Syntheses and Structures of the Five-Coordinate Complexes [M(N-N)([9]aneS$_3$)](PF$_6$)$_2$ (M = Pd, (N-N) = 2,2′-Bipyridine; M = Pt, (N-N) = 1,10-Phenanthroline; ([9]aneS$_3$) = 1,4,7-Trithiacyclononane)

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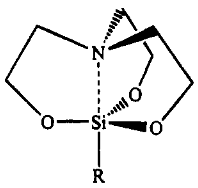
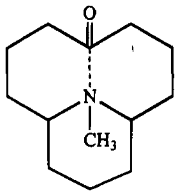
Syntheses and crystal structure determinations of [Pd(bpy)([9]aneS$_3$)][PF$_6$]$_2$ (bpy = 2,2′-bipyridine; [9]aneS$_3$ = 1,4,7-trithiacyclononane) and [Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$ (phen = 1,10-phenanthroline) are reported. The Pd compound ($C_{16}H_{20}N_2S_3PdP_2F_{12}$) crystallizes in triclinic space group $P\bar{1}$ (No. 2), with a = 10.376(3) Å, b = 10.810(2) Å, c = 10.907(2) Å, α = 84.25(1)°, β = 87.25(2)°, γ = 84.89(2)°, D_c = 2.009 g cm^{-3}, and Z = 2; the Pt compound ($C_{18}H_{20}N_2S_3PtP_2F_{12}$) crystallizes in orthorhombic space group *Pbca* (No. 61), with a = 15.422(3) Å, b = 10.618(2) Å, c = 31.335(6) Å, D_c = 2.189 g cm^{-3}, and Z = 8. Each structure features a five-coordinate metal center in a distorted square-pyramidal geometry. Two diimine nitrogens and two of the S-donors of [9]aneS$_3$ are bound in the square plane, (M−N 2.06−2.07 Å; M−S 2.27−2.29 Å), whereas the third sulfur of the thia crown ether occupies the apical position (Pd−S 2.81 Å; Pt−S 2.82 Å). The room-temperature ^{1}H NMR solution spectrum of each complex shows an AA′BB′ pattern in the methylene region. The NMR spectral properties of [Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$ between room temperature and −91 °C in acetone-d_6 solution are interpreted in terms of relatively rapid intracomplex rearrangements ($\Delta G^{\ddagger} \sim 38$ kJ mol^{-1}; $T_c = -80$ °C) similar to the nuclear motions associated with the formation and decay of the transition state in a Pt(II) associative substitution reaction.

Introduction

The coordination chemistry of the thia crown ether 1,4,7-trithiacyclononane ([9]aneS$_3$) with transition metals has been investigated over the past 15 years.[1] It has been shown that [9]aneS$_3$ is capable of stabilizing metal ions in unusual coordination geometries and oxidation states; for example, five-coordinate complexes of d^8 metals have been synthesized and characterized.[1,2] In the case of Pt(II), four sulfur atoms, two from each of two thia crown ethers, form the square-planar platform of a PtS$_5$ structure in which the apical sulfur (from one of the thia crowns) is weakly bonded.[3,4] Electrochemical experiments have established that this ligand environment supports Pt(III), a rare oxidation state for a mononuclear platinum complex.[5]

We are investigating d^8 complexes in which one thia crown ether is replaced with 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy). Solution structures in these cases can be determined readily, since assigning the methylene proton resonances of the remaining crown ether is relatively straightforward.[6] These structures are of great interest because five-coordinate complexes containing a weakly bonded ligand are related to the transition state of a d^8 associative substitution reaction in the same way as silethane complexes and medium-ring compounds with transannular N···C═O interactions model early stages of analogous associative processes at silicon and carbon centers.[7]





We have determined the structures of crystals of [Pd(bpy)([9]aneS$_3$)][PF$_6$]$_2$ (**I**) and [Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$ (**II**). Interestingly, in solution the Pt(II) complex undergoes rapid intramolecular rearrangements that have features in common with key steps in an associative substitution reaction of a square-planar complex.

Experimental Section

Materials. K$_2$PtCl$_4$ and K$_2$PdCl$_4$ were from Strem; 1,4,7-trithiacyclononane, 2,2′-bipyridine, 1,10-phenanthroline, and NH$_4$PF$_6$ were from Aldrich. Omnisol solvents (EM Science) were degassed by flushing them with argon for at least 30 min. Pt(phen)Cl$_2$[8] was prepared according to a literature procedure; Pd(bpy)Cl$_2$ was prepared by an analogous method.

