but we are unaware of previous X-ray studies that show this interaction.

Conclusion

Cyclodichlorophosphazene has been shown to be a viable reagent for scavenging NaC_5H_5 from mixtures containing organoyttrium complexes. The utility of this reagent depends on (1) the relative reaction rates for the cyclopentadienyl species to be removed versus the cyclopentadienyl complex to be isolated and (2) the relative solubility of the reaction products. The crystal structure of $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$ shows that the hydroxide ligand can exhibit normal bonding parameters in an organoyttrium complex and that unusual layered structures may be possible with hydroxide-containing organometallic compounds via hydrogen bonding.

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Registry No. **1**, 114199-08-5; $(C_5H_5)_2Y(OH)(THF)$, 114199-06-3; $(C_5H_5)_3Y(THF)$, 79533-63-4; $(C_5H_5)_2Y(t\text{-}C_4H_9)(THF)$, 80642-66-6; $C_6H_5C{\equiv}CC_6H_5$, 501-65-5; $(NPCl_2)_x$, 26085-02-9.

Supplementary Material Available: An alternative view of **1** plus tables of complete bond angles, thermal parameters, intermolecular contact distances, and hydrogen atom positions (5 pages); a table of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Multinuclear Magnetic Resonance Studies of the Reactions of Bidentate Ligands with $Pt(S_2P\{OEt\}_2)_2$. Crystal and Molecular Structure of $(apeS)Pt(S_2P\{OEt\}_2)_2$ (ApeS = $Ph_2AsCH_2CH_2P(S)Ph_2$)

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The interactions in dichloromethane solution of $Pt(S_2P\{OEt\}_2)_2$ with a number of potentially bidentate ligands have been studied by multinuclear (^{31}P, ^{77}Se, ^{195}Pt) magnetic resonance techniques. The ligands used (L-L′) were $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2AsCH_2CH_2PPh_2$ (ape), $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2P(E)Ph_2$ (E = S, Se to give dpmS, dpmSe), and $Ph_2AsCH_2CH_2P(E)Ph_2$ (apeS, apeSe). All the ligands except apeS and apeSe react with $Pt(S_2P\{OEt\}_2)_2$ in 1:1 proportions to give initially $[(L\text{-}L')Pt(S_2P\{OEt\}_2)]^+$ and free $[S_2P(OEt)_2]^-$, but a slower reaction gives $(L\text{-}L')Pt(S_2P\{O\}OEt)$ and $EtS_2P(OEt)_2$ by attack of the free anion on the coordinated dithiophosphate ligand. In 1:2 proportions these ligands give $[Pt(L\text{-}L')_2]^{2+}$ and free $[S_2P(OEt)_2]^-$, except for dpm which gives $[(\eta^1\text{-dpm})(\eta^2\text{-dpm})Pt(\eta^1\text{-}S_2P\{OEt\}_2)]^+$. The same products are obtained by reacting 1 mol of L-L′ with 1 mol of $[(L\text{-}L')Pt(S_2P\{OEt\}_2)]^+$, but the $(L\text{-}L')Pt(S_2P\{O\}OEt)$ compounds do not react with further L-L′ ligand. The ligands apeE react with $Pt(S_2P\{OEt\}_2)_2$ to give only $(\eta^1\text{-apeE})Pt(\eta^1\text{-}S_2P\{OEt\}_2)(\eta^2\text{-}S_2P\{OEt\}_2)$. The structures of all the complexes in solution were determined by multinuclear magnetic resonance studies and that of $(\eta^1\text{-apeS})Pt(\eta^1\text{-}S_2P\{OEt\}_2)(\eta^2\text{-}S_2P\{OEt\}_2)$ in the solid state was confirmed by a single-crystal X-ray diffraction study. Crystal data for $(apeS)Pt(S_2P\{OEt\}_2)_2$: $M_r = 1039.98$, monoclinic space group $P2_1$, $a = 10.107$ (1) Å, $b = 20.002$ (2) Å, $c = 11.278$ (2) Å, $\beta = 114.23$ (2)°, $Z = 2$, $\rho_{measd} = 1.65$ (1) g cm^{-3}, Mo Kα radiation, $R = 0.030$, $R_w = 0.034$ for 7695 independent reflections. The structure contains discrete molecules with the square-planar stereochemistry about platinum being defined by three sulfur atoms from one bidentate and one monodentate $[S_2P(OEt)_2]^-$ ligand and an arsenic atom from the monodentate apeS ligand.

Introduction

There have been extensive studies by Stephenson[1-5] and Fackler[6,7] and their co-workers on the interactions of monodentate group 15 ligands with platinum(II) bis(dithiolate) compounds $Pt(S\text{-}S)_2$ (S-S = $[S_2CNR_2]^-$, $[S_2COR]^-$, $[S_2P(OR)_2]^-$, $[S_2PR_2]^-$). In general, 1 mol of tertiary phosphine or phosphite reacts to generate the species $(PR_3)Pt(\eta^1\text{-}S\text{-}S)(\eta^2\text{-}S\text{-}S)$, which often, at room temperature, display exchange on the NMR time scale between the monodentate and bidentate dithiolate ligands. Reaction of a second mole of phosphine or phosphite causes displacement of the η^1-dithiolate ligand to give $[(PR_3)_2Pt(\eta^2\text{-}S\text{-}S)]^+$. In the *O*,*O′*-dialkyl dithiophosphate (and xanthate) systems these products must be isolated quickly; otherwise, interaction between the free dithiolate anion and the remaining coordinated dithiolate occurs to give $RS_2P(OR)_2$ and coordinated $[S_2P(O)OR]^{2-}$. These reactions have been studied in solution by using proton, phosphorus-31, and platinum-195 NMR spectroscopies,[1-7] and X-ray crystallographic studies on some of the isolated products have confirmed the stereochemistries of several of these compounds.[1,6,7]

In this paper the results of reactions between $Pt(S_2P\{OEt\}_2)_2$ and several potentially bidentate ligands L-L′ are described where L-L′ = $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2AsCH_2CH_2PPh_2$ (ape), $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2P(E)Ph_2$ (E = S, Se to give dpmS, dpmSe), and $Ph_2AsCH_2CH_2P(E)Ph_2$ (apeS, apeSe). The products of the reactions have been characterized by NMR (^{31}P, ^{77}Se, ^{195}Pt) spectroscopic studies and a crystal structure determination on $(apeS)Pt(S_2P\{OEt\}_2)_2$.

