

## The Mechanism of Synthesis and the Unexpected Structure of the Cluster [Pt<sub>2</sub>Re<sub>2</sub>(μ-CO)<sub>2</sub>(CO)<sub>6</sub>(μ-dppm)<sub>2</sub>] (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)

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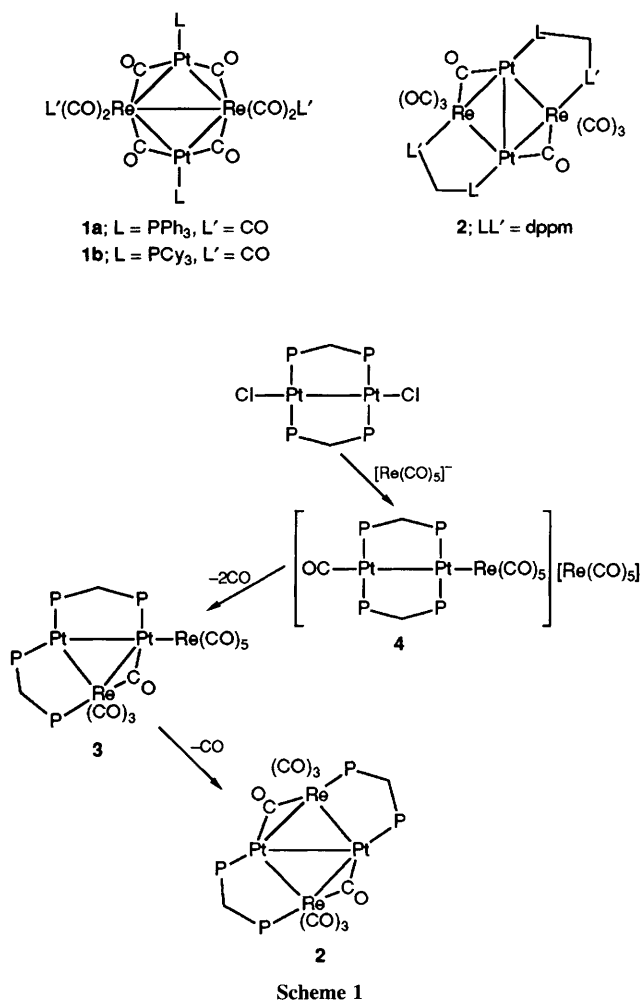
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The new cluster [Pt<sub>2</sub>Re<sub>2</sub>(μ-CO)<sub>2</sub>(CO)<sub>6</sub>(μ-dppm)<sub>2</sub>], **2**, dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, has a planar, diamond-shaped metal core and, for the first time in *triangulo*-Re<sub>2</sub>Pt<sub>n</sub> clusters, PtPt bonding is present while ReRe bonding is absent.

Heterogeneous catalysts containing platinum and rhenium are important in petroleum reforming,<sup>1</sup> and consequently there is interest in mixed-metal Pt-Re clusters which might mimic some of the properties of the bimetallic catalysts.<sup>2,3</sup> In the 58-electron clusters [Pt<sub>2</sub>Re<sub>2</sub>(μ-CO)<sub>4</sub>(CO)<sub>6</sub>(PR<sub>3</sub>)<sub>2</sub>], **1a**, R = Ph; **1b**, R = C<sub>6</sub>H<sub>11</sub>, the metal core is approximately

tetrahedral and PtPt bonding is weak or absent,<sup>2</sup> and so it is particularly interesting that in the new isoelectronic cluster [Pt<sub>2</sub>Re<sub>2</sub>(μ-CO)<sub>2</sub>(CO)<sub>6</sub>(μ-dppm)<sub>2</sub>], **2**, dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, the metal core is planar and, for the first time in *triangulo*-Re<sub>2</sub>Pt<sub>n</sub> clusters, ReRe bonding is absent.

