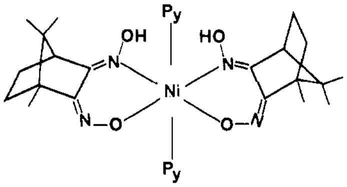

Figure 6. Proposed structure of $[Ni(\delta\text{-}HCQD)_2(py)_2]\cdot CHCl_3$.

absorption at 576 nm remains unchanged over a period of several days. Also there is no evidence of the 614-nm absorption characteristic of $Ni(\delta\text{-}HCQD)_2(py)_2$. Moreover, the pyridine solution remains diamagnetic, which suggests that the $Ni(\delta\text{-}HCQD)_2$ retains its square-planar geometry even in the presence of excess pyridine. These observations strongly indicate that $Ni(\delta\text{-}HCQD)_2(py)_2$ is not a simple trans adduct of $Ni(\delta\text{-}HCQD)_2$, Figure 1. A possible structure for this complex is the one shown in Figure 6 in which the $(HCQD^-)_2$ coordination around the Ni is now *cis*-N_2O_2 as suggested by the IR results. Further evidence in support of this structure is the fact that addition of $AgNO_3$ to a $H_2O/MeOH/CHCl_3$ solution of $[Ni(\delta\text{-}HCQD)_2(py)_2]\cdot CHCl_3$ readily yields the Ni–Ag cluster.

The solvent $(H_2O/MeOH/CHCl_3)$ plays an important role in the preparation of $Ni(\delta\text{-}HCQD)_2(py)_2$. Perhaps its high polarity promotes the isomerization of *trans*-N_2O_2 $Ni(\delta\text{-}HCQD)_2$ to the *cis*-N_2O_2 isomer which then reacts with pyridine.

Since our attempts to prepare similar Ni–Ag cluster complexes with $Ni(HDMG)_2$ and $Pd(\beta\text{-}HCQD)_2$ (in the ternary solvent system) failed, it becomes evident that N,O-chelation of the ligand to the metal is probably a necessary condition for the formation of these hexanuclear cluster complexes.

Acknowledgment. We are grateful to the National Institute of General Medical Sciences (PHS Research Grant No. GM-12626) and the U.S. Department of Energy, Division of Materials Science, for support of this research. Purchase of the JEOL FX-90Q NMR spectrometer was made possible through a grant from the National Science Foundation. We appreciate a useful suggestion made by a reviewer on the structure of one of the compounds.

Registry No. Ni–Ag, 74744-20-0; Pd–Ag, 74744-21-1; $Ni(\delta\text{-}HCQD)_2(py)_2$, 74511-62-9; $Ni(\alpha\text{-}HCQD)_2Ag$, 74498-59-2; $Pd(\alpha\text{-}HCQD)_2Ag$, 74511-63-0; $Ni(\delta\text{-}HCQD)_2$, 52139-64-7; $Pd(\delta\text{-}HCQD)_2$, 72100-35-7; $Ni(\alpha\text{-}HCQD)_2$, 52231-70-6; $Pd(PhCN)_2Cl_2$, 14220-64-5.

Supplementary Material Available: Tables of observed and calculated structure factors for $[Ni(\delta\text{-}HCQD)_2Ag]_3\cdot 2.5CHCl_3$ and for $[Pd(\delta\text{-}HCQD)_2Ag]_3\cdot 2CHCl_3$ and complete tables of interatomic distances and angles and least-squares planes (36 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Queen's University, Kingston, Canada K7L 3N6

Protonation of Dimethylmercury. Complexing Reactions of CH_3Hg^+ in the Gas Phase

JOHN A. STONE,* J. RICHARD M. CAMICIOLI, and MICHAEL C. BAIRD*

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The reactions of dimethylmercury have been examined in a high-pressure, field-free, chemical ionization source with methane as the reagent gas. Both CH_3Hg^+ and $(CH_3)_2HgH^+$ are formed by protonation of $(CH_3)_2Hg$, and both react with $(CH_3)_2Hg$ to yield $(CH_3)_3Hg_2^+$ as the final stable product. This ion reacts with added aromatic, olefinic, and n-donor bases to yield stable methylmercury adduct ions, CH_3HgB^+. The order of stability of these complexes parallels that of the protonated analogues BH^+. It is suggested that $(CH_3)_3Hg_2^+$ and $(CH_3)_2HgH^+$ have similar structures which arise from the attack of the electrophilic CH_3Hg^+ or H^+ on the $CH_3Hg\text{–}CH_3$ σ bond.

