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Multimode Coordination Chemistry of $[R_2P(X)CH_nP(Y)R'_2]^{(2-n)-}$ Ligands (X, Y = O, S, Se; *n* = 1, 2). Synthesis and ^{31}P NMR Spectroscopy of Platinum Complexes

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Reactions of the bis(phosphine chalcogenides) $CH_2\{P(X)R_2\}\{P(Y)R'_2\}$ (X, Y = O, S, Se) and their derived anions $[CH\{P(X)R_2\}\{P(Y)R'_2\}]^-$ with chloroplatinum complexes $PtCl_4^{2-}$, $[Pt_2Cl_4(PEt_3)_2]$, or $[Pt_2Cl_2(PEt_3)_4]^{2+}$ result in a wide variety of coordination complexes. For example, when R = R′ = Ph and X = Y = S, the following are all accessible in high yield: $[PtCl(PEt_3)\{CH_2(P(S)Ph_2)_2\text{-}S,S\}]^+$, $[PtCl(PEt_3)\{CH(P(S)Ph_2)_2\text{-}C,S\}]$, $[PtCl(PEt_3)\{CH(P(S)Ph_2)_2\text{-}S,S\}]$, $[Pt(PEt_3)_2\{CH_2(P(S)Ph_2)_2)\text{-}S,S\}]^{2+}$, $[Pt(PEt_3)_2\{CH(P(S)Ph_2)_2\text{-}C,S\}]^+$, $[PtCl_2\{CH_2(P(S)Ph_2)_2\text{-}S,S\}]$, $[Pt\{CH_2(P(S)Ph_2)_2\text{-}S,S\}_2]^{2+}$, and $[Pt\{CH(P(S)R_2)_2\text{-}C,S\}_2]$. A more limited range of complexes is also reported for X = Y = O, X = Y = Se, and X = O, Y = S. In general, the ligands exhibit at least five different coordination modes: (i) Bidentate X,Y coordination of neutral ligands; (ii) bidentate X,Y coordination of the anionic ligands; (iii) bidentate C,X coordination of the anions in a strained four-membered ring; (iv) monodentate C coordination of the anions; (v) complex C,S bridging mode involving a dianionic ligand and two metal centers. Interconversion reactions and characteristic ^{31}P NMR spectroscopy are described for all of the coordination modes, including dynamic NMR studies of the C,X modes. These last modes all exhibit some degree of fluxional behavior, involving an exchange of coordinated and noncoordinated P═X groups in essentially a classic "bimolecular" substitution reaction, except that the incoming ligand is actually part of one of the existing ligands.

Introduction

Although coordination complexes of the bis(phosphine chalcogenide) ligands $CH_2\{P(X)R_2\}\{P(Y)R'_2\}$ (X, Y = O, S, Se) and their derived anions $[CH\{P(X)R_2\}\{P(Y)R'_2\}]^-$ have been known for approximately twenty years, they remain an area of active research interest.[1-23] The ligands are loosely analogous to acetylacetone and acetylacetonate, but the literature indicates a coordination chemistry for the phosphine chalcogenides which is even more rich and varied than that of their famous analogues. For example, derivatives of $CH_2\{P(S)Ph_2\}_2$ exhibit monodentate S[6,20] and bidentate[7] or bridging[8] S,S coordination of the neutral ligand; bidentate S,S[2] and C,S[13] coordination of the monoanion; and a novel dimer in which the central carbon of the dianion forms a quaternary carbon bridge between two platinum centers and is C,S chelated at each platinum center.[24] Examples of most of these coordination modes are shown in Scheme I.

Despite the wide range of metals which have been studied and the large number of individual compounds which have been reported for these phosphine chalcogenide ligands, it is notable that there have been no studies of the inter-relationships between the various possible coordination modes. Moreover, some very recent studies indicate that closely related ligands may be effective in promoting catalysis at metal centers. Thus, the P,O chelate complex $[RhCl(CO)\{Ph_2PCH_2CH_2P(O)Ph_2\}]$ catalyzes carbonylation of methanol to acetic acid[25] and iridium complexes of $[C\{P(O)Ph_2\}_3]^-$ are under investigation as catalysts in alkyne hydrosilylation.[26] Earlier authors have suggested that lability of M–S bonds may occasion unusual reactivity and catalysis.[27,28]

In this context it is somewhat surprising that there have been relatively few studies of the bis(phosphine chalcogenide) ligands with the most catalytically active metals, namely the platinum group. Ainscough and co-workers[5] prepared rhodium and iridium cations $[M(cod)\{CH_2(P(S)Ph_2)_2\}]^+$, and in our preliminary work[24] we have shown that the related complex $[Ir(cod)\{CH(P(S)Ph_2)_2\}]$ shows sequential, two-center reactivity at one ligand and one metal site. Thus, reaction with methyl iodide yields first $[Ir(cod)\{CHMe(P(S)Ph_2)_2\}]I$ and only subsequently $[IrMeI(cod)\{CHMe(P(S)Ph_2)_2\}]I$. In platinum chemistry, our preliminary results included an X-ray diffraction study of $[PtCl(PEt_3)\{CH(P(S)Ph_2)_2\text{-}C,S\}]$, complex **4** in Scheme I, the first example of C,S coordination of the anion.[13] This coordination mode has also been observed subsequently in the gold(III) complex $[Au(C_6F_5)_2\{CH(P(S)Ph_2)_2\}]$.[19]

Another particularly interesting feature of the chemistry of these ligands, and one which is potentially relevant to catalytic applications, concerns the lability of the M–X/M–Y bonds and the resulting dynamic processes. For example, the η^2-C,S ligand in **4B** (R = R′ = Ph, X = Y = S) exhibits dynamic exchange between the two P═S groups,[13] and a closely related process occurs in $[PtCl(PEt_3)\{C(P(S)Ph_2)_3\text{-}S,S\}]$.[29] In each case, the exchange process is essentially a rotation about a strong metal–ligand bond, Pt–C in the first example and Pt–S in the second.

The present paper reports results of a full study of platinum complexes for a variety of bis(phosphine chalcogenide) ligands, including dioxides, disulfides, diselenides, and some mixed oxide sulfides. A wide variety of coordination modes is found, and it is possible to study their interconversion (Scheme I) and char-

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Table I. Phosphorus-31 Nuclear Magnetic Resonance Parameters for the Complexes Shown in Scheme I[q]

complex						chem shifts, ppm			coupling constants, Hz					
no.	X	Y	R	R′	notes	$\delta(P_A)$	$\delta(P_B)$	$\delta(P_C)$	$J(PtP_A)$	$J(PtP_B)$	$J(PtP_C)$	$J(P_AP_B)$	$J(P_AP_C)$	$J(P_BP_C)$
3	S	O	Ph	Ph	*a, b*	30.3 (dd)	41.5 (dd)	5.6 (t)	138	nr	3825	13	3	4
	S	S	Ph	Ph	*a, b*	28.9 (t)	32.7 (t)	12.8 (t)	143	60	3279	8	8	9
			Ph	Pr^i	*a, b*	27.7 (t)	59.7 (t)	11.6 (t)	154	69	3232	13	14	9
			Pr^i	Ph	*a, b*	58.3 (t)	30.9 (dd)	12.3 (dd)	149	60	3376	12	10	8
			Ph	Bu^t	*a, b*	27.2 (t)	65.0 (dd)	11.6 (dd)	161	87	3234	15	16	8
			Bu^t	Ph	*a, b*	63.6 (dd)	32.1 (dd)	13.6 (t)	165	65	3365	14	9	8
			Me	Me	*a, c*	33.8 (dd)	34.7 (dd)	12.0 (t)	153	60	3273	14	9	9
	Se	Se	Ph	Ph	*a, b, d, e*	8.9 (dd)	20.5 (dd)	11.8 (t)	147	66	3219	3	8	9
4a	S	O	Ph	Ph	*a, d*	62.9 (dd)	29.9 (t)	5.6 (dd)	446	74	2915	10	6	13
	S	S	Ph	Ph	*a, d, f*	69.9 (d)	42.2 (d)	4.9 (t)	448	80	2903	nr	9	7
			Ph	Pr^i	*g*	61.3 (dd)	71.0 (dd)	4.7 (dd)	456	52	2825	11	10	5
			Pr^i	Ph	*g*	105.2 (dd)	42.9 (dd)	3.4 (dd)	377	82	2928	2	9	4
			Me	Me	*g*	69.9 (d)	59.0 (d)	6.1 (t)	445	73	2954	10	5	nr
	Se	Se	Ph	Ph	*a, d, h*	$\underline{39.5}$ (d)	$\underline{39.5}$ (d)	4.5 (t)	$\underline{418}$	$\underline{418}$	2895	na	$\underline{9}$	$\underline{9}$
4b	S	S	Ph	Ph	*h, i*	$\underline{40.3}$ (d)	$\underline{40.3}$ (d)	4.1 (t)	$\underline{301}$	$\underline{301}$	3906	nr	$\underline{6}$	$\underline{6}$
	S	S	Ph	Ph	*i, j*	49.2	41.3	10.3	505	nr	3871	nr	nr	nr
	Se	Se	Ph	Ph	*a, d, h*	$\underline{39.4}$ (d)	$\underline{39.4}$ (d)	3.0 (t)	$\underline{368}$	$\underline{368}$	3297	na	$\underline{16}$	$\underline{16}$
5	S	S	Ph	Ph	*k*	$\underline{45.0}$ (d)	$\underline{45.0}$ (d)	4.7 (t)	$\underline{461}$	$\underline{461}$	3436	na	$\underline{20}$	$\underline{20}$
			Ph	Bu^t	*g*	34.5 (dd)	90.1 (dd)	−1.6 (dd)	478	366	3414	54	21	18
6	O	O	Ph	Ph	*c, l*	48.1 (s)	48.1 (s)	10.9 (s)	34	34	3845	nr	nr	nr
	S	O	Ph	Ph	*a, b, m*	32.3 (ddd)	46.8 (dd)	6.3 (dd)	66	nr	3693	12	3	nr
	S	S	Ph	Ph	*c, l*	33.2 (s)	33.2 (s)	13.5 (s)	72	72	3141	nr	nr	nr
7	O	O	Ph	Ph	*a, b, h, n*	$\underline{46.3}$ (m)	$\underline{46.3}$ (m)	16.2 (dt)	$\underline{157}$	$\underline{157}$	2673	nr	$\underline{10}$	$\underline{10}$
	S	O	Ph	Ph	*a, b, d, o*	48.8 (ddd)	26.6 (ddd)	5.2 (m)	385	91	2592	5	10	12
	S	S	Ph	Ph	*a, c, d, h, p*	$\underline{43.6}$ (d)	$\underline{43.6}$ (d)	3.5 (dt)	$\underline{243}$	$\underline{243}$	2623	nr	$\underline{10}$	$\underline{10}$

