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Complexes of mercuric halides with the tripod ligand np_3 ($=N(CH_2CH_2PPh_2)_3$). Molecular structure of $[(np_3)HgI]I \cdot 0.5C_2H_5OH$

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Abstract

Complexes of formulae $[(np_3)HgX]X$ (X = Cl, Br, I) have been prepared by reaction of the tripod-like ligand np_3 ($=N(CH_2CH_2PPh_2)_3$) with mercury halides. The molecular structure of the iodide derivative has been established by a single crystal X-ray diffraction study: triclinic, $P\bar{1}$, $a=10.495(6)$, $b=12.246(7)$, $c=18.368(9)$ Å, $\alpha=106.55(3)$, $\beta=98.16(4)$, $\gamma=96.66(4)°$, $Z=2$, final conventional R value of 0.060. The metal atom displays a pseudo-tetrahedral geometry being coordinated to three phosphorus and one iodine atoms, the central nitrogens of the tripod ligand being 3.13(1) Å apart. The NMR spectra, which are in agreement with the solid state structure, show the presence of a dynamic process in solution.

Key words: Crystal structures; Mercury complexes; Polydentate ligand complexes; Chelate complexes

Introduction

In the past the magnitude of the directly bonded transition metal–phosphorus coupling constant (J(MP)) in transition metal phosphine complexes has been related to several factors. Among these we recall the number of the ligands: actually the value of the coupling constant generally decreases with increasing number of coordinated phosphorus atoms. Other elements such as the s-electron density at the metal nucleus or the s-character of the phosphorus lone pair orbital are proportionally related to J(MP). In this framework a number of phosphine complexes with mercury(II) as metal atom has been considered. In particular the monomeric pseudotetrahedral $Hg(PR_3)_nX_{4-n}$ complexes, which are the most investigated, show one-bond Hg–P coupling constant in the range 6300–2700 Hz [1].

Recently we have reported that the tripod-like ligand $N(CH_2CH_2PPh_2)_3$, np_3, forms pseudo-tetrahedral complexes of formula $[(np_3)HgR]^+$ (R = Me, Et, Ph), which show unusually low Hg–P one-bond couplings (30–400 Hz) [2, 3]. Now we report the preparation and characterization of the related halide derivatives $[(np_3)HgX]X$, X = Cl, Br, I. The complete X-ray crystal structure of the iodide derivative has been carried out.

Experimental

Solvents were purified and dried by standard methods. $^{31}P\{^1H\}$ NMR, Bruker ACP 200 (CH_2Cl_2, 85% H_3PO_4 as external reference); ^1H NMR, Bruker ACP 200 (CD_2Cl_2, TMS as internal reference); electric conductivities (nitroethane), Analytical Control 111 (Orion 990101 conductance cell); IR, Perkin-Elmer 1600 FTIR, (Nujol mulls).

Preparations

$[(np_3)HgI]I \cdot 0.5C_2H_5OH$ (1)

A solution of HgI_2 (0.45 g, 1 mmol) in 20 ml of acetone was added, at room temperature, to a solution of np_3 (0.65 g, 1 mmol) in 30 ml of the same solvent. Addition of 20 ml of ethanol and evaporation of the solvent in air, allowed the precipitation of colorless crystals. These were filtered off, washed with ethanol, then with petroleum ether. Yield 0.98 g (87%), δ_H (ppm) = 7.90–7.20(m), 3.66 (q, ^3J(HH) = 7 Hz), 2.85 (broad), 2.50 (broad), 1.19 (t, ^3J(HH) = 7 Hz). *Anal.* Calc. for $C_{43}H_{45}I_2HgNO_{0.5}P_3$: C, 45.65; H, 4.01; N, 1.23. Found: C, 45.30; H, 3.91 N, 1.23%.

$[(np_3)HgBr]Br \cdot H_2O$ (2)

The complex was prepared by the method used for the previous compound. Yield 90%; δ_H

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(ppm) = 7.90–7.10 (m), 3.0–2.25 (m, broad), 1.64 (s). *Anal.* Calc. for $C_{42}H_{44}Br_2HgONP_3$: C, 48.87; H, 4.29; N, 1.37. Found: C, 48.75; H, 4.35; N, 1.35%.

