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Trinuclear and hexanuclear platinum clusters as building blocks for organometallic one-dimensional structures†

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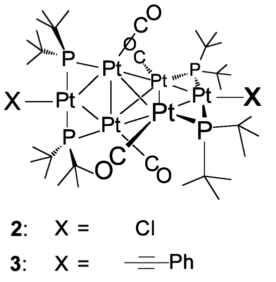
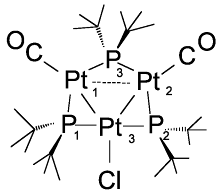
Received (in Cambridge, UK) 19th June 2003, Accepted 29th July 2003
First published as an Advance Article on the web 15th August 2003

The reaction between the new hexa- and trinuclear clusters {Pt_6}(CC–C_6H_4–CCH)$_2$, (4) [{Pt_6} = $Pt_6(CO)_4(\mu\text{-}PBu^t{}_2)_4$], and {$Pt_3$}Cl, (6) [{$Pt_3$} = $Pt_3(\mu\text{-}PBu^t{}_2)_3(CO)_2$], in CuI/Amine gives the thermally and air stable {Pt_6}(CC–C_6H_4–CC{Pt_3})$_2$ (7), where the cluster units are separated by conjugated 1,4-diethynylphenyl groups.

Several derivatives containing transition metals alternated with conjugate organic spacers in the main chain have been prepared[1] and are deeply investigated for their promising magnetic,[2] liquid-crystalline,[3] non-linear optical,[4] luminescence[5] or long-range electron transfer[1,6] properties. Most of them contain isolated transition metal centres located at the extremes[7] or regularly intercalated[8] in the main chain; some recent studies have reported oligomers containing bimetallic units.[9] Ordered structures containing metal *clusters* intercalated with conjugated organic spacers, although of great potential interest, are rare,[10] and are unknown with terminal σ-alkynyl spacers. This may be due to the tendency of metal clusters to undergo fragmentation or condensation processes.

We obtained suitable precursors for such materials by exploiting the remarkable stabilization of the central tri-[11] or hexametallic[12] core accomplished by bulky phosphido ligands in platinum clusters. Therefore, the dichloride {Pt_6}Cl_2 (**2**) [{Pt_6} = $Pt_6(CO)_4(\mu\text{-}PBu^t{}_2)_4$] was obtained† from [{$Pt_6$}$(CO)_2$]$(CF_3SO_3)_2$ (**1**).[12] By reacting **2** with phenylacetylene or 1,4-diethynylbenzene, in diethylamine with a catalytic amount of CuI, we prepared the bis-alkynyl derivatives {Pt_6}$(CCR)_2$ [(**3**), 90%, R = Ph; (**4**), 85%, R = C_6H_4-4-CCH].





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The NMR spectra of **3** and **4** exhibit a diagnostic complex signal at *ca.* 336 ppm (δ_P, four equivalent P nuclei) and at *ca.* −3000 and −4675 ppm (δ_{Pt}), respectively assigned to the central four and to the apical two equivalent platinum centers. Significant IR absorptions were found at *ca.* 2100 (ν_{CC}) and 2010 (ν_{CO}) cm^{-1}; moreover, the ethynyl CH resonances for **4** were found at 3.17 (δ_H) and 84.7 (δ_C) ppm. Fig. 1 shows an ORTEP view of the structure of **3**,‡ with the σ-alkynyl groups terminally bonded to the apical platinum centers of the Pt_6 core. Sigma-alkynyl moieties are found in many organometallic rigid-rod molecules. When attached to single metal centres, they exhibit terminal coordination modes (σ, η^1) not involving their π electrons, which can therefore take part in the conjugation along the chain.[13] In dinuclear, and still more in cluster complexes, the alkynyl function often adopts other coordination modes,[13,14] which have been suggested to decrease the electronic communication between the redox centres.[1a] These bonding modes are probably obstructed in **3** by the bulky phosphides. The metal core of **3** with the phosphido and carbonyl ligands show an approximately $\bar{4}\,2m$ (D_{2d}) local symmetry. Although the phenyl groups lie out of the *pseudo*-mirror planes and do not comply with this symmetry (dihedral angle *ca.* 56° between the phenyl planes), the CC, *ipso*- and *para*- carbon atoms of the PhCC units are nearly aligned with the major *pseudo*-C_2 axis.

