Synthesis and *X*-Ray Crystal Structure of a Cuboctahedral Platinum Cluster‡

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Reaction of [Pt(C_2H_4)$_2$(PBu$^t_3$)] and [Pt(C_2H_4)$_3$] in hexane solution with hydrogen (300 atm) and a trace of carbon monoxide affords the cluster [Pt$_{15}$H$_x$(CO)$_8$(PBu$^t_3$)$_6$] (*x* unknown) in small yield. Crystals are triclinic, $P\bar{1}$, with cell parameters a = 13.953(10), b = 14.361(9), c = 16.361(13) Å, α = 121.03(6), β = 91.21(6), γ = 99.38(5)° (200 K), and Z = 1. The molecule has a centred cuboctahedral core of thirteen platinum atoms with two exopolyhedral Pt(μ-CO)$_2$(PBu$^t_3$) groups.

Platinum has provided several examples of unusual metal cluster geometries such as the stacked triangles of [{Pt$_3$(μ-CO)$_3$(CO)$_3$}$_n$]$^{2-}$ (n = 2—5)[1] and the fused, bicapped, pentagonal prisms[2] of [Pt$_{19}$(μ-CO)$_{10}$(CO)$_{12}$]$^{4-}$. Metallic platinum adopts a face-centred cubic (f.c.c.) structure,[3] and although the frequently encountered triangles and tetrahedra may be viewed as fragments of the bulk structure, only two large clusters, [Pt$_{38}$H$_2$(CO)$_{44}$]$^{2-}$ and [Pt$_{24}$(CO)$_{30}$]$^{2-}$, adopt the f.c.c. geometry.[4]

Results and Discussion

In preparing[5] [Pt$_3$H$_6$(PBu$^t_3$)$_3$] from [Pt(C_2H_4)$_2$(PBu$^t_3$)] and hydrogen (300 atm, 15 °C) we have frequently isolated small quantities of well formed black crystals (**1**) which are sparingly soluble in aromatic solvents. Both ^{1}H and ^{31}P n.m.r. spectra ([^{2}H$_6$]benzene or [^{2}H$_8$]toluene) showed signals which were broad and ill defined, and were not improved by varying the temperature (−70 to +50 °C). However the crystals proved amenable to study by *X*-ray diffraction, and solution by Patterson methods revealed the molecular structure shown in Figures 1 and 2.

The metal core is a cuboctahedron with an interstitial platinum atom sited at a crystallographic centre of symmetry. Two exopolyhedral platinum atoms symmetrically bridge diametrically related edges of the cuboctahedron. Internuclear distances (Table 1) along the surface of the cage vary from 2.70(1) to 2.90(1) Å [mean 2.81(4) Å] and the radial distances lie between 2.75(1) and 2.86(1) Å [mean 2.81(6) Å]. On average these are slightly longer than the 2.77 Å observed in the f.c.c. metallic state.[3]

Four of the cage atoms are radially bound to PBu$^t_3$ ligands [mean Pt(1)–Pt–P 179°]. A further four platinum atoms bear linear carbonyl ligands [mean Pt(1)–Pt–C 173, Pt–C–O 167°]. The remaining four cage atoms are attached in pairs to the two exopolyhedral Pt(μ-CO)$_2$(PBu$^t_3$) groups with carbonyl ligands bridging symmetrically between the cage and the external platinum atoms. Both the surface and radial Pt–Pt bond lengths suggest that the bonding radius of platinum attached to CO is slightly less than that of platinum attached to PBu$^t_3$. However the complexity of the structure and the uncertainty in the Pt–Pt distances require that such conclusions be treated cautiously.

