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Synthesis, characterization and X-ray structure of the organomercurial complex $[Hg(C_6F_5)(np_3)](CF_3SO_3)$, $np_3 = N(CH_2CH_2PPh_2)_3$

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Abstract

The tetrahedral complex $[Hg(C_6F_5)(np_3)](CF_3SO_3)$, $np_3 = N(CH_2CH_2PPh_2)_3$ has been prepared and characterized by single-crystal diffraction study and NMR spectroscopy (^1H, ^{31}P, ^{199}Hg). The crystal structure consists of $[Hg(C_6F_5)(np_3)]^+$ cations, $(CF_3SO_3)^-$ anions and dichloromethane solvent molecules. In the cation the mercury atom is coordinated to the three phosphorus atoms of the np_3 ligand and by a C_6F_5 molecule with a geometry very close to that of tetrahedral. The NMR measurements, in dichloromethane solution at room temperature, are fully consistent, showing the formation of linkages between the $Hg(C_6F_5)$ fragment and the three phosphorus atoms of the np_3, which are non-labile in the NMR time scale. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In organomercury compounds, mercury(II) forms two essentially collinear primary bonds and retains appreciable Lewis acidity in the plane perpendicular to these bonds through the availability of empty p orbitals. Recently, we reported [1] that the interaction of the organomercurial cations $[HgR]^+$ ($R = CH_3$, C_6H_5) with the tripodal ligand tris(2-diphenylphosphinoethyl)amine, np_3, affords the complexes $[HgR(np_3)]^+$ which display an unique pseudotetrahedral geometry around the mercury ion, both in solid state and in solution. These complexes are fluxional in solution, at room temperature, indicating a labile coordination of the phosphorus atoms.

Since the use of electron-withdrawing substituents is an efficient method for increasing the acceptor properties of the mercury center [2], we have prepared the derivative $[Hg(C_6F_5)(np_3)](CF_3SO_3)$, in order to obtain a non-fluxional tetrahedral complex.

The complex has been structurally characterized in the solid state by X-ray diffraction and in solution by multinuclear magnetic resonance.

2. Experimental

2.1. Materials

All reagents and solvents were commercial products of analytical grade and were used without purification. $(C_6F_5)HgBr$ was prepared according to a literature procedure [3].

2.2. Preparation of $[Hg(C_6F_5)(np_3)](CF_3SO_3)\cdot CH_2Cl_2$

All operations were carried out in a dry nitrogen atmosphere. $(C_6F_5)HgBr$ (0.45 g, 1 mmol) and

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$Ag(CF_3SO_3)$ (0.26 g, 1 mmol) were stirred together in acetone (20 ml) for 2 h. The reaction mixture was then filtered to remove the AgBr precipitate. Ligand np_3 (0.65 g, 1 mmol) was added to the filtrate and the solution was stirred for 15 min, *n*-butanol (10 ml) was then added. Concentration of the solution with a current of nitrogen allowed the precipitation of a small amount of colorless crystals of $(np_3)HgBr_2$ [4], which were filtered off. Further concentration afforded colorless microcystals of the title complex. These were filtered, washed with *n*-butanol and then with pentane and dried in a current of nitrogen. Recrystallization of the product from dichloromethane/toluene afforded a 45% yield (0.54 g) of $[Hg(C_6F_5)(np_3)](CF_3SO_3){\cdot}CH_2Cl_2$, as well-shaped crystals. *Anal.* Calc. for $C_{50}H_{44}Cl_2F_8HgO_3NP_3S$: C, 47.84; H, 3.53; N, 1.12. Found: C, 50.0; H, 3.65; N, 1.05%. ^1H NMR (CD_2Cl_2, 295 K): δ 7.9–7.0 (m, 30H, C_6H_5), 2.93 (m, 6H, CH_2), 2.47 (s, broad, 6H, CH_2).

2.3. Crystallography

Diffraction data were collected at room temperature on an Enraf–Nonius CAD4 automatic diffractometer and graphite monochromatized Mo Kα radiation. Unit cell parameters were determined from a least-squares refinement of the setting angles of 25 carefully centered reflections. Crystal data and data collection details are given in Table 1. On the basis of the systematic extinctions, the space groups *Pc* and *P*2/*c* were both possible, but the solution and the refinement of the structure confirmed the acentric *Pc* was the correct one. On the other hand, the presence in the asymmetric unit of two independent molecules almost equal, pressed us to control very accurately also the possibility of the *P*2/*c* space group. The intensities were rescaled and assigned a standard deviation $\sigma(I)$ calculated using the value of 0.03 for the instability factor *k* [5]. The intensities were corrected for Lorentz–polarization effects and an empirical absorption correction was applied [6]. All the calculations were performed in a Pentium processor, using the programs SIR-92 [7], SHELX-93 [8] and ORTEP [9]. Atomic scattering factors were taken from Ref. [10] and an anomalous dispersion correction, real and imaginary parts, was applied [11]. The structure was solved by direct methods and refined by full-matrix F^2 refinement, with anisotropic thermal parameters assigned to mercury and phosphorus atoms. Hydrogen atoms were introduced in their calculated positions riding on their carbon atoms with thermal parameters 20% larger than those of the respective carbon atoms. The absolute structure was established, as described for polar space groups by Flack [12]. The function minimized during the refinement was $\Sigma w(F_o^2 - F_c^2)^2$, with $w = 1/[\sigma^2(F_o^2) + (0.098P)^2 + 46.04P]$ where $P = (\max(F_o^2,0) + 2F_c^2)/3$. Some disorder was detected in the regions of the triflate anions and of chloromethane solvent molecules.

