

Palladium(II) and Platinum(II) Complexes of Bis(phenylthio)methane and Bis(methylthio)methane

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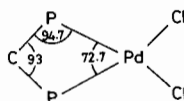
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Bis(phenylthio)methane, PhSCH₂SPh, reacts with Na₂[PdX₄] or K₂[PtX₄] (X = Cl, Br, I) to form planar trans-[ML₂X₂] (M = Pd, Pt) containing dithioether ligands bonding in a monodentate manner. An insoluble polymer [Pd(PhSCH₂SPh)Cl₂]_n with trans ligand bridges was also prepared. Bis(methylthio)methane, MeSCH₂SMe, produces only a chelating ligand complex [M(MeSCH₂SMe)X₂]. Attempts to produce halide free complexes using [M(MeCN)₄](ClO₄)₂ gave M:L stoichiometry of 1:2 but these complexes could not be obtained in a pure form. Other complexes of PhSCH₂SPh include [Rh(PhSCH₂SPh)₃Cl₃], [Ir(PhSCH₂SPh)₃Cl₃] and Ru(PhSCH₂SPh)₂Cl₃·EtOH. The differences in behaviour of these two ligands is discussed and rationalised.

Introduction

Ligands in which the donor atoms are separated by a single methylene group, for example bis(diphenylphosphino)methane, Ph₂PCH₂PPh₂ have been shown to bind to metal ions in a variety of ways. In contrast, ligands with two or three carbon atoms in the backbone usually bind as *cis* chelates. The short one carbon backbone produces a strained ring on chelation and monodentate or bridging bidentate behaviour may be preferred. This ring strain on chelation is evident from the large deviation of the internal angles of the chelate ring in [Pd(Ph₂PCH₂(PPh₂)Cl₂)] (1) from the expected values of 109°28' for <P–C–P and <C–P–M and 90° for <P–Pd–P [1]. In the case of Ph₂PCH₂PPh₂, chelation, monodentate and bridging bidentate behaviour are well established [2] in the complexes [Pd(Ph₂PCH₂PPh₂)Cl₂], chelated [1], [Ni(Ph₂PCH₂PPh₂)₂Br₂], monodentate [3] and [Fe(CO)₄]₂(Ph₂PCH₂PPh₂) brid-

ing bidentate [4]. More recently, attention has focussed on the ability of this ligand to bridge two metal–metal bonded atoms as in [PtCl(Ph₂PCH₂-



PPh₂)₂ [5] or [Fe₂(CO)₇(Ph₂PCH₂PPh₂)] [6]. The diarsine Ph₂AsCH₂AsPh₂ with metal carbonyls and metal halides [7] exhibits similar behaviour but the distibine Ph₂SbCH₂SbPh₂ usually bonds as a monodentate [8–10].

Recently [11] we reported a detailed study of palladium(II) and platinum(II) complexes of a series of structurally varied dithioethers PhS(CH₂)_nSPh (n = 2, 3, 6, 8, 12), MeS(CH₂)_nSMe (n = 2, 3), *cis*-RSCH=CHSR and *o*-C₆H₄(SR)₂ (R = Ph, Me). As an extension of this work we have examined the monomethylene backbone bis(phenylthio)methane, PhSCH₂SPh and bis(methylthio)methane MeSCH₂SMe (also called 2,4-dithiapentane). Methylplatinum(IV) halide complexes of the latter have recently been reported [12].

Experimental

Physical measurements were performed as previously described [11]. Dry ethanol was prepared by distillation of the calcium oxide dried commercial product from magnesium ethoxide.

Bis(phenylthio)methane PhSCH₂SPh

Benzenethiol (22.0 g, 0.2 mol) was added slowly under nitrogen to sodium ethoxide solution prepared from sodium (4.6 g, 0.2 g atom) in dry ethanol (500 cm³) and the mixture stirred for 30 minutes. It was then heated to reflux and dichloromethane (8.5 g, 0.1 mol) added dropwise. After addition the solution was stirred for 30 minutes, cooled and

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filtered and the filtrate evaporated to leave a light brown oil. This was dissolved in dichloromethane, filtered and evaporated and residual oil dissolved in ethanol. On standing at 0 °C waxy crystals were deposited. After filtration of the product it was dried at 50 °C and 1 torr to remove ethanol retained in the crystals. Yield 18.5 g (80%). *Anal.* Found: C, 68.0; H, 5.1%. $C_{13}H_{12}S_2$ requires: C, 67.8; H, 5.2%. 1H NMR 7.3 ppm (m) [5H], 4.21 ppm (s) [1H].

