$HClO_4$ (70%, 15 mL) yielded *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4 \cdot H_2O$ (9.16 g, 98%).

NMR Experiments. The SO_3^{2-} substitution reactions on *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ were followed in situ by ^{13}C NMR spectroscopy as follows: A sample of the complex (0.143 g, 5×10^{-4} mol), dissolved (trans) or suspended (cis) in H_2O (1.0 mL), was treated with Na_2SO_3 (0.069 g, 1.1 equiv) in H_2O (1.0 mL) with use of calibrated syringes. After 2.0 min of reaction, the mixture was treated with 1.0 mL of D_2O containing dioxane and $HClO_4$ (150 μL, 11.7 M; Gilson pipet) to provide a deuterium lock while H-D exchange at the amine centers was prevented. Spectra were accumulated immediately thereafter. Similar experiments were performed without the acid quench with use of D_2O rather than H_2O and also with use of a 1 M Na_2SO_3 solution (2.0 mL) and 0.1 g of complex (SO_3^{2-}:Co = ca. 4:1) rather than stoichiometric amounts.

Some unreacted $[Co(en)_2Cl_2]^+$ was observed in the ^{13}C NMR spectrum commencing with the cis isomer and, correspondingly, some *trans*-bis(sulfito) complex, whose signal coincides with that of the *trans*-chlorsulfito signal. When the reaction was begun with the trans isomer, no unreacted *trans*-$[Co(en)_2Cl_2]^+$ (−21.55 ppm in D_2O) was found because the ClO_4^- was sufficient to precipitate it quantitatively.

Spontaneous Aquation and Isomerization. Either the crystallized *cis*-$[Co(en)_2(SO_3)Cl]$ was used directly or *cis*-$[Co(en)_2(SO_3)Cl]$ was generated in situ as follows. Solid Na_2SO_3 (1 mmol) was stirred into an ice-cold solution (ca. 3 mL) containing 1.0 mmol of any of the chloro salts listed above; usually the *cis*- or *trans*-dichloro species was used. The solutions became deep burnt-orange in 10–20 s. After 60 s, the solution was loaded on a short (6 × 2 cm) Sephadex cation-exchange column at 5 °C. The charge-neutral chlorosulfito species washed off with ice-cold water and was cleanly separated from some anionic *cis*-bis(sulfito) complex, which elutes more rapidly than the charge-neutral species [λ, nm (ε, M^{-1} cm^{-1})]: 505 (105), 450 (110), 289 (ca. 16 000). Molar absorptivities are based on total cobalt concentrations determined by the Kitson[36] method.

The $[Co(en)_2(SO_3)OH_2]^+$ isomerization reaction, free from interference from the generating *cis*-$[Co(en)_2(SO_3)Cl]$ hydrolysis, was studied as follows. The neutral *cis*-$[Co(en)_2(SO_3)Cl]$ species isolated by ion exchange as above was allowed to aquate for 20 min at 20 °C and then cooled rapidly to 5 °C and was sorbed on and eluted from Sephadex as before. Washing with water removed residual reactant, and 0.25 M $NaClO_4$ eluted the desired yellow-orange $[Co(en)_2(SO_3)OH_2]^+$ band; its cis and trans isomers were not separated. Isosbestic points for the subsequent spectral changes were observed at 274 (ε = 15 400), 442 (ε = 116), 500 (ε = 90), and 587 nm (ε = 9.0); for the final equilibrium mixture, absorption maxima were at 465 (ε = 160) and 272 nm (ε = 15 600).

Hg^{2+}-Induced Hydrolysis. The *cis*-$[Co(en)_2(SO_3)Cl] \cdot 1.5H_2O$ complex (ca. 50 mg) was dissolved directly in prefiltered 0.01 M $Hg(ClO_4)_2$/0.01 M $HClO_4$ (25.00 mL). For a semiquantitative confirmation of the stereochemistry by ^{13}C NMR spectroscopy, the complex suspended in D_2O was treated dropwise with $Hg(CH_3CO_2)_2$ in 2 M CF_3SO_3H to complete dissolution and the spectrum was immediately recorded.

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Multinuclear Magnetic Resonance Studies of the Reactions of Bidentate Ligands with $Pt(S_2CNEt_2)_2$. Comparisons with the Reactions of $Pt(S_2P\{OEt\}_2)_2$

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The interactions in dichloromethane solution of $Pt(S_2CNEt_2)_2$ 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). In 1:1 proportions the ligands dpe, ape, and dpm all eventually give $[(\eta^2\text{-L-L}')Pt(\eta^2\text{-}S_2CNEt_2)]^+$. With dpe, the reaction is fast and no intermediate is observed; with ape, $(\eta^1\text{-ape})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ is observable and kinetic and thermodynamic data for its conversion to the final product were obtained. The overall reaction with dpm is very slow and involves both $(\eta^1\text{-dpm})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ and the dimer *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$. In 1:2 proportions $[(\eta^1\text{-L-L}')_2Pt(\eta^2\text{-}S_2CNEt_2)]^+$ (L-L′ = ape, dpm) are formed but there is no further reaction in the dpe system. The relative instability of chelated ape and dpm is confirmed by reaction of $[(\eta^2\text{-L-L}')Pt(\eta^2\text{-}S_2CNEt_2)]^+$ with PPh_3 to give $[(\eta^1\text{-L-L}')(PPh_3)Pt(\eta^2\text{-}S_2SNEt_2)]^+$. The reaction between $Pt(S_2CNEt_2)_2$ and dpmSe in 1:1 proportions is extremely complicated and is determined by the reactivity of the P=Se bond. The initial products include $(\eta^1\text{-L-L}')Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ (L-L′ = dpmSe, dpm) and $dpmSe_2$. The reaction proceeds slowly to give *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$ and $[(\eta^2\text{-dpm})Pt(\eta^2\text{-}S_2CNEt_2)]^+$ that then react with the generated $dpmSe_2$ to reinsert Se into a Pt–P bond to give $[(\eta^2\text{-dpmSe})Pt(\eta^2\text{-}S_2CNEt_2)]^+$ as the final product. In contrast, dpmS reacts cleanly to give $(\eta^1\text{-dpmS})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ and then $[(\eta^2\text{-dpmS})Pt(\eta^2\text{-}S_2CNEt_2)]^+$ due to the lower lability of the P=S bond. No further reaction occurs with either ligand in 1:2 proportions. The ligands apeE do not react with $Pt(S_2CNEt_2)_2$ in dichloromethane solution.

