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Preliminary communication

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE DIMETHYL-PLATINUM(II) COMPLEX OF 1,1,1-TRIS(DIPHENYLPHOSPHINOMETHYL)-ETHANE

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Summary

A single crystal X-ray study, as well as proton and phosphorus-31 NMR studies, show that the structure of $\text{Pt}(\text{CH}_3)_2(\text{tripod})$ [tripod = 1,1,1-tris(diphenylphosphinomethyl)ethane] consists of a four-coordinate, nearly planar platinum with the triphosphine functioning as a bidentate ligand.

Recent studies on dimethylplatinum(II)—phosphine complexes have focused on (1) the analysis of the ^1H NMR spectra [1], (2) the effect of the chelate ring size of ditertiary phosphines [2], (3) the mechanism of oxidation and cleavage with $[\text{IrCl}_6]^{2-}$ [3] and (4) metathesis of methyl groups for halides [4]. We have been studying the structures and dynamics of dimethylplatinum(II) complexes of a series of triphosphine ligands in attempts to stabilize a five-coordinate platinum(II) compound. We have found that the triphosphine ligands $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ (ttp), $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ (etp), and $\text{PhP}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2$ (dmetp) give complexes of composition $\text{Pt}(\text{CH}_3)_2(\text{triphosphine})$ that are fluxional on the ^{31}P NMR time scale at temperatures below 25°C [5]. In contrast, the dimethylplatinum(II) complex of $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ (tripod) does not exhibit fluxional behavior at room temperature. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Pt}(\text{CH}_3)_2(\text{tripod})$ (Fig. 1) is consistent with a planar four-coordinate platinum(II) complex in which the tripod ligand functions as a chelating diphosphine with one of the diphenylphosphino groups dangling free in solution.

The ^1H NMR spectrum of $\text{Pt}(\text{CH}_3)_2(\text{tripod})$ in the Pt—CH₃ region is similar to that of $\text{Pt}(\text{CH}_3)_2(\text{PPh}_3)_2$ reported by Greaves et al., as expected [6]. Goodfellow [1]

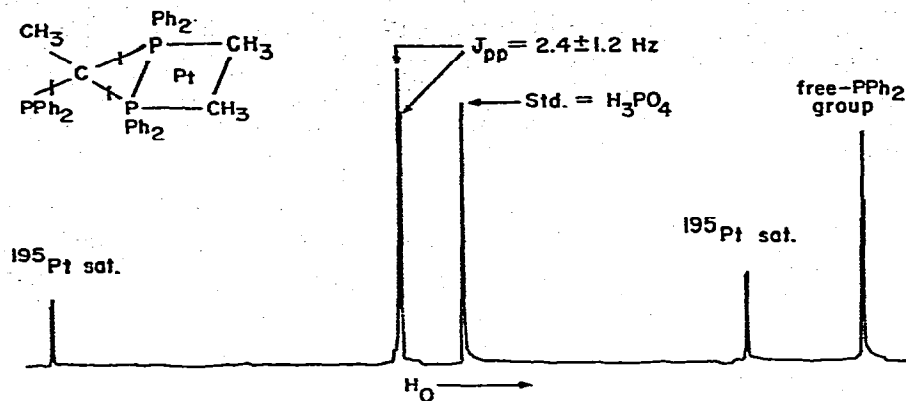


Fig. 1. A Fourier-transform $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Pt}(\text{CH}_3)_2$ (tripod) in $\text{CDCl}_3/\text{CH}_2\text{Cl}_2$ at room temperature.

pointed out that such a spectrum could not be analyzed on the basis of an $[\text{AX}_3]_2$ spin system. With ^{31}P decoupling, the methyl multiplet collapses to a single resonance with corresponding ^{195}Pt satellites and $^2J(\text{Pt}-\text{H})$ 69 Hz. An X-ray structural determination on $\text{Pt}(\text{CH}_3)_2$ (tripod) was performed to determine if the four-coordinate structure persisted in the solid state, and the results are presented in this communication.