Bis(methylthio)methane MeSCH₂SMe

This was prepared by the method of Brandsma [13] from methanethiol and paraformaldehyde in aqueous hydrochloric acid. Yield 76%, B.Pt. 150 °C, 1H NMR 2.06 ppm (s) [3H] and 3.55 ppm (s) [1H].

[Di{bis(phenylthio)methane}dichloropalladium(II)]

A solution of the ligand (0.46 g, 2 mmol) in dichloromethane (20 cm³) was heated dropwise with a solution of Na₂[PdCl₄] (0.3 g, 1 mmol) in ethanol (15 cm³) and the mixture stirred at room temperature for two hours. The solution was evaporated to dryness, extracted with chloroform, filtered and concentrated. The yellow solid which deposited was filtered and dried *in vacuo*. Yield 0.38 g, 60%.

The other [Pd(PhSCH₂SPh)₂X₂] (X = Br, I) and [Pt(PhSCH₂SPh)₂X₂] (X = Cl, Br, I) complexes were prepared similarly using K₂[PtCl₄] in aqueous ethanol for the platinum(II) complexes.

[{bis(methylthio)methane}dichloropalladium(II)]

A solution of the ligand (0.23 g, 1 mmol) in ethanol (10 cm³) was slowly added to a vigorously stirred solution of Na₂[PdCl₄] (0.3 g, 1 mmol) in ethanol (20 cm³) and the mixture stirred for one hour. The brown-orange precipitate was collected, washed with ethanol, chloroform and diethylether and dried *in vacuo*. Yield 0.37 g, 90%.

The same material was obtained from [Pd(PhCN)₂Cl₂] and the ligand in a 1:1 molar ratio in chloroform.

The reaction of rhodium(III) chloride hydrate with PhSCH₂SPh

Hydrated rhodium(III) chloride (0.25 g, *ca.* 1 mmol) was dissolved in ethanol (15 cm³) and PhSCH₂SPh (0.48 g, 2.1 mmol) in ethanol (10 cm³) added and the mixture refluxed gently for 30 minutes. An orange-yellow solid was deposited which was filtered and discarded. The filtrate was concentrated to *ca.* 5 cm³ and on standing a yellow-orange solid separated as [Rh(PhSCH₂SPh)₃Cl₃] 0.2 g.

[Di{bis(phenylthio)methane}trichlororuthenium(III)]·EtOH

This was prepared by reaction of RuCl₃·xH₂O (0.25 g, *ca.* 1 mmol) with the ligand (0.69 g, 3 mmol) in ethanol (20 cm³) under reflux for one hour. The brown product was filtered washed with diethylether and dried *in vacuo*. Yield 0.4 g, 60%.

[Tri{bis(phenylthio)methane}trichloroiridium(III)]

Iridium(III) chloride hydrate (0.35 g, *ca.* 1 mmol) was dissolved in a mixture of water (5 cm³) and ethanol (15 cm³) and the ligand (0.46 g, 2 mmol) in ethanol (10 cm³) added. The mixture was stirred for one hour under gentle reflux then cooled and the yellow solid filtered off (0.1 g unidentified C, 34.0%; H, 3.3%; Cl, 14.6%). The filtrate on concentration gave [Ir(PhSCH₂SPh)₃Cl₃] as a yellow powder 0.25 g.

[{Bis(methylthio)methane}dichloropalladium(II)]

A filtered solution of Na₂[PdCl₄] (0.3 g, 1 mmol) in ethanol (15 cm³) was treated with the ligand (0.1 g, 1 mmol) and the mixture stirred for two hours at room temperature. The mixture was concentrated *in vacuo* to *ca.* 5 cm³ and the solid which deposited filtered, washed with ethanol and diethylether and dried *in vacuo*. Yield 25%.