Table 1
Crystal data and structure refinement parameters for $[Hg(C_6F_5)(np_3)](CF_3SO_3){\cdot}CH_2Cl_2$

Empirical formula	$C_{50}H_{44}Cl_2F_8HgNO_3P_3S$
Formula weight	1255.32
Temperature (K)	293(2)
Wavelength (Å)	0.71070
Crystal system	monoclinic
Space group	*Pc*
Unit cell dimensions	
a (Å)	17.363(6)
b (Å)	10.280(6)
c (Å)	30.786(10)
α (°)	90.000
β (°)	104.01(3)
γ (°)	90.000
V (Å^3)	5332(3)
Z	4
D_{calc} (g cm^{-3})	1.564
Absorption coefficient (mm^{-1})	3.185
F(000)	2488
Crystal size (mm)	0.40 × 0.20 × 0.10
θ Range for data collection (°)	2.50–20.06
Index ranges	$-16 \le h \le 16$, $0 \le k \le 9$, $0 \le l \le 29$
Scan speed (° min^{-1})	1.49–8.24
Scan width	$0.8 + 0.35 \tan\theta$
Reflections collected	5098
Independent reflections	5098 [$R_{int} = 0.0000$]
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5098/2/438
Goodness-of-fit on F^2	1.034
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0660$, $wR_2 = 0.1591$
R indices (all data)	$R_1 = 0.1071$, $wR_2 = 0.1814$

2.4. NMR spectra

NMR spectra were recorded in 5 mm tubes, at 295 K, in a Bruker AC-200 spectrometer, operating at 200.13 MHz (^1H), 81.015 MHz (^{31}P) and 35.85 MHz (^{199}Hg). Chemical shifts are relative to internal TMS, external 85% H_3PO_4 and external 0.1 mol dm^{-3} $Hg(ClO_4)_2$ in 0.1 mol dm^{-3} $HClO_4$, respectively, with downfield values reported as positive.

3. Results and discussion

The crystal structure of the title compound consists of $[Hg(C_6F_5)(np_3)]^+$ cations, $(CF_3SO_3)^-$ anions and dichloromethane solvent molecules interspersed in the lattice. Fig. 1 shows a perspective view of one of the two crystallographically independent cationic molecules. Table 2 reports selected bond distances and angles.

In the asymmetric unit there are two independent complex cations (A and B), which substantially differ in

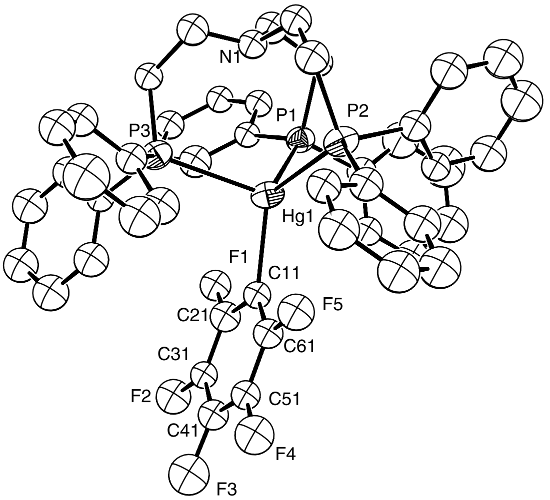


Fig. 1. Perspective view of the complex cation $[Hg(C_6F_5)(np_3)]^+$ (A). ORTEP drawing with 30% probability ellipsoids.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Hg(C_6F_5)(np_3)](CF_3SO_3)\cdot CH_2Cl_2$