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Table 1. Crystallographic Data

	[Pt(phen)([9]aneS$_3$)](PF$_6$)$_2$	[Pd(bpy)([9]aneS$_3$)](PF$_6$)$_2$
formula	$C_{18}H_{20}F_{12}N_2P_2PtS_3$	$C_{16}H_{20}F_{12}N_2P_2PdS_3$
mol wt	845.57	732.86
color	red	magenta
shape	prismatic rod	diamond shape
crystal system	orthorhombic	triclinic
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
a, Å	15.422(3)	10.376(3)
b, Å	10.618(2)	10.810(2)
c, Å	31.335(6)	10.907(2)
α, deg	90	84.25(1)
β, deg	90	87.25(2)
γ, deg	90	84.89(2)
V, Å^3	5131(2)	1211.4(5)
Z	8	2
D_x, g/cm^3	2.189	2.009
radiation	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
wavelength, Å	0.710 73	0.710 73
μ, cm^{-1}	59.39	12.60
temp, °C	25(2)	20(2)
transm factors	0.926−1.040	0.96−1.02
collection method	ω scans	ω scans
no. of rflns used ($I > 2\sigma(I)$)	4279	4252
$R(F_o)^a$	0.0538	0.0284
$R_w(F_o2)^b$	0.0815	0.0691
$(\Delta/\sigma)_{max}$	0.017	−0.001
goodness of fit	1.406	2.263

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}1/2$, $w = 1/[\sigma^2(F_o^2)]$.

[Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$. Pt(phen)Cl$_2$ (170 mg, 0.38 mmol) and [9]aneS$_3$ (68 mg, 0.38 mmol) were refluxed in a 1:1:1 mixture of distilled water, methanol, and acetonitrile (150 mL) for 3 h under argon. After cooling to room temperature, an excess of NH$_4$PF$_6$ was added to the resulting red solution. The solvent was partially removed, and red crystals of the product precipitated upon cooling to 4 °C. They were washed with ethanol and ether and dried *in vacuo*. FAB: *m/z* = 700.11, parent peak due to {[Pt(phen)([9]aneS$_3$)]PF$_6$}$^+$. ^{1}H NMR: (300 MHz, acetone-*d*$_6$, 22 °C): δ 3.59 (m, 12 H, CH$_2$), 8.32 (t, H$_3$, *J* = 8.4 Hz), 8.49 (s, H$_5$), 9.25 (d, H$_4$, *J* = 6.9 Hz), 9.62 (d, H$_2$, *J* = 5.4 Hz, *J*(PtH) = 36 Hz). ^{13}C NMR (75.47 MHz, acetone-*d*$_6$, 22 °C): δ 34.4 (s, CH$_2$), 128.4, 129.5, 142.6, 152.4 (s, phen).

[Pd(bpy)([9]aneS$_3$)][PF$_6$]$_2$. Reaction of Pd(bpy)Cl$_2$ (100 mg, 0.3 mmol) and [9]aneS$_3$ (55 mg, 0.3 mmol) (Pt conditions) gave magenta crystals. FAB: *m/z* = 586.95, parent peak due to {[Pd(bpy)([9]aneS$_3$)]PF$_6$}$^+$. ^{1}H NMR: (300 MHz, acetone-*d*$_6$, 22 °C): δ 3.66 (m, 12 H, CH$_2$), 8.92 (d, H$_6$, *J* = 5.4 Hz), 8.81 (d, H$_3$, *J* = 8.1 Hz), 8.56 (t, H$_4$, *J* = 8 Hz), 7.95 (t, H$_5$, *J* = 6.6 Hz). ^{13}C NMR (75.47 MHz, acetone-*d*$_6$, 22 °C): δ 35.0 (s, CH$_2$), 126.1, 129.9, 143.5, 151.9 (s, bpy).

Methods. ^{1}H NMR spectra were obtained on Bruker AM-500 and Varian Unity Plus 600 instruments (measurements were made in acetone-*d*$_6$ with TMS as standard). Variable-temperature NMR experiments were performed on a GE-300 MHz FT-NMR spectrometer. Mass spectra were obtained with a fast atom bombardment spectrometer (UC Riverside Mass Spectrometry Facility).