Experimental Section

Materials. $Pt(S_2P\{OEt\}_2)_2$ was prepared by the interaction of aqueous solutions of $K_2[PtCl_4]$ and $K[S_2P(OEt)_2]$.[8] The precipitate was filtered

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Table I. Crystal Structure Data for (apeS)Pt($S_2P\{OEt\}_2$)$_2$

formula	$C_{34}H_{44}AsO_4P_3PtS_5$
formula weight	1039.98
cryst system	monoclinic
space group	$P2_1$ (C_2^2; No. 4)
a, Å	10.107 (1)
b, Å	20.002 (2)
c, Å	11.278 (2)
β, deg	114.23 (2)
V, Å^3	2079 (1)
Z	2
ρ(calcd), g cm^{-3}	1.66
ρ(measd), g cm^{-3}	1.65 (1)
cryst dimens: dist from centroid, mm	±(010), 0.036; ±(100), 0.150; ±(001), 0.093
temp, K	295
radiation (λ, Å)	Mo Kα, graphite monochromator (0.71069)
F(000)	1032
μ, mm^{-1}	4.55
transmission factors	max 0.7249, min 0.4659
2θ limits, deg	$2 \leq 2\theta \leq 55$
no. of reflcns collcd	12921
no. of unique reflcns	9501
R_{amal}	0.017
no. of unique reflcns used ($I > 2\sigma(I)$)	7695
R	0.030
R_w	0.034

and dried in air at the pump. The ligands dpe, ape, and dpm (Strem) were used as received. The ligands dmpE and apeE were prepared as described previously.[9] DpmSe and apeSe were prepared by reaction of equimolar amounts of dpm or ape and elemental red selenium in tetrahydrofuran solution. The solvent was removed under vacuum and the white product recrystallized from CH_2Cl_2/n-hexane. DpmS was prepared by the slow addition of sulfur (in slight excess) to a toluene solution of dpm at 0 °C. Addition of n-hexane followed by cooling to −15 °C resulted in the precipitation of the desired product. ApeS was prepared by the reaction of equimolar quantities of ape and sulfur in CH_2Cl_2 at ambient temperatures. The solvent was removed under vacuum and the white product recrystallized from CH_2Cl_2/n-hexane.

NMR Spectra. NMR spectra were obtained by using a JEOL FX 100 spectrometer, phosphorus-31 at 40.32 MHz, selenium-77 at 18.98 MHz, and platinum-195 at 21.32 MHz. All spectra were acquired in the presence of $Cr(acac)_3$ by using 18-μs pulses and 200-ms pulse delays. External references used were 85% H_3PO_4, 1 M H_2SeO_3 in water, and 1 M H_2PtCl_6 in concentrated HCl. High-frequency positive convention is used for chemical shifts.

Crystal Structure Determination of (apeS)Pt($S_2P\{OEt\}_2$)$_2$. Data Collection. Yellow platelike crystals of (apeS)Pt($S_2P\{OEt\}_2$)$_2$ were grown by the slow evaporation of a dichloromethane/hexane solution of the compound. Preliminary oscillation and Weissenberg photographs of the crystals showed that they were monoclinic, possessing space group $P2_1$ or $P2_1/m$; the noncentrosymmetric space group $P2_1$ proved to be the correct space group. Integrated intensity data were collected at room temperature with Mo Kα radiation (graphite monochromator) by using an Enraf-Nonius CAD-4F diffractometer and the $\omega/2\theta$ scan mode. Accurate values of the unit cell parameters and the crystal orientation matrix were determined from a least-squares treatment of the angular settings of 25 carefully centered reflections. Crystal data together with details of data collection are given in Table I. Three strong reflections were used as orientation controls and no realignment of the crystal was necessary during data collection. There was no significant variation of the intensity values for three strong reflections recorded every 3600 s of X-ray exposure time. The intensity data, which included a complete set of Friedel pairs in the angular range measured, were corrected for Lorentz, polarization, and absorption effects,[10,11] but no correction was made for extinction; absorption corrections were numerically evaluated by Gaussian integration to a precision of 0.5%.

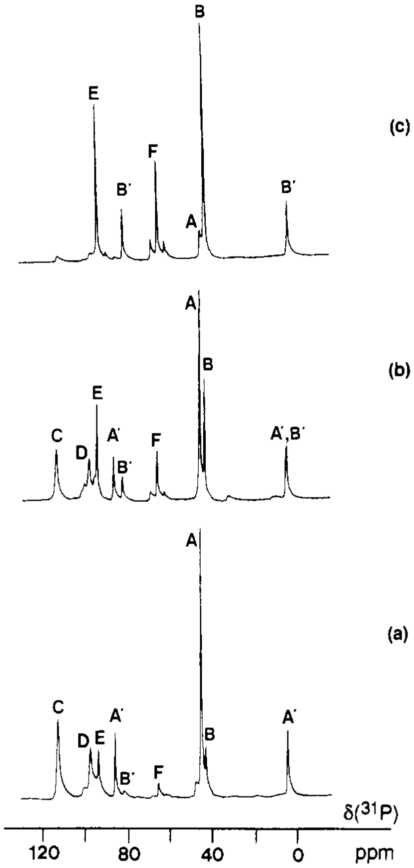

Figure 1. Phosphorus-31 NMR spectra of a dichloromethane solution containing equimolar quantities of Pt($S_2P\{OEt\}_2$)$_2$ and dpe: (a) soon after mixing; (b) 3 h after mixing; (c) 17 h after mixing.

Attempts to amalgamate the data in terms of the centrosymmetric space group $P2_1/m$ led to the relatively high R_{amal} value of 0.054. This, together with inconsistencies noted between the intensity values of 23 Friedel pairs, supported the initial assignment of $P2_1$ as the correct space group, which had been based on the number of formula units per unit cell and the expected asymmetry of the molecule. The amalgamation of equivalent reflections for the space group $P2_1$ yielded the value of R_{amal} of 0.017 with an absence of any inconsistencies between equivalent reflections.

Structure Determination and Refinement. The coordinates of Pt, As, and three S atoms were obtained by using the automatic Patterson interpretation routine of the SHELXS-86 system.[12] The remaining non-hydrogen atoms were located on subsequent difference maps. The y coordinates of all atoms were referred to that of the Pt atom, which was fixed at 0.0 throughout the structure determination. The structure was refined by using the full-matrix least-squares procedure of the SHELX-76 system,[10] which minimizes the function $\sum w\Delta^2$ where $\Delta = ||F_o| - |F_c||$ and w is is the weight assigned to each reflection; unit weights were used throughout the refinement. Anisotropic thermal parameters were assigned to all the non-hydrogen atoms; $R = 0.044$. At this stage the methylene and phenyl hydrogen atoms were clearly discernible in the difference maps, and all hydrogen atoms were included in the model at their calculated positions. Refinement was continued by employing a common isotropic temperature factor for all the methylene hydrogen atoms, and the methyl and phenyl hydrogen atoms were similarly treated. At convergence the maximum shift/esd for the non-hydrogen parameters was 0.01. The maximum residual electron density was 1.04 e/Å^3, 1.05 Å from the Pt atom.

An analysis of the variance showed no unusual features, indicating that the use of unit weights was appropriate. Final values of R and R_w are given in Table I.

