Large Dendrimeric Organoplatinum Complexes

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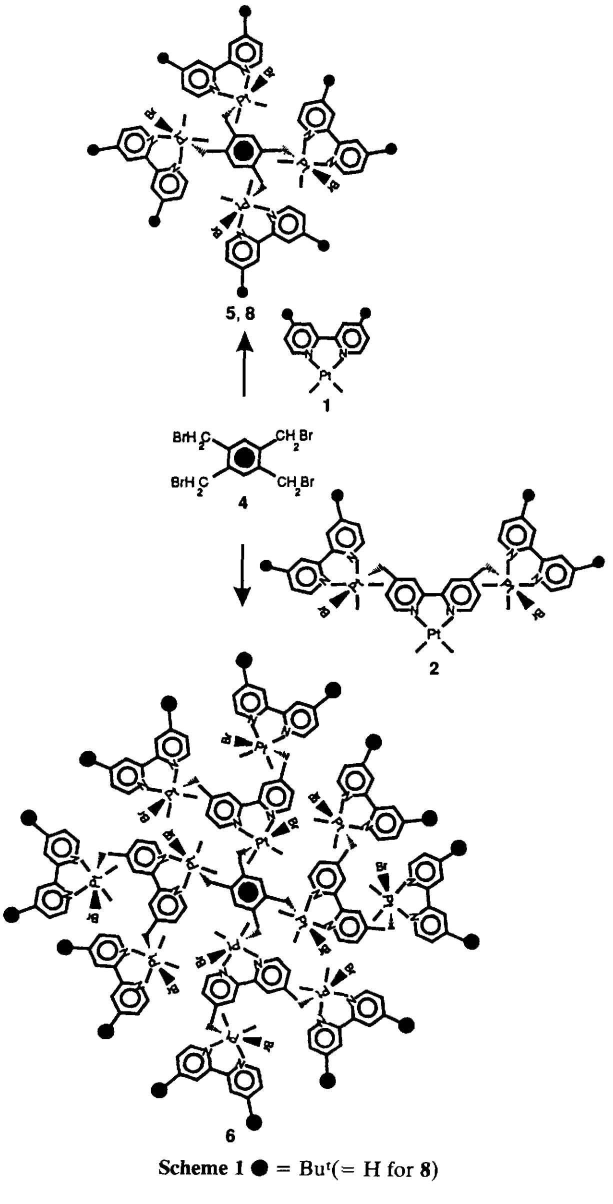
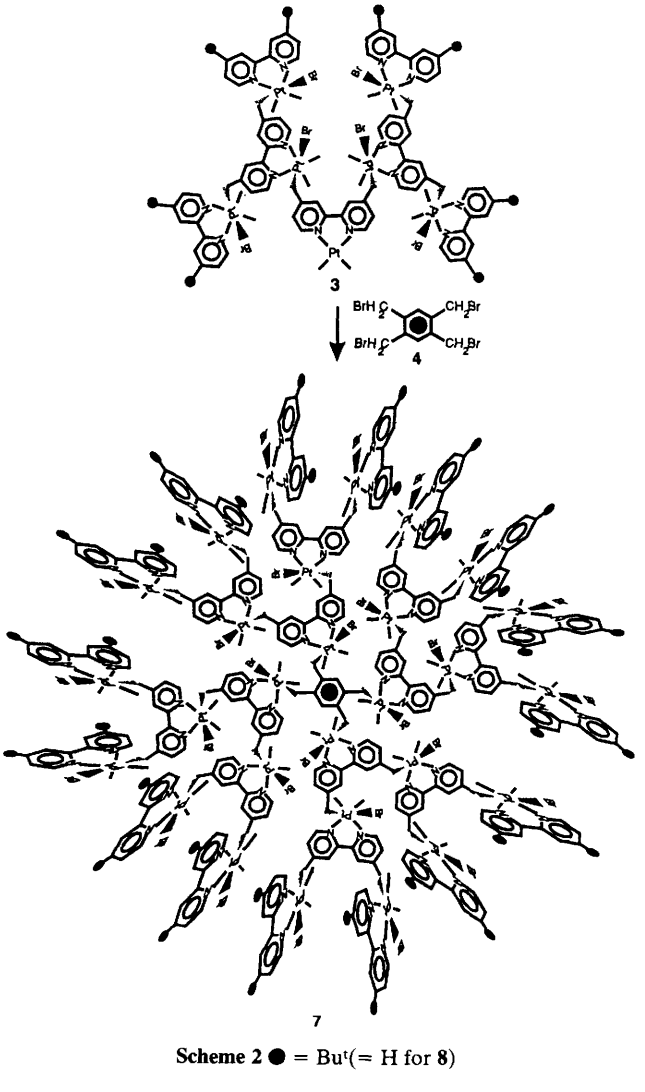
New dendrimeric organoplatinum complexes have been prepared by oxidative addition of precursors containing a dimethylplatinum(II) centre to 1,2,4,5-tetrakis(bromomethyl)benzene; the products include a Pt_{28} complex which is believed to be the largest reported transition-metal dendrimer.