The cleavage of transition metal–carbon σ bonds by electrophilic reagents has elicited considerable attention of late.[1] We have been particularly interested in the cleavage reactions of compounds of the type $\eta^5\text{-}C_5H_5Fe(CO)_2R$ with the halogens,[2] mercury(II),[3] and copper(II)[4] and have very recently investigated the stereochemistry of the acid (DCl, CF_3CO_2D) cleavage of the compounds *cis*- and *trans*-(4-methylcyclohexyl)$Fe(CO)_2(\eta^5\text{-}C_5H_5)$.[5] Cleavage in the latter cases yields the corresponding monodeuterated hydrocarbons, with retention of configuration, via a mechanism believed to involve direct protonation of a nonbonding metal d orbital, the highest occupied molecular orbital (HOMO).

During the course of the acid-cleavage work, there appeared a report on the gas-phase protonation of $CH_3Mn(CO)_5$, studied with the use of ICR spectrometry.[6] Interestingly, the ICR data were interpreted in terms of protonation of the manganese compound at *two* sites, either the essentially d orbitals of e and b_2 symmetry or the combination of an e orbital and the a_1 Mn–C σ-bonding orbital. It was possible to correlate the proton affinities of the two sites with photoelectron data for the compound, thus demonstrating the possibility of valuable correlations between the solution-phase and gas-phase protonation reactions of volatile organo transition-metal compounds and their gas-phase ionization potentials.

We have therefore initiated a study of the gas-phase chemistry of representative organometallic compounds, utilizing high-pressure mass spectrometry. We report here a chemical ionization study of dimethylmercury, $(CH_3)_2Hg$, surprisingly little studied heretofore in spite of its ready availability and high volatility. We also report preliminary results on the formation of complex ions by the electrophilic reactions of the methylmercury cation, CH_3Hg^+, with a series of donor ligands.

Experimental Section

A high-pressure, electron-impact ion source patterned on the one described by Kebarle[7] was built. It was usually operated in the field-free mode at ambient temperature, but a repeller field was available. Most results were obtained in the continuous-ionization mode, but time-resolved studies could be made with a pulsed electron beam.[7] The 2-kV beam was pulsed on for 58 μs, and the decay of

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the resultant ion signal was followed for a further 5 ms. Ion counting was employed, and data from repetitive pulses 10 ms apart were accumulated in a Nicolet 1170 signal averager. Conventional CI mass spectra were obtained with an electron beam current of 2 μA. A high-pressure photoionization source[8] was employed for a few ancillary experiments.

Samples were made up in a 5-L heated glass reservoir. A typical sample contained 1 atm of methane, 2 torr of sulfur hexafluoride to capture electrons, 2.5 torr of dimethylmercury, and 2 torr of complexing agent. The sample flowed into the ion source via a heated, all-metal leak valve. The dimethylmercury was >98% pure and was used as received (Strem).

Results and Discussion

Cleavage Reactions. The major ions generated in methane at pressures from 0.1 to 3 torr are CH_5^+ and $C_2H_5^+$. The presence of $\sim 2 \times 10^{-5}$ torr of $(CH_3)_2Hg$ in CH_4 at 0.1 torr resulted in the formation of CH_3Hg^+ and $(CH_3)_2HgH^+$ in roughly equal but small amounts. Increasing the total pressure and/or increasing the concentration of $(CH_3)_2Hg$ led to the appearance of the ion $(CH_3)_3Hg_2^+$, while the previously mentioned ions decreased in importance as did CH_5^+ and $C_2H_5^+$. Other ions which contained only one mercury atom also appeared and increased in yield with increasing pressure, to become the dominant ions at 2–3 torr. These ions arose from impurities, mainly tetrahydrofuran, present in the $(CH_3)_2Hg$, and will be discussed below.

