# Tetrahedral Platinum Carbonyl Clusters

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The first carbonylplatinum clusters established crystallographically to have tetrahedral $Pt_4$ cores are $[Pt_4H(CO)(\mu\text{-}CO)_3L_4]ReO_4$ **2** and $[Pt_4(\mu\text{-}CO)_2L_4(ReO_4)_2]$ **3**, L = $P(C_6H_{11})_3$, having 56 and 54 cluster valence electrons (CVE), respectively.

There are few tetrahedral platinum clusters; those characterized crystallographically include hydride derivatives $[Pt_4H_2L_4]^{2+}$ [48 CVE, L = $PBu^t_3$, Pt–Pt(av.) 2.68(5) Å], $[Pt_4H_2L_4]$ [50 CVE, L = $PBu^t$, Pt–Pt(av.) 2.74(3) Å] and $[Pt_4H_8L_4]$ [56 CVE, L = $PPr^i_2Ph$, Pt–Pt(av.) 2.94(5) Å], while $[Pt_4H_7L_4]^+$ [54 CVE, L = $PBu^t_3$, Pt–Pt(av.) 2.78(4) Å] has a butterfly structure.[1] For carbonylplatinum clusters, there are many with 58 CVE, including $[Pt_4(\mu\text{-}CO)_5L_4]$, L = phosphine, having butterfly structures,[2] and there is a recent report of an unstable tetranuclear cluster characterized only in solution as either $[Pt_4H(\mu\text{-}CO)_3L_4]^+$ (54 CVE) or $[Pt_4H(CO)(\mu\text{-}CO)_3L_4]^+$ [56 CVE, L = $P(C_6H_{11})_3$], the presence or absence of a terminal carbonyl ligand being uncertain. This cluster was formed on decomposition of $[Pt_3(\mu_3\text{-}H)(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}]^+$ in the presence of $HBF_4$; it was suspected to be tetrahedral based on its NMR properties but could not be isolated in pure form.[3] On theoretical grounds, it has been argued that stable tetrahedral clusters might include $[Pt_4L_8]$ (56 CVE) and $[Pt_4L_8]^{2+}$ (54 CVE).[4,5] Clearly, no empirical trend of structure *vs.* electron count is yet apparent. This article reports the first tetrahedral carbonylplatinum cluster complexes with 54 and 56 CVEs.

The reaction of $[Pt_3(\mu\text{-}CO)_3L_3]$ **1**, L = $P(C_6H_{11})_3$,[6] with $Re_2O_7$ in moist $CH_2Cl_2$ gave the complex $[Pt_4H(CO)(\mu\text{-}CO)_3L_4]ReO_4$, **2**, which could be isolated in high yield as a red–black crystalline solid. Its formation from **1** and $HReO_4$, presumed to be formed *in situ* by reaction of $Re_2O_7$ with adventitious water, can be described by eqn. (1).

$$4\,[Pt_3(\mu\text{-}CO)_3L_3] + 3\,HReO_4 \rightarrow 3\,[Pt_4H(CO)(\mu\text{-}CO)_3L_4]ReO_4 \qquad (1)$$

Further reaction of **2** with $HReO_4$ occurred more slowly to give a second platinum cluster complex $[Pt_4(\mu\text{-}CO)_2L_4(ReO_4)_2]$ **3**, according to eqn. (2).

$$[Pt_4H(CO)(\mu\text{-}CO)_3L_4]ReO_4 + HReO_4 \rightarrow [Pt_4(\mu\text{-}CO)_2L_4(ReO_4)_2] + 2CO + H_2 \qquad (2)$$

Both **2** and **3** were thermally stable and so could be fully characterized both in solution and in the solid state as described below. The structure of the $Pt_4$ cluster cation in **2** is shown in Fig. 1.† The platinum core is tetrahedral and can be considered to be based on a $[Pt_3(\mu\text{-}CO)_3L_3]$ unit capped by a $[PtH(CO)L]^+$ unit. The Pt–Pt distances within the $[Pt_3(\mu\text{-}CO)_3L_3]$ unit [2.689(1)–2.714(1) Å] are shorter than those to the capping Pt(4) atom [2.819(1)–2.878(1) Å]. A hydride ligand was identified in a difference Fourier map and it was successfully refined to give Pt(4)–H 1.7(2) Å. In this model, the Pt(4)H(CO)L unit has an angular structure with angles C–Pt–P 98.9(6), H–Pt–P 72(5) and H–Pt–C 131(5)° and the hydride is a terminal ligand. The simplest view of the bonding in the cation would be to consider the $[Pt_3(\mu\text{-}CO)_3L_3]$ unit to donate two electrons from its filled metal–metal bonding MO of $a_1$ symmetry to a vacant acceptor orbital of a T-shaped $[PtH(CO)L]^+$ unit as shown in **2a** (L = $PH_3$ in the EHMO calculations). In this model, the hydride is expected to be *trans* to the carbonyl ligand on $Pt^4$; according to the X-ray model the structure is distorted in the solid state since the angle H–Pt–C is 131(5) rather than 180°.‡