There have been many recent advances in the synthesis of highly branched molecules known as dendrimers.[1–7] Most known dendrimers are organic in nature, but organosilicon dendrimers containing up to 485 silicon atoms have also been prepared.[4] Dendrimers are prepared by stepwise growth, which may be divergent[1] (growth from the centre outwards) or convergent[2,3] (growth from the outside to the centre), but which can only be successful if very high yields are obtained in individual growth steps. Recently, the first inorganic and organometallic dendrimers of the transition elements have been synthesized in which the metal may be at the centre only, the periphery only or in each generational layer of the dendrimer.[2–6] A convergent synthesis of organoplatinum dendrimers, based on use of the trifunctional reagent 4,4′-bis(bromomethyl)-2,2′-bipyridine, whose bromomethyl groups were used to oxidatively add to two square planar dimethylplatinum(II) centres {initially $[PtMe_2(4,4'Bu^t_2\text{-bipy})]$ $4,4'\text{-}Bu^t_2$-bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine} and whose diimine group was then used to complex to a new dimethylplatinum(II) centre, has been reported.[7] Repetititon of this cycle gave the Pt_{14} dendrimer but further growth did not occur due to steric hindrance at the reaction centre. The Pt_1, Pt_3 and Pt_7 complexes **1–3** (Schemes 1 and 2) were prepared in this way and were shown to be reactive to further oxidative addition.[7] This paper reports that each of the complexes **1**, **2** and **3** react in a 4:1 molar ratio with 1,2,4,5-tetrakis(bromomethyl)benzene, **4**, to give new complexes **5**, **6** and **7** containing 4, 12 and 28 platinum(IV) centres respectively (Schemes 1 and 2). The Pt_{28} complex, containing a total of 1292 atoms, appears to be the largest transition-metal dendrimer yet known.[6]

The new reactions shown in Schemes 1 and 2 were carried out using acetone solutions at room temp. The precursor complexes **1–3** are red or orange, due to the presence of a



Scheme 1 ● = Bu^t(= H for **8**)



Scheme 2 ● = Bu^t(= H for **8**)

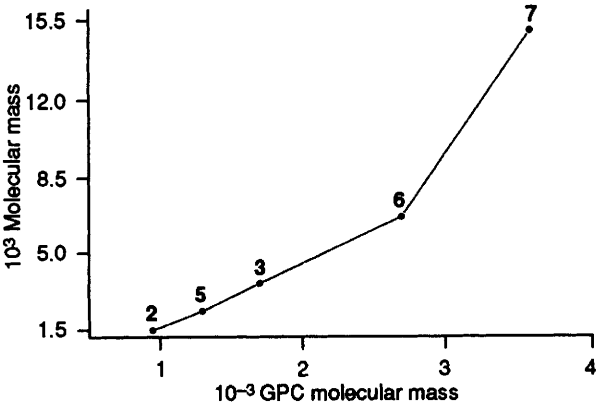


Fig. 1 Correlation of apparent molecular mass determined by GPC with the calculated molecular mass of the dendrimers

