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Ligand assisted dimerisation of a diplatinum(2+) system: a straightforward high yield access to tetranuclear platinum clusters

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The iodide induced dimerisation of a dppm-/diphenylphosphido-bridged Pt_2^{2+} system leads to a 56 CVE Pt_4 butterfly cluster which is diprotonated by HO_3SCF_3 to give a 60 CVE rectangular Pt_4 cluster.

An electron count of 56 or 54 for tetranuclear platinum clusters in tetrahedral geometry with a latitudinal or longitudinal ligand arrangement is predicted by theoretical studies based on $Pt(PH_3)_2$ fragments.[1] 54-electron CVE clusters are proposed to be stabilised by bridging dppm or phosphido ligands, which might be able to retain the less favourable longitudinal ligand arrangement. Taking into account that two additional electrons lead to a butterfly geometry of the Pt_4 core, we report here on a ligand controlled stabilisation of an unusual cluster electron count: a Pt_4 butterfly cluster with the hitherto unknown valence electron count of 56 is readily accessible *via* dimerisation of the diplatinum(2+) system in a suitable ligand sphere. The protonation of the cluster is associated with a novel structural rearrangement of the cluster core to a rectangular 60 CVE Pt_4 skeleton.

Treatment of $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)\{\eta^2\text{-bicyclo(2.2.1)hept-2-ene}\}_2](O_3SCF_3)$[2] **1**, (Scheme 1) with 1 mol equiv. of NBu_4I in toluene–dichloromethane (4/1) produces quantitatively the tetranuclear cluster $[Pt_4(\mu\text{-dppm})_2(\mu\text{-PPh}_2)_2I_2]$ **2** (Scheme 1, Fig. 1†) as dark red red crystals which are sparingly soluble in all common organic solvents. The reaction proceeds *via* the substitution of one bicyclo(2.2.1)hept-2-ene by iodide‡ which may in turn induce the dissociation of the remaining bicyclo-(2.2.1)hept-2-ene resulting in a reactive intermediate. The formation of **2** represents a ring opening dimerisation, the overall oxidation state of the platinum centres of +1 is maintained. We do not know whether the $Pt_2(\mu\text{-PPh}_2)$ or the $Pt_2(\mu\text{-dppm})$ ring is opened. The molecular structure of **2** exhibits a butterfly shaped Pt_4 skeleton. Complying with a crystallographically imposed C_2 symmetry, the two dppm and two diphenylphosphido ligands alternately bridge between the hinge and wingtip platinum atoms. One terminal iodide ligand is attached to each wingtip.

The wingtip to hinge Pt–Pt distances are 274.03(8) pm for the dppm-bridged and 287.40(8) pm for the diphenylphosphido-bridged platinum atoms. The distance between the two hinge Pt atoms of the butterfly framework amounts to 269.33(11) pm. The dihedral angle between the two wings [144.27(2)°] is substantially larger compared with other Pt_4 butterfly clusters (83.7–96.8°).[3] The Pt_2P_2C rings formed by the dppm ligands adopt twist conformations. The structure seems to be retained in solution according to ^{31}P NMR spectroscopy.§

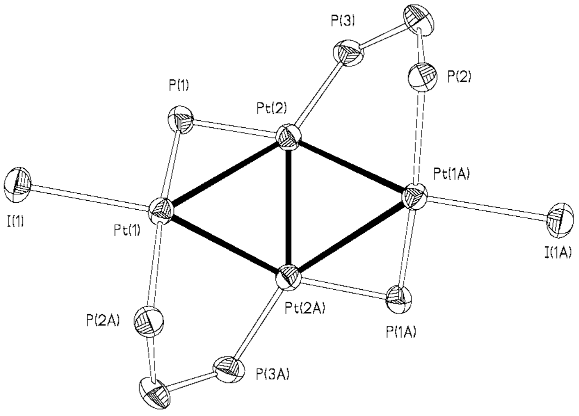
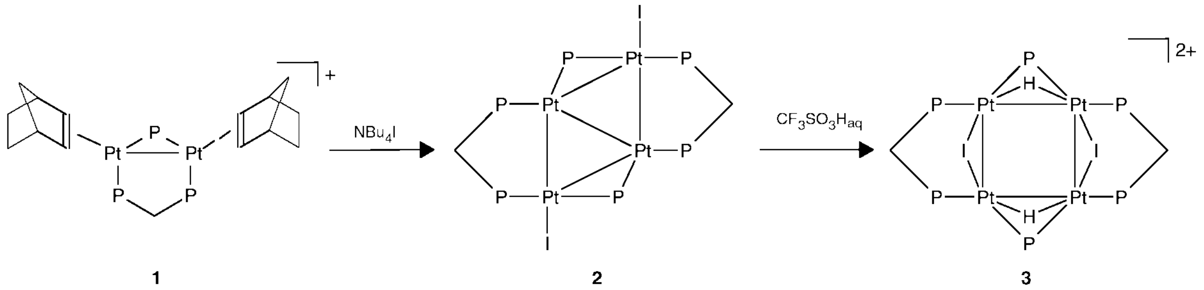


