New organomercury(II) compounds containing intramolecular N → Hg interactions: crystal and molecular structure of [2-(Me₂NCH₂)C₆H₄]HgCl and [2-(Me₂NCH₂)C₆H₄]Hg[S(S)PPh₂]

Oana Bumbu [a], Cristian Silvestru [a,*], M. Concepción Gimeno [b], Antonio Laguna [b]

[a] *Facultatea de Chimie si Inginerie Chimica, Universitatea Babes-Bolyai, RO-3400 Cluj-Napoca, Romania*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

Abstract

[2-(Me₂NCH₂)C₆H₄]HgCl (**1**) was prepared by reacting HgCl₂ with [2-(Me₂NCH₂)C₆H₄]Li in diethyl ether. The reactions of **1** with the sodium or ammonium salt of the appropriate thiophosphinato ligand, in 1:1 molar ratio, afford the isolation of [2-(Me₂NCH₂)C₆H₄]Hg[S(S)PR₂] [R = Me (**2**), Et (**3**), Ph (**4**)], [2-(Me₂NCH₂)C₆H₄]Hg[S(O)PPh₂] (**5**) and [2-(Me₂NCH₂)C₆H₄]Hg-[S(S)P(O^{i}Pr)₂] (**6**). The compounds were investigated by IR and multinuclear NMR (^{1}H, ^{13}C and ^{31}P) spectroscopy. The molecular structures of **1** and **4** were determined by single-crystal X-ray diffraction. Due to the strong intramolecular coordination of the N atom of the pendant CH₂NMe₂ arm [Hg(1)–N(1) 2.764(6) and 2.725(4) Å in **1** and **4**, respectively] both compounds exhibit a T-shaped (*C,N*)HgX core in the molecular unit, with almost linear arrangement of the covalent bonds [C(1)–Hg(1)–Cl(1) 176.93(18)° in **1**, and C(1)–Hg(1)–S(1) 169.54(16)° in **4**]. The crystals of **1** contain discrete monomeric molecules, while the crystals of **4** contain dimer associations built through asymmetric bridging dithiophosphinato ligands [Hg(1)–S(1) 2.3911(16) Å, Hg(1)···S(2a) 3.102(2) Å], thus resulting in an overall pseudo-trigonal bipyramidal (or seesaw) (*C,N*)HgS₂ core, with the nitrogen atom and the weekly bonded sulfur atom in equatorial positions [N(1)–Hg(1)···S(2a) 82.01(10)°].
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Organomercury(II) compounds of the type R₂Hg and RHgX (R = alkyl or aryl; X = halide) [1] have received a lot of attention for the last three decades mainly related to the search for biologically active compounds and versatile reagents in controlled transmetallation reactions [2]. The influence of secondary interactions between mercury and donor atoms as nitrogen on the structures of organomercury compounds was reviewed by Kuz'mina and Struchkov [3]. Cyclometallated organomercury(II) chlorides containing *N*-donor functionalised aryl ligands were investigated in the context of their use as transmetallation reagents [4–6]. The synthesis of few mercury(II) compounds containing phenyl groups with pendent arms was reported so far, i.e. [2-(R₂NCH₂)C₆H₄]₂Hg (R = Me [7,8], Et [9]), [2-(Me₂NCH₂)C₆H₄]HgCl [7], [2-{Me₂NC(Me)H}C₆H₄]HgX (X = Cl, Br, I) [10], and [2-{Me₂NC(Me)H}C₁₀H₆]HgX (X = Cl, Br, I) [11]. In the case of the above chlorides the solid state structure determinations revealed, in addition of internal N → Hg coordination, the association of the molecular units through weak Hg–Cl···Hg intermolecular bridges weak (often at the limit of the sum of the van der Waals radii, $\sum_{vdW}$(Hg,Cl) 3.4 Å [12]) into dimers [Fig. 1(a), Hg···Cl 3.239(10) Å] [4], tetramers [Fig. 1(b), Hg···Cl 3.184(5), 3.410(6), 3.442(6) Å] [5,6], single-bridged [Fig. 1(c), Hg···Cl 3.303(3) Å] [10] or doubly bridged polymers [Fig. 1(c), Hg···Cl 3.271(5), 3.330(5) Å] [11]. The Hg atom in these compounds was suggested to be a stereocenter in solid state since the (*C,N*)HgX core is slightly pyramidal [10,11].