Crystal Structure Analysis. Red crystals of [Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$ (**II**) were grown by vapor diffusion of diethyl ether into a saturated solution of the complex in nitroethane. Magenta crystals of [Pd(bpy)([9]aneS$_3$)][PF$_6$]$_2$ (**I**) were obtained by slow evaporation of an acetone solution. Suitable crystals of each were mounted on glass fibers and centered on an Enraf-Nonius CAD-4 diffractometer using Mo K$\bar{\alpha}$ radiation with experimental conditions given in Table 1. The usual Lp corrections were made as well as absorption corrections based on a series of Ψ scans using the program CRYM.[9] Atomic scattering factors and values for Δ*f*′ and Δ*f*″ were taken from Cromer[10] and Cromer and Waber,[11] SHELXL-93,[12] SHELXS-86,[13] and XP[14] computer programs were used. Both structures were solved using the Patterson method. For [Pd(bpy)([9]aneS$_3$)][PF$_6$]$_2$, the Pd and three S atoms were located; for [Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$, the Pt atom was located; other non-hydrogen atoms were positioned using Fourier difference synthesis. Hydrogen atoms were placed in expected chemical positions and included in final least-squares cycles as riding atoms. The PF$_6$ groups show disordering, but no attempt was made to model this disorder. The only peaks in the final Fourier difference synthesis were near Pt or Pd in the respective structures. For [Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$, a large libration of the complex cation in the plane of the phenanthroline ligand was found, indicating disorder or large thermal motion. Bond distances were corrected for libration using THMA14.[15] Atomic coordinates along with equivalent isotropic displacement parameters for both complexes are given in the Supporting Information.

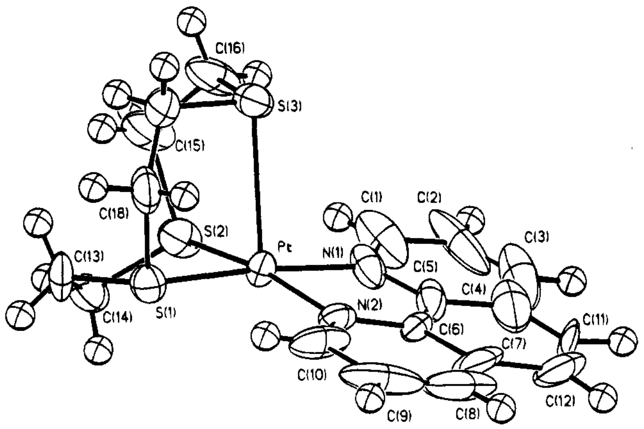

Figure 1. Structure of [Pt(phen)([9]aneS$_3$)]$^{2+}$ (40% probability ellipsoids) showing the atomic numbering scheme.

Table 2. Selected Bond Distances (Å) and Angles [deg]

bond	[Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$	[Pd(bpy)([9]aneS$_3$)][PF$_6$]$_2$
M−N(1)	2.074(10)	2.057(2)
M−N(2)	2.070(9)	2.063(2)
M−S(1)	2.272(3)	2.269(1)
M−S(2)	2.279(3)	2.293(1)
M−S(3)	2.821(3)	2.812(1)
N(1)−M−N(2)	82.1(5)	80.0(1)
N(2)−M−S(1)	93.7(3)	94.6(1)
S(1)−M−S(2)	88.5(1)	87.8(1)
S(1)−M−S(3)	86.5(1)	85.8(1)
S(2)−M−S(3)	85.9(1)	86.1(1)
N(1)−M−S(3)	98.1(3)	99.8(1)
N(2)−M−S(3)	104.6(3)	104.5(1)

Results and Discussion

Crystal Structure. The platinum atom in [Pt(phen)([9]aneS$_3$)]$^{2+}$ is coordinated by two nitrogen and two sulfur atoms in a slightly distorted square plane (Figure 1). The third sulfur occupies an apical position, thereby completing an elongated square pyramid (Table 2). The Pt−S(3) bond length of 2.821(3) Å is considerably longer than the equatorial ones but shorter than the apical distances in other square-pyramidal [9]aneS$_3$−Pt complexes (Table 3). The Pt−S bonds in the square plane are of comparable length. The structural parameters for [Pd(bpy)([9]aneS$_3$)]$^{2+}$ are very similar to those for the Pt compound

