Pt Dendrimer Synthesis

Assembling Metal Clusters with Covalent Linkers: Synthesis and Structure of a Quasi-Planar Pt_{18} Dendrimer Containing Five Clusters Connected by σ-Alkynyl Spacers**

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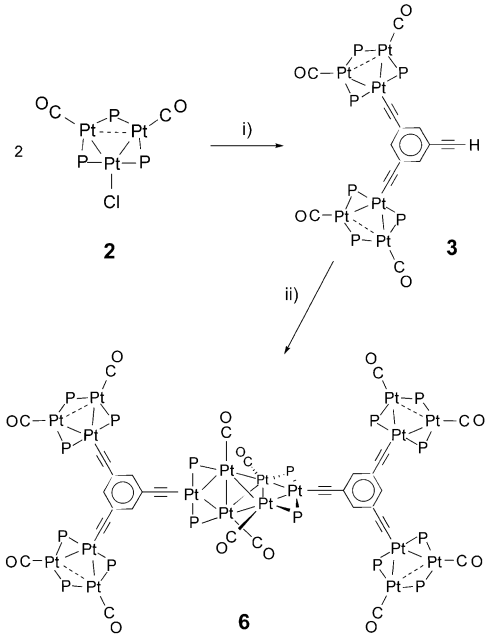
Transition-metal σ-alkynyl derivatives[1] are emerging as potentially useful precursors for advanced materials due to their promising magnetic,[2] liquid-crystalline,[3] nonlinear optical,[4] and luminescence[5] properties. Moreover, there is considerable and increasing interest for their application in the synthesis of metal-containing macrocyclic,[6] dendritic,[7] and rigid-rod molecular frameworks with delocalized π systems. These compounds include derivatives of various dimensions, actively investigated for their potential use in molecular electronics,[8,9] and contain isolated metal centers either located at the extremes[8–11] or regularly intercalated[8,12] into the main chain. Ordered structures with alternated metal clusters (or metal–metal-bonded bimetallic units[13]) and conjugated σ-alkynyl spacers[14–15] are extremely rare,[16] although of great potential interest.[10] This may be due to: 1) the tendency of metal clusters to undergo fragmentation or condensation, 2) their multiple and undistinguishable reactive positions, which facilitate the formation of complex mixtures of products, and 3) the preferred π interaction between the cluster and the alkynyl units[1,17] (the metal–alkynyl σ linkage usually results in increased electronic delocalization[9]).

In this paper we show that tri- and hexanuclear platinum clusters with sizable bridging phosphide groups are suitable precursors to ordered materials. Indeed, the bulky P*t*Bu_2 ligands in $[Pt_3(\mu\text{-}PtBu_2)_3(L)_2(X)]^{n+}$[18] and $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(X)_2]^{2n+}$[19] (X = neutral ligand, $n = 1$; X = monoanionic ligand, $n = 0$; L = neutral ligand) impart remarkable thermal and chemical stability to the $\{Pt_x(\mu\text{-}P)_y\}$ cores and leave a limited number of reactive sites properly positioned to build ordered structures. Moreover, they force alkynyl ligands to bind the polynuclear system with σ,η^1- rather than π,η^2-interactions.[20] Several structures with predefined molecular shape can therefore be engineered through the combination of these building blocks with well-chosen σ-alkynyl spacers, one of which is shown in Scheme 1. The trinuclear precursor



Scheme 1. Synthesis of complex **6**. i) 1,3,5-$C_6H_3(CCH)_3$, CuI, NEt_2H, 25 °C, 24 h (80%); ii) **3** (2 equiv), **5**, CuI, NEt_2H, 25 °C, 24 h (85%) (**5** = $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4Cl_2]$).