In order to establish the absolute configuration of the structure, an identical refinement procedure was carried out by using the inverse set of coordinates. This refinement converged with R and R_w values of 0.069 and 0.078, respectively, which clearly demonstrates that the correct configuration had resulted from the first refinement. A detailed comparison of the $|F_o|$ values of 25 Friedel pairs with the corresponding $|F_c|$ values calculated for both orientations supported, in every case, the assignment. These 25 paris were selected on the basis of the significant

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Table II. ^{31}P and ^{195}Pt NMR Data for the Dpe and Ape Derivatives of $Pt(S_2P\{OEt\}_2)_2$ in Dichloromethane Solution[a]

complex	$\delta(^{31}P)$	$\delta(^{195}Pt)$	$J_{Pt,P}$, Hz	temp, °C
$[(dpe)Pt(S_2P\{OEt\}_2)]^+$	44.0 (s)	−5010 (td)	$^1J_{Pt,P} = 3355$	25
	97.6 (s)[b]		$^2J_{Pt,P} = 275$	
$(dpe)Pt(S_2P\{O\}OEt)$	41.8 (s)	−5000 (td)	$^1J_{Pt,P} = 3200$	25
	64.8 (s)[b]		$^2J_{Pt,P} = 265$	
$[Pt(dpe)_2]^{2+}$	47.6 (s)	−5285 (q)	$^1J_{Pt,P} = 2320$	25
$[(ape)Pt(S_2P\{OEt\}_2)]^+$	48.0 (s)	−5115 (dd)	$^1J_{Pt,P} = 3315$	0
	99.2 (s)[b]		$^2J_{Pt,P} = 310$	
$(ape)Pt(S_2P\{O\}OEt)$	46.1 (s)	−5110 (dd)	$^1J_{Pt,P} = 3200$	0
	68.0 (s)[b]		$^2J_{Pt,P} = 300$	
cis-$[Pt(ape)_2]^{2+}$	53.1 (s)	−5485 (t)	$^1J_{Pt,P} = 2700$	−20
trans-$[Pt(ape)_2]^{2+}$	50.0 (s)	−5480 (t)	$^1J_{Pt,P} = 2255$	−20

[a] s = singlet, dd = doublet of doublets, td = triplet of doublets, t = triplet, and q = quintet. [b] Resonance due to the dithiolate ligand.

difference between the $|F_o|$ values and the range of their *hkl* values.

Results and Discussion

Reactions with Dpe. Figure 1 shows phosphorus-31 NMR spectra at different times after mixing equimolar quantities of $Pt(S_2P\{OEt\}_2)_2$ and dpe in dichloromethane at 25 °C. Figure 1a is the spectrum recorded a few minutes after mixing, and there are no signals due to the starting materials. The dominant signal A has platinum-195 satellites A′, and signal C at δ 113 is due to free $[S_2P(OEt)_2]^-$.[13] Resonance D also displays platinum-195 satellites, although obscured on one side, with a coupling constant of 275 Hz, which is typical for dithiophosphates chelated to platinum.[5,7] There are other weak peaks, B, E, and F, observable in the spectrum. The corresponding platinum-195 NMR spectrum is a triplet of doublets with coupling constants agreeing with those derived from the phosphorus-31 NMR spectrum. This confirms that dpe is chelated, and only one dithiolate ligand remains coordinated to platinum. Figure 1b is the phosphorus-31 NMR spectrum of the same mixture some 3 h later. The peaks labeled B (with satellites B′), E, and F have grown significantly while those labeled A, C, and D have decreased in intensity. Figure 1c is the spectrum after 17 h and shows that these changes have proceeded almost to completion. The corresponding platinum-195 NMR spectrum is a triplet of doublets very similar in appearance and chemical shift to that of the initial product, but with coupling constants corresponding to those derived from resonances B and F in Figure 1c. Once again, this spectrum confirms that dpe is chelated and one dithiolate type of ligand is coordinated to platinum in the compound giving rise to these spectra. The resonance labeled E in Figure 1c is due to $EtS_2P(OEt)_2$, and it is reasonable to interpret these spectra by reactions analogous to those with monodentate phosphines.[2] Thus, the spectrum in Figure 1a is predominantly due to $[(dpe)Pt(S_2P\{OEt\}_2)]^+$, which is the product of the fast reaction between $Pt(S_2P\{OEt\}_2)_2$ and dpe, and that in Figure 1c essentially is due to $(dpe)Pt(S_2P\{O\}OEt)$ and $EtS_2P(OEt)_2$, which are the products of the relatively slow nucleophilic attack of the free dithiolate anion on the remaining coordinated dithiolate. All NMR data for this system are given in Table II.

The phosphorus-31 NMR spectrum of a dichloromethane solution of $Pt(S_2P\{OEt\}_2)_2$ and dpe in 1:2 molar ratio at 25 °C shows the presence of only one species containing platinum and a singlet resonance at δ 113 due to free $[S_2P(OEt)_2]^-$. The integrated intensities of the main peak together with its platinum satellites and the free dithiolate anion are 2:1. This suggests that two molecules of dpe have completely displaced all the dithiolates to give $[Pt(dpe)_2]^{2+}$. This is fully confirmed by the platinum-195 NMR spectrum, which is a quintet. The reaction is therefore summarized in the simple equation

$$Pt(S_2P\{OEt\}_2)_2 + 2dpe \rightarrow [Pt(dpe)_2]^{2+} + 2[S_2P(OEt)_2]^- \quad (1)$$

The identity of $[Pt(dpe)_2]^{2+}$ has been confirmed by comparison of the NMR spectra with those of an authentic sample.[14]

If an additional mole of dpe is added to an aged (3 h) solution containing both $[(dpe)Pt(S_2P\{OEt\}_2)]^+$ and $(dpe)Pt(S_2P\{O\}OEt)$ (corresponding to the mixture in Figure 1b), it emerges that the latter does not react with further dpe at room temperature. The phosphorus-31 NMR spectrum at 25 °C of such a solution shows large resonances due to $[Pt(dpe)_2]^{2+}$ and $(dpe)Pt(S_2P\{O\}OEt)$. There is a resonance at δ 113 due to free dithiolate anion and another at δ 93.9 due to $EtS_2P(OEt)_2$. Significantly, a resonance due to free dpe is observed at δ −13.4. The corresponding platinum-195 NMR spectrum confirms that only $[(dpe)Pt(S_2P\{OEt\}_2)]^+$ reacts with further dpe since, in addition to the quintet due to $[Pt(dpe)_2]^{2+}$, the triplet of doublets due to $(dpe)Pt(S_2P\{O\}OEt)$ is clearly observed. Thus, the compound $[(dpe)Pt(S_2P\{OEt\}_2)]^+$ is a reactive species that interacts with both $[S_2P(OEt)_2]^-$ and dpe, while the compound $(dpe)Pt(S_2P\{O\}OEt)$ does not react with dpe up to 40 °C in dichloromethane.

Reactions with Ape. The reactions between $Pt(S_2P\{OEt\}_2)_2$ and ape show considerable parallels with the corresponding dpe reactions, although there are some interesting differences. The phosphorus-31 NMR spectrum at 25 °C of a freshly prepared dichloromethane solution of $Pt(S_2P\{OEt\}_2)_2$ and ape in equimolar proportions is dominated by a large resonance at δ 48 with platinum satellites, but the other resonances in the spectrum are broad. However, on cooling of the solution to 0 °C, these signals sharpen and may then be identified as being due to free dithiolate anion (δ 113) and coordinated dithiolate at δ 99.2. The corresponding platinum-195 NMR spectrum is a doublet of doublets and confirms that a chelating ape ligand has replaced one dithiolate ligand to give $[(ape)Pt(S_2P\{OEt\}_2)]^+$ and $[S_2P(OEt)_2]^-$. The broadening at room temperature of the signals due to free and coordinated dithiolate ligands indicates that exchange is occurring, although at a relatively slow rate on the NMR time scale.