In the $^1H$ NMR spectrum of **2** in $CD_2Cl_2$ at room temperature, the hydride resonance appeared at δ −5.24, as a doublet with $^2J(P^4H)$ 10 Hz. Coupling to $^{195}Pt$ gave a 1:4:1 multiplet due to $^1J(Pt^4H)$ 480 Hz and an apparent 1:4:7:4:1 quintet due to $^2J(PtH)$ 137 Hz [an average of the couplings $^2J(Pt^1H,Pt^2H,Pt^3H)$]. Clearly, the Pt(4)H(CO)L unit is rotating rapidly with respect to the $Pt_3(\mu\text{-}CO)_3L_3$ triangle so that the cluster appears to have threefold symmetry. In agreement, the $^{31}P$ NMR spectrum contains only two resonances, a quartet at δ 71.3 due to $P^4$ [q, 1P, $^1J(PtP)$ 3425, $^2J(PtP)$ 230, $^3J(PP)$ 30 Hz, a further doublet splitting was seen in the $^1H$ coupled spectrum, $^2J(P^4H)$ 10 Hz], and a doublet at δ = 49.7 due to $P^1$, $P^2$, $P^3$ [d, 3P, $^1J(PtP)$ 5180, $^2J(PtP)$ 280, $^3J(PP)$ 140, $^3J(PP)$ 29 Hz]. Similarly, the $^{13}C$ NMR spectrum contained only two carbonyl resonances at δ 191.4 due to $C^4$ [m, 1 C, $^1J(PtC)$ 1250, $^2J(PtC)$ 45 Hz] and at δ 244.5 due to $C^1$, $C^2$, $C^3$ [m, 3C, $^1J(PtC)$ = 590, $^2J(PtC)$ 35 Hz, μ-CO]. The averaging of the $P^1$, $P^2$, $P^3$ and $C^1$, $C^2$, $C^3$ resonances is clearly due to fluxionality.§

The molecular structure of **3** (Fig. 2)¶ contains a slightly distorted tetrahedral $Pt_4$ cluster with two opposing edges, related by a crystallographic diad axis, bridged by carbonyl

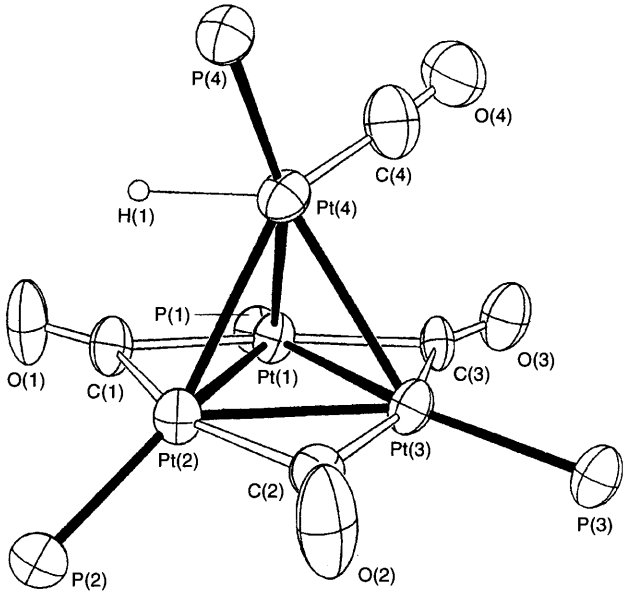
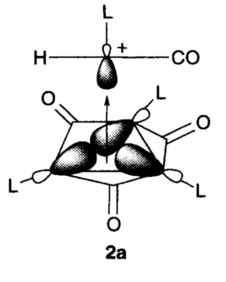
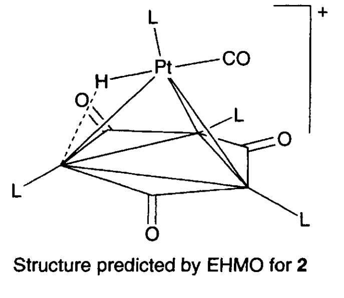