[a] $CDCl_3$ solution. [b] ClO_4^- salt. [c] BF_4^- salt. [d] −30 °C. [e] $^1J(P_A{-}Se) = 575$ Hz, $^1J(P_B{-}Se) = 597$ Hz. [f] $CDCl_3$ solution. Note that the slightly different values in ref 13 were recorded in tetrahydrofuran. [g] C_6D_6 solution. [h] Underlined values are averaged by exchange (see Results). [i] Tetrahydrofuran-d_8 solution. [j] −80 °C. [k] Toluene-d_8 solution. Underlined values are averages. Actual values are not available because this is a very strongly coupled ABX spin system (see Results). [l] CH_2Cl_2 solution. This AA′XX′ system appears as two singlets with no resolution of $J(P{-}P)$ values (see Results). $\delta(P_D) = \delta(P_C)$. [m] $\delta(P_D)$ 21.4(ddd); $J(Pt{-}P_D) = 3277$; $J(P_A{-}P_D) = 8.8$; $J(P_B{-}P_D) = 3.1$; $J(P_C{-}P_D) = 19.1$. [n] $\delta(P_D)$ 5.2(d); $J(Pt{-}P_D) = 3917$; $J(P_A{-}P_D)$ = nr; $J(P_B{-}P_D)$ = nr; $J(P_C{-}P_D) = 21.3$. [o] $\delta(P_D)$ 4.4(m); $J(Pt{-}P_D) = 3480$; $J(P_A{-}P_D) = 9.9$; $J(P_B{-}P_D)$ = nr; $J(P_C{-}P_D) = 19.3$. [p] $\delta(P_D)$ 2.2(d); $J(Pt{-}P_D) = 3558$; $J(P_A{-}P_D) = \underline{5}$; $J(P_B{-}P_D) = \underline{5}$; $J(P_C{-}P_D) = 18.9$. [q] The atom-labeling scheme is shown in Chart I. Chemical shifts (δ) are quoted in parts per million relative to 85% H_3PO_4. All shifts were positive. Coupling constants (J) are in Hz. Some ^{13}C and ^{195}Pt data for these complexes are given in the Experimental Section. Nr = not resolved. Na = not available from the observed spectrum.

acteristic spectroscopy (Table I).

Experimental Section

Data relating to the characterization of the complexes are given in Table I, under Results, and in the preparative descriptions below. Microanalysis was by the Canadian Microanalytical Service, Vancouver, BC, Canada. ^{31}P nuclear magnetic resonance (NMR) spectra were recorded in appropriate solvents (Table I) at either 24.3 MHz using a Nicolet TT14 Fourier transform spectrometer with a Varian HA60 magnet and an external C_6D_6 lock signal or at 101.3 MHz using a Bruker WP250 Fourier transform spectrometer locked to the solvent deuterium resonance. ^{13}C and ^{195}Pt spectra were recorded at 62.9 and 53.5 MHz, respectively, in $CDCl_3$ solution using the Bruker instrument. For all nuclei protons were decoupled by broad band ("noise") irradiation at appropriate frequencies. ^{31}P chemical shifts were measured relative to external $P(OMe)_3$ and are reported in parts per million relative to 85% H_3PO_4 using a conversion factor of +141 ppm. ^{13}C and ^{195}Pt chemical shifts are reported in ppm relative to $Si(CH_3)_4$ and $\Xi(^{195}Pt) = 21.4$ MHz,[30] respectively. Positive values are deshielded relative to the references. In all cases, Pt–P coupling constants in ^{195}Pt spectra were in acceptable agreement with those derived from ^{31}P spectra (Table I). Line shape analyses for the dynamic NMR spectra were carried out using a locally constructed program package based on DNMR3.[31]

All operations were carried out at ambient temperature (ca. 25 °C) under an atmosphere of dry nitrogen using standard Schlenk tube techniques. Solvents were dried by reflux over appropriate reagents (calcium hydride for dichloromethane, molecular sieves or K_2CO_3 for acetone, and potassium/benzophenone for diethyl ether, tetrahydrofuran, toluene, benzene, and hexane) and were distilled under nitrogen prior to use. Recrystallizations from solvent pairs were by dissolution of the complex in the first solvent (using about double the volume required for complete solution) followed by dropwise addition or layering of sufficient second solvent to cause turbidity at ambient temperature. Crystallization was then completed either by continued very slow dropwise addition of the second solvent or, in those cases where a temperature is indicated in the detailed descriptions below, by setting the mixture aside at a reduced temperature.

The metal complexes $[Pt_2Cl_4(PEt_3)_2]$ and $[Pt_2Cl_2(PEt_3)_4]Z_2$, Z = BF_4 or ClO_4, were prepared as previously described.[32,33] The ligands **1**, $CH_2\{P(X)R_2\}\{P(Y)R'_2\}$, where X = Y = O, R = R′ = Ph;[11,12] X = Y = S, R = R′ = Ph,[11,34] R = R′ = Me,[35] R = Ph, R′ = Pr^i,[34] R = Ph, R′ = Bu^t;[36] X = S, Y = O, R = R′ = Ph;[11] and X = Y = Se, R = R′ = Ph,[11] have all been reported previously and were prepared by methods similar to the literature procedures. There is a potential explosion hazard arising from the use of perchlorates in the presence of organic material, so quantities should be kept small and heating (especially to dryness) avoided. In general we preferred to prepare disulfides by heating the corresponding bisphosphines[37] with 2 molar equiv of elemental sulfur under reflux in benzene for 2 h rather than the more common literature method of reaction of $[CH_2\{P(S)R_2\}]^-$ with R'_2PCl followed by heating with sulfur. $CH_2\{P(S)Ph_2\}\{P(O)Ph_2\}$, prepared previously by oxidation of $CH_2\{P(S)Ph_2\}\{PPh_2\}$,[11] was more conveniently obtained from $CH_2\{PPh_2\}\{P(O)Ph_2\}$ and sulfur, and $CHMe\{P(S)Ph_2\}_2$[34] was obtained by treating a tetrahydrofuran solution of $Li[CH\{P(S)Ph_2\}_2]$ with 1 molar equiv of iodomethane.

The lithium salts $Li[CH\{P(X)Ph_2\}\{P(Y)R_2\}]$ were prepared by dropwise addition of a slight excess (ca. 1.1–1.2 molar equiv) of *n*-butyllithium (1.5 M in hexane) to stirred solutions of $CH_2\{P(X)Ph_2\}\{P(Y)R_2\}$ in tetrahydrofuran. ^{31}P and ^{13}C NMR spectra confirmed that the required anions were the sole phosphorus-containing products, and the solutions were used in situ without further workup.

^{31}P and ^{13}C NMR data for the neutral ligands, $CH_2\{P(X)R_2\}\{P(Y)R'_2\}$, were recorded in chloroform and for the anionic ligands, $[CH\{P(X)R_2\}\{P(Y)R'_2\}]^-$, in tetrahydrofuran. Many of these species have been reported previously, and where ^{31}P data are available,[11,34] our results are

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in good agreement. The following data show shifts in ppm and coupling constants in Hz. X = Y = O, R = R′ = Ph: neutral, δ(P) 24.6; anion, δ(P) 36.8. X = S, Y = O, R = R′ = Ph: neutral; δ(*P*–S) 36.1, δ(*P*–O) 23.2, ^2J(P–P) = 16; anion, δ(*P*–S) 36.0, δ(*P*–O) 34.8, ^2J(P–P) = 24. X = Y = S, R = R′ = Ph: neutral, δ(P) 34.6, δ(P–*C*–P) 38.8, ^1J(P–C) = 45; anion, δ(P) 38.6, δ(P–*C*–P) 19.9, ^1J(P–C) = 110. X = Y = S, R = Ph, R′ = Pr$^\mathrm{i}$: neutral, δ(*P*Ph$_2$) 31.9, δ(*P*Pr$^\mathrm{i}_2$) 69.5, ^2J(P–P) = 16, δ(P–*C*–P) 33.1, ^1J(C–PPh$_2$) = 41, ^1J(C–PPr$^\mathrm{i}_2$) = 32; anion, δ(*P*Ph$_2$) 37.4, δ(*P*Pr$^\mathrm{i}_2$) 62.1, ^2J(P–P) = 18. X = Y = S, R = Ph, R′ = Bu$^\mathrm{t}$: neutral, δ(*P*Ph$_2$) 37.8, δ(*P*Bu$^\mathrm{t}_2$) 73.9, ^2J(P–P) = 16, δ(P–*C*–P) 27.0, ^1J(C–PPh$_2$) = 50, ^1J(C–PBu$^\mathrm{t}_2$) = 28. X = Y = S, R = R′ = Me: neutral, δ(P) 32.7, δ(P–*C*–P) 39.6, ^1J(C–P) = 42. X = Y = Se, R = R′ = Ph: neutral, δ(P) 26.2, ^2J(P–P) = 18, ^1J(Se–P) = 745.

Complexes 3: [PtCl(PEt$_3$){CHR″(P(X)R$_2$)(P(Y)R′$_2$)-*X*,*Y*}][Z] [R″ = H (X = S, Y = O, R = R′ = Ph; X = Y = S, R = R′ = Ph; X = Y = S, R = Ph, R′ = Pr$^\mathrm{i}$; X = Y = S, R = Ph, R′ = Bu; X = Y = S, R = R′ = Me; X = Y = Se, R = R′ = Ph); R″ = Me (X = Y = S, R = R′ = Ph); Z = BF$_4^-$, ClO$_4^-$]. These complexes were obtained in 70–90% yields by procedures similar to the first example below, using NaClO$_4$·H$_2$O or NaBF$_4$ as appropriate.

[PtCl(PEt$_3$){CH$_2$(P(S)Ph$_2$)(P(S)Bu$^\mathrm{t}_2$)-*S*,*S*}]ClO$_4$. A solution of CH$_2${P(S)Ph$_2$}{P(S)Bu$^\mathrm{t}_2$} (0.13 g, 0.32 mmol) in acetone (5 mL) was added dropwise to a stirred solution of [Pt$_2$Cl$_4$(PEt$_3$)$_2$] (0.12 g, 0.16 mmol) and NaClO$_4$·H$_2$O (0.045 g, 0.32 mmol) in acetone (20 mL). The solution immediately became cloudy and lighter in color due to precipitation of NaCl. After 1 h the solvent was removed in vacuo, to ensure complete precipitation of the NaCl, and the residue extracted with dichloromethane. Solvent was again removed in vacuo and the residue recrystallized from acetone/hexane at −18 °C to give [PtCl(PEt$_3$){CH$_2$(P(S)Ph$_2$)(P(S)Bu$^\mathrm{t}_2$)-*S*,*S*}]ClO$_4$ as lemon yellow crystals (0.23 g, 0.27 mmol). Anal. Calcd for C$_{27}$H$_{45}$Cl$_2$O$_4$P$_3$PtS$_2$: C, 37.9; H, 5.29. Found: C, 37.6; H, 5.38. NMR: δ(Pt) 416.7 ppm (ddd, CDCl$_3$); δ(P–*C*–P) 22.7 ppm (dd, CDCl$_3$); ^1J(C–PPh$_2$) = 46; ^1J(C–PBu$^\mathrm{t}_2$) = 27 Hz.