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$\{Pt_3\}Cl$ (**2**) [$\{Pt_3\} = Pt_3(\mu\text{-}PtBu_2)_3(CO)_2$] was easily prepared from [$\{Pt_3\}(CO)$]-(CF_3SO_3) (**1**)[18] and a chloride salt. Coupling two equivalents of **2** with 1,3,5-triethynylbenzene,[21] under the classical Sonogashira conditions,[22] gave C_6H_3-1,3-(CC-$\{Pt_3\}$)$_2$-5-(CCH) (**3**) as a green solid. This can be further modified either by substituting the carbonyl ligands or by exploiting the reactivity of the residual CCH unit, and may thus be considered an interesting pivot intermediate for the synthesis of dendrimeric structures.

Finally, by coupling (2:1 ratio) complex **3** with the dichloride $\{Pt_6\}Cl_2$ (**5**) [$\{Pt_6\} = Pt_6(\mu\text{-}PtBu_2)_4(CO)_4$], which can straightforwardly be prepared from the known [$\{Pt_6\}(CO)_2$](CF_3SO_3)$_2$ (**4**),[19] we obtained (in 85% yield) the title compound [($\{Pt_3\}$-CC)$_2$-C_6H_3-CC]$_4${Pt_6} (**6**), as an orange, microcrystalline solid that was thermally and air stable. All complexes were characterized by microanalytical, IR, and multinuclear NMR data.

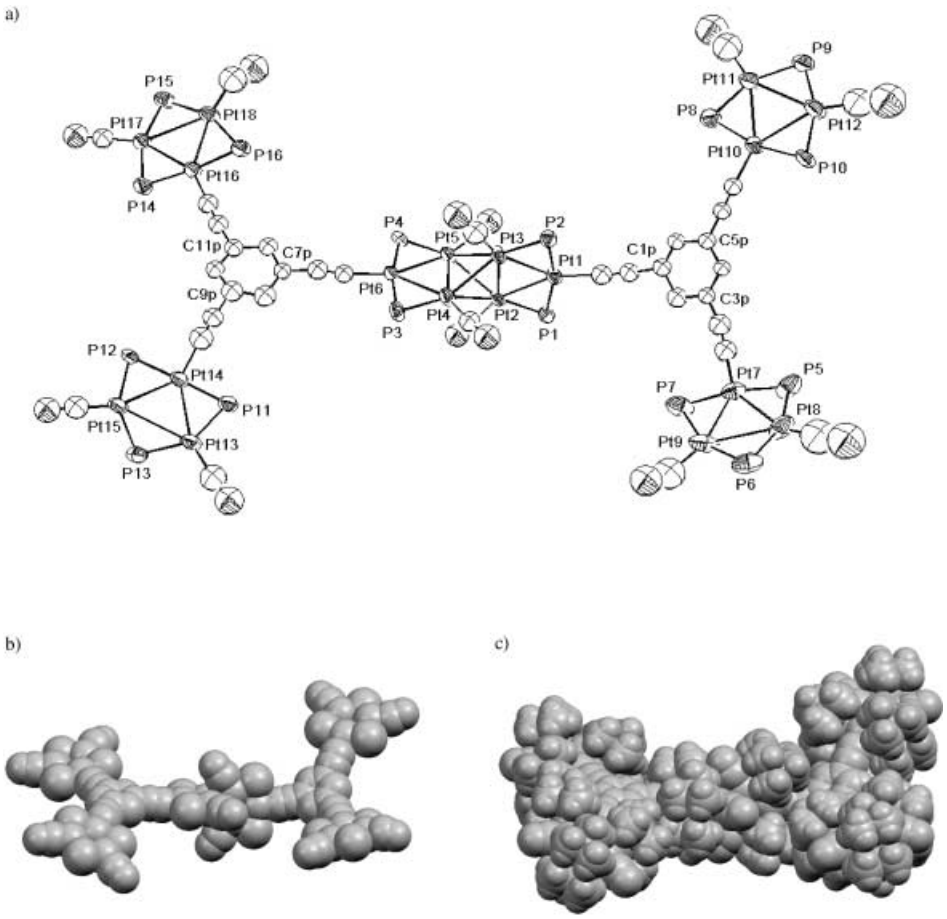

Figure 1. a) ORTEP view of **6** showing the atom numbering scheme; b,c) space-filling models of the molecular structure of **6** (*t*Bu groups omitted for clarity in a) and b)).

