Inorg. Chem. **1994**, *33*, 6163–6170

Metal Coordination and Hg–C Bond Protonolysis in Organomercury(II) Compounds. Synthesis, Characterization, and Reactivity of the Tetrahedral Complexes $[(np_3)HgR][(CF_3)SO_3]$ $\{np_3 = N(CH_2CH_2PPh_2)_3;\ R = CH_3,\ C_2H_5,\ C_6H_5\}$

Pierluigi Barbaro,[†] Franco Cecconi,[†] Carlo A. Ghilardi,[†] Stefano Midollini,*,[†] Annabella Orlandini,[†] and Alberto Vacca[‡]

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi, 39, I-50132 Firenze, Italy, and Dipartimento di Chimica, Università di Firenze, I-50144 Firenze, Italy

Received July 7, 1994[®]

The tetrahedral complexes $[(np_3)HgR][(CF_3)SO_3]$ ($np_3 = N(CH_2CH_2PPh_2)_3$, $R = CH_3$, C_2H_5, C_6H_5) have been prepared and characterized by NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{199}Hg) and X-ray crystal structure analyses. The reactivity of the methyl and phenyl derivatives toward CH_3COOH (or CF_3COOH) and thiols has been investigated through GC and/or NMR measurements. In both cases protonolysis of the Hg–C bond occurs at valuable rates, under mild conditions, with formation of alkane (arene) and $[(np_3)HgX][(CF_3)SO_3]$ or $[(np_3)Hg(SR)][(CF_3)SO_3]$ ($X = CH_3COO$, CF_3COO; $R = C_6H_5$, p-$CH_3C_6H_4$, $C(CH_3)_3$). Kinetics of the acetolysis suggests that, although the coordination of the three phosphorus atoms to the metal center does not substantially change the accepted mechanism of the protonolysis of the organomercurials, the resulting activation of the Hg–C bond strongly accelerates the cleavage reaction. In the case of the reaction with thiols the mechanism appears more complicated, the basicity of the amino group of np_3 playing a determining role. Crystallographic data are as follows: $[(np_3)Hg(CH_3)][(CF_3)SO_3]$·toluene, **3**, $Pb2_1a$, $a = 34.491(12)$ Å, $b = 12.694(5)$ Å, $c = 11.184(5)$ Å, $Z = 4$, $R = 0.060$, $R_w = 0.059$; $[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}][(CF_3)SO_3]$, **9**, $P2_1/a$, $a = 17.509(9)$ Å, $b = 16.805(7)$ Å, $c = 17.870(8)$ Å, $\beta = 113.83(6)°$, $Z = 4$, $R = 0.067$, $R_w = 0.066$. In both complexes the metal displays a distorted tetrahedral geometry, with the nitrogen atom of the tripod ligand being uncoordinated.

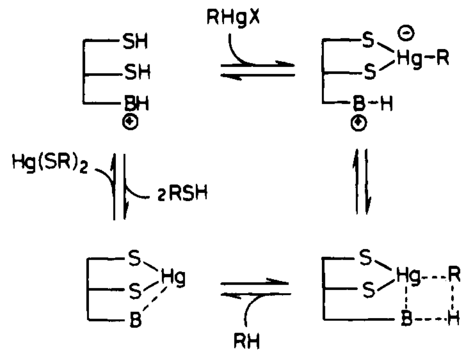
Introduction

The pollutant agent methylmercury(II) is especially dangerous since its lipophilic nature gives it a strong tendency toward bioaccumulation in the food chain.[1] Unfortunately the cleavage of the Hg–C bond in organomercury(II) salts is a quite difficult task. As a matter of fact it was known for several years that RHgX compounds (X = halide, pseudohalide, acetate, etc.; R = alkyl, aryl) virtually do not react with glacial acetic acid, the protonolysis occurring only by attack at high temperatures of strong mineral acids, such as HCl, $HClO_4$, and H_2SO_4.[2]

Recently it has been found that some bacteria have developed a strategy to detoxyficate, in mild conditions, organomercury(II) salts through enzymatic processes. The coordination of the organomercury(II) ion by one or more nucleophilic residues, in the organomercurial lyase active site, is agreed to be the initial step of the Hg-C bond cleavage process (Scheme 1).[3] On the other hand also the proposed mechanism for the symmetrization of arylmercuric salts is agreed to involve the coordination of the metal center by chelating agents.[4] These, by donating their lone-pair electrons to the mercury atom should enhance the Hg–C bond nucleophilicity, strongly favoring the attack by the electrophile agent and then the cleavage of the bond itself. Finally the nucleophilic acceleration of the bromolysis of alkylmercury bromides has been previously ascertained.[5]

Therefore it seems that the problem of the Hg–C bond cleavage is closely related to the coordination of the metal by a strongly donating ligand. However, as far as we know, the literature shows that the $[RHg]^+$ compounds, almost invariably, contain the metal in a linear dicoordinated geometry;[6] only some

Scheme 1[a]



[a] Reprinted with permission from ref 3.

[†] ISSECC-CNR.

[‡] Università di Firenze.

[®] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

(1) Summers, A. O.; Silver, S. *Annu. Rev. Microbiol.* **1978**, *32*, 637. Craig, P. J.; Mennie, D.; Bartlett, P. D. In *The Chemistry of the Copper and Zinc Triads*; Welch, A. J., Chapman, K., Eds.; The Royal Society of Chemistry: Cambridge 1993; pp 62–81 and references therein.

(2) (a) Jensen, F. R.; Rickborn, B. In *Electrophilic Substitution of Organomercurials*; Mc Graw-Hill: New York, 1968. (b) Makarova, L. G.; Nesmeyanov, A. N. In *Methods of Elemento-Organic Chemistry*; Nesmeyanov, A. N.; Kocheshkov, K. E., Eds.; North Holland: Amsterdam, 1967; Vol. 4. (c) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson G., Ed.; Pergamon Press: Oxford, 1982, Vol. 2, pp 863. (d) Corwin, A. H.; Naylor, M. A., Jr.; *J. Am. Chem. Soc.* **1947**, *69*, 1004. (e) Winstein, S.; Traylor, T. G. *J. Am. Chem. Soc.* **1955**, *77*, 3447. (f) Kreevoy, M. M. *J. Am. Chem. Soc.* **1957**, *79*, 5927. Kreevoy, M. M.; Hansen, R. L. *J. Am. Chem. Soc.* **1961**, *83*, 626. (g) Dessy, R. E.; Kim, J. Y. *J. Am. Chem. Soc.* **1961**, *83*, 1167.

(3) Moore, M. J.; Distefano, M. D.; Zydowsky, L. D.; Cummings, R. J.; Walsh, C. T. *Acc. Chem. Res.* **1990**, *23*, 301 and references therein.

(4) Halpern, Y.; Garti, N. *J. Organomet. Chem.* **1975**, *92*, 291. Jensen, F. J.; Rickborn, B.; Miller, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 340.

(5) Sayre, L. M.; Jansen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 6001.

0020-1669/94/1333-6163$04.50/0

further secondary interactions have been proved by X-ray structural analyses in few methylmercury complexes, mostly with chelating nitrogen donors.[7]

We report here the synthesis, the characterization and reactivity of the first examples of tetrahedral complexes of the $[RHg]^+$ ion (R = Me, Et, Ph), with the tripodal ligand tris(2-diphenylphosphinoethyl)amine, np$_3$. The complete X-ray structure determinations for the $[(np_3)Hg(CH_3)][(CF_3)SO_3]$ and $[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}][(CF_3)SO_3]$ derivatives are reported.

