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Symmetrization of methylmercury(II) and phenylmercury(II) salts induced by the tripodal ligand $N(CH_2CH_2PPh_2)_3$

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Abstract

Both ionic $[HgR(DMSO)][CF_3SO_3]$ (R = Me or Ph) and covalent HgMeI organomercury(II) compounds react with the tripodal ligand $N(CH_2CH_2PPh_2)_3$ (np_3) to yield as ultimate products Hg(II) complexes, the new five-coordinated $[Hg(OSO_2CF_3)(np_3)]^+$ or the known tetrahedral $[HgI(np_3)]^+$ and symmetric diorganomercurials respectively. Monitoring of the reactions by ^1H, ^{31}P and ^{13}C NMR spectroscopy has shown that the mechanistic pathways depend on the nature of the reagents.

Keywords: Methyl–mercury; Phenyl–mercury; Tripodal phosphine; Symmetrization reaction

1. Introduction

Methylmercury is exceedingly toxic to living organisms because of its high affinity for thiols. Moreover its lipophilic nature, strongly favouring bioaccumulation in the food chain, makes it especially dangerous to higher organisms [1]. Unfortunately $[HgMe]^+$ is relatively inert and difficult to degrade except under fairly severe conditions. However, recent reports have indicated that the coordination of organomercury(II) ions by donors so as to increase the metal coordination from the usual linear dicoordination to a higher coordination number is quite important in the activation of the Hg–C bond, both in enzymatic degradation processes and in laboratory chemical reactions [2]. In particular, we have shown that the coordination of the three phosphorus atoms of np_3 {$np_3 = N(CH_2CH_2PPh_2)_3$} to HgR^+ (R = Me or Ph) by activating the Hg–C bond, strongly accelerates the protonolysis reaction [3].

Symmetrization is a general reaction of organomercurials which allows the simultaneous formation of symmetric diorganomercurials HgR_2 and Hg(II) complexes [4]. This reaction, involving the cleavage of an Hg–C bond, is promoted by strongly complexing agents. The phosphines are very efficacious reagents in these reactions, arylmercury salts being more readily symmetrized than alkyl salts [4a,5,6]. However, the isolation and the inertness of the pseudotetrahedral complexes $[HgR(np_3)]^+$ (Scheme 1) contradict the above statements.

We report here further investigations about the reactivity of np_3 towards organomercury(II) salts, both ionic $[HgR(DMSO)][CF_3SO_3]$ (R = Me or Ph) and covalent HgMeI.

2. Experimental section

2.1. General data

All the solvents and chemicals were reagent grade and were used as received. HgMeI was purchased from Strem Chemicals and used without further purification. $[HgMe(DMSO)][CF_3SO_3]$, $[HgPh(DMSO)][CF_3SO_3]$. DMSO, $[HgMe(np_3)][CF_3SO_3]$.toluene (**1**) and $[HgPh(np_3)][CF_3SO_3]$ (**2**) (DMSO-dimethylsulphoxide) were prepared as described previously [3]. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 200.13, 50.32 and 81.015 MHz respectively on a Bruker AC-200 spectrometer. Peak positions are relative to tetramethylsilane (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P) as external references. Downfield values of the chemical shifts are

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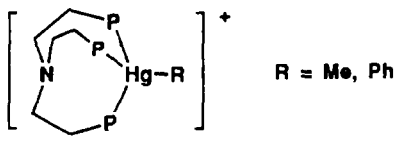


Scheme 1.

reported as positive. Solution conductivities were measured as previously reported.

Caution! Mercury compounds are extremely toxic and should be handled and manipulated with due care.

2.2. Synthesis of $[Hg(OSO_2CF_3)(np_3)][CF_3SO_3]$ (3)

2.2.1. Method 1.

A solution containing **1** (1110 mg, 1 mmol) and $[HgMe(DMSO)][CF_3SO_3]$ (445 mg, 1 mmol) in dichloromethane (20 ml) was put aside for 12 h. After the addition of toluene (15 ml) the solvent was evaporated under a current of dinitrogen at room temperature to give **3** as colourless crystals (945 mg (82%)). Anal. Found: C, 46.05; H, 3.75; N, 1.20; S, 5.45. $C_{44}H_{42}F_6HgNO_6P_3S_2$ calc.: C, 45.85; H, 3.66; N, 1.21; S, 5.56%. Selected NMR data (CD_2Cl_2, 295 K). $^{31}P\{^1H\}$: δ 21.7 (s with satellites, $^1J_{HgP} = 3720$ Hz) ppm. $^{19}F\{^1H\}$: δ 77.6 (s) ppm.