* Corresponding author. Tel.: +40-264-193833; fax: +40-264-190818.
E-mail address: cristi@chem.ubbcluj.ro (C. Silvestru).
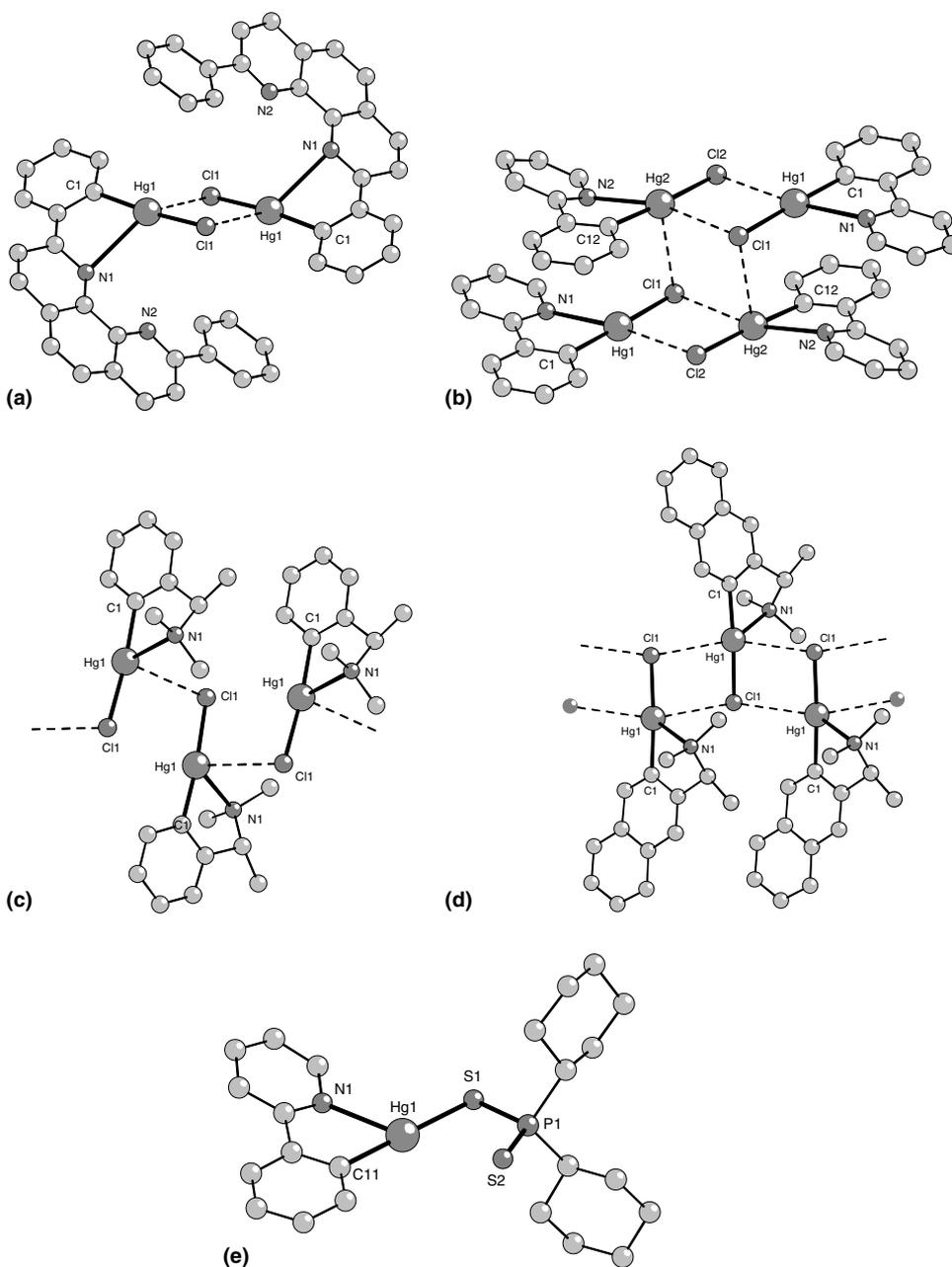
Fig. 1. Associations in the crystal of (a) [2-(9-Ph-1,10-phenanthrolinyl-2)phenyl]HgCl [4]; (b) [2-(2-pyridyl)phenyl]HgCl [5,6]; (c) [2-{Me$_2$NC-(Me)H}C$_6$H$_4$]HgCl [10]; (d) [2-{Me$_2$NC(Me)H}C$_{10}$H$_6$]HgCl [11]; and (e) [2-(2-pyridyl)phenyl]Hg[S(S)PCy$_2$] [19].

Variable temperature NMR studies in solution have revealed that the above chiral organomercury halides exhibit a temperature-dependent equilibrium between two- and three-coordinate species. The use of [2-{Me$_2$NC(Me)H}C$_6$H$_4$]HgCl as a transmetallation reagent in the synthesis of chiral Ru(II) complexes was reported [13,14].

However, no derivatives with anionic ligands containing a second potential coordinating atom, to compete the nitrogen atom of the C(R)HNMe$_2$ pending arm for coordination to the metal centre have been prepared so far. On the other hand, thiophosphorus ligands of the

type [R$_2$P(X)S]$^-$ (R = alkyl, aryl, alkoxy; X = O, S) are well known to involve usually both chalcogen atoms in coordination to the metal atom in organomercury(II) derivatives thus resulting in dimeric [MeHg{S(S)PPh$_2$}]$_2$ [15] and [PhHg{S(S)P(OEt)$_2$}]$_2$ [16] species [structure I – S,S-bimetallic biconnective phosphorus ligands] or polymeric [PhHg{S(S)PEt$_2$}]$_n$ [structure II – S,S',S'-bimetallic triconnective ligands] [17] and [MeHg{S(O)PPh$_2$}]$_n$ [structure III – S,O,O-trimetallic triconnective ligands] associations [18]. Only one example of an [organo-C,N]mercury(II) dithiophosphinate containing intramolecular N → Hg coordination was reported, i.e.

the monomeric [2-(2-pyridyl)phenyl-(C,N)]Hg[S(S)PCy$_2$] [Fig. 1(e)], in this case the dithio ligand acting as a monometallic monoconnective (monodentate) unit [19].

(I)   (II)   (III)
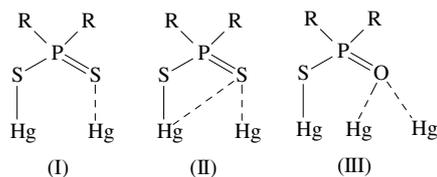
In the context of our interest in the coordination chemistry of 1,1-dichalcogenophosphorus ligands, we report here on the synthesis and spectroscopic characterization of some organomercury(II) derivatives, i.e. [2-(Me$_2$NCH$_2$)C$_6$H$_4$]HgCl (**1**), [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Hg-[S(S)PR$_2$] [R = Me (**2**), Et (**3**), Ph (**4**)], [2-(Me$_2$NCH$_2$)-C$_6$H$_4$]Hg[S(O)PPh$_2$] (**5**) and [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Hg-[S(S)P(O^{i}Pr)$_2$] (**6**), as well as the crystal and molecular structure of **1** and **4**.

2. Results and discussion

2.1. Preparation

The [2-(dimethylaminomethyl)phenyl]mercury(II) chloride, [2-(Me$_2$NCH$_2$)C$_6$H$_4$]HgCl (**1**), was prepared by reacting [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Li with HgCl$_2$ (1:1 molar ratio), in diethyl ether, at −78 °C [7]. The methatesis reaction between stoichiometric amounts of **1** and the sodium or ammonium salt of the appropriate organophosphorus acid affords the isolation of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Hg[S(S)PR$_2$] [R = Me (**2**), Et (**3**), Ph (**4**)], [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Hg[S(O)PPh$_2$] (**5**) and [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Hg[S(S)P(O^{i}Pr)$_2$] (**6**) (Scheme 1).