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 $(PR_3)Pt(\eta^1\text{-S-S})(\eta^2\text{-S-S})$ and reaction of a second 1 mol of ligand causes displacement of the monodentate dithiolate to give $[(PR_3)_2Pt(\eta^2\text{-S-S})]^+$. These reactions have been

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Table I. ^{31}P and ^{195}Pt NMR Data for the Dpe, Ape, and Dpm Derivatives of $Pt(S_2CNEt_2)_2$ in Dichloromethane Solution[a]

complex	$\delta(^{31}P)$	$\delta(^{195}Pt)$	J, Hz	temp, °C
$[(\eta^2\text{-dpe})Pt(S_2CNEt_2)]^+$	42.7 (s)	−4830 (t)	$^1J_{Pt,P}$ = 3135	25
$(\eta^1\text{-ape})Pt(\eta^1\text{-}S_2CNEt_2)\text{-}(\eta^2\text{-}S_2CNEt_2)$	7.9 (s)	−4370 (d)	$^1J_{Pt,P}$ = 3710	−20
$[(\eta^2\text{-ape})Pt(S_2CNEt_2)]^+$	45.7 (s)	−4930 (d)	$^1J_{Pt,P}$ = 3115	25
$[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+$	7.4 (s)	−4675 (t)	$^1J_{Pt,P}$ = 3180	−50
$[(PPh_3)_2Pt(S_2CNMe_2)]^+$ [b]		−4645 (t)	$^1J_{Pt,P}$ = 3280	25
$(\eta^1\text{-dpm})Pt(\eta^1\text{-}S_2CNEt_2)\text{-}(\eta^2\text{-}S_2CNEt_2)$	2.2 (d) −28.2 (d)	−4330 (d)	$^1J_{Pt,P}$ = 3760 $^3J_{Pt,P}$ = 64 $^2J_{P,P}$ = 59	25
cis,cis-$[Pt_2(S_2CNEt_2)_2\text{-}(\mu\text{-dpm})_2]^{2+}$	−9.2 (s)	−4275 (dd)	$^1J_{Pt,P}$ = 3645 $^2J_{Pt,P}$ = 127	25
$[(\eta^2\text{-dpm})Pt(S_2CNEt_2)]^+$	−56.1 (s)	−4270 (t)	$^1J_{Pt,P}$ = 2685	25
$[(\eta^1\text{-dpm})_2Pt(S_2CNEt_2)]^+$	3.3 (d) −28.2 (d)	−4615 (tt)	$^1J_{Pt,P}$ = 3245 $^3J_{Pt,P}$ = 59 $^2J_{P,P}$ = 59	−40

[a] Key: s = singlet; d = doublet; dd = doublet of doublets; t = triplet; tt = triplet of triplets. [b] Data from ref 5.

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 a recent paper,[8] we described the reactions between $Pt(S_2P\{OEt\}_2)_2$ and a series of potentially bidentate group 15 and mixed group 15/group 16 donor ligands L-L′. Most of the reactions yielded $[(\eta^2\text{-L-L}')Pt(\eta^2\text{-}S_2P\{OEt\}_2)]^+$ and $[Pt(L\text{-}L')_2]^{2+}$, but $Ph_2PCH_2PPh_2$ (dpm) gave $[(\eta^1\text{-dpm})(\eta^2\text{-dpm})Pt(\eta^1\text{-}S_2P\{OEt\}_2)]^+$ for the 1:2 reaction. In this paper, we describe a nuclear magnetic resonance study of the reactions of $Pt(S_2CNEt_2)_2$ with dpm, $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2AsCH_2CH_2PPh_2$ (ape), $Ph_2PCH_2P(E)Ph_2$ (E = S, Se to give dpmS, dpmSe) and $Ph_2AsCH_2CH_2P(E)Ph_2$ (apeS, apeSe).

Experimental Section

$Pt(S_2CNEt_2)_2$ was prepared by the interaction of aqueous solutions of $K_2[PtCl_4]$ and $Na[S_2CNEt_2]$,[9] and the precipitate was filtered and dried at the pump. The ligands dpe, ape, and dpm (Strem) were used as received while dpmS, dpmSe, apeS, and apeSe were prepared as described previously.[8]

$(\eta^1$-Dpm)$Pt(S_2CNEt_2)_2$. Equimolar quantities (1 mmol) of $Pt(S_2CNEt_2)_2$ and dpm were mixed in dichloromethane. The vessel was then placed in an ice/salt bath to prevent formation of $[(\eta^2\text{-dpm})Pt(S_2CNEt_2)]^+$. Hexane was added, and when the mixture was cooled to −15 °C, yellow crystals precipitated.

[(L-L)$Pt(S_2CNEt_2)][BPh_4]$ (L-L = Dpe, Ape, Dpm). Equimolar quantities (1 mmol) of $Pt(S_2CNEt_2)_2$ and the L-L ligand (dpe, ape) were stirred in dichloromethane for 30 min, and then the solvent was removed under vacuum. The yellow solids were dissolved in acetone and treated with $NaBPh_4$ in the same solvent. After removal of the solvent, the solids were recrystallized from dichloromethane/hexane. The preparation of $[(dpm)Pt(S_2CNEt_2)][BPh_4]$ is similar, except that the solution was aged for 1 month before the anion was added. However, the reaction time is a matter of hours in refluxing dichloromethane.