2.2.2. Method 2.

CF_3SO_3H (88.5 μl, 1 mmol) dissolved in 5 ml of dichloromethane was added to a solution of **1** (1110 mg, 1 mmol) in the same solvent (15 ml), at room temperature. After the solution was allowed to stand for 3 h in the dark, toluene (15 ml) was added and the solvent was evaporated in a current of dinitrogen, until colourless crystals of **3** formed (860 mg (75%)). The compound was identical with that obtained by method 1.

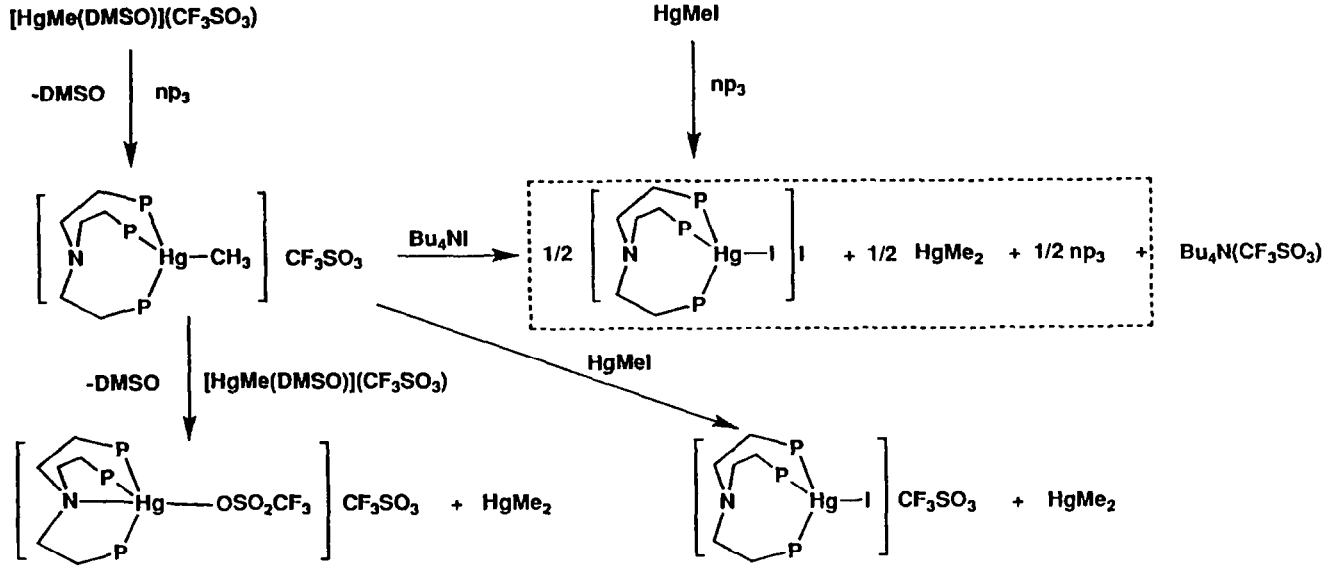
3. Results and discussion

The reactions of the complexes $[HgR(np_3)][CF_3SO_3]$ (R = Me or Ph) with both ionic $[HgR(DMSO)][CF_3SO_3]$ and covalent HgMeI compounds have been performed in dichloromethane solution at room temperature. The results are reported in Scheme 2. The reactions of the phenyl derivatives are quite rapid (minutes) whereas those of the corresponding methyl compounds take some hours to be complete. Therefore these latter can be monitored by NMR spectroscopy.

The reaction of **1** (or **2**) with an equimolar amount of $[HgMe(DMSO)][CF_3SO_3]$ {or $[HgPh(DMSO)][CF_3SO_3]$} allows the clean formation of $HgMe_2$ (or $HgPh_2$) and the new species $[(np_3)Hg(OSO_2CF_3)(np_3)][CF_3SO_3]$ (**3**):

$$[HgR(np_3)][(CF_3)SO_3] + [HgR(DMSO)][(CF_3)SO_3] \rightarrow [Hg(OSO_2CF_3)(np_3)][(CF_3)SO_3] + HgMe_2 + DMSO \quad (1)$$

The symmetric species have been identified in the final solution by ^1H and ^{13}C NMR spectroscopy. The ^{31}P



Scheme 2.

