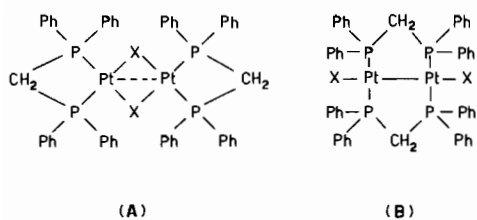


The Structure of Dimeric Platinum(I) Complexes with Bis(diphenylphosphino)methane as Ligand

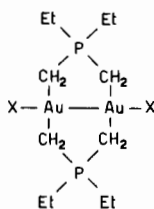
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The dimeric platinum(I) complex $[(\text{Ph}_2\text{PCH}_2\text{-PPh}_2)\text{PtCl}]_2$ (Ia) has recently been reported by Glockling and Pollock¹ who have assigned it a chlorine-bridged structure (A).



- (I) (a) X = Cl
 (b) X = Br
 (c) X = I



- (II) X = Cl, Br and I

Subsequently, Schmidbauer *et al.*,² by analogy with related gold(II) complexes (II), have suggested the alternative phosphine-bridged structure (B). We are therefore prompted to report briefly some results of our study of complex (Ia) and of the corresponding bromo- and iodo-derivatives (Ib) and (Ic), respectively.

The ¹H n.m.r. resonance of the CH₂ groups may be used as a criterion for testing the validity of the proposed structures since for (A) the familiar 1:4:1 triplet consisting of two ¹⁹⁵Pt satellites and a central peak is expected, whereas for (B) where the CH₂ group is part of a ligand bridging two Pt atoms, a 1:8:18:8:1 quintet is expected.³ The observed resonances (Table) for all three platinum(I) complexes conform in fact to the latter situation since, although not all five peaks can be observed, the area

TABLE. N.m.r. Resonances^a (60 MHz) for the CH₂ Groups.

| Complex | δ (ppm) ^b | ³ J(Pt–H) (Hz) |
|---------|-----------------------------|---------------------------|
| (Ia) | 4.46 | 54.0 ^c |
| (Ib) | 4.34 | 58.8 |
| (Ic) | 4.44 | 57.6 |

^a In 1,1,2,2-C₂D₂Cl₄. Spectra in CDCl₃ and CD₂Cl₂ were similar. ^b Downfield from TMS. ^c Ref. 1 gives 56.6 Hz.

ratios of the three major peaks are in good agreement ($\pm 5\%$) with 8:18:8. Further, in the case of compounds (Ia) and (Ib) which gave the best spectra (see figure for the spectrum of the latter compound) one of the weak outer peaks can also be clearly detected. The reason that the other outer peak cannot be seen is that it is obscured by resonance from CH₂Cl₂ derived from solvent of crystallization. Thus these resonances are in accord with a bridging situation for the phosphine ligands, such as that in structure (B) and preclude any structure, such as (A) in which the ligands are chelating. The integrated peak area ratio we observe is not in agreement with that (equivalent to 1:4:1) reported by Glockling and Pollock for (Ia) and we also fail to resolve the P–H coupling which they reported.

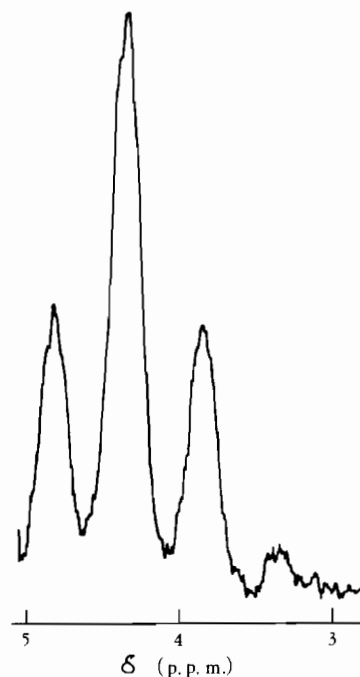


Figure. ¹H n.m.r. spectrum of compound (Ib).

Despite the possibility of isomerism between chelating and bridging structures for complexes of bis(diphenylphosphino)methane,⁴ there is little doubt that our compound (Ia) is identical to that reported

by Glockling and Pollock.¹ In this respect, satisfactory agreement on the Pt-H coupling constant (Table), the m.p., the i.r. band at 249 cm⁻¹ and the mass spectrum (see below) seem conclusive.

The chloro-complex (Ia) was previously prepared (92%) from reaction of [(Ph₂PCH₂PPh₂)PtCl₂] with [Hg(SiMe₃)₂].¹ An improved route (70%) is by reduction of [(Ph₂PCH₂PPh₂)PtCl₂] with NaBH₄ in MeOH followed by treatment of the uncharacterised Pt-H compound [ν (Pt-H), 2130 cm⁻¹] thus obtained with HCl and C₆H₆. The yellow solid (a benzene solvate) has a m.p. 292 °C (lit. 291 °C¹) and may be crystallised from CH₂Cl₂ (as a CH₂Cl₂ solvate). Both solvates have satisfactory microanalyses. The mass spectrum shows peaks centred at 1228 a.m.u. (lit. 1229 a.m.u.¹) which indicates probable H loss from a parent ion calculated as having an isotope pattern centred at 1230 a.m.u. The mass spectrum also has peaks due to the ions [(Ph₂PCH₂PPh₂)PtCl]⁺ and [(Ph₂PCH₂PPh₂)Pt]⁺. The vibrational spectra have bands at 249 cm⁻¹ (i.r.) (lit. 249 cm⁻¹) and 275 cm⁻¹ (Raman) tentatively assigned to *asym*- and *sym*- ν (Pt-Cl), respectively. A strong Raman band at 150 cm⁻¹ is tentatively assigned to ν (Pt-Pt) and compares with bands⁵ at 170 and 135

cm⁻¹ for ν (Pt-Pt) in [Pt₂Cl₄(CO)₂]²⁻ and [Pt₂Br₄(CO)₂]²⁻, respectively.

The bromo-complex (Ib) and the iodo-complex (Ic), CH₂Cl₂ solvates of which have satisfactory microanalyses, are best obtained by halide exchange from (Ia). Thus treatment with Et₄N⁺Br⁻ in CH₂Cl₂ gives (Ib) (76%) and with NaI in (CH₃)₂CO gives (Ic) (65%). Their i.r. spectra are closely similar to that of (Ia) but show no band at 249 cm⁻¹.

Acknowledgments

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