Identification of compounds was usually unambiguous from the NMR spectra, but comparisons were always made with data for the corresponding dithiophosphate complexes.[8]

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, neat $SeMe_2$, and 1 M H_2PtCl_6 in concentrated HCl. The high frequency positive convention is used for chemical shifts.

Results and Discussion

Initial NMR studies of the interaction between $Pt(S_2CNEt_2)_2$ and the ligands in dichloromethane solution were carried out in situ in the NMR tube. Some of the complexes were subsequently isolated and their NMR spectra (Table I) were the same as those for the complexes generated in situ.

Table II. Rate Constant Data for the Conversion of $(\eta^1\text{-Ape})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ to $[(\eta^2\text{-Ape})Pt(\eta^2\text{-}S_2CNEt_2)][S_2CNEt_2]$ in Dichloromethane

temp, °C	rate const, s^{-1}	temp, °C	rate const, s^{-1}
23.5	$(2.5 \pm 0.2) \times 10^{-3}$	−3.0	$(1.4 \pm 0.2) \times 10^{-4}$
6.2	$(6.5 \pm 0.3) \times 10^{-4}$		

Reactions of $Pt(S_2CNEt_2)_2$ with Group 15 Ligands. (i) Reactions with Dpe. The phosphorus-31 NMR spectrum obtained soon after mixing equimolar quantities of $Pt(S_2CNEt_2)_2$ and dpe in dichloromethane at 25 °C consists of a singlet with platinum-195 satellites; the platinum-195 NMR spectrum is a triplet with no evidence for unreacted $Pt(S_2CNEt_2)_2$. These data can be accommodated by either $(\eta^2\text{-dpe})Pt(\eta^1\text{-}S_2CNEt_2)_2$ or $[(\eta^2\text{-dpe})\text{-}Pt(\eta^2\text{-}S_2CNEt_2)]^+$, but the latter is shown to be the correct formulation by isolation of its tetraphenylborate salt. This reaction is an exact analogy of the 1:2 stoichiometric reactions with monodentate phosphines observed by Stephenson.[1] $[(Dpe)Pt\text{-}(S_2CNEt_2)]^+$ is stable for days in the presence of ionic $[S_2CNEt_2]^-$ in contrast with the analogous dithiophosphate complex, $[(dpe)Pt(S_2P\{OEt\}_2)]^+$, which undergoes nucleophilic attack by the dithiophosphate anion in solution.[8] This stability of the dithiocarbamate complexes was also noted by Stephenson.[1]

$Pt(S_2CNEt_2)_2$ and dpe in dichloromethane at 25 °C in 1:2 molar proportions give only $[(dpe)Pt(S_2CNEt_2)]^+$ and free dpe in contrast to $[(dpe)Pt(S_2P\{OEt\}_2)]^+$, which reacts to give $[Pt(dpe)_2]^{2+}$. However, mixing equimolar quantities of $[Pt(dpe)_2][BPh_4]_2$ and $[Bu_4N][S_2CNEt_2]$ in dichloromethane also gives $[(dpe)Pt\text{-}(S_2CNEt_2)]^+$ and free dpe so equilibria are involved but they are slow on the NMR time scale.

No reaction occurs on the addition of 1 mol of PPh_3 to a dichloromethane solution of $[(dpe)Pt(S_2CNEt_2)]^+$.

(ii) Reactions with Ape. Preliminary experiments on dichloromethane solutions of $Pt(S_2CNEt_2)_2$ and ape in equimolar proportions showed two products are formed, one of which is short-lived at room temperature. Separate dichloromethane solutions of equimolar amounts of $Pt(S_2CNEt_2)_2$ and ape were cooled in ice before being mixed in a cold NMR tube, which was then immediately inserted into the spectrometer probe precooled to −20 °C. The resulting phosphorus-31 NMR spectrum is dominated by the sharp singlet at δ 7.9 and only a small proportion of another signal at δ 45.3 is apparent, both with platinum−195 satellites. No change occurs in the spectrum over a period of 30 min at −20 °C, but when the solution is allowed to warm to room temperature, the signal at high frequency gains intensity at the expense of that at δ 7.9. The platinum-195 NMR spectrum of the freshly prepared cold mixture shows a strong and weak doublet. After the solution is warmed to room temperature and recooled to −20 °C for spectral acquisition, the spectrum consists only of the doublet at higher frequency; thus, both complexes have one phosphorus atom coordinated to platinum. The final stable product was isolated by precipitation as its tetraphenylborate salt and is identified as $[\eta^2\text{-ape})Pt(S_2CNEt_2)][BPh_4]$. It is therefore proposed that the sequence of events is as shown in Scheme I.

Scheme I

$$Pt(\eta^2\text{-}S_2CNEt_2)_2 + \text{ape} \rightarrow (\eta^1\text{-ape})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2) \rightarrow [(\eta^2\text{-ape})Pt(\eta^2\text{-}S_2CNEt_2)]^+ + [S_2CNEt_2]^-$$

The kinetics of the chelation of ape can be followed by NMR spectroscopy but they cannot, however, be followed accurately by direct continuous monitoring of the NMR spectra at or near room temperature because of the broadness of the resonances. The stoichiometric amount of ape was added to a dichloromethane solution of $Pt(S_2CNEt_2)_2$ at a controlled temperature between −3.0 and +23.5 °C. Aliquots of the reaction mixture were removed at recorded times and frozen in NMR tubes with liquid nitrogen. Phosphorus-31 NMR spectra of the aliquots were later obtained at −50 °C and the relative proportions of the two compounds readily determined.