Pt(5d)–diimine(π*) MLCT band in the visible region,[8] while the products **5**–**7** are pale yellow. Thus, the reactions could be monitored by the quantitative decay of the MLCT band in the UV–VIS spectrum. Alternatively, the quantitative disappearance of the CH_2Br resonance due to **4** allowed monitoring by NMR. Complexes **5**–**7** are soluble in acetone or dichloromethane, but the similar adduct, **8**, of [$PtMe_2$(2,2′-bipy)] is insoluble. Clearly the *tert*-butyl substituents and branched structures contribute to the greater solubilities compared to **8**. The melting points and temperatures requires to decompose completely to leave a platinum residue, as determined by differential scanning calorimetry and thermal gravimetric analysis, increased with molecular size. Characterization of **5** by NMR was straightforward.[†] There were two methylplatinum resonances at δ 0.65 [^2J(PtH) = 68 Hz] and 0.88 [^2J(PtH) = 68 Hz], while the CH_2Pt resonance occurred as an AB multiplet, part at δ 2.15 [^2J(PtH) = 91 Hz, ^2J(HH) *ca.* 8 Hz] and part obscured by the intense *tert*-butyl resonance at δ 1.5. Non-equivalence of the Me_2Pt and CH_2Pt protons is expected since there can be no plane of symmetry containing the $BrPtCH_2$ axis, and the magnitudes of the coupling constants ^2J(PtH) are characteristic for platinum(IV).[8–11] The NMR spectra of **6** and **7** are broader and individual resonances are not resolved,[‡] so that an alternative method of determining homogeneity and molecular weight was needed. So far, mass spectrometry (FAB or EI) of the larger dendrimers has failed to yield parent ions, but the molecular sizes can be monitored in a qualitative way by gel permeation chromatography (GPC). The apparent molecular masses by GPC (referenced to linear polystyrene standards) were 950, 1300, 1700, 2700 and 3600 for **2**, **5**, **3**, **6** and **7** respectively, giving a reasonable correlation with the calculated molecular masses (Fig. 1). In summary, it is clear that the methodology described above has succeeded in the synthesis of the largest known transition-metal dendrimers containing up to 28 platinum atoms. These are new types of dendrimers in which transition metals are contained in every layer of the dendrimer except in the core.[2,3]

We thank NSERC (Canada) and 3M (Canada) for financial support.

Received, 16th May 1994; Com. 4/02899F

Footnotes

[†] Pt_4 complexes; **5**: ^{1}H NMR in CD_2Cl_2; 0.65 [s, 12H, *J*(PtH) = 68 Hz, MePt], 0.88 [s, 12H, *J*(PtH) = 68 Hz, MePt], 1.45 (s, 72H, Bu^t), 2.1 [m, 4H, *J*(PtH) = 91 Hz, CH_2Pt], see text, 7.52 [d, 8H, $H^{5,5'}$, 4,4′Bu^t_2-bipy], 8.20 [s, 8H, $H^{3,3'}$, 4,4′Bu^t_2-bipy], 8.26 [d, 8H, $H^{6,6'}$, 4,4′Bu^t_2-bipy]. **8**: (Found: C, 35.0; H, 3.0; N, 6.0. Calc. for $C_{58}H_{66}Br_4N_8Pt_4$: C, 35.3; H, 3.4; N, 5.7%). FABMS; *m/z* = 1894. Calc. for M − Br; 1895; mp 279 °C, decomp. 300–800 °C.

[‡] Complex **6**. (Found: C, 39.5; H, 4.9; N, 4.8 Calc. for $C_{226}H_{314}Br_{12}N_{24}Pt_{12}$: C, 40.7; H, 4.7; N, 5.0%). NMR (CD_2Cl_2): δ 1.0–1.8 [br, 216H, Bu^t and MePt], 2.6–3.2 [br, 24H, CH_2Pt]; 5.8–8.8 [br, 74H, aromatic H]; mp 297 °C, decomp. 296–887 °C. Complex **7**: (Found: C, 38.1; H, 4.7; N, 4.70 Calc. for $C_{498}H_{682}Br_{28}N_{56}Pt_{28}$: C, 39.5; H, 4.5; N, 5.2%); mp 312 °C, decomp. 317–920 °C.

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