Fig. 1 Molecular structure of **2**. The phenyl groups have been omitted for clarity.

The protonation of **2** with 50% aqueous trifluoromethanesulfonic acid quantitatively produces the yellow tetranuclear dihydrido cluster $[Pt_4(\mu\text{-dppm})_2(\mu\text{-PPh}_2)_2(\mu_2\text{-H})_2(\mu_2\text{-I})_2](O_3SCF_3)_2$ **3** (Scheme 1, Fig. 2†) which is slightly soluble in CH_2Cl_2. The formation of **3** is accompanied by a rearrangement of the Pt_4 shape to a rectangle, a change of the geometry of the phosphido phosphorus relative to the dppm phosphorus atoms from *cis/trans* in **2** to *cis/cis* in **3** and a change to a bridging bonding mode of the iodide ligands. The phosphido bridged edges of the Pt_4 rectangle involve relatively short Pt–Pt distances [279.92(3) and 277.28(3) pm], whilst the distances of the dppm bridged platinum atoms [296.85(3) and 300.58(3) pm] indicate that the Pt–Pt interactions are weak. All sides are doubly bridged, either by dppm and iodide or by diphenylphosphido and hydride ligands making a 60-electron CVE. The hydride and iodide ligands are on the same side of the Pt_4 plane. The hydride ligands could be located *via* X-ray structure analysis and their position is confirmed by NMR spectroscopy:¶ the intensity of the hydride signal of the isotopomer containing one ^{195}Pt nucleus demonstrates a μ_2-H bonding. The P–H coupling constants involving the dppm and phosphido phospho-



Scheme 1

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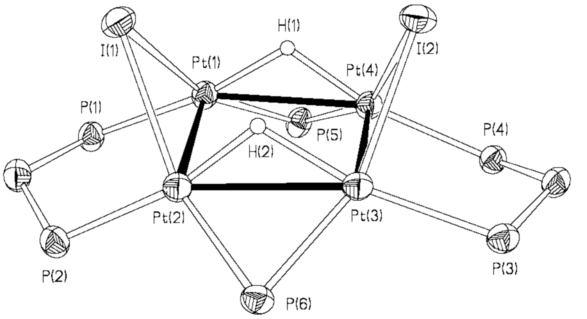

Fig. 2 Structure of the cation of **3**. The phenyl groups have been omitted for clarity.

rus atoms are 87.7 and 13.2 Hz respectively. This indicates the H–Pt–P_{dppm} angle to be distinctly larger compared with the H–Pt–$P_{phosphido}$ angle and this requires the hydride ligands to bridge the same edge as the phosphido ligands. The hydride ligands are kinetically stable on the NMR time scale at ambient temperature.

Dimerisation reactions related to the formation of **2** exist for the dipalladium(2+) system: the product of $[Pd_2(\mu\text{-dppm})_2Cl_2]$ and $NaBH_4$ was recently identified as $[Pd_4(\mu\text{-dppm})_4(\mu_4\text{-H})_2]^{2+}$ and the reaction with $[Cu(MeCN)_4]^+$ gave $[Pd_4(\mu\text{-dppm})_4(\mu_2\text{-Cl})_2]^{2+}$.[4,5] The X-ray structure of the latter product showed a rectangular Pd_4 skeleton [Pd–Pd 259.4(2) and 374.2(3) pm] consisting of two isolated Pd_2 moieties whereas no solid state structure of $[Pd_4(\mu\text{-dppm})_4(\mu_4\text{-H})_2]^{2+}$ is available. Analogous reactions of the platinum congener $[Pt_2(\mu\text{-dppm})_2Cl_2]$ leave the $[Pt_2(\mu\text{-dppm})_2]$ arrangement unchanged.[6] The different reactivities of the platinum and palladium $[M_2(\mu\text{-dppm})_2Cl_2]$ complexes have been attributed to different M–P bonding strengths. The reactivity of **1** in contrast to $[Pt_2(\mu\text{-dppm})_2Cl_2]$ is apparently due to the presence of both dppm and diphenylphosphido ligands.