Plots of ln (% η^1-ape) vs time at each temperature are linear and confirm the expected first-order kinetics, and rate constant

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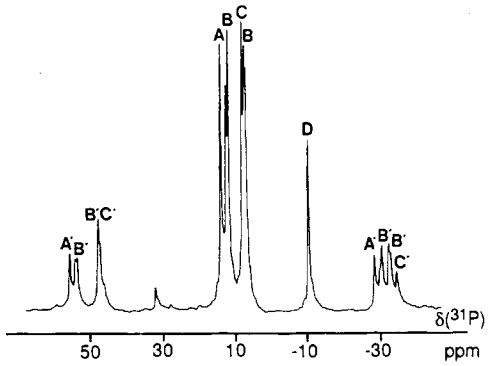


Figure 1. ^{31}P NMR spectrum at −70 °C of a dichloromethane solution of $[(ape)Pt(S_2CNEt_2)]^+$ to which 1 mol of PPh_3 has been added.

data are given in Table II. The Eyring plot is linear and gives the enthalpy of activation $\Delta H^\ddagger = 58 \pm 3$ kJ mol^{-1}. The entropy of activation, $\Delta S^\ddagger$, and the energy of activation, E_a, are -99 ± 133 J K^{-1} mol^{-1} and 54 ± 2 kJ mol^{-1}, respectively. By interpolation, a value of $k_{298} = (2.5 \pm 0.2) \times 10^{-3}$ s^{-1} was determined. The enthalpy of activation is typical for substitution reactions of platinum(II) complexes.[10]

$Pt(S_2CNEt_2)_2$ and ape in 1:2 molar proportions is labile at room temperature. At −50 °C the phosphorus-31 NMR spectrum is still somewhat broad but consists of two singlets (with satellites) of almost identical chemical shift (δ 7.4), and a further singlet at δ −14.7. One singlet at δ 7.4 is due to $(\eta^1\text{-ape})Pt(S_2CNEt_2)_2$ and that at δ −14.7 is due to free ape. A few hours after mixing, the spectrum (at −50 °C) contains only one sharp singlet at δ 7.4 (with satellites) and the signal due to free ape has disappeared. The corresponding platinum-195 NMR spectrum at −50 °C consists of a triplet showing that two phosphorus atoms must be coordinated to platinum, but the spectrum is not that of *cis*/*trans*-$[Pt(ape)_2]^{2+}$.[8] The spectra are consistent with the slow formation of $[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+$, with ape acting as a monodentate phosphine ligand.

All attempts to precipitate the $[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+$ cation from solution resulted in mixtures of $[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+$ and $[(\eta^2\text{-ape})Pt(S_2CNEt_2)]^+$. This indicates that the equilibrium

$$[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+ \rightleftharpoons [(ape)Pt(S_2CNEt_2)]^+ + ape \quad (1)$$

exists in solution, and this was confirmed by reacting $[(ape)Pt(S_2CNEt_2)][S_2CNEt_2]$ with ape to give $[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+$ showing that the Pt–As bond in $[(\eta^2\text{-ape})Pt(S_2CNEt_2)]^+$ is relatively weak. Exchange within this equilibrium is slow on the NMR time scale and the equilibrium in solution lies predominantly to the left. Addition of 1 mol of $[Bu_4N][S_2CNEt_2]$ to a dichloromethane solution of *cis*/*trans*-$[Pt(ape)_2][BPh_4]_2$[8] also gives $[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+$ suggesting that the equilibrium

$$[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+ \rightleftharpoons [Pt(ape)_2]^{2+} + [S_2CNEt_2]^- \quad (2)$$

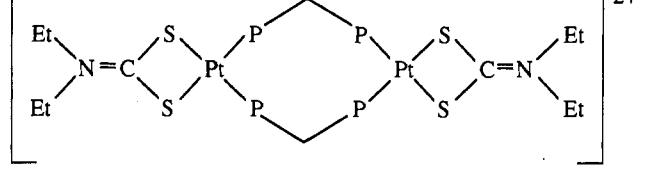
also exists in solution and, again, lies substantially to the left.

In order to further investigate the cleavage of the Pt–As bond by phosphorus ligands, the interaction of $[(ape)Pt(S_2CNEt_2)]^+$ with 1 mol of PPh_3 was studied. At 25 °C the phosphorus-31 NMR spectrum indicates exchange, but when the solution is cooled to −70 °C, the spectrum shown in Figure 1 is obtained. A sharp singlet at δ 14.6 with platinum-195 satellites is labeled A with satellites A′, and another singlet C with satellites C′ is observed at δ 7.5. The spectrum also contains two asymmetric doublets B (δ 12.6, 8.5; $^2J(P,P) = 22$ Hz) that have satellites B′: $^1J(Pt,P) = 3250$, 3100 Hz, the larger coupling constant being associated with the doublet at higher frequency. These doublets constitute an AB quartet but the ratio $J/\Delta\nu$ is small (0.13) and the spectrum approximates to an AX system. The singlet D at δ −12.5 is due to free PPh_3. The platinum-195 NMR spectrum consists of two overlapping triplets at δ −4690 and −4685 and a doublet of doublets at δ −4680. These resonances are assigned to compounds A, B, and C, respectively, by their platinum–phosphorus coupling constants. By comparison with the NMR data in Table I, compound C is identified as $[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+$ and compound A as $[(PPh_3)_2Pt(S_2CNEt_2)]^+$.[5] Compound B is identified as $[(PPh_3)(\eta^1\text{-ape})Pt(S_2CNEt_2)]^+$, in which the ape ligand is coordinated to platinum through the phosphorus atom. The three mixed phosphine complexes $[(PPh_3)_x(\eta^1\text{-ape})_{2-x}Pt(S_2CNEt_2)]^+$ are not produced in the statistical proportion expected for a random distribution of the phosphines. The relative integrated intensities of the three platinum-195 signals for compounds A, B, and C are approximately 1:4:1, rather than 1:2:1. This result suggests that the formation of either compound A or C is thermodynamically unfavorable, probably due to steric effects. Reaction of $[(ape)Pt(S_2CNEt_2)]^+$ with dpe gives $[(dpe)Pt(S_2CNEt_2)]^+$ and ape, confirming the superior chelating ability of dpe over ape.