The exopolyhedral Pt(μ-CO)$_2$(PBu$^t_3$) unit is reminiscent of

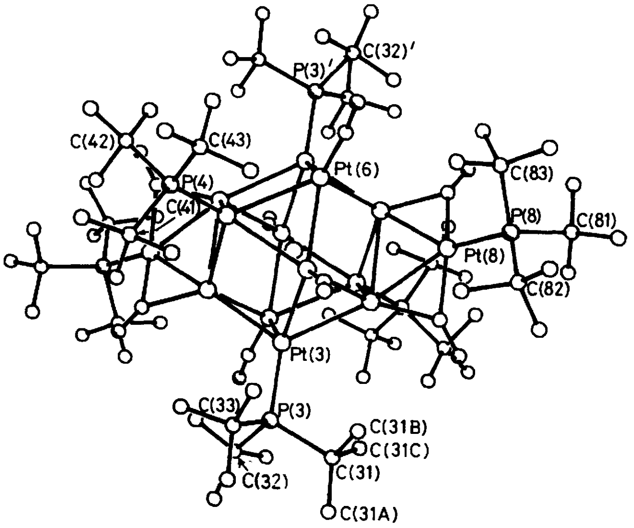

Figure 1. Molecular structure of [Pt$_{15}$H$_x$(CO)$_8$(PBu$^t_3$)$_6$] showing all non-hydrogen atoms and part of the numbering scheme

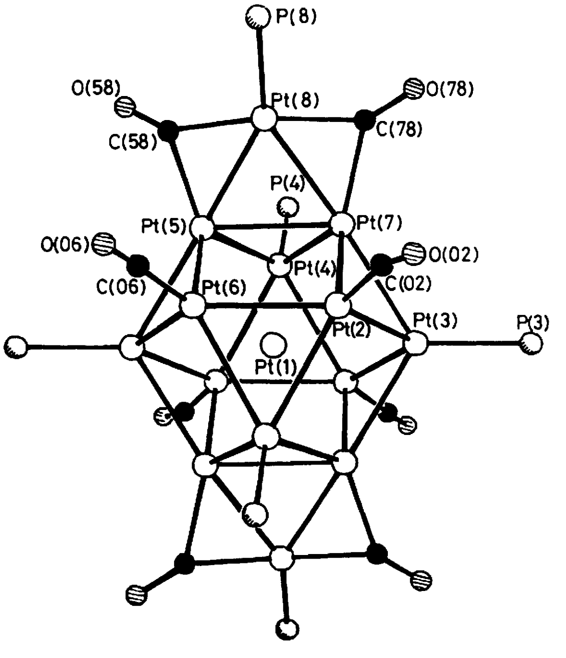

Figure 2. The core structure of [Pt$_{15}$H$_x$(CO)$_8$(PBu$^t_3$)$_6$] showing the core numbering scheme

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Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Important bond lengths (Å) and interbond angles (°) for $[Pt_{15}H_x(CO)_8(PBu^t_3)_6]$ with estimated standard deviations (e.s.d.s) in parentheses (primed and unprimed atoms related by the centre of inversion)

