

## Synthesis, X-Ray Crystal Structure and NMR Characterization of a Tetrahedral Methylmercury Complex with the Tripod Ligand $N(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$

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The complex  $[\text{Hg}(\text{np}_3)\text{Me}]\text{CF}_3\text{SO}_3$ , which is the first example of a methylmercury complex in an almost regular tetrahedral coordination, is obtained by the reaction of  $\text{np}_3$  [ $N(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ ] with  $(\text{HgMe})\text{CF}_3\text{SO}_3$ ; the complex has been studied by X-ray analysis in the solid state and NMR spectroscopy in solution.

Mercury and methylmercury complexes have been largely investigated owing to the growing concern about the complexation of mercury in the environment.<sup>1</sup> The  $\text{HgMe}^+$  ion has a strong tendency toward linear two-coordination, although for some complexes secondary (and weaker) interactions have been ascertained, mainly in the solid state.<sup>2</sup> Renewed interest for coordination numbers greater than two in methylmercury complexes stems from nature's mercury detoxification catalysts, which have been recently investigated.<sup>3</sup>

In this work, we report the complexation of the  $\text{HgMe}^+$  ion by the tripod-like ligand  $N(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  ( $\text{np}_3$ ). The latter, due to its flexibility, is known to stabilize several geometries, acting as a bi-, tri- or tetra-dentate ligand.<sup>4</sup>

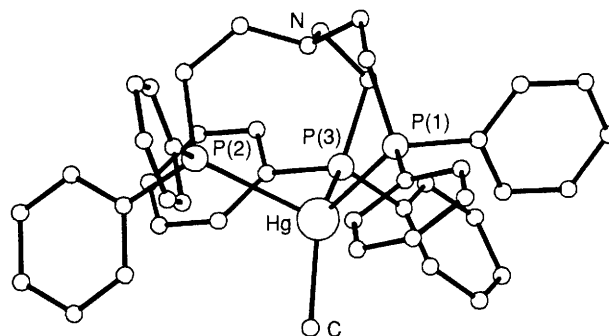
Equimolar addition of a toluene solution of  $\text{np}_3$  to a methylene chloride solution of  $(\text{HgMe})\text{CF}_3\text{SO}_3$ , at room temperature, resulted in the rapid, quantitative formation of the complex, which was isolated as colourless crystals of formula  $[\text{Hg}(\text{np}_3)\text{Me}]\text{CF}_3\text{SO}_3 \cdot \text{C}_7\text{H}_8$ , by solvent evaporation.<sup>†</sup>

The molecular structure<sup>‡</sup> of the complex, which has been established by a complete X-ray diffraction study, consists of

<sup>†</sup> Satisfactory C, H, N analyses were obtained. The complex is soluble in organic solvents, such as dichloromethane, acetone and methanol, but practically insoluble in water.

<sup>‡</sup> *Crystal data* for:  $\text{C}_{51}\text{H}_{53}\text{F}_3\text{HgNO}_3\text{P}_3\text{S}$ ,  $M = 1110.6$ , orthorhombic,  $Pb2_1a$ ,  $a = 34.491(12)$ ,  $b = 12.694(5)$ ,  $c = 11.184(5)$  Å,  $U = 4896.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.506$  g cm<sup>-3</sup>,  $F(000) = 2232$ ,  $\lambda(\text{Cu-K}\alpha) = 1.5418$  Å,  $\mu(\text{Cu-K}\alpha) = 78.2$  cm<sup>-1</sup>, Philips PW 1100 diffractometer,  $\omega$ - $2\theta$  scan,  $2\theta_{\text{max}} = 100^\circ$ . The structure was solved by the heavy atom method and refined by full-matrix least-squares procedures using SHELX76.<sup>5</sup> The phenyl rings were treated as rigid bodies and the hydrogen atoms were introduced in calculated positions and not refined. At convergence  $R$  and  $R_w$  factors are 0.060 and 0.059, respectively for 1753 observed [ $I > 3\sigma(I)$ ], absorption corrected reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

discrete  $[\text{Hg}(\text{np}_3)\text{Me}]^+$  cations,  $\text{CF}_3\text{SO}_3^-$  anions and toluene solvent molecules. A perspective view of the cation is shown in Fig. 1 together with selected bond distances and angles. Notwithstanding the great tendency of methylmercury to form strong collinear bonds, the nitrogen atom of the ligand *trans* to the methyl is definitely not coordinated, being 3.50(2) Å away. It is interesting to note that the  $\text{Hg}\cdots\text{N}$  distance is the longest ever found in complexes where  $\text{np}_3$  acts as tridentate ligand.<sup>4</sup> The three phosphorus atoms of the  $\text{np}_3$  ligand complete a slightly distorted tetrahedron around the metal with angles ranging from 97.1(3) to 121.6(9)°. As far as we know, this is the first example of a methylmercury complex containing the metal atom in a tetrahedral coordination geometry, albeit slightly distorted. The Hg-P bond distances appear rather long and one [2.808(7) Å] is significantly longer



**Fig. 1** Perspective view of the cation  $[\text{Hg}(\text{np}_3)\text{Me}]^+$  (PLUTO<sup>6</sup> drawing). Selected bond distances (Å) and angles (°): Hg-P(1) 2.600(8), Hg-P(2) 2.808(7), Hg-P(3) 2.615(9), Hg-C 2.18(3), Hg $\cdots$ N 3.50(2), P(1)-Hg-P(2) 100.6(3), P(1)-Hg-P(3) 100.7(3), P(2)-Hg-P(3) 97.1(3), P(1)-Hg-C 121.6(9), P(2)-Hg-C 111.0(9), P(3)-Hg-C 121.5(9).