(iii) Reactions with Dpm. The reactions of $Pt(S_2CNEt_2)_2$ with dpm were examined to investigate the effects of chelate ring size. All NMR data for this system are given in Table I.

The phosphorus-31 NMR spectrum of a freshly prepared dichloromethane solution containing equimolar proportions of $Pt(S_2CNEt_2)_2$ and dpm at 25 °C consists of two doublets of equal intensity, each having satellites, and one doublet is close to the position of the resonance for free dpm. The corresponding platinum-195 NMR spectrum is a doublet of doublets, but in order to observe this spectrum, it is necessary to accumulate the data at −20 °C since a second product (discussed below) forms at 25 °C during the long spectral acquisition. These spectra are consistent with the formation of $(\eta^1\text{-dpm})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$.

A second product slowly forms in solutions containing $Pt(S_2CNEt_2)_2$ and dpm in 1:1 molar proportions at 25 °C. The phosphorus-31 NMR spectrum at 25 °C of such a solution approximately 90 min after mixing shows $(\eta^1\text{-dpm})Pt(S_2CNEt_2)_2$ is still present, but an additional set of interesting signals is also observed. This consists of an apparent singlet at δ 9.2 flanked by what appear to be two pairs of platinum-195 satellites; the outer pair of satellites resembles doublets. The platinum-195 NMR spectrum also shows signals due to $(\eta^1\text{-dpm})Pt(S_2CNEt_2)_2$ together with a distorted doublet of doublets due to the new species. The complex platinum-195 satellites in the phosphorus-31 NMR spectrum are characteristic of binuclear complexes such as *cis*,*cis*-$[Pt_2Me_4(\mu\text{-dpm})_2]$.[11] This data suggests that $(\eta^1\text{-dpm})Pt(S_2CNEt_2)_2$ slowly rearranges in dichloromethane solution to form the dimer *cis*,*cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$ shown in structure I. Two days after mixing, the phosphorus-31 NMR spectrum



I

shows that no $(\eta^1\text{-dpm})Pt(S_2CNEt_2)_2$ remains, but in addition to the sharp signals due to *cis*,*cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$, there is a broad singlet at δ −56.1 with satellites. The coordination shift, defined as δ(coordinated phosphine) − δ(free phosphine), for this resonance is −33.8, and such a value is typical for a four-membered chelate complex.[12] The platinum-195 NMR spectrum is a distorted doublet of doublets due to *cis*,*cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$ and a triplet at δ −4270. This new species in solution is proposed to be $[(\eta^2\text{-dpm})Pt(\eta^2\text{-}S_2CNEt_2)]^+$ by a comparison with the NMR data for $[(dpm)Pt(S_2P\{OEt\}_2)]^+$.[8] However, its platinum-195 chemical shift is quite unlike those for $[(dpe)Pt(S_2CNEt_2)]^+$ and $[(ape)Pt(S_2CNEt_2)]^+$. Such deviations have been noted previously[12] and are thought to be due to the ring

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Table III. NMR Data for the DpmSe and DpmS Derivatives of $Pt(S_2CNEt_2)_2$ in Dichloromethane Solution[a]

complex	$\delta(^{31}P)$	$\delta(^{195}Pt)$	J, Hz	temp, °C
$(\eta^1$-dpmSe)Pt$(\eta^1$-$S_2CNEt_2)$-$(\eta^2$-$S_2CNEt_2)$	1.4 (d) 24.4 (d)	−4290 (dd)	$^1J_{Pt,P}$ = 3775 $^2J_{Pt,P}$ = 155 $^2J_{P,P}$ = 27	25
[$(\eta^2$-dpmSe)Pt-(S_2CNEt_2)]$^+$ [b]	20.5 (d) 43.7 (d)	−4495 (dd)	$^1J_{Pt,P}$ = 3370 $^2J_{Pt,P}$ = 125 $^1J_{Pt,Se}$ = 165 $^2J_{P,P}$ = 46 $^1J_{P,Se}$ = 517	25
$(\eta^1$-dpmS)Pt$(\eta^1$-$S_2CNEt_2)$-$(\eta^2$-$S_2CNEt_2)$	0.9 (d) 33.9 (d)	−4285 (dd)	$^1J_{Pt,P}$ = 3775 $^2J_{Pt,P}$ = 155 $^2J_{P,P}$ = 27	25
[$(\eta^2$-dpmS)Pt(S_2CNEt_2)]$^+$	16.7 (d) 61.7 (d)		$^1J_{Pt,P}$ = 3350 $^2J_{Pt,P}$ = 60 $^2J_{P,P}$ = 39	25

[a] Key: d = doublet; dd = doublet of doublets. [b] $\delta(^{77}Se)$ = −65 (d).

strain in the four-membered chelate ring produced by dpm.

Prolonged standing (1 month) at room temperature results in the formation of pure [(dpm)Pt(S_2CNEt_2)]$^+$, and this cation can then be isolated as its tetraphenylborate salt. The slow and complex interaction between equimolar quantities of $Pt(S_2CNEt_2)_2$ and dpm is therefore by Scheme II. It is not clear whether all the [(dpm)Pt(S_2CNEt_2)]$^+$ is formed via the dinuclear species or whether some is formed directly from (dpm)Pt$(S_2CNEt_2)_2$.