The other halide complexes of this ligand were prepared similarly.

Perchlorate Complexes

The reaction of PhSCH₂Ph with Na₂[PdX₄] (ClO₄)₂ (M = Pd, Pt) in a 2:1 ratio as dichloro- previously [11]. The crude products were recrystallised from nitromethane and obtained as solids by either evaporation to small volume or by slow addition of diethylether.

Results

Bis(phenylthio)methane

The reaction of PhSCH₂Ph with Na₂[PdX₄] (X = Cl, Br, I) in a 2:1 molar ratio in dichloromethane/ethanol produced [Pd(PhSCH₂SPh)₂X₂] complexes (Table I). The complexes are slightly soluble in chlorocarbons in which they are non-electrolytes and have molecular weights consistent with a monomeric structure. The far infrared spectra display one medium intensity absorption identified as the $\nu(Pd-X)$ related band. The band positions (Table I) are interpreted as the antisymmetric stretches of *trans*-PdX₂(B_{2u}) [11, 13]. Proton NMR spectra in d⁶ dmso show only resonances identical with those of the free ligand indicating solvent displacement of the ligand. Saturated solutions in deuteriochloroform show only a single -CH₂- resonance downfield from that of the free ligand

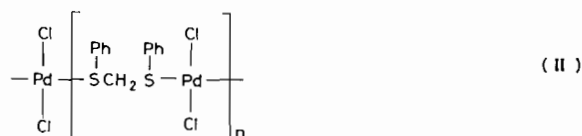
TABLE I. Analytical and Spectroscopic Data for the Complexes.