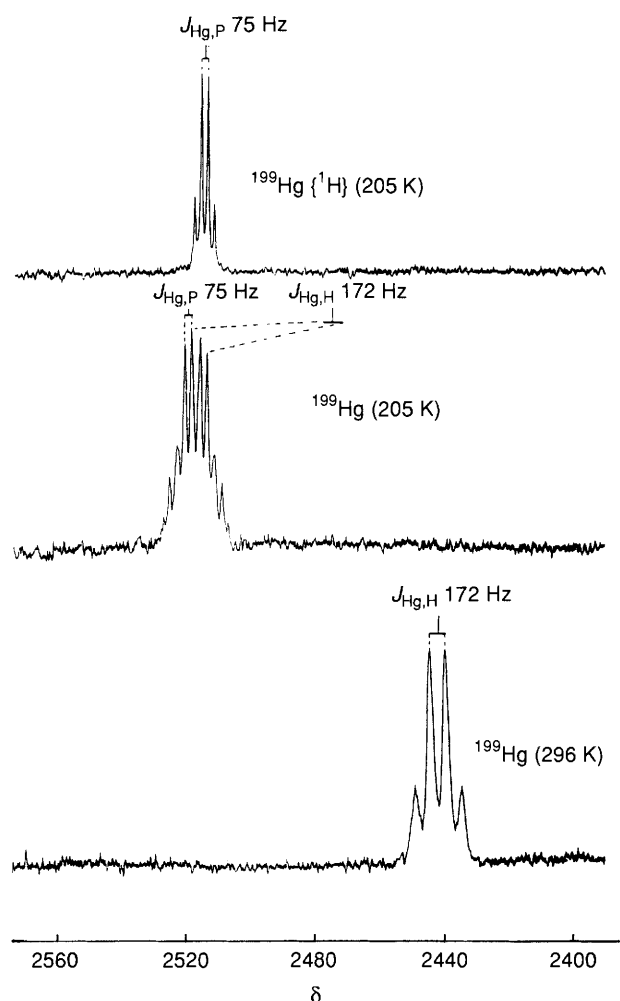


Fig. 2  $^{199}\text{Hg}$  NMR spectra of a solution of  $[\text{Hg}(\text{np}_3)\text{Me}]\text{CF}_3\text{SO}_3 \cdot \text{C}_7\text{H}_8$  ( $0.20 \text{ mol dm}^{-3}$ ) in  $\text{CH}_2\text{Cl}_2$  at 296 and 205 K. Chemical shifts are relative to external  $0.1 \text{ mol dm}^{-3} \text{Hg}(\text{ClO}_4)_2$  in  $0.1 \text{ mol dm}^{-3} \text{HClO}_4$ .

than the other two [2.600(8) and 2.615(9) Å]. The Hg–Me fragment is slightly distorted with respect to the pseudo threefold axis passing through the nitrogen and mercury atoms, the smallest P–Hg–C angle corresponding to the longest Hg–P distance.

The  $^{31}\text{P}$  and  $^{199}\text{Hg}$  NMR spectra of the complex in  $\text{CH}_2\text{Cl}_2$  solutions, show that the three phosphorus atoms of  $\text{np}_3$  are equivalent and coordinated to the mercury atom. However they are remarkably dependent on temperature and concentration, indicating the presence of dynamic processes.

The  $^{199}\text{Hg}$  NMR spectrum of a  $0.2 \text{ mol dm}^{-3}$  solution of the trifluorosulfonate, at 295 K (Fig. 2) is a broad quartet ( $^2J_{\text{Hg,H}}$  172 Hz); § at 205 K the signal, which is considerably shifted downfield, appears as a quartet of quartets ( $^2J_{\text{H,H}}$  172;  $^1J_{\text{Hg,P}}$  73 Hz). The Hg–P spin correlation is lost at ca. 230 K as shown by the  $^{31}\text{P}\{^1\text{H}\}$  variable temperature NMR spectra of the same solution, in the range 309–183 K (Fig. 3). Most probably, a rapid ligand dissociation occurs, this being responsible for the chemical exchange decoupling. The  $\text{np}_3$  dissociation has been confirmed by the  $^{31}\text{P}$  variable temperature NMR spectra of a complex solution, containing an excess of ligand. On the other hand, the rapid scrambling between the donor atoms of the ligand substrate is a peculiarity of the  $\text{HgMe}^+$  ion.<sup>7</sup>

