

Synthesis of *cis*- and *trans*-Bis(phosphine)bis(thiolato)platinum(II) Complexes, $(\text{PR}_3)_2\text{Pt}(\text{SR}')_2$

RABIN D. LAI and ALAN SHAVER*

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Complexes of the type $\text{L}_2\text{Pt}(\text{SR})_2$ are isolated in high purity and yield by treating the *cis*-dichlorides with thiols under nitrogen atmosphere in the presence of triethylamine, $\text{L} = \text{PPh}_3$, PMePh_2 , PMe_2Ph , and $1/2(\text{PPh}_2\text{CH}_2)_2$, and $\text{R} = \text{CH}_2\text{Ph}$, *i*- C_3H_7 , *n*- C_3H_7 , and 4- $\text{C}_6\text{H}_4\text{CH}_3$. For $\text{R} = \text{alkyl}$ the complexes have been assigned the *cis* geometry while for $\text{R} = \text{aryl}$ 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*- $\text{L}_2\text{Pt}(\text{SR})_2$ 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*- $\text{L}_2\text{Pt}(\text{SR})_2$, 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 some⁵⁻⁸ to depend upon R being an electron-withdrawing group. It is true that for many monomeric complexes of the type $\text{L}_2\text{Pt}(\text{SR})_2$ and $\text{L}_2\text{Pt}(\text{SR})\text{Y}$, 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 $\text{C}(\text{O})\text{R}$.²⁵ However, a

careful survey reveals some reports of complexes where R is an electron-releasing group such as $\text{H}^{4,10,20,26,27}$ 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* $\rightarrow$ *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) $_2\text{PtCl}_2$,^{33,34} *cis*-

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(PMePh₂)₂PtCl₂,³⁵ and (diphos)PtCl₂,^{36,37} (diphos = PPh₂CH₂CH₂PPh₂) were prepared by published procedures. Phosphines from Aldrich (PPh₃) and Strem Chemicals (PMePh₂, PMePh₂, diphos), mercaptans from Aldrich, and triethylamine were used without further purification. The complexes *cis*-(PMePh₂)₂PtCl₂ and additional *cis*-(PMePh₂)₂PtCl₂ were prepared by displacement of the neutral ligands in *cis*-(Et₂S)₂PtCl₂³⁸ or CODPtCl₂³⁹ (COD = 1,5-cyclooctadiene) in CH₂Cl₂ solution under N₂ atmosphere.

(A) *cis*-Bis(phenylmethanethiolato)bis(triphenylphosphine)platinum(II), *cis*-(PPh₃)₂Pt(SCH₂Ph)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 N₂ to a stirred suspension of *cis*-(PPh₃)₂PtCl₂ (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 CH₂Cl₂. This solution was washed with 4 × 100 mL (distilled) water, dried over anhydrous MgSO₄, and stripped to dryness on a rotary evaporator. The product was recrystallized in air from CH₂Cl₂/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 N₂, and pumped on for 24 h. The yield was 2.61 g (97%).

(B) *cis*-Bis(phenylmethanethiolato)bis(methyldiphenylphosphine)platinum(II), *cis*-(PMePh₂)₂Pt(SCH₂Ph)₂ (1b). As in part A, *cis*-(PMePh₂)₂PtCl₂ (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 CH₂Cl₂/hexane gave yellow crystals, 3.15 g (87%).

(C) *cis*-Bis(phenylmethanethiolato)bis(dimethylphenylphosphine)platinum(II), *cis*-(PMe₂Ph)₂Pt(SCH₂Ph)₂ (1c). As in part A, *cis*-(PMe₂Ph)₂PtCl₂ (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 CH₂Cl₂/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*-(PPh₃)₂Pt(SCH₂CH₂CH₃)₂ (2a). As in part A, *cis*-(PPh₃)₂PtCl₂ (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 CH₂Cl₂/hexane gave 2.3 g (83%) of yellow crystals.

(E) *cis*-Bis(1-propanethiolato)bis(methyldiphenylphosphine)platinum(II), *cis*-(PMePh₂)₂Pt(SCH₂CH₂CH₃)₂ (2b). *cis*-(PMePh₂)₂PtCl₂ (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 CH₂Cl₂/ether gave 0.82 g (69%) of yellow crystals.

(F) *cis*-Bis(2-propanethiolato)bis(triphenylphosphine)platinum(II), *cis*-(PPh₃)₂Pt(SCHMe)₂ (3a). As in part A, *cis*-(PPh₃)₂PtCl₂ (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 CH₂Cl₂/ether, 1.19 g (73%) of yellow crystals.

(G) *cis*-Bis(2-propanethiolato)bis(methyldiphenylphosphine)platinum(II), *cis*-(PMePh₂)₂Pt(SCHMe)₂ (3b). As in part A, *cis*-(PMePh₂)₂PtCl₂ (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(SCH₂Ph)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 N₂ from sodium/benzophenone) were added dropwise to (diphos)PtCl₂ (1.0 g, 1.5 mmol) in 100 mL of THF and stirred for 18 h. Recrystallization from CH₂Cl₂/hexane gave pale yellow microcrystals, 1.09 g (86%).

