Synthesis and Molecular Structures of Platinum and Mercury Complexes Chelated by (Phenylthiomethyl)silane Ligands

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Abstract. Metathesis reaction of the dithioether complex cis-[PtCl₂{(PhSCH₂)₂SiPh₂}] (2a) with NaBr and NaI yields the square planar complexes cis-[PtX₂{(PhSCH₂)₂SiPh₂}] (**2b**, X = Br; **2c**, X = I). The new compounds, which are fluxional in solution, have been studied by multinuclear NMR techniques; the crystal structures of 2a-c have been determined by X ray diffraction. This series allows to evaluate the trans-influence of the halide ligands on the lengths of the Pt-S bonds, which increase from 227.26(12) (2a), 228.46(13) (2b) to 229.96(15) (2c) pm due to a more pronounced trans-influence of I compared with Br and Cl. Complexation of (PhSCH₂)₂SiPh₂ (1a) on HgBr₂ gives the distorted tetrahedral compound [HgBr₂{(PhSCH₂)₂SiPh₂}] (3), having a quite loose coordination of the ligand both in solution and in the solid state [Hg-S =

291.88(2) pm]. Alternatively, the coordination around Hg may be described as distorted square pyramidal in the solid state, since to due to a weak intermolecular Hg. Br interaction [346.72(13) pm], a dimeric motif is formed. Furthermore, the functionalised cyclic silane (PhSCH₂)₂SiC₄H₆ (1b) has been prepared and co-ordinated as chelating dithioether ligands to [PtCl2(PhCN)2] affording the dithioether complex cis-[PtCl₂{(PhSCH₂)₂SiC₄H₆)}] (4). The crystal structure of 4 has also been determined by an X-ray diffraction study.

Keywords: Platinum; Mercury; Dithioether complexes; Trans-influence; Crystal structures; Silicon

Synthese und Molekülstrukturen einiger Dithioether-Platin- und Quecksilberkomplexe mit chelatisierenden (Phenylthiomethyl)silan-Liganden

Inhaltsübersicht. Die Metathesereaktion des Dithioetherkomplexes cis-[PtCl₂{(PhSCH₂)₂SiPh₂}] (2a) mit NaBr und NaI ergibt die quadratisch-planaren Komplexe cis-[PtX₂{(PhSCH₂)₂SiPh₂}] (**2b**, X = Br; 2c, X = I). Die neuen Verbindungen, welche mittels Multikern-NMR untersucht wurden, zeigen dynamisches Verhalten in Lösung. Die Kristallstrukturen von 2a-c wurden mittels Einkristall-Röntgenstrukuranalyse bestimmt. Diese Serie erlaubt eine Abschätzung des trans-Einflusses der Halogen- Liganden auf die Pt-S-Bindungslängen. Diese wachsen von 227.26(12) (2a), 228.46(13) (2b) auf 229.96(15) (2c) pm infolge eines ausgeprägteren trans-Einflusses von I im Vergleich mit Cl und Br. Koordination von (PhSCH₂)₂SiPh₂ (1a) an HgBr₂ ergibt den verzerrt tetraedrischen Komplex [HgBr₂{(PhSCH₂)₂SiPh₂}] (3). In dieser Verbindung ist der Ligand sowohl in Lösung als auch im Festkörper ziemlich locker gebunden [Hg-S = 291.88(2) pm]. Die Koordination um das Hg-Atom lässt sich im Festkörper besser als verzerrt quadratisch-pyramidal beschreiben, da infolge einer schwachen intermolekularen Hg. Br-Wechselwirkung [346.72(13) pm] ein dimeres Motiv vorliegt. Weiterhin wurde das funktionalisierte cyclische Silan (PhSCH₂)₂SiC₄H₆ (1b) hergestellt und als chelatisierender Dithioether-Ligand an [PtCl2(PhCN)2] gebunden. Die Kristallresultierenden Dithioether-Komplexes struktur des cis- $[PtCl_2{(PhSCH_2)_2SiC_4H_6}]$ (4) wurde ebenfalls ermittelt.