When the solution is allowed to stand at room temperature, the phosphorus-31 NMR spectrum shows changes entirely analogous to the corresponding dpe system, and the platinum-195 NMR spectrum at 25 °C after 20 h confirms that nucleophilic attack on the coordinated dithiolate by the free dithiolate anion occurs to give $(ape)Pt(S_2P\{O\}OEt)$. NMR data for this system are given in Table II.

The phosphorus-31 NMR spectrum of a dichloromethane solution containing $Pt(S_2P\{OEt\}_2)_2$ and ape in 1:2 molar proportions shows that the system is labile at room temperature. However, on cooling to −20 °C, the signals become sharp revealing a large resonance due to free dithiolate anion and two signals at δ 50 and 53.1, each having platinum satellites. The corresponding platinum-195 NMR spectrum at −20 °C shows two triplets of almost identical chemical shifts so that the central resonances overlap. Their relative intensities, as judged by the relative heights of the outer signals, are approximately the same as the two phosphorus signals mentioned above. Since the platinum signals are triplets, two ape ligands must be coordinated to each platinum so the two species must be *cis*- and *trans*-$[Pt(ape)_2]^{2+}$. It is proposed that, by analogy with many other cis and trans pairs of platinum(II) complexes containing two phosphorus ligands,[15,16] the compound with the smaller coupling constant is assigned to the trans isomer (minor component) and the compound with the larger coupling constant is assigned to the cis isomer (major component). These isomers of $[Pt(ape)_2]^{2+}$ have recently been prepared[14] by the interaction of $PtCl_2(cod)$ (cod = 1,4-cyclooctadiene) and ape, and the reported phosphorus-31 NMR spectra agree well with those given here. However, when prepared in this manner, the cation is not labile at room temperature, so the enhanced lability in the present case is clearly due to attack on platinum by the free $[S_2P(OEt)_2]^-$ ion. This was confirmed by adding $[S_2P(OEt)_2]^-$ to a solution of $[Pt(ape)_2]Cl_2$.

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Table III. ^{31}P and ^{195}Pt NMR Data for the Dpm Derivatives of $Pt(S_2P\{OEt\}_2)_2$ in Dichloromethane Solution[a]

complex	$\delta(^{31}P)$	$\delta(^{195}Pt)$	$J_{Pt,P}$, Hz	temp, °C
$[(dpm)Pt(S_2P\{OEt\}_2)_2]^+$	−59.6 (s)	−4435 (td)	$^1J_{Pt,P} = 2855$	−20
	101.4 (s)[b]		$^2J_{Pt,P} = 254$	
$(dpm)Pt(S_2P\{O\}OEt)$	−58.3 (s)	−4400 (td)	$^1J_{Pt,P} = 2735$	−20
	68.9 (s)[b]		$^2J_{Pt,P} = 264$	
$[(\eta^1\text{-dpm})(\eta^2\text{-dpm})Pt(S_2P\{OEt\}_2)]^+$	−45.5 (m)	−4440 (ddd)	$^1J_{Pt,P} = 2765$	−80
	−32.1 (m)		$^1J_{Pt,P} = 2580$	
	−27.3 (s)		$^1J_{Pt,P} = 2025$	
	−1.4 (m)			
	9.1 (m)			
	92.9 (s)[b]			

[a] s = singlet, ddd = doublet of doublet of doublets, td = triplet of doublets, and m = multiplet. [b] Resonance due to dithiolate ligand.

When 1 mol of ape is added to a partially aged (approximately 1 h) solution initially containing $Pt(S_2P\{OEt\}_2)_2$ and ape in 1:1 molar proportions, it is found that only $[(ape)Pt(S_2P\{OEt\}_2)]^+$ reacts with further ape to give $[Pt(ape)_2]^{2+}$, while the compound $(ape)Pt(S_2P\{O\}OEt)$ does not react with the ligand, similar to the situation described previously for the dpe system.

Reactions with Dpm. The phosphorus-31 NMR spectrum of a solution of $Pt(S_2P\{OEt\}_2)_2$ and dpm in 1:1 stoichiometric proportions soon after mixing at 25 °C consists of a strong singlet at δ −59.6 with platinum-195 satellites and a number of broad resonances at higher frequencies. On cooling to −20 °C, these other signals sharpen and may then be identified as being due to free and chelated $[S_2P(OEt)_2]^-$. A weak signal at δ −58.3 with platinum satellites is also apparent at the lower temperature. The corresponding platinum-195 NMR spectrum shows two triplets of doublets. These spectra are similar to those in the dpe system and are assigned to $[(dpm)Pt(S_2P\{OEt\}_2]^+$ and $(dpm)Pt(S_2P\{O\}OEt)$. NMR data for this system are given in Table III.

A solution of $Pt(S_2P\{OEt\}_2)_2$ and dpm in 1:2 stoichiometric proportions at 25 °C produces a phosphorus-31 NMR spectrum that consists mainly of a broad singlet at about δ 105 and a very broad resonance at about δ −30. On cooling to −80 °C, a complicated spectrum is obtained as shown in Figure 2a, and the rather broad signals at δ 111 and 93 due to free and monodentate $[S_2P(OEt)_2]^-$ show that exchange between them is still occurring, albeit slowly on the NMR time scale. The remaining resonances are also rather broad, but platinum-195 satellites can be discerned. The structure of the complex in solution is not obvious from this spectrum, but the corresponding platinum-195 NMR spectrum shown in Figure 2b is more informative. The eight lines comprise a doublet of doublet of doublets due to coupling of platinum to three magnetically nonequivalent phosphorus atoms. The values of the coupling constants (2765, 2580, and 2025 Hz) indicate that all three phosphorus atoms are directly bonded to the metal, and both spectra are consistent with the formation of $[(\eta^1\text{-dpm})(\eta^2\text{-dpm})Pt(\eta^1\text{-}S_2P\{OEt\}_2)]^+$ and free $[S_2P(OEt)_2]^-$. Coupling of platinum to the phosphorus in the monodentate dithiophosphate ligand is not observed in either spectrum due to the continuing slow-exchange process mentioned above, which broadens the signals. Thus, dpm does not form the known $[Pt(dpm)_2]^{2+}$ cation, analogous to the products obtained with dpe and ape, under these conditions. Presumably, this is associated with the lower stability of the four-membered chelate ring formed by this ligand compared with the five-membered ring formed by the other ligands. Another example of this type of behavior has recently been reported.[17] $[(\eta^2\text{-dpm})Pt(L)Cl]^+$ (L = PBu_3, $PMePh_2$) reacts with further L to give $[(\eta^1\text{-dpm})PtL_2Cl]^+$, but the corresponding reaction does not occur with $[(\eta^2\text{-dpe})Pt(L)Cl]^+$.