(*a*) Within the metal core

Pt(1)–Pt(2)	2.75(1)	Pt(4′)–Pt(1)–Pt(5)	61.9(3)	Pt(4)–Pt(6)–Pt(2)	60.3(3)
Pt(1)–Pt(3)	2.83(1)	Pt(5)–Pt(1)–Pt(6)	57.8(3)	Pt(3)–Pt(6′)–Pt(5′)	60.9(3)
Pt(1)–Pt(4)	2.86(1)	Pt(6)–Pt(1)–Pt(4)	60.3(3)	Pt(5)–Pt(8)–Pt(7)	62.6(3)
Pt(1)–Pt(5)	2.77(1)	Pt(3)–Pt(2)–Pt(4)	91.8(3)	Pt(7)–Pt(5)–Pt(8)	59.3(3)
Pt(1)–Pt(6)	2.82(1)	Pt(2)–Pt(3)–Pt(5′)	89.2(3)	Pt(5)–Pt(8)–Pt(7)	62.6(3)
Pt(1)–Pt(7)	2.80(1)	Pt(5′)–Pt(4)–Pt(2)	87.5(3)	Pt(5)–Pt(7)–Pt(8)	58.1(3)
Pt(2)–Pt(3)	2.85(1)	Pt(3)–Pt(5′)–Pt(4)	91.4(3)	Pt(3)–Pt(7)–Pt(8)	160.1(3)
Pt(2)–Pt(4)	2.82(1)	Pt(7)–Pt(2)–Pt(6)	91.5(3)	Pt(2)–Pt(7)–Pt(8)	98.2(3)
Pt(2)–Pt(6)	2.76(1)	Pt(2)–Pt(6)–Pt(5)	89.6(3)	Pt(6)–Pt(5)–Pt(8)	98.5(3)
Pt(2)–Pt(7)	2.72(1)	Pt(6)–Pt(5)–Pt(7)	90.7(3)	Pt(3)–Pt(5)–Pt(8)	159.2(3)
Pt(3)–Pt(7)	2.80(1)	Pt(5)–Pt(7)–Pt(2)	88.2(3)	Pt(8)–Pt(7)–Pt(4′)	104.6(3)
Pt(3)–Pt(5′)	2.79(1)	Pt(3)–Pt(7)–Pt(4′)	89.2(3)	Pt(8)–Pt(5)–Pt(4′)	104.7(3)
Pt(3)–Pt(6′)	2.79(1)	Pt(7)–Pt(4′)–Pt(6′)	89.2(3)	Pt(3)–Pt(5′)–Pt(6′)	61.2(3)
Pt(4)–Pt(6)	2.85(1)	Pt(4′)–Pt(6′)–Pt(3)	89.6(3)	Pt(5′)–Pt(3)–Pt(6′)	58.0(3)
Pt(4)–Pt(5′)	2.90(1)	Pt(6′)–Pt(3)–Pt(7)	91.9(3)	Pt(7)–Pt(5)–Pt(4′)	60.3(3)
Pt(4)–Pt(7′)	2.87(1)	Pt(7)–Pt(2)–Pt(3)	60.3(3)	Pt(7)–Pt(4′)–Pt(5)	58.4(3)
Pt(5)–Pt(6)	2.70(1)	Pt(2)–Pt(3)–Pt(7)	57.6(3)	Pt(4′)–Pt(7)–Pt(5)	61.4(3)
Pt(5)–Pt(7)	2.81(1)	Pt(3)–Pt(7)–Pt(2)	62.1(3)		
Pt(5)–Pt(8)	2.69(1)	Pt(6)–Pt(2)–Pt(4)	61.5(3)		
Pt(7)–Pt(8)	2.73(1)	Pt(6)–Pt(4)–Pt(2)	58.2(3)		

(*b*) Phosphine ligands

Pt(3)–P(3)	2.30(1)	Pt(1)–Pt(3)–P(3)	178.8(6)	Pt(2)–Pt(3)–P(3)	122.7(4)	Pt(6)–Pt(4)–P(4)	119.2(5)
Pt(4)–P(4)	2.29(1)	Pt(1)–Pt(4)–P(4)	178.3(5)	Pt(7)–Pt(3)–P(3)	121.5(6)	Pt(5′)–Pt(4)–P(4)	124.1(5)
Pt(8)–P(8)	2.31(2)	Pt(5)–Pt(8)–P(8)	145.5(6)	Pt(6′)–Pt(3)–P(3)	119.2(5)	Pt(2)–Pt(4)–P(4)	121.3(3)
		Pt(7)–Pt(8)–P(8)	146.7(6)	Pt(5′)–Pt(3)–P(3)	119.7(6)	Pt(7′)–Pt(4)–P(4)	122.4(4)

