Inorganica Chimica Acta, *77* (1983) L95–L96

Binuclear Platinum Complexes with Bis(dimethylphosphino)methane Ligands: the Molecular Structure and Chemistry of $[Pt_2Me_4(\mu\text{-}Me_2PCH_2PMe_2)_2]$

SAMSON S. M. LING, RICHARD J. PUDDEPHATT*,

Department of Chemistry, The University of Western Ontario, London, Ont. N6A 5B7, Canada

LUBICA MANOJLVOVIC-MUIR* and KENNETH W. MUIR

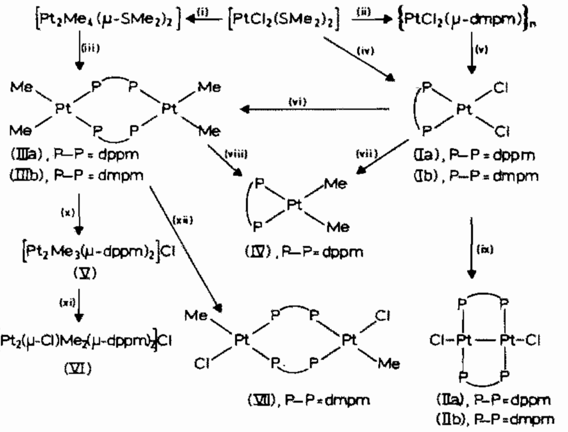
Department of Chemistry, The University of Glasgow, Glasgow G12 8QQ, U.K.

Received April 27, 1983

The ligand bis (diphenylphosphino)methane, dppm, has been widely used as a bridging ligand to lock together two transition metal centres, giving suitable systems for the systematic development of the organometallic chemistry and catalytic properties of binuclear transition metal complexes [1–4]. To further develop this field, a study of electronic and steric effects of related ligands $R_2PCH_2PR_2$ [5] on the structures and reactivities of binuclear complexes has been initiated. This article gives some results for the ligand $Me_2PCH_2PMe_2$, dmpm, which indicate that the smaller steric effect of methyl substituents can lead to different, and in some ways enhanced, reactivity compared to similar dppm complexes.

Some reactions to illustrate the similarities and differences between the ligands dmpm and dppm are shown in the Scheme. Similarities are seen in the formation of complexes (I), (II) [6] and (III) [7] for both ligands**.

We have determined the crystal structure of (IIIb) (see Fig. 1)*** in order to compare it with that of the analogous dppm complex [7]. In both complexes pairs of bridging diphosphinomethane ligands link two *cis*-square-planar dimethylplatinum units, so that eight-membered $Pt_2P_4C_2$ rings are formed. The ring conformations are however distinctly different in the two complexes. The dmpm complex adopts a symmetrical C_{2h} twist-chair conformation [internal ring torsion angles are 109–114° at P–Pt bonds and 42–45° at P–CH_2 bonds, angles involving the same P atom being of opposite signs]. The eight-membered



Scheme 1.

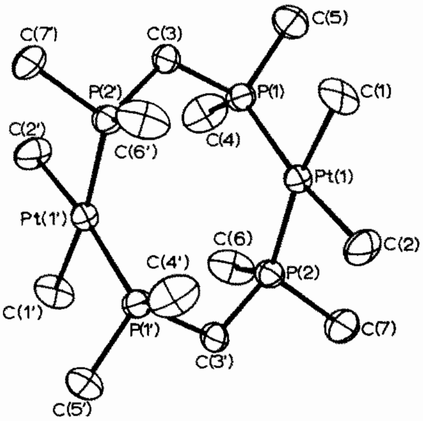


Fig. 1. A perspective view of one of the $Me_2Pt(Me_2PCH_2PMe_2)_2PtMe_2$ molecules showing 50% ellipsoids. Ranges of chemically equivalent distances and angles are: Pt–P 2.264(3)–2.280(3), Pt–C 2.124(12)–2.202(9), P–C 1.808(13)–1.870(13) Å, P–Pt–P 102.7(2)–102.9(2), C–Pt–C 82.3(5)–83.4(5), Pt–P–CH_2 114.1(5)–116.6(4), and P–C–P 114.4(7)–115.7(5)°.

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*Authors to whom correspondence should be addressed.

**Satisfactory analytical and ^1H and ^{31}P NMR data have been obtained for all complex. NMR data: (Ib) in $CDCl_3$; 1.77t [$^3J(PtH)22$, $^2J(PH) + {}^4J(PH) = 7.2$, *Me*P], 3.84t [$^3J(PtH)26$, $^2J(PH)9.6$ CH_2P_2], −17.1s from $(MeO)_3PO$ ref. [$^1J(PtP)2500$, Pt*P*]. (IIb) in CD_2Cl_2; 1.70m [$^3J(PtH)$-28.5, $^2J(PH) + {}^4J(PH) = 6.5$, *Me*P] 2.80q [$^3J(PtH)43$, $^2J(P^aH) + {}^4J(P^bH) = 7.0$, CH_2P_2], −43.4s from $(MeO)_3PO$ ref. [$^1J(PtP)2674.4$, $^3J(PtP)$ −147.9, $^2J(P^aP^b)49.6$, ^3J-$(P^aP^{b'})20.2$, Pt*P*]. (IIIb) in CD_2Cl_2; 0.29m [$^2J(PtH)66$, $^3J(PH) + {}^3J(P^1H)1.8$, *Me*Pt], 2.57m [$^3J(PtH)19$, *Me*P], 4.25m [$^3J(PtH)23$, CH_2P_2], −17.4m from $(MeO)_3PO$ ref. [$^1J(PtP)1835$, $^3J(PtP)65$, $^2J(P^aP^b)40$, $^3J(P^aP^{b'})10$, Pt*P*].

