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Methylmercury(II) and phenylmercury(II) chelated complexes with the ligand tris(2-diphenylphosphinoethyl)phosphine: synthesis, X-ray diffraction and NMR studies

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Abstract

The reaction of methyl and phenylmercury ions with the ligand tris(2-diphenylphosphinoethyl)phosphine, pp_3, allowed the isolation of the complexes $[(pp_3)HgR]BF_4$ (R = Me, Ph). The X-ray crystal structure of the methyl derivative established that in the cation the metal atom is coordinated to the central phosphorus atom of the tripod pp_3 ligand and to the methyl group. Two terminal phosphorus atoms of the ligand are additionally linked to the metal throught secondary bonding interactions. ^{31}P- and ^{199}Hg-NMR spectra indicated that the coordination of terminal phosphorus atoms of pp_3 to the mercury atom occurs also in solution. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organomercurials; Phosphine complexes; Crystal structure; NMR spectroscopy

1. Introduction

Methylmercury(II) and related organomercury(II) ions have been found preferentially to display linear dicoordination [1]. Polydentate nitrogen donor ligands have often been reported to induce higher coordination numbers in the solid state, although the geometries at mercury are with only one strong Hg–N interaction [2]. Therefore, there is the convinction that it is not possible to design suitable sequestering agents for methylmercury(II) because of the impossibility to include methylmercury into chelated rings [3].

However, in dealing with the interaction of MeHg(II) with biomolecules it has been pointed out recently that a coordination mode in which mercury has a coordination number higher than two is of great biological interest [4]. Thus, we have found that the tripod ligand tris(2-diphenylphosphinoethyl)amine (np_3) can really chelate RHg(II) ions to give tetrahedral complexes both in solid state and in solution [5].

We now report the preparation and the characterization of the complexes $[(pp_3)HgR]BF_4$ (R = Me, Ph), where pp_3 is the related ligand tris(2-diphenylphosphinoethyl)phosphine. The tetradentate phosphine pp_3 has been reported previously to occupy four coordination sites with various geometries such as the trigonal pyramidal [6], trigonal bipyramidal [7], square pyramidal [8] or octahedral [9]. Sometimes pp_3 can also act as a bidentate or tridentate ligand toward one or two metal centers [10,11].

2. Experimental

All the solvents and chemicals were reagent grade and were used as received by commercial suppliers. The organomercurials MeHgI and $HgPh_2$ were purchased from Strem and used without further purification. Proton NMR spectra were recorded at 200.133 MHz, on a

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Bruker AC-200 spectrometer. Peak positions are relative to TMS as external reference. $^{31}P\{^{1}H\}$- and $^{199}Hg\{^{1}H\}$-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.

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

2.1. Syntheses

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 dried under a stream of nitrogen.

2.1.1. [(pp$_3$)HgMe]BF$_4$, **1**

Solid $AgBF_4$ (195 mg, 1 mmol) was added to a solution of MeHgI (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 filtered and solid pp$_3$ (670 mg, 1 mmol) was added. Methanol (25 ml) was added to the solution and the solvent was evaporated under a stream of nitrogen till the volume was reduced to ca. 15 ml. Then diethyl ether (20 ml) and *n*-hexane (40 ml) were added in turn, and the resultant solution was held in the refrigerator at 253 K for 5 h. Well shaped colorless crystals precipitated. These were filtered and washed with diethyl ether (yield 818 mg, 84%). Anal. calc. for $C_{43}H_{45}BF_4HgP_4$: C, 53.07; H, 4.66; Hg, 20.61. Found: C, 53.25; H, 4.75; Hg, 20.50. Selected NMR data (CD_2Cl_2, solution 0.18 M): ^{1}H-NMR (293 K) δ 1.29 ppm (s with satellites, $^{2}J_{HgH} = 180$ Hz, CH_3Hg); $^{31}P\{^{1}H\}$-NMR (223 K) δ 31.17 ppm (q with satellites, $^{2}J_{PP} = 105$ Hz, $^{1}J_{HgP_{ap}} = 1740$ Hz, P_{ap}), δ −7.98 ppm (d with satellites, $^{1}J_{HgP_{ter}} = 583$ Hz, P_{ter}); $^{199}Hg\{^{1}H\}$-NMR (223 K) δ 2192 ppm (dq, $^{1}J_{HgP_{ap}} = 1745$ Hz, $^{1}J_{HgP_{ter}} = 584$ Hz).

