Structural/bonding insights from new geometrical varieties of two Pt–Au carbonyl/phosphine clusters, $[Pt_3(AuPPh_3)_5(\mu_2\text{-}CO)_2L_3]^+$ ($L_3 = (CO)_2PPh_3$) and $[(\mu_6\text{-}Au)\{Pt_3(\mu_2\text{-}CO)_3L_4\}_2]^+$ ($L = PMe_3$)†

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Structural/bonding considerations of two new Pt–Au clusters, $[Pt_3(AuPPh_3)_5(\mu_2\text{-}CO)_2(CO)_2PPh_3]^+$ (1) and $[(\mu_6\text{-}Au)\{Pt_3(\mu_2\text{-}CO)_3(PMe_3)_4\}_2]^+$ (2) isolated (as chloride salts), revealed: (i) that the heretofore unknown 20-electron Pt-centered Pt_2Au_5 icosahedral cage fragment (five missing vertices) of 1 is best viewed as a 44-electron triangular Pt_3 adduct of a nearly planar 39-electron $[Pt_3(\mu_2\text{-}CO)_2L_3]^+$ ($L_3 = (CO)_2PPh_3$) and five one-electron donating $AuPPh_3$ ligands; and (ii) that the geometrically distorted trimethylphosphine "full" Pt_3AuPt_3 sandwich of 2 is the first example of two nucleophilic 44-electron triangular $Pt_3(\mu_2\text{-}CO)_3L_4$ (3 : 3 : 4) units ($L = PMe_3$) which asymmetrically encapsulate a central electrophilic Au(I).

The current interest in heterometallic Au–Pt nanoparticles (both naked and ligated) and in the potential applicability of heterometallic Au–Pt clusters or its precursors as catalysts has motivated our exploration to synthesize and characterize new types of Au–Pt carbonyl phosphine clusters. Our particular use of $[Ni_6(CO)_{12}]^{2-}$ as both a reducing agent and carbonyl source has given rise to a series of geometrically unprecedented Pt–Au clusters.[1]

Herein we report the syntheses[2] and structural characterizations of two new varieties of Au–Pt clusters, $[Pt_3(AuPPh_3)_5(\mu_2\text{-}CO)_2L_3]^+$ ($L_3 = (CO)_2PPh_3$) (**1**) and $[(\mu_6\text{-}Au)\{Pt_3(\mu_2\text{-}CO)_3L_4\}_2]^+$ ($L = PMe_3$) (**2**). Their geometries were unequivocally established‡[3] from low-temperature CCD X-ray crystallographic determinations of their Cl^- salts. Both clusters have unusual geometrical features with intriguing structural/bonding implications.

In connection with the preparation of **1**, previous synthetic investigations have produced Au-rich Pt–Au clusters consisting of a central platinum surrounded by $AuPR_3$ units ($L = PPh_3$,[4] PEt_3[5]). Such clusters typically form Pt-centered $[Pt(AuPR_3)_n]^{m+}$ fragments with relatively strong Pt–Au bond connectivities and weaker Au–Au bond connectivities among the closed-shell Au(I) centers (at distances of 2.8–3.0 Å in **1**) that have been attributed to aurophilic bonding;[6] extensive experimental/theoretical evidence[6,7] has assigned these attractive interactions to strong dispersion forces (also described as correlation effects) markedly enhanced by relativistic effects which are especially pronounced for gold. *Phosphine-stabilized* M-Au clusters of general formula $[M(AuPR_3)_n]^{m+}$ (M = Pt, Pd, Au)[4,5] have generated extensive chemistry because of their ability to react with a wide variety of substrates. The structural/reactivity properties of these M-centered gold clusters have been rationalized by use of an electron-counting formalism,[4,5,8] which classifies each cluster as having 16 or 18 cluster valence electrons (CVEs). Clusters having 18 CVEs (*i.e.*, $(s^\sigma)^2(p^\sigma)^6$ MO's + 10 d(M) electrons) possess spheroidal geometries (mainly M-centered icosahedral cage fragments) and those having 16 CVE's (*i.e.*, $(s^\sigma)^2(p^\sigma)^4$ MO's + 10 d(M) electrons) normally have flattened toroidal geometries.