The only previously reported, well characterized phosphine–organomercury complex was the dicoordinated $[(PPh_3)HgPh]NO_3$.[8]

Preliminary accounts of part of this work have already been published.[9]

Experimental Section

General Data. All the solvents and chemicals were reagent grade and were used as received by commercial suppliers. The organomercurials CH_3HgI, $(C_6H_5)HgCl$, $(C_2H_5)_2Hg$, and $(C_6H_5)_2Hg$ were purchased from Strem Chem. and used without further purification. Deuterated solvents for NMR measurements (Merck) were dried over molecular sieves. Proton and $^{13}C\{^1H\}$ NMR spectra were recorded at 200.13 and 50.32 MHz respectively, on a Bruker AC-200 spectrometer. Peak positions are relative to tetramethylsilane as external reference. $^{31}P\{^1H\}$ and $^{199}Hg\{^1H\}$ NMR spectra were recorded on the same instrument operating respectively at 81.015 and 35.85 MHz. Chemical shifts are relative to 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. $^{19}F\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 spectrometer operating at 282.18 MHz. Chemical shifts are relative to fluorotrichloromethane, as external reference, with downfield values reported as positive. Conductivities were measured with an Orion Model 990101 conductance cell, connected to a Model 101 conductivity meter. The conductivity data were obtained using sample concentrations of ca. 1×10^{-3} M, in nitroethane solution, at room temperature (293 K). GC analyses were performed on a Shimadzu GC-14A gas cromatograph, equipped with a flame ionization detector and a 30m (0.25 mm i.d., 0.25 μm FT) SPB-1 Supelco fused silica capillary column.

Caution! Organomercurials are extremely toxic, and all experimentation involving these reagents should be carried out in a well-vented fume hood.

Synthesis of the Complexes. All reactions and manipulations were routinely performed under a nitrogen atmosphere, unless otherwise noted. The solid compounds were collected on a sintered-glass frit and washed with ethanol and petroleum ether (bp 323–343 K) before being dried under a stream of nitrogen.

$[(CH_3)Hg(DMSO)][(CF_3)SO_3]$, 1. Solid $Ag[(CF_3)SO_3]$ (257 mg, 1mmol) was added to a solution of $(CH_3)HgI$ (342 mg, 1 mmol) in methanol (20 mL). The mixture was stirred in the dark for 3 h, then AgI was filtered off. The solvent was removed from the filtrate under a vacuum, at room temperature, to leave a colorless material, which was dissolved in dichloromethane (25 mL). The solution was again filtered and DMSO (107 μL, 1.5 mmol) was added. Concentration and addition of *n*-hexane (20 mL) allowed the precipitation of a colorless microcrystalline product (yield 368 mg, 83%). Anal. Calcd for $C_4H_9F_3HgO_4S_2$: C, 22.66; H, 2.94; S, 16.50. Found: C, 22.55; H, 3.05; S, 16.35. ^1H NMR (CD_2Cl_2, 293 K): δ 2.98 ppm (s, 6H, CH_3S), 1.24 ppm (s with satellites, 3H, CH_3Hg, $^2J_{HgH}$ = 254 Hz).

$[(C_6H_5)Hg(DMSO)][(CF_3)SO_3]\cdot DMSO$, 2. A solution of $(C_6H_5)_2Hg$ (355 mg, 1 mmol) in THF (20 mL) was added to a solution of HgI_2 (454 mg, 1 mmol) in acetone (15 mL). After the solution became colorless, solid $Ag[(CF_3)SO_3]$ (257 mg, 1 mmol) was added. The mixture was stirred for 3 h, then AgI was filtered off. DMSO (178 μL, 2.5 mmol) was added to the filtrate and the solvent was removed under a vacuum, at room temperature, to give colorless crystals (yield 461 mg, 79%). Anal. Calcd for $C_{11}H_{17}F_3HgO_5S_3$: C, 22.66; H, 2.94; S, 16.50. Found: C, 22.50; H, 3.00; S, 16.40. ^1H NMR (CD_2Cl_2, 293 K): δ 8.15–6.75 ppm (m, 5H, C_6H_5), 2.72 ppm (s, 12H, CH_3S).

$[(np_3)Hg(CH_3)][(CF_3)SO_3]\cdot toluene$, 3. A solution of methylmercury triflate (1 mmol) in dichloromethane (20 mL) was prepared as previously described for the synthesis of $[(CH_3)Hg(DMSO)][(CF_3)SO_3]$, except for the addition of DMSO. A solution of np$_3$ (654 mg, 1 mmol) in toluene (20 mL) was added at room temperature. Evaporation of the solvent in a current of nitrogen afforded colorless crystals (yield 966 mg, 87%). Anal. Calcd for $C_{51}H_{53}F_3HgNO_3P_3S$: C, 55.15; H, 4.81; N, 1.26. Found: C, 55.20; H, 4.95; N, 1.20. Selected NMR data (CD_2Cl_2): ^1H (solution 0.05 M, 293 K) δ 1.18 ppm (s with satellites, $^2J_{HgH}$ = 174 Hz, CH_3Hg); $^{13}C\{^1H\}$ (solution 0.1 M, 223 K) δ 1.28 ppm (q, $^2J_{PC}$ = 32 Hz, CH_3Hg); $^{31}P\{^1H\}$ (solution 0.15 M, 203 K) δ 6.70 ppm (s with satellites, $^1J_{HgP}$ = 71 Hz); $^{199}Hg\{^1H\}$ (solution 0.2 M, 205 K) δ 2415 ppm (q, $^1J_{HgP}$ = 75 Hz).

$[(np_3)Hg(C_2H_5)][(CF_3)SO_3]\cdot$*n*-BuOH, 4. A solution of $(C_2H_5)_2Hg$ (259 mg, 1 mmol) in acetone (10 mL) was added, at room temperature, to a solution of HgI_2 (454 mg, 1 mmol) in the same solvent (10 mL). After the solution became colorless, $Ag[(CF_3)SO_3]$ (257 mg, 1 mmol) was added. The mixture was stirred for 3 h, then AgI was filtered off. A solution of np$_3$ (654 mg, 1 mmol) in acetone (10 mL) was added to the filtrate. Addition of *n*-butanol (20 mL) and evaporation of the solvent in a current of nitrogen afforded colorless crystals (yield 940 mg, 85%). Anal. Calcd for $C_{49}H_{57}F_3HgNO_4P_3S$: C, 53.18; H, 5.19; N, 1.26. Found: C, 53.05; H, 5.25; N, 1.30. Selected NMR data (CD_2Cl_2): ^1H (solution 0.05 M, 293 K) δ 2.12 ppm (q, $^3J_{HH}$ = 8 Hz, CH_3CH_2Hg), 1.60 ppm (t, CH_3CH_2Hg); $^{13}C\{^1H\}$ (solution 0.15 M, 293 K) δ 20.70 ppm (s, br, CH_3CH_2Hg), 17.93 ppm (s with satellites, $^2J_{HgC}$ = 88 Hz, CH_3CH_2Hg); $^{31}P\{^1H\}$ (solution 0.15 M, 243 K) δ 9.30 (s with satellites, $^1J_{HgP}$ = 443 Hz); $^{199}Hg\{^1H\}$ (solution 0.15 M, 243 K) δ 2380 ppm (q, $^1J_{HgP}$ = 443 Hz).

$[(np_3)Hg(C_6H_5)][(CF_3)SO_3]\cdot 0.25THF$, 5. A solution of np$_3$ (654 mg, 1 mmol) in acetone (10 mL) was added to a solution of phenylmercury triflate (1 mmol) in a mixture of acetone (15 mL) and THF (15 mL), prepared as above described for the synthesis of $[(C_6H_5)Hg(DMSO)][(CF_3)SO_3]\cdot DMSO$. Further addition of *n*-butanol and solvent evaporation allowed the precipitation of colorless crystals (yield 912 mg, 83%). Anal. Calcd for $C_{50}H_{49}F_3HgNO_{3.25}P_3S$: C, 54.66; H, 4.50; N, 1.27. Found: C, 54.60; H, 4.55; N, 1.25. Selected NMR data (CD_2Cl_2): $^{13}C\{^1H\}$ (solution 0.15 M, 293 K)(C_6H_5–Hg moiety) δ 162.5 ppm (q, $^2J_{PC}$ = 45 Hz, Cα), 140 ppm (q with ^{199}Hg satellites, $^3J_{PC}$ = 3 Hz, $^2J_{HgC}$ = 86 Hz, C*o*), 129 Hz (q with satellites, $^4J_{PC}$ = 2 Hz, $^3J_{HgC}$ = 175 Hz, C*m*), 127 ppm (s with satellites, $^4J_{HgC}$ = 32 Hz, C*p*)(the ^{199}Hg satellites of the Cα resonance were not observed due to the low intensity of the signal); $^{31}P\{^1H\}$ (solution 0.1 M, 294 K) δ 8.0 ppm (s with satellites, $^1J_{HgP}$ = 317 Hz); $^{199}Hg\{^1H\}$ (solution 0.1 M, 292 K) δ 2225 ppm (q, $^1J_{HgP}$ = 318 Hz).