2.1.2. [(pp$_3$)HgPh]BF$_4$, **2**

A solution of $HgPh_2$ (335 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 $AgBF_4$ (195 mg, 1 mmol) was added. The mixture was stirred in the dark for 3 h, then AgI was filtered off. The solvents were removed from the filtrate under a vacuum, at room temperature, to leave a colorless material, which was dissolved in dichloromethane (25 ml). Solid pp$_3$ (670 mg, 1 mmol) was added and the solution was filtered. Methanol (25 ml) was added to the filtrate; evaporation of the solvent in a current of nitrogen afforded colorless crystals. These were filtered and washed with methanol (yield 797 mg, 77%). Anal. calc. for $C_{48}H_{47}BF_4HgP_4$: C, 55.69; H, 4.58; Hg, 19.38. Found: C, 55.50; H, 4.70; Hg, 19.25. Selected NMR data (CD_2Cl_2, solution 0.175 M): $^{31}P\{^{1}H\}$-NMR (223 K) δ 22.76 ppm (q with satellites, $^{2}J_{PP} = 115$ Hz, $^{1}J_{HgP_{ap}} = 2255$ Hz, P_{ap}), δ − 5.66 ppm (d with satellites, $^{1}J_{HgP_{ter}} = 597$ Hz, P_{ter}); ^{199}Hg {^{1}H)-NMR (223 K) δ 2004 ppm (dq, $^{1}J_{HgP_{ap}} = 2258$ Hz, $^{1}J_{HgP_{ter}} = 598$ Hz).

2.2. X-ray crystallography

Diffraction data of **1** were collected at room temperature on an Enraf Nonius CAD4 automatic diffractometer. Unit cell parameters were determined from a least-squares refinement of the setting angles of 25 carefully centred reflections. Crystal data and data collection details are given in Table 1. During the data collection the stability of the crystal was checked by periodically measuring three standard reflections. After correction for background the intensities I were assigned standard deviations $\sigma(I)$ calculated using the value of 0.03 for the instability factor k [12]. The intensities were corrected for Lorentz and polarization effects and for absorption by means of ψ scans [13]. All the calculations were performed on a personal com-

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{43}H_{45}BF_4HgP_4$
Formula weight	973.07
Temperature (K)	293(2)
Wavelength (Å)	0.71070
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.498(7)
b (Å)	25.117(8)
c (Å)	17.890(7)
β (°)	95.94(6)
V (Å^3)	4245(2)
Z	4
Density$_{calc.}$ (Mg m^{-3})	1.523
Absorption coefficient (mm^{-1})	3.823
$F(000)$	1936
Crystal size	$0.12 \times 0.15 \times 0.45$
Theta range for data collection (°)	2.5–20.0
Index ranges	$-9 \le h \le 9$, $0 \le k \le 24$, $0 \le l \le 17$
Reflections collected	3949
Independent reflections	3949 [$R_{int} = 0.0000$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3949/0/189
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$, $wR_2 = 0.1005$
R indices (all data)	$R_1 = 0.0649$, $wR_2 = 0.1075$
Largest difference peak and hole (e Å^{-3})	0.649 and −0.455