The compound $\text{Pt}(\text{CH}_3)_2$ (tripod) was prepared by treating a solution of $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ (0.6600 g, 1.06 mmol in 30 ml of benzene) with 0.3525 g (1.06 mmol) of $\text{Pt}(\text{CH}_3)_2(\text{COD})$ (COD = 1,5-cyclooctadiene). The resulting solution was refluxed 3 h and then most of the benzene was removed on a rotary evaporator. The remaining solution was treated by adding 80 ml of diethyl ether, and crystals started appearing after 5 minutes. After the resultant mixture sat in the refrigerator overnight, the crystals were collected on a sintered glass frit, washed with ether, and dried in vacuo. Yield, 80%; dec. 234°C . Anal. Found: C, 60.77, H, 5.29%. $\text{C}_{43}\text{H}_{45}\text{P}_3\text{Pt}$ calcd.: C, 60.77; H, 5.35%.

Preliminary examination by precession techniques of a crystal mounted on a glass fiber showed that the crystal was monoclinic, space group $P2_1/c$ with four molecules in the unit cell. The cell constants, as determined by hand centering twelve reflections on a Picker four-circle diffractometer using graphite monochromatized $\text{Cu-K}\alpha_1$ radiation, are a 12.495(7), b 15.518(5), c 25.493(12) Å, and β $49.88(3)^\circ$. The X-ray structure of $\text{Pt}(\text{CH}_3)_2$ (tripod) was determined using 3188 independent reflections collected using counter methods. At the present stage of refinement (full-matrix least squares refinement in which Pt and P atoms are treated anisotropically, all other atoms treated isotropically, the phenyl rings treated as rigid groups, and the H atoms treated as a fixed atom contribution), the conventional unweighted R factor is 9.2%. A perspective view of the molecular structure is shown in Fig. 2.

The coordination geometry about the platinum is square planar. The Pt-P(1) and Pt-P(2) bond lengths of 2.26 and 2.28 Å, respectively, are comparable to Pt-P distances of 2.279(5) and 2.285(6) Å in $\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{PPh}_3)_2$ [7]. Also, the Pt-P distances are 2.254(3) Å and 2.289(3) Å in $\text{Pt}(\text{C}_6\text{H}_5)(\text{CH}_2\text{COC}_6\text{H}_5)_2$ (diphos) [8]. The Pt-C(1) and Pt-C(2) bond lengths of 2.18 and 2.15 Å are

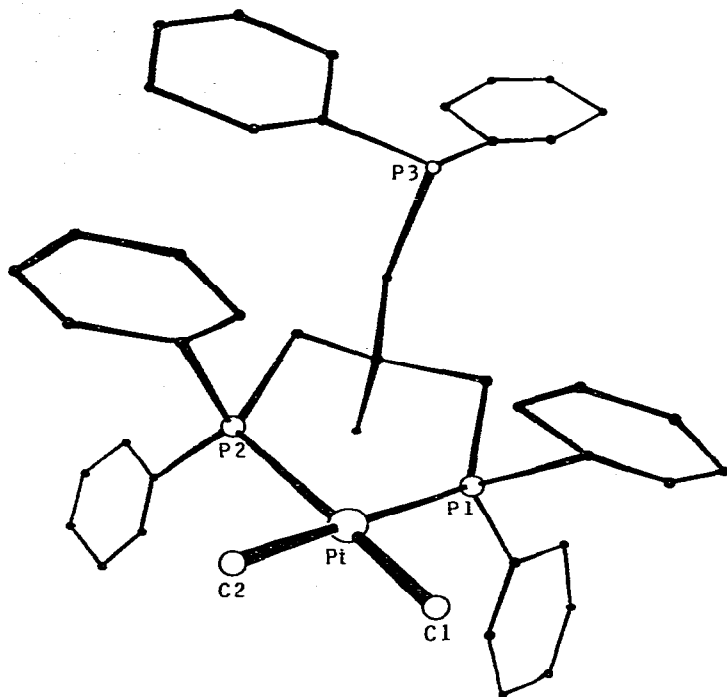


Fig. 2. A perspective view of the molecular structure of $\text{Pt}(\text{CH}_3)_2(\text{tripod})$.