Scheme II

$$Pt(S_2CNEt_2)_2 + dpm \rightarrow$$
$$(\eta^1\text{-dpm})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2) \rightarrow$$
$$\tfrac{1}{2}\ cis,cis\text{-}[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+} + [S_2CNEt_2]^- \rightarrow$$
$$[(dpm)Pt(S_2CNEt_2)]^+ + [S_2CNEt_2]^-$$

At 25 °C, the phosphorus-31 NMR spectrum of a dichloromethane solution containing $Pt(S_2CNEt_2)_2$ and dpm in 1:2 molar proportions indicates some exchange is occurring, but when the solution is cooled to −60 °C, the spectrum sharpens and shows that two species are present, both giving two doublets with the high-frequency doublet in each case having platinum-195 satellites. The platinum-195 NMR spectrum at −60 °C is a doublet of doublets due to $(\eta^1$-dpm)Pt$(S_2CNEt_2)_2$ and a triplet of triplets. Approximately 1 week after mixing, the phosphorus-31 NMR spectrum at −40 °C is two slightly broadened doublets. The platinum-195 NMR spectrum is a triplet of triplets, but the appropriate platinum satellites for the second coupling are not observable in the phosphorus NMR spectrum due to the comparative broadness of the phosphorus resonance and the small coupling constant. These spectra are consistent with the complex in solution being $[(\eta^1\text{-dpm})_2Pt(S_2CNEt_2)]^+$. Thus, the behavior of dpm resembles that of ape in the sense that addition of a second mole of ligand cleaves the original chelate ring and produces two monodentate ligands. Platinum complexes containing monodentate dpm ligands in a cis configuration have previously[13] been synthesized by reactions of $(\eta^2$-dpm)PtR_2 with dpm to give *cis*-$(\eta^1$-dpm)$_2PtR_2$ where R are alkyl and aryl groups which prefer to be mutually cis, and do not readily ionize as R^-.

Mixing equimolar quantities of $[(\eta^2$-dpm)Pt$(S_2CNEt_2)][BPh_4]$ and PPh_3 in dichloromethane produces a complex phosphorus-31 NMR spectrum showing the presence of three species. The platinum-195 NMR spectrum allows these to be identified as $[PPh_3)_2Pt(S_2CNEt_2)]^+$, $[(\eta^1\text{-dpm})_2Pt(S_2CNEt_2)]^+$, and $[(PPh_3)(\eta^1\text{-dpm})Pt(S_2CNEt_2)]^+$.

Reactions of $Pt(S_2CNEt_2)_2$ with Mixed Group 15/Group 16 Ligands. (i) Reactions with DpmSe. The reactions between $Pt(S_2CNEt_2)_2$ and dpmSe show some parallels with those of the group 15 ligands, but there are some very interesting differences. All NMR data for this system are given in Table III.

The phosphorus-31 NMR spectrum at 25 °C of a dichloromethane solution initially containing equimolar quantities of $Pt(S_2CNEt_2)_2$ and dpmSe soon after mixing is complex. Two intense doublets observed at δ 30.6 and −27.7 are due to unreacted dpmSe, and a singlet at δ 24.4 is due to $dpmSe_2$ ($Ph_2P(Se)$-$CH_2P(Se)Ph_2$).[14] Two doublets (compound E) appear at δ 1.4 and 24.4, each having satellites, and there are small resonances due to $(\eta^1$-dpm)Pt$(S_2CNEt_2)_2$. For the first time the ligand has not reacted completely, and side reactions are occurring. This is confirmed by the platinum-195 NMR spectrum, which is dominated by a singlet at δ −3830 due to $Pt(S_2CNEt_2)_2$. It also contains three doublets of doublets, two of which are assigned to $(\eta^1$-dpm)Pt$(S_2CNEt_2)_2$ and *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$. The most intense doublet of doublets is assigned to compound E by its platinum–phosphorus coupling constants, and it is identified as $(\eta^1$-dpmSe)Pt$(\eta^1$-$S_2CNEt_2)(\eta^2$-$S_2CNEt_2)$ (with dpmSe coordinated through phosphorus) by comparison of its NMR data with those for $(\eta^1$-dpm)Pt$(S_2CNEt_2)_2$.

Thus the unreacted dpmSe abstracts selenium from the pendent P=Se of the monodentate dpmSe ligand in $(\eta^1$-dpmSe)Pt-$(S_2CNEt_2)_2$ to produce $dpmSe_2$ and $(\eta^1$-dpm)Pt$(S_2CNEt_2)_2$. The dpm complex subsequently follows the reaction pathway described previously. This transfer of selenium between phosphorus atoms of different phosphines is well-known.[14-17] Two hours after mixing, the phosphorus spectrum clearly shows the presence of increased quantities of $dpmSe_2$ and cis,cis-$[Pt_2(S_2CNEt_2)_2(\mu$-$dpm)_2]^{2+}$.

After 3 days, the phosphorus-31 NMR spectrum shows $(\eta^1$-dpmSe)Pt$(S_2CNEt_2)_2$ is now absent, but signals due to *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$, dpmSe, and $dpmSe_2$ are still obvious. A singlet due to [(dpm)Pt(S_2CNEt_2)]$^+$ is now present, and two doublets at δ 20.5 and 43.7 with platinum satellites are observed. The latter phosphorus resonance is due to the P(Se) phosphorus atom of coordinated dpmSe, but no selenium-77 satellites are observable at this stage due to the low intensity of the signal. The corresponding platinum-195 NMR spectrum *still* contains a signal due to unreacted $Pt(S_2CNEt_2)_2$, and other resonances can be assigned to *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$ and [(dpm)Pt-(S_2CNEt_2)]$^+$. A doublet of doublets at δ −4505 due to the new compound suggests it contains a chelated dpmSe ligand. The selenium-77 NMR spectrum consists of doublets at δ −340 and −300 due to dpmSe and $dpmSe_2$, respectively, and a doublet at δ −95 with platinum-195 satellites. All the NMR data for this new dpmSe species in solution are consistent with the formulation $[(\eta^2$-dpmSe)Pt$(\eta^2$-$S_2CNEt_2)]^+$.