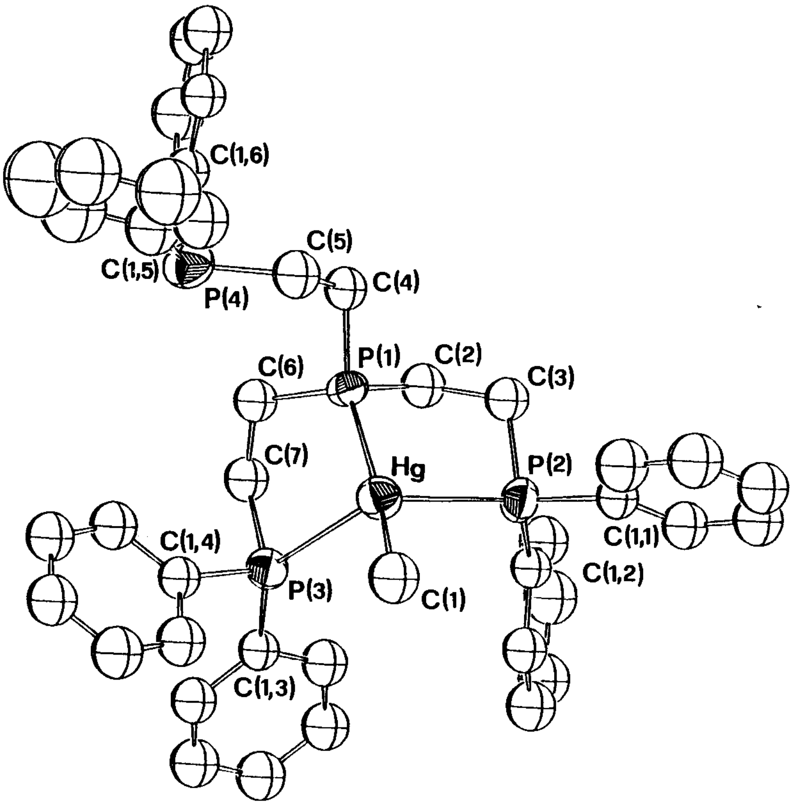

Fig. 1. Perspective view of the complex cation $[(pp_3)HgMe)]^+$. ZORTEP drawing with 30% probability ellipsoids.

puter, using the progams SHELXS86 [14], SHELXL93 [15], and ZORTEP [16]. Atomic scattering factors were taken from Ref. [17] and an anomalous dispersion correction, real and imaginary part, was applied [18]. Patterson and Fourier maps enabled the location of all the atoms. Full matrix least-squares refinements on F^2 were carried out with anisotropic thermal parameters assigned to mercury, phosphorus and fluorine 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 function minimized during the refinement was $\Sigma\, w(F_o^2 - F_c^2)^2$, with $w = 1/[\sigma^2(F_o)^2 + (0.0443P)^2 + 18.75P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

3. Discussion

3.1. X-ray structure

The molecular structure of **1** consists of discrete $[(pp_3)HgMe]^+$ cations and BF_4^- anions. Fig. 1 shows a perspective view of the cation and Table 2 reports selected bond distances and angles. In the cation the metal atom is linearly coordinated (P(1)–Hg–C(1) = 167.5(3)°) to the apical phosphorus atom of the tripod pp_3 ligand and to the methyl group. In addition to the two strong covalent bonds, Hg–P(1) 2.446(3) and Hg–C(1) 2.087(11) Å, the metal is linked to other two phosphorus donors of the tripod ligand which display bond distances of 2.879(3) and 3.078(3) Å. The fourth phosphorus atom of the pp_3 ligand is definitively not coordinated to the metal the Hg···P(4) contact being 5.04 Å. Therefore, the actual coordination geometry is somewhat in between the trigonal bipyramidal geometry (all the three terminal phosphorus coordinated in the equatorial plane) and the limit linear geometry when even P(2) and P(3) are not coordinated to the metal atom. Indeed the metal atom displays a 2 + 2 coordination mode which is rather frequent for the mercury [1]. Bond distances in the P_{ap}–Hg–C fragment appear normal for covalent bonds and in particular match for example those reported for $[(dpb)Hg(Me)]_2$ (dpb = diphenylphosphinobenzoate) [19] and for $[(PPh_3)HgPh]^+$ [20]. As concerns the two secondary bonds, if the sum of the van der Waals radii [21] of mercury and phosphorus is taken to be ca. 3.4 Å, the Hg–P distances of 2.879(3) and 3.078(3) Å may be considered as weak bond interactions.