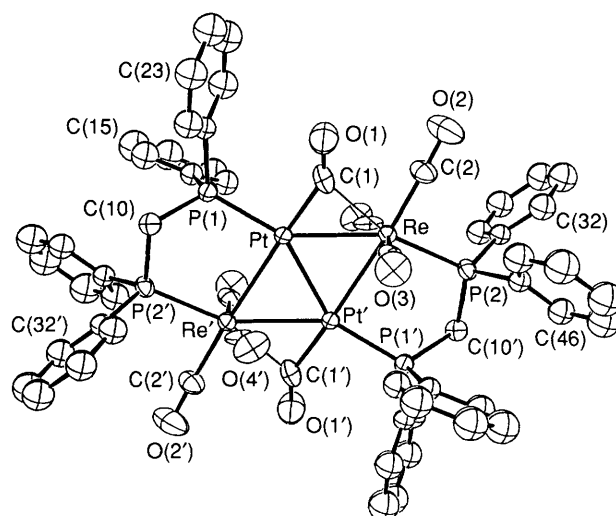
The cluster [Pt<sub>2</sub>Re<sub>2</sub>(μ-CO)<sub>2</sub>(CO)<sub>6</sub>(dppm)<sub>2</sub>], **2**, was pre-



pared by reaction of Na[Re(CO)<sub>5</sub>] with [Pt<sub>2</sub>Cl<sub>2</sub>(μ-dppm)<sub>2</sub>]<sup>4</sup> in tetrahydrofuran (thf) for several days.<sup>†</sup> Formation of **2** proceeds *via* several intermediates, of which the major ones are identified as **3** and **4**, Scheme 1, by monitoring the reaction mixture by <sup>31</sup>P NMR.<sup>†</sup> Braunstein and coworkers have shown that the reaction of [Pd<sub>2</sub>Cl<sub>2</sub>(μ-dppm)<sub>2</sub>] with Na[Mn(CO)<sub>5</sub>] gives the cluster [Pd<sub>2</sub>Mn<sub>2</sub>(CO)<sub>9</sub>(μ-dppm)<sub>2</sub>], which has a similar spiked triangle geometry as in **3**, but there appear to be no precedents for the further triangulation to give clusters analogous to **2**.<sup>5</sup> Clusters **2** and **3** are therefore formed by

<sup>†</sup> *Characterization data for 2*: IR (Nujol): ν(CO)/cm<sup>-1</sup> 1998s, 1935vs, 1904vs, 1821s; NMR ([<sup>2</sup>H<sub>6</sub>]acetone, 298 K): δ(<sup>1</sup>H) 4.78 (m, 4H, PCH<sub>2</sub>P); δ(<sup>13</sup>C) 216.1 (d, <sup>2</sup>J<sub>P,C</sub> 28, <sup>1</sup>J<sub>Pt,C</sub> 747 Hz, 2C, PtCRE), 208.3 (m, 4C, ReC axial), 204.8 (m, 2C, ReC equatorial); δ(<sup>31</sup>P) 44.2 (m, <sup>1</sup>J<sub>Pt,P</sub> 3317, <sup>2</sup>J<sub>Pt,P</sub> 310 Hz, PtP), 10.2 (m, ReP). *Crystal data for C<sub>58</sub>H<sub>44</sub>O<sub>8</sub>P<sub>4</sub>Pt<sub>2</sub>Re<sub>2</sub>·2C<sub>3</sub>H<sub>6</sub>O*: triclinic, space group *P* $\bar{1}$ ; *a* = 11.503(1), *b* = 14.069(3), *c* = 11.455(1) Å, α = 104.31(2), β = 119.10(9), γ = 91.53(2)°; *V* = 1545.8(5) Å<sup>3</sup>, *Z* = 1; Enraf Nonius CAD4 diffractometer with Mo-Kα radiation, λ = 0.71073 Å; *R* = 0.042, *R<sub>w</sub>* = 0.039 for 182 parameters varied and 5546 reflections with *I* > 2.5σ(*I*). Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

For **3**: NMR ([<sup>2</sup>H<sub>6</sub>]acetone, 298 K): δ(<sup>1</sup>H) 5.46 (m, 2H, CH<sub>2</sub>P<sub>2</sub>), 5.12 (m, 2H, CH<sub>2</sub>P<sub>2</sub>); δ(<sup>31</sup>P) 24.1 (m, <sup>1</sup>J<sub>Pt,P</sub> 2245, *J<sub>P,P</sub>* 22, 26, 53 Hz, PtP<sub>2</sub>), 18.0 (m, <sup>1</sup>J<sub>Pt,P</sub> 2773, *J<sub>P,P</sub>* 34, 53 Hz, PtP<sub>1</sub>), -11.0 (m, *J<sub>P,P</sub>* 22, 35, 35 Hz, ReP<sub>4</sub>), -23.2 (m, <sup>1</sup>J<sub>Pt,P</sub> 3195, <sup>2</sup>J<sub>Pt,P</sub> 302, *J<sub>P,P</sub>* 26, 35 Hz, PtP<sub>3</sub>). For **4**: IR (Nujol): ν(CO)/cm<sup>-1</sup> 2068m, 2004s, 1879vs; NMR ([<sup>2</sup>H<sub>6</sub>]acetone, 298 K): δ(<sup>1</sup>H) 4.60 (m, 4H, CH<sub>2</sub>P<sub>2</sub>); δ(<sup>13</sup>C) 167.6 (s, <sup>1</sup>J<sub>Pt,C</sub> 1106, <sup>2</sup>J<sub>Pt,C</sub> 417 Hz, PtC); δ(<sup>31</sup>P) -4.6 (m, <sup>1</sup>J<sub>Pt,P</sub> 2601, <sup>2</sup>J<sub>Pt,P</sub> 120 Hz, PtP), -6.2 (m, <sup>1</sup>J<sub>Pt,P</sub> 2714, <sup>2</sup>J<sub>Pt,P</sub> 84 Hz, PtP).