Compounds **1–5** were isolated as colorless crystalline solids, while compound **6** was a viscous oil. Compounds **1**, **4** and **5** are air-stable for weeks; the others decompose to a black material within two weeks both in solution and in the solid state. However, they were stable enough to be characterized by multinuclear NMR. Single crystals of **1** and **4** were obtained by slow difusion from a mixture of CH$_2$Cl$_2$ and hexane (1/4, v/v) and the crystal and molecular structures were determined by X-ray diffraction.

HgCl$_2$ + [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Li $\xrightarrow{\text{− LiCl}}$ [2-(Me$_2$NCH$_2$)C$_6$H$_4$]HgCl
1

$\downarrow$ + M[SXPR$_2$]
− MCl

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]Hg[S(X)PR$_2$]
2 - 6
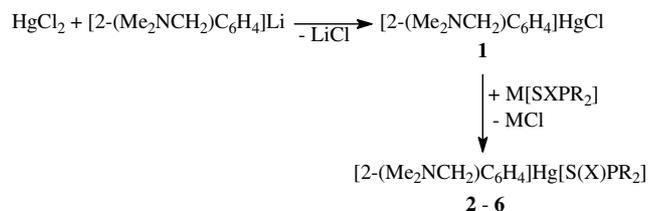
Scheme 1.

2.2. IR spectra

The infrared spectra of **4** and **5** exhibit, in addition to the expected strong absorptions due to the organic groups bonded to mercury, strong bands in the 650–540 cm^{-1} region and around 1165 cm^{-1} for **5**, which were assigned to phosphorus–sulfur and phosphorus–oxygen stretching vibrations. The presence of absorption bands corresponding to P–S single bond (575 cm^{-1}) and P=O double bond (1165 cm^{-1}) in the infrared spectrum of **5** indicates a primary coordination of the phosphorus ligand to the metal centre through the sulfur atom (cf. the methyl esters: 1027 (P–O), 635 (P=S) cm^{-1} for Ph$_2$P(S)OMe [20]; 1200 (P=O), 568 (P–S) cm^{-1} for Ph$_2$P(O)SMe [20]; for a detailed discussion, see [21]). For both compounds the infrared data are consistent with a basically S-monometallic monoconnective coordination pattern of the phosphorus ligand in solid state. This behavior of a monothiophosphinato moiety contrasts with its ability to exhibit a bridging pattern as found in the polymeric [MeHg{S(O)PPh$_2$}]$_n$ [18]. The primary S-coordination of the monothiophosphinato moiety in the solid state is consistent with the magnitude of the ^{31}P chemical shift found for compound **5** in solution (see subsequent discussion).

2.3. NMR spectra

The room temperature ^{1}H and ^{13}C NMR spectra of compounds **1–6** show resonances for the organic groups bonded to mercury and phosphorus atoms, respectively. The assignment of the ^{1}H and ^{13}C chemical shifts for the 2-(Me$_2$NCH$_2$)C$_6$H$_4$ group according to the numbering scheme (IV) was made using the literature data for related organomercury(II) compounds [7–11].

(IV)
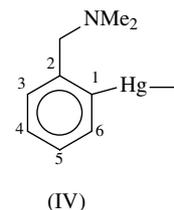
The presence of only one singlet resonance for the proton and carbon nuclei of the NMe$_2$ group in compounds **1–6** is consistent either with the absence of intramolecular N → Hg coordination or with a fast conformational change of the chelate five-membered HgC$_3$N ring [assuming a planar (C,N)HgX core] in solution, thus yielding averaged NMR resonances. The spectra of compound **1** remained unchanged until down to −70 °C, so that no conclusion concerning possible Hg–N interaction could be drawn.

The ^{1}H and ^{13}C NMR spectra of compounds **2–6** also exhibit the resonances for the organic groups attached to the phosphorus atom with the expected splitting

pattern due to phosphorus–proton and phosphorus–carbon couplings.

Only one singlet $^{31}P\{^1H\}$ resonance was observed in the ^{31}P NMR spectra of compounds **2–6**. For compound **5** two isomers are possible, i.e. containing the mono-thiophosphinato ligand connected to the metal through the oxygen (structure V) or through sulfur atom (structure VI). The magnitude of the observed ^{31}P chemical shift (δ 48.5 ppm) is indicative for a structure VI with *S*-monodentate monothiophosphinato moiety [cf. δ (^{31}P) 83.5 ppm for $Ph_2P(S)OMe$ [22]; 42.8 ppm for $Ph_2P(O)SMe$ [22]; and, for example, 64.9 ppm for $Ph_3SnOSPPh_2$ – for a detailed discussion, see [21]]. This behavior suggests that the coordination pattern of the phosphorus ligand in the CHCl$_3$ solution of compound **5** is the same as found in solid state.

(V)   (VI)
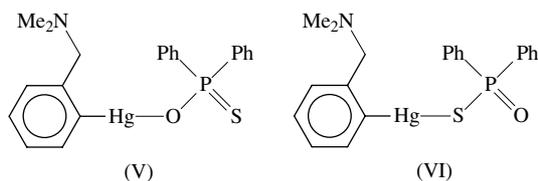
2.4. Crystal and molecular structure of [2-(Me₂NCH₂)C₆H₄]HgCl (1) and [2-(Me₂NCH₂)-C₆H₄]Hg[S(S)-PPh₂] (4)

The ORTEP diagrams for compounds **1** and **4** with the atom numbering scheme is shown in Figs. 2 and 3, respectively, and selected interatomic distances and angles are listed in Table 1.