Samples containing equal quantities of $(CH_3)_2Hg$ and C_6H_6 in methane showed only a small peak due to $C_6H_7^+$, whereas samples containing equal quantities of $(CH_3)_2Hg$ and $C_6H_5CH_3$ showed large yields of $C_6H_5CH_3H^+$. Time-resolved studies showed that $C_6H_7^+$ transferred a proton to $(CH_3)_2Hg$ whereas $C_6H_5CH_3H^+$ was unreactive. The proton affinity (PA) of $(CH_3)_2Hg$ is therefore between that of benzene (757 kJ mol^{-1}) and that of toluene (791 kJ mol^{-1}), and proton transfer from both CH_5^+ and $C_2H_5^+$ to $(CH_3)_2Hg$ is exothermic.[9]

If PA[$(CH_3)_2Hg$] is taken as 774 kJ mol^{-1}, then ΔH_f[$(CH_3)_2HgH^+$] is $\sim$586 kJ mol^{-1}. Proton transfer from both CH_5^+ and $C_2H_5^+$ is sufficiently exothermic to cause decomposition to CH_3Hg^+. See reactions 1 and 2.

$$CH_5^+ + (CH_3)_2Hg \rightarrow 2CH_4 + CH_3Hg^+ \qquad \Delta H \approx -230 \text{ kJ mol}^{-1} \tag{1}$$

$$C_2H_5^+ + (CH_3)_2Hg \rightarrow CH_4 + CH_3Hg^+ + C_2H_4 \qquad \Delta H \approx -105 \text{ kJ mol}^{-1} \tag{2}$$

Collisional stabilization of some of the initially excited $(CH_3)_2HgH^+$ must therefore occur to explain the relatively high initial yield of $(CH_3)_2HgH^+$.

Both CH_3Hg^+ and $(CH_3)_2HgH^+$ react with $(CH_3)_2Hg$ to yield $(CH_3)_3Hg_2^+$ (eq 3 and 4).

$$CH_3Hg^+ + (CH_3)_2Hg \xrightarrow{M} (CH_3)_3Hg_2^+ \tag{3}$$

$$(CH_3)_2HgH^+ + (CH_3)_2Hg \rightarrow (CH_3)_3Hg_2^+ + CH_4 \tag{4}$$

The integrity of the methyl group in the product ions is suggested by experiments in which mixtures of $(CH_3)_2Hg$ and $(C_2H_5)_2Hg$ were used. Trialkyldimercury ions were observed corresponding to $(CH_3)_3Hg_2^+$, $(CH_3)_2(C_2H_5)Hg_2^+$, $CH_3(C_2H_5)_2Hg_2^+$, and $(C_2H_5)_3Hg_2^+$. A sample containing $(CH_3)_2Hg$ and $(C_2H_5)_2Hg$ in the molar ratio of 1:14 showed relative yields of the above ions of 1:7:7:<1 at 1.6 torr with no repeller field. On the other hand, the ratio became 1:3:2:<1 with a repeller field of 26 V cm^{-1}.

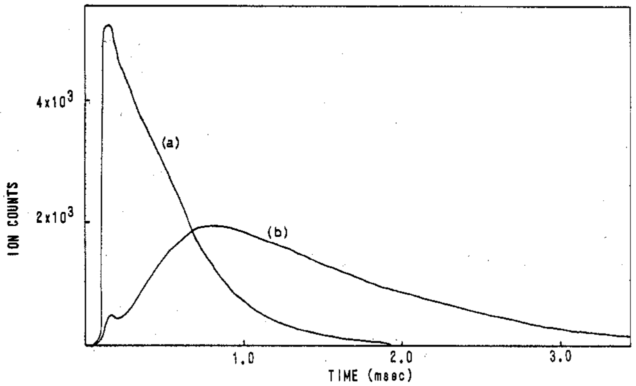
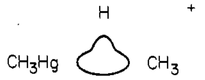


Figure 1. The intensities of (a) $(CH_3)_3Hg_2^+$ and (b) $CH_3HgC_6H_6^+$ ion currents as functions of time after an initial 2-kV electron pulse of 58-μs duration. Each curve is obtained by summing the ions obtained from 3×10^4 pulses.

