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Synthesis of *cis*- and *trans*-Bis(phosphine)bis(thiolato)platinum(II) Complexes, $(PR_3)_2Pt(SR')_2$

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Complexes of the type $L_2Pt(SR)_2$ are isolated in high purity and yield by treating the *cis*-dichlorides with thiols under nitrogen atmosphere in the presence of triethylamine, L = PPh_3, $PMePh_2$, PMe_2Ph, and $^1/_2(PPh_2CH_2)_2$, and R = CH_2Ph, *i*-C_3H_7, *n*-C_3H_7, and 4-$C_6H_4CH_3$. For R = alkyl the complexes have been assigned the cis geometry while for R = aryl they have been assigned the trans configuration on the basis of NMR studies. The *cis*-bis(thiolato) complexes tend to rearrange to a complex mixture of the trans complexes and other species upon exposure to air in solution. It is proposed that this surprising sensitivity accounts for the relative rarity of complexes of the type *cis*-$L_2Pt(SR)_2$ where L_2 or the thiolato ligands are not chelates.

Introduction

Given the technological importance of platinum as a catalyst and the well-known poisoning abilities of thiols, it is reasonable to conclude that platinum–thiolato complexes have been well studied. They have had a long history of investigation, thio-bridged dimers being first prepared in the last century.[1] Our need for complexes of the type *cis*-$L_2Pt(SR)_2$, where L is a phosphine and R is an alkyl or aryl group, led to a survey of the literature which revealed little information concerning the preparative requirements for the cis and trans isomers of such compounds. Monomeric thiolato complexes have the reputation of being unstable with respect to polymerization,[2–6] and their preparation and stability is thought by some[5–8] to depend upon R being an electron-withdrawing group. It is true that for many monomeric complexes of the type $L_2Pt(SR)_2$ and $L_2Pt(SR)Y$, where Y is a negative ligand, R has been C_6H_5[6,8–16] or a monosubstituted derivative,[17–20] C_6X_5, where *X* is a halogen,[5,7,15,21,22] CF_3,[23,24] or C(O)R.[25] However, a careful survey reveals some reports of complexes where R is an electron-releasing group such as H[4,10,20,26,27] or CH_2R.[4,11,12,20,28,29] Stable monomers with chelating neutral ligands such as bis(diphenylphosphino)ethane[8,11,22,23,28,29] and/or chelating dithiolato[4,8,15,26] ligands are known. In those cases where the geometry of the monomers has been studied, they have usually been assigned the trans configuration except for a few where cis geometry[5,24,26,28,30] was indicated and of course for the chelated examples. As part of a study on the reactions of metal thiolates with sulfur-transfer reagents,[31a] the cis-complexes were required. Thus, it became necessary to determine the conditions that lead to this geometry and to examine the nature of the cis → trans isomerization and the dimerization[31b] of these complexes.

Experimental Section

Reactions were carried out in three-necked round-bottom flasks of the appropriate size equipped with an inlet for nitrogen gas under which the reactions were conducted. The purification and characterization of the products were carried out in air. The preparation of **1a** below (part A) has been described in detail with respect to the use of inert-atmosphere conditions and is typical. Such details have been omitted from the descriptions of the other preparations for the sake of brevity. Nitrogen gas (Linde "High Purity" grade, 10 ppm O_2) was used without further purification. Toluene was freshly distilled (under N_2) from sodium/benzophenone. Other solvents were of Spectrograde quality. Deuterated NMR solvents from Merck, Sharp and Dohme of Montreal were used. Melting points were determined in air on a Thomas-Hoover Uni-melt apparatus and are uncorrected. Proton NMR spectra were recorded on a Varian T-60 instrument in $CDCl_3$ solution. Chemical shifts are reported in ppm relative to Me_4Si as internal standard. Phosphorus NMR spectra were obtained on a Bruker-WH90 spectrometer, operating in the pulsed Fourier transform mode in $CDCl_3$ or C_6D_6 solution. Chemical shifts are reported in ppm downfield (positive) from 85% H_3PO_4 as external standard, with D_2O as the lock signal. Elemental analyses were performed by Midwest Microlab Ltd., Indianapolis, Ind.