$[(np_3)HgCl]Cl \cdot H_2O$ (3)

The complex was prepared by the method used in the previous preparations. Yield 92%; δ_H (ppm) = 7.90–7.10 (m); 3.0–2.25 (m, broad); 1.67 (s). *Anal.* Calc. for $C_{42}H_{44}Cl_2HgONP_3$: C, 53.47; H, 4.70; N, 1.48. Found: C, 53.20; H, 4.70; N, 1.50%.

$[(np_3)HgI]BPh_4$ (4)

A solution of HgI_2 (0.45 g, 1 mmol) in acetone (10 ml) was added, at room temperature, to a solution of np_3 (0.65 g, 1 mmol) in acetone/dichloromethane (10/20 ml). Then a solution of $NaBPh_4$ (0.32 g, 1 mmol) in 30 ml of ethanol was added; after evaporation of the solvent in air colorless crystals precipitated. They were recrystallized from dichloromethane/ethanol. Yield 1.05 g (81%); δ_H (ppm) = 7.70–6.70 (m), 2.70–1.90 (m, broad). *Anal.* Calc. for $C_{66}H_{62}BIHgNP_3$: C, 60.93; H, 4.80; N, 1.08. Found: C, 61.05; H, 4.85; N, 1.10%.

Crystallography

Crystal data for $[(np_3)HgI]I \cdot 0.5C_2H_5OH$

$M = 2262.33$, triclinic, $P\bar{1}$, $a = 10.495(6)$, $b = 12.246(7)$, $c = 18.368(9)$ Å, $\alpha = 106.55(3)$, $\beta = 98.16(4)$, $\gamma = 96.66(4)°$, $V = 2209.34$ Å^3, $Z = 2$, $D_c = 1.700$ g/cm^3, μ(Mo Kα) = 50.0 cm^{-1}, $\lambda = 0.7107$ Å. A white regular prism of dimensions $0.15 \times 0.25 \times 0.70$ mm was mounted on an Enraf Nonius CAD4 automatic diffractometer. The unit cell were determined by a least-squares refinement of the setting angles of 24 reflections. Intensity data were collected by the ω–2θ scan method with a scan speed of 16.48° min^{-1} and a scan width = $0.8 + 0.35 \tan \theta$ within $2\theta < 40°$. After correction for decay (25%) the standard deviations $\sigma(I)$ were calculated by using the value of 0.03 for the instability factor k [4]. Data were corrected for Lorentz–polarization effects and for absorption [5]. 3300 reflections, with intensity larger than $3\sigma(I)$, were considered observed.

All the calculations were carried out on an HP 486 PC using the SHELX76 [6] and ORTEP [7] programs. Atomic scattering factors for the appropriate neutral atoms were taken for non-hydrogen and hydrogen atoms from refs. 8 and 9, respectively. Corrections for anomalous dispersion effects, real and imaginary parts, were applied to the calculated structure factors amplitudes [10]. The structure was solved by the heavy atom method and full-matrix least-squares refinements were carried out assigning anisotropic thermal parameters to mercury, iodine, phosphorus and nitrogen atoms and treating the phenyl rings as rigid groups. Hydrogen atoms were introduced in their calculated positions but not refined. The iodine atom out of the coordination sphere was found to be disordered, being located in two distinct positions with a population parameter of 0.5. Moreover a half molecule of ethanol is alternatively present in the same region with one of these iodine atoms (I_3). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, w being set equal to $1/\sigma^2(F_o)$. At convergence R and R_w factors are equal to 0.060 and 0.059, respectively. Final atomic parameters are given in Table 1.