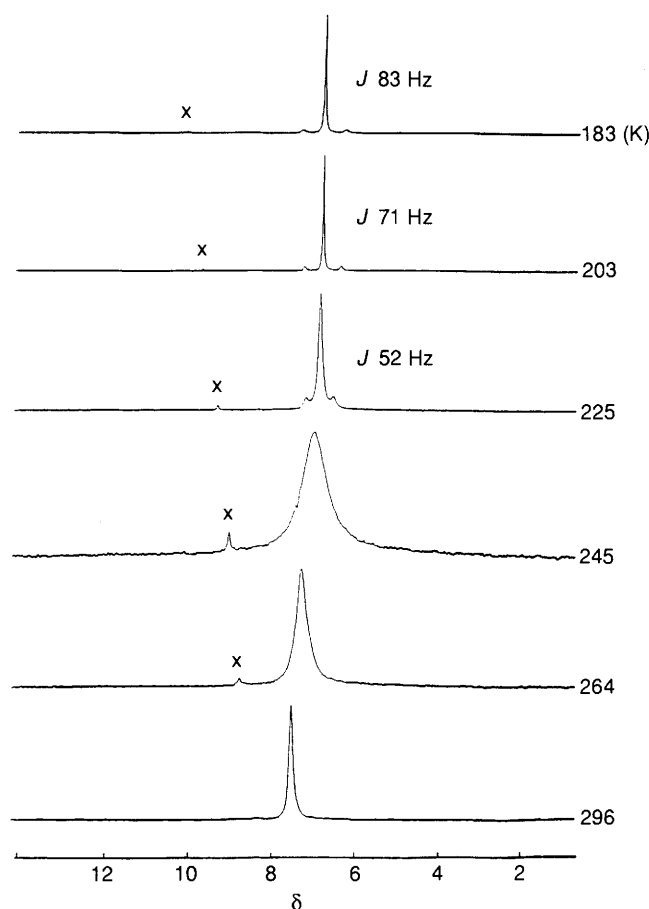


Fig. 3 Variable temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of a solution of  $[\text{Hg}(\text{np}_3)\text{Me}]\text{CF}_3\text{SO}_3 \cdot \text{C}_7\text{H}_8$  ( $0.15 \text{ mol dm}^{-3}$ ) in  $\text{CH}_2\text{Cl}_2$ . Chemical shifts are relative to external  $\text{H}_3\text{PO}_4$ . The signals marked by  $\times$  are due to impurities.

At temperatures  $< 230 \text{ K}$  the value of the  $^1J_{\text{Hg,P}}$  coupling constant, which is exceptionally small,<sup>¶</sup> continuously increases as the temperature drops. This value also increases when the concentration of the solution increases: *i.e.* at 225 K  $^1J_{\text{Hg,P}}$  is 47, 52, 57 and 70 Hz for solutions *ca.* 0.1, 0.15, 0.2 and  $0.4 \text{ mol dm}^{-3}$ , respectively. The variation of the coupling constant with the temperature generally is consistent with the presence of a rapidly interconverting set of isomers.<sup>9</sup> In the present case the  $^{31}\text{P}$  chemical shift at high frequencies seems to exclude the hypothesis of isomers containing uncoordinated phosphorus atoms. On the other hand, the small values of  $J_{\text{Hg,P}}$  could be related to the small *s* character of the phosphorus–mercury bonds, the Hg 6s orbital being mainly involved in the organometallic bond. A comparable small  $^1J_{\text{Hg,P}}$  (125 Hz) has been previously reported for the complex  $[\text{Hg}(\text{triphos})(\mu\text{-PPh}_2)\text{Cr}(\text{CO})_5]$  [triphos =  $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ].<sup>10</sup> A temperature dependence of the P–Hg–P angles and subsequently of the Hg–P hybridization may account for the  $^1J_{\text{Hg,P}}$  variation. However the concentration dependence, which seems to involve a more complicated intermolecular process, is still not clear. Further experimental measurements and calculations are in progress in order to rationalize the process.

§ The  $^1\text{H}$  NMR spectrum of the same solution shows a singlet at  $\delta 1.16$  due to Hg–Me with  $^{199}\text{Hg}$  satellites ( $^2J_{\text{Hg,H}}$  172 Hz).

¶ Interestingly the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the closely related pseudo-tetrahedral complex  $[\text{Hg}(\text{np}_3)\text{I}](\text{PF}_6)$  [P–Hg–P =  $107.7(3)$ – $109.9(3)^\circ$ ], in  $\text{CH}_2\text{Cl}_2$ , at room temperature, shows a singlet at  $\delta 7.7$ , with  $^{199}\text{Hg}$  satellites ( $J_{\text{Hg,P}}$  2696 Hz).<sup>8</sup>

This work has been partially supported by the Progetto Finalizzato, Chimica Fine II, CNR, Rome.

Received, 31st July 1992; Com. 2104140E

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