Platinum sponge (Engelhard Industries of Canada) was converted to K_2PtCl_4.[32] The complexes *cis*-$(PPh_3)_2PtCl_2$,[33,34] *cis*-

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$(PMePh_2)_2PtCl_2$,[35] and $(diphos)PtCl_2$[36,37] (diphos = $PPh_2CH_2CH_2PPh_2$) were prepared by published procedures. Phosphines from Aldrich (PPh_3) and Strem Chemicals ($PMePh_2$, $PMePh_2$, diphos), mercaptans from Aldrich, and triethylamine were used without further purification. The complexes *cis*-$(PMe_2Ph)_2PtCl_2$ and additional *cis*-$(PMePh_2)_2PtCl_2$ were prepared by displacement of the neutral ligands in *cis*-$(Et_2S)_2PtCl_2$[38] or $CODPtCl_2$[39] (COD = 1,5-cyclooctadiene) in CH_2Cl_2 solution under N_2 atmosphere.

(A) ***cis*-Bis(phenylmethanethiolato)bis(triphenylphosphine)platinum(II), *cis*-$(PPh_3)_2Pt(SCH_2Ph)_2$ (1a).** Benzyl mercaptan (0.75 mL, 6.4 mmol) and triethylamine (2.0 mL, 14.4 mmol) in 75 mL of toluene were added dropwise under N_2 to a stirred suspension of *cis*-$(PPh_3)_2PtCl_2$ (2.21 g, 2.8 mmol) in 125 mL of toluene. The mixture was stirred at room temperature for 20 h after which the volatile components were removed by vacuum distillation at room temperature. The yellow residue was dissolved (in air) in about 20 mL of CH_2Cl_2. This solution was washed with 4 × 100 mL (distilled) water, dried over anhydrous $MgSO_4$, and stripped to dryness on a rotary evaporator. The product was recrystallized in air from CH_2Cl_2/ether at −12 °C (crystals form quite rapidly, minimizing loss due to reaction in air) to yield yellow crystals. These were collected on a sintered-glass funnel in air, washed with diethyl ether, dried in a stream of N_2, and pumped on for 24 h. The yield was 2.61 g (97%).

(B) ***cis*-Bis(phenylmethanethiolato)bis(methyldiphenylphosphine)platinum(II), *cis*-$(PMePh_2)_2Pt(SCH_2Ph)_2$ (1b).** As in part A, *cis*-$(PMePh_2)_2PtCl_2$ (2.87 g, 4.3 mmol), benzyl mercaptan (1.1 mL, 9.4 mmol), and triethylamine (3.0 mL, 21.6 mmol) were stirred in toluene (220 mL) for 17 h. Recrystallization from CH_2Cl_2/hexane gave yellow crystals, 3.15 g (87%).

(C) ***cis*-Bis(phenylmethanethiolato)bis(dimethylphenylphosphine)platinum(II), *cis*-$(PMe_2Ph)_2Pt(SCH_2Ph)_2$ (1c).** As in part A, *cis*-$(PMe_2Ph)_2PtCl_2$ (2.78 g, 5.1 mmol), benzyl mercaptan (1.2 mL, 10.2 mmol), and triethylamine (4.0 mL, 28.8 mmol) were stirred for 17 h in 300 mL of toluene. Recrystallization from CH_2Cl_2/ether gave pale yellow crystals, 3.0 g (83%), which were contaminated by the trans complex **6c** (about 10%).

(D) ***cis*-Bis(1-propanethiolato)bis(triphenylphosphine)platinum(II), *cis*-$(PPh_3)_2Pt(SCH_2CH_2CH_3)_2$ (2a).** As in part A, *cis*-$(PPh_3)_2PtCl_2$ (2.44 g, 3.1 mmol), 1-propanethiol (0.6 mL, 6.6 mmol), and triethylamine (3.0 mL, 21.6 mmol) in 200 mL of toluene were stirred for 5 h. Recrystallization from CH_2Cl_2/hexane gave 2.3 g (83%) of yellow crystals.