This product has two possible isomers: **3A** (X = Y = S, R = Ph, R′ = Bu$^\mathrm{t}$) and **3B** (X = Y = S, R = Bu$^\mathrm{t}$, R′ = Ph). ^{31}P NMR spectrum of the initial reaction mixture showed the presence of both possible isomers in approximately a 3:2 ratio, but the final crystals consisted entirely of isomer **3A** and other spectroscopy was carried out on this isomer. A similar situation pertained for the R = Ph, R′ = Pr$^\mathrm{i}$ complex below. For the other complexes **3**, involving symmetrical bis(phosphine sulfide) ligands, only a single isomer is possible.

[PtCl(PEt$_3$){CH$_2$(P(S)Ph$_2$)(P(O)Ph$_2$)-*S*,*O*}]ClO$_4$. Recrystallization: acetone/diethyl ether. Anal. Calcd for C$_{31}$H$_{37}$Cl$_2$O$_5$P$_3$PtS: C, 42.3; H, 4.24. Found: C, 42.8; H, 4.21.

[PtCl(PEt$_3$){CH$_2$(P(S)Ph$_2$)$_2$-*S*,*S*}]ClO$_4$·Me$_2$CO. Recrystallization: acetone/diethyl ether. Anal. Calcd for C$_{34}$H$_{43}$Cl$_2$O$_5$P$_3$PtS$_2$: C, 42.8; H, 4.54. Found: C, 43.1; H, 4.59. NMR: δ(Pt) 420.9 ppm (dd, CDCl$_3$); δ(P–*C*–P) 31.5 ppm (t, CDCl$_3$); ^1J(C–P) = 46 Hz.

[PtCl(PEt$_3$){CH$_2$(P(S)Me$_2$)$_2$-*S*,*S*}]BF$_4$. Recrystallization: dichloromethane/hexane at −18 °C. Anal. Calcd for C$_{11}$H$_{29}$BClF$_4$P$_3$PtS$_2$: C, 20.8; H, 4.60. Found: C, 21.0; H, 4.58. NMR: δ(P–*C*–P) 31.2 (t, CDCl$_3$); ^1J(C–PPh$_2$) = 45 Hz.

[PtCl(PEt$_3$){CH$_2$(P(S)Ph$_2$)(P(S)Pr$^\mathrm{i}_2$)-*S*,*S*}]ClO$_4$. Recrystallization: acetone/hexane at −18 °C. Anal. Calcd for C$_{25}$H$_{41}$Cl$_2$O$_4$P$_3$PtS$_2$: C, 36.2; H, 4.99. Found: C, 36.2; H, 5.17. NMR: δ(Pt) 412.2 ppm (ddd, CDCl$_3$); δ(P–*C*–P) 25.1 ppm (dd, CDCl$_3$); ^1J(C–PPh$_2$) = 49; ^1J(C–PPr$^\mathrm{i}_2$) = 34 Hz.

[PtCl(PEt$_3$){CHMe(P(S)Ph$_2$)$_2$-*S*,*S*}]BF$_4$. Recrystallization: tetrahydrofuran/diethyl ether at −18 °C. Anal. Calcd for C$_{32}$H$_{39}$BClF$_4$P$_3$PtS$_2$: C, 42.8; H, 4.38. Found: C, 42.4; H, 4.45. NMR: δ(P$_\mathrm{A}$) 42.3 ppm; δ(P$_\mathrm{B}$) 43.9 ppm; δ(P$_\mathrm{C}$) 12.6 ppm; *J*(Pt–P$_\mathrm{A}$) = 147 Hz; *J*(Pt–P$_\mathrm{B}$) = 65 Hz; *J*(Pt–P$_\mathrm{C}$) = 3269 Hz; *J*(P$_\mathrm{A}$–P$_\mathrm{B}$) = nr; *J*(P$_\mathrm{A}$–P$_\mathrm{C}$) = 8 Hz; *J*(P$_\mathrm{B}$–P$_\mathrm{C}$) = 8 Hz; δ(Pt) 482.2 ppm (ddd, CDCl$_3$); δ(P–*C*–P) 31.4 ppm (t, CDCl$_3$); ^1J(P–C) = 42 Hz. The ligand {CHMe(P(S)Ph$_2$)$_2$} had δ(P) 46.6 ppm (CDCl$_3$).

[PtCl(PEt$_3$){CH$_2$(P(Se)Ph$_2$)$_2$-*Se*,*Se*}]BF$_4$. This complex was characterized only by ^{31}P NMR spectroscopy in solution (Table I).

Complexes 4: [PtCl(PEt$_3$){CH(P(X)R$_2$)(P(Y)R′$_2$)-*C*,*X*}] [X = S, Y = O, R = R′ = Ph; X = Y = S, R = R′ = Ph; X = Y = S, R = Ph, R′ = Pr$^\mathrm{i}$; X = Y = S, R = R′ = Me; X = Y = Se, R = R′ = Ph]. [PtCl(PEt$_3$){CH(P(S)Ph$_2$)(P(S)Pr$^\mathrm{i}_2$)-*C*,*S*}]. A solution (1.3 M in hexane) of *n*-butyllithium (0.28 mL, 0.36 mmol) was added dropwise to a stirred suspension of CH$_2${P(S)Ph$_2$}{P(S)Pr$^\mathrm{i}_2$} (0.14 g, 0.37 mmol) in tetrahydrofuran (10 mL). The resulting orange solution was added dropwise to a stirred solution of [Pt$_2$Cl$_4$(PEt$_3$)$_2$] (0.14 g, 0.18 mmol) in tetrahydrofuran (10 mL). After 1 h, the solvent was removed in vacuo leaving a viscous orange oil which was extracted with benzene (5 mL) to leave precipitated LiCl as residue. Addition of hexane (20 mL) to the benzene extract gave [PtCl(PEt$_3$){CH(P(S)Ph$_2$)(P(S)Pr$^\mathrm{i}_2$)-*C*,*S*}] as a yellow powder (0.26 g, 0.36 mmol). Anal. Calcd for C$_{25}$H$_{40}$ClP$_3$PtS$_2$: C, 41.2; H, 5.54. Found: C, 41.7; H, 5.60. The product contained approximately equal amounts of the two possible isomers of structure **4A**, namely R = Ph, R′ = Pr$^\mathrm{i}$ or R = Pr$^\mathrm{i}$, R′ = Ph. NMR for R = Ph, R′ = Pr$^\mathrm{i}$: δ(Pt) 792.7 ppm (ddd, C$_6$D$_6$). NMR for R = Pr$^\mathrm{i}$, R′ = Ph: δ(Pt) 801.1 ppm (ddd, C$_6$D$_6$).

[PtCl(PEt$_3$){CH(P(S)Ph$_2$)$_2$-*C*,*S*}]. This preparation was similar to that above, but the product was unusual in that although ^{31}P spectroscopy of the initial orange oil showed structure **4A** as in the example above, during attempted recrystallization procedures increasing proportions of structure **4B** were formed. A small, pure sample of **4B** was finally obtained from a florisil column, eluted with hexane, diethyl ether, and finally tetrahydrofuran. The first two eluates were discarded, and the product was obtained by reducing the volume of the tetrahydrofuran under reduced pressure followed by addition of diethyl ether to give yellow crystals. Anal. Calcd for C$_{31}$H$_{36}$ClP$_3$PtS$_2$: C, 46.8; H, 4.56. Found: C, 47.6; H, 4.88. NMR for **4A**: δ(Pt) 780.7 ppm (ddd, C$_6$D$_6$). NMR for **4B**: δ(Pt) 747.4 ppm (ddd, C$_6$D$_6$). Crystals suitable for study by X-ray diffraction were obtained by recrystallization from a tetrahydrofuran/hexane mixture, and the structure was determined as described previously.[13] A ^{31}P NMR study was carried out in tetrahydrofuran-*d*$_8$ solution over the temperature range −100 to +30 °C, and the line shapes were analyzed using DNMR3.[31]

[PtCl(PEt$_3$){CH(P(S)Me$_2$)$_2$-*C*,*S*}]. This compound was obtained in almost quantitative yield by similar procedures, and its ^{31}P NMR spectrum was consistent with structure **4A**.

[PtCl(PEt$_3$){CH(P(Se)Ph$_2$)$_2$-*C*,*Se*}]. This compound was prepared by addition of 1,8-bis(dimethylamino)naphthalene to solutions of [PtCl(PEt$_3$){CH$_2$(P(Se)Ph$_2$)$_2$-*Se*,*Se*}]ClO$_4$ in acetone or chloroform at −30 °C. The product was shown by ^{31}P NMR spectroscopy to consist mainly of structure **4B**, but small quantities of isomer **4A** were observed in some preparations. The product was relatively unstable, with decomposition beginning about 0 °C and being complete after several hours in solution at ambient temperature.

Complexes 5: [PtCl(PEt$_3$){CH(P(S)Ph$_2$)(P(S)R′$_2$)-*S*,*S*}] (R′ = Ph or Bu$^\mathrm{t}$). [PtCl(PEt$_3$){CH(P(S)Ph$_2$)(P(S)Bu$^\mathrm{t}_2$)-*S*,*S*}]. Sodium hydride (0.039 g, 1.30 mmol, 80% in oil) was added to a solution of [PtCl(PEt$_3$){CH(P(S)Ph$_2$)(P(S)Bu$^\mathrm{t}_2$)-*S*,*S*}]ClO$_4$ (0.25 g, 0.29 mmol) in tetrahydrofuran (3 mL). After being stirred for 3 h, the orange supernatant was decanted from unreacted sodium hydride and the solvent removed in vacuo. The orange residue was extracted with benzene (10 mL) and the solvent removed from the extract in vacuo. The residue was recrystallized from tetrahydrofuran/hexane to give [PtCl(PEt$_3$){CH(P(S)Ph$_2$)(P(S)Bu$^\mathrm{t}_2$)-*S*,*S*}] (0.17 g, 0.22 mmol) as a yellow powder. Anal. Calcd for C$_{27}$H$_{44}$ClP$_3$PtS$_2$: C, 42.9; H, 5.86. Found: C, 42.6; H, 5.47. NMR: δ(Pt) 722.0 ppm (ddd, C$_6$D$_6$).

Note that both the starting material, **3**, and the product, **5**, have two possible isomers depending on the positions of the Ph and Bu$^\mathrm{t}$ groups. The configuration of the starting material corresponded to structure **3** (R = Ph, R′ = Bu$^\mathrm{t}$) in Scheme I, and the product had the same configuration.