(I) Bis(4-methylbenzenethiolato)[1,2-bis(diphenylphosphino)ethane]platinum(II), (diphos)Pt(SC₆H₄Me)₂ (5). As in part A, (diphos)PtCl₂ (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*-(PPh₃)₂Pt(SCH₂Ph)₂ (6a). This reaction was performed as in part A, but in air, with *cis*-(PPh₃)₂PtCl₂ (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 CH₂Cl₂. Reaction time was 22 h. The yield was 2.3 g (63%) of yellow crystals (CH₂Cl₂/ether).

(K) *trans*-Bis(4-methylbenzenethiolato)bis(triphenylphosphine)platinum(II), *trans*-(PPh₃)₂Pt(SC₆H₄Me)₂ (7a). As in part A, *cis*-(PPh₃)₂PtCl₂ (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 CH₂Cl₂/ether gave 2.6 g (95%) of orange crystals.

(L) *trans*-Bis(4-methylbenzenethiolato)bis(methyldiphenylphosphine)platinum(II), *trans*-(PMePh₂)₂Pt(SC₆H₄Me)₂ (7b). As in part A, *cis*-(PMePh₂)₂PtCl₂ (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 CH₂Cl₂/hexane gave yellow crystals, 3.7 g (95%).

(M) *trans*-Bis(4-methylbenzenethiolato)bis(dimethylphenylphosphine)platinum(II), *trans*-(PMe₂Ph)₂Pt(SC₆H₄Me)₂ (7c). As in part A, *cis*-(PMe₂Ph)₂PtCl₂ (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 CH₂Cl₂/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 K₂PtCl₄ via the method of Roundhill.⁸

Results

The anaerobic treatment of a suspension of *cis*-L₂PtCl₂ in toluene with an alkanethiol in the presence of triethylamine leads to the isolation of complexes of the type *cis*-L₂Pt(SR)₂ in high yield and purity, where L = PPh₃, PMePh₂, and PMe₂Ph and R = CH₂Ph, *n*-C₃H₇, and *i*-C₃H₇. 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 N₂ atmosphere. Use of the diphos ligand, Ph₂PCH₂CH₂PPh₂, constrains the geometry to be *cis*. In this case, under similar conditions, complexes 4 and 5 were isolated for R = CH₂Ph and 4-C₆H₄CH₃, 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*-L₂Pt(SR)₂ react when fused in vacuo to produce dimeric complexes of the type [L₂Pt(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 PMePh₂ and PMe₂Ph is also a sensitive

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Table I. Analytical and Physical Data

compd	no.	mp, °C	% C		% H	
			calcd	found	calcd	found
<i>cis</i> -(PPh ₃) ₂ Pt(SCH ₂ Ph) ₂	1a	150–152	62.2	61.9	4.56	4.48
<i>cis</i> -(PMePh ₂) ₂ Pt(SCH ₂ Ph) ₂	1b	130–132	57.1	56.4	4.76	4.66
<i>cis</i> -(PMe ₂ Ph) ₂ Pt(SCH ₂ Ph) ₂	1c	161–162	50.2	50.6	5.02	5.10
<i>cis</i> -(PPh ₃) ₂ Pt(SCH ₂ CH ₂ CH ₃) ₂	2a	142–144	58.0	57.1	5.06	5.28
<i>cis</i> -(PMePh ₂) ₂ Pt(SCH ₂ CH ₂ CH ₃) ₂	2b	126–128	51.5	52.1	5.37	5.31
<i>cis</i> -(PPh ₃) ₂ Pt(SCHMe ₂) ₂ ^a	3a	139–140	58.0	56.8	5.06	5.23
<i>cis</i> -(PMePh ₂) ₂ Pt(SCHMe ₂) ₂ ^a	3b	134–136	51.5	50.4	5.37	5.30
(diphos)Pt(SCH ₂ Ph) ₂	4	173–175	57.2	57.9	4.53	4.49
(diphos)Pt(4-SC ₆ H ₄ Me) ₂	5	155–157	57.2	56.7	4.53	4.74
<i>trans</i> -(PPh ₃) ₂ Pt(SCH ₂ Ph) ₂	6a	184–185	62.2	62.0	4.56	4.56
<i>trans</i> -(PPh ₃) ₂ Pt(4-SC ₆ H ₄ Me) ₂ ^a	7a	185–187	62.2	61.3	4.56	4.52
<i>trans</i> -(PMePh ₂) ₂ Pt(4-SC ₆ H ₄ Me) ₂	7b	177–179	57.1	56.7	4.76	4.82
<i>trans</i> -(PMe ₂ Ph) ₂ Pt(4-SC ₆ H ₄ Me) ₂	7c	209–210	50.2	49.7	5.02	5.09

^a The analysis was calculated by assuming 1/2CH₂Cl₂ of crystallization was present per molecule of complex. CH₂Cl₂ was observed in the ¹H NMR of these complexes.