The Pt_3Au_5 core-geometry of **1** may be viewed as a Pt-centered icosahedral Pt_2Au_5 cage fragment with five missing vertices (Fig. 1). This fragment consists of one centered Pt atom, Pt1, that is directly connected to each of the five tangential Au(cage) atoms and to the

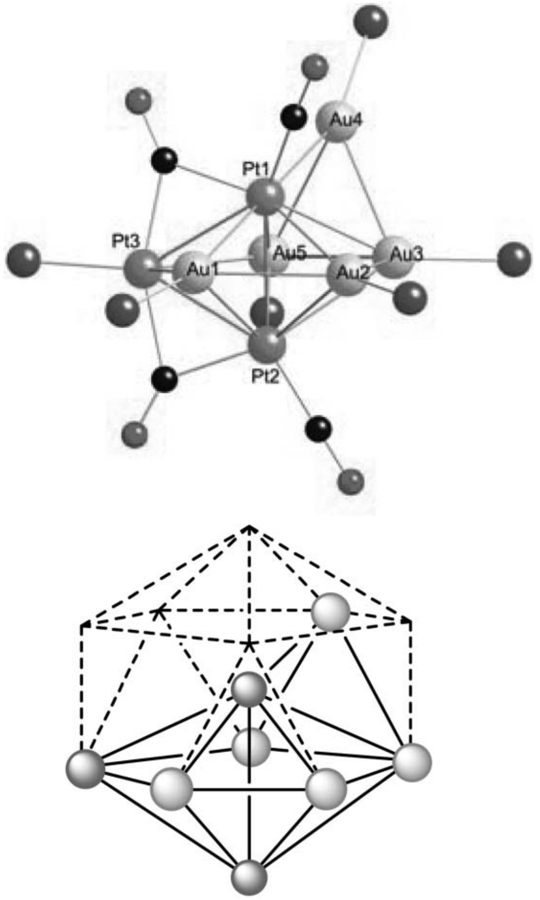

Fig. 1 Configuration (top view) of $[Pt_3(AuPPh_3)_5(\mu_2\text{-}CO)_2L_3]^+$ ($L_3 = (CO)_2PPh_3$) (**1**) with the P-attached phenyl rings omitted (for clarity). The bottom view depicts this cluster as a 20-electron Pt1-centered Pt_2Au_5 icosahedral cage with five missing vertices.

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† The HTML version of this article has been enhanced with colour images

other two Pt2, Pt3 atoms. But unlike the known Pt–Au icosahedral-based fragment geometries, the Pt_3Au_5 core of **1** has two Pt atoms occupying cage sites. The means of the seven radial Pt1–M(cage) and 12 tangential M(cage)–M(cage) distances are 2.74 and 2.87Å, respectively. However, the tangential Pt2–Pt3 bond connectivity of 2.726(1) Å is equivalent to (instead of being longer than) the two radial Pt1–Pt2, Pt1–Pt3 bond connectivities of 2.739(1), 2.697(1) Å, respectively. A CVE-counting scheme for **1** based upon its geometry being formulated as a Pt1-centered icosahedral Pt_2Au_5 cage fragment (Fig. 1) gives rise to 20 CVEs (namely, 10d[Pt1] + 0[Pt2(CO)] + 0[$Pt3(PPh_3)$] + 5 × 1[$AuPPh_3$] + 3 × 2[CO] − 1[+1 charge] = 20) instead of normally 18 CVEs for a gold-rich cluster with spheroidal geometry; an alternative consideration as a triangular Pt_3 cluster (Fig. 2) results in 44 CVEs (namely, 3 × 10[Pt] + 5 × 1[$AuPPh_3$] + 4 × 2[CO] + 1 × 2[PPh_3] − 1[+1 charge] = 44).

Hence, we greatly prefer to classify **1** as a carbonyl-stabilized triangular Pt_3 cluster (Fig. 2) that may be formally derived from well-known planar 42-electron triangular $Pt_3(\mu_2\text{-}CO)_3L_3$ clusters (L_3 = $(CO)_2PPh_3$) by the replacement of one two-electron CO-bridging ligand and one electron (to give a positive charge) with five one-electron donating $AuPPh_3$ ligands; the resulting mono-charged 44-electron Pt_3 cluster (**1**) is electronically equivalent to known $Pt_3(\mu_2\text{-}CO)_3L_4$ systems.[9] The formation of **1** is presumed to originate from the interactions of $AuPPh_3$ ligands with a preformed Pt_3 triangular moiety to give the 44-electron **1**, with its concomitant rearrangement to an icosahedral-based metal-core geometry to maximize the number of nearest neighbors for metal–metal attractive interactions.

