

### Preliminary communication

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## TRINUCLEAR PLATINUM HYDRIDES

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### Summary

The isolation of trinuclear platinum cations containing hydrido ligands, viz.  $[\text{H}_x\text{Pt}_3(\text{dpe})_3]^+$  and  $[\text{H}_x\text{Pt}_3(\text{dpae})_3]^+$ , is reported (dpe =  $(\text{Ph}_2\text{PCH}_2)_2$  and dpae =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ ).

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In the field of polynuclear hydrides of transition metals stabilized by phosphorus ligands, pairs of di- and trinuclear species have been recently characterized in the case of rhodium [1] and iridium [2], e.g.  $\text{H}_2\text{Rh}_2[\text{P}(\text{OR})_3]_4$ ,  $\text{H}_3\text{Rh}_3[\text{P}(\text{OR})_3]_6$  and  $[\text{H}_2\text{Ir}_2(\text{L}-\text{L})_2]^+$ ,  $[\text{H}_7\text{Ir}_3(\text{L}-\text{L})_3]^{2+}$  ( $\text{L}-\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ ). In the case of platinum, although several dinuclear hydrides are now well known, both with chelating [3] or bridging [4] diphosphines or even with monodentate phosphines [5],  $[\text{H}_3\text{Pt}_2(\text{L}-\text{L})_2]^+$  and  $[\text{H}_3\text{Pt}_2\text{L}_4]^+$ , no homotrimeric species has been described. We report here the isolation of two trinuclear derivatives, namely  $[\text{H}_x\text{Pt}_3(\text{dpe})_3]$  [A] (dpe = 1,2-bis(diphenylphosphino)ethane, A =  $\text{BF}_4$ , I,  $\text{BPh}_4$ ) and  $[\text{H}_x\text{Pt}_3(\text{dpae})_3][\text{BF}_4]$  (dpae = 1-diphenylphosphino-2-diphenylarsinoethane). The first was obtained by three different routes: (i) reaction of  $[(\text{dpe})\text{Pt}(\text{pzH})_2]^{2+}$  [6] (pzH = 3,5-dimethylpyrazole) with  $\text{KBH}_4$  (molar ratio 1/5) in methanol solution; (ii) reaction of  $[(\text{dpe})\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{dpe})]^{2+}$  [7] with  $\text{KBH}_4$ , molar ratio  $\text{Pt}/\text{BH}_4 = 1/1$ ; and (iii) reaction of  $[\text{H}_3\text{Pt}_2(\text{dpe})_2][\text{BF}_4]$  [3] with  $\text{KBH}_4$  ( $\text{Pt}/\text{BH}_4 = 1/1$ ).

Full details will be described elsewhere, but a few comments are as follows:

Path i, which utilizes the good leaving ability of the coordinated pyrazole, was previously employed to obtain the dinuclear species ( $\text{Pt}/\text{BH}_4 = 1/1$ ). With

excess  $\text{KBH}_4$ , the trinuclear hydride is isolated as  $[\text{H}_x\text{Pt}_3(\text{dpe})_3][\text{OH}]$ , from which other salts can be obtained by exchange with the appropriate anion (e.g.  $\text{BF}_4$ ).

Path ii gives both the dinuclear and trinuclear species: the yield of the trinuclear hydride can be improved if the reaction is carried out in dilute methanol solution (1 g Pt complex/250 ml): in any case, separation of the mixture is required and the yield of the  $\text{Pt}_3$  species is low (<20%).

Path iii is similar to the first; and once again the isolation of a pure complex requires treatment with a solution of an anion having a low coordinating ability, such as  $\text{BF}_4$  (yield ca. 30%).