Reactions with DpmSe and DpmS. The phosphorus-31 NMR spectrum of a dichloromethane solution containing equimolar quantities of $Pt(S_2P\{OEt\}_2)_2$ and dpmSe at 25 °C soon after mixing shows a large resonance at δ 113 assigned to free $[S_2P(OEt)_2]^-$ and one at δ 96.3, with platinum-195 satellites ($^2J_{Pt,P}$ = 340 Hz), which is typical for chelated $[S_2P(OEt)_2]^-$. Two doublets appear at δ 40.5 and 20.5 ($^2J_{P,P}$ = 40 Hz). The one at lower frequency displays platinum satellites, while the doublet at higher frequency has selenium-77 satellites with a coupling constant $^1J_{Se,P}$ = 510 Hz. This is much reduced from that of the free ligand, strongly suggesting coordination of the selenium to platinum, but platinum-195 satellites for this doublet are not observed. There are in addition to these features a small resonance at δ 93.9 assigned to $EtS_2P(OEt)_2$ and multiplets near δ 33.5 and 24.4 that, as will be shown later, are due to a small proportion of a complex containing two dpmSe ligands. The spectrum is consistent with the formation of $[(dpmSe)Pt(S_2P\{OEt\}_2)]^+$ containing both chelated dpmSe and dithiolate. The phosphorus-31 NMR spectrum after approximately 17 h is consistent with the formation of $EtS_2P(OEt)_2$ and $(dpmSe)Pt(S_2P\{O\}OEt)$.

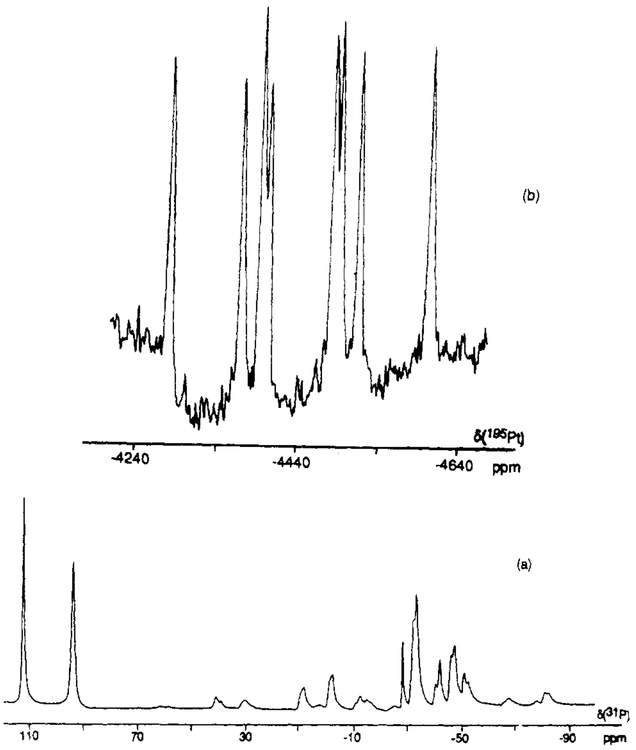

Figure 2. NMR spectra at −80 °C of a dichloromethane solution containing equimolar quantities of $Pt(S_2P\{OEt\}_2)_2$ and dpm: (a) ^{31}P; (b) ^{195}Pt.

The formation of $[(dpmSe)Pt(S_2P\{OEt\}_2)]^+$ is confirmed by the platinum-195 NMR spectrum, which appears as a doublet of doublets of doublets due to coupling with three nonequivalent phosphorus atoms with coupling constants $^1J_{Pt,P}$ = 3525 Hz, $^2J_{Pt,P}$ = 340 Hz (dithiolate), and $^2J_{Pt,P}$ = 68 Hz. This last small coupling involves the P=Se phosphorus of dpmSe, but platinum satellites are not observable in the phosphorus-31 NMR spectrum due to the comparative broadness of the phosphorus resonance and the small coupling constant. Selenium-77 satellites were not observed in the platinum-195 spectrum because of the low signal to noise ratio. The platinum-195 NMR spectrum of the 17-h-old solution of $Pt(S_2P\{OEt\}_2)_2$ and dpmSe shows a new doublet of doublets of doublets, due to $(dpmSe)Pt(S_2P\{O\}OEt)$, which is obvious although it is partly obscured by the resonances due to $[(dpmSe)Pt(S_2P\{OEt\}_2)]^+$.

The selenium-77 NMR spectrum of the 1:1 stoichiometric solution of $Pt(S_2P\{OEt\}_2)_2$ and dpmSe consists of two doublets. One at δ −1300 has platinum-195 satellites ($^1J_{Pt,Se}$ = 180 Hz). This selenium-77 resonance is approximately 300 ppm to higher frequency compared to that of free dpmSe, confirming the coordination of selenium in this complex. The second, less intense, doublet at δ −1350 with $^1J_{Se,P}$ = 530 Hz is assigned to

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[17] Anderson, G. K.; Lumetta, G. J. *Inorg. Chem.* **1987**, *26*, 1518.

Table IV. NMR Data for the DpmSe and DpmS Derivatives of $Pt(S_2P\{OEt\}_2)_2$ in Dichloromethane Solution[a]

complex	$\delta(^{31}P)$	$\delta(^{77}Se)$	$\delta(^{195}Pt)$	J, Hz	temp, °C
$[(dpmSe)Pt(S_2P\{OEt\}_2)]^+$	20.5 (d)[b] 40.5 (d)[c] 96.3 (s)[d]	−1300 (d)	−4680 (ddd)	$^1J_{Pt,P} = 3525$ $^2J_{Pt,P} = 68$ $^2J_{Pt,P} = 340$ $^1J_{Pt,Se} = 180$ $^1J_{Se,P} = 510$ $^2J_{P,P} = 40$	25
$(dpmSe)Pt(S_2P\{O\}OEt)$	18.3 (d)[b] 40.3 (d)[c] 63.0 (s)[d]	−1350 (d)	−4660 (ddd)	$^1J_{Pt,P} = 3455$ $^2J_{Pt,P} = 78$ $^2J_{Pt,P} = 310$ $^1J_{Se,P} = 530$ $^2J_{P,P} = 51$	25
$[(dpmS)Pt(S_2P\{OEt\}_2)]^+$	17.7 (d)[b] 60.0 (d)[c] 95.8 (s)[d]		−4550 (ddd)	$^1J_{Pt,P} = 3505$ $^2J_{Pt,P} = 59$ $^2J_{Pt,P} = 352$ $^2J_{P,P} = 34$	25
$(dpmS)Pt(S_2P\{O\}OEt)$	15.1 (d)[b] 59.5 (d)[c] 62.6 (s)[d]		−4530 (ddd)	$^1J_{Pt,P} = 3415$ $^2J_{Pt,P} = 51$ $^2J_{Pt,P} = 308$ $^2J_{P,P} = 42$	25
cis-$[Pt(dpmSe)_2]^{2+}$	22.5 (d)[b] 33.5 (d)[c]	−1327 (ddd)	−4880 (tt)	$^1J_{Pt,P} = 3250$ $^2J_{Pt,P} = 54$ $^1J_{Pt,Se} = 270$ $^1J_{Se,P} = 508$ $^2J_{Se,P} = 76$ $^2J_{Se,P} = 51$ $^2J_{P,P} = 29$	−40
trans-$[Pt(dpmSe)_2]^{2+}$	24.4 (t)[b] 39.3 (t)[c]	−1225 (d)	−5015 (tt)	$^1J_{Pt,P} = 2360$ $^2J_{Pt,P} = 88$ $^1J_{Pt,Se} = 260$ $^1J_{Se,P} = 498$ $^2J_{P,P} = 43$	−40
cis-$[Pt(dpmS)_2]^{2+}$	17.0 (d)[b] 47.1 (d)[c]		−4700 (t)	$^1J_{Pt,P} = 3255$ $^2J_{P,P} = 22$	25
trans-$[Pt(dpmS)_2]^{2+}$	24.1 (t)[b] 61.3 (t)[c]		−4775 (tt)	$^1J_{Pt,P} = 2270$ $^3J_{P,P} = 44$ $^2J_{Pt,P} = 80$	25

[a] s = singlet, ddd = doublet of doublet of doublets, t = triplet, and tt = triplet of triplets. [b] Resonance due to P(III). [c] Resonance due to P=Se. [d] Resonance due to the dithiolate ligand.

