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Some Binuclear Bis(diphenylphosphino)methane Complexes of Platinum with Bridging and Terminal Hydrido Groups

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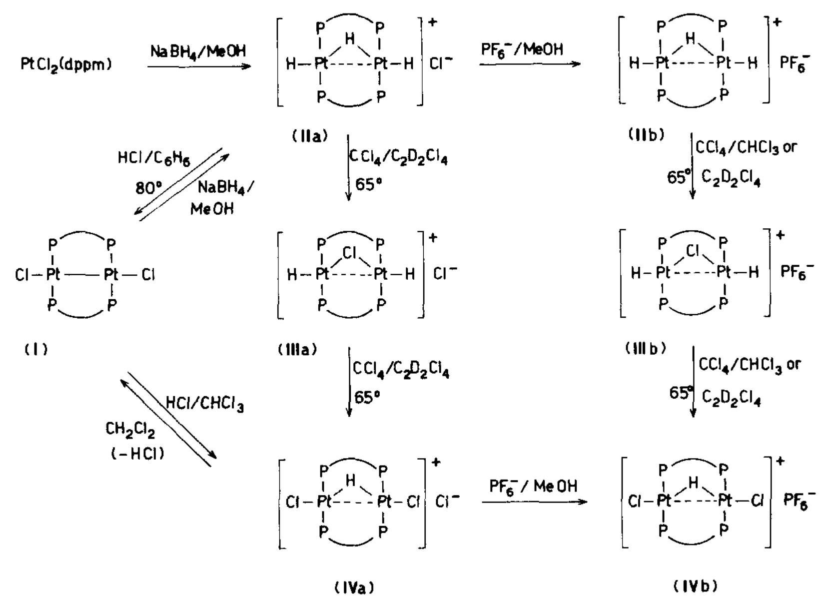
The bis(diphenylphosphino)methane (dppm) complex $[Pt_2Cl_2(dppm)_2]$, which contains two platinum atoms in the formal oxidation state one, has been shown to have structure (I) (scheme) [1, 2]. The Pt–Pt bond in (I) is exposed and should be susceptible to attack by electrophiles [2]. We now report some hydride derivatives which contain the same $Pt_2(dppm)_2$ skeleton as in (I), but which also contain hydride or chloride ligands bridging between the platinum atoms. The preparation and proposed structures of the complexes are shown in the scheme.

Reduction of $[PtCl_2(dppm)]$ with $NaBH_4$ gives a hydrido-platinum complex now shown to be $[Pt_2H_3(dppm)_2]Cl$, (IIa). This complex (IIa) reacts with chlorinated solvents such as CCl_4 to give first the dihydrido complex, (IIIa), and then the monohydrido complex, (IVa). All these complexes are thought to be ionic and can be converted to the more stable PF_6^- salts (IIb)–(IVb). Of particular interest is the observation that (IVa) can be obtained by reversible protonation of the Pt–Pt bond of (I) by hydrogen chloride.

The presence of the $Pt_2(dppm)_2$ unit in (II)–(IV) is proved by the ^1H n.m.r. spectra in the CH_2 group region and by the ^{31}P n.m.r. spectra, which are very similar to those reported earlier for the parent (I) [1]. The nature of the hydridoplatinum groups is determined from the ^1H n.m.r. spectra in the Pt–H region (Table). Thus a grouping H–Pt–Pt–H containing one ^{195}Pt atom (I = 1/2, natural abundance 33%), will give a resonance with *two* sets of satellites corresponding to $^1J(Pt–H)$ and $^2J(Pt–H)$, each satellite intensity being 1/4 that of the central peak. This pattern is observed for (III). In contrast the grouping $\mathrm{Pt}\overset{\mathrm{H}}{\cdots}\mathrm{Pt}$ will give a hydride resonance with only one $^{195}Pt–H$ coupling constant but the peak intensities will be approximately 1:8:18:8:1 with the inner satellites having almost half the intensity of the central peak [1]. This pattern, less the weak outer peaks, is observed for (IV). Complexes (II) contain two hydride resonances with relative intensity 2:1 corresponding to the terminal H–Pt–Pt–H and bridging $\mathrm{Pt}\overset{\mathrm{H}}{\cdots}\mathrm{Pt}$ groups respectively, each resonance having the expected ^{195}Pt satellites. At higher temperatures (70 °C) coalescence of the peaks due to terminal and bridging groups occurred, indicating that exchange between bridging and terminal hydride groups in (II) occurs readily. The n.m.r. data (Table) for corresponding chlorides and PF_6^- derivatives of complexes (II) and (III) are very similar, indicating



Scheme. (Bridging $Ph_2PCH_2PPh_2$ (dppm) groups denoted by P⌒P).

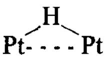
TABLE. ^{1}H n.m.r. Data[a] (Pt–H).

Complex	Terminal Hydride			Bridging Hydride	
	δH	^{1}J(Pt–H)	^{2}J(Pt–H)	δH	^{1}J(Pt–H)
(IIa) $[Pt_2H_3(dppm)_2]^+Cl^-$	−6.76	1162	116	−5.85	540
(IIb) $[Pt_2H_3(dppm)_2]^+PF_6^-$	−6.86	1138	103	−5.86	540
(IIIa) $[Pt_2H_2Cl(dppm)_2]^+Cl^-$	−12.35	1184	271	–	–
(IIIb) $[Pt_2H_2Cl(dppm)_2]^+PF_6^-$	−12.00	1174	305	–	–
(IVb) $[Pt_2HCl_2(dppm)_2]^+PF_6^-$	–	–	–	−16.60	810

[a] Spectra recorded at 60 MHz in $C_2H_2Cl_4$ or $C_2D_2Cl_4$ except for (IVb) which was examined in CD_2Cl_2. δ values ± 0.05 (relative to tetramethylsilane), J. values ± 10Hz. Hydride resonance was not observed for complex (IVa).

that the chlorides are also ionic, at least in solution.

The Pt–Pt bond shown to be present in (I) is not necessarily present in (II)–(IV) and it is predicted that the Pt–Pt bond in (IV) should be at least considerably weaker than in (I). This aspect is being investigated further. The preference for a bridging hydride in (IV) but a bridging chloride in (III) is also as yet unexplained.

Previous workers have been unable to detect  $\overset{H}{\mathrm{Pt}\cdots\mathrm{Pt}}$ bridging groups by n.m.r. spectroscopy [3]. The present work shows that this is possible and that valuable structural information can be obtained from the spectra.

Acknowledgement

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References

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