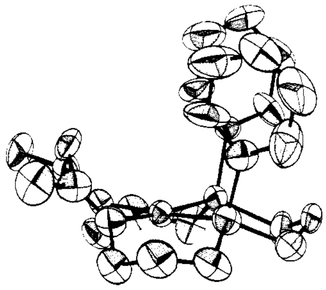

Figure 2. Side view of the macrocyclic cation illustrating the cavity created by the phenyl rings and tilted diimine ring.

(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$_4$)·H$_2$O](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$_2$P$_2$)]$^{2+}$ 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$_4$)·H$_2$O]$^{2+}$ system.[16]

A significant structural difference between the N$_4$ and N$_2$P$_2$ 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$_2$P$_2$ 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$_4$)·H$_2$O](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$_2$P$_2$)](PF$_6$)$_2$ may be more stable due to the presence of the cavity in the coordinated N$_2$P$_2$ 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$_2$P$_2$ ligands of varying ring size and charge.

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Supplementary Material Available: Positional and thermal parameters for [Ni(Me$_2$[16]dieneN$_2$P$_2$)](PF$_6$)$_2$·0.5H$_2$O (3 pages). Ordering information is given on any current masthead page.

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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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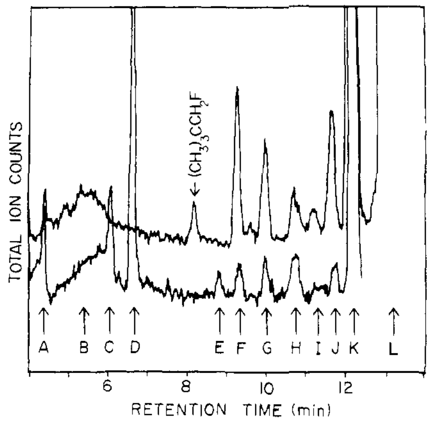

Figure 1. Desorption gas chromatograms from 1-h collections of flow tube gases. Lower trace: no ions present. Upper trace: ions present. All peaks were characterized by their mass spectrum and are identified as (A) NF_3; (B) C_6H_5COOH; (C) CH_2Cl_2; (D) $(CH_3)_2CO$; (E) $(CH_3)_2CHOH$; (F) $CHCl_3$; (G) CF_2ClCCl_2F; (H) $CH_2{=}CHCH_2CH_2Cl$; (I) CH_3CCl_3; (J) CCl_4; (K) $CH_3CHClCH_2CH_3$; (L) $(CH_3)_3CCH_2Cl$.

to the flow reactor. By addition of approximately 2 mtorr of NH_3 to the buffer gas, all positive ion reactions of **1** were suppressed.

The sampling port is 20 cm downstream from the neutral addition inlet. A 10-mm id borosilicate glass collection column was packed with glass wool that had been coated with 2,6-diphenyl-*p*-phenylene oxide–polymer (Tenax-GC[6]). This porous polymer is a relatively inert, reversible sorbent for collection of volatile, environmental samples.[7] Polymer-coated glass wool provides an inert surface for low-temperature condensation of volatile compounds. A small fraction (1.5×10^{-4}) of the gases in the flow tube was diverted to the cooled (−198 °C) collection column. A fluoride ion density of 3×10^8 cm^{-3} produces a like number of **2**, and, with 100% sampling efficiency, we should find about 8 ng of neopentyl fluoride in 1 h.

After collection (15 min to 1 h), the sampling column was removed and connected to the inlet port of a HP 5982A GC/MS/DS. The neutrals were then backflushed at 190 °C and focused at −78 °C onto the head of a $^1/_4$ in. × 6 ft chromatographic column (0.1% SP1000 on Carbopak C). Subsequent temperature-programmed elution coupled with full mass scanning detection by the MS allow unambiguous identification of collected species. Comparison with appropriate standards allows quantitative determination of the collected products.[8]

Figure 1 depicts the results of a typical GC/MS study for a 1-h collection. The lower trace shows neutrals collected with the ion source off (all reagents present but no ions). The upper trace shows a sample collected in the presence of F^-; the only additional peak is due to 6 ng of neopentyl fluoride. A full mass scan of the new peak at 8.3 min absolutely identifies it as the reaction product. Methylene chloride, acetone, and 2-propanol (peaks C, D, and E) are ubiquitous solvents, and all other peaks are due to trace-level impurities in the starting material (**1**). This proves that **2** has been produced by a chemical reaction in our flow tube.

Some serious objections remain. How can we be sure that surface reactions (either on the walls of the flow tube or on the collection column) were not responsible for **2**? Can we say that **2** is produced by a negative ion reaction such as in eq 1 and not an atom or radical reaction? We certainly produce F and NF_2 at the ion source as well as F^-.

Two control experiments answered these questions. Neopentyl chloride alone was injected into the flowing afterglow with no ions present. After deposition of **1** onto the cooled collection column for 30 min, the neopentyl chloride was turned off; F^- was then generated from NF_3, and sampling was continued for 1 h. A chromatogram of this sample shows that **2** is not present. Therefore, our neopentyl fluoride was not produced by surface reactions. Our afterglow is equipped with an ion shutter.[5c] This is a tungsten mesh astride the flow tube. When biased at −100 V, the quadrupole MS indicated that all negative ions were blocked, and yet all neutrals (NF_3, F, NF_2, etc.) were free to pass. We then added **1** downstream from the shutter and collected as before. Again, we could not detect the presence of **2** with our GC/MS/DS (sensitivity for **2** around 100 pg). Both F^- and **1** must interact in the flow tube to produce neopentyl fluoride; radical reactions do not produce our product. These experiments establish that eq 1 is correct as written by Olmstead and Brauman.[3]

Neutral product analysis uniquely characterizes the chemistry of gas-phase ions. This powerful new technique now clears the way for a more complete understanding of ion–molecule reactions in the absence of solvent.

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Facile Syntheses of Tetraalkylchlorin and Tetraalkylporphyrin Complexes and Comparison of the Structures of the Tetramethylchlorin and Tetramethylporphyrin Complexes of Nickel(II)

Sir:

We report facile syntheses of meso-substituted tetraalkylchlorin and tetraalkylporphyrin complexes of some first-row transition metals and provide a comparison of the structures of Ni(TMC) and Ni(TMP), where TMC = 5,10,15,20-tetramethylchlorinato and TMP = 5,10,15,20-tetramethylporphyrinato. The use of metalloporphyrins as models for coordination sites in metallobiomolecules is now of recognized importance.[1] That reduced hemes occur in certain biological systems[2,3] has led to interest in the synthesis of model systems[4,5] involving reduced porphyrins, e.g., chlorins, bacteriochlorins, and isobacteriochlorins. In no instance has there been available an easy route to analytically and isomerically pure samples of metal complexes of reduced porphyrins. To this end, we have turned our attention to the synthesis of the simple TMP and TMC and related tetraalkyl systems.

All suggested syntheses for H_2TMP[6-8] report problems with "contamination" by H_2TMC, probably because H_2TMC has a higher oxidation potential than tetraphenyl- or octaethylchlorin. We find that a template synthesis increases the "contamination" of TMP by TMC to make it the major product. Reaction 1 with R = Me affords different M(TMC)/M(TMP) ratios, depending upon the metal M and the amount of anhydride present. In the presence of 2% acetic anhydride, the following products[9] were

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