$(dpmSe)Pt(S_2P\{O\}OEt)$. This species is apparent since the spectral acquisition time was approximately 15 h, which allowed time for its formation. NMR data for this system are given in Table IV.

Figure 3a is the phosphorus-31 NMR spectrum of a solution containing $Pt(S_2P\{OEt\}_2)_2$ and 2 mol of dpmSe. The spectrum does not vary with temperature down to −60 °C so the singlet at δ 113 may be assigned to the free dithiolate anion rather than an exchange average signal between free and coordinated dithiolate. The remainder of the spectrum is composed of a series of multiplets between δ 39 and 22 together with their satellites. The doublet at δ 22.5 has platinum-195 satellites, while the doublet at δ 33.5 has no discernible satellites. The remaining signals are two triplets, with the one at lower frequency (partially obscured by the doublet at δ 22.5) showing platinum-195 satellites.

Figure 3b shows the platinum-195 NMR spectrum of the same solution recorded at −40 °C. Although there was no apparent change in the phosphorus-31 NMR spectrum as a function of temperature, the platinum-195 NMR spectrum failed to show resolution of the fine couplings at room temperature. The spectrum consists of two triplets of triplets, and no selenium-77 satellites are observed. The spectrum shows that two species are formed, each containing two chelated dpmSe molecules, and no coordinated dithiolate remains. Thus, the only possibilities, on the basis of the platinum-195 NMR spectrum, are cis and trans isomers of $[Pt(dpmSe)_2]^{2+}$. On the basis of the magnitudes of the $^1J_{Pt,P}$ couplings, the more intense triplet is assigned to the cis isomer.

Unambiguous confirmation of this assignment is provided by the selenium-77 NMR spectrum of the solution at −40 °C shown in Figure 3c. The spectrum shows two resonances, a doublet of doublet of doublets at δ −1325 and a broad doublet at δ −1225, and their relative intensities are approximately the same as for the two platinum signals in Figure 3b. Each signal has platinum satellites with coupling constants of 270 and 260 Hz, respectively, and these small coupling constants explain why the weak selenium-77 satellites were not observed in the platinum-195 NMR spectrum. The more intense multiplet at δ −1325 confirms that *cis*-$[Pt(dpmSe)_2]^{2+}$ is the more abundant isomer since it would be expected to produce a complex multiplet due to coupling of each selenium atom with three magnetically nonequivalent phosphorus atoms.

The fact that the trans isomer displays no fine structure in the doublet in its selenium-77 NMR spectrum is probably due to the small magnitude of cis $^2J_{Se,P}$. Pan and Fackler[18] noted cis $^2J_{Se,P}$ to be less than 10 Hz in compounds of the type $M(Se_2CNEt_2)PPh_3X$ (M = Pt, Pd; X = CH_3, Cl). Under the spectral acquisition conditions of Figure 3c, this small coupling is not resolved, leading to a broad doublet. Very recently, Peringer[19] has reported briefly on the phosphorus-31 and platinum-195 NMR spectra of *cis*- and *trans*-$[Pt(dpmSe)_2]^{2+}$ in a complex system involving selenium insertion into $[Pt(dpm)_2]^{2+}$. The NMR parameters reported here for these compounds agree well with his values.

Previous values of $^1J_{Pt,Se}$ have been reported by Pan and Fackler.[20] In $Pt(Se_2CNR_2)_2$ they were 100–115 Hz, but in $Pt(Se_2CNR_2)(PR_3)X$ (X = Cl, Br, I) the values were typically 116 and 289 Hz for selenium trans and cis to phosphorus, respectively. The values reported here are within these limits.

DpmS reacts with $Pt(S_2P\{OEt\}_2)_2$ in a similar manner, and NMR data are also given in Table IV.

Reactions with ApeSe and ApeS. The reaction between $Pt(S_2P\{OEt\}_2)_2$ and apeSe is quite unlike any of the systems described so far, and all NMR data are given in Table V. The phospho-

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[18] Pan, W.-H.; Fackler, J. P., Jr.; Chen, H. W. *Inorg. Chem.* **1981**, *20*, 856.

[19] Peringer, P.; Schwald, J. *J. Chem. Soc., Chem.* Commun. **1986**, *22*, 1625.

[20] Pan, W.-H.; Fackler, J. P., Jr *J. Am. Chem. Soc.* **1978**, *100*, 5783.

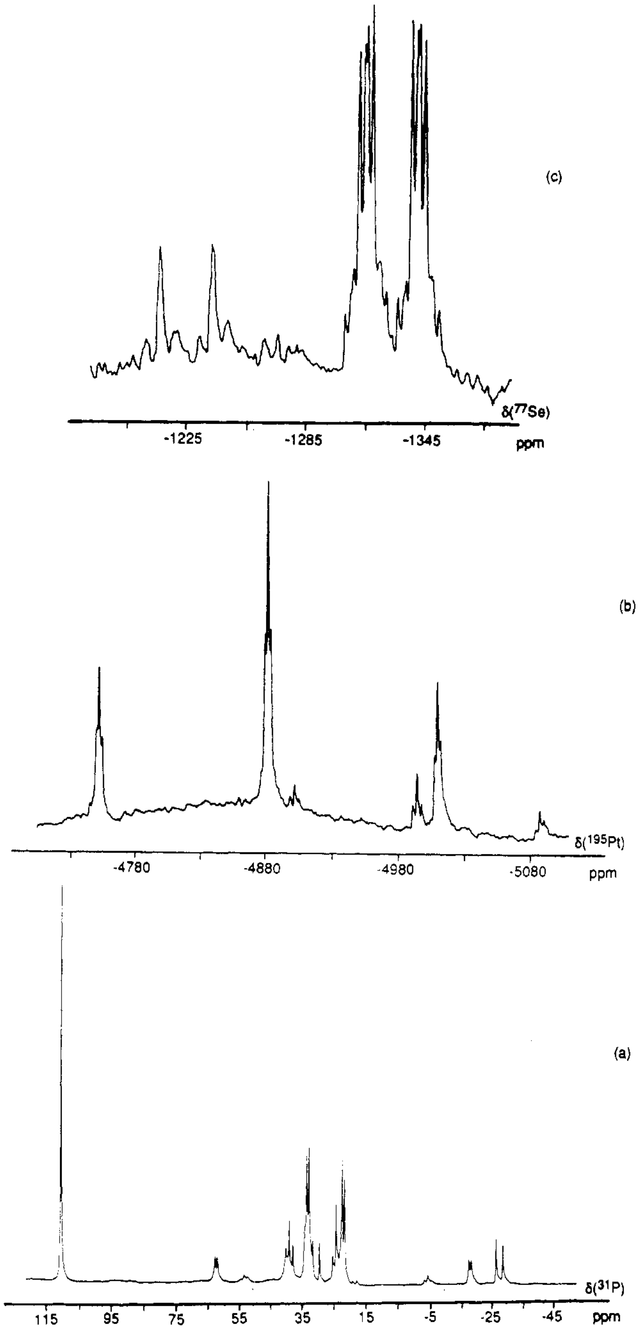

Figure 3. NMR spectra at −40 °C of a dichloromethane solution containing $Pt(S_2P\{OEt\}_2)_2$ and dpmSe (1:2 proportions): (a) ^{31}P; (b) ^{195}Pt; (c) ^{77}Se.