**Fig. 1** A view of the structure of the cation $[Pt_4H(CO)(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_4]^+$. Cyclohexyl groups are omitted for clarity. Selected distances (Å) are Pt(1)–Pt(2) 2.7131(9), Pt(1)–Pt(3) 2.6888(8), Pt(2)–Pt(3) 2.7144(9), Pt(1)–Pt(4) 2.8526(9), Pt(2)–Pt(4) 2.8193(10), Pt(3)–Pt(4) 2.8784(9).



**2a**



Structure predicted by EHMO for **2**

ligands. Each platinum atom is thus coordinated by one carbonyl C atom and also by a terminal $P(C_6H_{11})_3$ ligand. In addition, Pt(2) and Pt(2A) are each attached to one oxygen atom of a terminal $ReO_4^-$ anion [Pt(2)–O(2)–Re(1) 163.8(7)°]. The Pt–Pt distances [2.692(1)–2.871(1) Å] are indicative of single bonds,[8,9] and their wide variation may reflect the coordination of Pt(2) and Pt(2A) by an additional ligand. Although **3** is a 54-electron cluster, EHMO calculations suggest that the perrhenate ligands have little effect on the frontier orbitals and the bonding resembles that discussed for the 50-electron $[Au_4L_4]^{2+}$ and related compounds.[5a,10]

The crystal structure of **3** is remarkable (Fig. 3): 18 molecules of the cluster are present in a cell of volume 46 608 Å$^3$. The molecules aggregate through polar O···H–C interactions [O···H 2.42–2.50 Å] to form open channels lined with cyclohexyl groups. These channels are parallel to the *c*-axis and have a circular cross-section with a diameter of *ca.* 9 Å. Thus **3** can be considered a *tubuland*,[11] with vacant channels large enough to act as hosts for a variety of small molecules.

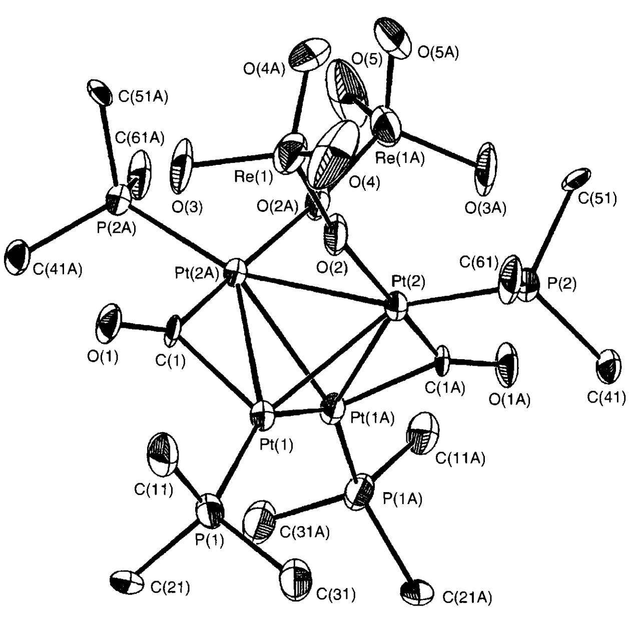


**Fig. 2** A view of the metal coordination in $[Pt_4L_4(\mu\text{-}CO)_2(ReO_4)_2]$, L = $P(C_6H_{11})_3$. Only the *ipso* carbon atom of each cyclohexyl ring is shown for clarity. The operation of the crystallographic diad axis is indicated by a terminal letter A in the atom name. 30% probability ellipsoids are displayed. Selected bond distances are as follows: Pt(1)–Pt(1A) 2.692(1), Pt(1)–Pt(2) 2.725(1), Pt(1)–Pt(2A) 2.796(1), Pt(2)–Pt(2A) 2.871(1), Pt(1)–C1 1.94(1), Pt(1)–P(1) 2.268(5), Pt(2)–C(1A) 1.91(2), Pt(2)–O(2) 2.153(9), Pt(2)–P(2) 2.328(4), Re(1)–O(2) 1.74(1), Re(1)–O(3) 1.72(1), Re(1)–O(4) 1.69(1), Re(1)–O(5) 1.70(1) Å.