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Table 3. M−S Bond Distances (Å) for ML([9]aneS$_3$) Complexes

L	Pd(II)		Pt(II)	
	S_{apical}	S_{eq}	S_{apical}	S_{eq}
[9]aneS$_3$	2.95[a]	2.31−2.33	2.88, 2.93[b]	2.25−2.30
Cl$_2$	3.14[c]	2.25−2.27		
Br$_2$	3.13[d]	2.26−2.28		
Ph$_2$			nonbonded[e]	2.35
bpy	2.81,[f] 2.91[g]	2.27−2.29		
phen	2.95[g]		2.82[f]	2.27−2.28

[a] References 1, 18, and 19. [b] References 1−4. [c] References 1 and 20. [d] Reference 19. [e] Reference 6. [f] This work. [g] Reference 1.

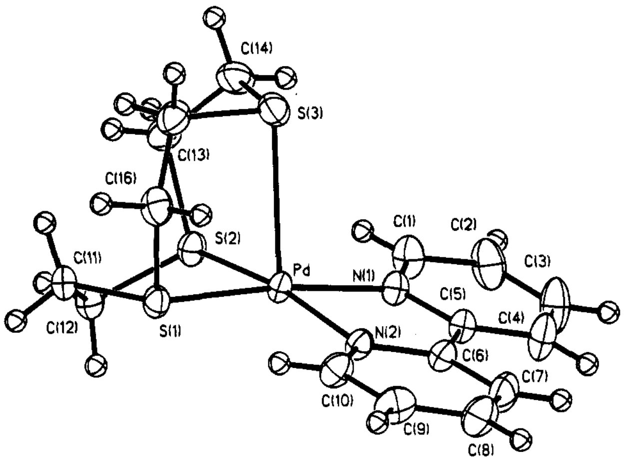

Figure 2. Structure of [Pd(bpy)([9]aneS$_3$)]$^{2+}$ (50% probability ellipsoids) showing the atomic numbering scheme.

(Figure 2, Table 2).[16] It is likely that the π-acceptor character of the diimine ligand is responsible for the relatively enhanced apical bonding in [Pt(phen)([9]aneS$_3$)]$^{2+}$ and [Pd(bpy)([9]aneS$_3$)]$^{2+}$. Back-bonding of metal d_{xz} and d_{yz} electrons into diimine π* orbitals increases the positive charge at the metal center and, as a consequence, enhances the electrostatic interaction between the metal and the apical sulfur. Strong σ donors like phenyl ligands, on the other hand, reduce the metal positive charge and disfavor apical bonding interactions (Table 3). It is apparent that apical interactions in square pyramidal Pd and Pt complexes can be influenced significantly by the electronic nature of the equatorial ligands.

Solution Structure. The 500 MHz ^{1}H NMR solution spectrum of the thia crown ether in [Pt(phen)([9]aneS$_3$)]$^{2+}$ shows an AA'BB' pattern centered at $\delta = 3.59$ ppm (Figure 3). It is likely that the observed slight asymmetry is caused by additional coupling to ^{195}Pt (34% natural abundance).[17] Raising the solution temperature to 50 °C did not alter the signal. However, upon cooling, the sharp signal present at room temperature started to broaden; then it collapsed and eventually coalesced at $T_c \approx -80$ °C. Further cooling led to a splitting into two bands with a ratio of 2:1 (Figure 4). Unfortunately, the freezing point of acetone (−94 °C) prevented further resolution. Our data indicate that the free energy of activation $\Delta G^{\ddagger}$ for the process at T_c is approximately 38 kJ mol^{-1}.[21] The Pd analog showed similar behavior; however, the point of coalescence lies at even lower temperature and could not be reached within the limits imposed by the solvent.

