. The $^{31}P\{^1H\}$ NMR spectrum

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* Compound 1 may be considered either as a closed triangular cluster of ruthenium atoms capped over one of its faces by a phenylphosphinidene ligand and bridged across two of its edges by diphenylphosphido groups or, alternatively, as a closed tetrahedral cluster of three rutheniums and one phosphorus atom with two of the ruthenium–ruthenium edges being bridged by diphenylphosphido groups.

** Spectroscopic data. Compound 2: $\nu(CO)$: 2078m, 2058s, 2030vs, 2002m, 1995m, 1980m (measured in cyclohexane). $^{31}P\{^1H\}$ NMR: AXY pattern, ν_A −60.4, ν_X −93.10, ν_Y −93.16 (J_{AX} 132.9, J_{AY} 152.8, J_{XY} ≈ 0 Hz) (δ scale in ppm relative to H_3PO_4) (measured in CDCl$_3$). Compound 3: $\nu(CO)$. 2018s, 1992vs, 1975w, 1955m, 1940m, 1920w (measured in cyclohexane). $^{31}P\{^1H\}$ NMR: ν_A 265.6 ddd, ν_M 198.9 ddd, ν_X 160.2 ddd, ν_Z 97.7 ddd, (J_{AM} 150.0, J_{AX} 5.6, J_{AZ} 73.5, J_{MX} 22.8, J_{MZ} 103.3, J_{XZ} 9.8) (measured in CD$_2$Cl$_2$ at −56°C). Compound 4: $\nu(CO)$: 1990m, 1955s, 1915m, (measured in CH$_2$Cl$_2$). $^{31}P\{^1H\}$ NMR: ABX pattern, ν_A 191.82, ν_B 191.81, ν_X 137.0, (J_{AX} 91.52, J_{BX} 86.78, J_{AB} ≈ 0,) (measured in acetone-d_6). Compound 5: $\nu(CO)$: 2030s, 1998vs, 1980s, 1960s, 1945m, 1937m (measured in cyclohexane. $^{31}P\{^1H\}$ NMR: ν_A 228.8 dd, ν_M 123.5 dd, ν_X 76.6 dd, (J_{AM} 141.7, J_{AX} 25.1, J_{MX} 87.3) (measured in CDCl$_3$).

of this compound, recorded under an atmosphere of CO, exhibited an AXY, approaching a typical AX_2, pattern of peaks considerably upfield of those of the parent reflecting firstly that a single compound was present in solution, secondly that the phosphorus atoms of the diphenylphosphido groups are essentially equivalent and thirdly that a possible change in the mode of co-ordination of the capping and bridging groups has occurred with the configuration reverting from a closed to an open one. Any one of three products is possible, *viz.* [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_8$], [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_9$] or [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_{10}$] depending on whether compound **1** adds one, two or three mole equivalents of carbon monoxide. These compounds will have structures **2A**, **2B** and **2C** respectively on the basis
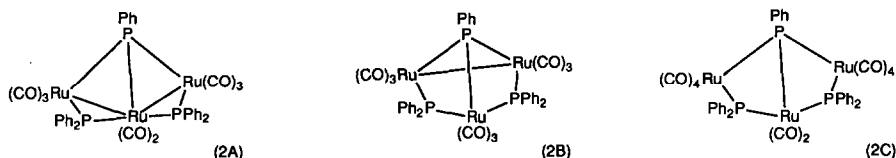
of the ^{31}P{^{1}H} NMR spectral data although the formation of the decacarbonyl product, **2C**, can be considered as being unlikely in view of a redistribution of the carbonyl groups being required from **2B** to **2C**. A limited number of examples of this type of cluster framework opening through CO addition are known and include those involving the capped triangular cluster [Fe$_2$Mn(μ_3-PPh)(η^5-C$_5$H$_5$)(CO)$_8$] which reversibly affords [Fe$_2$Mn(μ_3-PPh)(η^5-C$_5$H$_5$)(CO)$_9$] and [Fe$_2$Mn(μ_3-PPh)(η^5-C$_5$H$_5$)(CO)$_{10}$] in consecutive steps [1] and [Ru$_3$(μ_3-η^2-PPhC$_5$H$_4$N)(μ_2-PPh$_2$)(μ-CO)$_2$(CO)$_6$] which reversibly affords [Ru$_3$(μ_3-η^2-PPhC$_5$H$_4$N)(μ_2-PPh$_2$)(CO)$_9$] [6].