$[(np_3)Hg(OOCCH_3)][(CF_3)SO_3]$, 6. CH_3COOH (57.5 μL, 1 mmol) was added to a solution of **5** (1098 mg, 1 mmol) in dichloromethane (20 mL), at room temperature. After the mixture was allowed to stand for 24 h in the dark, *n*-butanol (15 mL) was added and the solvent was evaporated in a current of nitrogen till colorless crystals precipitated (yield 860 mg, 81%). Anal. Calcd for $C_{45}H_{45}F_3HgNO_5P_3S$: C, 50.87; H, 4.26; N, 1.32. Found: C, 50.75; H, 4.25; N, 1.25. Selected NMR data (CD_2Cl_2, solution 0.02 M 293 K): ^1H δ 2.17 (s, CH_3C); $^{31}P\{^1H\}$ δ 12.4 ppm (s with satellites, $^1J_{HgP}$ = 3480 Hz).

$[(np_3)Hg(OOCCF_3)][(CF_3)SO_3]\cdot 0.25$*n*-BuOH, 7. The complex was prepared with the same method used for **6** (yield 942 mg, 83%). Anal. Calcd for $C_{46}H_{44.5}F_6HgNO_{5.25}P_3S$: C, 48.67; H, 3.95; N, 1.23. Found:

---

(6) (a) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson G., Ed.; Pergamon Press: Oxford, 1982; Vol. 2, p 901. (b) Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1993**, 3117 and references therein.

(7) (a) Canty, A. J.; Lee, C. V. *Organometallics* **1982**, *1*, 1063. (b) Canty, A. J.; Chaichit, N.; Gatehouse, B. M.; George E. E. *Inorg. Chem.* **1981**, *20*, 4293. (c) Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 2201. (d) Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Vacca, A. *J. Organomet. Chem.* **1994**, 471, 29.

(8) Lobana, T. S.; Sandhy, M. K.; Povey, D. C.; Smith, G. W. *J. Chem. Soc., Dalton Trans.* **1988**, 1913.

(9) Ghilardi, C. A.; Innocenti, P.; Midollini, S.; Orlandini, A.; Vacca, A. *J. Chem. Soc., Chem. Commun.*, **1992**, 1691. Ghilardi, C. A.; Midollini, S.; Orlandini, A. In *The Chemistry of the Copper and Zinc Triads*; Welch, A. J., Chapman, S. K., Eds.; The Royal Society of Chemistry: Cambridge, England, 1993; pp 141–144.

C, 48.70; H, 4.05; N, 1.30. Selected NMR data: $^{19}F\{^{1}H\}$ (acetone, solution 0.02 M, 293 K) δ −73.5 ppm (s, CF_3C), −78.0 ppm (s, CF_3S); $^{31}P\{^{1}H\}$ (CD_2Cl_2, solution 0.02 M, 293 K) δ 15.9 ppm (s with satellites, $^{1}J_{HgP}$ = 3700 Hz).

$[(np_3)Hg\{S(C_6H_5)\}][(CF_3)SO_3]$, 8. $(C_6H_5)SH$ (102 μL, 1 mmol) was added, at room temperature to a solution of **5** (1098 mg, 1 mmol) in dichloromethane (20 mL). After the mixture was allowed to stand for 24 h, benzene (25 mL) was added and the solvent was evaporated in a current of nitrogen till colorless crystals precipitated (yield 877 mg, 78%). Anal. Calcd for $C_{49}H_{47}F_3HgNO_3P_3S_2$: C, 52.89; H, 4.25; N, 1.26; S, 5.76. Found: C, 52.80; H, 4.30; N, 1.30; S, 5.65. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, solution 0.05 M, 293 K): δ 7.01 ppm (s with satellites, $^{1}J_{HgP}$ = 1845 Hz).

$[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}][(CF_3)SO_3]$, 9. The complex was prepared with the same method used for **8** (yield 893 mg, 80%). Anal. Calcd for $C_{50}H_{49}F_3HgNO_3P_3S_2$: C, 53.30; H, 4.38; N, 1.24; S, 5.69. Found: C, 53.25; H, 4.45; N, 1.20; S, 5.60. Selected NMR data (CD_2Cl_2, solution 0.033 M, 293 K): ^{1}H δ 2.18 ppm (s with satellites, $^{7}J_{HgH}$ = 15 Hz); $^{31}P\{^{1}H\}$ δ 6.98 ppm (s with satellites, $^{1}J_{HgP}$ = 1776 Hz).

$(C_6H_5)Hg\{S(p\text{-}CH_3C_6H_4)\}$, 10. A solution of $Na\{S(p\text{-}C_6H_4CH_3)\}$ (146 mg, 1 mmol) in methanol (15 mL) was added dropwise to a solution of $(C_6H_5)HgCl$ (313 mg, 1 mmol) in THF (15 mL), at room temperature. After 30 min of stirring, the solvent was evaporated under a vacuum, at room temperature. The residue was dissolved in dichloromethane (15 mL) and filtered. Addition of methanol (20 mL) and evaporation of the solvent in air afforded a colorless microcrystalline material (yield 289 mg, 72%). Anal. Calcd for $C_{13}H_{12}HgS$: C, 38.95; H, 3.01; S, 7.99. Found: C, 38.85; H, 3.05, S, 7.85. ^{1}H NMR (CD_2Cl_2, 293 K): δ 7.8−6.8 ppm (m, 9H, C_6H_5/C_6H_4), 2.30 ppm (s, 3H, CH_3).

Kinetic Studies. Reactions between **5** and CH_3COOH were performed in CH_2Cl_2 thermostated solutions at 291 K. In a typical experiment, equimolar amounts of acetic acid and **5** (in CH_2Cl_2 solution containing *n*-eptane as internal standard) were mixed under stirring. The mixture composition was analyzed periodically (*ca.* every 15 min) by GC. The organic products were identified by comparison of their retention times with those of authentic specimens. Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an internal standard method. The concentration of benzene was measured with a relative mean error of *ca.* 2%. The temperature of the solution was controlled with an accuracy of 0.5 °C. The kinetic data were obtained from a wide number of measurements for initial concentrations of **5** ranging from 0.5×10^{-2} to 5×10^{-2} M. Kinetic data were achieved also by integration of the $^{31}P\{^{1}H\}$ NMR spectra, recorded in the absolute intensity mode, in dichloromethane-d_2 solutions. The reactions were run in sealed NMR tubes, at 294 K. Since in these conditions the reactions are rather slow it was assumed that the acquisition time (ca. 1 min) was negligible in the respect to the sampling time (*ca.* 30 min). So the time between the two first halves of two successive acquisitions was assumed to be the sampling time and used in the rate calculations. The [**5**]/[**6**] concentration ratio was calculated by integration of the relative resonances. Then [**6**] was obtained on the basis of the integration of the resonance of this complex at the end of the reaction, on account of the fact that **6** was the only containing phosphorus species.

Crystal Structure Determinations. Colorless prismatic crystals of dimensions 0.05 × 0.07 × 0.42 and 0.07 × 0.17 × 0.30 mm were used for data collection of **3** and **9** respectively. The unit cell constants were determined by a least-squares refinement of the setting angles of 25 reflections. Intensity data were collected by the $\omega - 2\theta$ scan method within $2\theta < 100$ and 40 for **3** and **9** respectively. Three check reflections measured every 2 h. showed no significant intensity reduction for both the compounds. Crystal data parameters are presented in Table 1.

The structures were solved by the heavy atom method and full-matrix least-squares refinements were carried out assigning anisotropic thermal parameters only to the heavier atoms and treating the phenyl rings as rigid groups. The function minimized was $\sum w(|F_o| - |F_c|)^2$, w being set equal to $1/\sigma^2(F_o)$. Hydrogen atoms were introduced in their calculated positions but not refined. In both complexes some residual electron density (*ca.* 1 e Å^{-3}) was present in the region of $(CF_3)SO_3$, which in **9** has been refined by using bond length constraints. Owing to the polarity of *Pb*2$_1$*a* space group of **3**, the absolute configuration of the structure was determined. All the calculations were carried out on an HP 486 PC using the SHELX76[10] and ORTEP[11] programs. The standard deviations $\sigma(I)$ were calculated by using the value of 0.03 for the instability factor *K*.[12] The data were corrected for Lorentz−polarization and absorption effects.[13] Atomic scattering factors for the appropriate neutral atoms were taken for non hydrogen and hydrogen atoms from refs 14 and 15 respectively. Corrections for anomalous dispersion effects, real and imaginary parts, were applied to the calculated structure factors amplitudes.[16] Final atomic parameters are given in Tables 2 and 3 for **3** and **9** respectively.