The molecular structures of compounds **1** and **4** reveal some similar features with respect to the [2-(Me₂NCH₂)C₆H₄]HgX (X = Cl, S) moiety. The coordination arrangement around the mercury atom is best
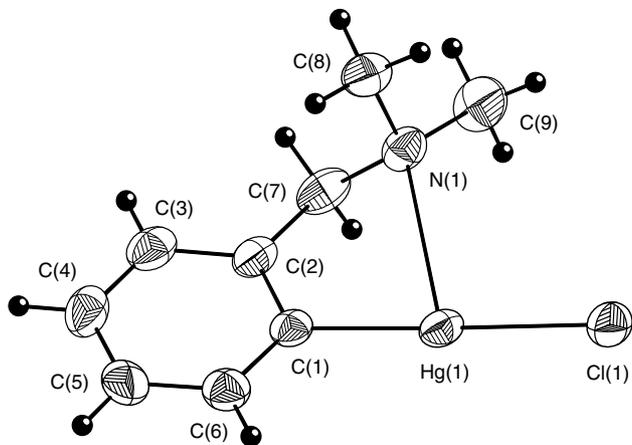
Fig. 2. ORTEP representation at 30% probability and atom numbering scheme for the (λ-*S*)-**1** isomer.
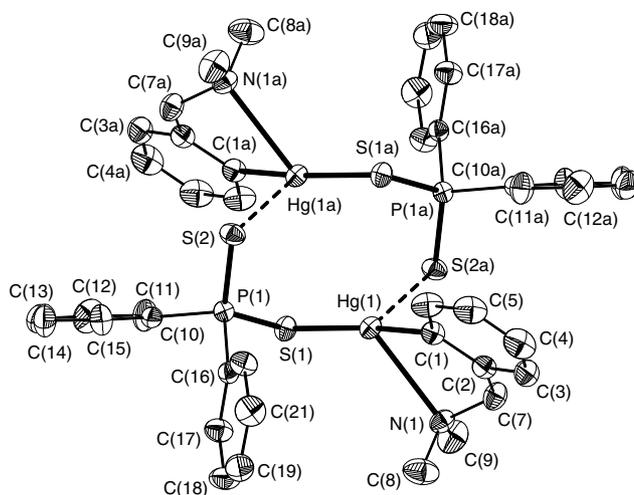
Fig. 3. Dimer association in the crystal of **4**.

Table 1
Selected interatomic distance (Å) and angles (°) in **1** and **4**

	1 (X = Cl)	**4** (X = S)
Hg(1)–C(1)	2.047(6)	2.063(6)
Hg(1)–N(1)	2.764(6)	2.725(4)
Hg(1)–X(1)	2.319(2)	2.3911(16)
N(1)–C(7)	1.451(10)	1.452(7)
N(1)–C(8)	1.461(10)	1.424(8)
N(1)–C(9)	1.467(10)	1.460(7)
P(1)–S(1)		2.052(2)
P(1)–S(2)		1.9652(19)
P(1)–C(10)		1.811(5)
P(1)–C(16)		1.811(5)
Hg(1)···S(2a)		3.102(2)
C(1)–Hg(1)–X(1)	176.93(18)	169.54(16)
C(1)–Hg(1)–N(1)	75.0(2)	74.69(18)
X(1)–Hg(1)–N(1)	104.93(14)	108.11(11)
S(2a)···Hg(1)–C(1)		106.34(15)
S(2a)···Hg(1)–N(1)		82.01(10)
S(2a)···Hg(1)–S(1)		84.11(5)
C(7)–N(1)–C(8)	110.9(6)	111.3(5)
C(7)–N(1)–C(9)	111.2(6)	111.1(5)
C(8)–N(1)–C(9)	109.8(6)	111.2(5)
Hg(1)–N(1)–C(7)	92.3(4)	94.6(3)
Hg(1)–N(1)–C(8)	111.4(4)	106.5(4)
Hg(1)–N(1)–C(9)	120.1(4)	121.0(4)
S(2)–P(1)–S(1)		115.98(9)
C(10)–P(1)–C(16)		106.3(2)
Hg(1)–S(1)–P(1)		95.53(7)
Hg(1)···S(2a)–P(1a)		92.78(7)

described as T-shaped due to the intramolecular N → Hg interaction, with the electronegative X atom *trans* to the aromatic carbon attached to mercury [C(1)–Hg(1)–Cl(1) 176.93(18)° in **1**, and C(1)–Hg(1)–S(1) 169.54(16)° in **4**]. The Hg(1)–N(1) distances [2.764(6) Å in **1**, and 2.725(4) Å in **4**] are considerably shorter that

the sum of the van der Waals radii for Hg and N [$\sum_{vdW}$(Hg,N) 3.05 Å] [12]; they are intermediate between the values of 2.89(1) Å for [2-(Me$_2$NCH$_2$)-C$_6$H$_4$]$_2$Hg [8] and 2.65(1) Å in (S)-[2-{Me$_2$NC(Me)H}-C$_6$H$_4$]HgCl [10], 2.69(1) Å in (S)$_C$(R)$_{Hg}$-[2-{Me$_2$NC-(Me)H}C$_{10}$H$_6$]HgCl [11] or 2.694(8) Å in [2-(2-pyr-idyl)phenyl-(C,N)]Hg[S(S)PCy$_2$] [19]. The Hg(1)–Cl(1) distance of 2.319(2) Å in **1** is similar to those observed for the related (S)-[2-{Me$_2$NC(Me)H}C$_6$H$_4$HgCl [2.323(3) Å] [10] and (S)$_C$(R)$_{Hg}$-[2-{Me$_2$NC(Me)H}-C$_{10}$H$_6$]HgCl [2.330(4) Å] [11]. In **4** the Hg(1)–S(1) bond length [2.391(2) Å] is slightly longer than in [2-(2-pyr-idyl)phenyl-(C,N)]Hg[S(S)PCy$_2$] [2.365(3) Å] [19], a be-havior which is consistent with the asymmetric bridging pattern in the former compound (see subsequent dis-cussion) in contrast to the monodentate nature of the dithio ligand in the second one.

The distortion of the three-coordinate (C,N)HgX core from the ideal T-shaped arrangement is mainly due to the restrictions imposed by the formation of the C$_3$NHg ring, the small bite of the C,N-bidentate organic ligand being reflected in the magnitude of the C(1)–Hg(1)–N(1) angle [75.0(2)° and 74.69(18)° in **1** and **4**, respectively].