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Introduction

In the past, chelating dithioether ligands RSX_nSR have been used as innocent spectator ligands in coordination chemistry [1]. However, a growing number of recent papers deals on the application of dithioether complexes for homogeneous catalysis. For example, rhodium(I) complexes ligated by atropisomeric dithioether ligands are catalytically

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active in hydroformylation of styrene, iridium(I) complexes chelated by 1,4-bis(isopropylthio)butane have been applied in hydrogenation of olefins [2, 3]. Square-planar Pd^{II} dithioether complexes are known to catalyze the alternating copolymerization of CO/ *tert*-butylstyrene [4], other catalytic applications have been very recently summarized in a review article [5]. In the context of our interest on the reactivity of the Pt-alkyl bond towards small insaturated molecules [6], we have prepared a series of platinum dithioether complexes of the type *cis*-[PtX₂{(PhSCH₂)₂SiR₂}] (X = hal). These precursor compounds, chelated with a potentially hemilabile dithioether ligand, may present after alkylation promising complexes for organometallic chemistry.

Results and Discussion

Synthesis of platinum complexes chelated by diphenylbis[(phenylthio)methyl]silane

In a previous paper we have described the synthesis of *cis*- $[PtCl_2{(PhSCH_2)_2SiPh_2}]$ (2a') by reaction of diphenylbis-[(phenylthio)methyl]silane (1a) with $[PtCl_2(PhCN)_2]$ in toluene and presented the molecular structure of this compound recorded at 298 K. The pale yellow crystals, obtained by recrystallisation from CH₂Cl₂, crystallized in the triclinic space group P1 [7]. However, using CHCl₃, as solvent for recrystallisation, orthorhombic crystals of 2a (space group Pbca) were formed and subjected to an X-ray diffraction study at 173 K (Fig. 3 and Table 1, see below). In order to evaluate the *trans*-influence of halide ligands situated trans with respect to the thioether groups of complexes of the type cis-[PtX₂{(PhSCH₂)₂SiPh₂}] (X = Cl, Br, I), we reacted 2a with a 10-fold excess of NaBr or NaI in acetone as solvent. This metathesis reaction afforded the air stable derivatives cis-[PtBr₂{(PhSCH₂)₂SiPh₂}] (**2b**) and cis-[PtI₂{(PhSCH₂)₂SiPh₂}] (2c), respectively.

As already noticed for 2a, bright yellow 2b also exhibits dynamic behaviour in solution due to a facile inversion process at the sulphur atoms in solution (Scheme 1). This tem-



Scheme 1

perature-dependent coexistence of meso(syn)and DL(anti)-isomers was examined by ¹H and ¹⁹⁵Pt NMR only in a qualitative manner, since more detailed studies on this phenomena have been published in the past by other groups [1]. The presence of meso- and DL-isomers of 2b is evidenced from the ¹⁹⁵Pt{¹H} NMR spectrum recorded at 298 K, which displays two broad humps at δ -2292 and -2303. At 323 K the pyramidal inversion is sufficiently fast, so that only one "averaged planar" conformation is observed resulting in broadened singlet resonance centred at δ -2289 (Figure 2). In the ¹H NMR spectrum of **2b** recorded at 298 K, the methylene resonance appears in form of a very broad resonance at δ 3.01, which sharpens on progressive heating to give finally (328 K) a sharp singlet at δ 3.12 with a ${}^{3}J_{\text{Pt,H}}$ coupling of 56 Hz. In the case of the iodo-derivative 2c, a broad singulet resonance centered at δ 2.99 is already observable at 298 K.

Figure 2 presents the normalized UV-vis spectra of ligand **1a** and complex **2c**. The superposition shows that both compounds exibit an intense absorption at 227 nm with molecular extinction coefficients around $62000 \text{ M}^{-1}\text{cm}^{-1}$. The complex **2c** possesses a second low energy absorption at 258 nm and a third broad, less intense band at 411 nm with ε 1300 M⁻¹cm⁻¹, which is absent in **1a**.



Fig. 1 $^{195}\text{Pt}\{^{1}\text{H}\}$ NMR spectrum of 2b in CDCl3 recorded at 298 and 323 K

-2296

-2300

-2304

-2308 (ppm)

- 2202

. 2288



Fig. 2 Absorption spectra of 1a and 2c carried out in CH_2Cl_2 at 298 K.

