DALTON COMMUNICATION

Linkage of heteronuclear rhodium–platinum clusters †

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Two coupled clusters $[Rh_8Pt_2(CO)_{21}(dppm)_2]$ (1) and $[Rh_6Pt_4(CO)_{16}(dppm)_3]$ (2) have been synthesised and characterised; the mixed metal Rh_2Pt_2 cluster in 1 and the tetranuclear Pt_4 cluster in 2 are bonded to the Rh_6 metal core *via* Rh–Rh and Pt–Rh bonds.

Clusters of variable nuclearity, heterometallic composition and with a great variety of ligands have been widely reported. However, the direct coupling of clusters has been much less studied, the best known example is from the early days of cluster chemistry. Albano and Bellon have reported the synthesis and characterization of $[Rh_{12}(CO)_{30}]^{2-}$, in which two $[Rh_6(CO)_{14}]^-$ moieties are linked by a carbonyl bridged Rh–Rh σ bond.[1] $[Ir_8(CO)_{22}]^{2-}$ is another example of this type of homometallic cluster coupling.[2] Here we report the synthesis and structural characterization of two new cluster compounds, where homo- and hetero-metallic units are linked by direct metal–metal bonds. During the course of a systematic study of heterometallic Pt–Rh clusters[3] we investigated the reactions of binuclear platinum complexes: $[PtCl(dppm)]_2$ and $[Pt_2(CO)_3(dppm)_2]$, with the hexanuclear rhodium clusters $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}(NCMe)]$, respectively.

$$[Rh_6(CO)_{15}][NBu_4]_2 + [PtCl(dppm)]_2 \longrightarrow [Rh_2Pt_2(CO)_6(dppm)_2] + [Rh_8Pt_2(CO)_{21}(dppm)_2] \quad (1)$$

$$[Rh_6(CO)_{15}(NCMe)] + [Pt_2(CO)_3(dppm)_2] \longrightarrow [Rh_6Pt_4(CO)_{16}(dppm)_3] \quad (2)$$

Both reactions (1) and (2) afford as main products the novel decanuclear clusters shown in Fig. 1 and 2.†[4]

Complexes **1** and **2** are examples of an unusual structural pattern where "Rh_6" and a tetranuclear fragment are linked by a direct metal–metal bond supported by two bridging CO groups. The bonding arrangement is similar to that in $[Rh_{12}(CO)_{30}]^{2-}$ where the linked $[Rh_6(CO)_{14}]^-$ octahedral moieties fit precisely to the electron count of the *closo* hexanuclear clusters (86 electrons).[1] The electron counting procedure for the clusters **1** and **2** gives an unexpected result for the both hexa- and tetra-nuclear cluster cores. If the metal–metal bond between two structural units is considered as a two electron covalent interaction the counting procedures would give 85 electrons for the Rh_6 units, 59 electrons for the Rh_2Pt_2 core in **1** and 55 electrons for the Pt_4 core in **2**. A reasonable way to rationalize the structures of **1** and **2** is by using the donor–acceptor nature of the metal–metal bond connecting two cluster units. There are several examples of donor–acceptor interactions between two cluster moieties but typically the donor fragment is bonded to the acceptor through a non-transition element.[5] The assumption of a dative metal–metal bond in the case of **1** and **2** leads to the expected even numbers of electrons for both linked units. In such a case one of the linked units would be the two electron donor and the other the two electron acceptor. The question of direction of the donor–acceptor interaction, however, plays an important role in the bonding description. The Rh center has been reported to act both as a two electron donor as in a Pt_2Rh chain structure[6] and on the other hand, as a two electron acceptor as in a

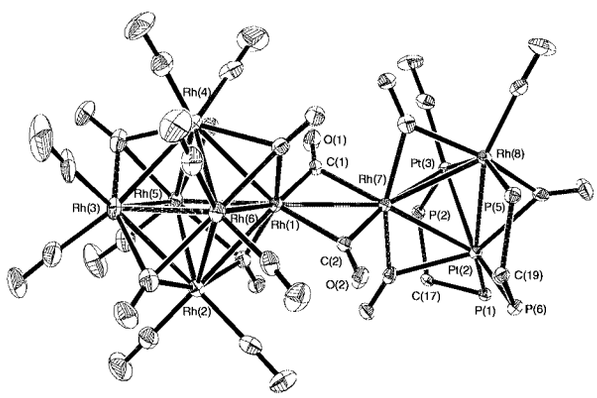

Fig. 1 Structure of $[Rh_8Pt_2(CO)_{21}(dppm)_2]$ (**1**). Hydrogens and aromatic rings have been omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–Rh(7) 2.7684(5), Rh(7)–Pt(2) 2.7687(4), Rh(7)–Pt(3) 2.9575(4), Rh(7)–Rh(8) 2.6807(4), Rh(8)–Pt(2) 2.6626(3), Rh(8)–Pt(3) 2.6803(4), Pt(2)–Pt(3) 2.5889(2), Rh(1)–C(1) 2.005(5), Rh(1)–C(2) 1.994(4), Rh(7)–C(1) 2.068(4), Rh(7)–C(2) 1.994(4), C(1)–O(1) 1.153(5), C(2)–O(2) 1.170; Rh(1)–C(1)–Rh(7) 85.63(17), Rh(1)–C(2)–Rh(7) 87.93(17).