As suggested previously by Nelson and co-workers [10,11], the Hg atom in the title compounds can be considered a stereocenter in solid state: the metal atom deviates from the C(1)N(1)X(1) plane by 0.058 Å in **1** and 0.190 Å in **4**, and the sum of the three angles around Hg is less (356.9° in **1**, and 352.3° in **4**, respectively) than 360° as expected for a planar structure. The molecules are thus pyramidal, with the metal atom in the apex and three different substituents on mercury describing the triangular base. The chelate, five-membered C$_3$NHg ring is not planar, but folded along the Hg(1)···C$_{methylene}$ axis (HgC$_3$/HgCN dihedral angle: 41.1° in **1**, and 39.9° in **4**, respectively), with the nitrogen atom 0.819 Å (**1**) and 0.788 Å (**4**) out from the best plane of the rest of the atoms. This induces a second source of chirality. Indeed, both compounds **1** and **4** crystalize as racemates. The molecular structure of the λ-S isomer of **1** is shown in Fig. 2 [assuming the priority numbers 1 (Cl, S), 2 (N), 3 (C) and 4 (the apex of the pyramid)] [23]. The crystal of **1** consists of discrete monomeric molecular enantiomers separated by normal van der Waals distances (the closer intermolecular Hg···Cl distance, 3.575(3) Å, is larger than the sum of the van der Waals radii, $\sum_{vdW}$(Hg,Cl) 3.4 Å [12]). For compound **4** the crystal contains dimers (Fig. 3) between pairs of (δ-R)–(λ-S) isomers connected through weak intermolecular Hg···S(=P) interactions [Hg(1)···S(2a) 3.102(2) Å; cf. the sum of the van der Waals radii, $\sum_{vdW}$(Hg,S) 3.3 Å [12] in a similar way as found for the dimeric [MeHg{S(S)PPh$_2$}]$_2$ [Hg···S 3.152(3)] [15].

With respect to the dithiophosphinato ligand in compound **4** the phosphorus–sulfur bond distances are consistent with P–S single and P=S double bonds [P(1)–S(1) 2.052(2) Å, P(1)–S(2) 1.965(2) Å; cf. Ph$_2$P(S)SH [24]: P–S 2.077(1) Å and P=S 1.954(1) Å], although the sulfur atom doubly bonded to phosphorus is bridging weakly a metal atom of a neighboring molecule. Similar phosphorus–sulfur distances [2.067(4), 1.963(4) Å] were also found for the monomeric [2-(2-pyridyl)phenyl-(C,N)]Hg[S(S)PCy$_2$] [19].

3. Conclusions

The substitution of the Cl atom in [2-(Me$_2$NCH$_2$)-C$_6$H$_4$]HgCl (**1**) by a potential bidentate ligand as the [S(S)PPh$_2$]$^-$ group in [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Hg[S(S)PPh$_2$] (**4**) does not influence the intramolecular coordination of the nitrogen atom of the CH$_2$NMe$_2$ pending arm to the metal centre. The distorted T-shaped coordination ge-ometry of the (C,N)HgX (X = Cl, S) core is preserved in the molecular unit of both compounds and the mercury atom acts as a stereocenter. Differences in the associa-tion degree in the crystal were noted, i.e. discrete mo-nomeric enantiomers for **1** and dimers associations of (δ-R)–(λ-S) isomers through weak intermolecular Hg···S interactions for **4**.

4. Experimental

4.1. Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and freshly distilled prior to use. Mercury(II) dichlo-ride, N,N-dimethylbenzylamine and butyllithium were commercially available. The other starting materials were prepared according to the literature methods: [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Li [25], Na[S$_2$PMe$_2$]·2H$_2$O [26], Na[S$_2$PEt$_2$]·2H$_2$O [27], NH$_4$[S$_2$P(O^{i}Pr)$_2$] [28], NH$_4$[S$_2$PPh$_2$] [29] and NH$_4$[OSPPh$_2$] [30,31]. Infrared spectra were recorded in the range 4000–250 cm^{-1} as KBr pellets on a Jasco FT/IR-615 instrument. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at room tem-perature on a VARIAN GEMINI 300S instrument op-erating at 299.5, 75.4 and 121.4 MHz, respectively, using solutions in dried CDCl$_3$. The chemical shifts are reported in ppm relative to TMS and H$_3$PO$_4$ 85%, respectively.

4.2. Preparation of [2-(dimethylaminomethyl)phenyl]-mercury(II) chloride, [2-(Me$_2$NCH$_2$)C$_6$H$_4$]HgCl (1)

The compound was prepared from [2-(Me$_2$NCH$_2$)-C$_6$H$_4$]Li (4.52 g, 0.032 mol) and HgCl$_2$ (8.70 g, 0.032 mol) in diethyl ether according to the literature method [7]. It was crystallized from hot hexane to give of **1** as colorless crystals. Yield: 10.1 g (85%), m.p. 76–77 °C

(dec.) (lit. [7]: 73 °C). ^{1}H NMR: δ 2.33s (6H, N–CH_3), 3.47s (2H, –CH_2–, $^{4}J_{\text{HgH}}$ 13.2 Hz), 7.23m (3H, H$_{3,4,5}$), 7.45m (1H, H$_6$, $^{3}J_{\text{HgH}}$ 207.7 Hz); ^{13}C NMR: δ 44.54s (N–CH$_3$, $^{5}J_{\text{HgC}}$ 10.3 Hz), 64.56s (–CH$_2$–, $^{3}J_{\text{HgC}}$ 103.0 Hz), 127.44s (C$_5$, $^{3}J_{\text{HgC}}$ 215.2 Hz), 128.61s (C$_4$, $^{4}J_{\text{HgC}}$ 34.3 Hz), 129.02s (C$_3$, $^{3}J_{\text{HgC}}$ 164.9 Hz), 137.18s (C$_6$, $^{2}J_{\text{HgC}}$ 139.7 Hz), 143.82s (C$_2$), 149.20s (C$_1$).

4.3. Preparation of [2-(Me₂NCH₂)C₆H₄]Hg[S(X)PR₂]

Mixtures of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]HgCl and the appropriate salt, M[SXPR$_2$] (1:1 molar ratio) in 40 ml dichloromethane were stirred for 18 h at room temperature and then filtered to remove the resulting alkali or ammonium chloride. The filtrate was evaporated under reduced pressure and an oily product was obtained. After stirring for 30 min. with *n*-hexane, a white solid deposited. It was separated by filtration, washed with *n*-hexane and dried in vacuum. Details of the preparations and melting points are given in Table 2. Microanalysis (C, H, N) and NMR spectra are consistent with the given composition of the isolated products.