   Treatment of compound **1** with P(OMe)$_3$ in solution at room temperature also led to a colour change but to a deep orange, to afford a reaction mixture from which a purple derivative characterized as [Ru$_3$(μ_3-PPh)(μ_2-PPh$_2$)$_2$(CO)$_6$-{P(OMe)$_3$}] (**3**) was isolated as the major product. A crystal structure determina-

tion *** of this compound confirmed its identity and showed it to have a structure based on that of its parent with a carbonyl group coordinated to the ruthenium containing three carbonyl groups, having been substituted by the trimethyl phosphite (Fig. 1). It is assumed that the original deep orange colour of the reaction
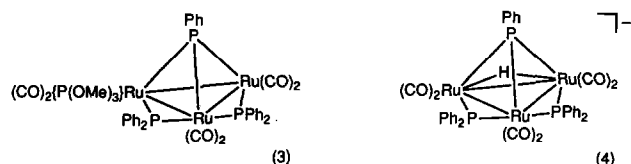
Fig. 1.

mixture stemmed from the formation of $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7\{P(OMe)_3\}]$, a substituted derivative of compound **2A** and resulting from an associative attack of the ligand on $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ (**1**), and that this substituted heptacarbonyl derivative readily decarbonylates to compound **3**. Consistent with these assumptions compound **3** was found to react readily and reversibly with carbon monoxide but the product mixture gave a highly complex $^{31}P\{^1H\}$ NMR spectrum indicating the presence of a number of products which could not be formally identified.

Compound **1** was also found to react readily in solution at room temperature with an excess of sodium borohydride to afford a mixture from which a product characterized as $[(PPh_3)_2N][Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})(CO)_6]$ (PPN, **4**) [†] could be isolated in high yield on addition of $[(PPh_3)_2N]Cl$. The ^1H NMR spectrum of this salt exhibits a doublet of triplets at -11.56 ppm, assigned to a bridging hydride ligand, while the $^{31}P\{^1H\}$ NMR spectrum displays an ABX, approaching a typical A_2X, pattern of peaks with the chemical shift of the phenylphosphinidene phosphorus being upfield of that of the diphenylphosphido phosphorus atoms, similar to that found for compound **1**. These data are interpreted in terms of the structure illustrated, *i.e.*, with the hydride ligand bridging the ruthenium–ruthenium edge not bridged by the diphenylphosphido groups and with the phosphorus atoms of the latter being essentially equivalent. Again it is assumed that the reaction involves an associative attack leading to the formation of $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})(CO)_7]^-$ and that the latter decarbonylates to $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(\mu_2\text{-H})(CO)_6]^-$ (**4**).

Diphenylacetylene was also found to react with compound **1** although a temperature slightly above ambient was required. The major product isolated from the

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[†] Protonation of compound PPN, **4** did not lead to the formation of $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ (**1**) which would have been expected if **4** was a heptacarbonyl species.

reaction mixture was identified as $[Ru_3(\mu_3\text{-}\eta^3\text{-PhPCPhCPh})(\mu_2\text{-PPh}_2)_2(CO)_6]$ (5), previously synthesized by Carty *et al.* by reaction of $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu\text{-H})(CO)_7]$ with PhC≡CPh in toluene under reflux conditions [7]. A crystal structure determination of this species revealed that the formation results from the formal insertion of the acetylene into a Ru–P bond of the phenylphosphinidene [7]. On the basis that $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu\text{-H})(CO)_7]$ is readily converted to $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ in toluene under reflux [5], it is clear that the formation of compound **5** from $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu\text{-H})(CO)_7]$ occurs via $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ as intermediate.

(5)   (6)

The reaction of compound **1** with acetylene was also investigated and significantly a major product found to be formed at temperatures of 40°C and at pressures of five atmospheres, was identified as $[Ru_3(\mu_3\text{-}\eta^2\text{-PhPC}_6H_4PPh)(\mu_2\text{-PPh}_2)(\mu_2\text{-H})(CO)_7]$ (6), previously isolated from the thermolysis of $[Ru_3(\mu_2\text{-PPh}_2)_3(\mu_2\text{-H})(CO)_7]$ or $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ (1) in xylene under reflux [5]. It is not clear why the acetylene should promote the isomerism of compound **1** to **6**.

We conclude that $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-PPh}_2)_2(CO)_7]$ (1) can be expected to react with a wide range of small molecule nucleophiles under mild conditions, thereby exhibiting a reactivity pattern essentially typical of metal clusters that are co-ordinatively unsaturated. However, as described above, compound **1** is co-ordinatively saturated in terms of the E.A.N. and Wade–Mingos Rules, and so we prefer to associate co-ordinative unsaturation in metal clusters with a small HOMO-LUMO gap as found in **1** on the basis of its colour.

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