Isolation of an Electronically Saturated Cluster of Platinum; Synthesis of $[Pt_4(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(CO)_2]^+$

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Protonation of $[Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2]$ with HBF_4 affords the electronically saturated sixty-electron cluster $[Pt_4(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(CO)_2]^+BF_4^-$.

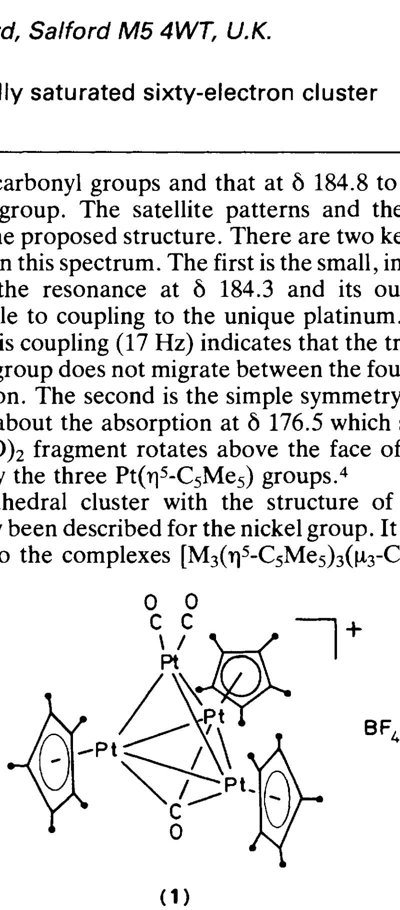
Homonuclear cluster chemistry of platinum is dominated by electron deficient, phosphine-stabilized complexes.[1] We now demonstrate that the pentamethylcyclopentadienyl ligand allows isolation of the electronically saturated sixty-electron cluster $[Pt_4(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(CO)_2]^+$ (**1**).

Addition of $HBF_4{\cdot}OEt_2$ to ethereal solutions of $[Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2]^2$ results in its quantitative conversion into dark microcrystals of $[Pt_4(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(CO)_2]^+$ (**1**). The cluster was characterised spectroscopically.†

The i.r. spectrum of (**1**) in dichloromethane shows the presence of triply bridging and terminal carbonyl groups.[3] The $^{195}Pt\text{-}\{^1H\}$ spectrum (Figure 1) is consistent with a tetrahedron of platinum atoms in which one vertex is unique. The spectrum is thus built up of AB and AB_2 subspectra superimposed on two singlets, the AB_3 subspectrum being too weak to be observed.

The $^{13}C\text{-}\{^1H\}$ spectrum (50% ^{13}CO enriched) of (**1**) (Figure 2) contains two complex absorptions to high frequency of δ 160. The absorption centred at δ 176.5 is assigned to the terminal carbonyl groups and that at δ 184.8 to the bridging carbonyl group. The satellite patterns and the J_{PtC} values support the proposed structure. There are two key features to be found in this spectrum. The first is the small, inner satellites on both the resonance at δ 184.3 and its outer satellites attributable to coupling to the unique platinum. The magnitude of this coupling (17 Hz) indicates that the triply bridging carbonyl group does not migrate between the four faces of the tetrahedron. The second is the simple symmetry of the inner satellites about the absorption at δ 176.5 which suggests that the $Pt(CO)_2$ fragment rotates above the face of the triangle defined by the three $Pt(\eta^5\text{-}C_5Me_5)$ groups.[4]

A tetrahedral cluster with the structure of (**1**) has not previously been described for the nickel group. It is possible to relate it to the complexes $[M_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^+$ (M =



(**1**)

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† Satisfactory analytical data (C, H) were obtained for (**1**). *Spectroscopic data* for (**1**): Fast atom bombardment m.s. 1269 (P^+); i.r. (CH_2Cl_2), ν(CO) 2050s, 2006m, 1699br. cm^{-1}; $^{195}Pt\text{-}\{^1H\}$ n.m.r. (Me_2CO; Ξ = 21.4 MHz) δ 938 $[Pt(CO)_2]$ −897 p.p.m. $[Pt(\eta^5\text{-}C_5Me_5)$, $^1J_{PtPt}$ 6127 Hz]; $^{13}C\text{-}\{^1H\}$ n.m.r. $[(CD_3)_2CO]$ δ 184.8 (μ-CO, $^1J_{PtC}$ 687, $^2J_{PtC}$ 17 Hz), 176.5 (CO, $^1J_{PtC}$ 1604, $^2J_{PtC}$ 63 Hz), 108.3 (*C*Me, $^1J_{PtC}$ 34 Hz), 10.5 (Me); ^1H n.m.r. ($CDCl_3$) δ 2.05 ($^3J_{PtH}$ 19.8 Hz).