Crystal structures of 2a-c

Suitable single crystals were grown from CHCl₃/heptane (2a) or CH₂Cl₂/heptane (2b,c). Figure 3 shows a platinum(II) atom in a square planar environment with a cisarrangement of the two chloro ligands [Cl(1)-Pt-Cl(2)] =90.11(5)°]. The root mean square deviation from the plane defined by Cl(1)-Cl(2)-Pt-S(1)-S(2) amounts to 0.031 Å. The six membered Pt-S(1)-S(2)-C(1)-C(2)-Si chelate ring adopts a distorted chair conformation very similar to that reported for cis-[PtCl₂{PhS(CH₂)₃SPh}] ligated by a 1,3-bis-(phenylthio)propane ligand [8]. In contrast to the latter complex, in which the phenyl substituents of the sulphur atoms are in an anti-mode with respect to the chelate ring, the two phenyl groups of 2a are syn-orientated corresponding to a meso-conformation. The Pt-S(1) and Pt-S(2) bond distances of 227.23(12) and 227.30(13) pm parallel that of [PtCl₂{PhS(CH₂)₃SPh}] [227.1(2) and 227.4(2) pm]. The averaged Pt-Cl bond length of 2a [231.72(13) pm] is also almost equal to that of the 1,3-bis(phenylthio)propane counterpart [232.50 pm].

A view of the square planar molecular structure of the dibromo derivative **2b**, which is isomorphous (orthorhom-



Fig. 3 View of the molecular structure of cis-[PtCl₂{(PhSCH₂)₂SiPh₂}] (2a)



Fig. 4 View of the molecular structure of *cis*-[PtBr₂{(PhSCH₂)₂SiPh₂}] (2b)

Pt-S(1) Pt-S(2)	227.23(12) 227.30(13)	228.61(12) 228.30(14)	230.3(2) 229.61(14)	227.05(12) 226.51(11)
Pt-Cl(1) Pt-Cl(2) Pt-Br(1) Pt-Br(2) Pt-I(1) Pt-V(2)	232.58(13) 230.85(12)	245.57(7) 243.99(7)	262.64(8)	230.42(12) 229.16(13)
S(1)-C(1) S(2)-C(2) S(1)-C(3) S(2)-C(9) Si-C(1) Si-C(1)	181.0(5) 181.3(5) 177.0(5) 177.5(5) 188.5(5) 188.6(5)	182.9(6) 182.1(6) 178.0(6) 178.2(6) 188.9(6) 189.6(6)	182.8(5) 182.0(6) 179.4(5) 180.8(6) 187.6(5) 188.9(5)	180.8(5) 189.4(5) 178.8(5) 176.9(4) 188.8(4) 119.4(3)
Cl(1)-Pt-Cl(2) Cl(1)-Pt-S(1) Cl(2)-Pt-S(1) Cl(1)-Pt-S(2) Cl(2)-Pt-S(2)	90.11(5) 83.15(5) 172.53(4) 177.32(4) 92.57(5)			88.69(4) 85.87(4) 173.31(4) 177.01(4) 93.51(4)
S(1)-Pt-S(2) C(1)-Si-C(2) S(1)-C(1)-Si S(2)-C(2)-Si C(1)-S(1)-Pt C(2)-S(2)-Pt	94.17(4) 107.3(2) 119.4(3) 108.7(2) 112.8(2) 105.6(2)	93.60(5) 108.1(3) 119.4(3) 107.9(3) 113.3(2) 106.3(2)	99.55(6) 109.5(2) 115.9(3) 117.6(3) 112.1(2) 107.1(2)	92.07(4) 108.3(2) 110.4(2) 119.4(3) 109.36(15) 105.5(2)
Br(1)-Pt-Br(2) Br(1)-Pt-S(1) Br(2)-Pt-S(1) Br(1)-Pt-S(2) Br(2)-Pt-S(2)		89.58(3) 83.61(4) 172.46(4) 177.11(4) 93.17(4)		
I(1)-Pt-I(2) I(1)-Pt-S(1) I(2)-Pt-S(1) I(1)-Pt-S(2) I(2)-Pt-S(2)			89.11(4) 86.01(5) 174.26(3) 170.11(3) 85.72(5)	