(*c*) Carbonyl ligands

Pt(2)–C(02)	2.00(9)	Pt(2)–C(01)–O(02)	166(10)	Pt(5)–C(58)	1.99(10)	Pt(5)–C(58)–O(58)	131(7)
C(02)–O(02)	1.09(14)	Pt(3)–Pt(2)–C(02)	121(4)	Pt(8)–C(58)	2.04(7)	Pt(8)–C(58)–O(58)	145(8)
		Pt(6)–Pt(2)–C(02)	116(4)	C(58)–O(58)	1.08(11)	Pt(5)–C(58)–Pt(8)	84(4)
		Pt(7)–Pt(2)–C(02)	111(5)				
		Pt(4)–Pt(2)–C(02)	125(5)	Pt(7)–C(78)	2.5(11)	Pt(7)–C(78)–O(78)	126(8)
Pt(6)–C(06)	1.70(7)	Pt(6)–C(06)–O(06)	165(5)	Pt(8)–C(78)	2.00(8)	Pt(8)–C(78)–O(78)	152(9)
C(06)–O(06)	1.22(8)	Pt(4)–Pt(6)–C(06)	126(3)	C(78)–O(78)	1.19(10)	Pt(7)–C(78)–Pt(8)	82(4)
		Pt(5)–Pt(6)–C(06)	113(3)			Pt(1)–Pt(6)–C(06)	174(3)
		Pt(2)–Pt(6)–C(06)	123(3)			Pt(1)–Pt(2)–C(02)	171(5)
		Pt(3′)–Pt(6)–C(06)	117(2)				

similar fragments in small platinum clusters, notably $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$.[6] The Pt–Pt distances to the *exo*-platinum (mean 2.71 Å) are 0.1 Å shorter than the average cage separation but slightly longer (0.05 Å) than in $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$. Both carbonyl ligands bridge the Pt–Pt bonds symmetrically.

Formulated as $[Pt_{15}(CO)_8(PBu^t_3)_6]$ the cluster appears to be electron deficient according to the expectations of current electronic theories. If the $Pt(\mu\text{-}CO)_2(PBu^t_3)$ fragment is regarded as contributing four electrons to the core, then there are 154 cluster valence electrons, far short of the 170 electrons predicted by Lauher,[7] and observed[8] for the anti-cuboctahedral anion $[Rh_{13}H_3(CO)_{24}]^{2-}$. It is well known however that certain platinum orbitals are frequently too high in energy to take part effectively in cluster bonding. Therefore a closer analogy may be with the icosahedral cation $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$,[9] which has 162 cluster valence electrons. A low electron count would also be predicted by Teo's application of the Hume–Rothery rule.[10] Thus it is tempting to suggest a stoicheiometry, $[Pt_{15}H_8(CO)_8(PBu^t_3)_6]$, which includes eight hydride ligands, possibly on the eight triangular faces or within the eight tetrahedral interstices of the cuboctahedron. However it should be stressed that there is no direct evidence for hydride ligands although it may be significant that we have succeeded in making the Pt_{15} cluster only under high pressure of hydrogen.

Table 2. Crystal data for $[Pt_{15}H_x(CO)_8(PBu^t_3)_6]$

M	4 364.4*	U/Å^3 at 200 K	2 750(4)
Space group	$P\bar{1}$	U/Å^3 at 293 K	2 818(5)
F(000)	1 975*	λ/Å	0.710 69
a/Å	13.953(10)	μ/cm^{-1}	193.2*
b/Å	14.361(9)	*T*/K	200
c/Å	16.361(13)	*Z*	1
α/°	121.03(6)	D_c/g cm^{-3} at 293 K	5.29*
β/°	91.21(6)	2θ range/°	2.9—50
γ/°	99.38(5)		

* Contribution from H_x not included.

Experimental

Nuclear magnetic resonance spectra were recorded on a JEOL FX 90Q Fourier-transform spectrometer. Infrared spectra were measured in Nujol mulls on a Perkin-Elmer 297 spectrophotometer. Starting materials and products were handled under dry oxygen-free nitrogen or argon using Schlenk-tube techniques. Solvents were dried and distilled under nitrogen prior to use. Hydrogen was BOC 'White Spot.'