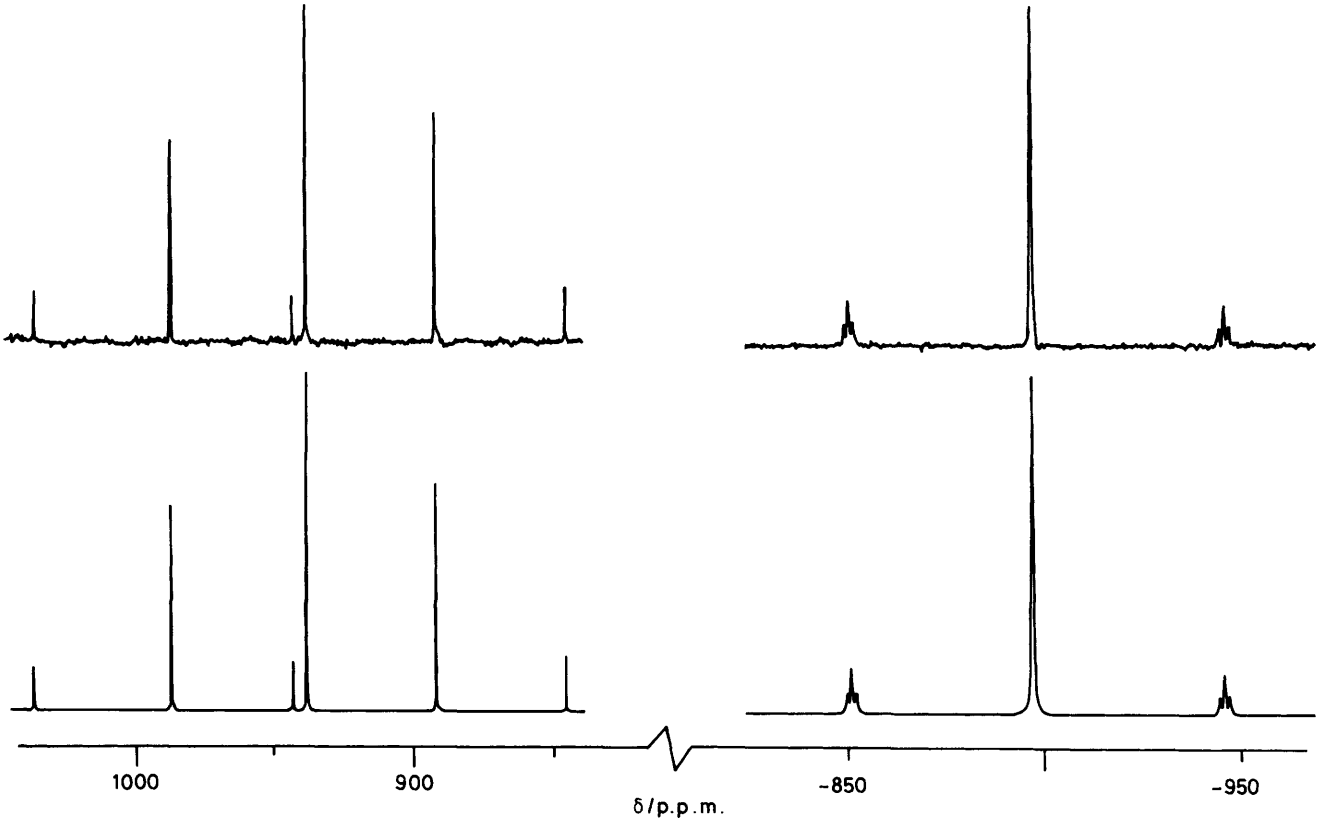

Figure 1. ^{195}Pt-{^{1}H} n.m.r. spectrum of (**1**) in $CDCl_3$ at 295 K with Ξ = 21.4 MHz. The simulated spectrum is shown below.