[PtCl(PEt$_3$){CH(P(S)Ph$_2$)$_2$-*S*,*S*}]·THF. This preparation was similar to that above except that the benzene extract was purified by passage through a Florisil column. Yield: 22%. Anal. Calcd for C$_{35}$H$_{44}$ClOP$_3$PtS$_2$: C, 48.4; H, 5.11; Cl, 4.08. Found: C, 48.6; H, 5.03; Cl, 4.42. NMR: δ(Pt) 800.5 ppm (dt, C$_6$D$_6$); δ(P–*C*–P) 16.3 ppm (t, C$_6$D$_6$); ^1J(P–C) = 71 Hz. When the reaction time was reduced to 30 min in an attempt to improve the yield, the desired product, [PtCl(PEt$_3$){CH(P(S)Ph$_2$)$_2$-*S*,*S*}], was mixed with [PtCl(PEt$_3$){CH(P(S)Ph$_2$)$_2$-*C*,*S*}] (**4A**) in about a 4:1 ratio.

Complexes 6: [Pt(PEt$_3$)$_2${CH$_2$(P(X)Ph$_2$)(P(Y)Ph$_2$)-*X*,*Y*}]Z$_2$ (X = Y = O; X = S, Y = O; X = Y = S; Z = BF$_4$, ClO$_4$). These complexes were all prepared by procedures similar to the first example below.

[Pt(PEt$_3$)$_2${CH$_2$(P(S)Ph$_2$)$_2$-*S*,*S*}][BF$_4$]$_2$. A solution of CH$_2${P(S)Ph$_2$}$_2$ (0.17 g, 0.26 mmol) in dichloromethane (5 mL) was added dropwise to a stirred solution of [Pt$_2$Cl$_2$(PEt$_3$)$_4$][BF$_4$]$_2$ (0.10 g, 0.13 mmol) in dichloromethane (10 mL). After 30 min, the solvent was removed in vacuo and the residue washed with diethyl ether and recrystallized from dichloromethane/diethyl ether to give [Pt(PEt$_3$)$_2${CH$_2$(P(S)Ph$_2$)$_2$-*S*,*S*}][BF$_4$]$_2$ as colorless crystals (0.22 g, 0.20 mmol). Anal. Calcd for C$_{37}$H$_{52}$B$_2$F$_8$P$_4$PtS$_2$: C, 42.2; H, 4.98. Found: C, 42.2; H, 5.18.

[Pt(PEt$_3$)$_2${CH$_2$(P(O)Ph$_2$)$_2$-*O*,*O*}][BF$_4$]$_2$. Anal. Calcd for C$_{37}$H$_{52}$B$_2$F$_8$O$_2$P$_4$Pt: C, 43.5; H, 5.13. Found: C, 43.1; H, 5.16.

[Pt(PEt$_3$)$_2${CH$_2$(P(S)Ph$_2$)(P(O)Ph$_2$)-*S*,*O*}][ClO$_4$]$_2$. Anal. Calcd for C$_{37}$H$_{52}$Cl$_2$O$_9$P$_4$PtS: C, 41.8; H, 4.93. Found: C, 41.5; H, 5.08.

Complexes 7: [Pt(PEt$_3$)$_2${CH(P(X)Ph$_2$)(P(Y)Ph$_2$)-*C*,*X*}]Z (X = Y = O; X = S, Y = O; X = Y = S; Z = BF$_4$, ClO$_4$, Cl). [Pt(PEt$_3$)$_2${CH(P(S)Ph$_2$)$_2$-*C*,*S*}]Cl. A solution (1.3 M in hexane) of *n*-butyllithium (0.20 mL, 0.26 mmol) was added dropwise to a stirred suspension of CH$_2${P(S)Ph$_2$}$_2$ (0.12 g, 0.27 mmol) in tetrahydrofuran (10 mL). The resulting orange solution was added dropwise to a stirred solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.10 g, 0.13 mmol) in tetrahydrofuran (10 mL), followed by addition of PEt_3 (0.04 mL, 0.27 mmol). After 1 h, the solvent was removed in vacuo, the residue extracted with dichloromethane, and the extract recrystallized from dichloromethane/hexane to give $[Pt(PEt_3)_2\{CH(P(S)Ph_2)_2\text{-}C,S\}]Cl$ as yellow crystals (0.20 g, 0.22 mmol). Anal. Calcd for $C_{37}H_{51}ClP_4PtS_2$: C, 48.6; H, 5.62. Found: C, 48.6; H, 6.11.

Reaction of **6** (R = R = Ph, X = Y = S) in chloroform with 1,8-bis(dimethylamino)naphthalene also gave the same complex cation and similar reactions were used to prepare $[Pt(PEt_3)_2\{CH(P(O)Ph_2)_2\text{-}C,O\}]ClO_4$ and $[Pt(PEt_3)_2\{CH(P(S)Ph_2)(P(O)Ph_2)\text{-}C,S\}]ClO_4$. The latter complexes had ^{31}P NMR spectra consistent with structure **7**, X = Y = O and X = S, Y = O, respectively.

Interconversion Reactions. These were carried out on a small scale in 10-mm NMR tubes. In all cases monitoring of the reactions by ^{31}P NMR spectroscopy (Table I) indicated rapid conversions in high yields. Protonations of **4** to **3** and **5** to **3** used approximately 1 molar equiv of $HBF_4{\cdot}Et_2O$ in either diethyl ether or tetrahydrofuran solution. Deprotonations of **3** to **4** and **6** to **7** used 1,8-bis(dimethylamino)naphthalene in chloroform solution at −78 °C followed by warming to ambient temperature.

$[PtCl_2\{CH_2(P(S)Ph_2)_2\text{-}S,S\}]$. A solution of $CH_2\{P(S)Ph_2\}_2$ (0.54 g, 1.2 mmol) in ethanol (10 mL) and acetone (5 mL) was added dropwise to a stirred solution of K_2PtCl_4 (0.5 g, 1.2 mmol) in water (15 mL) and ethanol (5 mL). After 24 h, the precipitate was collected and washed with water, ethanol, dichloromethane, and ether to yield $[PtCl_2\{CH_2(P(S)Ph_2)_2\}]$ (0.77 g, 1.1 mmol) as a buff precipitate which was too insoluble for recrystallization and in consequence gave relatively poor microanalytical results. Anal. Calcd for $C_{25}H_{22}Cl_2P_2PtS_2$: C, 42.0; H, 3.10. Found: C, 40.8; H, 3.01. NMR: $\delta(P)$ 29.6 ppm (s, CH_3NO_2); $^2J(Pt\text{-}P)$ = 123 Hz.

$[Pt\{CH_2(P(S)Ph_2)_2\text{-}S,S\}_2](ClO_4)_2$. $CH_2\{P(S)Ph_2\}_2$ (0.70 g, 1.6 mmol) was added to a stirred solution of $[PtCl_2\{CH_2(P(S)Ph_2)_2\}]$ (0.80 g, 1.1 mmol) and $NaClO_4{\cdot}H_2O$ (0.16 g, 1.1 mmol) in acetone (10 mL) and nitromethane (10 mL). After 15 h, solvent was removed in vacuo and the residue extracted into dichloromethane and crystallized by addition of diethyl ether to yield $[Pt\{CH_2(P(S)Ph_2)_2\}_2](ClO_4)_2$ (1.3 g, 1.0 mmol) as yellow crystals. Anal. Calcd for $C_{50}H_{44}Cl_2O_8P_4PtS_4$: C, 46.5; H, 3.44; Cl, 5.5. Found: C, 46.0; H, 3.26; Cl, 6.7. NMR: $\delta(P)$ 33.0 ppm (s, CH_2Cl_2); $^2J(Pt\text{-}P)$ = 100 Hz.

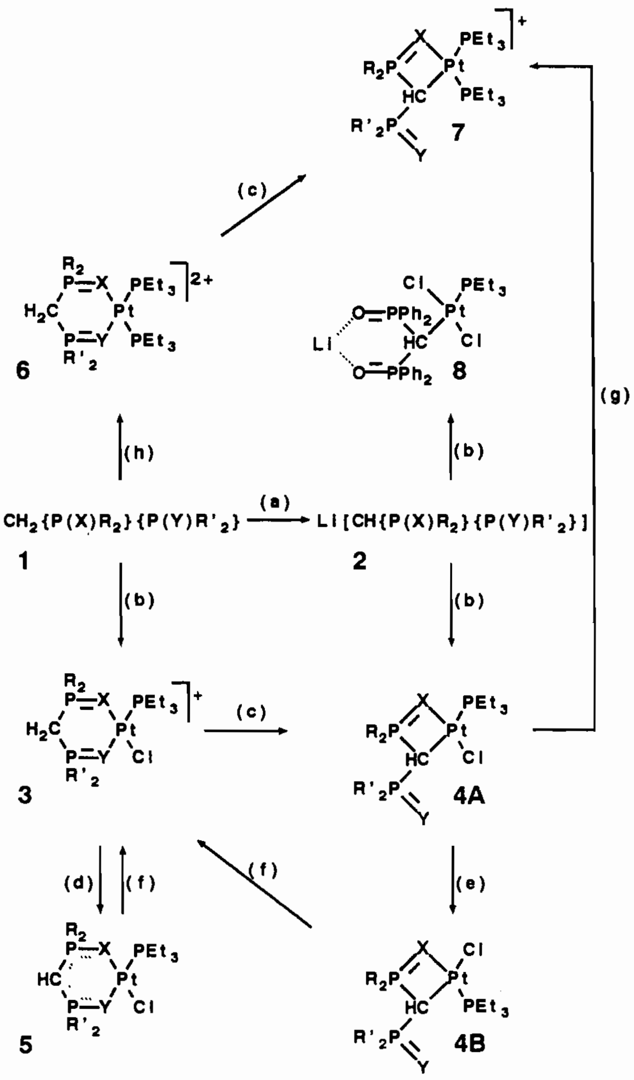
$[Pt\{CH(P(S)Ph_2)_2\text{-}C,S\}_2]$. This product was obtained by reaction of sodium hydride (in tetrahydrofuran) or 1,8-bis(dimethylamino)naphthalene (in chloroform) with $[Pt\{CH_2(P(S)Ph_2)_2\}_2](ClO_4)_2$. ^{31}P NMR spectroscopy of the impure product was consistent with a structure containing mutually trans-C,S-bonded ligands. NMR in tetrahydrofuran: $\delta(P_A)$ 64.7 (s) ppm; $\delta(P_B)$ 39.6 (s) ppm; $^2J(Pt\text{-}P_A)$ = 495 Hz; $^2J(Pt\text{-}P_B)$ = 104 Hz.