Preparation of $[Pt_{15}H_x(CO)_8(PBu^t_3)_6]$.—Crystalline tris(ethylene)platinum (0.212 g, 0.76 mmol) was dissolved in hexane (8 cm^3) under ethylene, and tri-t-butylphosphine (0.137 g, 0.68

Table 3. Final atomic positional (fractional co-ordinates) parameters for $[Pt_{15}H_x(CO)_8(PBu^t_3)_6]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pt(1)*	0	0	0
Pt(2)	0.114 1(2)	0.178 2(2)	0.160 6(2)
Pt(3)	−0.089 9(2)	0.171 1(2)	0.134 6(2)
Pt(4)	0.139 2(1)	0.155 7(2)	−0.018 8(2)
Pt(5)	0.704 2(2)	−0.138 4(2)	0.047 0(2)
Pt(6)	0.202 3(2)	0.010 4(2)	0.031 2(2)
Pt(7)	−0.017 1(2)	0.032 7(2)	0.182 6(2)
Pt(8)	0.112 8(2)	−0.054 5(3)	0.236 3(2)
P(3)	−0.163 7(8)	0.310 9(6)	0.241 4(10)
P(4)	0.253 7(10)	0.280 1(5)	−0.032 4(4)
P(8)	0.227 6(8)	−0.025 7(10)	0.354 7(14)
C(31)	−0.185(3)	0.308(3)	0.361(2)
C(31A)	−0.237(3)	0.397(3)	0.435(2)
C(31B)	−0.082(3)	0.323(3)	0.407(2)
C(31C)	−0.244(3)	0.192(3)	0.329(2)
C(32)	−0.293(2)	0.303(3)	0.181(3)
C(32A)	−0.369(2)	0.208(3)	0.174(3)
C(32B)	−0.281(2)	0.280(3)	0.079(3)
C(32C)	−0.328(2)	0.413(3)	0.240(3)
C(33)	−0.078(2)	0.457(2)	0.283(3)
C(33A)	0.029(2)	0.462(2)	0.313(3)
C(33B)	−0.115(2)	0.555(2)	0.365(3)
C(33C)	−0.083(2)	0.466(2)	0.193(3)
C(41)	0.223(4)	0.423(2)	0.025(4)
C(41A)	0.285(4)	0.507(2)	0.006(4)
C(41B)	0.251(4)	0.455(2)	0.129(4)
C(41C)	0.113(4)	0.423(2)	0.009(4)
C(42)	0.274(5)	0.234(6)	−0.161(2)
C(42A)	0.363(5)	0.299(6)	−0.178(2)
C(42B)	0.179(5)	0.263(6)	−0.185(2)
C(42C)	0.269(5)	0.109(6)	−0.227(2)
C(43)	0.379(2)	0.301(5)	0.029(4)
C(43A)	0.457(2)	0.399(5)	0.044(4)
C(43B)	0.406(2)	0.191(5)	−0.048(4)
C(43C)	0.375(2)	0.303(5)	0.124(4)
C(81)	0.192(3)	−0.149(3)	0.379(4)
C(81A)	0.080(4)	−0.176(3)	0.378(4)
C(81B)	0.244(3)	−0.116(3)	0.477(4)
C(81C)	0.225(3)	−0.252(3)	0.299(4)
C(82)	0.236(3)	0.120(2)	0.477(2)
C(82A)	0.146(3)	0.110(2)	0.526(2)
C(82B)	0.226(3)	0.196(2)	0.438(2)
C(82C)	0.329(3)	0.170(2)	0.550(2)
C(83)	0.355(4)	−0.032(4)	0.300(4)
C(83A)	0.422(2)	−0.046(4)	0.367(4)
C(83B)	0.400(2)	0.074(4)	0.301(4)
C(83C)	0.344(2)	−0.133(4)	0.197(4)
C(06)	0.321(4)	0.008(5)	0.058(4)
O(06)	0.409(3)	0.026(4)	0.081(3)
C(02)	0.190(8)	0.284(9)	0.269(8)
O(02)	0.235(6)	0.362(7)	0.328(6)
C(58)	0.128(4)	−0.203(5)	0.116(5)
O(58)	0.143(4)	−0.283(4)	0.091(4)
C(78)	0.005(5)	0.025(6)	0.306(5)
O(78)	−0.030(3)	0.063(4)	0.378(3)