Complex	Colour	%C ^a	%H	%X	M. Wt ^b	$\nu(\text{M}-\text{X}) \text{ cm}^{-1}$	$\epsilon_{\text{max}} (\text{emol}) \times 10^{-3} \text{ cm}^{-1} \text{ c}$	$\epsilon_{\text{max}} \times 10^{-3} \text{ cm}^{-1} \text{ d}$	¹ H NMR (δ) ^e
Pd(PhSCH ₂ SPh) ₂ Cl ₂ ·1/3CHCl ₃	Yellow	45.4(45.3)	3.5(3.5)	17.3(17.8)	645(640)	360	28.2(8700), 27.5(1430)	28.6, 23.0	4.65
Pd(PhSCH ₂ SPh) ₂ Br ₂	Orange	42.6(42.2)	2.9(3.2)	21.8(21.8)	696(730)	248	31.35(15900), 28.8(17390), 23.5(8290)	36.5, 23.9	4.75
Pd(PhSCH ₂ SPh) ₂ I ₂	Dark brown	37.3(37.9)	3.0(2.9)	30.7(30.8)	—	218	30.2(1940), 20.4(1177)	33.5, 22.5, 20.0sh	4.35
Pt(PhSCH ₂ SPh) ₂ Cl ₂	Yellow	42.6(42.4)	2.9(3.2)	9.4(9.6)	—	356	27.9(8600), 25.3sh(2760)	31.75, 25.32	4.70(34)
Pt(PhSCH ₂ SPh) ₂ Br ₂	Buff	38.9(38.2)	2.9(2.7)	19.5(19.5)	783(819)	256	32.8(9342), 23.8(210)	31.5, 24.3, 20.7sh	4.80(28)
Pt(PhSCH ₂ SPh) ₂ I ₂	Yellow-brown	33.8(34.1)	2.6(2.6)	17.4(27.8)	940(920)	204	30.75(4787), 28.75(9940), 21.35(727)	27.8, 24.5, 21.9sh	4.68(30)
[Pd(PhSCH ₂ SPh) ₂ Cl ₂] _n ^f	Orange-brown	39.6(38.2)	3.1(2.9)	16.8(17.5)	insol	355	—	27.6sh, 23.8, 20.0sh	—
[Pd(PhSCH ₂ SPh) ₂ Cl ₂] _n ^g	Orange-brown	38.9(38.2)	3.1(2.9)	17.0(17.5)	insol	355	—	—	—
Pd ₂ (PhSCH ₂ SPh) ₂ Cl ₄	Brick red	26.5(26.6)	1.8(2.0)	23.7(24.2)	insol	—	—	27.2sh, 24.3, 19.6	insol
mer-Ir(PhSCH ₂ SPh) ₃ Cl ₃	Orange	51.7(51.7)	4.3(4.0)	12.2(11.8)	—	—	—	32.6, 28.8, 24.0, 21.0sh	5.2, 4.35 2:1
mer-Ir(PhSCH ₂ SPh) ₃ Cl ₃	Yellow	47.5(47.0)	3.8(3.6)	10.6(10.6)	—	—	—	32.0(3390), 27.7sh(790), 25.4(sh)	—
Ru(PhSCH ₂ SPh) ₂ Cl ₃ ·EtOH	Brown-black	46.3(46.5)	3.5(3.7)	14.8(14.8)	—	—	—	32.2(4411), 28.0sh(3556), 23.6(2593)	5.2 4.3 2:1
Pd(MeSCH ₂ SMe)Cl ₂	Yellow	12.8(12.7)	2.8(2.8)	24.6(25.0)	—	—	—	30.0sh, 26.6, 23.0	—
Pd(MeSCH ₂ SMe)Br ₂	Brown	9.5(9.6)	2.2(2.2)	42.9(43.0)	—	—	—	31.3sh, 26.7, 22.0	—
Pd(MeSCH ₂ SMe)I ₂	Brown-black	7.5(7.7)	1.5(1.7)	55.3(54.5)	—	—	—	27.0sh, 24.0, 20.6sh	—
Pt(MeSCH ₂ SMe)Cl ₂	Yellow	10.0(9.7)	2.2(2.2)	18.4(19.0)	—	—	—	26.45, 24.8sh	—
Pt(MeSCH ₂ SMe)Br ₂	Yellow	7.6(7.8)	1.7(1.7)	34.0(34.7)	—	—	—	27.3, 24.0	—
Pt(MeSCH ₂ SMe)I ₂	Brown-yellow	6.5(6.5)	1.4(1.5)	46.0(45.8)	—	—	—	24.0, 21.0sh	—
Pd(PhSCH ₂ SPh) ₂ (ClO ₄) ₂	Yellow	42.7(40.6)	3.1(3.1)	16.4(16.6) ^h	—	—	—	22.2	—
Pt(PhSCH ₂ SPh) ₂ (ClO ₄) ₂	Pale yellow	31.5(36.3)	3.3(2.9)	—	—	—	—	25.6	—
Pd(MeSCH ₂ SMe) ₂ (ClO ₄) ₂	Yellow	16.9(13.8)	3.6(3.1)	23.0(24.6) ^h	—	—	—	>30.0	—
Pt(MeSCH ₂ SMe) ₂ (ClO ₄) ₂	Yellow	11.5(11.8)	2.5(2.6)	—	—	—	—	29.2	—
								>30.0	—

^aFound (calc). ^bOsmometric in $10^{-3} M C_2H_4Cl_2$. ^cSolutions in CH_2Cl_2 , ϵ mol in $dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$. ^dDiffuse reflectance (diluted with $BaSO_4$). ^eIn $CDCl_3$, ppm relative to TMS. ^f $^3J_{Pt-H}$ in brackets. ^gFrom $Na_2 [PdCl_4]$. ^hSulphur analysis.

($\delta_{\text{CH}_2} = 4.26$ ppm). This suggests that only one isomer is present in solution. The ^{13}C NMR was recorded for $\text{X} = \text{Cl}$ and the $-\text{CH}_2-$ resonance at 46.6 ppm compares with that of the free ligand at 40.0 ppm (relative to TMS). Poor solubility was a major problem in the NMR studies. On the basis of the above evidence a *trans* planar structure with monodentate dithioether ligands is assigned to these complexes.