Complex **4** reasonably retains the main structural features observed for **3** and bears two terminal ethynyl groups still aligned with the main axis. Their reactivity and their location make complex **4** a promising building block for the construction of ordered structures containing the hexanuclear {Pt_6} unit. Chain elongation of ethynyl derivatives to give linear, polygonal or 3-D ordered structures has been previously achieved through self-coupling of CCH groups or their condensation with aryl- or transition metal halides.[1a,7,8,13,15]

The trinuclear platinum cluster {Pt_3}Cl (**6**) [{Pt_3} = $Pt_3(\mu\text{-}PBu^t{}_2)_3(CO)_2$] contains a halide ligand which can easily be substituted with σ-alkynyl groups;[16] the steric bulkiness of the six *tert*-butyls again prevents π-bonding of the alkynyl moiety.

For these reasons complex **6** was believed to be suitable to insert the {Pt_3} unit at the extremes of the main chain of complex **4**. It was easily prepared in 70% yield by reacting the known tricarbonyl [{Pt_3}(CO)]CF_3SO_3 (**5**)[11] with chloride salts and was characterised by single crystal X-ray diffraction[16] and by IR and multinuclear NMR spectroscopy. The signals in the ^1H, $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were satisfactorily simulated by the following parameters: $\delta_{P1,2}$ = 167.8, δ_{P3} =

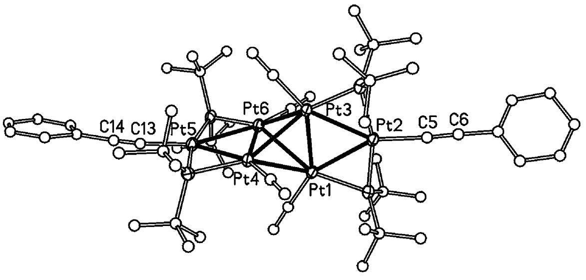

Fig. 1 Molecular structure of **3**. H atoms are omitted (thermal ellipsoids of Pt and P atoms are at 30% probability). Relevant bond distances (Å) and angles (°): Pt1–Pt3, 2.681(2); Pt1–Pt2, 2.737(2); Pt1–Pt4, 2.854(2); Pt1–Pt6, 2.856(2); Pt2–C5, 2.00(3); Pt2–Pt3, 2.728(2); Pt3–Pt1–Pt2, 60.45(5); Pt3–Pt1–Pt4, 62.09(5); Pt2–Pt1–Pt4, 115.60(6); Pt3–Pt1–Pt6, 61.83(5); Pt2–Pt1–Pt6, 113.79(6); Pt4–Pt1–Pt6, 56.09(4); C5–Pt2–Pt3, 150.6(10); C5–Pt2–Pt1, 150.6(10); Pt3–Pt2–Pt1, 58.76(5); Pt1–Pt3–Pt2, 60.79(5); Pt1–Pt3–Pt6, 62.10(5); Pt2–Pt3–Pt6, 114.30(6); Pt1–Pt3–Pt4, 61.92(5); Pt2–Pt3–Pt4, 115.75(6); Pt6–Pt3–Pt4, 56.12(4); Pt4–Pt6–Pt1, 61.92(5); Pt3–Pt6–Pt1, 56.07(5); C6–C5–Pt2, 175(3); C14–C13–Pt5, 174(3).

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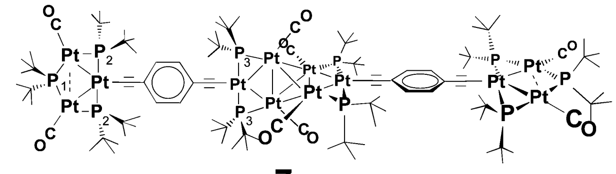
† Electronic supplementary information (ESI) available: experimental procedures and characterization data. See http://www.rsc.org/suppdata/cc/b3/b307003d/

DOI: 10.1039/b307003d



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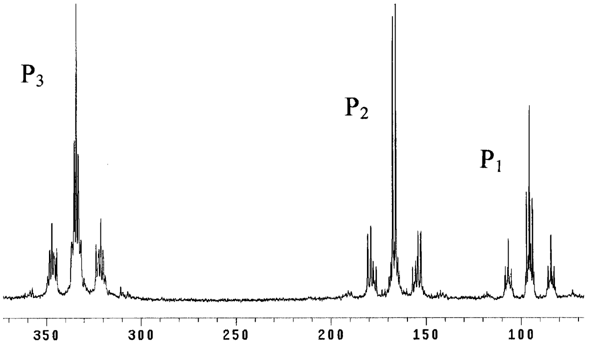

Fig. 2 ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2, 298 K) of complex **7**.