The trimethylphosphine "full" Pt_3AuPt_3 sandwich, $[(\mu_6\text{-}Au)\{Pt_3(\mu_2\text{-}CO)_3(PMe_3)_4\}_2]^+$ sandwich (**2**), was isolated from an analogous room-temperature redox reaction in acetonitrile of $PtCl_2(COD)$ and $Au(SMe_2)Cl$ with $[Ni_6(CO)_{12}]^{2-}$ in the presence of PMe_3. Our choice of PMe_3 as a potential platinum-linked phosphine ligand was based upon its relatively smaller ligand cone-angle size[10] and greater basicity compared to that of PPh_3 and thereby was presumed to favor the formation and stabilization of large PMe_3-ligated Pt clusters. This premise is consistent with the unprecedented geometry of **2** (*vide infra*). The configuration of **2** (Fig. 3), consists of two nucleophilic 44-electron triangular $Pt_3(\mu_2\text{-}CO)_3L_4$ (3 : 3 : 4) units (L = PMe_3) that asymmetrically encapsulate an electrophilic $5d^{10}$ Au(I). Although the "open-face" sandwiches, $[(\mu_3\text{-}AuPCy_3)\{Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3\}]^+$ (**3**)[11a] with one 42-electron $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$ (3 : 3 : 3) unit and $[(\mu_3\text{-}AuPPh_3)\{Pt_3(\mu_2\text{-}CO)_3(PPh_3)_4\}]^+$ (**4**)[11b] with one 44-electron $[Pt_3(\mu_2\text{-}CO)_3(PPh_3)_4]$ (3 : 3 : 4) unit, have been prepared and crystallographically analyzed, the only previously reported example of a structurally determined "full" Pt_3AuPt_3 sandwich (with unconnected triangular Pt_3 units) is $[(\mu_6\text{-}Au)\{Pt_3(\mu_2\text{-}CO)_3(PPh_3)_3\}_2]^+$(**5**),[11c] which has two 42-electron $[Pt_3(\mu_2\text{-}CO)_3(PPh_3)_3]$ (3 : 3 : 3) units.

The architecture of **2** constitutes the first reported "full" Pt_3MPt_3 sandwich (M = Cu, Ag, Au) in which the central M(I) is encapsulated between two 44-electron $[Pt_3(\mu_2\text{-}CO)_3L_4]$ (3 : 3 : 4) units.[12,13] Fig. 3 reveals that its salient structural feature is the large *pseudo*-C_{2h} distortion of the Pt_3AuPt_3 core from that of *pseudo*-D_3 symmetry in **5**; the two centrosymmetrically staggered 44-electron $Pt_3(\mu_2\text{-}CO)_3(PMe_3)_4$ triangles are oriented such that the Au–Pt1 distance (2.754(1) Å) is 0.2 Å shorter than the Au–Pt2, Au–Pt3 distances (2.922(1); 2.938(1) Å). In **5** the three Au–Pt distances from Au(I) to each twofold-equivalent $[Pt_3(\mu_2\text{-}CO)_3(PPh_3)_3]$ (3 : 3 : 3) unit are virtually identical (mean, 2.728 Å). An analogous *pseudo*-C_{2h} asymmetry is found in the three independent Pt–Pt distances of **2** with one shorter (2.647(1) Å) and the other two

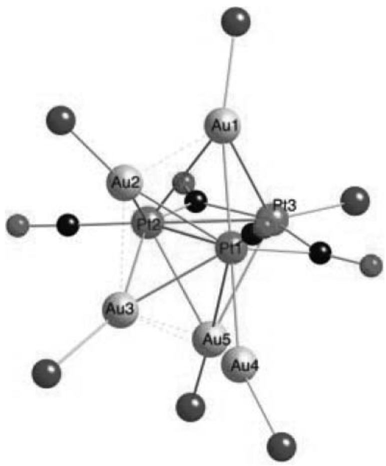

Fig. 2 Different orientation of $[Pt_3(AuPPh_3)_5(\mu_2\text{-}CO)_2L_3]^+$ (L_3 = $(CO)_2PPh_3)^+$ (**1**) which emphasizes that its geometry is best considered from a structural/bonding viewpoint as a 44-electron triangular Pt_3 system. Metal-core connectivities (Å) are: Pt1–Pt2, 2.739(1); Pt2–Pt3, 2.697(1); Pt2–Pt3, 2.726(1); Pt1–Au1, 2.795(1); Pt1–Au2, 2.776(1); Pt1–Au3, 2.748(1); Pt1–Au4, 2.648(1); Pt1–Au5, 2.783(1); Pt2–Au1, 2.872(1); Pt2–Au2, 2.855(1); Pt2–Au3, 2.924(1); Pt2–Au5, 2.852(1); Pt3–Au1, 2.851(1); Pt3–Au5, 3.007(1); Au1–Au2, 2.837(1); Au2–Au3, 2.784(1); Au3–Au4, 2.966(1); Au3–Au5, 2.883(1); Au4–Au5, 2.850(1).