Repeated attempts were made to prepare 1:1 complexes and only $[\text{Pd}(\text{PhSCH}_2\text{SPh})\text{Cl}_2]$ could be obtained in a pure form. This orange-brown powder is prepared by reacting $\text{Na}_2[\text{PdCl}_4]$ with the ligand in a ratio of 1: *ca.* 0.9 in ethanol. The complex is insoluble in or decomposed by all common solvents. The far infrared spectrum show a single band at 355 cm^{-1} assigned to $\nu(\text{Pd}-\text{Cl})$ suggesting that the ligand acts in a bridging bidentate manner(II). A number of orange



materials were obtained in attempts to prepare this complex under various conditions. The composition by analysis fell in the range $\text{Pd}(\text{PhSCH}_2\text{SPh})_n\text{Cl}_2$ ($n = 1$ to *ca.* 1.3) and these have infrared spectra identical to that of complex (II). Insolubility prevented a more detailed characterisation but it is probable that these are oligomers of varying chain length related to structure (II) with PhSCH_2SPh end groups. Somewhat similar materials are obtained by reaction of $\text{Na}_2[\text{PdCl}_4]$ with $[\text{Pd}(\text{PhSCH}_2\text{SPh})_2\text{Cl}_2]$ but this reaction also yields an insoluble crimson powder $\text{Pd}_2\text{Cl}_4(\text{PhSCH}_2\text{SPh})$.

The platinum(II) complexes were more straightforward only $[\text{Pt}(\text{PhSCH}_2\text{SPh})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) being obtained irrespective of the metal:ligand ratio used. These are rather less soluble than the palladium(II) analogues and also decomposed in d^6 dmso.

Using $[\text{M}(\text{MeCN})_2\text{X}_2]$ or $[\text{M}(\text{PhCN})_2\text{X}_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) offered no advantage over $[\text{MX}_4]^{2-}$ ($\text{M} = \text{Pd}, \text{Pt}$) as starting materials.

The reaction of $[\text{M}(\text{MeCN})_4](\text{ClO}_4)_2$ ($\text{M} = \text{Pd}, \text{Pt}$) [14] with two equivalents of PhSCH_2SPh in acetonitrile produced yellow materials of approximate stoichiometry $\text{ML}_2(\text{ClO}_4)_2$ which retain small amounts of MeCN. Typical analyses are given in Table I. The infrared spectra indicate that the perchlorate groups are ionic ν_3 at 1090 cm^{-1} being unsplit. Insolubility and/or decomposition by all solvents prevented solution studies, however, it is probable that the complexes are ligand bridged oligomers.

The reactions of PhSCH_2SPh with various other transition metal salts was briefly investigated. Rho-

dium(III) and iridium(III) chlorides produce $[\text{Rh}(\text{PhSCH}_2\text{SPh})_3\text{Cl}_3]$ and $[\text{Ir}(\text{PhSCH}_2\text{SPh})_3\text{Cl}_3]$ respectively. In chlorocarbon solvents these complexes are non-electrolytes and the ^1H NMR spectra show two well separated methylene resonances in a 2:1 ratio indicating that they are *mer* isomers with monodentate dithioether coordination (*cf.* $[\text{M}(\text{MeSPh})_3\text{Cl}_3]$ [16]). A number of other complexes of these metals with metal:ligand ratios of *ca.* 1:2 were isolated but these have insufficient solubility for ^1H NMR studies to establish whether these contain ligand or halide bridges. Ruthenium(III) chloride and PhSCH_2SPh react in refluxing ethanol to give a brown-black paramagnetic ($\mu_{\text{eff}} = 2.1$ B.M.) material $\text{Ru}(\text{PhSCH}_2\text{SPh})_2\text{Cl}_3 \cdot \text{EtOH}$. Even with excess dithioether the tris-ligand complex could not be isolated. The presence of ethanol is confirmed by infrared spectroscopy and the complex is presumably analogous to $[\text{Ru}(\text{Pr}^1\text{SPh})_2\text{Cl}_3 \cdot \text{MeOH}]$ [17] and $[\text{Ru}(\text{PPh}_3)_2\text{Cl}_3 \cdot \text{MeOH}]$ [18]. When the reaction was conducted in boiling 2-methoxyethanol in an attempt to prepare the ruthenium(II) complex a metallic mirror and a fine black powder precipitates which may be either metallic ruthenium or ruthenium sulphide. No reaction appears to occur between sodium hexachloroosmate(IV) and PhSCH_2SPh in 2-methoxyethanol. This is not unexpected since neither Ph_2S or Me_2S react under these conditions [19]. There is no reaction between PhSCH_2SPh and the bromides of nickel(II), cobalt(II) or copper(II) in acetone or ethanol.