The initially formed products of the proton-cleavage reaction are completely consistent with known solution chemistry.[12,13] Dialkylmercury compounds, R_2Hg, normally react with protic acids to yield an alkane and an RHg^+ cation, the latter combining with either the solvent or the conjugate base of the reactant acid, i.e.

$$R_2Hg + HX \rightarrow RH + RHgX \tag{5}$$

The mechanism of the reaction is believed to involve overlap of the vacant 1s orbital of the proton with the HOMO of the alkyl compound.[14] In contrast to the iron system discussed above,[1] the HOMO of $(CH_3)_2Hg$ is of essentially mercury–carbon σ-bonding character[14,15] and lies some 5.6 eV above the filled mercury 5d^{10} levels.[15] In the present study, the postulated intermediate, $(CH_3)_2HgH^+$, is observed and probably involves a two-electron, three-centered orbital as in I.

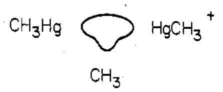


I

Elimination of methane from I is clearly rather facile,[16] and the highly electrophilic product ion, CH_3Hg^+, can interact either with a variety of complexing agents (see below) or with a second dimethylmercury.

$$CH_3Hg^+ + (CH_3)_2Hg \rightarrow \underset{\text{II}}{(CH_3)_3Hg_2^+} \tag{6}$$

The trimethyldimercury cation II is stable in the gas phase and probably has a structure similar to that of I.



II

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Similar species are believed to be intermediates in the cleavage of organomercurials by mercury(II) salts.[13]

Complex Formation. $(CH_3)_3Hg_2^+$ is a methylmercury cation donor, and the introduction of suitable ligands into the reaction mixture leads to the formation of complexes containing the CH_3Hg^+ moiety. For example, in the presence of benzene the only new product ion observed is $CH_3HgC_6H_6^+$ (eq 7). Figure 1 shows that $(CH_3)_3Hg_2^+$ is indeed the precursor of this complex ion.

$$(CH_3)_3Hg_2^+ + C_6H_6 \rightarrow CH_3HgC_6H_6^+ + (CH_3)_2Hg \qquad (7)$$

When two complexing agents are present in comparable concentrations, competition for CH_3Hg^+ occurs, and equilibrium concentrations of the two complex ions can be determined provided that the methylmercury cation affinities of the two complexing agents are comparable. For example, a reaction mixture containing toluene and ethylbenzene yielded $CH_3HgC_6H_5CH_3^+$ and $CH_3HgC_6H_5C_2H_5^+$. These ions were in equilibrium after a residence time of $\sim$400 μs at 0.8 torr. The equilibrium constant

$$K = \frac{[CH_3HgC_6H_5C_2H_5^+]}{[CH_3HgC_6H_5CH_3^+]}\,\frac{[C_6H_5CH_3]}{[C_6H_5C_2H_5]}$$

has a value of 2.6, which leads to a difference in methylmercury cation affinity ($\Delta G°$) of 2.4 kJ mol^{-1} in favor of the ethylbenzene at 298 K.

Even if equilibrium is not attained due to too large a value of $\Delta G°$, the ordering of affinities may be determined. In time-resolved studies, the more stable ion shows a continually increasing relative yield with increasing reaction time. In continuous-ionization studies, the ion current of this complex increases relative to others with increasing ion source pressure, i.e., increasing ion residence time.