Approximately 3 weeks after the equimolar quantities of Pt-$(S_2CNEt_2)_2$ and dpmSe were mixed, the phosphorus-31 NMR spectrum still shows signals due to $dpmSe_2$ and the dimeric dpm complex but is dominated by the resonances due to [(dpmSe)-Pt(S_2CNEt_2)]$^+$. Both the platinum-195 and selenium-77 satellites for the P(Se) phosphorus resonance are now clearly visible. The resonance due to $dpmSe_2$ is significantly reduced in intensity, while resonances due to [(dpm)Pt(S_2CNEt_2)]$^+$ and dpmSe are absent. The corresponding platinum-195 NMR spectrum is dominated by the doublet of doublets due to [(dpmSe)Pt(S2CNEt$_2$)]$^+$. No signal due to unreacted $Pt(S_2CNEt_2)_2$ remains. The selenium-77 NMR spectrum shows resonances due to [(dpmSe)Pt(S_2CNEt_2)]$^+$ and $dpmSe_2$.

It appears that a selenium atom from $dpmSe_2$ is being inserted into the Pt–P bond of [(dpm)Pt(S_2CNEt_2)]$^+$ and/or *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$ to form [(dpmSe)Pt(S_2CNEt_2)]$^+$ and dpmSe. Confirmation of this reaction is obtained by adding $dpmSe_2$ to a dichloromethane solution containing a mixture of *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$ and [(dpm)Pt(S_2CNEt_2)]$^+$. A reference solution of PPh_3 enclosed in a narrow NMR tube concentric with the normal 10-mm NMR tube was included to enable a direct measure of changes in the intensities of the various resonances to be made. Immediately after mixing, the phos-

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phorus-31 NMR spectrum shows two doublets due to dpmSe as well as an intense singlet due to $dpmSe_2$ indicating that the transfer of some selenium is very rapid. Approximately 2 weeks after the addition of $dpmSe_2$, the doublets due to $[(dpmSe)Pt(S_2CNEt_2)]^+$ are clearly visible and the absolute intensity of the resonance for $dpmSe_2$ is significantly decreased. Insertion of selenium into the four-membered chelate ring of dpm has previously been observed by Peringer.[15] He found that in the presence of $[Cl]^-$ ion, $[Pt(dpm)_2]^{2+}$ reacts with selenium to produce $[(dpm)Pt(dpmSe)]^{2+}$ and finally *cis/trans*-$[Pt(dpmSe)_2]^{2+}$.

Clearly, the interaction between equimolar quantities of $Pt(S_2CNEt_2)_2$ and dpmSe is very complex and involves a number of competing equilibria; Scheme III outlines the proposed mechanism. It is difficult to ascertain whether $(\eta^1\text{-dpmSe})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ forms any $[(dpmSe)Pt(S_2CNEt_2)]^+$ directly by simple chelation. This process may very well accompany the unusual selenium abstraction and insertion reactions described above.

Scheme III

$$Pt(S_2CNEt_2)_2 + dpmSe \xrightarrow{\text{partial reaction}}$$
$$(\eta^1\text{-dpmSe})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2) \xrightarrow{dpmSe\ (-Se)}$$
$$(\eta^1\text{-dpm})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2) + dpmSe_2 \rightarrow$$
$$\tfrac{1}{2}\,cis,cis\text{-}[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+} + dpmSe_2 +$$
$$[S_2CNEt_2]^- \rightarrow [(dpm)Pt(S_2CNEt_2)]^+ + dpmSe_2 +$$
$$[S_2CNEt_2]^- \rightarrow [(dpmSe)Pt(S_2CNEt_2)]^+ +$$
$$dpmSe + [S_2CNEt_2]^-$$

Dichloromethane solutions of $Pt(S_2CNEt_2)_2$ and dpmSe in 1:2 molar proportions produce NMR spectra similar to those for the equimolar reaction mixture. Evidently a second mole of dpmSe cannot compete with the chelation of dpmSe to give the $(\eta^1\text{-dpmSe})_2$ complex.

(ii) Reactions with DpmS. The dpmS samples used in the in situ NMR studies to be described here all contained some $dpmS_2$ (9.7%). All NMR data for this system are given in Table III.

The phosphorus-31 NMR spectrum at 25 °C of a dichloromethane solution containing equimolar quantities of $Pt(S_2CNEt_2)_2$ and dpmS soon after mixing shows two doublets at δ −28.8 and 39.6 due to unreacted dpmS and a singlet at δ 34.2 due to the $dpmS_2$ impurity. Two doublets also appear at δ 0.9 and 33.9 each having platinum-195 satellites. The platinum-195 NMR spectrum contains a singlet due to unreacted $Pt(S_2CNEt_2)_2$, and a doublet of doublets at δ −4285, suggesting that $(\eta^1\text{-dpmS})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ is formed slowly. However, unlike dpmSe, the unreacted dpmS does not abstract the sulfur atom from the pendent P=S in $(\eta^1\text{-dpmS})Pt(S_2CNEt_2)_2$. This result is in accordance with previous observations[17,18] which show that phosphine sulfides are less labile than their selenium analogues.

Ten days later, the phosphorus-31 NMR spectrum shows weak resonances due to dpmS and $(\eta^1\text{-dpmS})Pt(S_2CNEt_2)_2$, but the intensity of the singlet due to $dpmS_2$ impurity is unchanged. Two new doublets at δ 16.7 and 61.7 are also visible, each having platinum satellites. The platinum-195 NMR spectrum still contains resonances due to $Pt(S_2CNEt_2)_2$ and $(\eta^1\text{-dpmS})Pt(S_2CNEt_2)_2$ and another doublet of doublets at δ −4415. This new species is proposed to be $[(dpmS)Pt(S_2CNEt_2)]^+$. One month after mixing, only $dpmS_2$ and $[(dpmS)Pt(S_2CNEt_2)]^+$ remain. Consequently, it appears that the monodentate dpmS ligand in the neutral species $(\eta^1\text{-dpmS})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ slowly chelates to form $[(dpmS)Pt(S_2CNEt_2)]^+$.