Bis(methylthio)methane

This ligand reacts with $[\text{MX}_4]^{2-}$ ($\text{M} = \text{Pd}, \text{Pt}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) salts to produce 1:1 complexes $[\text{M}(\text{MeSCH}_2\text{SMe})\text{X}_2]$ ($\text{M} = \text{Pd}, \text{Pt}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) irrespective of the metal:ligand ratio used. In contrast to the phenyl analogue ligand all attempts to produce 1:2 complexes failed. The $[\text{M}(\text{MeSCH}_2\text{SMe})\text{X}_2]$ complexes are insoluble in ethanol or acetone and very slightly soluble in chlorocarbons. This low solubility prevented molecular weight and solution electronic spectroscopy measurements. ^1H NMR could not be observed in CDCl_3 or CD_3NO_2 and in $(\text{CD}_3)_2\text{SO}$ a resonance at 2.05 ppm is observed due to free ligand. If the d^6 dmso solutions are run instantly on preparation weak resonances are observed in the region 2.4–2.6 ppm which in the case of $[\text{Pt}(\text{MeSCH}_2\text{SMe})\text{X}_2]$ sometimes exhibit ^{195}Pt satellites. The resonances decrease rapidly on ageing leaving only free ligand signals.

The solid state electronic spectra are unexceptional and consistent with planar MS_2X_2 coordination spheres [11]. The far infrared spectra contain a number of medium intensity bands in the range expected for *cis*- MX_2 groups with *X trans* to thioether sulphur [11].

The properties of these complexes are similar to those of dithioethers with longer backbones, e.g., 2,5-dithiahexane and 2,6-dithioheptane, which are monomers with chelating dithioether, although these are not appreciably decomposed in dmsO solution. Since the chelate ring formed by MeSCH₂SMe will be considerably strained compared to the five and six membered rings formed by MeS(CH₂)_nSMe (n = 2,3), ring opening and subsequent ligand displacement is not unreasonable. As no solvent suitable for molecular weight determinations could be found we cannot rule out dimers or polymeric structures with *cis* bridging dithioethers. However, we do feel that monomers with chelating bis(methylthio)methane are most likely. This is supported by the diperchlorate complexes [M(MeSCH₂SMe)₂](ClO₄)₂ formed from [M(MeCN)₄](ClO₄)₂ (M = Pd, Pt) plus ligand in a 1:2 ratio. Conductivity measurements in nitromethane gave Λ_M (10⁻³ molar solution) values of 135 and 146 ohm⁻¹ cm² M⁻¹ for palladium and platinum complexes respectively. These results are consistent with a 2:1 electrolyte structure suggesting that they are monomers with chelating dithioether ligands.

Discussion

The ligand PhSCH₂SPh has been shown to bind predominantly in a monodentate fashion to soft metal ions. The PhS-group is a relatively poor donor and it would seem that the energy gained in binding the second PhS-group to the same metal atom and hence producing chelation is insufficient to overcome the strain produced. Bridging bidentate behaviour has been identified in a few complexes. It seems unlikely that this ligand will have an extensive coordination chemistry like Ph₂PCH₂PPh₂ and characterisation of many of its complexes is greatly hindered by a combination of poor solubility and ease of ligand displacement in solution. The behaviour of MeSCH₂SMe is more straightforward. Monodentate coordination of this ligand was not observed, the greater σ donor power of MeS-groups no doubt being the reason why chelation is observed. Although solubility problems again prevented some solution studies it is probable that [M(MeSCH₂SMe)₂X₂]

(M = Pd, Pt; X = Cl, Br, I) do contain chelating dithioether ligand and are formulated as shown. If a bridging mode were favoured by this ligand it is difficult to explain why monodentate behaviour is not seen. Our attempts to produce [M(MeSCH₂SMe)₂X₂] even with a large excess of ligand were unsuccessful, only [M(MeSCH₂SMe)X₂] being isolated. This behaviour parallels that of MeS(CH₂)_nSMe (n = 2, 3) where the 1:1 complexes contain chelating ligands [11].

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