Results and discussion

The reaction of np_3 with mercury halides in acetone/ethanol solution allows the formation of complexes of formulae $[(np_3)HgX]X$, X = Cl, Br, I. The $[(np_3)HgX]BPh_4$ derivatives can be prepared by simple methatetical reactions of **1**, **2** or **3** with $NaBPh_4$. All the compounds are air stable, colorless crystalline solids. These, with values of Λ_M (Ω^{-1} cm^2 mol^{-1}) in the range 72–60 for **1**–**3** and 50 for **4** (nitroethane solutions 10^{-3} M, 25 °C), behave as 1:1 electrolytes. The ^{1}H NMR spectra of the complexes show, in addition to the resonances due to the ligand protons, the signals of uncoordinated C_2H_5OH (**1**) or H_2O (**2**, **3**). Accordingly the IR spectra of the solid **1**–**3** show the expected absorption bands due to the O–H stretching vibrations of C_2H_5OH (**1**) or H_2O (**2**, **3**).

The molecular structure of **1** consists of discrete $[(np_3)HgI]^+$ cations, I^- anions and ethanol solvating molecules. Figure 1 shows a perspective view of the cation and selected bond distances and angles are reported in Table 2.

The metal atom displays a pseudo-tetrahedral geometry being coordinated to the three phosphorus atoms of the ligand and to the iodine, the central nitrogen of the tripod ligand being 3.13(1) Å apart. This value which is of the same order of the sum of the van der Waals radii [11] seems to exclude any significant bond interaction.

Neglecting the nitrogen atom the four ligands are arranged in an almost regular geometry with angles ranging from 107.3(1) to 113.8(1)°. The Hg–P bond distances (2.521(5)–2.555(7) Å) and Hg–I1 (2.851(2) Å) are fully comparable with the sum of the covalent radii. A wide range of values, 2.45–2.91 Å [12], has been reported for Hg–P distances in complexes of the type $[HgX_2(PPh_3)_2]$ confirming the easy deformability of the coordination sphere of a d^{10} metal ion.

It is interesting to compare the title compound with the closely related complex $[(np_3)HgCH_3]^+$, where the replacement of the iodine ligand with a methyl group induces in the chromophore very significant differences [2]. As a matter of fact the nitrogen ligand is completely expelled from the coordination sphere with an Hg–N separation of 3.50(2) Å, which is the largest ever found

TABLE 1. Positional (×10000) and thermal (×1000) parameters

Atom	x	y	z	U or U_{eq}[a]
Hg	1786(1)	2043(1)	3038(1)	41(1)*
I1	1442(2)	3127(1)	4575(1)	53(1)*
I2	2844(4)	3091(3)	9446(2)	79(2)*
I3	4319(6)	2365(4)	9395(3)	123(3)*
P1	3794(5)	1095(5)	3052(3)	43(2)*
P2	−201(5)	529(4)	2383(3)	41(3)*
P3	1978(6)	3421(5)	2229(3)	46(3)*
N	2055(17)	648(14)	1366(10)	50(9)*
C1	3124(21)	69(19)	1431(13)	56(6)
C2	4254(21)	755(18)	2101(12)	52(6)
C3	819(20)	−86(18)	1013(12)	47(6)
C4	210(22)	−572(18)	1592(13)	57(6)
C5	2336(19)	1637(16)	990(11)	40(5)
C6	1506(20)	2567(17)	1202(12)	46(6)
C7	6934(110)	3600(90)	9469(62)	172(40)
C8	5964(68)	2410(59)	9098(40)	116(22)
O	8364(57)	3489(46)	9729(33)	154(20)
C1,1	5222(12)	1977(12)	3683(9)	45(5)
C2,1	5124(12)	3004(12)	4232(9)	64(7)
C3,1	6248(12)	3721(12)	4701(9)	80(8)
C4,1	7470(12)	3411(12)	4621(9)	68(7)
C5,1	7569(12)	2385(12)	4072(9)	75(8)
C6,1	6445(12)	1667(12)	3603(9)	71(7)
C1,2	3571(17)	−218(14)	3313(8)	53(6)
C2,2	3664(17)	−1296(14)	2820(8)	75(8)
C3,2	3489(17)	−2274(14)	3063(8)	88(9)
C4,2	3221(17)	−2174(14)	3800(8)	97(9)
C5,2	3128(17)	−1096(14)	4293(8)	121(11)
C6,2	3303(17)	−118(14)	4049(8)	90(9)
C1,3	−1016(11)	−284(12)	2935(8)	39(5)
C2,3	−380(11)	−260(12)	3661(8)	62(7)
C3,3	−1005(11)	−849(12)	4094(8)	93(9)
C4,3	−2268(11)	−1462(12)	3799(8)	70(7)
C5,3	−2905(11)	−1487(12)	3073(8)	67(7)
C6,3	−2279(11)	−897(12)	2641(8)	65(7)
C1,4	−1433(14)	1156(9)	1944(8)	44(5)
C2,4	−2285(14)	536(9)	1257(8)	57(6)
C3,4	−3196(14)	1076(9)	920(8)	78(8)
C4,4	−3257(14)	2235(9)	1270(8)	79(8)
C5,4	−2405(14)	2855(9)	1958(8)	95(9)
C6,4	−1494(14)	2316(9)	2295(8)	56(6)
C1,5	990(15)	4556(13)	2395(8)	47(6)
C2,5	714(15)	5051(13)	3127(8)	59(6)
C3,5	36(15)	5982(13)	3257(8)	84(8)
C4,5	−367(15)	6419(13)	2655(8)	75(8)
C5,5	−92(15)	5925(13)	1922(8)	101(10)
C6,5	587(15)	4993(13)	1793(8)	89(9)
C1,6	3580(17)	4178(14)	2329(8)	47(6)
C2,6	4337(17)	4570(14)	3070(8)	81(8)
C3,6	5578(17)	5216(14)	3198(8)	119(11)
C4,6	6062(17)	5471(14)	2586(8)	96(9)
C5,6	5306(17)	5079(14)	1845(8)	95(9)
C6,6	4064(17)	4433(14)	1716(8)	73(7)