Table V. NMR Data for the ApeSe and ApeS Derivatives of $Pt(S_2P\{OEt\}_2)_2$ in Dichloromethane Solution[a]

complex	δ(^{31}P)	δ(^{77}Se)	δ(^{195}Pt)	*J*, Hz	temp, °C
(apeSe)Pt(S_2P-{OEt}$_2$)$_2$	37.0 (s)[b] 93.7 (s)[c] 96.5 (s)[d]	−1670 (d)	−4435 (dd)	$^2J_{Pt,P}$ = 117 $^2J_{Pt,P}$ = 376 $^1J_{Se,P}$ = 730	−20
(apeS)Pt(S_2P-{OEt}$_2$)$_2$	43.9 (s)[b] 93.4 (s)[c] 96.6 (s)[d]		−4425 (dd)	$^2J_{Pt,P}$ = 117 $^2J_{Pt,P}$ = 371	−20

[a] s = singlet, d = doublet, and dd = doublet of doublets. [b] Resonance due to the ape ligand. [c] Resonance due to the monodentate dithiolate. [d] Resonance due to the chelated dithiolate.

Table VI. Fractional Atomic Coordinates for (apeS)Pt(S_2P\{OEt\}$_2$)$_2$

Pt	0.11080 (2)	0.00000	0.21503 (2)
As	0.02615 (7)	−0.11011 (4)	0.15403 (6)
S1	0.2866 (2)	−0.0219 (1)	0.1349 (2)
S2	0.1029 (2)	0.0955 (1)	−0.0938 (2)
S3	0.1906 (2)	0.1103 (1)	0.2861 (2)
S4	−0.0642 (2)	0.0246 (1)	0.2930 (2)
S5	−0.2428 (2)	−0.1998 (1)	−0.3076 (2)
P1	0.2857 (2)	0.0609 (1)	0.0296 (2)
P2	0.0119 (2)	0.1188 (1)	0.3188 (2)
P3	−0.1402 (2)	−0.1147 (1)	−0.2859 (2)
O1	0.3841 (5)	0.0422 (3)	−0.0452 (5)
O2	0.3812 (5)	0.1125 (2)	0.1388 (5)
O3	0.0307 (7)	0.1499 (3)	0.4523 (6)
O4	−0.1003 (6)	0.1708 (3)	0.2291 (6)
C1	0.0008 (7)	−0.1337 (3)	−0.0205 (6)
C2	−0.0843 (7)	−0.0813 (3)	−0.1221 (6)
C3	0.5376 (8)	0.0257 (5)	0.0266 (9)
C4	0.6086 (9)	0.0270 (6)	−0.0628 (10)
C5	0.3881 (9)	0.1826 (4)	0.1114 (8)
C6	0.5111 (10)	0.2116 (4)	0.2264 (9)
C7	0.1308 (12)	0.1209 (5)	0.5742 (8)
C8	0.2456 (14)	0.1656 (7)	0.6456 (12)
C9	−0.1233 (10)	0.1823 (6)	0.0955 (9)
C10	−0.2514 (10)	0.2240 (6)	0.0309 (10)
C11	−0.1552 (7)	−0.1336 (3)	0.1618 (6)
C12	−0.1654 (8)	−0.1298 (4)	0.2799 (7)
C13	−0.2957 (10)	−0.1433 (5)	0.2878 (8)
C14	−0.4142 (9)	−0.1615 (5)	0.1791 (9)
C15	−0.4071 (9)	−0.1651 (4)	0.0618 (8)
C16	−0.2782 (8)	−0.1512 (4)	0.0511 (7)
C21	0.1561 (7)	−0.1802 (3)	0.2523 (6)
C22	0.1089 (9)	−0.2464 (4)	0.2396 (7)
C23	0.2037 (10)	−0.2964 (4)	0.3049 (10)
C24	0.3447 (9)	−0.2827 (5)	0.3793 (8)
C25	0.3947 (8)	−0.2167 (5)	0.3960 (7)
C26	0.2980 (7)	−0.1664 (4)	0.3314 (6)
C31	0.0223 (7)	−0.1210 (4)	−0.3149 (6)
C32	0.1287 (8)	−0.0715 (4)	−0.2733 (8)
C33	0.2513 (8)	−0.0770 (5)	−0.2968 (9)
C34	0.2697 (9)	−0.1320 (5)	−0.3632 (8)
C35	0.1651 (9)	−0.1809 (4)	−0.4052 (8)
C36	0.0424 (8)	−0.1755 (4)	−0.3812 (7)
C41	−0.2523 (7)	−0.0494 (3)	−0.3893 (6)
C42	−0.3968 (9)	−0.0462 (5)	−0.4082 (9)
C43	−0.4862 (8)	0.0036 (7)	−0.4846 (9)
C44	−0.4355 (9)	0.0479 (5)	−0.5463 (8)
C45	−0.2964 (10)	0.0456 (5)	−0.5316 (9)
C46	−0.2027 (7)	−0.0034 (6)	−0.4511 (7)

Table VII. Interatomic Distances (Å) for (apeS)Pt(S_2P\{OEt\}$_2$)$_2$

Pt–As	2.361 (1)	Pt–S1	2.342 (2)
Pt–S3	2.373 (2)	Pt–S4	2.328 (2)
As–C11	1.929 (8)	As–C21	1.930 (6)
As–C1	1.936 (7)	C1–C2	1.530 (8)
P3–C2	1.822 (7)	P3–S5	1.956 (3)
P3–C31	1.806 (8)	P3–C41	1.807 (6)
P1–S1	2.036 (3)	P1–S2	1.928 (2)
P2–S3	1.993 (3)	P2–S4	2.011 (3)
P1–O1	1.590 (7)	P1–O2	1.593 (5)
P2–O3	1.567 (7)	P2–O4	1.565 (6)
O1–C3	1.463 (8)	O2–C5	1.444 (9)
O3–C7	1.452 (10)	O4–C9	1.446 (13)
C3–C4	1.458 (17)	C5–C6	1.497 (11)
C7–C8	1.424 (16)	C9–C10	1.459 (14)

rus-31 NMR spectrum at 25 °C of a dichloromethane solution of $Pt(S_2P\{OEt\}_2)_2$ and apeSe in equimolar proportions is dominated by a large singlet that has only selenium-77 satellites, with chemical shift and coupling constant similar to those of free apeSe. This stronly implies that the selenium atom is not coordinated to platinum. The other resonances in the spectrum are broad, but on cooling of the solution to −20 °C, these signals sharpen and may then be identified as being due to chelated and monodentate dithiolate. The corresponding platinum-195 NMR spectrum is a doublet of doublets. These data suggest that the neutral species (η^1-apeSe)Pt(η^1-S_2P\{OEt\}$_2$)(η^2-S_2P\{OEt\}$_2$) has been generated, in which the apeSe ligand is coordinated to platinum in a monodentate fashion through the arsenic atom.