Table 1 Selected bond lengths/pm and bond angles/° of 2a-c and 4



Fig. 5 View of the molecular structure of cis -[PtI₂{(PhSCH₂)₂SiPh₂}] (2c)

bic, space group Pbca) with **2a**, is given in Figure 4. Table 1 shows that substitution of the chloro ligands by two bromo ligands does not affect the most pertinent structural features in a significant manner. However, substitution by two voluminous iodo ligands alters the structural parameters noticeably. Derivative **2c** crystallizes (solvated with two molecules of CH_2Cl_2) within the triclinic space group $P\overline{l}$. The coordination around the metal atom (Figure 5) exhibits

now a more pronounced deviation from ideal square planar, the rms deviation fitted through I(1)-I(2)-Pt-S(1)-S(2) being 0.1075 Å. In particular the angle I(1)-Pt-S(2) is more acute than the angle Cl(1)-Pt-S(2) of 2a [170.11(3) vs. 177.32(4)°], whereas the angles I(2)-Pt-S(1) and Cl(1)-Pt-S(2) remain in a similar range [174.26(3) vs. 172.53(4)°]. The angle S(1)-Pt-S(2) which is in the case of 2a and 2b about 94°, opens to 99.55(6)° in the case of 2c. The Pt-S(1) and Pt-S(2) bond distances of 230.3(2) and 229.61(14) pm are also significantly longer than those of 2a. This elongation of the Pt-S bonds within the series 2a-c is probably due to thermodynamic trans-influence exerted by the halide, which is known to increase from Cl < Br < I [9]. The comparison with the literature-known five-membered chelate complexes cis-[PtX₂(PhSCH₂CH₂SPh)] (X = Cl, Br, I) [10] reveals that chelatation by a six-membered chelate ring causes a systematic lengthening of the average Pt-S bond distances by ca. 3 pm [224.7 vs 227.26(12) 2a], [224.8 vs 228.46(13) 2b] and 226.5 vs. 229.96(15) 2c pm].

Synthesis of [HgBr₂{(PhSCH₂)₂SiPh₂}]

For structural comparison with $[PtBr_2{(PhSCH_2)_2SiPh_2}]$ (2b), we prepared also the analogous mercury complex $[HgBr_2{(PhSCH_2)_2SiPh_2}]$ (3) by reacting $HgBr_2$ with 1a in toluene. This compound, which crystallizes in form of stable colourless crystals, displays in the proton NMR spectrum a sharp resolved singlet resonance at δ 2.98 due to the methylene groups. The absence of any noticeable ¹⁹⁹Hg couplings as well a chemical shift close to that of non-coordinated 1a ($\delta = 2.84$) may be indicative for labile coordination of the dithioether ligand on HgBr₂ in solution. Note that UV-vis, conductivity and molecular weight measurements on addition compounds between aliphatic thioethers and mercury(II) chloride have evidenced a strong dissociation in solution [11]. More recentlely, Sanger has reported on the facile dissociation of dithioether complexes of the type $[HgCl_2{PhS(CH_2)_nSPh}]$ (n = 1-4) in solution [12]. This hypothesis of a loose bonding of 1a on HgBr₂ is corroborated by the findings of an X-ray diffraction study performed on single crystals of 3. Figure 6 shows that the "tetrahedral" coordination around the Hg atom is severely distorted. The angle Br(1)-Hg-Br(2) [160.39(4)°] is close to linearity, the angle S(1)-Hg-S(2) [76.24(6)°] deviates also significantly from tetrahedral (table 2). Despite the soft nature of mercury, the averaged Hg-S bond distance of 3 is far longer than that of 2b (291.85 vs. 228.46 pm; atomic radii 1.62 vs. 1.373 Å). Even compared to other Hg^{II} complexes ligated by chelating thioether ligands, the bond distances of 3 are considerably elongated [13]. Thus, an averaged Hg-S bond length of 261.2 pm has been encountered for the cationic compound [N(CH₂CH₂S-*i*-Pr)₃HgCl]⁺ chelated by a tripod-like tristhioether ligand [14], 269.3 pm have been reported for the macrocyclic complex [bis(1,4,7-trithiacyclodecane)Hg]₂ [15, 16]. Bond distances closer to those of 3 have been reported for the macrocyclic dinuclear complex trabromo(1,4,7,10,13,16-hexathiahiacyclooctadecane)Hg₂],