Diagnostic signals at $\approx$166 (4P) and 96 ppm (2P) and at ≈ -6100 (2Pt) and -5700 ppm (4Pt) were observed in the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of **3**, which suggested the presence of two equivalent triangular cluster units. This was confirmed by the ethynyl CH resonances, found at $\delta = 3.08$ (δ_H) and 75.7 ppm (δ_C), and by the features of the aromatic C–H region (signals in the 2:1 ratio at $\delta = 7.22$ and 7.38 ppm and at $\delta = 131.0$ and 134.3 ppm, respectively, observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra). Significant IR absorptions were found at 3300 ($\nu_{CC\text{-}H}$), 2094 (ν_{CC}) and 2024 cm^{-1} (ν_{CO}).

Similar spectral parameters were observed for complex **6**, whose spectra showed additional resonances due to the central hexanuclear cluster ($\delta_P = 335.1$ (4P); $\delta_{Pt} = -4664$ (2Pt), -2996 ppm (4Pt)), while the signals of the CCH unit disappeared. Single crystals of **6** suitable for X-ray crystallographic analysis were obtained by slow solvent evaporation from a $CHCl_3$ solution. Figure 1 shows space-filling and ORTEP views of **6**.[23]

The hexanuclear core of the structure may be described as being obtained by the condensation of two "Pt_3" units resulting in two edges of the triangles (i.e., Pt4–Pt5 and Pt2–Pt3) at bonding distances in the range of 2.62–2.87 Å. This gives rise to a central tetrahedral unit with two edge-bridging "PtP_2" moieties (the "Pt1Pt3" and "Pt4Pt6" triangles are mutually perpendicular, the dihedral angle defined by their mean planes being 89.8°). All the Pt–Pt separations are shorter relative to those found in other triangular clusters such as [$Pt_3(\mu\text{-}PtBu_2)_3(H)(CNR)_2$][18] (2.91–3.03 Å) or [$Pt_3(\mu\text{-}PtBu_2)_3(H)(CO)_2$][24] (2.72–3.61 Å); distances that fall in the lower end of the reported range.

The four chemically identical peripheral triangular units contain one long and two short Pt–Pt bonds[25] and lie approximately in the same mean planes defined by the alkynyl spacers (dihedral angles between planes in the range 16–18°) with the exception of the "Pt7-Pt9" cluster, for which the dihedral angle is $\approx$37°. Moreover, one of the alkynyl groups is roughly coplanar with the nearby triangular portion of the central Pt_6 core, while the other is more tilted (dihedral angles between the mean planes C7P–C12P/Pt4–Pt6 and C1P–C6P/Pt1–Pt3 are 13.6 and 51.3°, respectively). Given these distortions, possibly due to steric hindrance, compound **6** can be described as being only approximately planar. It is worth noting that the atoms in this dendrimer show quite large displacement parameters indicating the presence of positional disorder, consistent with the large amount of conformational freedom allowed by the long alkynyl spacers.

We are presently pursuing the utilization of compounds **1**–**6** in the synthesis of other ordered structures. The spectroscopic characterization of a linear analogue of complex **6** has also been recently described.[27]

Experimental Section

$[Pt(\mu\text{-}PtBu_2)(CO)]_3(CF_3SO_3)$ (**1**),[18] $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_6](CF_3SO_3)_2$ (**4**),[19] and 1,3,5-triethynylbenzene[21] were prepared as previously described.

