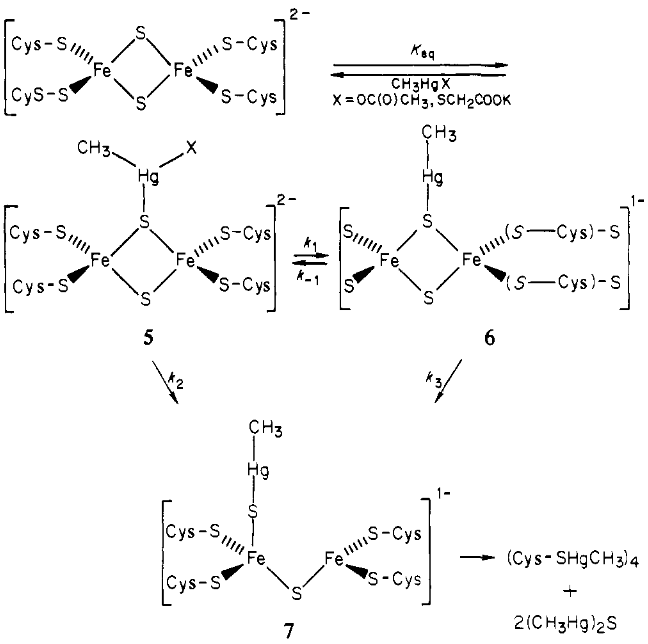
Scheme I



the sulfur-bound mercurial CH_3HgSCH_2COOH. Since we note the *opposite* behavior in the present study, we conclude that the relative electrophilicity of the attacking mercurial is more important than the bridging capacity of the ligands. These observations tend to preclude a concerted four-center transition state such as **3** and suggest an intermediate like **5** where the bioligand is initially bonded to CH_3HgX at the more nucleophilic labile sulfur (Scheme I). The facile extrusion of sulfur from AD with CH_3HgOAc is consistent with a rapid preequilibrium where the effective concentration of complex **5** would be much higher for the more ionic mercurial CH_3HgOAc.[15] In aqueous medium, complex **6** may arise directly either by collision with CH_3Hg^+ or by loss of acetate anion from **5**. Our kinetic data do not allow us to make this distinction. However, with CH_3HgSCH_2COOK, prior ionization to CH_3Hg^+ would be highly improbable, and the rate-limiting step in the reaction should depend upon the ratio k_2/k_1. It seems unlikely that simple ionization with loss of RS^- from **5** (k_1) would be either rapid or reversible in the hydrophobic environment of the iron–sulfur chromophore. We therefore suggest a rate-limiting Fe–S bond rupture in **5** with concerted loss of RS^- (k_2) and subsequent rapid stepwise extrusion of the remaining mercaptides in **7** as a consequence of the disruption of the core ion stability afforded by the intercluster electron delocalization.

In conclusion, we have provided kinetic data which provide a clear distinction between a concerted-type extrusion pathway and one that proceeds by initial attack of CH_3Hg^{II} at nucleophilic sulfur. The observed reaction of an alkyl mercury mercaptide with the iron–sulfur cluster provides yet another demonstration of the tenacity with which mercury bonds to sulfur, providing a target for methylmercury poisoning.

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[15] The equilibrium constant for complexation of CH_3SCH_3 with CH_3HgOAc in CH_2Cl_2 is surprisingly small, $K_f = 0.04$. However, complexation of dimethyl sulfide with CH_3HgSCH_3 was too small to measure by our highly sensitive ^{199}Hg NMR method. Since we see no discernable change in the mercury resonance upon addition of excess dimethyl sulfide, we suggest that K_f is at least two orders of magnitude lower than that with CH_3HgOAc (unpublished results).

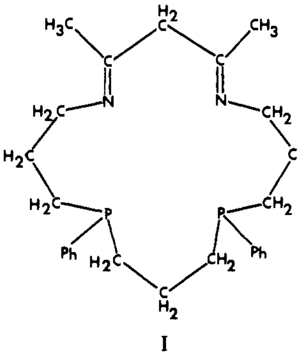
Communications to the Editor

First Synthesis, Characterization, and X-ray Structural Determination of the Macrocyclic Phosphineamine Complex $[Ni(Me_2[16]dieneN_2P_2)](PF_6)_2 \cdot 0.5H_2O$

Sir:

The chemical literature is replete with examples of macrocyclic metal complexes containing tetradentate ligands with N_4, O_4, N_2O_2, and N_2S_2 donor sets.[1,2] Similar complexes with PN_3, P_4, and P_2S_2 type ligands are few in number and have been reported only recently.[3-8] To date, the only method reported for the synthesis of complexes with any mixed macrocyclic P–N ligands has involved refluxing 2,6-diacetylpyridine with the required phosphinodiamine and metal salt.[3,9]

In this communication, we report the synthesis of the first metal complex containing a cyclic N_2P_2 Schiff base ligand, 14,16-dimethyl-5,9-diphenyl-5,9-diphosphino-1,13-diazacyclohexadeca-13,16-diene, hereafter abbreviated $Me_2[16]dieneN_2P_2$.[10] The ligand has two phosphorus and two nitrogen donor atoms equally distributed along the 16-membered ring as shown in I.