Notes and references

† *Crystal data* for **2**: $C_{74}H_{64}I_2P_6Pt_4$, M = 2173.23, monoclinic, a = 1272.88(5), b = 2578.7(2), c = 2115.80(10) pm, β = 97.689(4)°, V = 6.8824(7) nm^3, T = 218(2) K, space group $C2/c$ (no. 15), Z = 4, Mo-Kα radiation (λ = 71.073 pm), 15160 reflections measured, 4166 reflections unique (R_{int} = 0.0597), reflections with $I > 2\sigma(I)$ 3670, $R1$ [$I > 2\sigma(I)$] = 0.0478, $wR2$ [$I > 2\sigma(I)$] = 0.1055, Goodness of fit 1.253. The structure was solved by direct methods (SHELXS-86),[7] and refined by full matrix least squares methods on F^2 (SHELXL-93).[8]

For **3**: $C_{76}H_{66}F_6I_2O_6P_6Pt_4S_2\cdot 2.5HO_3SCF_3\cdot 4H_2O\cdot 0.5CH_2Cl_2$, M = 2963.11, triclinic, a = 1452.98(2), b = 1850.66(2), c = 1873.47(3) pm, α = 104.854(1), β = 96.059(1), γ = 99.961(1)°, V = 4.73613(11) nm^3, T = 218 (2) K, space group $P\bar{1}$ (no. 2), Z = 2, Mo-Kα radiation (λ = 71.073 pm), 83252 reflections measured, 14013 reflections unique (R_{int} = 0.0661), reflections with $I > 2\sigma(I)$ 12327, $R1$ [$I > 2\sigma(I)$] = 0.0326, $wR2$ [$I > 2\sigma(I)$] = 0.0767, Goodness of fit 1.017. The structure was solved by direct methods (SHELXS-86),[7] and refined by full matrix least squares methods on F^2 (SHELXL-93).[8]

CCDC 182/1656. See http://www.rsc.org/suppdata/cc/b0/b003101l/ for crystallographic files in .cif format.

‡ *NMR data* for $[Pt_2(\mu\text{-dppm})(\mu\text{-PPh}_2)\{\eta^2\text{-bicyclo(2.2.1)hept-2-ene}\}I]$. ^{31}P NMR (CD_2Cl_2): δ 198.3 [P^1 (phosphido), $J(P^1P^2)$ 332.1, $J(P^1P^3)$ 181.3, $J(Pt^1P^1)$ 2422, $J(Pt^2P^1)$ 3152 Hz], 7.3 [P^2 (dppm, phosphorus *cis* to I), $J(P^2P^3)$ 62.8, $J(Pt^1P^2)$ 54, $J(Pt^2P^2)$ 3493 Hz], −2.7 [P^3 (dppm, phosphorus *cis* to bicyclo(2.2.1)hept-2-ene), $J(Pt^1P^3)$ 2896, $J(Pt^2P^3)$ 105.9 Hz]; ^{195}Pt NMR (CD_2Cl_2): δ −5807 [Pt^1 (Pt bound to bicyclo(2.2.1)hept-2-ene), $J(Pt^1Pt^2)$ 3137 Hz], −5240 [Pt^2 (Pt bound to I)].

§ *NMR data* for **2** (labelling of the atoms as in Fig. 1). ^{31}P NMR (CD_2Cl_2): δ 170.0 [P^1, $J(PtP^1)$ 2563, 2343, 238 Hz], 9.5 [P^3, $J(PtP^3)$ 3865, 813 Hz], −2.4 [P^2, $J(PtP^2)$ 2824 Hz].

¶ *NMR data* for **3** (labelling of the atoms as in Fig. 2). ^{31}P NMR (CD_2Cl_2): δ 142.2 [P^5, $J(Pt^1P^5)$ 3236, $J(Pt^2P^5)$ 54 Hz], 17.3 [P^1, $J(Pt^1P^1)$ 3974, $J(Pt^4P^1)$ 274 Hz]; ^1H NMR (CD_2Cl_2): δ −7.39 [$^2J(PH)$ 13.2 (PPh_2), 87.7 (dppm), $^1J(PtH)$ 403 Hz].

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