2: nBu_4NCl (250 mg, 0.90 mmol) was added to a brown solution of **1** (825 mg, 0.66 mmol) in acetone (20 mL). After stirring for 12 h at room temperature, the mixture was concentrated to ≈5 mL. Addition of H_2O (5 mL) caused the precipitation of **2** as a microcrystalline brown solid (720 mg, 98%). Elemental analysis calcd (%) for $C_{26}H_{54}ClO_2P_3Pt_3$: C 28.1, H 4.89; found: C 28.0 H 4.93. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C) (in this spectrum and the following ones # denotes the presence of ^{195}Pt satellites): $\delta = 167.8^{\#}$ (d, $^2J_{PP} = 130$ Hz), $46.7^{\#}$ (t, $^2J_{PP} = 130$ Hz); ^1H NMR (200 MHz, C_6D_6, 25°C): $\delta = 1.47$ (vt, $^3J(H,P) + {}^5J(H,P) = 7.4$ Hz, 36H, CCH_3), 1.27 ppm (d, $^3J(H,P) = 15$ Hz, 18H, CCH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): $\delta = 172.6^{\#}$ (s, *C*O), $39.8^{\#}$ (m, *C*CH_3), $38.8^{\#}$ (m, *C*CH_3) 33.4 ppm (br s, C*C*H_3); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): $\delta = -6389.8$ (1Pt), −5320.0 ppm (2Pt). IR (CH_2Cl_2): 2025 cm^{-1} (CO).

5: NH_4Cl (9.6 mg, 0.18 mmol) was added to a red solution of complex **4** (120 mg, 0.054 mmol) in acetone (5 mL). Complex **5** precipitated out as a red solid and was filtered and vacuum dried (101 mg, 97%). Elemental analysis calcd (%) for $C_{36}H_{72}Cl_2O_4P_4Pt_6$: C 22.3, H 3.75; found: C 22.1, H 3.70. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): $\delta = 328.9^{\#}$ ppm (s); ^1H NMR (200 MHz, $CDCl_3$, 25°C): $\delta =$ 1.51 ppm (vt, $^3J(H,P) + {}^5J(H,P) = 7.2$ Hz); $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): $\delta = -4152.9$ (2Pt), −3462.7 ppm (4 Pt); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): $\delta = 203.7^{\#}$ (weak br s, 4CO), 44.8 (s, P*C*), 31.5 ppm (s, *C*H_3). IR (CH_2Cl_2): 2017 cm^{-1} (CO).

3: 1,3,5-triethynylbenzene (14.1 mg, 0.094 mmol) and CuI (0.38 mg, 0.002 mmol) were added to a solution of complex **2** (210 mg, 0.189 mmol) in diethylamine (25 mL). After 24 h the solvent was evaporated and the green/brown residue was extracted with Et_2O to give, after chromatography (silica gel, eluent: CH_2Cl_2/*n*-hexane 1:5), 172.6 mg of **3** (80%). Elemental analysis calcd (%) for $C_{64}H_{112}O_4P_6Pt_6$: C 33.4, H 4.90; found: C 33.3, H 4.86. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): $\delta = 165.7^{\#}$ (d, $^2J(PP) = 128$ Hz), 95.8# ppm (t, $^2J(PP) = 128$ Hz). ^1H NMR (200 MHz, CD_2Cl_2, 25°C): $\delta = 7.38$ (s, 1H), 7.22 (s, 2H), 3.08 (s, 1H, ≡C-*H*), 1.41 (vt, $^3J(H,P) + {}^5J(H,P) =$ 7.4 Hz, 36H), 1.32 ppm (d, $^3J(H,P) = 15.4$ Hz, 18H). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25°C): $\delta = 175.2^{\#}$ (s, CO), 134.3, 131.0, 129.3, 121.1 (s, C_6H_3), $86.4^{\#}$ (s, Pt-*C*C), 84.7 (s, *C*≡C-H), 75.7 (C≡*C*-H), 39.0, 38.7 (s, *C*-CH_3), 33.5 ppm (s, C-*C*H_3). $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): $\delta = -6104.1$ (dt, 2Pt), −5708.3 ppm (dd, 4Pt). IR (CH_2Cl_2): 3300 (≡C-H), 2094 (C≡C), 2024 cm^{-1} (CO).