4.3.1. [2-(Me₂NCH₂)C₆H₄]Hg[S(S)PMe₂] (2)

Anal. Found: C, 28.6; H, 3.7; N, 3.2. Calc. for C$_{11}$H$_{18}$HgNPS$_2$: C, 28.7; H, 3.9; N, 3.1%. ^{1}H NMR: δ 2.16d (6H, P–CH_3, $^{2}J_{\text{PH}}$ 13.2 Hz), 2.37s (6H, N–CH_3), 3.44s (2H, –CH_2–, $^{4}J_{\text{HgH}}$ 13.2 Hz), 7.20m (3H, H$_{3,4,5}$), 7.49dd (1H, H_6, $^{3}J_{\text{HH}}$ 6.6, $^{4}J_{\text{HH}}$ 1.6, $^{3}J_{\text{HgH}}$ 196.6 Hz). ^{13}C NMR: δ 32.18d (P–CH$_3$, $^{1}J_{\text{PC}}$ 53.8 Hz), 45.01s (N–CH$_3$, $^{5}J_{\text{HgC}}$ 9.2 Hz), 65.25s (–CH$_2$–, $^{3}J_{\text{HgC}}$ 98.5 Hz), 127.27s (C$_5$, $^{3}J_{\text{HgC}}$ 201.5 Hz), 128.17s (C$_4$, $^{4}J_{\text{HgC}}$ 29.8 Hz), 128.88s (C$_3$, $^{3}J_{\text{HgC}}$ 160.3 Hz), 137.32s (C$_6$, $^{2}J_{\text{HgC}}$ 135.1 Hz), 144.40s (C$_2$); the resonance for C$_1$ was not observed. ^{31}P NMR: δ 63.2s.

4.3.2. [2-(Me₂NCH₂)C₆H₄]Hg[S(S)PEt₂] (3)

Anal. Found: C, 32.2; H, 4.4; N, 2.7. Calc. for C$_{13}$H$_{22}$HgNPS$_2$: C, 32.0; H, 4.5; N, 2.9%. ^{1}H NMR: δ 1.39dt (6H, P–CH$_2$–CH_3, $^{3}J_{\text{HH}}$ 7.7, $^{3}J_{\text{PH}}$ 21.4 Hz), 2.13dq (4H, P–CH_2–CH$_3$, $^{3}J_{\text{HH}}$ 7.7, $^{2}J_{\text{PH}}$ 10.7 Hz), 2.36s (6H, N–CH_3), 3.44s (2H, –CH_2–, $^{4}J_{\text{HgH}}$ 13.2 Hz), 7.21m (3H, H$_{3,4,5}$), 7.51dd (1H, H_6, $^{3}J_{\text{HH}}$ 7.5, $^{4}J_{\text{HH}}$ 1.6, $^{3}J_{\text{HgH}}$

194.4 Hz). ^{13}C NMR: δ 7.59d (P–CH$_2$–CH$_3$, $^{2}J_{\text{PC}}$ 4.6 Hz), 33.57d (P–CH$_2$–CH$_3$, $^{1}J_{\text{PC}}$ 50.4 Hz), 45.07s (N–CH$_3$, $^{5}J_{\text{HgC}}$ 9.2 Hz), 65.42s (–CH$_2$–, $^{3}J_{\text{HgC}}$ 96.2 Hz), 127.20s (C$_5$, $^{3}J_{\text{HgC}}$ 199.2 Hz), 128.06s (C$_4$, $^{4}J_{\text{HgC}}$ 27.5 Hz), 128.82s (C$_3$, $^{3}J_{\text{HgC}}$ 160.3 Hz), 137.32s (C$_6$, $^{2}J_{\text{HgC}}$ 132.8 Hz), 144.45s (C$_2$), 156.65s (C$_1$). ^{31}P NMR: δ 85.0s ($^{1}J_{\text{PC}}$ 50.7 Hz).

4.3.3. [2-(Me₂NCH₂)C₆H₄]Hg[S(S)PPh₂] (4)

Anal. Found: C, 43.1; H, 3.8; N, 2.3. Calc. for C$_{21}$H$_{22}$HgNPS$_2$: C, 43.2; H, 3.8; N, 2.4%. IR (cm^{-1}): 650s [ν_{as} (PS$_2$)], 546v [ν_{s} (PS$_2$)]. ^{1}H NMR: δ 2.22s (6H, N–CH_3), 3.41s (2H, –CH_2–, $^{4}J_{\text{HgH}}$ 13.2 Hz), 7.20m (3H, H$_{3,4,5}$), 7.46m (7H, H$_6$ + P–C$_6$H$_5$-*meta* + *para*), 8.06dm (4H, P–C$_6$H$_5$-*ortho*, $^{3}J_{\text{PH}}$ 14.8 Hz). ^{13}C NMR: δ 44.92s (N–CH$_3$), 65.33s (–CH$_2$–, $^{3}J_{\text{HgC}}$ 98.5 Hz), 127.24s (C$_5$, $^{3}J_{\text{HgC}}$ 201.5 Hz), 128.11s (C$_4$, $^{4}J_{\text{HgC}}$ 32.0 Hz), 128.31d (P–C$_6$H$_5$-*meta*, $^{3}J_{\text{PC}}$ 13.7 Hz), 128.84s (C$_3$, $^{3}J_{\text{HgC}}$ 160.3 Hz), 130.72d (P–C$_6$H$_5$-*ortho*, $^{2}J_{\text{PC}}$ 11.6 Hz), 131.10d (P–C$_6$H$_5$-*para*, $^{4}J_{\text{PC}}$ 3.4 Hz), 137.30s (C$_6$, $^{2}J_{\text{HgC}}$ 135.1 Hz), 139.65d (P–C$_6$H$_5$-*ipso*, $^{1}J_{\text{PC}}$ 82.4 Hz), 144.39s (C$_2$), 156.50s (C$_1$). ^{31}P NMR: δ 65.5s ($^{1}J_{\text{PC}}$ 81.9 Hz).