Table 1. Crystal Data for $[(np_3)Hg(CH_3)][(CF_3)SO_3]$·toluene, **3**, and $[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}][(CF_3)SO_3]$, **9**

	3	**9**
formula	$C_{51}H_{53}F_3HgNO_3P_3S$	$C_{50}H_{49}F_3HgNO_3P_3S_2$
fw	1110.6	1126.6
space group	*Pb*2$_1$*a*	*P*2$_1$/*a*
a, Å	34.491(12)	17.509(9)
b, Å	12.694(5)	16.805(7)
c, Å	11.184(5)	17.870(8)
β, deg	90.0	113.83(6)
V, Å^3	4896.7	4809.8
Z	4	4
T, °C	22	22
λ, Å	1.5418	0.7107
μ, cm^{-1}	78.2	34.3
d_{calcd}, gcm^{-3}	1.506	1.555
diffractometer	Philips PW 1100	Enraf Nonius CAD4
scan width, deg	$0.70 + 0.15 \tan \theta$	$0.80 + 0.35 \tan \theta$
scan speed, deg min^{-1}	4.2	1.50−8.24
reflcns measd	$+h,+k,+l$	$\pm h,+k,+l$
no. of data ($I \geqslant 3\sigma(I)$)	1753	2131
no. of variables	192	209
R, R_w[a]	0.060, 0.059	0.067, 0.066

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Results and Discussion

Synthesis and Characterization of the $[(np_3)HgR][(CF_3)SO_3]$ Complexes. The complexes $[(np_3)HgR][(CF_3)SO_3]$ {R = Me (**3**), Et (**4**), Ph (**5**)} have been cleanly prepared by reaction of $[HgR][(CF_3)SO_3]$ salts with equimolar amounts of np_3. The colorless crystalline solids appear indefinitely stable in air when stored in the dark. The compounds are soluble in polar organic solvents such as dichloromethane, acetone, nitroethane, where they behave as 1:1 electrolytes.

The $^{31}P\{^{1}H\}$ and $^{199}Hg\{^{1}H\}$ NMR spectra of the three complexes, which are quite similar, well agree with the results of the X-ray structure determination of **3**, indicating the coordination of all the three phosphorus atoms (vide infra). As a matter of fact the ^{31}P spectra, at low temperature, consist of a singlet with ^{199}Hg satellites, whereas the ^{199}Hg ones consist of a quartet. Both the signal shape and the NMR parameters (chemical shifts and coupling constants) are temperature and concentration dependent. The ^{31}P variable temperature spectra of **3**, recorded in the range 183−309 K, in dichloromethane solution, have shown that the singlet broadens at ca. 230 K, and at ca. 245 K the $^{199}Hg-^{31}P$ spin correlation is lost. This behavior is due to a rapid ligand dissociation, as confirmed by

---

(10) Sheldrick, G. M. *SHELX76, System of Computing Programs*, University of Cambridge: Cambridge, England; 1976.

(11) Johnson, C. K. *ORTEP.* ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(12) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(13) Walker, N.; Steward, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England 1974; Vol 4, p 99.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T., *J. Chem. Phys.* **1965**, *42*, 3175.

(16) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, p 149.

Table 2. Fractional Coordinates (×10000) of $[(np_3)Hg(CH_3)][(CF_3)SO_3]$·toluene

atom	*x*	*y*	*z*
Hg	1125(1)	0	2036(1)
P1	1007(2)	1031(7)	60(8)
P2	1937(2)	−140(12)	2022(9)
P3	1070(3)	1522(7)	3602(8)
N	1666(7)	2297(19)	1568(21)
C	862(10)	−1535(30)	2353(33)
C1	1416(10)	1887(29)	−417(32)
C2	1512(10)	2735(28)	477(29)
C3	2212(9)	1112(25)	2272(30)
C4	2079(9)	1983(27)	1494(31)
C5	1183(10)	2851(26)	3104(32)
C6	1589(10)	2966(29)	2577(29)
C1,1	581(7)	1850(22)	150(23)
C2,1	546(7)	2752(22)	−554(23)
C3,1	208(7)	3354(22)	−507(23)
C4,1	−95(7)	3054(22)	246(23)
C5,1	−61(7)	2152(22)	950(23)
C6,1	277(7)	1550(22)	903(23)
C1,2	923(7)	168(16)	−1190(24)
C2,2	706(7)	449(16)	−2192(24)
C3,2	652(7)	−273(16)	−3118(24)
C4,2	816(7)	−1275(16)	−3042(24)
C5,2	1034(7)	−1556(16)	−2040(24)
C6,2	1087(7)	−834(16)	−1114(24)
C1,3	2147(6)	−640(20)	644(24)
C2,3	1974(6)	−1551(20)	192(24)
C3,3	2111(6)	−1998(20)	−866(24)
C4,3	2421(6)	−1535(20)	−1471(24)
C5,3	2594(6)	−625(20)	−1019(24)
C6,3	2457(6)	−178(20)	38(24)
C1,4	2132(6)	−1023(15)	3151(20)
C2,4	2457(6)	−766(15)	3830(20)
C3,4	2580(6)	−1435(15)	4745(20)
C4,4	2376(6)	−2362(15)	4980(20)
C5,4	2050(6)	−2619(15)	4301(20)
C6,4	1928(6)	−1949(15)	3387(20)
C1,5	1381(6)	1274(15)	4928(18)
C2,5	1498(6)	239(15)	5141(18)
C3,5	1750(6)	17(15)	6084(18)
C4,5	1884(6)	830(15)	6813(18)
C5,5	1767(6)	1865(15)	6601(18)
C6,5	1515(6)	2087(15)	5658(18)
C1,6	593(8)	1673(20)	4248(26)
C2,6	505(8)	2496(20)	5029(26)
C3,6	133(8)	2579(20)	5511(26)
C4,6	−150(8)	1840(20)	5212(26)
C5,6	−61(8)	1018(20)	4432(26)
C6,6	310(8)	934(20)	3950(26)
C1,7	716(10)	5450(23)	1861(23)
C2,7	946(10)	5529(23)	2883(23)
C3,7	1341(10)	5741(23)	2777(23)
C4,7	1507(10)	5874(23)	1648(23)
C5,7	1277(10)	5795(23)	627(23)
C6,7	881(10)	5583(23)	733(23)
C7	329(14)	5336(47)	2084(47)
C8	1548(10)	5187(47)	6832(31)
F1	1661(10)	5144(57)	5851(37)
F2	1458(14)	4133(37)	7810(40)
F3	1676(12)	6090(36)	7152(40)
S	1141(8)	5138(42)	6998(24)
O1	852(12)	5706(36)	7691(39)
O2	989(12)	4368(36)	5908(38)
O3	908(33)	4562(94)	7943(88)