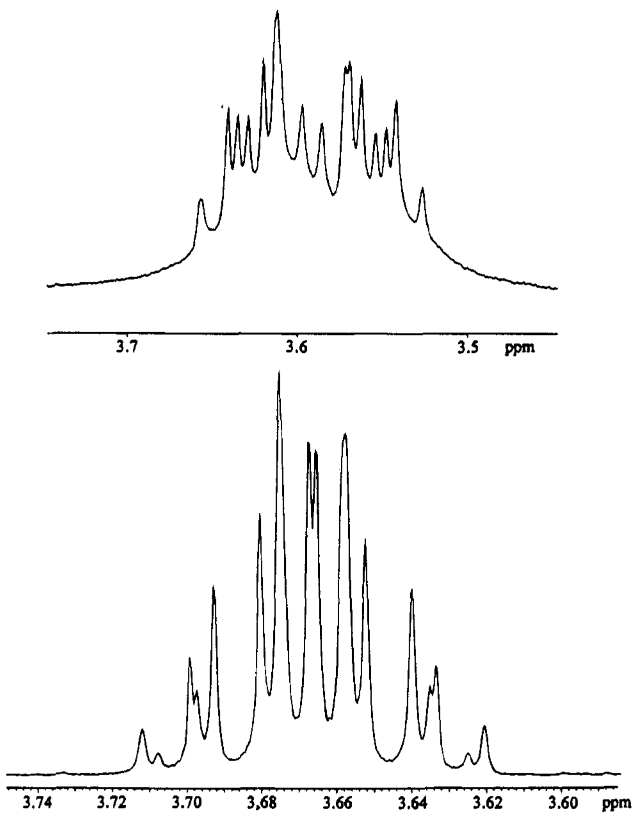

Figure 3. ^{1}H NMR spectra (methylene region) of [Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$ (top, 500 MHz) and [Pd(bpy)([9]aneS$_3$)][PF$_6$]$_2$ (bottom, 600 MHz) in acetone-d_6 solution.

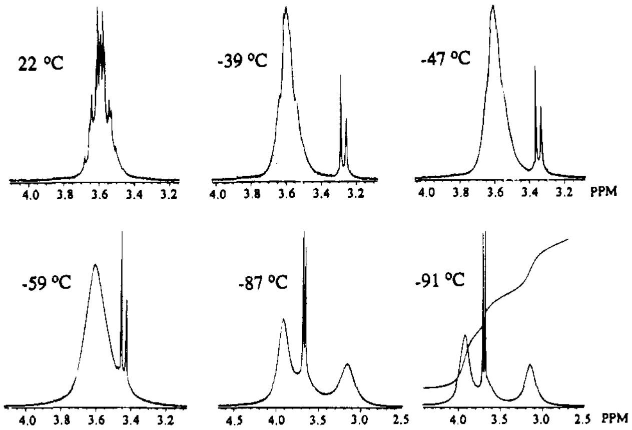

Figure 4. ^{1}H NMR spectra (methylene region) of [Pt(phen)([9]aneS$_3$)][PF$_6$]$_2$ between room temperature and −91 °C in acetone-d_6 solution. The additional sharp double peak seen at lower temperatures is due to H$_2$O; it is strongly temperature dependent.

It is likely that the thia crown ether in [Pt(phen)([9]aneS$_3$)]$^{2+}$ undergoes a rapid intramolecular rearrangement at room temperature similar to that of a dimethylplatinum−tripod complex.[22] In this rearrangement, the apical sulfur approaches the platinum center, forming a square-pyramidal structure (with three equal

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(16) The phenanthroline ligand in [Pt(phen)([9]aneS$_3$)]$^{2+}$ shows strong disorder at the outer carbon positions; this disorder is probably caused by large thermal motions. In the Pd analog with bpy as the π-acceptor, there is no disorder of the cation.

(17) The 600 MHz spectrum (methylene proton region) of the Pd analog shows the expected symmetric resonance pattern (Figure 2), since the methylene protons are not coupled to the metal center.

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(21) $\Delta G^{\ddagger} = RT_c[22.96 + \ln(T_c/\delta\nu)]$ [J mol^{-1}]: Günther, H. *NMR-Spektroskopie: Grundlagen, Konzepte und Anwendungen der Protonen- und Kohlenstoff-13-Kernresonanz-Spektroskopie in der Chemie*; Georg Thieme Verlag: Stuttgart, New York, 1983; Chapter 9.