(E) ***cis*-Bis(1-propanethiolato)bis(methyldiphenylphosphine)platinum(II), *cis*-$(PMePh_2)_2Pt(SCH_2CH_2CH_3)_2$ (2b).** *cis*-$(PMePh_2)_2PtCl_2$ (1.07 g, 1.6 mmol), 1-propanethiol (0.35 mL, 3.9 mmol), and triethylamine (1.0 mL, 7.2 mmol) were stirred for 17 h in 130 mL of toluene as in part A. Recrystallization from CH_2Cl_2/ether gave 0.82 g (69%) of yellow crystals.

(F) ***cis*-Bis(2-propanethiolato)bis(triphenylphosphine)platinum(II), *cis*-$(PPh_3)_2Pt(SCHMe_2)_2$ (3a).** As in part A, *cis*-$(PPh_3)_2PtCl_2$ (1.47 g, 1.9 mmol), 2-propanethiol (0.4 mL, 4.3 mmol), and triethylamine (2.0 mL, 14.4 mmol) were stirred in 150 mL of toluene for 5 h to give, after recrystallization from CH_2Cl_2/ether, 1.19 g (73%) of yellow crystals.

(G) ***cis*-Bis(2-propanethiolato)bis(methyldiphenylphosphine)platinum(II), *cis*-$(PMePh_2)_2Pt(SCHMe_2)_2$ (3b).** As in part A, *cis*-$(PMePh_2)_2PtCl_2$ (0.51 g, 0.77 mmol), 2-propanethiol (0.3 mL, 3.2 mmol), and triethylamine (1.0 mL, 7.2 mmol) in toluene (100 mL) were stirred for 5 h. After the final evaporation the yellow oil was triturated with hexane and the resulting yellow powder was collected and dried (0.38 g (67%)).

(H) **Bis(phenylmethanethiolato)[1,2-bis(diphenylphosphino)ethane]platinum(II), (diphos)$Pt(SCH_2Ph)_2$ (4).** Benzyl mercaptan (0.35 mL, 3.0 mmol) and triethylamine (1.0 mL, 7.2 mmol) in 80 mL of THF (distilled under N_2 from sodium/benzophenone) were added dropwise to (diphos)$PtCl_2$ (1.0 g, 1.5 mmol) in 100 mL of THF and stirred for 18 h. Recrystallization from CH_2Cl_2/hexane gave pale yellow microcrystals, 1.09 g (86%).

(I) **Bis(4-methylbenzenethiolato)[1,2-bis(diphenylphosphino)ethane]platinum(II), (diphos)$Pt(SC_6H_4Me)_2$ (5).** As in part A, (diphos)$PtCl_2$ (1.0 g, 1.5 mmol), 4-methylbenzenethiol (0.39 g, 3.2 mmol), and triethylamine (2.0 mL, 14.4 mmol) were stirred for 19 h in toluene (120 mL). Recrystallization from acetone/hexane gave 0.8 g (63%) of yellow crystals.

(J) ***trans*-Bis(phenylmethanethiolato)bis(triphenylphosphine)platinum(II), *trans*-$(PPh_3)_2Pt(SCH_2Ph)_2$ (6a).** This reaction was performed as in part A, but in air, with *cis*-$(PPh_3)_2PtCl_2$ (3.0 g, 3.8 mmol) in 200 mL of toluene to which was added dropwise benzyl mercaptan (0.9 mL, 7.7 mmol) and triethylamine (3.0 mL, 21.6 mmol) in 100 mL of CH_2Cl_2. Reaction time was 22 h. The yield was 2.3 g (63%) of yellow crystals (CH_2Cl_2/ether).