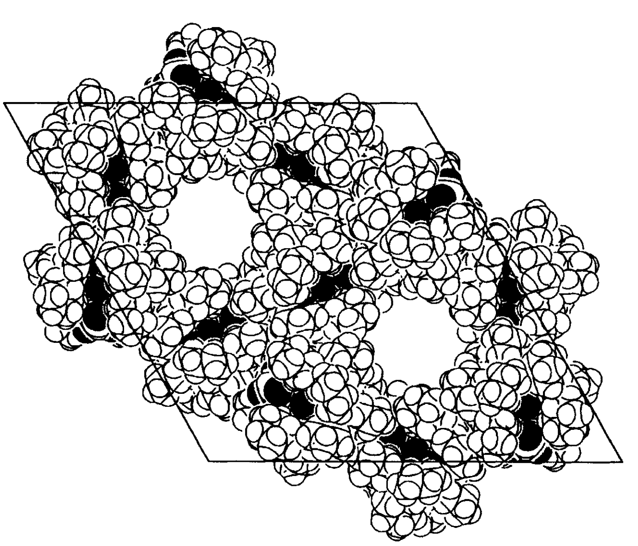


**Fig. 3** CPK space-filling model of the crystal structure of **3** viewed down the *c*-axis. Oxygen atoms are shown in black.

The clusters **2** and **3** appear to be the first examples of carbonyl clusters of platinum established to have 56 and 54 CVEs, respectively, and **3** appears to be the first tetrahedral $Pt_4$ cluster having a 54-electron count.[1–5] It is interesting that, although the ligation and electron counts in **2** and **3** are different, the $Pt_4$ core structures are the same and the average Pt–Pt distances [2.778 Å in **2**, 2.767 Å in **3**] are similar.

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## Footnotes

† *Crystal data* for **2**: $C_{76}H_{133}O_8P_4Pt_4Re$, *M* = 2265.26, triclinic, $P\bar{1}$, *a* = 14.245(2), *b* = 16.856(2), *c* = 17.558(2) Å, $\alpha$ = 90.135(7), $\beta$ = 91.945(9), $\gamma$ = 98.317(8)°, *U* = 4169(1) Å$^3$, *Z* = 2, $D_c$ = 1.805 g cm$^{-3}$, $R_1$ = 0.0595, $wR_2$ = 0.1396.

‡ Extended Huckel MO calculations indicate that the structrue with T-shaped $[Pt^4H(CO)L]^+$ unit, with hydride edge-bridging as in the line drawing **2a**, is preferred. We note that there is support for this structure from spectroscopic data in solution. For example, the magnitude of $^1J(Pt^4H)$ is in the normal range for a bridging hydride (low for a terminal hydride) and $^1J(Pt^4C)$ suggests a carbonyl *trans* to a bridging hydride; the small magnitude of $^2J$(PPtH) shows that the hydride is *cis* to the phosphine.[7] Comparison of the spectroscopic properties of **2** with the more limited data for the cluster proposed to be $[Pt_4H(\mu\text{-}CO)_3L_4]BF_4$ or $[Pt_4H(CO)(\mu\text{-}CO)_3L_4]BF_4$[3] indicates that the cations are the same and that the latter formulation is the correct one.

§ The fluxionality was partially frozen out in the NMR spectra in $CD_2Cl_2$ at −90 °C, but in the $^1$H NMR spectrum, *two* PtH resonances were observed at δ −4.9 [$^1J$(PtH) 480 Hz, isomer A] and −5.2 [$^1J$(PtH) 460 Hz, isomer B), indicating the presence of two isomers (or rotamers) in approximately a 2 : 1 ratio.

¶ *Crystal data* for **3**: $C_{74}H_{132}O_{10}P_4Pt_4Re_2$, *M* = 2458.44, trigonal, space group *R3c* (No. 167), hexagonal axes, *a* = 45.067(7), *c* = 26.498(2) Å, *U* = 46,608(11) Å$^3$, $D_c$ = 1.577 g cm$^{-3}$, *Z* = 18, $R_1$ = 0.047, $wR_2$ = 0.111.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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