The present compound can be compared with the related reported np_3 derivative, where the mercury atom displays a tetrahedral coordination with the apical nitrogen atom definitively away from the metal (Hg···N = 3.50 Å), and the three phosphorus atoms covalently bonded in the equatorial plane [5]. In the pp_3 case the apical phosphorus binds the metal centre,

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths (Å)			
Hg(1)–C(1)	2.087(11)	P(3)–C(1,3)	1.824(5)
Hg(1)–P(1)	2.446(3)	P(3)–C(1,4)	1.825(6)
Hg(1)–P(2)	2.879(3)	P(3)–C(7)	1.838(10)
Hg(1)–P(3)	3.078(3)	P(4)–C(1,5)	1.838(8)
P(1)–C(4)	1.812(10)	P(4)–C(1,6)	1.851(6)
P(1)–C(2)	1.826(10)	P(4)–C(5)	1.859(11)
P(1)–C(6)	1.843(10)	C(2)–C(3)	1.530(13)
P(2)–C(1,2)	1.830(6)	C(4)–C(5)	1.523(13)
P(2)–C(3)	1.834(10)	C(6)–C(7)	1.513(13)
P(2)–C(1,1)	1.840(6)		
Bond angles (°)			
C(1)–Hg(1)–P(1)	167.5(3)	C(7)–P(3)–Hg(1)	102.0(3)
C(1)–Hg(1)–P(2)	109.4(3)	C(1,5)–P(4)–C(1,6)	101.7(4)
P(1)–Hg(1)–P(2)	80.66(9)	C(1,5)–P(4)–C(5)	101.6(5)
C(1)–Hg(1)–P(3)	111.0(3)	C(1,6)–P(4)–C(5)	99.3(5)
P(1)–Hg(1)–P(3)	74.04(9)	C(3)–C(2)–P(1)	113.4(7)
P(2)–Hg(1)–P(3)	97.46(8)	C(2)–C(3)–P(2)	111.6(7)
C(4)–P(1)–C(2)	105.2(5)	C(5)–C(4)–P(1)	118.3(7)
C(4)–P(1)–C(6)	107.1(5)	C(4)–C(5)–P(4)	114.2(7)
C(2)–P(1)–C(6)	104.3(5)	C(7)–C(6)–P(1)	115.3(7)
C(4)–P(1)–Hg(1)	116.6(3)	C(6)–C(7)–P(3)	114.4(7)
C(2)–P(1)–Hg(1)	108.1(3)	C(6,1)–C(1,1)–P(2)	117.4(4)
C(6)–P(1)–Hg(1)	114.5(3)	C(2,1)–C(1,1)–P(2)	122.5(4)
C(1,2)–P(2)–C(3)	106.8(4)	C(6,2)–C(1,2)–P(2)	124.4(4)
C(1,2)–P(2)–C(1,1)	105.4(3)	C(2,2)–C(1,2)–P(2)	115.6(4)
C(3)–P(2)–C(1,1)	103.6(4)	C(6,3)–C(1,3)–P(3)	115.9(4)
C(1,2)–P(2)–Hg(1)	122.0(3)	C(2,3)–C(1,3)–P(3)	124.1(4)
C(3)–P(2)–Hg(1)	95.6(3)	C(6,4)–C(1,4)–P(3)	115.3(4)
C(1,1)–P(2)–Hg(1)	120.4(2)	C(2,4)–C(1,4)–P(3)	124.7(4)
C(1,3)–P(3)–C(1,4)	104.7(3)	C(6,5)–C(1,5)–P(4)	116.3(6)
C(1,3)–P(3)–C(7)	100.7(4)	C(2,5)–C(1,5)–P(4)	123.7(6)
C(1,4)–P(3)–C(7)	104.4(4)	C(6,6)–C(1,6)–P(4)	116.9(4)
C(1,3)–P(3)–Hg(1)	142.0(2)	C(2,6)–C(1,6)–P(4)	122.9(4)
C(1,4)—P(3)–Hg(1)	98.7(2)		