Table 3. Fractional Coordinates (×10000) of $[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}][(CF_3)SO_3]$

atom	*x*	*y*	*z*
Hg	480(1)	1765(1)	7417(1)
P1	271(4)	3319(5)	7325(4)
P2	1517(5)	1580(4)	6736(5)
P3	1234(5)	1346(5)	8902(5)
S1	−1005(5)	1284(5)	6605(5)
N	2194(12)	2722(14)	8313(13)
C1	1240(16)	3838(16)	7591(16)
C2	1950(18)	3550(16)	8346(17)
C3	2576(16)	1843(18)	7425(15)
C4	2689(18)	2640(16)	7822(17)
C5	2019(18)	2079(17)	9494(17)
C6	2581(18)	2336(18)	9083(17)
C7	−1829(32)	−2140(28)	7098(31)
C1,1	−102(12)	3677(10)	8082(11)
C2,1	−319(12)	4473(10)	8110(11)
C3,1	−548(12)	4735(10)	8730(11)
C4,1	−562(12)	4202(10)	9323(11)
C5,1	−345(12)	3407(10)	9296(11)
C6,1	−116(12)	3144(10)	8675(11)
C1,2	−426(13)	3733(10)	6353(13)
C2,2	−1147(13)	3301(10)	5902(13)
C3,2	−1719(13)	3596(10)	5156(13)
C4,2	−1570(13)	4322(10)	4861(13)
C5,2	−849(13)	4753(10)	5312(13)
C6,2	−278(13)	4459(10)	6058(13)
C1,3	1228(9)	2232(13)	5871(12)
C2,3	1820(9)	2650(13)	5689(12)
C3,3	1568(9)	3118(13)	4985(12)
C4,3	724(9)	3169(13)	4464(12)
C5,3	132(9)	2751(13)	4646(12)
C6,3	384(9)	2283(13)	5350(12)
C1,4	1643(16)	582(20)	6417(19)
C2,4	906(16)	174(20)	5966(19)
C3,4	939(16)	−594(20)	5684(19)
C4,4	1709(16)	−954(20)	5853(19)
C5,4	2446(16)	−546(20)	6305(19)
C6,4	2413(16)	222(20)	6587(19)
C1,5	584(12)	1203(11)	9466(9)
C2,5	−194(12)	855(11)	9029(9)
C3,5	−753(12)	751(11)	9398(9)
C4,5	−534(12)	996(11)	10204(9)
C5,5	243(12)	1344(11)	10641(9)
C6,5	802(12)	1447(11)	10272(9)
C1,6	1796(15)	425(14)	9013(12)
C2,6	2536(15)	242(14)	9681(12)
C3,6	2942(15)	−476(14)	9701(12)
C4,6	2609(15)	−1013(14)	9054(12)
C5,6	1870(15)	−830(14)	8386(12)
C6,6	1464(15)	−112(14)	8365(12)
C1,7	−1171(23)	337(24)	6794(22)
C2,7	−830(29)	−318(30)	6509(27)
C3,7	−1019(27)	−1125(26)	6637(25)
C4,7	−1542(26)	−1259(26)	7015(24)
C5,7	−1909(24)	−659(24)	7311(23)
C6,7	−1725(22)	125(22)	7155(20)
C8	4441(22)	1707(20)	1804(20)
F1	5247(21)	1413(19)	2256(19)
F2	4190(21)	1494(19)	990(18)
F3	4445(23)	2539(18)	1913(20)
S2	3663(14)	1379(13)	1966(13)
O1	2903(23)	1910(21)	1549(20)
O2	3607(26)	604(18)	1539(21)
O3	3963(25)	1337(23)	2873(14)

the ^{31}P variable temperature spectra of a complex solution, containing free np_3 ligand. In the case of the complexes **4** and **5** the signal broadening temperatures are considerably higher, namely 285 and 305 K. Remarkable temperature effects on chemical shifts and coupling constants have been previously reported for mercury(II) complexes.[17] In the present study we have to stress both the large temperature dependence of the ^{199}Hg chemical shifts (e.g. in the case of **3** δ is 2440 ppm at 299 K and 2525 ppm at 205 K), and the continuous variation of the $^{1}J_{HgP}$ coupling constants in the overall range of the investigated temperatures (Tables 4−6). Since the values of the one bond mercury−phosphorus coupling constant of **3**, **4**, and **5** are among the smallest ones reported for phosphine-complexes of Hg(II), the temperature per cent variation of these

---

(17) Granger, P. In *Transition Metal Nuclear Magnetic Resonance*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991; pp 306−332 and references therein.

Table 4. $^{31}P\{^1H\}$ Chemical Shifts (δ, ppm) and $^1J_{HgP}$ Coupling Constant (Hz) of $[(np_3)Hg(CH_3)][(CF_3)SO_3]$ in CH_2Cl_2

	soln 0.1 M		soln 0.15 M		soln 0.2 M	
T (K)	δ	J	δ	J	δ	J
225	6.8	47	6.8	52	6.8	57
215	6.75	57	6.8	62	6.8	66
203	6.7	66	6.8	71	6.8	75
193	6.7	73	6.8	77	6.8	82
183	6.7	80	6.8	83	6.8	90

Table 5. $^{31}P\{^1H\}$ Chemical Shift (δ, ppm) and $^1J_{HgP}$ Coupling Constant (J, Hz) of $[(np_3)Hg(C_2H_5)][(CF_3)SO_3]$ in CH_2Cl_2[a]

	soln 0.15 M			soln 0.15 M	
T (K)	δ	J	T (K)	δ	J
289	9.6	463	223	9.2	429
263	9.45	452	203	9.1	412
243	9.3	443	183	9.1	397

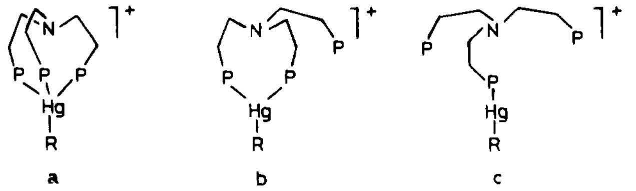
[a] $\delta = 9.5$, $J = 468$ for a solution 0.05 M, at 290 K.

Table 6. $^{31}P\{^1H\}$ Chemical Shift (δ, ppm) and $^1J_{HgP}$ Coupling Constant (J, Hz) for $[(np_3)Hg(C_6H_5)][(CF_3)SO_3]$ in CH_2Cl_2[a]

	soln 0.1 M			soln 0.1 M	
T (K)	δ	J	T (K)	δ	J
284	8.0	317	235	7.6	378
275	7.85	333	215	7.55	400
255	7.7	356	195	7.55	4.18

[a] $\delta = 9.5$, $J = 468$ for a solution 0.05 M, at 290 K.

Chart 1



values is cleanly the highest so far found. It is also of interest to point out that whereas for **3** and **5** the temperature effect on ^1J is that commonly observed (e.g. ^1J increases when the temperature decreases) in the case of **4** the opposite trend occurs. Concerning the concentration effect, a concentration decrease gives rise to a variation of ^1J similar to that determined by a temperature increase in all the cases.[18]

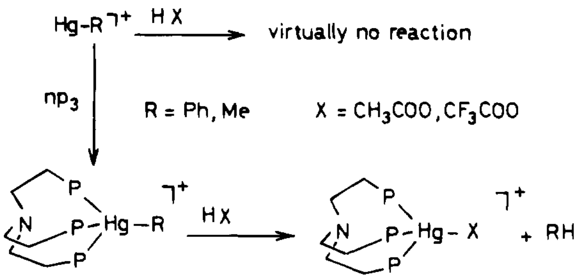
As regard as the temperature dependence of the NMR parameters it would be tempting to suggest the presence of an interconverting set of isomers such as those reported in Chart 1. In species b and c the three phosphine groups would be undergoing rapid exchange, in the overall range of the investigated temperatures, preventing the observation of the signals of uncoordinated phosphorus atoms. The maintenance of the ^{199}Hg-^{31}P spin correlation, during such a process, could likely occur due to the time of the M−P bond breaking and forming, being short relative to the phosphorus nuclear relaxation time.[19] This has been already observed for tripodal phosphine complexes.[20] Preliminary calculations performed for complex **3**, on the basis of two interconverting species, a and b, allowed a satisfactory simulation of the temperature dependence of the ^1J values. However, due to the contribution of species containing not-coordinating phosphorus atoms, the average values of the chemical shifts resulted shifted high field and did not fit the observed ones. On the other hand, it appears rather surprising that the slow-exchange limit is not observed in anyone of the NMR spectra for **3**, **4**, and **5**. Since large variations of ^1J and δ have been previously reported for phosphino-complexes of Hg(II), without ascertaining the presence of isomers, it is likely to suppose that the solvation mode plays a determining role in these phenomena even if the exact nature of these remains unclear.