[a] U_{eq} (*) defined as one third of the trace of the orthogonalized thermal tensor.

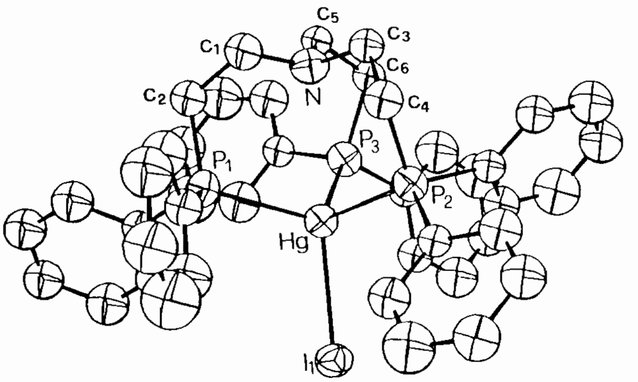


Fig. 1. Perspective view of the complex cation $[(np_3)HgI]^+$. ORTEP drawing with 30% probability ellipsoids.

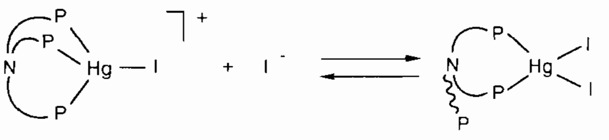
TABLE 2. Selected bond distances (Å) and angles (°)