competing with the strong σ-donor CH_3 group in utilizing the metal orbitals suitable for axial linkages (i.e. s and p_z). It follows that, since the Hg(II) d orbitals are all full, only two orbitals (p_x and p_y) remain available for the linkages of the equatorial phosphines. The different role of the phosphine with respect to the amine axial donor (i.e. the better σ-donor capabilities of the phosphine) has been again enlighted, in agreement with what has been discussed already for the series $[LHgX]^+$, where $L = N(CH_2CH_2PPh_3)_3$ $X = Me$, p-$C_6H_5S^-$, halide, $CF_3SO_3^-$; $L = N(CH_2CH_2NMe_2)_3$, $X = Me$, Ph; $L = N(CH_2CH_2SCHMe_2)_3$, $X = Cl$ [22].

3.2. NMR spectra

The ^{31}P- and ^{199}Hg-NMR spectra of the two complexes in CD_2Cl_2 solution are quite similar indicating analogous coordination geometries. The room temperature ^{31}P-NMR spectra of **1** and **2** consist of a downfield quartet and a high-field doublet, due respectively, to the apical and the terminal phosphorus atoms. These spectra show that the two compounds are labile in solution. Indeed the signals are broad and no metal/phosphine coupling is observed (Fig. 2). However the fact that the ^{31}P resonances are shifted to higher frequences and the phosphorus to phosphorus coupling constant is remarkably higher than in the free pp_3 ligand is indicative of some metal/phosphine interaction. This behaviour is consistent with a rapid phosphine dissociation as confirmed by the spectra of the complexes solution containing free pp_3 ligand. In fact these consist of two broad signals the chemical shifts of which are the weighted averages of those of the corresponding resonances of the complexes and the free pp_3.

The variable temperature ^{31}P-NMR spectra of complex **2** are reported in Fig. 3 (the pattern of the corresponding spectra of **1** is quite similar). When the temperature of the solution decreases both the signals sharpen and the ^{199}Hg satellites loom out of the baseline. The slow exchange limit of the two systems is reached below 230 K in the present concentration conditions, ca. 0.2 M. It is worthwhile to note that a concentration decrease lowers the slow exchange limit. The low temperature ^{199}Hg spectra of **1** and **2** (Fig. 4)