(K) ***trans*-Bis(4-methylbenzenethiolato)bis(triphenylphosphine)platinum(II), *trans*-$(PPh_3)_2Pt(SC_6H_4Me)_2$ (7a).** As in part A, *cis*-$(PPh_3)_2PtCl_2$ (2.2 g, 2.8 mmol) in 150 mL of toluene was treated dropwise with 4-methylbenzenethiol (0.77 g, 6.2 mmol) and triethylamine (1.7 mL, 12.2 mmol) in 50 mL of ether and stirred for 8 h. Recrystallization from CH_2Cl_2/ether gave 2.6 g (95%) of orange crystals.

(L) ***trans*-Bis(4-methylbenzenethiolato)bis(methyldiphenylphosphine)platinum(II), *trans*-$(PMePh_2)_2Pt(SC_6H_4Me)_2$ (7b).** As in part A, *cis*-$(PMePh_2)_2PtCl_2$ (3.0 g, 4.6 mmol), 4-methylbenzenethiol (1.2 g, 9.5 mmol), and triethylamine (4.0 mL, 28.8 mmol) were stirred for 16 h in 300 mL of toluene. Recrystallization from CH_2Cl_2/hexane gave yellow crystals, 3.7 g (95%).

(M) ***trans*-Bis(4-methylbenzenethiolato)bis(dimethylphenylphosphine)platinum(II), *trans*-$(PMe_2Ph)_2Pt(SC_6H_4Me)_2$ (7c).** As in part A, *cis*-$(PMe_2Ph)_2PtCl_2$ (2.8 g, 5.2 mmol), 4-methylbenzenethiol (1.3 g, 10.5 mmol), and triethylamine (3.0 mL, 21.6 mmol) in 170 mL of toluene were stirred for 17 h. Recrystallization from boiling CH_2Cl_2/hexane gave 2.3 g (62%) of yellow crystals.

Comments on the Preparations. The complexes **7a–c** may be equally well prepared in air, in the same manner as **6a**. Compounds **6a** and **7c** were also obtained in somewhat poorer yields directly from K_2PtCl_4 via the method of Roundhill.[8]

Results

The anaerobic treatment of a suspension of *cis*-L_2PtCl_2 in toluene with an alkanethiol in the presence of triethylamine leads to the isolation of complexes of the type *cis*-$L_2Pt(SR)_2$ in high yield and purity, where L = PPh_3, $PMePh_2$, and PMe_2Ph and R = CH_2Ph, *n*-C_3H_7, and *i*-C_3H_7. On the other hand, treatment of the *cis*-dichlorides with 4-methylbenzenethiol under similar conditions produced only the *trans*-bis(thiolates) when the reaction was run under air or N_2 atmosphere. Use of the diphos ligand, $Ph_2PCH_2CH_2PPh_2$, constrains the geometry to be cis. In this case, under similar conditions, complexes **4** and **5** were isolated for R = CH_2Ph and 4-$C_6H_4CH_3$, respectively. The yellow compounds were stable to air in the solid state and were characterized by elemental analysis (Table I) and infrared and NMR (Table II) spectroscopy. They were not amenable to mass spectral analysis. The complexes *cis*- and *trans*-$L_2Pt(SR)_2$ react when fused in vacuo to produce dimeric complexes of the type $[LPt(SR)_2]_2$.[31b]

The ^1H NMR of these complexes is the most important physical evidence upon which the assignment of their geometry is based.[40] The triplet of doublets observed for the methylene protons of the phenylmethanethiolato ligand in complexes **1a–c** and **4** is consistent with cis geometry.[28] In complexes **6a** (isolated) and **6b–c** (identified in solution) the methylene protons appear in a triplet pattern consistent with trans geometry. The pattern observed for the methyl groups of the phosphine ligands $PMePh_2$ and PMe_2Ph is also a sensitive

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Table I. Analytical and Physical Data