I

The macrocyclic structure has been verified by single-crystal X-ray diffraction analysis of the hydrated Ni(II) complex, $[Ni(Me_2[16]dieneN_2P_2)](PF_6)_2 \cdot 0.5H_2O$. This work represents the first X-ray structure determination on any metal complex containing a P–N macrocyclic ligand. Preliminary to the preparation of this 16-membered ring complex, a 14-membered ring complex, $[Ni(Me_2[14]dienatoN_2P_2)] \cdot PF_6$, was prepared as well as two 5-coordinate chlorobis(tertiary phosphino)diamine metal complexes of cobalt(II) and nickel(II). Structures of the latter

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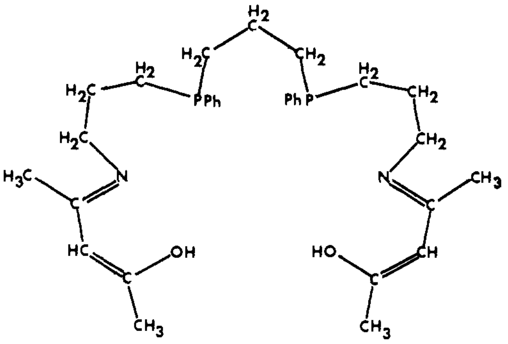
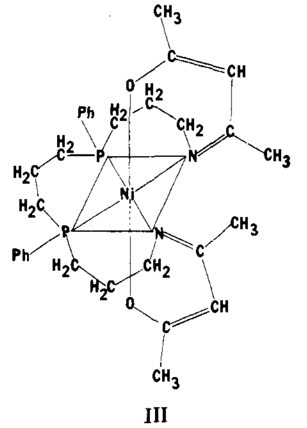
two complexes also have been completed and will be reported later.[11]

Synthesis of $[Ni(Me_2[16]dieneN_2P_2)](PF_6)_2\cdot 0.5H_2O$ first required preparation of the linear tetradentate phosphineamine ligand, $3,3,3\text{-}P_2N_2$, by the method of Isslieb[12] except that THF rather than liquid NH_3 was used as solvent. Attempts to prepare the macrocyclic complex by the in situ reaction of $3,3,3\text{-}P_2N_2$, H(acac), and $Ni(OAc)_2\cdot 4H_2O$ in aqueous solution, analogous to the method we developed earlier for tetraaza systems,[13] proved unsuccessful. We therefore used an alternate method which required synthesis of the linear, sexadentate Schiff base ligand bis(acetylacetone)trimethylenebis[(3-aminopropyl)phenylphosphine] (II) by condensation of 2 equiv of H(acac) with 1 equiv of $3,3,3\text{-}P_2N_2$ in methanol. During 16 h of reflux under N_2, the solution changed from colorless to pale yellow. The ^1H NMR spectrum of the sexadentate ligand exhibits signals at δ 7.6–7.3 (m), 4.9 (s), 3.5–3.0 (m), and 2.1–1.6 (m) downfield from Me_4Si, with relative intensities close to 5:1:2:13. The peaks have been assigned to the phenyl, vinyl, methylene adjacent to >C=N, remaining methylene, and methyl protons, respectively. The presence of a broad singlet at 10.7 ppm due to two OH protons, as well as the singlet which integrates for two vinyl protons, indicates that the ligand exists predominantly in the enol form.



II

When 1 equiv of $Ni(OAc)_2\cdot 4H_2O$, dissolved in methanol, was added dropwise to a methanolic solution of the sexadentate ligand, and the resulting solution was refluxed for 16 h, the solution became reddish brown [a color which suggests formation of the sexadentate Schiff base Ni(II) complex]. At this point, 90% of the methanol was removed by distillation and replaced with deaerated water which had been adjusted to pH 4 with HOAc. A second reflux period of 16 h caused a color change from red-brown to orange. Yellow crystals of $[Ni(Me_2[16]dieneN_2P_2)](PF_6)_2\cdot 0.5H_2O$ were isolated from the orange solution after 2 equiv of $NaPF_6$ were added and the solution was chilled. The successful synthesis of the macrocyclic complex presumably involves acid-catalyzed intramolecular rearrangement of the 6-coordinate Schiff base Ni(II) complex III although this species was never isolated. Other work in our laboratory has led to the isolation of Co(III) complexes of this type.[14] Rearrangement requires the elimination of 1 equiv of H(acac) as the ring is closed. We have reported similar procedures for the synthesis of tetraaza macrocycles; however, in these cases, the sexadentate precursors were always isolated before further reaction.[15]