Table 7. $^1J_{HgP}$ Coupling Constants (J, Hz) of the pseudotetrahedral Hg(II) Complexes $[(np_3)HgX]^+$, in CH_2Cl_2

complex	J	ref
$[(np_3)Hg(OOCCF_3)]^+$	3700	this work
$[(np_3)Hg(OOCCH_3)]^+$	3480	this work
$[(np_3)HgCl]^+$	3340	21
$[(np_3)HgBr]^+$	3160	21
$[(np_3)HgI]^+$	2780	21
$[(np_3)Hg(SC_6H_5)]^+$	1845	this work
$[(np_3)Hg(C_2H_5)]^+$	443[a]	this work
$[(np_3)Hg(C_6H_5)]^+$	318[b]	this work
$[(np_3)Hg(CH_3)]^+$	75[c]	this work

[a] Solution: 0.15 M, 243 K. [b] Solution: 0.1 M, 294 K. [c] Solution: 0.2 M, 205 K.

Scheme 2



Finally when we consider in general the series of the pseudotetrahedral complexes $[(np_3)HgX]^+$ (Table 7), the values of the $^1J_{HgP}$ increase as the donor ability of the X ligand decreases, in agreement with that previously reported for other Hg(II) phosphine complexes.[17,21] Particularly, in the case of the **3**−**5** derivatives the quite small values of ^1J could be related to the small s character of the phosphorus−mercury bond, the Hg 6s orbital being mainly involved in the organometallic linkage.

Reactivity of $[(np_3)HgR][(CF_3)SO_3]$ with CR'_3COOH (R′ = H, F). The complexes **3** and **5** react with equimolar amounts of CF_3COOH, in dichloromethane solution, at room temperature (Scheme 2). The reactions, which can be easily monitored by NMR spectroscopy result in the almost quantitative formation of RH and $[(np_3)Hg(OOCCF_3)][(CF_3)SO_3]$, **7**. The phenylmercury derivative reacts more rapidly than the methyl one (the reaction is complete within minutes vs. hours), according to the previously reported acetylation of diorganomercurials.[2c] The analogous reaction of CH_3COOH with **5** to yield C_6H_6 and $[(np_3)Hg(OOCCH_3)][(CF_3)SO_3]$, **6**, occurs in hours; on the other hand, acetylation of the complex **3** requires the use of glacial acetic acid, at *ca.* 40 °C (ca. 2 h). The $[(CH_3)Hg(DMSO)][(CF_3)SO_3]$ or $[(C_6H_5)Hg(DMSO)][(CF_3)SO_3]$ salts virtually do not react, in the same conditions not even with CF_3COOH. Of course, when equimolar amounts of np_3 are added, the reactions proceed as above described for compounds **3** and **5**.

---

(18) All the NMR spectra are also solvent dependent, such a variation having not be investigated because outside the aim of this work.

(19) Jesson, J. P.; Muetterties, E. L. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 256.

(20) Cecconi, F.; Innocenti, P.; Midollini, S.; Moneti, S.; Vacca, A.; Ramirez, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1129.

(21) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chim. Acta* **1994**, *217*, 155.

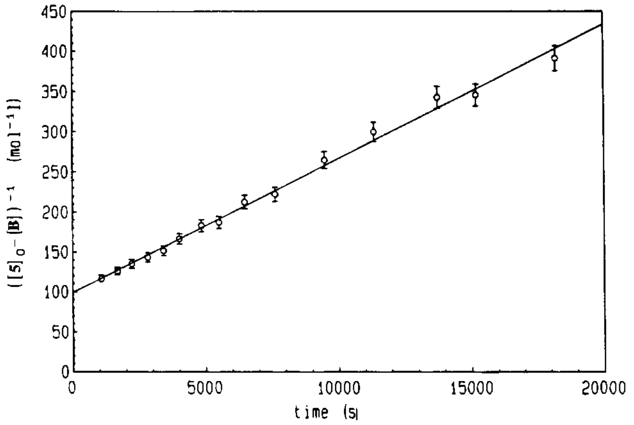


Figure 1. Plot of $([\mathbf{5}]^0 - [\mathbf{B}])^{-1}$ versus reaction time for reaction 1. Experimental conditions: $[\mathbf{5}]^0 = [\mathbf{HAc}] = 0.0101$ M, $T = 291$ K. $k = 0.0167 \pm 3$ (mol^{-1} dm^3 s^{-1}), correlation coefficient = 99.80%.

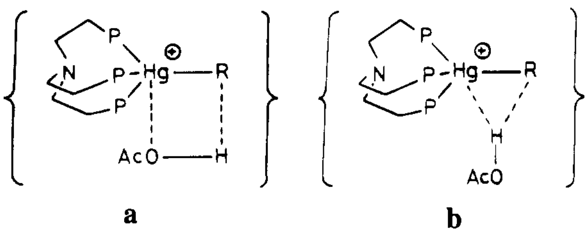
The complexes **6** and **7** can be easily isolated, in almost quantitative yield, as colorless crystals, by addition of *n*-butanol and evaporation of the solvent. Both the compounds behave as 1:1 electrolytes in nitroethane solution. Their $^{31}P\{^1H\}$ NMR spectra (solutions $2 \cdot 10^{-2}$ M in CH_2Cl_2, 293K), are quite similar, consisting of a singlet at δ 15.9 (**7**) or 12.4 ppm (**6**) with ^{199}Hg satellites $\{^1J_{HgP} = 3700$ (**7**) or 3480 Hz (**6**)$\}$. These spectral parameters are closely related to those of the complexes $[(np_3)HgX]X$ (X = Cl, Br, I) for which a tetrahedral geometry, with the apical nitrogen atom uncoordinated, has been definitively ascertained through an X-ray diffractometric analysis.[21] Therefore, we can assign an analogous structure to **6** and **7**, with the $[(CR'_3COO)]^-$ anion coordinated through one oxygen atom.

The reactions between **5** and CH_3COOH, performed at room temperature, in CH_2Cl_2 solutions, using different initial concentrations of equimolar reagents ($[\mathbf{5}]_0 = [\mathbf{B}]_0$, in the range 0.5×10^{-2} to 5×10^{-2} M), were investigated by GC analysis. The

$$[(np_3)Hg(C_6H_5)][(CF_3)SO_3] + HAc \rightarrow [(np_3)HgAc][(CF_3)SO_3] + C_6H_6 \quad (1)$$

only organic product detected in the course of each reaction was benzene (**B**). The kinetics of the reaction was followed by determining the concentration of benzene formed in the reaction solutions, as a function of time, by GS sampling the reaction mixture periodically. Plots of $([\mathbf{5}]_0 - [\mathbf{B}])^{-1}$ versus time were found to be linear for all the experiments indicating that the kinetic of the protonolysis reaction conforms to the following law: $1/\{[\mathbf{5}]_0 - [\mathbf{B}]\} = kt + 1/[\mathbf{5}]_0$. A typical plot is shown in Figure 1 for one of the experiments. This confirms that the reaction between **5** and **HAc** is first order with respect to both the concentration of the phenylmercury complex and acetic acid, *i.e.*: $d[\mathbf{B}]/dt = k[\mathbf{5}][\mathbf{HAc}]$. The reaction remained second order for the whole time the experiments were observed (ca. 5 h). The kinetic constant k can be calculated from least squares linear regression of the kinetic data of each experiment. A mean value of $k = (1.65 \pm 4) \times 10^{-2}$ mol^{-1} dm^3 s^{-1}, at 291K was obtained.[22] Comparable results ($k = 2.23 \times 10^{-2}$, at 293 K) have been, more easily though less rigorously, obtained from NMR spectroscopy. In this case the kinetics was followed by determining the concentration of **6** ($[\mathbf{6}] = [\mathbf{B}]$), through periodically recorded $^{31}P\{^1H\}$ NMR spectra. NMR measurements of the effect of substituting CH_3COOD for CH_3COOH have given a K_H/k_D ratio of ca. 3, indicating that the proton transfer is involved in the rate determining step of the reaction.[23] This finding agrees with the observed acceleration of reaction 1 when the stronger acid CF_3COOH is used in the place of CH_3COOH. As generally expected, an increase of the reaction rate occurs when the temperature is increased.

Chart 2



The above results appear to be consistent with a concerted S_E2 path to protonolysis, involving either a four-centered transition state (Chart 2a) or a three-centered one (Chart 2b), such as those proposed for the organomercury(II) salts cleavage by bacterial organomercurial lyase[24] and the acetolysis of diorganomercurials[23b] respectively. Therefore, although the coordination of np_3 to the $[HgR]^+$ ion does not seem to change substantially the mechanism of the protonolysis, the resulting activation of the carbon−mercury bond strongly accelerates the reaction.