			% C		% H	
compd	no.	mp, °C	calcd	found	calcd	found
cis-$(PPh_3)_2Pt(SCH_2Ph)_2$	**1a**	150–152	62.2	61.9	4.56	4.48
cis-$(PMePh_2)_2Pt(SCH_2Ph)_2$	**1b**	130–132	57.1	56.4	4.76	4.66
cis-$(PMe_2Ph)_2Pt(SCH_2Ph)_2$	**1c**	161–162	50.2	50.6	5.02	5.10
cis-$(PPh_3)_2Pt(SCH_2CH_2CH_3)_2$	**2a**	142–144	58.0	57.1	5.06	5.28
cis-$(PMePh_2)_2Pt(SCH_2CH_2CH_3)_2$	**2b**	126–128	51.5	52.1	5.37	5.31
cis-$(PPh_3)_2Pt(SCHMe_2)_2$[a]	**3a**	139–140	58.0	56.8	5.06	5.23
cis-$(PMePh_2)_2Pt(SCHMe_2)_2$[a]	**3b**	134–136	51.5	50.4	5.37	5.30
(diphos)$Pt(SCH_2Ph)_2$	**4**	173–175	57.2	57.9	4.53	4.49
(diphos)$Pt(4\text{-}SC_6H_4Me)_2$	**5**	155–157	57.2	56.7	4.53	4.74
trans-$(PPh_3)_2Pt(SCH_2Ph)_2$	**6a**	184–185	62.2	62.0	4.56	4.56
trans-$(PPh_3)_2Pt(4\text{-}SC_6H_4Me)_2$[a]	**7a**	185–187	62.2	61.3	4.56	4.52
trans-$(PMePh_2)_2Pt(4\text{-}SC_6H_4Me)_2$	**7b**	177–179	57.1	56.7	4.76	4.82
trans-$(PMe_2Ph)_2Pt(4\text{-}SC_6H_4Me)_2$	**7c**	209–210	50.2	49.7	5.02	5.09

[a] The analysis was calculated by assuming $^1/_2CH_2Cl_2$ of crystallization was present per molecule of complex. CH_2Cl_2 was observed in the ^1H NMR of these complexes.

Table II. ^1H and ^{31}P NMR Data for Platinum Bis(thiolate) Complexes[a]

		$P\text{–}CH_3$[b]			S–R[b,c]			P[d]	
compd	no.	τ	*J*-(Pt–H)	*J*-(P–H)	τ	*J*-(Pt–H)	*J*-(P–H)	α	*J*-(Pt–P)
cis-$(PPh_3)_2Pt(SCH_2Ph)_2$	**1a**				5.62 (td)	47	6	−24.1	2888
cis-$(PMePh_2)_2Pt(SCH_2Ph)_2$	**1b**	8.34 (td)	28	10	5.58 (td)	44	6	−6.7	2856
cis-$(PMe_2Ph)_2Pt(SCH_2Ph)_2$	**1c**	8.52 (td)	28	10	5.64 (td)	38	6	9.5	2788
cis-$(PPh_3)_2Pt(SCH_2CH_2CH_3)_2$	**2a**				9.18 (t)[e]			−24.3	2864
cis-$(PMePh_2)_2Pt(SCH_2CH_2CH_3)_2$	**2b**	8.17 (td)	27	9	9.12 (t)[e]			−5.6	2807
cis-$(PPh_3)_2Pt(SCHMe_2)_2$	**3a**				8.70 (d)[f]			−23.8	2852
cis-$(PMePh_2)_2Pt(SCHMe_2)_2$	**3b**	8.10 (td)	27	9	8.61 (d)[f]			−6.6	2825
(diphos)$Pt(SCH_2Ph)_2$	4	7.82 (m)[g]			5.99 (td)	33	4	−47.2	2798
(diphos)$Pt(4\text{-}SC_6H_4Me)_2$	**5**	7.89 (m)[g]			7.92 (s)			−45.6	2896
trans-$(PPh_3)_2Pt(SCH_2Ph)_2$	**6a**				7.50 (t)	18		−25.2	2925
trans-$(PMePh_2)_2Pt(SCH_2Ph)_2$	**6b**	7.82 (tt)	30	4	7.22 (t)	28			
trans-$(PMe_2Ph)_2Pt(SCH_2Ph)_2$	**6c**	8.18 (tt)	30	4	6.85 (s)[h]	35			
trans-$(PPh_3)_2Pt(4\text{-}SC_6H_4Me)_2$	**7a**				7.81 (s)[h]			−22.3	2954
trans-$(PMePh_2)_2Pt(4\text{-}SC_6H_4Me)_2$	**7b**	8.07 (tt)	29	4	7.85 (s)[h]			−6.4	2739
trans-$(PMe_2Ph)_2Pt(4\text{-}SC_6H_4Me)_2$	**7c**	8.34 (tt)	27	4	7.80 (s)[h]			6.6	2603