Results and Discussion

Our principal synthetic results are summarized in Scheme I. The ligands **1**, $CH_2\{P(S)R_2\}\{P(S)R'_2\}$ (X = Y = O, R = R′ = Ph;[11,12] X = Y = S, R = R′ = Ph,[11,34] R = R′ = Me,[35] R = Ph, R′ = Pr^i,[34] R = Ph, R′ = Bu^t;[36] X = S, Y = O, R = R′ = Ph;[11] X = Y = Se, R = R′ = Ph),[11] and most of the derived salts **2** have been reported previously and were prepared by methods similar to the literature procedures. We were not successful in preparing the salts **2** for X = Y = Se, since in these cases attempted reactions of the ligands **1** with Bu^nLi resulted only in deselenation of the ligand and formation of $Li[SeBu^n]$.

Our most complete study is for derivatives of $CH_2\{P(S)Ph_2\}_2$ (**1**; X = Y = S, R = R′ = Ph), and for this example the complete reaction sequence shown in Scheme I, with the single exception of **8**, is established with all complexes **3**–**7** isolated and fully characterized. Complex **8** has been reported previously.[12] It is only accessible when X = Y = O and is included in the scheme for completeness. Results for other ligands are somewhat less extensive than those for $CH_2\{P(S)Ph_2\}_2$, but they indicate a generally similar chemistry for all the ligands studied. The majority of complexes have been isolated and fully characterized by microanalysis, detailed ^{31}P NMR studies (Table I), some ^{13}C and ^{195}Pt NMR results (Experimental Section), and in one case, $[PtCl(PEt_3)\{CH(P(S)Ph_2)_2\text{-}C,S\}]$ (**4B**; X = Y = S, R = R′ = Ph), by a full X-ray diffraction study which has been reported previously.[13] In a few cases where products are close relatives of well-characterized complexes it has been sufficient to study reactions by in situ ^{31}P NMR experiments. This is especially the situation X = Y = Se complexes, since these are rather unstable in solution and attempts at isolation were unsuccessful.

Scheme I. Structures and Interconversion Reactions for Complexes **1**–**8**[a]



[a] Reagents: (a) *n*-butyllithium; (b) $[Pt_2Cl_4(PEt_3)_2]$; (c) 1,8-bis(dimethylamino)naphthalene in chloroform; (d) sodium hydride in tetrahydrofuran; (e) recrystallization from tetrahydrofuran; (f) H^+; (g) triethylphosphine; (h) $[Pt_2Cl_2(PEt_3)_4]^{2+}$.

In section A of the following discussion we present first a detailed account of the synthesis and interconversion of each class of X = Y = S derivatives, followed in each case by summaries for the other ligands indicating the ranges of complexes prepared and any differences between their chemistry and that of the disulfides. In addition to the derivatives outlined in Scheme I, we report a few complexes of $CH_2\{P(S)Ph_2\}_2$ which contain no other phosphine ligands. These were obtained from the reaction of K_2PtCl_4 with $CH_2\{P(S)Ph_2\}_2$. In section B, we describe details of ^{31}P NMR results, and resultant structural assignments, and the dynamic solution behavior of some of the complexes (section B(4)).

(A) Synthesis and Interconversion Reactions. Derivatives of $CH_2\{P(S)R_2\}\{P(S)R'_2\}$. Cleavage of chloro bridges is often a convenient route to platinum coordination complexes, and in the present work either $[Pt_2Cl_4(PEt_3)_2]$ or $[Pt_2Cl_2(PEt_3)_4]^{2+}$ reacted smoothly with **1** (R = R′ = Ph, X = Y = S) under mild conditions to form respectively **3** or **6** in high yield. In order to facilitate formation of **3** by precipitation of NaCl and to provide a counterion, the former reaction was carried out in acetone in the presence of $NaClO_4$. The S,S coordination in **3** contrasts strongly with the products from reactions of $[Pt_2Cl_4(PEt_3)_2]$ with the ligand anions $[CH\{P(S)R_2\}\{P(S)R'_2\}]^-$ (**2**). These latter reactions invariably yield derivatives **4** with C,S coordination.

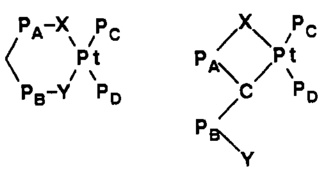
Complexes containing similar ligand coordination arrangements are also accessible via displacement of chloride from the tetrachloroplatinate(II) anion. Thus, K_2PtCl_4 reacts with 1 equiv of $CH_2\{P(S)Ph_2\}_2$ to yield $[PtCl_2\{CH_2(P(S)Ph_2)_2\text{-}S,S\}]$, and excess ligand in the presence of added $NaClO_4$ results in complete removal of chloride to give $[Pt\{CH_2(P(S)Ph_2)_2\text{-}S,S\}_2]^{2+}$. This cation is deprotonated by either sodium hydride or 1,8-bis(dimethylamino)naphthalene to form $[Pt\{CH(P(S)Ph_2)_2\text{-}C,S\}_2]$.

The acidity of the methylene protons in **3** and the possible reorganization from S,S to C,S coordination which accompanies its removal is of considerable interest. Several research groups have been interested in reactivity of the methylene group of coordinated $CH_2\{PPh_2\}_2$, and it is known that the protons are relatively acidic. Both alkylation and metalation reactions are known and can result in either mono- or disubstituted products.[38-43] Addition of sulfur should enhance the acidity (reactivity) of the methylene protons, but little is known about this aspect of the chalcogenide chemistry.[24]

As expected, reactions of **3** with bases do result in the removal of a methylene proton, but surprisingly, the structure of the products is strongly dependent on the nature of the base, possibly on the solvent, and on the particular R,R′ groups on the ligand. Thus, **3** (R = R′ = Ph, X = Y = S) reacts with 1,8-bis(dimethylamino)naphthalene in chloroform to give **4A** under mild conditions and this product rearranges during workup or on heating to **4B**. When the base is sodium hydride in tetrahydrofuran, the product is primarily the S,S-coordinated complex, **5**, with some evidence that **4A** is formed at shorter reaction times. The simplest reaction path for both bases would be an initial deprotonation to **5**, with subsequent reorganization to **4A** and/or **4B** under some conditions. However, the observation of **4A** at short reaction times in the sodium hydride reaction and a lack of conversion of **5** to **4** during solution studies are both at variance with this simple interpretation and preclude definite conclusions.

The initial formation of isomer **4A** (rather than **4B**) in reactions of **2** with $[Pt_2Cl_4(PEt_3)_2]$ or **3** with 1,8-bis(dimethylamino)naphthalene may be understood in terms of kinetic control. In each case a carbanionic reagent is either used or generated and the bond trans to the labilizing triethylphosphine ligand is attacked in preference to the bond trans to chloride. In general we would expect **4B** to be the thermodynamically more stable isomer since P is not trans to C. Thus, when R = R′ = Ph, X = Y = S, **4A** rearranges slowly in solution to **4B**, and when R = R′ = Ph, X = Y = Se, isomer **4B** is the main product of deprotonation of **3** by 1,8-bis(dimethylamino)naphthalene, even when the reaction is carried out at −30 °C. The selenium complexes are sensitive to decomposition, and it is likely that donors such as PEt_3 or P=Se groups are liberated. Since we have also noticed some tendency for the rate of isomerization of **4A** (R = R′ = Ph, X = Y = S) to depend on the method of preparation of the sample, it seems probable that adventitious impurities or products of decomposition play a significant role in the isomerization. This behavior would parallel that for the complexes $[PtClMe(PEt_3)_2]$, where the cis isomer, with C trans to P as in **4A**, readily isomerizes to the more stable trans isomer and the transformation is catalyzed by addition of donors such as PEt_3.[44] However, it is also clear that **4B** is not necessarily the most stable isomer in all cases, and overall the products are determined by a subtle blend of steric and electronic factors. For example, **4A** (R = R′ = Ph, X = S, Y = O), **4A** (R = R′ = Me, X = Y = S), and **4A** (R = Ph, R′ = Pr^i, X = Y = S) all fail to isomerize. The first example is perhaps understandable in view of the known low affinity of platinum for oxygen, but the reasons in the other cases are not clear.

Chart I. Schematic Structures of Complexes **6** and **7** To Show Labeling for NMR Parameters[a]



6 **7**

[a] Labels for complexes **3**–**5** are similar except that P_D is absent (replaced by Cl).

Other reactions in which base causes reorganization from an S,S-coordinated ligand to C,S coordination are reaction of **6** with 1,8-bis(dimethylamino)naphthalene to yield **7** and, as mentioned above, the reaction of $[Pt\{CH_2(P(S)Ph_2)_2\}_2]^{2+}$ with either sodium hydride or 1,8-bis(dimethylamino)naphthalene to yield $[Pt\{CH(P(S)Ph_2)_2\text{-}C,S\}_2]$. Compound **7** is also obtained from reactions of **4** with triethylphosphine, which is a useful confirmation of its structure. Both S,S- and C,S-coordinated derivatives revert to **3** on reaction with H^+.

Other reactions of X = Y = S derivatives include preparations of **3** and **4A** for R = R′ = Me and a preparation of **3** for $CHMe\{P(S)R_2\}_2$. This last product is somewhat puzzling since it failed to react with bases (NaH) and we were also unsuccessful in preparing the lithium salt, **2**, of this ligand. Consequently, no Pt–C-bound complexes of this ligand are available. The reason for this lack of reactivity is not obvious, since corresponding rhodium derivatives are readily deprotonated.[24]

Derivatives of $CH_2\{P(O)Ph_2\}_2$. This ligand does not react with $[Pt_2Cl_4(PEt_3)_2]$ under mild conditions. Evidently the oxygen atoms are insufficiently nucleophilic toward platinum to cleave the chloro bridges. However, compound **6** is easily prepared from $[Pt_2Cl_2(PEt_3)_4]^{2+}$, indicating that the positive charge in this starting material enhances the ease of bridge cleavage by nucleophilic reagents. Reaction of **6** with 1,8-bis(dimethylamino)naphthalene gives deprotonation and rearrangement to the C,O-coordinated derivative **7**, but this complex proved relatively unstable, decomposing during attempted workup procedures.

The reaction of $Li[CH\{P(O)Ph_2\}_2]$ with $[Pt_2Cl_4(PEt_3)_2]$ is different from all the others which we studied. Evidently, in the cases involving at least one sulfur or selenium donor atom, the ligand is a sufficiently good donor to displace Cl^- after the initial coordination to platinum via a Pt–C linkage. The dioxide ligand evidently cannot do this, and the complex is stabilized instead by an unusual coordination rearrangement to a lithium ion as shown in structure **8**. This complex has been reported in detail previously[12] and is included here only for completeness.