III

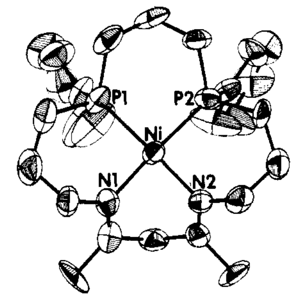


Figure 1. Above the plane view of the macrocyclic $[Ni(Me_2[16]dieneN_2P_2)]^{2+}$ cation.

Table I. Bond Lengths and Angles within the Cationic Macrocycle[a]

type	length, Å	type	angle, deg
Ni-P1	2.193 (4)	P1-Ni-P2	91.5 (2)
Ni-P2	2.191 (5)	N1-Ni-N2	87.2 (3)
Ni-N1	1.919 (9)	P1-Ni-N1	90.7 (3)
Ni-N2	1.927 (8)	P2-Ni-N2	90.4 (3)

[a] Numbers in parentheses following each datum are the estimated standard deviations in the last significant figure.

Yellow crystals of $[Ni(Me_2[16]dieneN_2P_2)](PF_6)_2\cdot 0.5H_2O$ are diamagnetic in the solid state with $\mu_{eff} = 0.9\ \mu_B$ (296 K). Conductivity studies in dry, deaerated acetone give values ($\Lambda_M = 212\ \Omega^{-1}\ cm^2\ mol^{-1}$) which are indicative of a 2:1 electrolyte. The visible spectrum was nearly identical in acetone and the solid state, and showed a single absorption band at 380 μm (ϵ 606) or 390 μm, respectively. The spectral and magnetic data are consistent with singlet ground state, square planar Ni(II).

Infrared, NMR, and elemental analyses also indicated the macrocyclic structure. A strong infrared active band at 1670 cm^{-1} is assigned to the >C=N stretching vibration. No absorptions attributable to NH_2 or >C=O groups are observed. Elemental analyses and the integrated intensities from ^1H NMR measurements indicate that one ketoimine moiety has been eliminated. Proton NMR spectra (90 MHz in acetone-d_6) showed signals in four distinct regions, δ 7.9–7.3 (m), 4.7 (s), 4.0–3.8 (m), and 2.8–2.1 (m), downfield from Me_4Si. The signals are assigned to protons of the phenyl rings, protons of the CH_2 group of the diimine ring, methylene protons adjacent to the >C=N group, and the remaining methylene and methyl protons. The integrated relative intensities are in good agreement with the required ratios of 5:1:2:10. The presence of two methylene protons in the diimine ring suggests the diene rather than dienato form of the macrocyclic ligand. The $^{31}P\{^1H\}$ NMR spectrum consists of a sharp singlet at −4.30 ppm from H_3PO_4. The presence of only one type of phosphorus indicates that the complex exists as one geometric isomer, either meso or racemic.

X-ray analysis confirms the meso structure of the macrocyclic complex. The molecule crystallizes in the monoclinic space group $P2_1/c$, with $a = 14.10$ (2), $b = 12.38$ (2), $c = 20.21$ (3) Å, and $\beta = 105.0$ (1)° ($\lambda = 0.71069$ Å, Mo Kα radiation). Intensity data were gathered at room temperature by means of a computer-controlled Picker FACS-1 diffractometer with $2\theta < 37°$. Refinement by block matrix with 2626 unique reflections yielded a conventional R factor of 0.076. There were four molecules of $[Ni(Me_2[16]dieneN_2P_2)](PF_6)_2$ with some disordered H_2O

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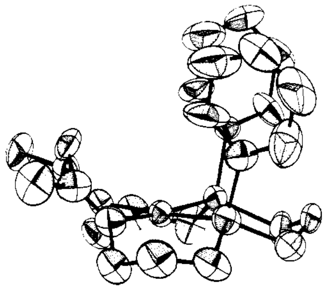

Figure 2. Side view of the macrocyclic cation illustrating the cavity created by the phenyl rings and tilted diimine ring.

(population factor 0.47) per unit cell. The experimental value of the density, 1.53 (1) g/cm^3, vs. a calculated value of 1.55 g/cm^3 is consistent with the X-ray data. Figure 1 shows the general features of the cation. The bond distances and angles of five atoms in the coordination sphere are listed in Table I.