[a] In $CDCl_3$ solvent. All *J* values in Hz; s = singlet, d = doublet, t = triplet, tt = triplet of triplets, td = triplet of doublets, m = multiplet. [b] Phenyl resonances observed in the range τ 2–3. [c] Resonances for the various thiolate ligands as indicated: $R = C\mathit{H}_2Ph, CH_2CH_2C\mathit{H}_3, CH(C\mathit{H}_3)_2, 4\text{-}C_6H_4C\mathit{H}_3$. [d] All ^{31}P chemical shifts in ppm upfield (negative) from 85% H_3PO_4. [e] $C\mathit{H}_2C\mathit{H}_2CH_3$: τ ~7.1 (m), 8.4 (m). [f] $C\mathit{H}(CH_3)_2$: τ ~5.9 (m) (*J*(H–H) = 7 Hz). [g] $[C\mathit{H}_2PPh_2]_2$. [h] $4\text{-}C_6\mathit{H}_4CH_3$: τ ~3.1–3.4.

probe of geometry.[41] For complexes **1b–c**, **2b**, and **3b** the peaks due to the methyl groups appear as a triplet of doublets consistent with cis geometry whereas they appear as a triplet of triplets for complexes **6b–c** and **7b–c** consistent with trans geometry. Thus the geometry of complexes can be directly assigned: **1a–c**, **2b**, **3b**, and **4** as cis and **6a–c** and **7b–c** as trans. Complexes **2a**, **3a**, and **7a** were assigned cis, cis, and trans geometry, respectively, on the basis of their analogy to the other complexes within the same series.

It was of interest to test the possibility of assigning the geometry of the complexes by using ^{31}P NMR (Table II). In the cis geometry the phosphorus atoms are trans to thiolato ligands, hence *J*(P–Pt) might be expected to be different for the trans geometry when they are trans to each other. Although only a small number of complexes of both geometries are available, there did not appear to be a distinct separation of the range of the *J*(P–Pt) values as a function of geometry. The *J* values were highly dependent upon the nature of the phosphine and thiolato ligands.

All of the purified cis complexes are unstable to air in solution as evidenced by the disappearance of their NMR signals and the growth of peaks due to other species. The stability of complex **1b** in deuterated solvents in air was monitored by NMR methods. Its concentration decreased with time at a rate that varied somewhat from solvent to solvent, being fastest in $CDCl_3$ and slowest in $(CD_3)_2CO$. The presence of added thiol, triethylamine, or phosphine had no noticeable effect on the decomposition. Thus, the preparation of cis complexes in high yield and purity requires inert-atmosphere conditions. Performing the preparations in air invariably led to contamination of the cis monomer by the trans monomer and the corresponding dimer in amounts which increased with the length of exposure to air in solution. In some cases the corresponding disulfide, the free phosphine, and its oxide were identified by NMR methods. Thus the attempt to prepare **1a** in air led to the isolation of only **6a** and the dimer which were separated by fractional crystallization. Heavily contaminated samples of the complexes **1b–c** were isolated when the appropriate reactions were conducted in air. Some preparative reactions with alkanethiols were performed in NMR tubes in C_6D_6 solvent and were monitored by NMR methods. No reaction occurred in the absence of triethylamine; however, the reaction proceeded rapidly once the latter was added. The initial product in all cases, under N_2 or air, was the cis monomer which underwent reaction to produce the other species when air was present. The complexes *trans*-L_2PtCl_2, where L = PPh_3 and $PMePh_2$, were prepared[42] and treated with phenylmethanethiol/triethylamine in N_2 atmosphere. In both