46.7, $\delta_{\mathrm{Pt1,2}} = -5320.0$, $\delta_{\mathrm{Pt3}} = -6389.8$ ppm, $^2J_{\mathrm{P1P2}} = 252$, $^2J_{\mathrm{P1,2P3}} = 130$, $^1J_{\mathrm{Pt1P1}} = {}^1J_{\mathrm{Pt2P2}} = 1972$, $^2J_{\mathrm{Pt1P2}} = {}^2J_{\mathrm{Pt2P1}} = -32$, $^1J_{\mathrm{Pt1,2P3}} = 1709$, $^1J_{\mathrm{Pt3P1,2}} = 2236$, $^2J_{\mathrm{Pt3P3}} = -153$, $^1J_{\mathrm{Pt1,2Pt3}} = 2058$, $^1J_{\mathrm{Pt1Pt2}} = 1300$ Hz.

The Pt_3–Pt_6–Pt_3 linear complex **7** was prepared by reacting **4** with 2 equiv. of **6** in diethylamine/CuI (1%); it was isolated as a deep orange air- and thermally stable solid in 92% yield, and was characterised by microanalytical, IR and multinuclear NMR and MALDI-TOF MS data. Fig. 2 shows its ^{31}P{^{1}H} NMR spectrum exhibiting the expected signals for the P nuclei of the tri- and hexanuclear moieties. The ^{195}Pt{^{1}H} NMR spectrum of **7** exhibits four signals with the expected shape at -6081.1 (2 Pt), -5717.8 (4 Pt), -4467.5 (2 Pt) and -2993.8 (4 Pt) ppm. The ^{1}H and ^{13}C{^{1}H} NMR spectra are compatible with structure **7** and significant IR absorptions were found at 2102 (ν_{CC}), and 2030, 2013 (ν_{CO}) cm^{-1}. The utilization of tri- or hexanuclear clusters derived from complexes **5** and **1** as building blocks for the construction of other 1-, 2- and 3-D molecular architectures, and the extent of the charge delocalization between the cluster units are currently under investigation.

We thank the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR), Programmi di Interesse Nazionale, 2002–2003 for financial support and Dr Giovanna Tripepi (Bruker Daltonics SrL) for the MALDI-TOF MS spectrum of complex **7**.

Notes and references

‡ Crystal data for **3**: $C_{52}H_{82}O_4P_4Pt_6$, crystal dimensions 0.28 × 0.24 × 0.10 mm, space group *C*2/*c* (No. 15), $a = 24.797(4)$, $b = 17.712(2)$, $c = 31.646(6)$ Å, $\beta = 112.72(2)°$, $V = 12821(4)$ Å^3, $Z = 8$, $D_c = 2.140$ g cm^{-3}, μ(Mo–K_α) = 13.180 mm^{-3}, $F(000) = 7632$, $\lambda_{\mathrm{MoK}\alpha} = 0.71073$ Å, $T = 293(2)$ K, $R(F_0) = 0.0647$. CCDC 199125. See http://www.rsc.org/suppdata/cc/b3/b307003d/ for crystallographic data in .cif or other electronic format.

7. Complex **6** (33 mg, 0.029 mmol) and CuI (0.05 mg, 2.6 × 10^{-4} mmol) were added to a diethylamine (20 mL) solution of complex **4** (30 mg, 0.014 mmol). After stirring 24 h at RT the solvent was evaporated and the orange residue was washed with H_2O to give, after column chromatography on alumina (Eluent CH_2Cl_2/*n*-hexane), 55 mg of **7** (92%). Calcd. for $C_{108}H_{188}O_8P_{10}Pt_{12}$: C, 30.4; H, 4.44. Found: C, 30.1; H, 4.53.

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