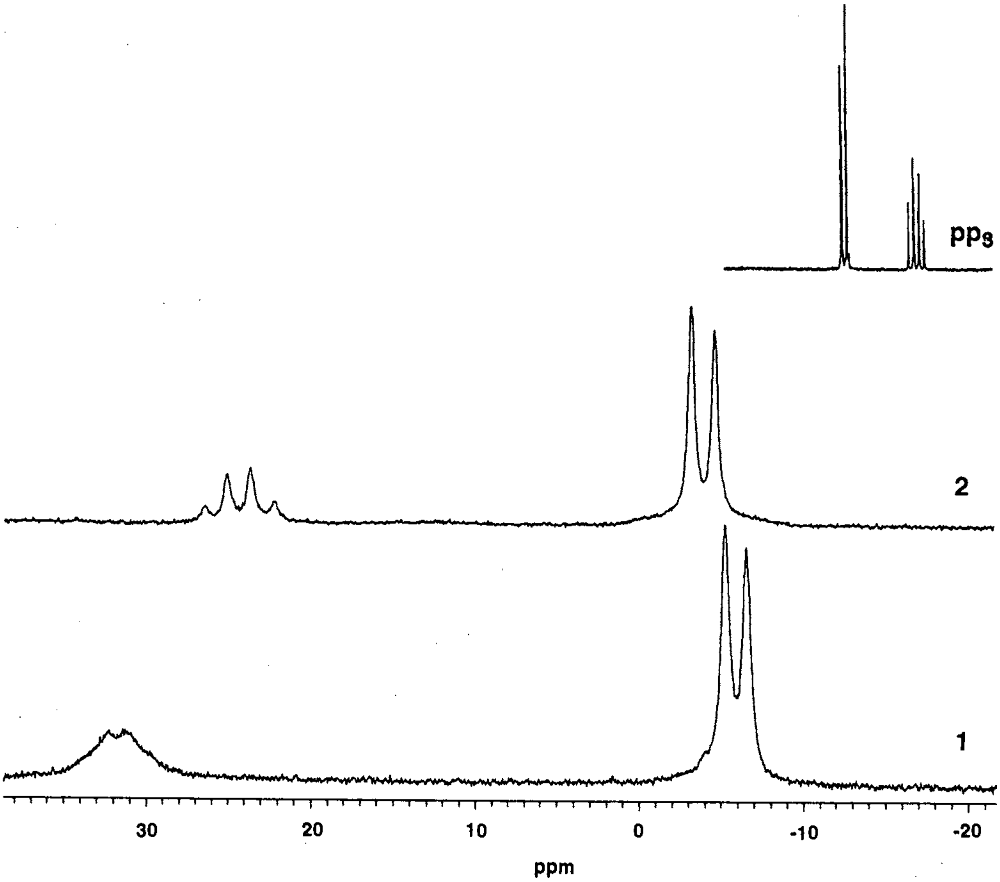

Fig. 2. $^{31}P\{^1H\}$-NMR spectra (CD_2Cl_2, 298 K) of **1**, **2** and pp_3.

are in perfect agreement with the ^{31}P spectra. Then, at low temperature, all the phosphorus atoms of the ligand pp_3 appear to be coordinated to the metal, the terminal ones being magnetically equivalent. The $^2J_{PP}$ coupling constants remain practically unchanged in the temperature range investigated. The values of the $^1J_{HgP}$ coupling constants, which are in the range reported previously for phosphine organo–mercury(II) complexes [23], increase when the temperature decreases (**1**: $^1J_{HgPap}$ is 1740 Hz at 223 K vs. 1777 at 213 K, $^1J_{HgPter}$ is 583 at 223 K vs. 591 at 213 K; **2**: $^1J_{HgPap}$ is 2255 at 223 K vs. 2334 at 203 K, $^1J_{HgPter}$ is 597 at 223 K vs. 621 at 203 K), and also when the concentration increases, as found previously for the related $[(np_3)HgMe]CF_3SO_3$ complex [5]. The $^1J_{HgPap}$ is remarkably higher than the $^1J_{HgPter}$ suggesting that the Hg–P_{ap} bond is stronger than the Hg–P_{ter} ones, in agreement with X-ray structural findings. However a five-coordinated geometry in solution does not agree with the results of the solid state structure. Even if the structure of a complex can be different in the solid state and in solution, in the case of an organomercury(II) derivative it appears at least surprising to find a coordination number of the metal higher in solution than in the solid state. We propose that the complexes in solution retain the coordination geometry found in the solid state, the two weakly coordinated terminal phosphorus atoms rapidly scrambling with the dangling one, also at low temperature. The maintenance of the ^{199}Hg–^{31}P spin correlation during such a process, could likely occur if the time of the Hg–P bond breaking and forming is short relative to the observed nucleus relaxation time [24]. In this case the observed value of the $^1J_{HgPter}$ should be an average of the mercury–phosphorus coupling of the two coordinated atoms and the uncoordinated ($J = 0$) one. This has to be expected especially in complexes of chelating ligands and has been observed already [24,25].

The results of this work confirm that polydentate ligands, containing soft donor atoms, engaged in a suitable skeleton, can chelate the mercury atom of organomercury(II) ions also in solution. This agrees with the recent hypothesis that in certain enzymatic active sites (i.e. organomercurial lyase) the mercury of the $HgMe^+$ ion has a coordination number higher than one [4].