For the purpose of comparison we have investigated the reactivity of the species $[(PPh_3)Hg(C_6H_5)]^+$ [8] toward trifluoroacetic acid. An X-ray crystal structure, recently determined on the nitrate salt, has ascertained that this cation complex contains a linearly dicoordinated mercury atom. A dichloromethane solution of this species is prepared by dissolving equimolar amounts of $[(C_6H_5)Hg(DMSO)][(CF_3)SO_3]$ and PPh_3. The $^{31}P\{^1H\}$ and $^{199}Hg\{^1H\}$ NMR spectra, containing a singlet at δ 48.34 ppm with ^{199}Hg satellites ($^1J_{HgP} = 2400$ Hz) and a doublet at δ 2401 ppm ($^1J_{HgP} = 2400$ Hz) respectively, are quite consistent with the results of the solid state structure. The above solution virtually does not react with an equimolar amount of CF_3COOH, at room temperature. On the contrary preliminary investigations have shown that the solutions of the complex $[(pp_3)Hg(C_6H_5)]^+$ $\{pp_3 = P(CH_2CH_2PPh_2)_3\}$ readily react with equimolar amount of CF_3COOH, at room temperature, to release benzene. Then it is evident that also the number of the coordinated phosphorus atoms to the $[RHg]^+$ ion is important in order to promote the Hg−C cleavage.

Reactivity of $[(np_3)HgR][(CF_3)SO_3]$ with Thiols. Since in the catalytic protonolysis of organomercury(II) derivatives (Scheme 1) the proton sources are probably the cysteinic residues of the enzymatic active sites, it seemed of interest to investigate the reactions of the title complexes towards thiols.

The complex **5** reacts with equimolar amounts of phenylthiol or *p*-thiocresol, in dichloromethane solution, at room temperature, to form benzene and the derivatives $[(np_3)HgSE][(CF_3)SO_3]$ ($E = C_6H_5$, **8**; $E = p\text{-}CH_3C_6H_4$, **9**) as the only products (reaction time ca. 18 h in solution 0.1 M) (Scheme 3). Also in this case the processes can be monitored by ^{1}H and ^{31}P NMR spectroscopy. Evidence has been obtained for an initial rapid step which allows the separation of free np_3 followed by the slow formation of $[(np_3)HgSE]^+$ and R-H. Namely in the case of the reaction with *p*-thiocresol the $^{31}P\{^1H\}$ NMR spectrum, recorded immediately after the addition of the thiol to the **5** solution, shows only the signals due to free np_3 and **5** (molar

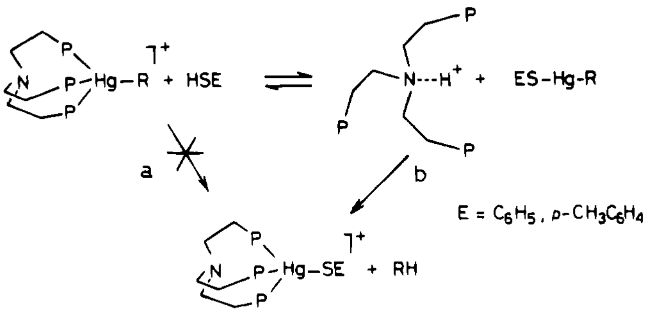
---

(22) Mean value of the kinetic constant $\langle k \rangle$ and its standard deviation $\sigma(\langle k \rangle)$, calculated as $\langle k \rangle = (\Sigma_i w_i k_i / \Sigma_i w_i)$ and $\sigma(\langle k \rangle) = [\Sigma_i w_i (k_i - \langle k \rangle)^2 / (n-1)\Sigma_i w_i]^{1/2}$, where $w_i = 1/\sigma_i^2(k_i)$.

(23) (a) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *J. Am. Chem. Soc.* **1965**, *87*, 1235. (b) Nugent, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5979.

(24) Begley, T.; Walts, A. E.; Walsh, C. T. *Biochemistry* **1986**, *25*, 7192.

Scheme 3



ratio ca. 1.6). The corresponding ^{1}H NMR spectrum shows a singlet at δ 2.29 ppm attributable to the CH_3 protons of both free thiol and $[(C_6H_5)Hg\{S(p\text{-}CH_3C_6H_4)\}]$.[25] The formation of this latter complex is likely promoted by the amino group of np$_3$. Later the reaction slowly proceeds with formation of the species **9** and benzene. At the end of the overall process **9** is the only containing phosphorus species. The reaction of equimolar amounts of authentic samples of np$_3$, $(CF_3)SO_3H$ and **10**, dissolved in this order in dichloromethane, well agreed with the pathway b in Scheme 3. Indeed we observed the formation of benzene and **9**, but any evidence has not been obtained for the formation of **5**.

The complexes **8** and **9**, which can be easily isolated, in high yield, as colorless crystals behave as 1:1 electrolytes in nitromethane solution.

The $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2, room temp.) of **8** and **9**, with singlets respectively at δ 7.01 ppm and 6.98 ppm (with ^{199}Hg satellites, $^1J_{HgP}$ = 1845 Hz and 1776 Hz) are consistent with a pseudotetrahedral geometry also in solution. Concerning complex **9** it is worth remarking that the singlet due to the CH_3 protons of the coordinated $p\text{-}CH_3C_6H_4S$ group in the ^{1}H NMR spectrum shows ^{199}Hg satellites with $^7J_{HgH}$ = 15 Hz. As a matter of fact the failure to observe mercury coupling associated with the SR moiety in Hg(II) thiolate complexes, due to the rapid exchange of the mercaptide ligands, had been reported for several years.[26]

The reactions of the above thiols with **3** or of alkyl thiols such as 2-propanethiol or 2-methyl-2-propanethiol with **5** occur with analogous mechanisms but the reaction rates are remarkably slower. As a matter of fact the ^{31}P NMR spectrum of the CH_2Cl_2 solution containing equimolar amounts of **3** and C_6H_5SH, after standing 24 h at room temperature, showed signals due to unreacted **3**, **8**, and free np$_3$. Analogously the reaction of **5** with $(CH_3)_3CSH$, performed with the same method used for the synthesis of **8** (time 48 h) gave a mixture of $[(np_3)Hg\{SC(CH_3)_3\}][(CF_3)SO_3]$ {^{31}P NMR (CH_2Cl_2, room temp.): δ 4.14 ppm (s with satellites, $^1J_{HgP}$ = 1318 Hz) and **5** in molar ratio *ca.* 1:1}.

Description of the Structures of 3 and 9. The molecular structure of **3** consists of $[(np_3)Hg(CH_3)]^+$ cations, $[(CF_3)SO_3]^-$ anions and solvating toluene molecules. Figure 2 shows a perspective view of the cation and selected bond distances and angles are reported in Table 8. At first sight it is remarkable that, in spite of the great tendency of methylmercury to form strong collinear bonds, the trans nitrogen atom of the np$_3$ ligand is 3.50(2) Å away. Indeed the mercury is fourcoordinated by the three phosphorus atoms of the tripod ligand and by the methyl group. The coordination geometry is distorted tetrahedral with angles ranging from 97.1(3) to 121.6(9)°. It is interesting to note that one Hg–P bond distance is significantly longer (2.808(7) Å) than the other two (2.600(9) and 2.615(9) Å). On the other hand a wide range of values, 2.45–2.91 Å, have been reported for Hg–P distances in complexes of the type $[HgX_2(PPh_3)_2]$[27] confirming the easy deformability of the coordination sphere of a d^{10} metal ion. The CH_3 group is bent with respect to the pseudo threefold axis passing through the nitrogen and the mercury atoms, the smallest P–Hg–C angle corresponding to the longest Hg–P distance. Due to the lack of genuine four-coordinated methylmercury complexes the Hg–C bond distance of 2.18(3) Å may be compared with a wide range of values, reported for a variety of methylmercury complexes.[6a]

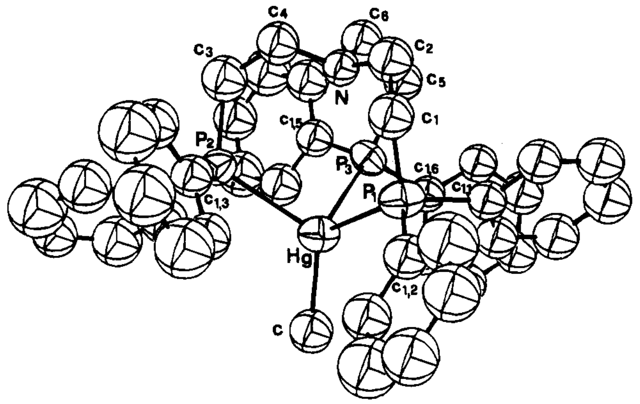


Figure 2. Perspective view of the complex cation $[(np_3)Hg(CH_3)]^+$ (ORTEP drawing with 30% probability ellipsoids).