6: Complex **3** (93 mg, 0.040 mmol) and CuI (0.08 mg, 0.4×10^{-3} mmol) were added to a solution of complex **5** (39.1 mg, 0.02 mmol) in diethylamine (20 mL). After 24 h the solvent was evaporated and the orange residue was extracted with Et_2O to give, after chromatograpy on silica gel (eluent: CH_2Cl_2/*n*-hexane 1:3), 110 mg of **6** (85%). Elemental analysis calcd (%) for $C_{164}H_{294}O_{12}P_{16}Pt_{18}$: C 30.5, H 4.58; found: C 30.6, H 4.65. $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$, 25°C): $\delta = 335.1^{\#}$ (s), $164.7^{\#}$ (d, $^2J(PP) = 128$ Hz), $96.7^{\#}$ ppm (t, $^2J(PP) = 128$ Hz). ^1H NMR (200 MHz, CD_2Cl_2, 25°C): $\delta = 7.23$ (s, 2H), 7.16 (s, 4H), 1.55 (vt, $^3J(H,P) + {}^5J(H,P) = 7.0$ Hz, 72H), 1.45 (vt, $^3J(H,P) + {}^5J(H,P) = 7.8$ Hz, 144H), 1.34 ppm (d, $^3J(H,P) = 14.8$ Hz, 72H). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 25°C): $\delta = 217.2^{\#}$ (s, 4*C*O), $175.7^{\#}$ (s, 8*C*O), 130.7, 129.3, 129.0 (s, C_6H_3), $123.4^{\#}$, $122.0^{\#}$ (s, Pt-*C*C), $99.5^{\#}$, $84.9^{\#}$ (s, Pt-*C*C), 44.3, 39.3, 39.1 (s, *C*-CH_3), 33.7, 31.8 ppm (s, C-*C*H_3). $^{195}Pt\{^1H\}$ NMR (42.8 MHz, $CDCl_3$, 25°C): $\delta = -6093$ (dt, 4Pt), −5712 (dd, 8Pt), −4664 (m, 2Pt), −2996 ppm (m, 4Pt). IR (CH_2Cl_2): 2098 (C≡C), 2019 cm^{-1} (br, CO).

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[23] Crystal data for **6**·($CHCl_3$): $C_{165}H_{295}Cl_3O_{12}P_{16}Pt_{18}$, triclinic, space group $P\bar{1}$ (no. 2), $a = 17.341(1)$, $b = 22.574(1)$, $c = 30.140(2)$ Å, $\alpha = 80.375(2)$, $\beta = 86.231(2)$, $\gamma = 79.132(2)°$, $V = 11\,416.7(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.915$ g cm^{-3}, μ ($Mo_{K\alpha}$) = 111.67 cm^{-1}, dimensions $0.08 \times 0.1 \times 0.25$ mm. 99 337 data were collected, at room temperature, on a Bruker APEX CCD diffractometer, of which 40 489 were unique ($R_{int} = 0.1805$). A multi-scan absorption correction was applied using the program SADABS (transmission factors in the range 1.0000–0.4122). Structure solution was by direct and Fourier methods and refinement by full-matrix least-squares on F^2 (SHELX-PC program) using anisotropic displacement parameters for the Pt and P atoms and the CO groups. Final agreement factors were $R_1 = 0.0844$, $R_{w2} = 0.2016$ for 14 218 observed reflections [$I \geq 2\sigma(I)$]; data/restraints/parameters 40489/0/1087; GOF = 0.908. A disordered molecule of solvent ($CHCl_3$) was found in the final Fourier-difference maps and its contribution was taken into account. CCDC-217686 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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