Dichloromethane solutions of $Pt(S_2CNEt_2)_2$ and dpmS in 1:2 molar proportions produce NMR spectra similar to those for the equimolar reaction mixture.

(iii) Reactions with ApeSe and ApeS. Remarkably, neither apeSe nor ApeS react with $Pt(S_2CNEt_2)_2$ at room temperature in dichloromethane solution.

Conclusions

The most striking result to emerge from the data presented in this paper is the inability of any of the potentially chelating ligands to displace both dithiocarbamate ligands from $Pt(S_2CNEt_2)_2$. In the $Pt(S_2P\{OEt\}_2)_2$ systems described previously, several of the ligands studies were able to completely displace $[S_2P(OEt)_2]^-$. This provides unequivocal evidence that diethyldithiocarbamate is more strongly bound to platinum than *O,O*-diethyl dithiophosphate.

Although all the ligands, except apeE, are capable of displacing one dithiocarbamate ligand, the chemistry is quite varied and reflects the differences between the chelating powers of the ligands. Dpe reacts rapidly with $Pt(S_2CNEt_2)_2$ to give $[(dpe)Pt(S_2CNEt_2)]^+$, and no further reaction occurs with additional dpe or any monodentate phosphine. However, ape reacts with $Pt(S_2CNEt_2)_2$ to give $(\eta^1\text{-ape})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$, which slowly gives $[(ape)Pt(S_2CNEt_2)]^+$. Since the ring sizes of dpe and ape are identical, these results suggest that the platinum–arsenic bond is weaker than the platinum–phosphorus bond, and it has been suggested that arsenic is a weaker σ-donor than phosphorus.[18] This was confirmed by reacting $[(ape)Pt(S_2CNEt_2)]^+$ with other phosphine ligands.

The evidence indicates that the chelating power of dpm is also significantly weaker than that of dpe. Although the formation of $[(dpm)Pt(S_2CNEt_2)]^+$ is complex, nevertheless, once formed, its chemical behavior is similar to that of $[(ape)Pt(S_2CNEt_2)]^+$ in the sense that the chelate ring is cleaved by other phosphines. Consequently, the chelating ability of dpm is comparable to that of ape but their poor chelating powers relative to that of dpe are due to different reasons. In the case of ape, the poor chelating ability is due to the weak platinum–arsenic bond but with dpm it is due to strain in the four-membered chelate ring.

The behavior of the dpmE ligands is also varied, despite the fact that the final product in both cases is $[(dpmE)Pt(S_2CNEt_2)]^+$. Both initially give $(\eta^1\text{-dpmE})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ in which dpmE is bonded to platinum through phosphorus, and the subsequent behavior is dependent upon the kinetics of reaction at the P=E bond rather than the Pt—P or Pt—E bond. The conversion of $(\eta^1\text{-dpmSe})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ to $[(dpmSe)Pt(S_2CNEt_2)]^+$ is extremely complex and involves selenium abstraction and then selenium insertion so that the formation of the final product is achieved via dpm complexes. In contrast, while the conversion of $(\eta^1\text{-dpmS})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ to $[(dpmS)Pt(S_2CNEt_2)]^+$ is slow, no other intermediates are detected.

The nonreaction of the apeE igands with $Pt(S_2CNEt_2)_2$ is surprising. In the dithiophosphate system, the apeE ligands generate $(\eta^1\text{-apeE})Pt(\eta^1\text{-}S_2P\{OEt\}_2)(\eta^2\text{-}S_2P\{OEt\}_2)$, but in the dithiocarbamate system, even this limited complex formation is not achieved, probably due to the stronger chelating ability of the dithiocarbamate ligand compared with that of the dithiophosphate and the relatively weak donor ability of arsenic.

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Registry No. dpmSe, 23176-19-4; $dpmSe_2$, 16675-12-0; apeS, 114582-76-2; apeSe, 77386-60-8; dpm, 2071-20-7; $Pt(\eta^2\text{-}S_2CNE_2)_2$, 15730-38-8; $(\eta^1\text{-ape})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$, 119480-09-0; $[(\eta^2\text{-ape})Pt(\eta^2\text{-}S_2CNEt_2)]^+[BPh_4]^-$, 119480-11-4; $(\eta^1\text{-dpm})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$, 119480-12-5; $[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$, 119480-13-6; $[(dpm)Pt(S_2CNEt_2)]^+[BPh_4]^-$, 119502-85-1; $(\eta^1\text{-dpmSe})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$, 119480-14-7; $[(dpmSe)Pt(S_2CNEt_2)]^+$, 119480-15-8; $[(\eta^2\text{-dpe})Pt(S_2CNEt_2)]^+[BPh_4]^-$, 119480-17-0; $[(\eta^1\text{-ape})_2Pt(S_2CNEt_2)]^+$, 119480-18-1; $[(\eta^1\text{-dpm})_2Pt(S_2CNEt_2)]^+$, 119480-19-2; $(\eta^1\text{-dpmS})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$, 119480-20-5; $[(\eta^2\text{-dpmS})Pt(S_2CNEt_2)]^+$, 119480-21-6; ^{195}Pt, 14191-88-9; $[(PPh_3)_2Pt(S_2CNEt_2)]^+$, 47865-97-4; $[(PPh_3)(\eta^1\text{-ape})Pt(S_2CNEt_2)]^+$, 119480-22-7; $[(PPh_3)(\eta^1\text{-dpm})Pt(S_2CNEt_2)]^+$, 119480-23-8.

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