Derivatives of $CH_2\{P(S)Ph_2\}\{P(O)Ph_2\}$. The chemistry of this ligand is basically similar to that of $CH_2\{P(S)Ph_2\}_2$ except that the poorer donor ability toward platinum of oxygen relative to sulfur means that **3** exists as only one isomer, namely that with X = S, Y = O, an arrangement that places the stronger trans-influence ligands trans to the weaker ones. Also, complex **4** is nonfluxional and exists only as isomers **4A** with coordinated sulfur and noncoordinated oxygen.

Derivatives of $CH_2\{P(Se)Ph_2\}_2$. The chemistry of this ligand is also basically similar to that of $CH_2\{P(S)R_2\}_2$ except that the complexes tend to be unstable due to deselenation reactions and also because the Pt–Se bonds appear to be somewhat more labile than corresponding Pt–S bonds. Thus, reaction of **1** (R = R′ = Ph, X = Y = Se) with $[Pt_2Cl_4(PEt_3)_2]$ gives a deselenated product, $[PtCl(PEt_3)\{CH_2(PPh_2)(P(Se)Ph_2)\text{-}P,Se\}]$, which has been prepared previously by the reaction of $[Pt_2Cl_4(PEt_3)_2]$ with $CH_2\{PPh_2\}\{P(Se)Ph_2\}$.[45] Complexes **3** and **4** are accessible by reactions of $CH_2\{P(Se)Ph_2\}_2$ or $[CH\{P(Se)Ph_2\}_2]^-$ with $[Pt_2Cl_4(PEt_3)_2]$, but

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whereas only isomer **4B** is fluxional in the S,S case, both **4A** and **4B** are fluxional when X = Y = Se. Isomer **4B** is the major product with about 15% of **4A**. Reaction of $CH_2\{P(Se)Ph_2\}_2$ with $[Pt_2Cl_2(PEt_3)_4]^{2+}$ gave no evidence of formation of **6**, which is more evidence of the weaker donor character of Se relative to S.

(B) ^{31}P NMR and Structural Assignments. The structures of the complexes discussed in this section are shown in Scheme I, and the detailed ^{31}P NMR data are given in Table I. Some ^{13}C and ^{195}Pt NMR data are included in the Experimental Section. The atom-labeling scheme used in Table I and in the following descriptions is shown in Chart I.

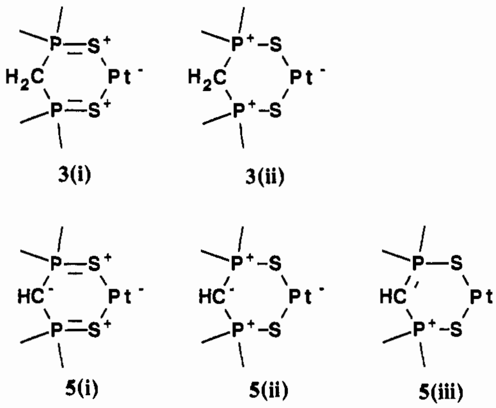
1. X,Y-Coordinated Neutral Ligands. (i) Complexes 3. The ^{31}P NMR spectrum of **3** (X = Y = S, R = R′ = Ph) shows three resonances at 12.8, 28.9, and 32.7 ppm, each consisting of a small triplet (ca. 8-Hz spacing) and each having sidebands attributable to ^{195}Pt (33.8% abundant, $I = {}^1/_2$) with Pt–P couplings of 3279, 143, and 60 Hz, respectively. The minor triplet structures are evidently due to P–P couplings of very similar magnitude so that the expected double doublets appear as triplets, and with this proviso, the spectrum is easily assigned to structure **3**. The chemical shift and platinum coupling for the first resonance are typical of PEt_3 trans to a ligand of low to medium trans influence. The smaller Pt–P couplings are consistent with two-bond couplings via sulfur, one trans to P and one trans to Cl. The trans influence of the P═S group, as measured by $^1J(Pt–P_C)$ = 3279 Hz, is clearly greater than that of chloride (*cis*-$[PtCl_2(PEt_3)_2]$, 3560 Hz) and much less than that of PEt_3(*trans*-$[PtCl_2(PEt_3)_2]$, 2435 Hz).[46] The present value is most comparable to those obtained for PEt_3 trans to ligands such as azide (3223 Hz) or thiocyanate (3360 Hz).[47]

The spectra of other complexes **3** are basically similar to this example except for the occurrence of two isomers when R and R′ are different. Two isomers are also possible for the S,O derivative, but in fact only the isomer with P═O trans to PEt_3 was obtained. This complex and the Se,Se derivative also provide a trans-influence series, P═O < P═S < P═Se, with $^1J(Pt–P_C)$ = 3825, 3279, and 3219 Hz, respectively. Within the ligand, weakening of the P═Se bond is shown by a reduction in ^1J(Se–P) from 745 to 575/597 (Se–P_A/P_B) Hz on coordination.

Although coordination shifts in ^{31}P NMR spectroscopy are often useful and informative when phosphorus is directly coordinated to a metal, they are generally less dramatic and more erratic in direction when phosphorus is not the directly bound atom. In most of the present cases, the phosphorus of the P═S groups experiences a small increase in shielding on coordination. The range for $\Delta\delta$ is +2 to −11 ppm, with only R = R′ = Me in the positive region. Similarly, the phosphorus of P═Se groups becomes more shielded on coordination of the selenium, from 26.2 ppm in the free ligand to 8.9 and 20.5 ppm in **3**, but in contrast, the P═O ligands all experience significant deshielding of phosphorus on coordination, for example from 24.6 ppm in the free ligand to 41.5 ppm in **3** (X = S, Y = O). There is thus a progression from negative to positive coordination shifts in the sequence P═O, P═S, and P═Se.

(ii) Complexes 6. When R = R′ = Ph and X = Y = O or S, the ^{31}P spectra of these complexes show only two singlets, each with ^{195}Pt sidebands. There is no evidence of the expected AA′XX′ character or indeed of any P–P coupling. This is probably because the three-bond P–P couplings are too small to introduce any significant magnetic inequivalence, but it could also be due to labile exchange between the two X,Y coordination sites at ambient temperature. The greater trans influence of P═S relative to P═O and the complementarity of trans bonds is nicely illustrated by the Pt–P couplings in these complexes. Thus, ^1J(Pt–P) is 3141 Hz trans to P═S in **6** (X = Y = S) and 3845 Hz trans to P═O when X = Y = O. The corresponding trans couplings are ^2J(Pt–S–P) = 72.4 Hz and ^2J(Pt–O–P) = 34.0 Hz. When X = S, Y = O, the four phosphorus atoms are all chemically inequivalent and the four Pt–P couplings reflect the same effects. Thus, ^2J(Pt–S–P) is 66 Hz while ^2J(Pt–O–P) is less than the spectrum resolution. ^1J(Pt–P) trans to S is 3277 Hz whereas trans to O is 3693 Hz.

Chart II. Possible Resonance Forms for Complexes 3 and 5



3(i) **3(ii)**

5(i) **5(ii)** **5(iii)**

(iii) $[PtCl_2\{CH_2(P(S)Ph_2)_2\text{-}S,S\}]$ and $[Pt\{CH_2(P(S)Ph_2)_2\text{-}S,S\}_2]^{2+}$. These complexes both show single ^{31}P resonances at 29.6 and 33.0 ppm, respectively, and with ^2J(Pt–P) = 123 and 100 Hz. By comparison with results for **3** these shifts and couplings are indicative of P═S coordinated trans to Cl.

2. X,Y-Coordinated Anionic Ligands. Complexes 5. These complexes were observed only for X = Y = S. When R = Ph, R′ = Bu^t, all three phosphorus resonances are clearly resolved and consist of the expected doublets of doublets with ^{195}Pt sidebands. When R = R′ = Ph, the spectrum is an ABX pattern with Pt sidebands, but unfortunately the AB region is so strongly coupled that only the center lines of the normal AB quartet are visible. Thus, only an average chemical shift is available for the two P═S groups and it is not possible to determine J(AB). However, it is clear that the conversion of **3** to **5**, i.e. deprotonation of the ligand without rearrangement, is accompanied by several important changes in the ligand ^{31}P NMR spectrum:

(a) The intrachelate coupling, $^2J(P_A–P_B)$, increases sharply, from 15 to 54 Hz when R = Ph, R′ = Bu^t and from 8 Hz to the value responsible for the strongly coupled AB pattern when R = R′ = Ph. (b) There is a sharp increase in ^2J(Pt–S–P) from 143 and 60 Hz to an averaged value of 461 Hz when R = R = Ph and from 161 and 87 Hz to 478 and 366 Hz when R = Ph, R′ = Bu^t. (c) The phosphorus atoms of the chelate ligand are deshielded by an average 14.2 ppm when R = R′ = Ph and by 7.3 and 25.1 ppm when R = Ph, R′ = Bu^t.

Coordination of a phosphine chalcogenide to a metal creates a formal positive charge on the ligand, and some representative resonance forms for **3** and **5** are shown in Chart II. The NMR changes described above are all consistent with a shift in the relative importance of structures i and ii on deprotonation. Thus, if phosphorus becomes more positively charged in **5** relative to **3**, then the phosphorus should be deshielded and the coupling constants should increase due to the higher effective nuclear charge at phosphorus. In previously known simple phosphorus ylides, structures involving a P═C double bond are considered less important than those involving some charge separation, $P^+–C^-$, since the ^{13}C NMR shifts are not deshielded as they are in alkenes.[48] In the present case it seems that structures such as **5(iii)** are relatively unimportant since the methyne carbon resonance of **5** (R = R′ = Ph, X = Y = S) is fairly strongly shielded at 16.3 ppm (^1J(P–C) = 71 Hz), compared with 31.5 ppm (46 Hz) for complex **3** and 38.8 ppm (45 Hz) for the noncoordinated ligand.