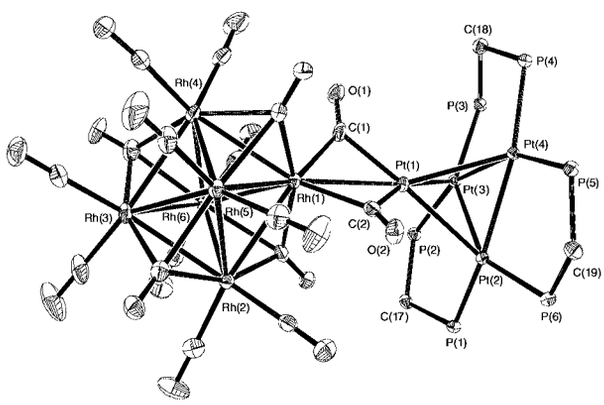

Fig. 2 Structure of $[Rh_6Pt_4(CO)_{16}(dppm)_3]$ (**2**). Hydrogens and aromatic rings have been omitted for clarity. Selected bond lengths (Å): Rh(1)–Pt(1) 2.6857(3), Pt(1)–Pt(2) 2.6522(2), Pt(1)–Pt(3) 2.6792(2), Pt(1)–Pt(4) 2.6921(2), Pt(2)–Pt(3) 2.6037(2), Pt(2)–Pt(4) 2.6219(2), Pt(3)–Pt(4) 2.6465(2), Rh(1)–C(1) 2.031(4), Rh(1)–C(2) 2.030(4), Pt(1)–C(1) 1.964(4), Pt(1)–C(2) 1.972(4), C(1)–O(1) 1.170(5), C(2)–O(2) 1.168(5).

† Electronic supplementary information (ESI) available: detailed reaction procedures for $[Rh_8Pt_2(CO)_{21}(dppm)_2]$ (**1**) and $[Rh_6Pt_4(CO)_{16}(dppm)_3]$ (**2**). See http://www.rsc.org/suppdata/dt/b1/b108224h/

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pentanuclear Rh_4Cr[7] cluster. We believe that in **1** and **2** the Rh_6 octahedral unit is the acceptor in both cases thus achieving a stable 86 electron configuration by withdrawal of two electrons from the tetranuclear cluster neighbor. Among the hexanuclear octahedral rhodium clusters characterized at the present time there are no exceptions to the 86 electron count,[8] whereas tetranuclear clusters containing platinum ($Pt_{4-x}M_x$, $x = 0$–2) shows high flexibility in the number of electrons.[9,10] In the $Pt_{4-x}M_x$ type clusters the electron count ranges from 48[9a] and 50[9b] up to 58[9c,10c–m] to give either a tetrahedral or a butterfly framework. By this hypothesis, we believe that the Rh_6 unit in **1** and **2** accepts an electron pair donated by the tetrahedral counterparts of the corresponding complexes.

For the cluster **1** the idea of donor–acceptor bonding described above gives 86 electrons for the Rh_6 core and 56 electrons for the Rh_2Pt_2 unit, the latter falling well within the range of electron counts found earlier for this type of cluster unit. The structure of the "$Rh_6(CO)_{14}$" fragment in **1** is thus a typical example of a neutral $Rh_6(CO)_{16}$ derivative,[9] where the main structural motif consists of the metal octahedron surrounded by four symmetrically positioned triply bridging CO groups along with two terminal CO at each rhodium atom, excluding Rh(1) which takes part in the "intercluster" bonding. Nevertheless, even for this atom the contribution from two bridging COs and donation of two electrons from the Rh(7) center simulates the four electron donicity of two terminal carbonyls typical for all other metal atoms of the octahedron. The structural parameters found for this fragment also fall in the range typical for the regular arrangement of the octahedral Rh_6 clusters.[8]