The two P and two N atoms are coplanar within ±0.004 (4) Å, and the Ni atom lies 0.07 Å out of plane on the side opposite the two phenyl rings. The diimine ring exists in the boat conformation with two C=N bond distances of 1.28 (2) and 1.29 (2) Å. This compares to C=N bond distances of 1.285 (9) and 1.265 (9) Å found in the tetraaza macrocyclic complex, $[Co(Me_2[14]dieneN_4)\cdot H_2O](PF_6)_2$.[16] The difference in ring strain in the 16-membered macrocycle compared to the 14-membered one is illustrated by distortion of the bond angle at the methylene carbon in the diimine ring. Puckering of this ring in the $[Ni(Me_2[16]dieneN_2P_2)]^{2+}$ system results in a bond angle of 112.9°, which is much closer to the expected sp^3 angle of 109.5° than the 121.9° angle observed in the more highly strained $[Co(Me_2[14]dieneN_4)\cdot H_2O]^{2+}$ system.[16]

A significant structural difference between the N_4 and N_2P_2 complexes is apparent when the angles between planes defined by the four donor atoms and the two C=N bonds are compared for the two molecules. This difference is highlighted in the ORTEP drawing shown in Figure 2 which shows that the plane defined by the two imine bonds is oriented at 45° with respect to the N_2P_2 plane. The angle between similar planes in the Co(II) complex is ~0°. The required conformation of the trimethylene chains connecting the P and N donor atoms in the 16-membered ring complex induces the 45° angle and creates a saddle-shaped cavity on one side of the molecule. Recent work in our laboratory on the tetraaza macrocyclic systems has shown that $[Co(Me_2[14]dieneN_4)\cdot H_2O](PF_6)_2$ reacts with dioxygen in low-temperature solutions containing Lewis bases to form 1:1 oxygen adducts.[17] We anticipate that 1:1 oxygen adducts of $[Co(Me_2[16]dieneN_2P_2)](PF_6)_2$ may be more stable due to the presence of the cavity in the coordinated N_2P_2 ligand which could provide a protective, somewhat hydrophobic pocket for the coordinated dioxygen. Work is in progress to test this hypothesis, and to extend the synthetic methods described here to other metal complexes with macrocyclic N_2P_2 ligands of varying ring size and charge.

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Supplementary Material Available: Positional and thermal parameters for $[Ni(Me_2[16]dieneN_2P_2)](PF_6)_2\cdot 0.5H_2O$ (3 pages). Ordering information is given on any current masthead page.

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[18] (a) Department of Chemistry. (b) Department of Geology.

Neutral Products of Ion-Molecule Reactions

Sir:

We have developed a technique for the collection and characterization of neutral products formed in gas-phase ion-molecule reactions. Our new procedure involves the collection of neutral reaction products from a flowing afterglow with an inert sampling column. We then employ a combined gas chromatograph/mass spectrometer/data system (GC/MS/DS) to separate and analyze the products.

Past mechanistic studies of gaseous ion reactions have generally been based upon identification of the ionic products.[1] A method of neutral product characterization would provide a new, complementary avenue for studying these reactions. Given the great rewards to be gained from the analysis of these neutrals, it is not surprising that several efforts have been made in this direction.[2] Our approach is centered on a flowing afterglow because it generates an immense number of ions, which can then be converted into large quantities of neutral products.

The reaction we have studied involves fluoride ion and neopentyl chloride (**1**) (eq 1). Olmstead and Brauman have measured the rate of this reaction in an ion cyclotron resonance spectrometer

$$\underset{\mathbf{1}}{(CH_3)_3CCH_2Cl} + F^- \rightarrow \underset{\mathbf{2}}{(CH_3)_3CCH_2F} + Cl^- \qquad (1)$$

(ICR) ($k_1 = 4.9 \times 10^{-10}$ cm^3 s^{-1}) and conjecture that **2** is the neutral product.[3] If this is so, the rate of reaction 1 is remarkably fast in light of what is known about direct displacements at neopentyl centers in solution.[4]

Reaction 1 was carried out by using a flowing afterglow which has been described elsewhere.[5] At the front of the flow tube, fluoride ions were produced by electron impact on NF_3 and entrained by a helium buffer gas (p = 0.5 torr, Q = 12 STP L min^{-1}). Downstream from the ion source, a continuous flow of neopentyl chloride was maintained at a constant pressure of 0.5 mtorr. The reaction is complete within a few centimeters of flow (about 0.5 ms). A quadrupole mass spectrometer at the end of the flow tube continuously monitored ions from m/z 10 to 200. Fluoride is the only ion depleted and Cl^- the only ion produced when **1** is added

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