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Preliminary communication

PLATINUM(I) DINUCLEAR HYDRIDES

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Summary

The novel complexes $[(dpe)_2Pt_2(CO)(H)][X]$ and $[(dpe)_2Pt_2(CNR)(H)][X]$ ($X = BF_4$, I; dpe = 1,2-bis(diphenylphosphino)ethane; R = *p*-tolyl, methyl and t-butyl) were obtained by reaction of $[(dpe)_2Pt_2H_3][X]$ with CO or isocyanides.

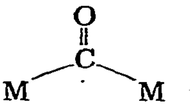
Several dinuclear polyhydrido derivatives of platinum(II) are known, including the species $[(dpe)_2Pt_2H_3][X]$ (I: $X = BF_4$, II: X = I) (dpe = 1,2-bis(diphenylphosphino)ethane) recently described by us [1]. We now describe the reactions of these hydrides with CO and isocyanides.

Bubbling CO at room temperature into the pale yellow solution of complex I (CH_2Cl_2 or $CHCl_3$ or acetone) gives a deep blue solution from which a crude product can be obtained by concentration and addition of methanol. Chromatography on deactivated Al_2O_3 (10% H_2O) to remove a trace amount of a yellow product, and precipitation with methanol, affords the analytically pure, turquoise-green species $[(dpe)_2Pt_2(CO)(H)][BF_4]$ (III) dec. > 225°C, yield ~90%. From this, the corresponding iodide (IV) dec. > 180°C, is easily obtained by reaction with KI in methanol.

The conductivity values ($\Lambda_0 - \Lambda/\sqrt{c}$) of the tetrafluoroborate III are in agreement with a 1/1 electrolyte, while the ^1H NMR spectra give evidence of a diamagnetic behaviour. In the IR spectra the lack of any absorptions in the 2200—1800 cm^{-1} region clearly shows the absence of terminal hydrido or carbonyl ligands: a strong band at 1730 and 1720 cm^{-1} (Nujol mull) for III and IV respectively, i.e. at a very low value for a positively charged complex, is assigned to the bridging carbonyl group.

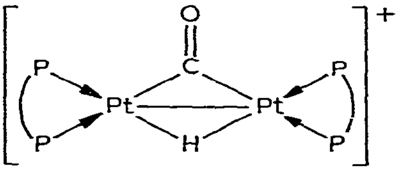
Carbonyl stretchings as low as these or lower were recently observed in other dinuclear platinum and palladium complexes [2], which were described as dimetallated formaldehyde derivatives [3]. In the case of the complexes

$[\{MCl(\mu\text{-dpam})\}_2(\mu\text{-CO})]$ (V: M = Pd [2b]; VI: M = Pt [4] (dpam = bis(diphenylarsino)methane)), the angles and distances reported below were taken as a proof that the carbonyl bridges two metal atoms not directly bonded, with the C atom in a nearly sp^2 hybridization. The complexes were therefore considered to be in the formal oxidation state of two [4].



	Pd	Pt
M—C—M	119°	106°
M—C—O	~120°	127°
M—M	3.27 Å	3.16 Å

Although the low ν(CO) value might suggest an analogous behaviour of the carbonyl in our case, the deep colour of complexes I and II, both in the solid state and in solution, makes the existence of a platinum(II) system less likely. On the basis of the available data, a dinuclear platinum(I) structure (A) may be suggested. Indeed, preliminary X-ray data on complex I [5], show that the carbonyl group bridges two platinum atoms held at a distance of ca. 2.7 Å and the Pt—C—Pt angle (ca. 84°) fit the value expected for a bridging carbonyl supported by a metal—metal bond [6]. The complexes are therefore examples of platinum(I) derivatives.



(A)

In the solid state, the bridging hydrogen atom has not yet been located, but evidence for the hydride ligand is obtained through the ^{1}H NMR spectrum, where a resonance centered at ca. τ 11.9 ppm (unresolved multiplet) is found. The species I reacts with CO even in the solid state. After several days at 68°C under a stream of CO a dark powder is obtained (ν(CO) at 1740(br) and 1785 cm^{-1}, Nujol mull): work up affords complex III in moderate yield.

A violet complex (ν(CO) at 1740 cm^{-1}) (VII) analogous to the hydrido carbonyl complex III, is obtained similarly from the species $[(dpp)_2Pt_2H_3][BF_4]$ (dpp = 1,3-bis(diphenylphosphino)propane) [7]. The arrangement of ligands in the space between the two platinum atoms is not likely to be limited to the carbonyl derivatives mentioned above. Indeed the reaction of I and II (or III and IV) with isocyanides (molar ratio 1/1) affords the violet derivatives $[(dpe)_2Pt_2(CNR)(H)][X]$ (VIII: R = p-tolyl, X = BF_4; ν(CN) 1650; IX: X = I, ν(CN) 1645; X: R = methyl, X = BF_4, ν(CN) 1660(br); XI: X = I, ν(CN) 1660(br) cm^{-1}, Nujol mull), which are likely to be of the same type.

Not unexpectedly, the reaction of an isocyanide having a bulky substituent (R = t-butyl) with complexes I and III (1/1 ratio) gives the yellow complex XII, dec. > 185°C, $[(dpe)_2Pt_2(CNR)(H)][BF_4]$, ν(CN) 2160, ν(Pt—H) 1995 cm^{-1} (disappears on deuteration) where both the isocyanide and the hydrido ligands are terminal.

Acknowledgements

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