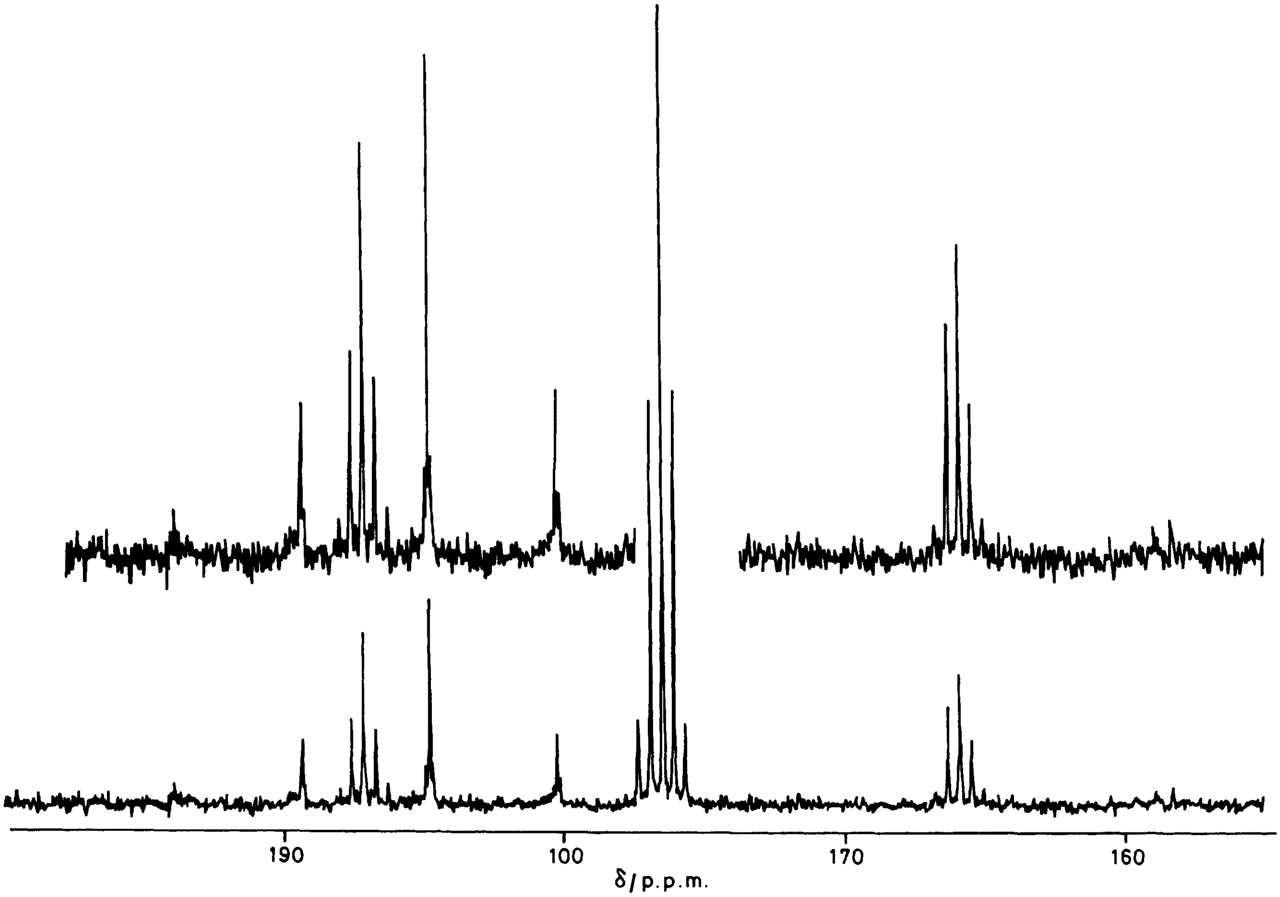

Figure 2. ^{13}C-{^{1}H} spectrum of the metal carbonyl region of (**1**) in $(CD_3)_2CO$ at 293 K.

Ni, Pd)[5,6] through the similarity of the frontier orbitals of the face bridging $Pt(CO)_2$ fragment with a μ_3-CO.[7] What distinguishes (**1**) from other homonuclear platinum clusters, however, is its electronic saturation. Previously described clusters, invariably stabilized by tertiary phosphines, are all unsaturated. For example, clusters of the type $[Pt_4(\mu\text{-}CO)_5(PR_3)_4]$ contain only 58 valence electrons.[8]

This strong predilection for unsaturation has been ascribed to the inability of the molecular orbitals derived from the platinum 6p atomic orbitals to fully contribute to cluster bonding.[1] The presence of pentamethylcyclopentadienyl groups on the cluster (**1**) overcomes this deficiency by providing a means by which these under-utilised metal-based orbitals can contribute to the overall bonding scheme of the cluster.

The formation of (**1**) contrasts with the reaction of $[Pd_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ with $HBF_4{\cdot}OEt_2$ which generates the trimer $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^+$.[4] Although initial protonation presumably occurs at the metal–metal bond in both systems,[9] the reaction pathways for the two metals must subsequently differ. For palladium, the next step is metal–metal cleavage. For platinum, however, the proton must be then transferred to the bound C_5Me_5 group, followed by loss of C_5Me_5H and condensation of the unsaturated fragment with unreacted $[Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2]$.

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