Table 2Selected bond lengths/pm and bond angles/° of 3

Hg-S(1)	288.9(2)	Br(1)-Hg-Br(2)	160.39(4)
Hg-S(2)	294.7(2)	Br(1)-Hg-S(1)	97.98(5)
Hg-Br(1)	244.99(10)	Br(2)-Hg-S(1)	100.21(5)
Hg-Br(2)	244.74(10)	Br(1)-Hg-S(2)	94.69(5)
S(1)-C(1)	181.1(8)	Br(2)-Hg-S(2)	96.69(5)
S(2)-C(2)	179.4(8)	S(1)-Hg-S(2)	76.24(5)
S(1)-C(3)	177.5(8)	C(1)-S(1)-C(3)	106.4(4)
S(2)-C(9)	179.3(7)	S(1)-C(1)-Si	112.8(4)
Si-C(1)	187.5(8)	S(2)-C(2)-Si	117.9(5)
Si-C(2)	189.2(7)	C(1)-S(1)-Hg	110.7(2)
$Hg-Br(1)^{\#}$	346.72(13)	C(2)-S(2)-Hg	100.5(3)
Hg-Br(2) [#]	513.3(2)	Br(1)-Hg-Br(1)#	91.66(3)
		S(1)-Hg-Br(1) [#]	94.98(4)



Fig. 6 View of the dimeric motif of 3

with averaged bond length of 277.2(5) pm between the thia donors and the two Hg^{II} atoms [17]. The Hg-Br distances of 248.1(3) and 254.0(5) pm of the latter complex are markedly longer than those of 3 [244.99(10) and 244.74(10) pm], the angle Br-Hg-Br of 141.55° being closer to tetrahedral than that of 3. As shown in Figure 6, the Hg center of 3 forms additionally an intermolecular contact of 346.72(13) pm with the bromo ligand $Br(1^{\#})$ of a second molecule, thus giving rise to a dimeric motif. Therefore, the effective coordination around each Hg atom of the dimeric unit is better described as distorted square pyramidal. The Hg...Hg# separation of 418.70(15) pm excludes any bonding interactions between the two d10 centers. An intermolecular Hg...Br contact of 342.7(3) pm exists also in the afore-mentioned compound [(1,4,7,10,13,16-hexathiahiacyclooctadecane)-Hg₂Br₄], which forms thus a 1D polymer considering the effective coordination around Hg as trigonal bipyramidal [17].

Synthesis of cis-[PtCl₂{(PhSCH₂)₂SiC₄H₆}]

We synthesized furthermore the functionalized dithioether ligand 1,1-bis(phenylthiomethyl)-2,5-dihydro-1*H*-silole (1b) incorporating a five-membered silacyclopentene unit by reaction of 1,1-dichlorosilacyclopenten-3-ene [18] with [(phenylthio)methyl]lithium at -40 °C according Scheme 2. The interest in this ligand system which was isolated as a waxy solid, stems from the presence of a potentially reactive olef-

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inic double bond. This functionalization may allow subsequent transformations like hydrosilylation or polymerization reactions. Compound **1b** was then coordinated on [PtCl₂(PhCN)₂] as chelating dithioether ligand forming the complex *cis*-[PtCl₂{(PhSCH₂)₂SiC₄H₆] (**4**), which was isolated in form of air-stable yellow crystals from chloroform. This complex which is only moderately soluble in halogenated solvents, is also fluxional according the ¹H NMR spectra recorded at variable temperature. At 298 K, the CH₂SPh protons give rise to a very broad hump at δ 2.64, which sharpens on heating to give finally (323 K) a broadened singlet at δ 2.76 with a ³J_{Pt,H} coupling of 52 Hz.





An X-ray diffraction study (Figure 7) shows that the coordination around Pt is close to ideal square planar (rms deviation from the plane defined by Pt-Cl(1)-Cl(2)-S(1)-S(2) 0.053 Å), the angles Cl(1)-Pt-Cl(2) and S(1)-Pt-S(2) being 88.69(4) and 92.07(4)°, respectively. The comparison with **2a** (Table 1) reveals that the Pt-S distances are almost the same, however the averaged Pt-Cl distances are slightly shorter [231.72(13) vs. 229.79(12) pm]. Again, the phenyl substituents of the sulphur atoms are in a *cis*-mode with respect to the chelate ring, corresponding to a *meso*-conformation.