An estimate of the strength of the CH_3Hg^+–aromatic bond may be gained from the results of an additional experiment. $C_6H_6^+$ was prepared by photoionization using krypton resonance radiation (10.0 and 10.6 eV) in a high-pressure photoionization source.[8] Helium was the buffer gas, and the pressure was sufficiently low that little $(C_6H_6)_2^+$ was formed. A very small amount of $(CH_3)_2Hg$ was bled into the source from a gas chromatograph, and the $C_6H_6^+$ signal decreased as $CH_3HgC_6H_6^+$ was formed (reaction 8). The same product ion appeared when C_6H_6 entered from the chromatograph to react with $CH_3HgCH_3^+$ formed by photoionization (reaction 9). The ionization potentials of C_6H_6 and $(CH_3)_2Hg$ are 9.24 and 9.10 eV, respectively, and hence in reaction 8 electron transfer is probably the initial event in the reaction complex.

$$(CH_3)_2Hg + C_6H_6^+ \rightarrow CH_3HgC_6H_6^+ + \cdot CH_3 \qquad (8)$$

$$(CH_3)_2Hg^+ + C_6H_6 \rightarrow CH_3HgC_6H_6^+ + \cdot CH_3 \qquad (9)$$

With the assumptions that reaction 9 is thermoneutral and that the initial ion is not excited, $\Delta H_f°(CH_3HgC_6H_6^+) \approx 909$ kJ mol^{-1}. With use of eq 10, a maximum value for the dissociation energy of the complex is $\sim$100 kJ mol^{-1}, which implies a much stronger bond than that due to simple electrostatic attraction.[18]

$$CH_3HgC_6H_6^+ \rightarrow CH_3Hg^+ + C_6H_6 \qquad (10)$$

A series of complexing agents was studied and the ordering of stability found is $(C_2H_5)_3N > (C_2H_5)_2NH \gg i\text{-}C_3H_7C_6H_5 > C_2H_5C_6H_5 > CH_3C_6H_5 > C_6H_5I > C_6H_6 > C_6H_5Br > C_6H_5Cl > C_6H_5F$. At this time only the ordering is reported since the differences in some of the methylmercury cation affinities are too large for accurate equilibrium studies to be carried out. Complexing agents to bridge the gaps are being sought.

The methylmercury cation affinities of the alkylbenzenes are in the same order as their proton affinities, the implication being that the site of attack by H^+ and CH_3Hg^+ is the same. A similar correlation has been reported by Beauchamp et al.[19] for the reaction of $C_5H_5Ni^+$ with a series of n-donor bases, and it is interesting to note that arene–mercury(II) complexes in solution are believed to involve η^1 rather than η^2 or η^6 coordination.[20,21] The gas-phase basicity of fluorobenzene is almost identical with that of chlorobenzene, but very little $CH_3HgC_6H_5F^+$ is present in samples containing equimolar mixtures of C_6H_5F and C_6H_5Cl. No value is available for the gas-phase basicity of iodobenzene, but it is expected to be lower than that of benzene. The greater stability of the iodobenzene complex relative to that of benzene may imply, in this case, bonding through halogen.

The affinities of the amines with respect to CH_3Hg^+ are much greater than those of the substituted benzenes, a not unexpected result since the same behavior is observed with respect to the proton. Complexes containing both one and two basic molecules were observed for $N(C_2H_5)_3$ and $NH(C_2H_5)_2$. In the absence of other complexing agents, the tetrahydrofuran impurity in the $(CH_3)_2Hg$ also gave rise to large yields of $CH_3Hg(THF)_2^+$ as well as the expected $CH_3Hg(THF)^+$. There is obviously no steric hindrance to the attachment of two "typical" bases to the CH_3Hg^+ ion, although 1:1 complexes are the norm in solution.[22]

Studies with olefins led to the series cycloheptatriene > *cis*-1,3-pentadiene > cyclohexene > benzene, but the spectra observed for these are rather complex because of the presence of impurities in the olefins and also, in some cases, because of the formation of more than one complex ion. For example, with cycloheptatriene an ion corresponding to $C_9H_{13}Hg^+$ is observed. This appears to be formed from $C_7H_7^+$, obtained by the reaction of c-C_7H_8 with CH_5^+ or $C_2H_5^+$ (eq 11 and 12).

$$CH_5^+ + c\text{-}C_7H_8 \rightarrow CH_4 + H_2 + C_7H_7^+ \qquad (11)$$

$$C_7H_7^+ + CH_3HgCH_3 \rightarrow C_9H_{13}Hg^+ \qquad (12)$$

The structure of the latter ion may be $CH_3HgC_7H_7CH_3$; i.e., a methyl has been transferred to the ring so that the complex is that of a substituted cycloheptatriene. There are no values for the proton affinities of most of the olefins employed. However, analogies with other olefins suggest that proton affinity increases with the number of double bonds, and therefore again there is a correlation between proton affinity and methylmercury cation affinity.