The selenium-77 NMR spectrum at −20 °C consists of a doublet at δ −1670 with a chemical shift and coupling constant very similar to those of the free ligand, confirming that selenium is not coordinated to platinum.

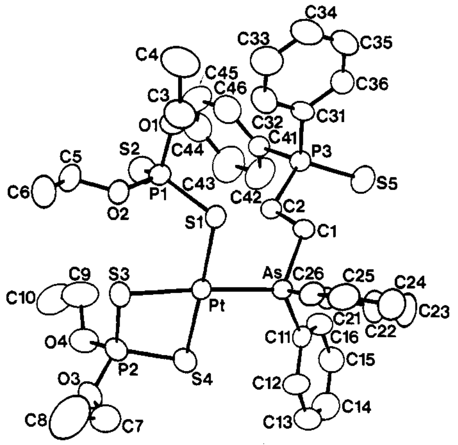

Figure 4. ORTEP drawing showing the molecular structure of $(apeS)Pt(S_2P\{OEt\}_2)_2$.

Table VIII. Interatomic Bond Angles (deg) for $(apeS)Pt(S_2P\{OEt\}_2)_2$

As–Pt–S1	87.4 (1)	As–Pt–S3	176.6 (1)
As–Pt–S4	93.8 (1)	S1–Pt–S3	95.6 (1)
S1–Pt–S4	178.5 (1)	S3–Pt–S4	83.2 (1)
Pt–As–C1	113.9 (2)	Pt–As–C11	116.8 (2)
Pt–As–C21	115.5 (2)	C1–As–C11	104.8 (3)
C1–As–C21	100.5 (3)	C11–As–C21	103.4 (3)
Pt–S1–P1	104.5 (1)	Pt–S3–P2	86.2 (1)
Pt–S4–P2	87.0 (1)	S1–P1–S2	119.1 (2)
S1–P1–O1	105.3 (2)	S1–P1–O2	102.7 (2)
S2–P1–O1	108.9 (2)	S2–P1–O2	115.0 (2)
O1–P1–O2	104.5 (3)	S3–P2–S4	102.4 (1)
S3–P2–O3	116.7 (3)	S3–P2–O4	114.1 (3)
S4–P2–O3	113.5 (3)	S4–P2–O4	113.4 (3)
O3–P2–O4	97.3 (3)	S5–P3–C2	111.9 (3)
S5–P3–C31	113.1 (3)	S5–P3–C41	112.9 (3)
C2–P3–C31	106.4 (3)	C2–P3–C41	103.9 (3)
C31–P3–C41	108.0 (3)	P1–O1–C3	120.8 (5)
P1–O2–C5	122.1 (4)	P2–O3–C7	120.9 (5)
P2–O4–C9	122.9 (5)	As–C1–C2	113.2 (4)
P3–C2–C1	110.7 (4)	O1–C3–C4	108.9 (7)
O2–C5–C6	106.7 (6)	O3–C7–C8	112.0 (8)
O4–C9–C10	110.0 (7)		

A 1:2 stoichiometric solution of $Pt(S_2P\{OEt\}_2)_2$ and apeSe produces a phosphorus-31 NMR spectrum at −20 °C that is essentially the same as that of an equimolar reaction mixture, but with an additional singlet (δ 36) with selenium satellites. This resonance is assigned to free apeSe, and the spectrum therefore suggests that only 1 mol of apeSe reacts with $Pt(S_2P\{OEt\}_2)_2$.

The reactions of $Pt(S_2P\{OEt\}_2)_2$ with apeS are entirely analogous to those with apeSe, and data are included in Table V. A crystal structure determination of $(apeS)Pt(S_2P\{OEt\}_2)_2$ has been completed, and it completely vindicates the structure determined by NMR studies.

Description of the Structure of $(apeS)Pt(S_2P\{OEt\}_2)_2$. The crystal structure consists of discrete molecules of $(apeS)Pt(S_2P\{OEt\}_2)_2$. The geometry about platinum is square planar, the donor atoms being three sulfurs, from bidentate and monodentate dithiophosphate ligands, and arsenic, from the monodentate apeS ligand. Figure 4 is an ORTEP[21] diagram showing the molecular geometry of $(apeS)Pt(S_2P\{OEt\}_2)_2$ together with the atomic numbering scheme. Positional parameters and important bond lengths and bond angles are given in Tables VI–VIII.

The Pt–S3 distance (trans to As) is significantly longer than the other Pt–S distances, and as a result the bidentate $[S_2P(OEt)_2]^-$ ligand is chelated slightly asymmetrically. The Pt–S distances are very similar to those found[7] in the compound $(PPh_3)Pt(S_2P\{OEt\}_2)_2$. The P–S bond distances for those sulfur atoms bonded to platinum are also similar to those in $(PPh_3)Pt(S_2P\{OEt\}_2)_2$, while those to nonbonded sulfurs are, of course, significantly shorter. There are no unexpected features in the remainder of the structure.

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Registry No. $[(dpe)Pt(S_2P\{OEt\}_2)]^+$, 114183-91-4; $(dpe)Pt(S_2P\{O\}OEt)$, 114183-92-5; $[Pt(dpe)_2]^{2+}$, 47895-52-3; $[(ape)Pt(S_2P\{OEt\}_2)]^+$, 114183-93-6; $(ape)Pt(S_2P\{O\}OEt)$, 114183-94-7; *cis*-$[Pt(ape)_2]^{2+}$, 114183-95-8; *trans*-$[Pt(ape)_2]^{2+}$, 114183-96-9; $[(dpm)Pt(S_2P\{OEt\}_2)]^+$, 114183-97-0; $(dpm)Pt(S_2P\{O\}OEt)$, 114183-98-1; $[(\eta^1\text{-}dpm)(\eta^2\text{-}dpm)Pt(\eta^1\text{-}S_2P\{OEt\}_2)]^+$, 114197-82-9; $[(dpmSe)Pt(S_2P\{OEt\})]^+$, 114183-99-2; $(dpmSe)Pt(S_2P\{O\}OEt)$, 114184-00-8; $[(dpmS)Pt(S_2P\{OEt\}_2)]^+$, 114197-76-1; $(dpmS)Pt(S_2P\{O\}OEt)$, 114184-01-9; *cis*-$[Pt(dpmSe)_2]^{2+}$, 107283-73-8; *trans*-$[Pt(dpmSe)_2]^{2+}$, 107380-70-1; *cis*-$[Pt(dpmS)_2]^{2+}$, 114184-02-0; *trans*-$[Pt(dpmS)_2]^{2+}$, 114248-21-4; $(apeSe)Pt(S_2P\{OEt\}_2)$, 114184-03-1; $(apeS)Pt(S_2P\{OEt\}_2)_2$, 114184-04-2; $K_2[PtCl_4]$, 10025-99-7; $HS_2P(OEt)_2$, 298-06-6.

Supplementary Material Available: Tables S-I–S-V, listing thermal parameters, the derived hydrogen positions, angles and distances associated with the phenyl rings, and least-squares equations of mean planes (8 pages); tables of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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[21] Johnson, C. K. "ORTEP"; Report No. ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.