4.3.4. [2-(Me₂NCH₂)C₆H₄]Hg[S(O)PPh₂] (5)

Anal. Found: C, 44.3; H, 3.7; N, 2.5. Calc. for C$_{21}$H$_{22}$HgNOPS: C, 44.4; H, 3.9; N, 2.4%. IR (cm^{-1}): 1165vs [ν(PO)], 575vs [ν(PS)]. ^{1}H NMR: δ 2.26s (6H, N–CH_3), 3.47s (2H, –CH_2–), 7.20m (3H, H$_{3,4,5}$), 7.35m (1H, H$_6$), 7.45m (6H, P–C$_6$H$_5$-*meta* + *para*), 7.95ddd (4H, P–C$_6$H$_5$-*ortho*, $^{3}J_{\text{HH}}$ 7.1, $^{4}J_{\text{HH}}$ 1.7, $^{3}J_{\text{PH}}$ 13.2 Hz). ^{13}C NMR: δ 44.49s (N–CH$_3$), 65.04s (–CH$_2$–, $^{3}J_{\text{HgC}}$ 96.2 Hz), 127.35s (C$_5$), 128.26s (C$_4$), 128.29d (P–C$_6$H$_5$-*meta*, $^{3}J_{\text{PC}}$ 13.7 Hz), 128.99s (C$_3$), 130.67d (P-C$_6$H$_5$-*ortho*, $^{2}J_{\text{PC}}$ 11.5 Hz), 131.30d (P–C$_6$H$_5$-*para*, $^{4}J_{\text{PC}}$ 3.4 Hz), 137.30s (C$_6$, $^{2}J_{\text{HgC}}$ 132.8 Hz), 139.15d (P–C$_6$H$_5$-*ipso*, $^{1}J_{\text{PC}}$ 105.4 Hz); the resonances for C$_1$ and C$_2$ were not observed. ^{31}P NMR: δ 48.5s.

4.3.5. [2-(Me₂NCH₂)C₆H₄]Hg[S(S)P(OⁱPr)₂] (6)

Anal. Found: C, 32.7; H, 4.7; N, 2.5. Calc. for C$_{15}$H$_{26}$HgNO$_2$PS$_2$: C, 32.9; H, 4.9; N, 2.6%. ^{1}H NMR: δ 1.42d [12H, P–OCH(CH_3)$_2$, $^{3}J_{\text{HH}}$ 6.0 Hz], 2.39s (6H, N–CH_3), 3.50s (2H, –CH_2–), 4.92dh [2H, P–

Table 2
Preparation data and m.p. for R′Hg[S(X)PR$_2$] [R′ = 2-(Me$_2$NCH$_2$)C$_6$H$_4$–] derivatives

Starting materials		Product [yield: g (%)]	m.p. (°C)
R′HgCl (g (mmol))	M[SXPR₂] (g (mmol))		
0.222 (0.6)	Na[S₂PMe₂]·2H₂O 0.110 (0.6)	[2-(Me₂NCH₂)C₆H₄]Hg[S(S)PMe₂] (**2**) 0.179 (65)	97
0.222 (0.6)	Na[S₂PEt₂]·2H₂O 0.125 (0.6)	[2-(Me₂NCH₂)C₆H₄]Hg[S(S)PEt₂] (**3**) 0.208 (71)	83
0.222 (0.6)	NH₄[S₂PPh₂] 0.160 (0.6)	[2-(Me₂NCH₂)C₆H₄]Hg[S(S)PPh₂] (**4**) 0.252 (72)	121
0.222 (0.6)	NH₄[SOPPh₂] 0.150 (0.6)	[2-(Me₂NCH₂)C₆H₄]Hg[S(O)PPh₂] (**5**) 0.225 (66)	89 (dec.)
0.222 (0.6)	NH₄[S₂P(OⁱPr)₂] 0.138 (0.6)	[2-(Me₂NCH₂)C₆H₄]Hg[S(S)P(OⁱPr)₂] (**6**) 0.25 (76)	–[a]

[a] Viscous oil.

Table 3
X-ray crystal data and structure refinement for **1** and **4**

	1	**4**
Empirical formula	$C_9H_{12}ClHgN$	$C_{42}H_{44}Hg_2N_2P_2S_4$
Formula weight	370.24	1168.19
T (K)	297(2)	297(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimension		
a (Å)	5.838(3)	9.451(3)
b (Å)	13.118(6)	10.943(3)
c (Å)	13.886(6)	11.128(3)
α (°)		77.450(4)
β (°)	93.648(9)	80.274(4)
γ (°)		78.596(4)
V (Å³)	1061.3(9)	1091.7(5)
Z	4	1
D_{calc} (g cm⁻³)	2.317	1.777
Absorption coefficient (mm⁻¹)	14.702	7.319
$F(000)$	680	564
Crystal size (mm)	$0.20 \times 0.20 \times 0.34$	$0.28 \times 0.18 \times 0.07$
θ range for data collection (°)	2.1–26.4	1.9–25.7
Reflections collected	8378	8332
Independent reflections (R_{int})	2169 (0.042)	4106 (0.0386)
Data/restraints/parameters	2169/0/111	4106/0/237
Goodness-of-fit on F^2	1.02	1.037
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0324$, $wR_2 = 0.0630$	$R_1 = 0.0342$, $wR_2 = 0.0725$
R indices (all data)	$R_1 = 0.0472$, $wR_2 = 0.0677$	$R_1 = 0.0391$, $wR_2 = 0.0746$
Largest difference peak and hole (e Å⁻³)	0.61 and −0.84	1.094 and −0.986

$OCH(CH_3)_2$, $^3J_{HH}$ 6.6, $^3J_{PH}$ 12.6 Hz], 7.22m (3H, $H_{3,4,5}$), 7.49d (1H, H_6, $^3J_{HH}$ 6.3, $^3J_{HgH}$ 197.8 Hz). ^{13}C NMR: δ 23.81d [P–$OCH(CH_3)_2$, $^3J_{PC}$ 4.6 Hz], 44.80s (N–CH_3), 65.31s (–CH_2–, $^3J_{HgC}$ 98.5 Hz), 73.20d (P–$OCH(CH_3)_2$, $^2J_{PC}$ 6.9 Hz), 127.41s (C_5, $^3J_{HgC}$ 197.0 Hz), 128.24s (C_4, $^4J_{HgC}$ 32.1 Hz), 129.17s (C_3, $^3J_{HgC}$ 160.4 Hz), 137.83s (C_6, $^2J_{HgC}$ 132.8 Hz), 144.40s (C_2); the resonance for C_1 was not observed. ^{31}P NMR: δ 97.4s.