***Crystal data*: $C_{14}H_{40}P_4Pt_2$, $M = 722.6$. Monoclinic, $a = 16.634(4)$, $b = 11.112(3)$, $c = 12.469(3)$ Å, $\beta = 103.40(2)°$, $U = 2242$ Å^3, $Z = 4$, $D_c = 2.141$ g cm^{-3}, $F(000) = 1360$, space group $P2_1/a$ (C^5_{2h}–No. 14), Mo-K$_\alpha$, radiation, $\lambda = 0.71069$ Å, μ(Mo-K$_\alpha$) = 128.7 cm^{-1}.

The structure is based on 3646 independent, absorption-corrected intensities [$I \geqslant 3\sigma(I)$, $2 \leqslant \theta(\text{Mo-K}_\alpha) \leqslant 27°$] derived from 6926 individual measurements made on an Enraf-Nonius CAD4F diffractometer. The non-hydrogen atoms were located using Patterson and Fourier methods and their parameters were refined by the full-matrix least-squares technique to R 0.043, R_w 0.055. The crystallochemical unit consists of two independent half molecules. Each molecule has crystallographic C_i symmetry but approximates to C_{2h} point symmetry, with the diad axis defined by the vector between the two methylene carbon atoms.

0020-1693/83/$3.00

ring in the dppm complex is flatter and much less regular, approximating to a twist-saddle conformation [8]. In the dmpm complex ring angles at P and C atoms [mean values 115.2 and 115.0°] are only *ca.* 6° greater than the tetrahedral value, whereas in the dppm complex these angles are 120–123°. By contrast the P–Pt–P angle in the dppm complex [98(1)°] is appreciably *less* obtuse than the corresponding mean angle of 102.8(2)° in the dmpm complex. The main source of steric strain in the dmpm complex appears to be the C(axial)...C(axial) [*e.g.* C(4)...C(6), see Figure] interactions of 3.22–3.26(2) Å. Inspection of models suggests that this conformation would not be stable if methyl substituents are replaced by the more sterically demanding phenyl substituents at phosphorus. The different conformations and steric strain patterns in the dmpm and dppm complexes thus reflect the differing steric properties of the substituents on phosphorus atoms. The activation energy for inversion of the chair conformation in (IIIb) as determined from the splitting of the MeP resonance in the H NMR spectra at low temperature ($\Delta\nu$ 323 at 400 MHz, T_c 293 K) is $\Delta G^{\ddagger}$ 56 kJ mol^{-1}.

As well as the differences in conformation and fluxional behaviour, the following important differences between (IIIa) and (IIIb) should be noted:

(1) Complexes with chelating diphosphine ligands are more easily formed with dppm than with dmpm. This can be seen from the easier formation of complex (I) with the ligand dppm (Scheme), but is illustrated particularly clearly in the dimethylplatinum(II) derivatives (III) and (IV). With dppm, both isomers can be isolated and the monomeric isomer (IV) is the more stable [7]. However, with dmpm ligand, the monomeric isomer could not be detected and the observed formation of dimeric (IIIb) by methylation of monomeric (Ib) strongly suggests that this dimeric isomer, (IIIb), is thermodynamically favored. This is apparently an example of the Thorpe–Ingold effect, according to which the stability of the strained 4-membered ring in the chelate complexes should be relatively greater when the substituents on the phosphorus are bulkier [9].

(2) Reaction of HCl with (IIIa) gives the ionic A-frame derivative (VI) [10], but with (IIIb) this reaction gives the neutral derivative (VII)*, which does not readily rearrange. Again, it is likely that steric hindrance in the dppm derivatives facilitates the chloride dissociation to give (VI).

(3) Complex (IIIb) readily undergoes oxidative addition with reagents such as MeI, $I(CH_2)_4I$, I_2 and Br_2 whereas (IIIa) is either unreactive (alkyl halides) or undergoes electrophilic cleavage of a methyl group (halogens) [7]. Again steric crowding at platinum in (IIIa) precludes oxidative addition.

Further comparisons of the ligand behaviour of dmpm, dppm and the more hindered derivative $^tBu_2PCH_2P^tBu_2$ are in progress, since the above results indicate that more quite new chemistry may be expected.

Acknowledgements

Financial support from NSERC (Canada) and Imperial Oil Ltd. is gratefully acknowledged.

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*NMR data in CD_2Cl_2: 0.54 m [$^2J(PtH)$52, $^3J(PH)$ 7.0, 4.0 *Me*Pt]; 1.78m [*Me*P]; 2.53m [$^3J(PtH)$ 34, CH_2P_2], −8.1m form $(MeO)_3PO$ ref. [$^1J(PtP)$ 1780, $^3J(PtP)$ 62.5, $J(P^aP^b) + J(P^aP^{b'}) = 6.0$, Pt$P^a$ *trans* to Me], −21.2m [^1J-(PtP) 4160, $^3J(PtP)$ 60.5, PtP^b *trans* to Cl]. These data prove the *cis*-[$PtClMeP_2$] stereochemistry at each Pt centre, and the observation of only one CH_2P_2 resonance indicates the overall *trans* structure shown for (VII).