Table 8. Selected Bond Distances and Angles for $[(np_3)Hg(CH_3)]^+$, **3**, and $[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}]^+$, **9**

	X = C	X = S
Hg–P1	2.600(9)	2.633(8)
Hg–P2	2.808(7)	2.581(8)
Hg–P3	2.615(9)	2.539(7)
Hg–X	2.18(3)	2.543(7)
Hg···N	3.50(2)	3.21(2)
P1–C1	1.86(3)	1.79(3)
P1–C1,1	1.80(3)	1.83(2)
P1–C1,2	1.80(2)	1.81(2)
P2–C3	1.87(3)	1.82(2)
P2–C1,3	1.82(3)	1.79(2)
P2–C1,4	1.82(2)	1.81(3)
P3–C5	1.82(3)	1.83(3)
P3–C1,5	1.86(2)	1.82(2)
P3–C1,6	1.80(3)	1.80(2)
S1–C1,7		1.68(4)
P1–Hg–P2	100.6(3)	101.3(2)
P1–Hg–P3	100.7(3)	109.9(2)
P2–Hg–P3	97.1(3)	107.0(3)
P1–Hg–X	121.6(9)	101.3(2)
P2–Hg–X	111.0(9)	116.4(3)
P3–Hg–X	121.5(9)	119.2(3)
N–Hg–P1	62.5(4)	67.1(4)
N–Hg–P2	61.3(4)	66.5(5)
N–Hg–P3	61.5(4)	68.3(4)
N–Hg–X	172.3(10)	168.3(4)
Hg–P1–C1	114.8(11)	112.0((9)
Hg–P1–C1,1	111.7(9)	111.3(7)
Hg–P1–C1,2	112.3(8)	117.6(7)
Hg–P2–C3	116.8(11)	111.7(10)
Hg–P2–C1,3	115.1(8)	109.0(7)
Hg–P2–C1,4	113.8(8)	117.2(11)
Hg–P3–C5	117.7(12)	111.7(10)
Hg–P3–C1,5	111.6(7)	116.0(6)
Hg–P3–C1,6	114.4(9)	112.5(8)

---

[25] The resonances of the CH_3 protons of $p\text{-}CH_3C_6H_4SH$ and **10** in CD_2Cl_2 solution are respectively at 2.290 and 2.295 ppm.

[26] Bach, R. B.; Weibel, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 6241.

[27] Buergi, H. B.; Fischer, E.; Kunz, R. W.; Parvez, M.; Pregosin, P. S. *Inorg. Chem.* **1982**, *21*, 1246.

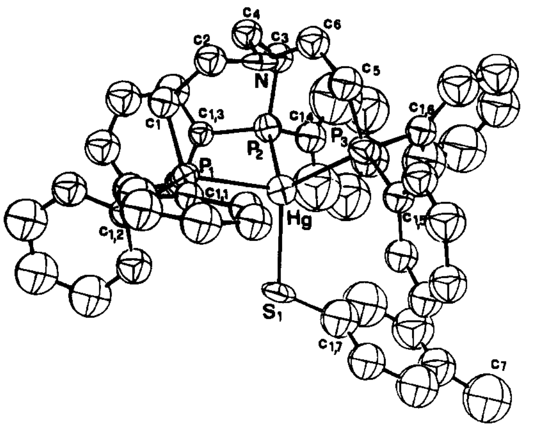


Figure 3. Perspective view of the complex cation $[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}]^+$ (ORTEP drawing with 30% probability ellipsoids).

The molecular structure of **9** consists of discrete $[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}]^+$ cations and $[(CF_3)SO_3]^-$ anions. Figure 3 shows a perspective view of the cation and Table 8 reports selected bond distances and angles. The mercury atom is fourcoordinated by the three phosphorus atoms of the np_3 ligand and by the sulfur atom of the *p*-thiocresol group. Indeed the tripod ligand acts as a tridentate one, the central nitrogen atom being 3.21(2) Å apart. The coordination geometry is distorted tetrahedral with angles which range from 101.3(2) to 119.3(3)°. The distortion from the limit geometry seems consistent with the steric arrangement of the *p*-thiocresol fragment. As a matter of fact the larger P−Hg−S angles involve the phosphines whose phenyl rings display shorter contacts with the *p*-thiocresol group. The Hg−P distances ranging from 2.539(7) to 2.633(8) Å compare well with the sum of the covalent radii (2.58 Å)[28] and the Hg−S bond distance of 2.543(7) Å is fully comparable with those of 2.537(1) and 2.552(1) Å, reported for the tetrahedral complex $[Hg(SC_6H_4Cl)_4]^{-2}$.[29]

Notwithstanding the gross geometrical features are preserved, the substitution of a methyl with a *p*-thiocresol group induces very significant differences. In the methyl derivative, **3**, the Hg−P distances are significantly longer than in **9**, moreover the average P−Hg−X angle is larger (118.0° vs. 112.3°) with a consequent[30] difference in the Hg$\cdots$N distance (3.50(2) vs. 3.21(2) Å). These differences may be explained on the basis of the stronger σ-donor capability of the methyl group with respect to the *p*-thiocresol ligand. In this context it is useful to compare the title compounds with the closely related tetrahedral complex $[(np_3)HgI]^+$.[21] Indeed in the latter complex the Hg$\cdots$N separation is 3.13(1) Å, the P−Hg−X angles average 110.6(9)° and the Hg−P distances are even shorter than in $[(np_3)Hg\{S(p\text{-}CH_3C_6H_4)\}]^+$ averaging to 2.533 Å. The correlation between the Hg−P bond distances and the σ donor capability of the X ligand in $[HgX_2(PPh_3)_2]$ complexes has been previously reported.[21,31]

Conclusions

Organomercurial salts are quite resistant to chemical hydrolysis by acids and bases. However the enzyme organomercurial lyase has evolved a mechanism to perform this difficult reaction in aqueous solutions (pH 7−10), at reasonable rates. The products of the reaction are alkane (or arene) and mercury thiolates. It has been suggested that such a mechanism involves, as a fundamental step, the binding of the organomercurial to one or two cysteine SH groups (Scheme 1). Now we have prepared the first examples of tetrahedral complexes of alkyl- or arylmercury(II), in which $[RHg]^+$ is linked to three phosphorus atoms of the tripodal ligand np_3, both in the solid state and in solution. The strong donor ability of the phosphorus atoms is capable to activate the carbon-mercury bond for protonolysis. As a matter of fact our complexes react in mild conditions, at valuable rates, with trifluoroacetic or acetic acid in organic solutions, with evolution of arene or alkane. The np_3 complexes are attacked also by thiols, this reaction being favoured by the presence of the np_3 amino group which likely acts as a base. The products of the latter reactions are RH and mercury−np_3 thiolate complexes. Then these findings are substantially in agreement with the proposed mechanism of the enzymatic protonolysis.

Acknowledgment. Thanks are due to Mrs. F. Nuzzi and P. Innocenti for technical assistance.

Supplementary Material Available: Tables of hydrogen atom coordinates, thermal factors, and complete bond distances and angles (11 pages). Ordering information is given on any current masthead page.

---

[28] Grdenic, D. *Q. Rev. Chem. Soc.* **1965**, *19*, 303.

[29] Choudhury, S.; Dance, I. G.; Guerney, P. J.; Rae, A. D. *Inorg. Chim. Acta* **1983**, *70*, 227.

[30] Mealli, C.; Ghilardi, C. A.; Orlandini, A. *Coord. Chem. Rev.* **1992**, *120*, 361.

[31] Buergi, H. B.; Kunz, R. W.; Pregosin, P. S. *Inorg. Chem.* **1980**, *19*, 3707.