These changes in the chelate ligand are also accompanied by increased shielding of the PEt_3 phosphorus and by deshielding of the platinum, but the reasons for these changes are less obvious. Interestingly, the trans influence of the chelate ligand, as indicated by the Pt–PEt_3 coupling, is reduced on deprotonation: $^1J(Pt–P_C)$

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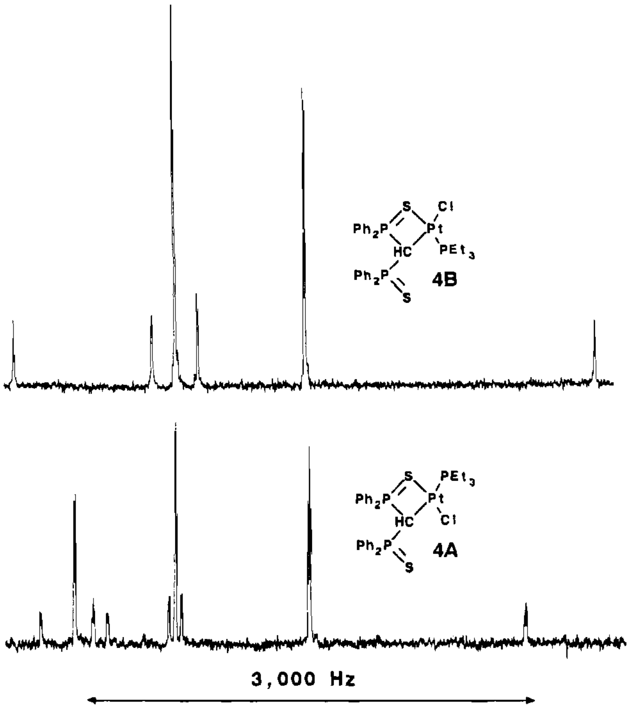

Figure 1. $^{31}P\{^1H\}$ NMR spectra of complexes **4A** (R = R′ = Ph, X = Y = S) and **4B** (R = R′ = Ph, X = Y = S). The central triplets due to PEt_3 are at 4.9 and 4.1 ppm, respectively, relative to 85% H_3PO_4.

increases from 3279 to 3436 Hz for R = R′ = Ph and from 3234 to 3414 Hz for R = Ph, R′ = Bu^t. Normally, the Fermi contact theory of the trans influence in NMR coupling constants would indicate that a decreased trans influence for the chelate ligand should be accompanied by decreased coupling from the chelate ligand to platinum. This is a consequence of the "σ only" nature of the Fermi contact term and the complementary demands of the chelate and the trans PEt_3 for the platinum 6s orbital. The fact that in the present complexes the Pt–P couplings to both chelate and PEt_3 phosphorus increase on deprotonation is an indication of the importance of π-bonding in the chelate ligands.

3. C,X-Coordinated Anionic Ligands. (i) Complexes 4. Complexes **4A**, **4B**, and **5** all have the same composition, and one example of **4B** (X = Y = S, R = R′ = Ph) has been fully characterized by an X-ray diffraction study.[13] Thus, the other structures are based on the relationships between their ^{31}P NMR parameters and those of the structurally characterized example, **4B**, and also on relationships to parameters of the neutral ligand complexes **3**. The comparison between **4A** and **4B** (R = R′ = Ph, X = Y = S) is shown in Figure 1. Thus, the ^{31}P NMR spectrum of **4A** consists of a triplet for the PEt_3 phosphorus (4.9 ppm) and two doublets (29.9 and 69.9 ppm) for the chelate ligand. The inter-phosphorus couplings, $^3J(P_A-P_C)$ = 9.1 Hz and $^3J(P_B-P_C)$ = 7.2 Hz, are sufficiently similar to account for the appearance of the PEt_3 resonance as a triplet rather than the expected doublet of doublets, and the third P–P coupling, $^2J(P_A-P_B)$, is not resolved. All three resonances have ^{195}Pt sidebands (J(Pt–P) = 2903, 80, and 448 Hz, respectively). The ambient-temperature spectrum of **4B**, shown in Figure 1, is basically similar except that platinum coupling to the PEt_3 phosphorus is much larger ($\delta(P_C)$ 4.1, $^3J(P_{A/B}-P_C)$ = 5.6 Hz, $^1J(Pt-P_C)$ = 3906 Hz), and there is only a single doublet ($\delta(P_{A/B})$ 40.3 ppm, $^2J(Pt-P_{A/B})$ = 301 Hz) for the phosphorus atoms of the chelate ligand. This spectrum for **4B** indicates dynamic solution interchange of the coordinated and noncoordinated P═S groups and is discussed in more detail below. However, with allowance for the effect of fluxionality in **4B**, the parameters for **4A** are basically similar except for the dramatic reduction in $^1J(Pt-PEt_3)$ coupling. The value of 2903 Hz in **4A** may be compared to those found in **3** (3279 Hz), **4B** (3906 Hz), and **5** (3436 Hz) and indicates that the PEt_3 group of **4A** is trans to a ligand of higher trans influence than any of the P═S groups of the former complexes. The only reasonable choice for this high trans influence group is a Pt–C bond.

In the chelate ligand region of the spectrum of **4A**, the intraligand coupling, $^2J(P_A-P_B)$, is not resolved but is clearly a small value as in **3** or **4B** rather than the much larger values observed in **5**. This suggests that the central ligand carbon of **4A** is sp^3 hybridized.

These comparisons are all consistent with the assignment of **4A** as an isomer of the structurally characterized **4B**, as shown in Scheme I. The value of $^1J(Pt-P_C)$ = 2903 Hz is relatively large for phosphorus trans to a σ-carbyl ligand, but it is comparable to values in $[PtMe\{CH(COMe)_2\}(dppe)]$, 2948 Hz,[49] and complex **8**, 2756 Hz, which has also been fully characterized by X-ray diffraction.[12]

Two other features of the ^{31}P NMR parameters within the four-membered rings of **4A** and **4B** merit comment:

(a) The ring phosphorus is strongly deshielded relative to **3**, for example by +41 ppm for **4A** (X = Y = S, R = R′ = Ph). This deshielding is puzzling since small rings normally have a shielding effect on phosphorus shifts.[50] This has been observed both in simple phosphorus ring compounds, $(RP)_n$,[51] and in metal complexes, $[PtCl_2\{Ph_2P(CH_2)_nPPh_2\}]$.[52]

(b) Platinum coupling to the deshielded intra-ring phosphorus is sharply increased relative to **3**, for example $^2J(Pt-S-P_A)$ increases from 143 Hz in **3** (X = Y = S, R = R′ = Ph) to 448 Hz in **4A**. The large coupling probably derives at least in part from the availability of two two-bond routes (through C or X) for the coupling. However, the coupling to the noncoordinated P═S is so much smaller (80 Hz) that it does not seem probable that this is the whole explanation. It suggests strongly that some other special factor affects the couplings within the four-membered ring, presumably an orbital difference caused by the angular constraints within the ring. For example, in **4B** (R = R′ = Ph, X = Y = S) the endocyclic Pt–C–P angle is 92° compared with 112° for the exocyclic angle.[13] We also note a large increase in ^2J(Pt–P) between **3** and **5**. Both of these complexes have two possible coupling pathways, the difference being in the amount of delocalization, again an orbital difference.

(ii) $[Pt\{CH(P(S)Ph_2)_2\text{-}C,S\}_2]$. Treatment of the cation $[Pt\{CH_2(P(S)Ph_2)_2\text{-}S,S\}_2]^{2+}$ with an excess of 1,8-bis(dimethylamino)naphthalene in $CDCl_3$ gives a product whose ^{31}P NMR spectrum indicates that both ligands have undergone deprotonation. Two resonances are observed; for one of these the shift (39.6 ppm, tetrahydrofuran) and platinum coupling (104 Hz) are similar to those for the noncoordinated P═S group in **4A** (R = R′ = Ph, X = Y = S), and the other resonance has a shift (64.7 ppm) and coupling constant (^2J(Pt–P) = 495 Hz) which are similar to those for P in the four-membered ring of **4A**. A structure with two C,S-bonded ligands is therefore indicated. There remains the possibility of cis/trans isomers of this structure. The trans isomer might be expected as a result of kinetic control similar to that observed above in synthesis of **4A**. In the present case the carbanion generated by deprotonation of the second ligand is expected to attack trans to the labilizing Pt–C bond formed during deprotonation of the first ligand. On the other hand, the cis isomer in which the σ-carbyl ligands are trans to low trans influence P═S groups may be expected to be more stable than the isomer in which the σ-carbyl groups are mutually trans. On balance we prefer the trans formulation because of the kinetic control established in the previous deprotonations and the probability that a cis complex, with P═S trans to labilizing σ-carbyl groups, would be fluxional at ambient temperatures.

(4) Dynamic Exchange of Coordinated and Noncoordinated P═S Groups. (i) Complex 4B (R = R′ = Ph, X = Y = S). As shown in Figure 1, the ^{31}P NMR spectrum of this complex at ambient temperature shows a triplet (J(P–P) = 5.6 Hz) for the

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PEt_3 phosphorus and only one doublet for the phosphorus atoms of the P=S groups. Thus, the expected difference between the coordinated and noncoordinated P=S groups is not observed. However, a low-temperature study in tetrahydrofuran-d_8 solution gives separate resonances for P_A and P_B below ca. −50 °C and optimally at ca. −80 °C. Since spin correlation between platinum and phosphorus in each of the ligands is maintained throughout, the process responsible for the changes in the spectra is clearly intramolecular and a fluxional process is indicated in which P_A and P_B become equivalent through interchange of free and coordinated P=S moieties. Detailed line shape analyses over the temperature range −80 to −20 °C, using the DNMR3 computer program,[31] give 40 kJ mol^{-1} for the free energy of activation. This relatively low value is not surprising in view of the long Pt–S bond (2.390 Å),[13] the labilizing trans effect of the PEt_3 ligand, and the proximity of the noncoordinated P=S group as seen in the solid-state structure.[13]

The low-temperature ^{31}P NMR parameters for P_A (δ 49.2 ppm, $^2J(Pt–P_A)$ = 505 Hz) and P_B (δ 41.3 ppm, $^2J(Pt–P_B)$ not resolved) should average to values close to those obtained at ambient temperature (δ 45.0 ppm, $^2J(Pt–P_A)$ = 291 Hz). The average value of the shift (45.2 ppm) is in satisfactory agreement, and the calculated value of $^2J(Pt–P_B)$ = 77 Hz is satisfactory in the sense the line width of our low-temperature spectra precluded resolution of ^{195}Pt satellites with this separation.

(ii) Complex 4A (R = R′ = Ph, X = Y = S). In view of the fluxional behavior of complexes **4B**, we examined the ^{31}P NMR spectra of complex **4A** (R = R′ = Ph, X = Y = S) from ambient temperature to +75 °C. As might be expected from our experience with interconversion of **4A** to **4B** during synthetic workup procedures, the spectra showed the growth of new lines assignable to complex **4B**. However, as the temperature is raised, it is clear from the gradual broadening of the resonances of **4A**, while those of **4B** remain sharp, that intramolecular exchange between coordinated and noncoordinated P=S groups also occurs in **4A** over this temperature range. The problems with conversion to **4B** precluded a proper line shape analysis, but the coalescence temperature for P_A and P_B is about 65 °C, corresponding to a free energy of activation of about 63 kJ mol^{-1}. The higher free energy of activation for this interchange in **4A** compared with **4B** is to be expected since the Pt–S bond in **4A** is subject to the relatively small trans effect of chloride whereas the Pt–S bond in **4B** is labilized by the trans PEt_3 ligand.