Bond lengths	
Hg(1)–P(1)	2.584(13)
Hg(1)–P(2)	2.612(10)
Hg(1)–P(3)	2.603(10)
Hg(1)–C(1,1)	2.20(2)
Hg(1)···N(1)	3.31(2)
Hg(2)–P(4)	2.542(12))
Hg(2)–P(5	2.609(10)
Hg(2)–P(6)	2.616(10)
Hg(2)–C(1,8)	2.21(2)
Hg(2)···N(2)	3.28(2)
Bond angles	
C(1,1)–Hg(1)–P(1)	122.0(7)
C(1,1)–Hg(1)–P(2)	119.2(6)
C(1,1)–Hg(1)–P(3)	103.2(7)
P(1)–Hg(1)–P(2)	100.0(4)
P(1)–Hg(1)–P(3)	104.9(3)
P(2)–Hg(1)–P(3)	106.0(3)
C(1,8)–Hg(2)–P(4)	123.6(7)
C(1,8)–Hg(2)–P(5)	119.9(7)
C(1,8)–Hg(2)–P(6)	100.7(7)
P(4)–Hg(2)–P(5)	101.8(4)
P(4)–Hg(2)–P(6)	104.0(4)
P(5)–Hg(2)–P(6)	104.1(3)

the bending of the fluorobenzene group with respect to the N–Hg direction (N1–Hg1–C1,1 167.2, Hg1–C1,1–C4,1 166.1° (A), N2–Hg2–C1,8 163.9, Hg2–C1,8–C4,8 170.1° (B)). Such a different arrangement of the group C_6F_5 is likely to be ascribed to the presence of different contacts in the two molecules (the C_6F_5 group in molecule A displays a shorter contact with one triflate anion, F2···F14A = 2.77 Å). In each cation the mercury is surrounded by three phosphorus atoms of the tripodal np_3 ligand and by a C_6F_5 molecule with a geometry very close to that of tetrahedral, the central nitrogen atom being 3.30(2) Å apart. The bond distances and angles within the coordination sphere evidence a sort of distortion, which is perfectly following the trend observed for the series of Hg complexes containing the tripodal ligands np_3 [1,4,13,14], $trenMe_6$ ($trenMe_6 = N(CH_2CH_2NMe_2)_3$) [15] and ns_3 ($ns_3 = N(CH_2CH_2SCHMe_2)_3$) [16]. For such compounds a linear relationships between the N_{ap}–M–L_{eq} angles and the N_{ap}–M distance has been already described and rationalized [16]. Actually the increase of distortion of the trigonal bipyramid toward the tetrahedron parallels an increase of the Hg–N_{ap} apical bond till the rupture in the limit compound $[HgCH_3(np_3)]^+$ [1]. It is clear that the electronegativity and the sigma-bonding capabilities of the axial ligands *trans* to the apical nitrogen are the main determinant factors in such kind of distortion. Stronger is the bond of the ligand in axial position *trans* to the nitrogen, weaker is the linkage of the nitrogen, which shares with the other axial ligand a three center four electron bond.

The distortion of the coordination sphere of the title compound is evidenced by the values of the P_{eq}–Hg–C_{ax}, averaging 115(4)° and the values of the Hg–N and Hg–C bonds, respectively, of 3.30(1) and 2.205(5) Å. These values, together with the Hg–P of 2.59(1) Å, put the compound in the reported series immediately before the methyl-derivative $[HgCH_3(np_3)]^+$ [1] (see Table 3). As a matter of fact, the limit compound, which displays an almost regular tetrahedral coordination, shows a Hg–N bond definitively broken (3.50(2) Å), a short Hg–C bond (2.18(3) Å), a large Hg–P (2.67(7) Å) and the P_{eq}–Hg–C averaging 118(3)°. The sigma-bonding capability of the C_6F_5 group, where the presence of the strongly withdrawing fluorine increases the electronegativity of the whole fragment, is therefore weaker than that of the methyl group. Thus the metal s orbital, when involved with axial ligand of lower sigma-bonding capability, remains more available to the linkage with the other ligands, both apical and equatorial. (It is worth to recall that for mercury there are only four metal orbitals available for five bonds.)

The $^{199}Hg\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra, recorded at 295 K in dichloromethane solution, are shown in Fig. 2. The spectra have been analyzed according to the spin system $A_3QX_2Y_2Z$ by computer simulation and the spectral data are reported in Scheme 1.