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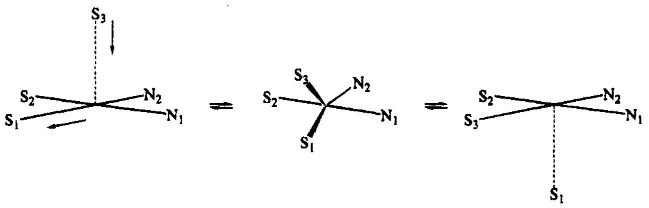
Pt−S bond distances) that relaxes first to a trigonal bipyramid (Berry mechanism) and then to a 4+1 geometry that is equivalent to the starting configuration.[23]



The nuclear rearrangement in $[Pt(phen)([9]aneS_3)]^{2+}$ is a 6-fold degenerate rotation of the thia crown ether (each rotation is a 1,4-metallotropic shift; Figure 5). Owing to this fluxionality, the sulfur atoms and the methylene protons are equivalent in solution. The molecule in the crystal can be considered as a substrate (Pt)−reactant (S) pair in spatial proximity (fixed by $[9]aneS_3$) that is about to start its journey toward a five-coordinate transition state. The fluxional process in $[Pt(phen)([9]aneS_3)]^{2+}$ is closely analogous to that of $[PtMe_3([12]aneS_4)]^+$.[24] In this octahedral Pt(IV) complex, $[12]aneS_4$ is bound with three sulfurs *fac* to the Pt center, and the remaining sulfur is not coordinated. The thia crown ether undergoes a series of rapid 1,4-metallotropic shifts ($\Delta G^{\ddagger}_{298} \sim 57$ kJ mol^{-1}). The low activation barrier is most likely related to the favorable position of the noncoordinated sulfur in the Pt(IV) molecule. In line with this interpretation, we suggest that the preorganized ligand configuration in $[Pt(phen)([9]aneS_3)]^{2+}$ accounts for its minimal intramolecular nuclear reorganization energy.[25] The intramolecular rearrangements of $[Pt(phen)([9]aneS_3)]^{2+}$ are closely related to the nuclear motions that have been proposed for the formation and decay of the five-coordinate transition state in a Pt(II) ligand substitution reaction.[26]

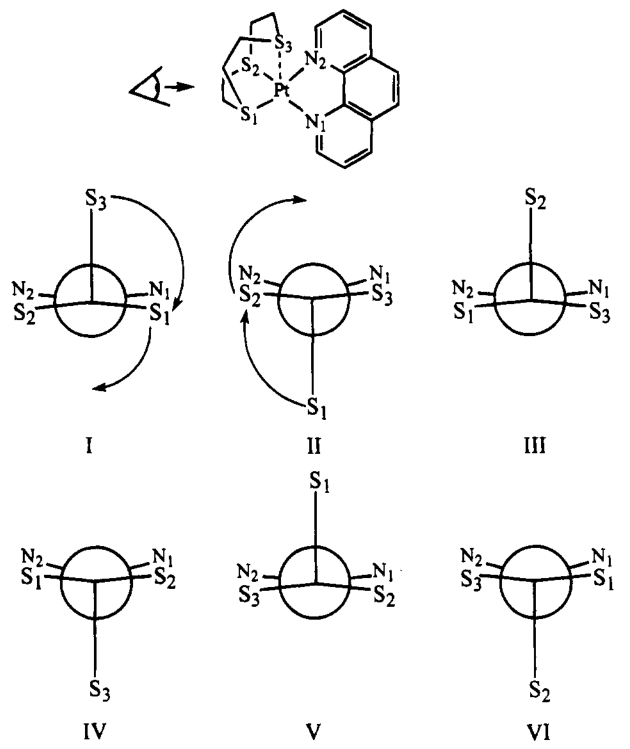


Figure 5. Sequence of 1,4-metallotropic shifts [I−VI (Newman projections)] in the 6-fold degenerate intramolecular rearrangement in $[Pt(phen)([9]aneS_3)]^{2+}$.

Acknowledgment. We thank Scott Ross for the 600 MHz ^1H NMR measurements. H.N. acknowledges the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship. This work was supported by NSF Grant CHE93-11587.

Supporting Information Available: Tables giving a summary of crystallographic data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates for $[Pd(bpy)([9]aneS_3)][PF_6]_2$ (**I**) and $[Pt(phen)([9]aneS_3)][PF_6]_2$ (**II**) (13 pages). Ordering information is given on any current masthead page.

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(23) A dissociative pathway (as discussed as an alternative process for the tripod complex[22]) can be ruled out due to steric constraints present in the thia crown ether.

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