Fig. 7 View of the molecular structure of $[PtCl_2{(PhSCH_2)_2SiC_4H_6}]$ (4)

Conclusion and Perspectives

We have shown that dithioether ligand (PhSCH₂)₂SiPh₂ (1a) forms stable coordination compounds upon complexation on platinum(II), however in the case of mercury(II) the coordination is loose both in solution and the crystalline state. We are currently investigating the possibility to alkylate or arylate the Pt-complex 2a by transmetallation reaction with SnR_4 [19, 20] in order to exploit the reactivity of cis-[PtR(Cl){(PhSCH₂)₂SiPh₂}] in organometallic chemistry and catalysis. As an extension of this of work we will also report in a forthcoming paper on the use of the tetrakis-thioether (PhSCH₂)₄Si and (PhSCH₂)₄Ge [21, 22] as tetradentate assembling ligands for the construction of heterodinuclear homoand systems of type $[L_nM{(PhSCH_2)_2Si(CH_2SPh)_2}ML_n]$ (M = Cd, Hg, Cu, Mn, Re, Pt).

Experimental Part

All reactions were performed in Schlenk-tube flasks under purified nitrogen. Solvents were dried and distilled under nitrogen before use, toluene and hexane over sodium, dichloromethane from P_4O_{10} . – IR spectra have been recorded on a Nicolet Nexus 470 spectrometer, UV-vis spectra on a Uvikon-XLspectometer. – Elemental C, H analyses were performed on a Leco Elemental Analyser CHN 900. – The ¹H NMR spectra were recorded at 300.13 MHz on a Bruker Avance 300 instrument. ¹⁹⁵Pt chemical shifts were measured on a Bruker ACP 200 instrument (42.95 MHz) and externally referenced to K₂[PtCl₄] in water with downfield chemical shifts reported as positive. NMR spectra were recorded in pure CDCl₃. Diphenylbis[(phenylthio)methyl]silane (**1a**) was prepared as previously described [23].

Preparation of $(PhSCH_2)_2SiC_4H_6$ (1b)

A cooled solution of 0.24 mol of (phenylthiomethyl)lithium in 200 mL of diethyl ether/hexane, prepared from thioanisole and *n*-BuLi in diethyl ether, was added at -40 °C to a solution of 0.08 mol of 1,1-dichlorosilacyclopent-3-ene in 30 mL of diethyl ether. The reaction mixture was warmed to room temperature and filtered. The solvent was evaporated in vacuo, and the residue was purified by Kugelrohr distillation.Yield: 54 %. *Anal.* Calc. for C₁₈H₂₀SiS₂ (328.5): C, 65.80; H 6.14. Found: C, 66.3; H 6.3 %. ¹H NMR: $\delta = 1.58$ (m, 4H, SiCH₂, ³*J*_{H, H} = 1.1 Hz), 2.49 (s, 4H, SiCH₂S), 5.95 (m, 2H, C=CH, ³*J*_{H,H} = 1.1 Hz), 7.1–7.34 (m, 10 H, SC₆H₃).

Preparation of $PtBr_2\{(PhSCH_2)_2SiPh_2\}$ (2b)

To a solution of **2a** (347 mg, 0.5 mmol) in a 50:50 mixture of 12 ml of dichloromethane/acetone was added an 10-fold excess of NaBr. The suspension was then stirred for 24 h. The solvent then was removed under reduced pressure and the residue extracted with CH₂Cl₂. After concentration of the extract, layering with hexane gave yellow crystals. (265 mg, 76 % yield). *Anal.* Calc. for C₂₆H₂₄Br₂PtS₂Si (783.57): C, 39.85; H 3.09. Found: C, 39.77; H 3.01 %. ¹H NMR (328 K): $\delta = 3.12$ (s, 2H, ³*J*_{Pt,H} = 56 Hz). ¹⁹⁵Pt{¹H} NMR (323 K): $\delta = -2289$ (s,br).

Preparation of $PtI_2\{(PhSCH_2)_2SiPh_2\}$ (2c)

This complex was obtained in a similar manner by adding NaI. After concentration of the extract, layering with heptane gives orange crystals of **2c** • 2 CH₂Cl₂, which loose the solvent molecules during drying *in vacuo*. (355 mg, 81 % yield). *Anal.* Calc. for C₂₆H₂₄I₂PtS₂Si (876.59): C, 35.59; H 2.76. Found: C, 35.17; H 2.64 %. ¹H NMR: δ = 2.99 (s, 2H, ³J_{Pt,H} = 55 Hz), 7.28 – 7.83 (m, 20H, phenyl).