(iii) Complexes 7 (R = R′ = Ph). When X = Y = S or X = Y = O, these complexes show equivalence of the P_A and P_B resonances at ambient temperature and the coupling constants (X = Y = S, $^2J(Pt–P)$ = 243 Hz; X = Y = O, $^2J(Pt–P)$ = 157 Hz) have values which suggest that they are an average of values for noncoordinated P=X and P=X coordinated in a four-membered ring. Structures with C,X coordination as shown in Scheme I are therefore indicated. When X = S, Y = O, there is some slight evidence of fluxionality at ambient temperature, but the complex is definitely static at −30 °C. Structure **7** (X = S, Y = O), with coordinated sulfur and noncoordinated oxygen, is expected and is consistent with the results. The values of $^1J(Pt–P)$ = 2592–2673 Hz do not vary greatly with the nature of the X and Y atoms, indicating that the methyne carbon atom has a similar trans influence in all these compounds, and this behavior parallels that for $^1J(Pt–P_C)$ in compounds **4A**. The coupling constants $^1J(Pt–P_D)$ are closely similar for complexes **7** when X = Y = S, 3558 Hz, or X = S, Y = O, 3480 Hz, but when X = Y = O, 3917 Hz, there is a significant difference. This supports the structure assigned to **7** (X = S, Y = O), since the atom trans to P_D is then sulfur for both this complex and for **7** (X = Y = S) whereas P_D is trans to an oxygen atom in **7** (X = Y = O). Also consistent with this assignment is the similarity in chemical shift of the noncoordinated P=O groups of **4A** (X = S, Y = O), $\delta(P_B)$ 29.9 ppm, and **7** (X = S, Y = O), 26.6 ppm, as compared with the rather different shift of the noncoordinated P=S group of **4A**, $\delta(P_B)$ 42.2 ppm.

A low-temperature study of **7** (R = R′ = Ph, X = Y = S) showed a gradual improvement in spectrum resolution down to −60 °C, but there was no real change in the observed patterns. Lower temperatures gave loss of resolution but whether due to slower exchange or to viscosity and solubility problems was not clear. On the basis of trans-effect considerations alone, the exchange rate for **7** should be similar to that for **4B**, since both contain P=S groups trans to triethylphosphine. Thus, the fact that **7** is fast fluxional even at −60 °C indicates a further labilization due to the added cis-PEt_3 ligand. Our spectra suggest a coalescence temperature below −70 °C, and assuming a chemical shift difference of 1000 Hz (similar to **4B**) between P_A and P_B, this gives about 36 kJ mol^{-1} as the maximum free energy of activation.

Summary and Conclusions

This work establishes that, within the chemistry of a single metal (platinum), the bis(phosphine chalcogenides) and their derived anions exhibit at least five different coordination modes. The simplest is the expected X,Y coordination of the neutral ligands (**3** and **4**). The anionic ligands show a similar X,Y-coordination mode (**5**), but it is rarer and more difficult to prepare than a mode involving C,X coordination in a strained four-membered chelate ring (**4** and **7**). Single examples of two other coordination modes have also been observed: monodentate via carbon (**8**) and the complex C,S-briding mode observed in the dianion complex $[Pt_2(MeOcod)_2\{C(P(S)Ph_2)_2\}]$.[24]

Three major points of interest emerge from the preceding results and discussion:

(a) The stability of the neutral ligand complexes contrasts with the situation for acetylacetone (acac)[53] and its dithio analogue (SacSac).[54] The coordination chemistry of these latter ligands is essentially entirely that of the derived anions, and there appear to be no stable complexes of the neutral ligands. (b) There is a delicate and interesting balance between the isomeric forms (**4** and **5**) of the anion complexes, with the C,X-chelate form **4** being more common, at least in platinum chemistry. The formation of **4** or **5** and the isomerization from **4A** to **4B** show a complex and subtle dependence on the choice of synthetic method, the nature of the base employed in deprotonation methods, and the bulk of the substituents. Evidence to date indicates that this relative balance between isomers is also strongly dependent on the metal, since in corresponding work on rhodium and iridium complexes we have obtained only X,Y coordination (analogous to **5**) with no evidence for metal–carbon bonds.[24] This would correspond to the situation for acac complexes, since these are normally O,O-bonded except for a few complexes of the late platinum metals (Pd, Pt, Au, Hg).[53] In contrast to our C,S-coordinated bis(phosphine sulfide) complexes, there appear to be no known examples of C-bonded SacSac complexes. They are all S,S-coordinated.[54] Evidently, the methyne carbon of the present ligands is more nucleophilic than that in the acac or SacSac anions, a conclusion which is supported by the highly shielded methyne carbon resonance of **5** relative to the deshielding experienced by acac complexes on deprotonation. (c) All of the C,X-bonded complexes exhibit some degree of fluxional behavior. The process is an exchange of coordinated and noncoordinated P=X groups, essentially by a rotation about the Pt–C bond. This produces what is essentially a classic "bimolecular" substitution reaction within the coordination sphere of the platinum, except that the incoming ligand is actually part of one of the existing ligands. This appears to be a very unusual process, quite different from the more common simple exchange of coordination sites in a "dangling" ligand. It is also noteworthy that the process inverts the chirality at the coordinated carbon atom. This occurs by interchange of the roles of the two X/Y atoms, despite the fact that the actual motion is simply a rotation about the Pt–C bond.

The rates of these exchange processes increase in the sequence **4A** < **4B** < **7** with corresponding activation energies (R = R′ = Ph, X = Y = S): 63, 40, and <36 kJ mol^{-1}. These values reflect the effect of trans ligands in labilizing the Pt–S bond with the

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trans effect of triethylphosphine (**4B**) greater than that of chloride (**4A**) and possibly an additional cis effect for the extra triethylphosphine in **7**. Relative to the closely related $[PtCl(PEt_3)\{C(P(S)Ph_2)_3\text{-}S,S'\}]$,[29] where exchange of two P=S groups occurs by rotation about a Pt–S bond with an activation energy of 67 kJ mol^{-1}, the exchange in **4B** is facilitated by the proximity of the P=S group. Examination of the two solid-state structures[13,29] shows that the exchange process in the tris(phosphine sulfide) complex requires more structural reorganization.

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Stereochemical Nonrigidity in Heterobimetallic Complexes Containing the Bent Metallocene–Thiolate Fragment

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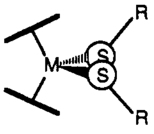
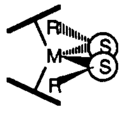
The physical properties and reactions of $Cp_2Ti(S\text{-}p\text{-}C_6H_4X)_2$ (**1**) and $Cp_2Ti(\mu\text{-}S\text{-}p\text{-}C_6H_4X)_2Mo(CO)_4$ (**2**) (X = Cl, H, CH_3, OCH_3) complexes as well as the mechanism of the Cp site equilibration process in bimetallic complexes were investigated. Cyclic voltammographs recorded in CH_2Cl_2 showed two reversible waves for Ti(IV) $\rightleftarrows$ Ti(III) and Mo(0) $\rightleftarrows$ Mo(I) processes in **2** and one reversible wave for Ti(IV) $\rightleftarrows$ Ti(III) in **1**. Positions of these waves varied uniformly with the Hammett σ parameter of the X substituent. Variable-temperature ^1H NMR studies provided values for $\Delta G^{\ddagger}$ of the Cp equilibration process which are ca. 30 kJ/mol smaller than $\Delta G^{\ddagger}$ for $Cp_2Ti(S\text{-}p\text{-}C_6H_4X)_2$ displacement from **2** by CO. This indicates that the fluxional process in **2** does not occur through a ligand dissociation process and argues for a mechanism of pyramidal inversion on sulfur. The X-ray structure for $Cp_2Ti(\mu\text{-}S\text{-}p\text{-}C_6H_4Cl)_2Mo(CO)_4$ (**2a**) is reported. Complex **2a** crystallizes in the monoclinic space group $P2_1/n$, with a = 12.396 (7) Å, b = 16.78 (2) Å, c = 12.838 (9) Å, β = 94.29 (5)°, Z = 4, and V = 2662 (3) Å^3. The Ti atom is in pseudotetrahedral coordination environment whereas the Mo is octahedrally coordinated. The S1–Ti–S2 and S1–Mo–S2 angles are obtuse (100.8 (1) and 97.6 (1)°, respectively) and Ti–S–Mo angles are acute (80.8 (1)°) in the planar $Ti\text{–}S_2\text{–}Mo$ ring, supportive of metal-metal interactions implied by spectroscopic and electrochemical data. The phenyl groups are in an anti arrangement with respect to the $Ti\text{–}S_2\text{–}Mo$ plane.

Introduction

The conformations of bent metallocene–thiolate complexes, $Cp_2M(SR)_2$, and their heterobimetallic analogues, $Cp_2M(\mu\text{-}SR)_2M'L_n$, are attractive subjects for structure/bonding arguments.[1] Solid-state and theoretical studies of the mononuclear metal complexes find the orientation of the SR ligands relative to the Cp rings to be coupled to the S–M–S angle.[1e,f,2,3] That is, maximization of sulfur π-donor interactions with the metal in d^0 and light metal d^1 complexes leads to wide (94–100°) S–M–S angles and, as well, orients the SR groups in the endo(anti) configuration. [Interestingly the endo(syn) configuration (with both R groups on the same side of the MS_2 plane) has never been observed for mononuclear complexes, although several examples of this configuration are known in binuclear compounds; vide infra.] Acute S–M–S angles (72–85°) suggestive of severe repulsion between the electrons in the metal-based $1a_1$ HOMO and the M–S bonded pair[3] are found in d^2 complexes and most heavier metal d^1 complexes. Additionally, the sulfur lone-pair density is directed away from the filled or half-filled metal frontier orbitals, generating the exo configuration, and, as well, projects sterically unhindered electron pair sites for further interaction with electrophiles.



Endo(anti)



Exo

In fact, both configurational types of the bent metallocene–thiolates may be used as synthons for the formation of heterobimetallic complexes. The known orientations of thiolates in the bimetallics, endo(syn), endo(anti), and exo, may be rationalized by minor rotations of the SR ligand about the M–S bond of the monomer precursor to align sulfur lone pairs for bonding to an electron-deficient $M'L_n$ fragment (Figure 1). This leads to a puckered MS_2M' core for the exo precursors and a planar MS_2M' core for the endo precursors. Solid-state structures of binuclear complexes derived from precursors of the endo(anti) configuration have been observed to either have sulfur-bound groups on the same side of the MS_2M' plane in the endo(syn) conformation or on opposite sides of the MS_2M' plane in an endo(anti) conformation. Although we have represented the endo(syn) monomer as precursor to the endo(syn) bimetallic in Figure 1, there is no requirement that rearrangement to this (evidently) less favored configuration occurs prior to binding to M′. These bimetallics are fluxional, and in fact, the structural interconversion between bimetallic endo(anti) and endo(syn) is a focus of this work.

Several of the heterobimetallics derived from d^0 bent metallocene–thiolates have been noted to be stereochemically nonrigid in solution as evidenced by variable-temperature ^1H NMR spectra. The nonequivalent Cp ligands in the syn conformation have two resonances in the limit of slow exchange whereas a single resonance

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