According to spectroscopic data obtained the minor product of reaction (1) contains the Rh_2Pt_2 core surrounded by six CO and two dppm ligands. The ^{31}P NMR spectrum of this cluster displays two resonances one of which corresponds to rhodium bound (^1J(Rh–P) = 135 Hz) and another to platinum bound (^1J(Pt–P) = 3257 Hz) phosphorus. This spectroscopic pattern clearly points to a symmetrical disposition of the dppm ligands, which very likely bridge two adjacent Pt–Rh bonds of the tetranuclear framework. Single-crystal X-ray structure determination of this compound is now in progress. The butterfly arrangement of the Pt_2M_2 frameworks is typical for the 58 electron clusters.[10d–g,i,j] In all these examples, the wingtip positions of the framework are occupied by platinum atoms. A related butterfly framework with a Pt–M wingtip arrangement has also been found in Pt_3Ir[10n] and Pt_3Ru[10o] clusters, where all three Pt–Pt bonds are spanned by dppm ligands, which evidently makes it impossible to open a Pt–Pt bond to form the more usual butterfly core configuration. Without metal–metal bonding between the two cluster fragments in **1**, the Rh_2Pt_2 core would also be a 58 electron system. However, formation of the donor–acceptor bond, suggested above, changes the electron count for the Rh_2Pt_2 framework to 56 electrons, which is unusual for this type of compound. Thus, cluster **1** represents the first example of a 56 electron M_2Pt_2 cluster with an open M–Pt edge. The ^{31}P NMR spectrum of the cluster **1** displays three platinum multiplets centered at −22.8, −16.5 and −7.45 ppm, ^1J(Pt–P) = 2550, 3190 and 3350 Hz, respectively, and a doublet for the P(5) phosphorus atom bonded to Rh(8), −8.8 ppm, ^1J(Rh–P) = 160 Hz that is typical for the Rh–P coupling. This set of ^{31}P resonances is consistent with the soilid state structure being retained in solution.

Formation of cluster **2** is evidently the result of reaction between the coordinatively unsaturated species "$Rh_6(CO)_{15}$", which forms upon dissociation of acetonitrile from the starting cluster, and two molecules of the binuclear platinum complex. The resulting compound contains two cluster cores, which are connected by two bridging carbonyls and a donor–acceptor metal–metal bond in a similar manner to that described for **1**, where the Pt_4 unit donates two electrons to the Rh_6 core. The donor–acceptor approach gives 52 electrons for the Pt_4-framework that fall in the relatively wide range of electron counts found for Pt_4 clusters.[9] The shorter Rh(1)–Pt(1) bond length in **2** compared to the corresponding Rh(1)–Rh(7) in **1** indicates a stronger Rh–Pt interaction suggesting a higher electron donating ability for the electron rich Pt_4 cluster.

Four platinum atoms can form tetrahedral[9a,b] or butterfly[9c–f] frameworks. The tetrahedral clusters typically have 48 or 50 electrons, whereas the electron counts for the butterfly structures[9c–f] range from 54 to 58. Thus, the structure **2** can be seen as the first example of an "electron rich" Pt_4 cluster, which forms a closed tetrahedral framework. The solid state structure of **2** remains unchanged in solution. The ^{31}P spectrum of **2** displays one phosphorus resonance at −4.8 ppm with the satellite structure typical for a symmetrical "$Pt_3(dppm)_3$" moiety, see for example refs. 10*n*,*o* and references therein.

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4 Crystal data for $[Rh_8Pt_2(CO)_{21}(dppm)_2]\cdot\frac{1}{2}(CH_3OH)$ (**1**): $C_{71.5}H_{46}O_{21.5}P_4Pt_2Rh_8$, M = 2586.42 g mol^{-1}, monoclinic, a = 18.2642(3) Å, b = 13.22680(10) Å, c = 31.5765(5) Å, β = 97.135(5)°, V = 7569.08(18) Å^3, T = 120 K, space group $P2_1/n$ (no. 14), Z = 4, D_c = 2.270 g cm^{-3}, μ(Mo-Kα) = 5.534 mm^{-1}, 62103 reflections collected, 13344 unique (R_{int} = 0.0458). The final R_1 was 0.0244 [$I > 2\sigma(I)$] and $wR_2(F^2)$ = 0.0572 [$I > 2\sigma(I)$]. Crystal data for $[Rh_6Pt_4(CO)_{16}(dppm)_3]\cdot 1\frac{1}{2}(CH_2Cl_2)$ (**2**): $C_{92.5}H_{69}Cl_3O_{16}P_6Pt_4Rh_6$, M = 3126.47 g mol^{-1}, triclinic, a = 13.6211(2) Å, b = 16.1772(1) Å, c = 24.2056(3) Å, α = 109.1330(10)°, β = 93.0890(10)°, γ = 109.2140(10)°, V = 4679.53(9) Å^3, T = 120 K, space group $P\bar{1}$ (no. 2), Z = 2, D_c = 2.219 g cm^{-3}, μ(Mo-Kα) = 7.234 mm^{-1}, 62380 reflections collected, 16920 unique (R_{int} = 0.0337). The final R_1 was 0.0233 [$I > 2\sigma(I)$] and $wR_2(F^2)$ = 0.0528 [$I > 2\sigma(I)$]. Data were collected with a Nonius KappaCCD diffractometer at 120 K using Mo-Kα radiation (λ = 0.71073 Å). CCDC reference numbers 155132 and 155133. See http://www.rsc.org/suppdata/dt/b1/b108224h/ for crystallographic data in CIF or other electronic format.

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