In the IR spectra (Nujol and  $\text{CHCl}_3$  solution), sharp absorptions around  $2000\text{ cm}^{-1}$  give evidence for terminal Pt—H bonds and allow a distinction to be made between the di- and the trinuclear species (Fig. 1). A better means of

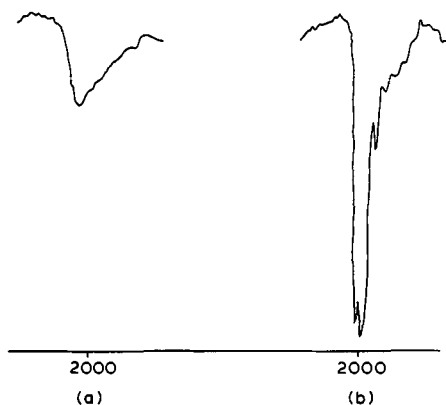


Fig. 1. IR spectra (Nujol,  $2000\text{ cm}^{-1}$  region) of the species  $[\text{H}_3\text{Pt}_2(\text{dpe})_2][\text{BF}_4]$  (a) and  $[\text{H}_x\text{Pt}_3(\text{dpe})_3][\text{BF}_4]$  (b).

distinguishing between the species of different nuclearity is by  $^1\text{H}$  NMR spectroscopy; as in the case of the  $[\text{H}_3\text{Pt}_2(\text{L}-\text{L})_2]^+$  complexes, the spectra of the trinuclear species indicate a rapid exchange among all hydride ligands, showing only one hydride signal over a wide range of temperature ( $\text{CDCl}_3$ ,  $-55$ ,  $+50^\circ\text{C}$ ). The hydride resonance of the  $[\text{H}_x\text{Pt}_3(\text{dpe})_3]^+$  cation, in agreement with the presence of six equivalent phosphorus nuclei, is observed as a binomial septet ( $^2J(\text{P}-\text{H}) = 29\text{ Hz}$ ) centered at  $\tau$  11.5, with satellites due to coupling with the  $^{195}\text{Pt}$  atoms ( $^1J(\text{Pt}-\text{H}) = 387\text{ Hz}$ ). The  $J(\text{Pt}-\text{H})$  value should be compared with the value of  $500\text{ Hz}$  found in the corresponding dinuclear complex: a reduction of the coupling on going from a di- to a trinuclear species has been observed previously [1] and is likely to be related to a lower bond order in the  $\text{M}_3\text{H}$  system. The presence of three ligand molecules is more evident in the spectrum of the other isolated species,  $[\text{H}_x\text{Pt}_3(\text{dpae})_3][\text{BF}_4]$ , which is shown in Fig. 2 together with the spectrum of the dinuclear complex. In the latter, coupling to two P atoms gives rise to a triplet, while in the trinuclear derivative, the presence of three equivalent phosphorus atoms is unambiguously shown by the splitting of all the signals into quartets ( $\tau$  14.1,  $^2J(\text{P}-\text{H}) = 17$ ,  $^1J(\text{Pt}-\text{H}) = 440\text{ Hz}$ ). The equivalence of the P nuclei in the



Fig. 2.  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , room temperature), central peak of the hydride resonance; (a)  $[\text{H}_3\text{Pt}_2(\text{dpae})_2]^+$ , (b)  $[\text{H}_x\text{Pt}_3(\text{dpae})_3]^+$ .

$[\text{H}_x\text{Pt}_3(\text{dpe})_3]^+$  complex was also indicated by the  $^{31}\text{P}\{^1\text{H}\}$  spectrum (57.8 ppm downfield from  $\text{H}_3\text{PO}_4$ ,  $\text{CDCl}_3$ , room temperature). The number of hydridic hydrogens  $x$ , is likely to be five; however, since formally platinum(I) hydrido species have been recently reported [8], in the absence of unequivocal evidence, such as a  $^1\text{H}$  non-decoupled  $^{195}\text{Pt}$  spectrum, we prefer not to specify it.

Although the trinuclear cations are fairly stable and several salts can be isolated by treatment with different anions, no crystal suitable for an X-ray investigation has been obtained. Furthermore, because of the dynamic behaviour in solution, the NMR spectra do not provide information on the coordination of the hydride ligands. Thus, at present suggestions for the structures of these trinuclear species would be only speculation.

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