long compared to the sum of the atomic radii [9], $\text{Pt}-\text{C}(\text{sp}^3)$ 2.09 Å; but they are very close to the $\text{Pt}-\text{C}$ distance (2.175(10) Å) of the $\text{PtCH}_2\text{COC}_6\text{H}_5$ unit in $\text{Pt}(\text{C}_6\text{H}_5)(\text{CH}_2\text{COC}_6\text{H}_5)(\text{diphos})$. However, the $\text{Pt}-\text{C}$ distances are 2.05(2) and 2.12(2) Å in $\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{PPh}_3)_2$. Also, the $\text{Pt}-\text{C}$ distance *trans* to a halide ion in some platinum(II) phosphine complexes (e.g., 2.086(7) Å in *trans*- $\text{Pt}(\eta^1\text{-C}_3\text{H}_5)\text{Br}(\text{PEt}_3)_2$ [10], 2.090(4) Å in *trans*- $\text{Pt}(\eta^1\text{-C}_3\text{H}_5)\text{Cl}(\text{PPh}_3)_2$ [11], 2.079(14) Å in *trans*- $\text{Pt}(\text{CH}_2\text{SiMe}_3)\text{Cl}(\text{PMe}_2\text{Ph})_2$ [12], and 2.07(1) Å in *trans*- $\text{Pt}(\text{Me})\text{Cl}(\text{PMePh}_2)_2$ [13] are short compared to the values found in this investigation. Although Pidcock et al. showed a correlation of bond length with $^1J(\text{Pt}-\text{P})$ for platinum(II) complexes [14], our data, $^1J(\text{Pt}-\text{P})$ 1818 Hz and the mean $\text{Pt}-\text{P}$ distance 2.27 Å, do not fit the trend. This may be attributed to the fact that the reported correlation does not take the *cis*-influence of ligands into account.

As shown in Fig. 2, the tripod ligand of $\text{Pt}(\text{CH}_3)_2(\text{tripod})$ is coordinated to the platinum atom in a bidentate fashion. One arm of the ligand is extended away from the platinum, similar to what was observed for each tripod ligand in $\text{Pt}(\text{tripod})_2$ [15]. In $\text{Pt}(\text{CH}_3)_2(\text{tripod})$ the non-coordinated or "dangling" phosphorus atom, P(3), is 6.29 Å from the Pt atom of the same molecule, and 7.18 Å from the Pt atom of the closest adjacent molecule at $x, 1/2 - y, 1/2 + z$. The closest intermolecular contact for P(3) is with a carbon atom of an adjacent phenyl ring. The methyl group of the tripod ligand projects over the coordination plane, but the $\text{Pt}-\text{C}$ distance of 4.04 Å indicates that there is no significant interaction between the metal and this methyl group.

The combined evidence of the X-ray, ^1H and ^{31}P NMR experiments shows that

in contrast to other platinum complexes with chelating triphosphine ligands that give transient, five-coordinate dimethylplatinum(II) complexes [5], the present complex is four-coordinate, with the fifth potential donor atom being nonbonded both in solution and in the solid state. The coordination behavior of the tripod ligand with dimethylplatinum(II) differs significantly from that of three other triphosphines $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, and $\text{PhP}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2$. The difference may be attributed to the structure of a trigonal-bipyramidal intermediate that leads to exchange of the terminal phosphino groups in the case of the three open-chained triphosphines. If tripod functions as a tridentate ligand, its structure requires that it bond to a face of a coordination polyhedron. Thus, tripod could not span the axial-equatorial-axial sites of a trigonal bipyramid, as can the three other triphosphines. Also, a facial arrangement of tripod in a trigonal-bipyramidal $\text{Pt}(\text{CH}_3)_2(\text{tripod})$ complex would force one of the methyl groups into an unfavorable axial coordination site.

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