* Lies at a centre of inversion, 0,0,0.

mmol) was added dropwise, with stirring. The solution was transferred under ethylene to a glass tube (100 cm^3) which was then placed in a steel autoclave (150 cm^3). This was filled with carbon monoxide (*ca.* 5 mmol) and hydrogen (300 atm) for 20 h. Small black *crystals* of $[Pt_{15}H_x(CO)_8(PBu^t_3)_6]$ were removed from the walls of the tube (0.04 g) (Found: C, 20.9, H, 3.9; P, 4.0. $C_{80}H_{162}O_8P_6Pt_{15}$ requires C, 22.0; H, 3.7; P, 4.3%). The poor agreement between the experimental and calculated analysis figures for carbon is probably a consequence of the difficulty in obtaining a homogeneous sample from the reaction mixture. Recrystallization was not successful owing to the small quantities of material available and the limited stability of the compound in solution.

Red *crystals* of $[Pt_3(\mu\text{-}CO)_3(PBu^t_3)_3]$ (0.06 g) were also recovered from the walls of the tube, and identified[11] by ^{31}P n.m.r. spectroscopy and by elemental analysis of the toluene solvate isolated on recrystallization from toluene (Found: C, 40.2; H, 6.80. $C_{46}H_{89}O_3P_3Pt_3$ requires C, 40.3; H, 6.55%); $\nu_{max.}$(CO)(Nujol) 1 788s and 1 730vs cm^{-1}; δ_P (36.2 MHz, C_7D_8) 95.9 [^1J(PtP) 5 234, ^2J(PP) 380, ^3J(PP) 41 Hz].

The supernatant was investigated by ^{31}P n.m.r. spectroscopy and found to contain almost exclusively $[Pt_3H_6(PBu^t_3)_3]$.[5]

Crystal Structure Determination.—The black air sensitive prisms of (**1**) were sealed into Lindemann glass capillaries under argon and cooled to 200 K. Diffracted intensities were recorded on a Nicolet *P*3*m* four-circle automated diffractometer using the parameters in Table 2. Of the 5 658 data, 3 256 with $I > 3\sigma(I)$ were used to solve and refine the structure after corrections had been applied for Lorentz, polarization and absorption effects. The crystals showed noticeable decay in the *X*-ray beam at room temperature (*ca.* 50% in 24 h), but this reduced dramatically to a much slower and acceptable rate at lower temperatures, thus allowing the collection of a more extensive data set. Scattering factors were taken from ref. 12, and all computations were carried out using the SHELXTL system of programs,[13] implemented on a Data General S230 computer. All Pt and P atoms were refined with anisotropic thermal parameters, while the methyl carbon atoms of the Bu^t groups were constrained to refine with a regular geometry and their isotropic thermal parameters linked for chemically equivalent atoms. This was done because the chemically sensible arrangements of the Bu^t group atoms located from the difference electron-density syntheses, when refined freely, gave unreasonably high thermal parameters and unstable positional parameters for some of the methyl C atoms. If, however, these are constrained to be part of a rigid group (C–C 1.54 Å) their common thermal parameters are quite reasonable and no other model, such as a partial occupancy of two sites for the errant C atoms, gave a better fit to the data. Refinement of the model illustrated converged at $R(R')$ 0.080 (0.084) using a weighting scheme of the form $w = [\sigma^2(F) + 0.006|F|^2]^{-1}$. Selected bond lengths and interbond angles are given in Table 1, and the final positional parameters in Table 3.

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