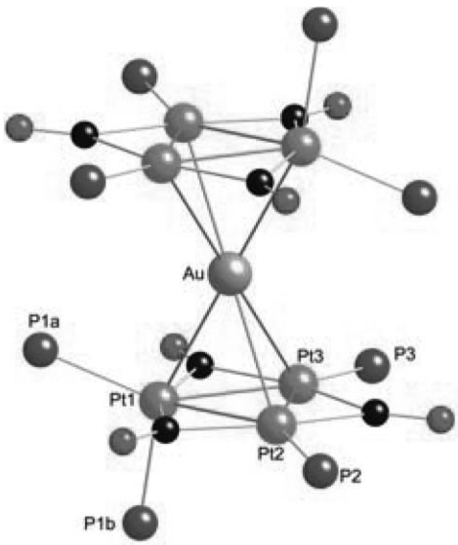

Fig. 3 Configuration of the "full" $[(\mu_6\text{-}Au)\{Pt_3(\mu_2\text{-}CO)_3(PMe_3)_4\}_2]^+$ sandwich (**2**) with the P-attached methyl substituents omitted (for clarity). Its highly deformed geometry (from the *pseudo*-D_3 symmetry of **5**) of crystallographic $C_i(-1)$ site symmetry ideally conforms to C_{2h} ($2/m$) symmetry. The much stronger Au(I) bonding to the highly nucleophilic $Pt(PMe_3)_2$ site in each Pt_3 triangle is evident from the 0.2 Å-shorter Au–Pt1 distance. The nearly linear Au–Pt1–P1b angle of 161° provides further support that the "full" Pt_3AuPt_3 sandwich **2** is stabilized primarily by the Au–Pt1 bonding interactions.

longer (2.665(1), 2.667(1) Å) compared to the three experimentally identical Pt–Pt distances (2.683(1) Å) of **5**. These bond-length variations in **2** emphasize the much stronger Au(I) bonding to the highly nucleophilic $Pt(PMe_3)_2$ and furthermore definitely suggest that the "full" Pt_3AuPt_3 sandwich of **2** is stabilized largely by linear Pt1–Au–Pt1′ bonding interactions.

An examination of the geometric differences between the corresponding "open-face" 56-electron $[(\mu_3\text{-}AuPPh_3)\{Pt_3(\mu_2\text{-}CO)_3L_4\}]^+$ (L = PPh_3) (**4**)[11b] and 54-electron $[(\mu_3\text{-}AuPCy_3)\{Pt_3(\mu_2\text{-}CO)_3L_3\}]^+$ (L = PCy_3) (**3**)[11a] shows that the $AuPt_3$ tetrahedron of **4** undergoes a similar large *pseudo*-C_{2v} distortion from that of **3**; the resulting metal-core parameters of **4** (Au–Pt, 2.700(1) Å *vs.* 2.902(2), 2.910(1) Å; Pt–Pt, 2.666(1) Å *vs.* 2.702(1), 2.708(1) Å) are remarkably close to those of **2**. A MO study by Mingos and Slee[14] of trinuclear platinum clusters including **4** provided reduced overlap populations in complete agreement with the experimental bond-lengths of **4** and theoretically accounted for the orientation of the electrophilic $[AuPPh_3]^+$ fragment with its s-p Au(I) LUMO pointing directly toward the higher coordinated PtL_2 site.

We conclude that the "existence" of the "full" Pt_3AuPt_3 sandwich with two $(Pt_3(\mu_2\text{-}CO)_3L_4)$ (3 : 3 : 4) units for **2** with L = PMe_3, but not for **5** with L = PPh_3, is a consequence of steric over-crowding that would result between two Au-centered $Pt_3(\mu_2\text{-}CO)_3L_4$ (3 : 3 : 4) units for L = PPh_3. In summary, the unprecedented formation and stabilization of the "full" PtAuPt sandwich of **2** with two 44-electron $Pt_3(\mu_2\text{-}CO)_3L_4$ (3 : 3 : 4) units (only with L = PMe_3) provides a further striking illustration of the crucial importance of steric requirements of the L ligands as well as electronic effects.