NMR spectra showed only one phosphorus resonance at $\delta = 21.7$ ppm ($^1J_{HgP} = 3720$ Hz), due to species 3, which was isolated as colourless crystals and can be prepared alternatively by protonolysis of **1** or **2** with CF_3SO_3H:

$$[HgR(np_3)][CF_3SO_3] + CF_3SO_3H \rightarrow [Hg\{OSO_2CF_3\}(np_3)][CF_3SO_3] + RH \quad (2)$$

An X-ray analysis of **3** was carried out but, owing to the poor quality of the crystal data [7], consisting of a small number of low intensity and small-angle reflections, we consider it correct to report only the connectivity of the atoms. The molecular structure of **3** consists of complex cations $[Hg\{OSO_2CF_3\}(np_3)]^+$ and $[CF_3SO_3]^-$ anions. The mercury center displays a five-coordinated geometry surrounded by the four donor atoms of the np_3 ligand and by the triflate group through an oxygen atom. The coordination polyhedron with three strong equatorial Hg–P bonds (2.48(2) Å) and two weaker axial linkages (Hg–N, 2.7(1) Å; Hg–O, 2.6(1) Å) displays expected bond lengths when a very electronegative axial ligand is present [3,8,9].

The value of $^1J_{HgP}$ of **3** (3720 Hz), the largest in the series of the Hg(II)–np_3 complexes so far described [3], fits well with the correlations of the $^1J_{HgP}$ coupling constants, the strength of the M–P bonds and the electronegativity of the axial ligand previously reported [10,11].

The $^{19}F\{^1H\}$ spectrum of **3** in dichloromethane solution shows only one signal at -76.6 ppm, suggesting rapid interchange between triflate anions. Conductivity measurements in nitromethane solution (1×10^{-3} M) ($\Lambda_M = 131$ cm^2 Ω^{-1} M^{-1} for **3** vs. 86 cm^2 Ω^{-1} M^{-1} for **1**) indicate that **3** behaves as a 1:2 electrolyte. These data are consistent with only a slight interaction between the metal and the triflate ion in solution.

Monitoring the reaction of $[HgMe(np_3)]^+$ with $[HgMe(DMSO)]^+$ by ^{31}P NMR spectroscopy showed the formation of an intermediate species (broad singlet at $\delta = 31.5$ ppm) the intensity of which gradually decreases as that of **3** increases. Remarkably, the signal of **1** was never observed. This finding is not consistent with the generally accepted S_E2 substitution mechanism which involves a three-centre two-electron transition state in which the group R should leave as the group $[HgR]^+$ enters [12].

The complexes $[HgR(np_3)]^+$ are easily attacked by the $[HgR(DMSO)]^+$ ions but nevertheless, when the molar ratio of $[HgR(DMSO)]^+$ to np_3 is 1, the very low concentration of the $[HgR(DMSO)]^+$ ions virtually prevents completion of the symmetrization process.

When $[HgR(DMSO)][CF_3SO_3]$ is treated with 0.5 equivalents of np_3 in dichloromethane solution at room temperature, the reaction occurs at the same rate and with formation of the same products as reaction (1), apart from the relative amount of DMSO:

$$2[HgMe(DMSO)][CF_3SO_3] + np_3 \rightarrow [Hg(OSO_2CF_3)(np_3)][CF_3SO_3] + HgMe_2 + 2DMSO \quad (3)$$

This indicates that DMSO is only weakly coordinated to mercury in CH_2Cl_2 solution and does not play a determining role in the symmetrization process.

When **1** reacts with an equimolar amount of HgMeI, the reaction proceeds towards the formation of $[HgI(np_3)][CF_3SO_3]$ and $HgMe_2$ without spectroscopic evidence of the presence of any intermediate species. The ^{31}P NMR spectrum of the reaction mixture showed only the resonance of the starting complex **1** (singlet at $\delta \approx 7.9$ ppm) and the resonance of $[HgI(np_3)]^+$ being formed [8] ($\delta = -5$ ppm (s with satellites, $^1J_{HgP} = 1720$ Hz)), the reaction being complete in about 3 h (**2** is symmetrized through an analogous reaction, in minutes). The complex $[HgI(np_3)][CF_3SO_3]$, completely analogous to the previously reported tetraphenylborate derivative, can be isolated as colourless crystals, through the addition of toluene and solvent evaporation (yield, about 90%).

The closely related derivative $[HgI(np_3)]I$ [8] can be obtained by the reaction of **1** or **2** with I^-, which is a well-known symmetrizing agent (Scheme 2) [4]. In this case, I^- first rapidly displaces np_3 to form HgMeI, which successively reacts with free np_3 to give $[HgI(np_3)]I$ and $HgMe_2$.

The results of this paper are fully consistent with those of the previous investigation [3], in that the coordination of the three phosphorus atoms of np_3 to the metal strongly activates the Hg–C bond.

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[7] Cell constants: $a = 10.225(7)$, $b = 13.447(4)$ and $c = 19.787(5)$ Å; $\alpha = 88.31(6)$, $\beta = 80.80(5)$ and $\gamma = 87.97(6)°$; triclinic; $P1$; $Z = 2$.

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