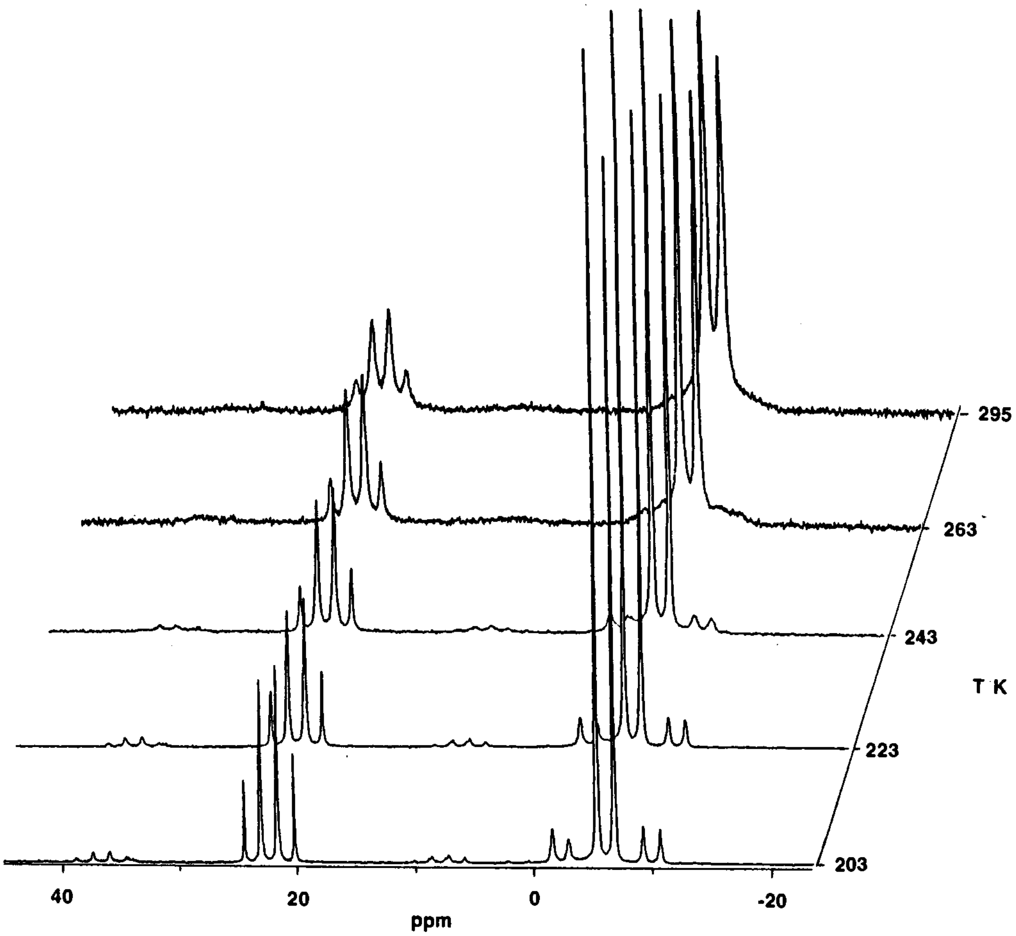

Fig. 3. $^{31}P\{^1H\}$ variable temperature NMR spectra (CD_2Cl_2) of **2**.

4. Supplementary material

Supplementary materials consist of coordinates, thermal parameters, complete bond distances and angles and F_o/F_c listings.

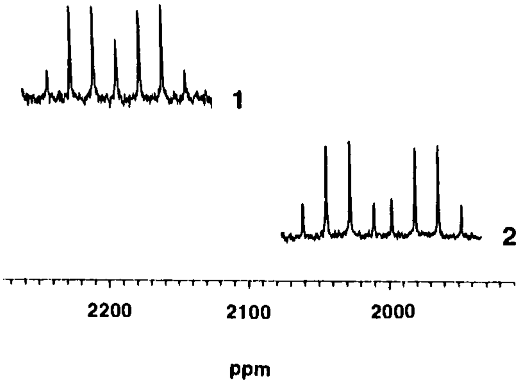

Fig. 4. $^{199}Hg\{^1H\}$-NMR spectra (CD_2Cl_2, 223K) of **1** and **2**.

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