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(41) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963); *J. Chem. Soc. A*, 770 (1966).

(42) S. H. Mastin and P. Haake, *J. Chem. Soc., Chem. Commun.*, 202 (1970).

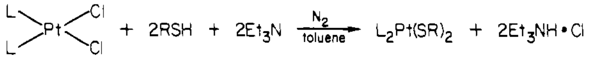
cases the *cis*-bis(thiolato) complex was the major product.

The treatment of $(PPh_3)_4Pt$ with benzyl disulfide under a variety of conditions including ultraviolet irradiation did not result in oxidative addition of the disulfide to give $(PPh_3)_2Pt(SCH_2C_6H_5)_2$. Oxidative addition has been reported to occur with phenyl disulfide, but alkyl disulfides such as $(C_2H_2)_2S_2$ and $(t\text{-}C_4H_9)_2S_2$ were found to be unreactive.[4] Benzyl disulfide did not react with *cis*-$(PPh_3)_2Pt(CH_3)_2$.

Cleavage of the thiolate polymer $[Pt(SPh)_2]_2$ with PMe_2Ph to give $(PMe_2Ph)_2Pt(SPh)_2$ has been reported.[8] We briefly investigated this type of reaction to see if it was a general route to monomeric complexes with nonchelating ligands. The polymers, prepared by treatment of K_2PtCl_4 with the thiol in ethanol/water, in air, at room temperature, gave a range of products depending on the thiol and the phosphine. When R = CH_2Ph and L = PPh_3, a mixture of mainly the trans complex **6a** and some dimer were identified by NMR methods. For R = CH_2Ph and L = PMe_2Ph a mixture of the cis complex **1c** and the trans **6c** was obtained in the ratio 4:1, respectively, as determined by NMR methods. Where R = 4-C_6H_4Me and L = PMe_2Ph the pure trans **7c** was isolated in low yield (24%). While this procedure does lead to some monomeric complexes, all of them are available by the reaction of the dichlorides with the thiols under the appropriate atmosphere.

Discussion

The displacement of chloride ligands from bis(phosphine)platinum dichloride complexes by thiols under N_2 atmosphere in the presence of triethylamine is a facile general route to monomeric bis(thiolates) (eq 1). Arenethiols give complexes of trans geometry whereas alkylthiols give cis complexes which were previously unavailable. The cis complexes are air sensitive in solution, reacting to give a complex mixture of species that usually contain both the cis and the trans complexes and the dimer. Thus the historical scarcity of the cis compounds may simply be due to previous studies being conducted in air.



$$L_2PtCl_2 + 2RSH + 2Et_3N \xrightarrow[\text{toluene}]{N_2} L_2Pt(SR)_2 + 2Et_3NH\cdot Cl \quad (1)$$

While this study was primarily directed toward the synthesis of complexes of the type *cis*-$L_2Pt(SR)_2$, the results obtained are somewhat unusual and raise some interesting questions. The NMR tube reactions show that the first complexes produced are of cis geometry for R = alkyl, regardless of the type of atmosphere. The presence of triethylamine is necessary for the reaction to proceed. Once added, however, all the NMR reactions were rapid, being essentially complete within 10 min. The subsequent rearrangement/dimerization of the cis complexes in solution proceeds at varying rates depending upon the phosphine, the R group and the solvent.