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Notes and references

‡ Crystal data for **1** and **2**: X-Ray data were collected at 100(2) K on a Bruker SMART CCD-1000 area-detector diffractometer with graphite-monochromated MoKα radiation from a sealed-tube generator. Least-squares refinements were carried out with SHELXTL.[3] $[Pt_3Au_5(PPh_3)_6(CO)_4]Cl.1.5(CH_3OH).0.5H_2O$: M_r = 3330.26, triclinic, P(−1), a = 13.898(2), b = 20.414(2), c = 20.878(2) Å, α = 89.765(2)°, β = 75.475(2)°, γ = 75.352(2)°, V = 5536.4(5) $Å^3$, Z = 2; $F(000)$ = 3114; ρ_{calcd} = 2.009 Mg m^{-3}. The crystallographically independent unit consists of one Pt_3Au_5 cluster (**1**), one Cl^-, and three half-weighted CH_3OH and one half-weighted H_2O solvated molecules. Full-matrix least-squares refinement (on F^2) of 15090 independent merged reflections [R(int) = 0.0357] converged at $wR_2(F^2)$ = 0.1247 for all data; $R_1(F)$ = 0.0489 for $I > 2\sigma(I)$; GOF (on F^2) = 0.993. $[Au\{Pt_3(CO)_3(PMe_3)_4\}_2]Cl.\ 2CH_2Cl_2$: M_r = 2349.44, triclinic, $P(-1)$, a = 11.444(1), b = 11.728(1), c = 13.142(1) Å, α = 68.521(2)°, β = 73.391(2)°, γ = 64.811(1)°, V = 1467.5(3) $Å^3$, Z = 1; $F(000)$ = 1068; ρ_{calcd} = 2.658 Mg m^{-3}. The centrosymmetric triclinic unit cell contains one $Au(Pt_3)_2$ cluster (**2**) located on an inversion center and two whole-weighted CH_2Cl_2 solvated molecules. Full-matrix least-squares refinement (on F^2) of 7088 independent merged reflections [R(int) = 0.0294] converged at $wR_2(F^2)$ = 0.0730 for all data; $R_1(F)$ = 0.0516 for $I > 2\sigma(I)$; GOF (on F^2) = 1.057. CCDC 605765 and 605766. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609380a

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2 Reactions were carried out by use of standard Schlenk techniques on a preparative vacuum line under a nitrogen atmosphere. *Preparation of **1***: To a stirred solution of $PtCl_2(COD)$ (0.071 g; 0.18 mmol), $AuPPh_3Cl$ (0.156 g; 0.31 mmol), and PPh_3 (0.091 g; 0.34 mmol) in 10 mL of DMSO was added $[NMe_4]_2[Ni_6(CO)_{12}]$ (0.34 g; 0.41 mmol) in 10 mL of DMSO. The resulting mixture was stirred under N_2 for 2–3 days. The solution was then crashed with water (at 0 °C) and filtered to isolate a dark brown residue. The residue was extracted with MeOH, and the solvent removed by evaporation. Single dark brown crystals of **1** (as the solvated Cl^- salt) were obtained by CH_2Cl_2–hexane layer diffusion (yield, ~10%). *Preparation of **2***: To a stirred solution of $PtCl_2(COD)$ (0.11 g; 0.29 mmol), $AuSMe_2Cl$ (0.079 g; 0.27 mmol) in 10 mL of MeCN was added PMe_3 (0.02 mL; 0.27 mmol). Separately dissolved $[NMe_4]_2$ $[Ni_6(CO)_{12}]$ (0.22 g; 0.265 mmol) in 10 mL of MeCN was added to the above mixture, and the resulting solution was stirred under N_2 for 5 h. The red solution was filtered to separate insoluble products, and the solvent was then removed by evaporation. Single red crystals of **2** (as the solvated Cl^- salt) were obtained by CH_2Cl_2–hexane layer diffusion (yield, ~15%).

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12 The other two coinage congeners (M = Cu, Ag) also form "full" Pt_3MPt_3 and "open-face" MPt_3 sandwiches analogous to those with M = Au. Those crystallographically determined are the triephenylphosphine "full" Pt_3CuPt_3 sandwich[11c] and triisopropylphosphine Pt_3AgPt_3 sandwich[13a] with two 42-electron $Pt_3(\mu_2\text{-}CO)_3L_3$ (3 : 3 : 3) units (L = PPh_3 and L = $P(^iPr_3)$, respectively) and triphenylphosphine "open-face" $(PPh_3)MPt_3$ sandwiches (M = Cu[13b], Ag[13c]) with one 44-electron $Pt_3(\mu_2\text{-}CO)_3L_4$ (3 : 3 : 4) unit (L = PPh_3). The MPt_3 cores in these latter two clusters possess highly distorted tetrahedral geometries similar to that of the $AuPt_3$ core in **4**.[11b].

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