Preparation of $HgBr_2\{(PhSCH_2)_2SiPh_2\}$ (3)

To a suspension of HgBr₂ (360.5 mg, 1 mmol) in 10 ml of toluene was added **1a** (428 mg, 1 mmol). The solution was stirred at 25 °C for 24 h. Layering the clear solution with hexane afforded colorless crystals, suitable for X-ray diffraction. (594 mg, 75 % yield). *Anal.* Calc. for $C_{26}H_{24}Br_2HgS_2Si$ (789,08): C, 39.07; H 3.07. Found: C, 39.48; H 3.49 %.

Preparation of $PtCl_2\{(PhSCH_2)_2SiC_4H_6\}$ (4)

To a solution of [PtCl₂(PhCN)₂] (471.8 mg, 1 mmol) in 8 ml of dichloromethane was added **1b** (361 mg, 1.1 mmol). The solution was stirred at 25 °C for 24 h. The solvent then was removed under reduced pressure and the residue rinsed with hexane. Recrystallisation from dichloromethane/hexane gave yellow crystals, which were filtered off and dried under vacuum. (619 mg, 89 % yield). *Anal.* Calc. for C₁₈H₂₀Cl₂PtS₂Si (594.54): C, 36.36; H 3.39. Found: C, 36.01; H 3.19 %. ¹H NMR (323 K): δ = 1.56 (s, 4H, SiCH₂, ³J_{H, H} = 1.1 Hz), 2.76 (s, 4H, SiCH₂S), 5.92 (s, 2H, C=CH, ³J_H. $_{\rm H}=1.1$ Hz), 7.44–7.86 (m, 10 H, SC₆H₅), UV-vis (CH₂Cl₂) $\lambda_{max}nm$ ($\epsilon,~M^{-1}cm^{-1}$) 230 (18000), 251 (16000).

Crystal structure determinations

A suitable crystal of each complex was mounted in a glass capillary (3) or in an inert oil (perfluoropolyalkylether) (2a-c and 4) and used for X-ray crystal structure determinations. Data of 3 were collected on a Siemens AED2 diffractometer at 293(2) K. The intensities were collected using $\Omega/2\theta$ scans, and the intensities of three standard reflections, which were measured after 90 min, remained stable throughout each data collection. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction based on the ψ -scans of three reflections was employed. Data of 2a-c and 4 were collected on a Stoe IPDS diffractometer at 173(2) K. The intensities were determined and corrected by the program INTEGRATE in IPDS (Stoe & Cie, 1999). An empirical absorption correction was employed using the FACEIT-program in IPDS (Stoe & Cie, 1999)

All structures were solved applying direct and Fourier methods, using SHELXS-90 (G. M. Sheldrick, University of Göttingen 1990) and SHELXL-97 (G. M. Sheldrick, SHELXL97, University of Göttingen 1997). For each structure, the non-hydrogen atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and each was assigned a fixed isotropic displacement parameter based on a riding-model. Refinement of the structures was carried out by full-matrix least-squares methods based on F_o^2 using SHELXL-97. All calculations were performed using the WinGX crystallographic software package, using the pro-

Table 3Crystallographic data for compounds 2a-c.