The spectra clearly show that the three phosphorus atoms of np_3 are equivalent and coordinated to the HgC_6F_5 fragment in solution, at room temperature. The comparison of the values of the $^1J_{HgP}$ coupling constants within the homogeneous $[HgX(np_3)]^+$ series {X = Cl (3340 Hz) [4] > X = Br (3160 Hz) [4] > X = I (2780 Hz) [4] > X = C_6F_5 (1706 Hz) > X = C_6H_5 (418 Hz, 250 K) [1] > X = CH_3 (90 Hz, 195 K) [1]}, shows that the title complex is located between $[HgI(np_3)]^+$

Table 3
Mean [a] values of selected bond distances (Å) and bond angles (°) of the series $[HgX(np_3)]^+$ [b]

X	CF_3SO_3 [13]	I [4]	p-MeC_6H_4S [1]	C_6F_5 [this work]	Me [1]
Hg–N_{ap}	2.72(6)	3.13(1)	3.21(2)	3.30(1)	3.50(2)
Hg–X	2.63(4)	2.851(2)	2.543(7)	2.205(5)	2.18(3)
Hg–P (av.)	2.48(2)	2.53(1)	2.58(3)	2.59(1)	2.67(7)
P–Hg–X (av.)	102(5)	111(2)	112(5)	115(4)	118(3)

[a] The estimated error on the means was calculated according to the formula $[\Sigma_n(d_n-d)^2/n(n-1)]^{1/2}$.
[b] Sums of the covalent radii (Å): Hg–C = 2.26, Hg–I = 2.82; Hg–N = 2.24, Hg–O = 2.22, Hg–P = 2.58, Hg–S = 2.50 [17].

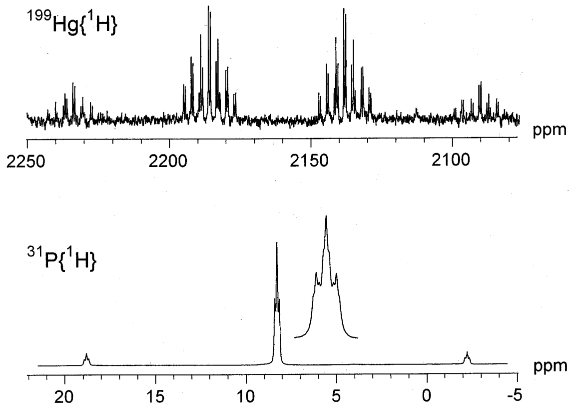
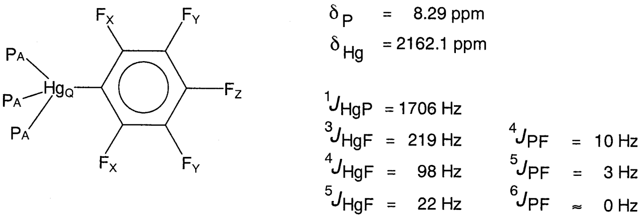


Fig. 2. $^{199}Hg\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of $[Hg(C_6F_5)(np_3)](CF_3SO_3)$, recorded at 295 K in CD_2Cl_2 solution.



Scheme 1.

and $[Hg(C_6H_5)(np_3)]^+$, according to the electron-withdrawing capability of the X ligand.

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 162521 for $[Hg(C_6F_5)(np_3)](CF_3SO_3)\cdot CH_2Cl_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) C.A. Ghilardi, P. Innocenti, S. Midollini, A. Orlandini, A. Vacca, J. Chem. Soc., Chem. Commun. (1992) 1691;
(b) P. Barbaro, F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca, Inorg. Chem. 33 (1994) 6163.
[2] (a) J.D. Werest, Acc. Chem. Res. 32 (1999) 91;
(b) M. Tschinkl, A. Schier, J. Riede, F.P. Gabbai, Organometallics 18 (1999) 2040.
[3] R.D. Chambers, G.E. Coates, J.G. Livingstone, W.K.R. Musgrave, J. Chem. Soc. (1962) 4367.
[4] F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini, Inorg. Chim. Acta 217 (1994) 155.
[5] P.W.R. Corfield, R.J. Doedens, J.A. Ibers, Inorg. Chem. 6 (1967) 197.
[6] S. Parkin, B. Moezzi, H. Hope, J. Appl. Crystallogr. 28 (1995) 53.
[7] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[8] G.M. Sheldrick, SHELX-93, University of Göttingen, Göttingen, Germany, 1993.
[9] C.K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976; as modified by L. Zsolnai and H. Pritzkow, Heidelberg University, 1994.
[10] A.J.C. Wilson (Ed.), International Tables for X-Ray Crystallography, vol. C, Kluwer Academic, Dordrecht, 1992, p. 500.
[11] A.J.C. Wilson (Ed.), International Tables for X-Ray Crystallography, vol. C, Kluwer Academic, Dordrecht, 1992, p. 219.
[12] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.
[13] F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca, J. Organomet. Chem. 510 (1996) 153.
[14] C.A. Ghilardi, C. Mealli, A. Orlandini, Coord. Chem. Rev. 120 (1990) 361.
[15] C.A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca, J. Organomet. Chem. 47 (1994) 29.
[16] F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini, Inorg. Chim. Acta 29 (1998) 274.
[17] (a) L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, NY, 1959;
(b) D. Grdenic, Q. Rev. Chem. Soc. 19 (1965) 303.