The qualitative observations of the preparations are consistent with chloride ligand displacement via an S_N2 mechanism. The triethylamine probably increases the concentration of the RS^- ion which is a much better nucleophile than RSH with respect to displacement of chloride ligands from platinum complexes.[43] However, treatment of *cis*-$(PMePh_2)_2Pt(SCH_2Ph)_2$ and *trans*-$(PMePh_2)_2Pt(4\text{-}SC_6H_4CH_3)_2$ with excess HCl gave the *cis*- and *trans*-dichlorides, respectively. Thus, by forming the hydrochloride the amine also prevents the HCl liberated in the preparation from reversing the reaction. The retention of geometry which occurs when *cis*-dichlorides are converted to *cis*-bis(thiolates) is also in accord with an S_N2 mechanism. However, the isolation of the cis complexes **1a–b** from the *trans*-dichlorides appears to be inconsistent.

The preparative results can also be discussed in terms of an oxidative addition of the thiol followed by reductive elimination of HCl (the amine serving to prevent the back reaction with HCl). Thiols are known to oxidatively add to low valent platinum group metal complexes.[4,8,10,44] The reaction of the *cis*-bis(thiolato) complexes with HCl is also consistent with an oxidative addition followed by reductive elimination of RSH. Such mechanisms are involved in the cleavage of the M–C bond of platinum(II) alkyl complexes.[45] Oxidative cleavages have been established for complexes of the type $CpFe(CO)_2R$, where R is an alkyl group.[45] The complex *trans*-$(PEt_3)_2Pt(H)(SH)$ has been reported[27] to react with HCl to give oxidative addition products which were detected at low temperature. Upon warming, elimination of H_2S occurred. However, simple electrophilic attack of the sulfur atom of the coordinated thiolato group be ruled out in this case.

The sensitivity of the *cis*-bis(alkanethiolato) complexes is of interest. It seems that O_2 leads to the observed changes. This rearrangement might be initiated by radicals in solution. Air-generated thiyl radicals, RS·, are involved in the cleavage of the platinum–carbon bonds in *cis*-$(PMe_2Ph)_2Pt(CH_3)_2$ by benzenethiol.[14] It is of particular interest that only trans products were isolated in the latter case and that these reactions were apparently conducted in air. These authors noted that cleavage with HCl on the other hand gave *cis*-$(PMe_2Ph)_2Pt(CH_3)(Cl)$. We have tested the effects of radical inhibitors and initiators on *cis*-$(PPh_3)_2Pt(SCH_2Ph)_2$ in solution under N_2 in order to determine if the rearrangement would be slowed or promoted, respectively. Unfortunately, complete decomposition occurred to give intractable mixtures of products. However, in the absence of added reagents the disulfide $PhCH_2SSCH_2Ph$ has been identified by NMR methods as one of the air rearrangement products of *cis*-$(PPh_3)_2Pt(SCH_2Ph)_2$ in C_6D_6. The formation of this product is consistent with radical coupling.

The different behavior of arenethiols which invariably lead to trans complexes compared to alkanethiols which give cis complexes is also of interest. The isolation of (diphos)Pt(*S*-aryl)$_2$ complexes by us and others suggests that a cis configuration is possible if the ligands are constrained in the cis geometry.

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Registry No. **1a**, 75365-64-9; **1b**, 75365-65-0; **1c**, 75365-66-1; **2a**, 75365-67-2; **2b**, 75365-68-3; **3a**, 72137-83-8; **3b**, 75365-69-4; **4**, 75365-70-7; **5**, 75365-71-8; **6a**, 75420-25-6; **6b**, 75420-26-7; **6c**, 75420-27-8; **7a**, 75420-28-9; **7b**, 75365-72-9; **7c**, 69596-87-8; *cis*-$(PPh_3)_2PtCl_2$, 15604-36-1; *cis*-$(PMePh_2)_2PtCl_2$, 16633-72-0; (diphos)$PtCl_2$, 14647-25-7; *cis*-$(PMe_2Ph)_2PtCl_2$, 15393-14-3.

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