Identification code	2a	2b	2c
Empirical formula	$C_{26}H_{24}Cl_2PtS_2Si$	C ₂₆ H ₂₄ Br ₂ PtS ₂ Si	C ₂₆ H ₂₄ I ₂ PtS ₂ Si x 2 CH ₂ Cl ₂
Formula weight	694.65	783.57	1047.40
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	Pbca	Pbca	PĪ
Unit cell dimensions	a = 10.159(2) Å,	a = 10.234(2) Å,	a = 13.238(3) Å,
	b = 20.696(4) Å,	b = 20.867(4) Å,	b = 13.628(3) Å,
	c = 23.695(5) Å,	c = 24.146(5) Å,	c = 14.383(3) Å,
	$\alpha = 90$	$\alpha = 90$	$\alpha = 114.11(3)^{\circ}$
	$\beta = 90^{\circ}$	$\beta = 90^{\circ}$	$\beta = 114.45(3)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 92.82(3)^{\circ}$
Volume	$4982.1(17) \text{ Å}^3$	5156.5(18) Å ³	1693.3(6) Å ³
Z	8	8	2
Density (calculated)	1.852 Mg/m^3	2.019 Mg/m ³	2.054 Mg/m^3
Absorption coefficient	6.077 mm^{-1}	8.764 mm^{-1}	6.459 mm^{-1}
F(000)	2704	2992	988
Crystal size mm	0.20 x 0.20 x 0.10	0.20 x 0.20 x 0.10	0.30 x 0.20 x 0.20
Theta range for data collection	2.39 to 25.0°	2.13 to 25.0°	2.25 to 27.0°
Index ranges	$-12 \le h \le 12,$	$-12 \le h \le 12,$	$-15 \le h \le 15$,
-	$-24 \le k \le 24$,	$-24 \le k \le 24$,	$-15 \le k \le 16$,
	$-28 \le 1 \le 28$	$-28 \le 1 \le 28$	$-15 \le 1 \le 17$
Reflections collected	40707	38348	12432
Independent reflections	4380	4546	6863
	[R(int) = 0.1130]	[R(int) = 0.0755]	[R(int) = 0.0386]
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	4380 / 0 / 289	4549 / 0 / 274	6863 / 0 / 343
Goodness-of-fit on F ²	1.031	1.052	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0349,	R1 = 0.0360,	R1 = 0.0446,
	wR2 = 0.0841	wR2 = 0.0822	wR2 = 0.1133
R indices (all data)	R1 = 0.0432,	R1 = 0.0459,	R1 = 0.0465,
~ /	wR2 = 0.0868	wR2 = 0.0852	wR2 = 0.1147
Largest diff. peak and hole	$1.037 \text{ and } -1.841 \text{ e.} \text{\AA}^{-3}$	0.937 and -1.988 e.Å^{-3}	4.340 and $-4.319 \text{ e.}\text{\AA}^{-3}$

Identification code	3	4
Empirical formula	C ₂₆ H ₂₄ Br ₂ HgS ₂ Si	C ₁₈ H ₂₀ Cl ₂ PtS ₂ Si
Formula weight	789.07	594.54
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /n
Unit cell dimensions	a = 14.557(3) Å,	a = 10.327(2) Å,
	b = 20.108(4) Å,	b = 12.623(4) Å,
	c = 9.367(2) Å,	c = 14.903(3) Å,
	$\alpha = 90$	$\alpha = 90$
	$\beta = 97.33(3)^{\circ}$	$\beta = 91.19(3)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume	2728.1(10) Å ³	1942.3(7) Å ³
Z	4	4
Density (calculated)	1.921 Mg/m ³	2.033 Mg/m ³
Absorption coefficient	8.781 mm ⁻¹	7.774 mm^{-1}
F(000)	1504	144
Crystal size (mm)	0.20 x 0.20 x 0.10	0.30 x 0.30 x 0.20
Theta range for data collection	2.41 to 25.0°	2.42 to 26.99°
Index ranges	$-17 \le h \le 17$,	$-13 \le h \le 13$,
0	$0 \le k \le 23$,	$-16 \le k \le 11$,
	$0 \le 1 \le 10^{-1}$	$-15 \le l \le 18$
Reflections collected	4517	10024
Independent reflections	4517	4136
*		[R(int) = 0.0412]
Refinement method	Full-matrix	Full-matrix
	least-squares on F2	least-squares on F2
Data / restraints / parameters	4517/0/289	4136/0/217
Goodness-of-fit on F ²	1.063	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0650,	R1 = 0.0342,
	wR2 = 0.1593	wR2 = 0.0899
R indices (all data)	R1 = 0.0712,	R1 = 0.0378,
	wR2 = 0.1658	wR2 = 0.0932
Largest diff. peak and hole	2.657 and $-1.875e.{\ensuremath{\text{A}^{-3}}}$	1.544 and -2.860 e.Å-

Table 4Crystallographic data for compounds 3 and 4.

grams SHELXS-90 and SHELXL-97. The crystallographic data for each complex are given in Tables 3 and 4. The figures were drawn using CrystalMaker for Mac 6.35.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos CCDC 239987 – 239991 for compounds **2a-c**, **3** and **4**. Copies of this information may be obtained free of charge from: The director, CCDC, Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)

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