Hg–P1	2.522(6)	P2–C1,4	1.79(2)
Hg–P2	2.521(5)	P3–C6	1.84(2)
Hg–P3	2.555(7)	P3–C1,5	1.81(2)
Hg–I1	2.851(2)	P3–C1,6	1.78(2)
Hg...N	3.131(15)	N–C1	1.40(3)
P1–C2	1.82(2)	N–C3	1.44(2)
P1–C1,1	1.78(2)	N–C5	1.57(3)
P1–C1,2	1.80(2)	C1–C2	1.55(3)
P2–C4	1.82(2)	C3–C4	1 54(3)
P2–C1,3	1.84(2)	C5–C6	1.51(3)
P1–Hg–P2	109.5(2)	C1,3–P2–C1,4	106.1(7)
P1–Hg–P3	108.2(2)	Hg–P3–C6	108.3(7)
P2–Hg–P3	107.3(2)	Hg–P3–C1,5	116.6(6)
I1–Hg–P1	110.6(1)	Hg–P3–C1,6	115.2(6)
I1–Hg–P2	107.3(1)	C6–P3–C1,5	107.0(8)
I1–Hg–P3	113.8(1)	C6–P3–C1,6	105.5(9)
Hg–P1–C2	109.9(8)	C1,5–P3–C1,6	103.5(8)
Hg–P1–C1,1	114.9(5)	C1–N–C3	115.2(16)
Hg–P1–C1,2	112.9(6)	C1–N–C5	111.8(17)
C2–P1–C1,1	103.8(8)	C3–N–C5	112.4(16)
C2–P1–C1,2	108.4(9)	P1–C2–C1	113.9(16)
C1,1–P1–C1,2	106.3(8)	C2–C1–N	113.7(17)
Hg–P2–C4	109.5(7)	P2–C4–C3	113.7(15)
Hg–P2–C1,3	120.3(5)	C4–C3–N	111.7(17)
Hg–P2–C1,4	109.8(4)	P3–C6–C5	111.3(14)
C4–P2–C1,3	104.6(9)	C6–C5–N	112.9(17)
C4–P2–C1,4	105 5(9)		

in complexes where np_3 acts as tridentate ligand [13]. This difference seems well explained on the basis of the stronger σ-donor capability of the methyl with respect to the more electronegative iodide. Moreover the Hg–P distances in the methylmercury derivative (2.600(8)–2.808(7) Å) are significantly larger than those reported in the title compound.

The above differences are in agreement with the NMR results (*vide infra*). As a matter of fact the coupling constants of the compounds considered (halides and methyl derivative) present values increasing with the electronegativity of the axial ligand (chloride (3340 Hz) > bromide (3160 Hz) > iodide (2780 Hz) > methyl (30–90 Hz)). It is known that the magnitude of the directly bonded coupling constant J(MP) is closely related, according to a relation of direct proportionality, to the s character of the metal hybrid and of the phosphorus lone pair [14]. On the other hand the larger the electronegativity of the axial ligand, the larger is the s character of the metal hybrid orbital, which remains available for the equatorial linkages. It ensues that in the iodide complex there are shorter Hg–P bonds and a stronger J(HgP) than in the methyl derivative.

Each room temperature $^{31}P\{^1H\}$ NMR spectrum of the complexes consists of a broad singlet ($\delta_P = -4.5$ (**1**), 3.7 (**2**) and 8.4 (**3**) ppm) flanked by quite broad, collapsing ^{199}Hg satellites. These data indicate a dynamic process. Indeed at 230 K the slow exchange limit has been reached, the spectra showing a sharp singlet with ^{199}Hg satellites: $\delta_P = -4.0$ ppm, ^1J(HgP) = 2780 Hz (**1**); $\delta_P = 4.4$ ppm, ^1J(HgP) = 3160 Hz (**2**); $\delta_P = 9.3$ ppm, ^1J(HgP) = 3340 Hz (**3**); since free np$_3$ shows $\delta_P = -21$ ppm (CD_2Cl_2) the coordination shifts are respectively 17 (**1**), 25.4 (**2**) and 30.3 (**3**) ppm. The values of the chemical shifts and those of the coupling constants decrease and increase, respectively, with the electronegativity of the halogens. The order of these variations is the same as has been previously observed in related mono-tertiary phosphine Hg(II)–halide complexes [15]. Concerning the temperature dependence of the NMR spectra, the dissociation of the ligand np$_3$ could account for the spectroscopic results. However, we have ascertained that this dynamic process is due to the presence in solution of halide ions. As a matter of fact we have found that the ^{31}P NMR spectrum of the CD_2Cl_2 solution of the complex [(np$_3$)HgI]BPh$_4$ shows a sharp signal, also at room temperature, ($\delta_P = -5.7$ ppm, ^1J(HgP) = 2700 Hz). When iodide ions (Bu$_4$NI) are added to the latter solution the resulting spectra are virtually identical to those of complex **1**. Then it appears likely to suggest a rapid exchange reaction of the following type, the equilibrium lying sharply to the left:



Complexes **2** and **3** have been found to show a completely analogous behavior.

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