**Fig. 1** A view of the structure of cluster **2**. The Pt-Re distances are 2.7281(9) and 2.7994(9) Å for the CO and dppm bridged edges, respectively. The dppm ligands are twisted slightly out of the Pt<sub>2</sub>Re<sub>2</sub> plane such that the dihedral angle P(1)-Pt-Re'-P(2)' is 13.1(1)° and the μ-CO ligand is asymmetrically bonded [Pt-C 1.95(1), Re-C 2.34(1) Å, Pt-C-O 146(1), Re-C-O 135(1)°].

sequential loss of CO from **4** as shown in Scheme 1. Thus, **4** is stable under a CO atmosphere and it may be formed cleanly by reaction of [Pt<sub>2</sub>Cl(CO)(μ-dppm)<sub>2</sub>]<sup>+</sup> with [Re(CO)<sub>5</sub>]<sup>-</sup>.

The structure of **2**, determined by single crystal X-ray diffraction,<sup>†</sup> is shown in Fig. 1. The molecule has a crystallographically imposed centre of inversion and hence the metal core is strictly planar. This geometry is unusual in tetranuclear clusters containing platinum,<sup>2,3,5-7</sup> and is quite different from the tetrahedral structure of the related 58-electron clusters [Pt<sub>2</sub>Re<sub>2</sub>(μ-CO)<sub>4</sub>(CO)<sub>6</sub>(PR<sub>3</sub>)<sub>2</sub>], **1**.<sup>2</sup> It is especially significant that the ReRe distance in **1** [ReRe 3.094(1) in **1a**, 3.0560(9) Å in **1b**] is in the range expected for a single bond {*c.f.* 3.041(1) Å in [Re<sub>2</sub>(CO)<sub>10</sub>]} but that in **2** [ReRe 4.840(1) Å] is clearly non-bonding. Also, the PtPt distance in **2** [2.671(1) Å] is in the usual range for a single bond (2.6-2.8 Å)<sup>4</sup> but in **1** it is outside this range [2.982(1) in **1a**, 3.0417(8) Å in **1b**]. It has been argued convincingly that the relatively short non-bonding PtPt distance in **1** is due to geometric constraints and not to PtPt bonding<sup>2</sup> and, if this is accepted, the structures of both **1** and **2** conform with electron counting rules. Each has five metal-metal bonds, and a minor change in carbonyl ligand binding allows each metal centre to have its preferred electron count (16 for Pt, 18 for Re).

What are the precedents for this remarkable difference in structures of **1** and **2**? The clusters [Pt<sub>2</sub>Mo<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>6</sub>(PR<sub>3</sub>)<sub>2</sub>] can exist in both planar and tetrahedral forms, with steric effects of the ligands PR<sub>3</sub> determining the preferred structure,<sup>7</sup> and there are several examples of the dihedral angle of a butterfly structure being affected in a less dramatic way by the ligand spanning the wingtip positions of the butterfly.<sup>6</sup> The present case is different and it is clear that it is the presence of monodentate or bridging phosphine ligands that mainly influences the preferred structure. The metal core in structure **1** is probably the more stable but it is not compatible with the presence of a bridging ligand (LL' in **1** or **2**) and so structure **2** is adopted instead. The core in cluster **2** appears to be rigid since the NMR spectra in solution are fully consistent with the solid state structure.<sup>†</sup>

In the context of heterogeneous Pt-Re catalysts, the planar structure of **2** makes it an interesting model for a flat PtRe surface and the chemistry of **2** is under active investigation.

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