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

compd	no.	P-CH ₃ ^b			S-R ^{b,c}			P ^d	
		τ	J- (Pt-H)	J- (P-H)	τ	J- (Pt-H)	J- (P-H)	α	J- (Pt-P)
<i>cis</i> -(PPh ₃) ₂ Pt(SCH ₂ Ph) ₂	1a				5.62 (td)	47	6	-24.1	2888
<i>cis</i> -(PMePh ₂) ₂ Pt(SCH ₂ Ph) ₂	1b	8.34 (td)	28	10	5.58 (td)	44	6	-6.7	2856
<i>cis</i> -(PMe ₂ Ph) ₂ Pt(SCH ₂ Ph) ₂	1c	8.52 (td)	28	10	5.64 (td)	38	6	9.5	2788
<i>cis</i> -(PPh ₃) ₂ Pt(SCH ₂ CH ₂ CH ₃) ₂	2a				9.18 (t) ^e			-24.3	2864
<i>cis</i> -(PMePh ₂) ₂ Pt(SCH ₂ CH ₂ CH ₃) ₂	2b	8.17 (td)	27	9	9.12 (t) ^e			-5.6	2807
<i>cis</i> -(PPh ₃) ₂ Pt(SCHMe ₂) ₂	3a				8.70 (d) ^f			-23.8	2852
<i>cis</i> -(PMePh ₂) ₂ Pt(SCHMe ₂) ₂	3b	8.10 (td)	27	9	8.61 (d) ^f			-6.6	2825
(diphos)Pt(SCH ₂ Ph) ₂	4	7.82 (m) ^g			5.99 (td)	33	4	-47.2	2798
(diphos)Pt(4-SC ₆ H ₄ Me) ₂	5	7.89 (m) ^g			7.92 (s)			-45.6	2896
<i>trans</i> -(PPh ₃) ₂ Pt(SCH ₂ Ph) ₂	6a				7.50 (t)	18		-25.2	2925
<i>trans</i> -(PMePh ₂) ₂ Pt(SCH ₂ Ph) ₂	6b	7.82 (tt)	30	4	7.22 (t)	28			
<i>trans</i> -(PMe ₂ Ph) ₂ Pt(SCH ₂ Ph) ₂	6c	8.18 (tt)	30	4	6.85 (s) ^h	35			
<i>trans</i> -(PPh ₃) ₂ Pt(4-SC ₆ H ₄ Me) ₂	7a				7.81 (s) ^h			-22.3	2954
<i>trans</i> -(PMePh ₂) ₂ Pt(4-SC ₆ H ₄ Me) ₂	7b	8.07 (tt)	29	4	7.85 (s) ^h			-6.4	2739
<i>trans</i> -(PMe ₂ Ph) ₂ Pt(4-SC ₆ H ₄ Me) ₂	7c	8.34 (tt)	27	4	7.80 (s) ^h			6.6	2603

^a In CDCl₃ 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 = CH₂Ph, CH₂CH₂CH₃, CH(CH₃)₂, 4-C₆H₄CH₃. ^d All ³¹P chemical shifts in ppm upfield (negative) from 85% H₃PO₄. ^e CH₂CH₂CH₃: τ ~7.1 (m), 8.4 (m).

^f CH(CH₃)₂: τ ~5.9 (m) (*J*(H-H) = 7 Hz). ^g [CH₂PPh₃]₂. ^h 4-C₆H₄CH₃: 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 ³¹P 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 CDCl₃ and slowest in (CD₃)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 C₆D₆ 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 N₂ or air, was the *cis* monomer which underwent reaction to produce the other species when air was present. The complexes *trans*-L₂PtCl₂, where L = PPh₃ and PMePh₂, were prepared⁴² and treated with phenylmethanethiol/triethylamine in N₂ atmosphere. In both

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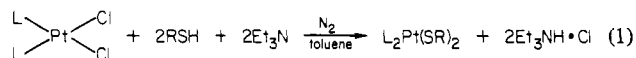
cases the *cis*-bis(thiolato) complex was the major product.

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 $(C_2H_5)_2S_2$ and $(i-C_4H_9)_2S_2$ were found to be unreactive.⁴ Benzyl disulfide did not react with *cis*-(PPh_3)₂Pt(CH₃)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.

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 $R = \text{alkyl}$, 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*-(PMe_2Ph)₂Pt-(SCH_2Ph)₂ and *trans*-(PMe_2Ph)₂Pt(4- $SC_6H_4CH_3$)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 reported²⁷ 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, $RS^\cdot$, are involved in the cleavage of the platinum-carbon bonds in *cis*-(PMe_2Ph)₂Pt(CH₃)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(CH₃)₂(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($S\text{-aryl}$)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)₂PtCl₂, 15604-36-1; *cis*-(PMe_2Ph)₂PtCl₂, 16633-72-0; (diphos)PtCl₂, 14647-25-7; *cis*-(PMe_2Ph)₂PtCl₂, 15393-14-3.

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