4.4. X-ray structure determination

Colourless, block crystals of [2-(Me₂NCH₂)C₆H₄]HgCl (**1**) and [2-(Me₂NCH₂)C₆H₄]Hg[S(S)PPh₂] (**4**) were mounted on a cryoloop. Data collection and processing was carried out using a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca). Cell refinement gave cell constants corresponding to a monoclinic cell for **1** and a triclinic cell for **4**, whose dimensions are given in Table 3 along with other experimental parameters.

An absorption correction was applied [32]. The structures were solved by direct methods [32,33] and refined using SHELX-97 [32,34]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 and 1.5 times that of the aromatic/methylene and methyl carbon atom, respec-

tively, to which they were attached. The drawings were created with the DIAMOND program [35].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 215788 for compound **1** and 215787 for compound **4**. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] (a) K. Brodersen, H.-U. Hummel, in: G. Wilkinson, R. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, 1987, p. 1047;
(b) J.L. Wardell, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon Press, Oxford, 1982, p. 863;
(c) J.L. Wardell (Ed.), Organometallic Compounds of Zn, Cd and Hg, Chapman & Hall, London, 1985;
(d) D.K. Breitinger, W.A. Herrmann, in: W.A. Herrmann (Ed.), Synthetic Methods of Organometallic and Inorganic Chemistry, vol. 5, Georg Thieme Verlag, Stuttgart, 1989, p. 193.

[2] (a) A. Spencer, in: G. Wilkinson, R. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 6, Pergamon Press, Oxford, 1987, p. 1026;
(b) W. Carruthers, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 7, Pergamon Press, Oxford, 1982, p. 671.

[3] L.G. Kuz'mina, Y.T. Struchkov, Croat. Chim. Acta 57 (1984) 701.

[4] M. Ali, W.R. McWhinnie, T.A. Hamor, J. Organomet. Chem. 371 (1989) C37.

[5] E.C. Constable, T.A. Leese, D.A. Tocher, J. Chem. Soc., Chem. Commun. (1989) 570.

[6] E.C. Constable, A.M.W. Cargill Thompson, T.A. Leese, D.G.F. Reese, D.A. Tocher, Inorg. Chim. Acta 182 (1991) 93.

[7] A.F.M.J. van der Ploeg, C.E.M. van der Kolk, G. van Koten, J. Organomet. Chem. 212 (1981) 283.

[8] J.L. Atwood, D.E. Berry, S.R. Stobart, M.J. Zaworotko, Inorg. Chem. 22 (1983) 3480.

[9] H. Schumann, S. Freitag, F. Girgsdies, H. Hemling, G. Kociok-Köhn, Eur. J. Inorg. Chem. (1998) 245.

[10] S. Attar, J.H. Nelson, J. Fischer, Organometallics 14 (1995) 4476.

[11] N. Gül, J.H. Nelson, J. Mol. Struct. 475 (1999) 121.

[12] N. Wiberg, Holleman-Wiberg – Lehrbuch der Anorganischen Chemie, Walter de Gruyter, Berlin, 1995.

[13] H.C.L. Abbenius, M. Pfeffer, J.P. Sutter, A. de Cian, J. Fischer, H.-J. Li, J.H. Nelson, Organometallics 12 (1993) 4464.

[14] S. Attar, V.J. Catalano, J.H. Nelson, Organometallics 15 (1996) 2932.

[15] J. Zukerman-Schpector, E.M. Vazquez-Lopez, A. Sanchez, J.S. Casas, J. Sordo, J. Organomet. Chem. 405 (1991) 67.

[16] E.M. Vazquez-Lopez, A. Castineiras, A. Sanchez, J.S. Casas, J. Sordo, J. Crystallogr. Spectrosc. Res. 22 (1992) 403.

[17] J.S. Casas, A. Castineiras, A. Sanchez, J. Sordo, E.M. Vazquez-Lopez, J. Organomet. Chem. 468 (1994) 1.

[18] J.S. Casas, A. Castineiras, I. Haiduc, A. Sanchez, J. Sordo, E.M. Vazquez-Lopez, Polyhedron 16 (1997) 781.

[19] J.S. Casas, E.E. Castellano, M.S. Garcia Tasende, A. Sanchez, J. Sordo, E.M. Vazquez-Lopez, J. Zukerman-Schpector, Acta Crystallogr., Sect. C 56 (2000) 182.

[20] E. Lindner, H.M. Ebinger, Chem. Ber. 107 (1974) 135.

[21] A. Silvestru, C. Silvestru, I. Haiduc, J.E. Drake, J. Yang, F. Caruso, Polyhedron 16 (1997) 949, and references therein.

[22] J.C. Tebby (Ed.), CRC Handbook of Phosphorus-31 Nuclear magnetic Resonance Data, vol. 13, CRC Press, Boca Raton, FL, 1991, p. 364.

[23] IUPAC Nomenclature of Organic Chemistry, 1979 ed., Pergamon Press, Oxford, 1979.

[24] B. Krebs, G. Henkel, Z. Anorg. Allg. Chem. 475 (1981) 143.

[25] A. Meller, H. Hoppe, W. Meringgele, A. Haase, M. Noltemeyer, Organometallics 17 (1998) 123.

[26] R.G. Cavell, W. Byers, E.D. Day, Inorg. Chem. 10 (1971) 2710.

[27] W. Kuchen, K. Strolenberg, J. Metten, Chem. Ber. 96 (1963) 1733.

[28] C. Silvestru, Ph.D. Thesis, Babes-Bolyai University, Cluj-Napoca, Romania, 1990.

[29] C. Silvestru, A. Silvestru, I. Haiduc, R. Gavino Ramirez, R. Cea-Olivares, Heteroatom. Chem. 5 (1994) 327.

[30] W.A. Higgins, R.W. Vogel, W.G. Craig, J. Am. Chem. Soc. 77 (1955) 1864.

[31] C. Silvestru, I. Haiduc, K.H. Ebert, H.J. Breunig, D.B. Sowerby, J. Organomet. Chem. 468 (1994) 113.

[32] Bruker, SADABS (Version 2.03), SHELXTL (Version 6.10) and SMART (Version 5.625), Bruker AXS Inc., Madison, WI, 2000.

[33] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[34] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

[35] DIAMOND – Visual Crystal Structure Information System, CRYSTAL IMPACT: Postfach 1251, D-53002 Bonn, Germany, 2001.