Using ICR techniques, Bach et al.[23] observed the gas-phase formation of stable ions derived from the reaction of the methylmercury cation with a series of methyl-substituted ethylenes. The reactions were observed to be second order, with the rate constant increasing with increasing methyl substitution. It was observed that the rate constants are in the reverse order of the strengths of the complexes formed between alkenes and Ag^+ ions in solution. The intrinsic reactivity was deemed to be shown by the gas-phase results, the reverse behavior in solution being due to solvent effects.

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Molecular orbital calculations suggested that bonding is due mainly to the overlap of the filled π orbital (HOMO) of the alkene with the vacant orbital of the metal. NMR studies of mercury(II)–olefin complexes in solution appear to be in agreement with this conclusion.[24]

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Registry No. $(CH_3)_2Hg$, 593-74-8; CH_3Hg^+, 22967-92-6; $(CH_3)_3Hg_2^+$, 74381-05-8; $CH_3HgC_6H_6^+$, 74366-54-4.

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Contribution from the Department of Chemistry,
Case Western Reserve University, Cleveland, Ohio 44106

Studies of a Series of Haloaluminum, -gallium, and -indium Phthalocyanines[1]

JOHN P. LINSKY, THOMAS R. PAUL, RONALD S. NOHR, and MALCOLM E. KENNEY*

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Physical and chemical studies have been carried out on the series of phthalocyanines AlPcF, AlPcCl, AlPcBr, AlPcI, GaPcF, GaPcCl, and InPcCl. It is concluded on the basis of mass spectroscopic, infrared, microscopic, X-ray, and other data collected in these studies that AlPcF and GaPcF are polymeric and have $(M–F)_x$ backbones. It is further concluded that the remaining compounds are nonpolymeric.

Introduction

In some of the very early work on phthalocyanines, the compound $(AlPc)_2O$ was discovered.[2] From the findings in this work and work done later,[3] it became clear that $(AlPc)_2O$ is a μ-oxo-bridged compound (Figure 1).

Now a number of other such μ-oxo bridged compounds are known.[3-7] Among these are $(MnPc)_2O\cdot 2py$,[5] $[(Me_3SiO)_2MeSiO][GePcO]_2[SiMe(OSiMe_3)_2]$,[6] AlPcOSiPcOAlPc,[3] $[(Me_3SiO)_2MeSiO][SiPcO]_3[SiMe(OSiMe_3)_2]$,[6] $Me_3SiO(SiPcO)_4SiMe_3$,[7] and $[(Me_3SiO)_2MeSiO][SiPcO]_5[SiMe(OSiMe_3)_2]$[6] (so far no compounds of this type with more than five rings have been reported). The structures of two of these compounds $(MnPc)_2O\cdot 2py$[8] and $[(Me_3SiO)_2MeSiO][SiPcO]_3[SiMe(OSiMe_3)_2]$[9] have been determined.

In addition to these (relatively) low molecular weight μ-oxo-bridged species, three μ-oxo-bridged phthalocyanine polymers are known. These are $(SiPcO)_x$,[10] $(GePcO)_x$,[11] and $(SnPcO)_x$.[12] The silicon polymer is quite stable and has attracted some notice because of this.[13] Recently all three have drawn attention because they become conducting when oxidized with iodine.[14]

In view of this, other phthalocyanines which have similar polymeric structures are of interest. In the present paper, we report on procedures for making two such polymers and on some of the properties of these polymers. The conductivities of these compounds, when oxidized, are described elsewhere.[15]

Experimental Section

AlPcCl. Part of the AlPcCl used was made by a procedure reported earlier.[16] Some of this was sublimed twice at 430 °C under vacuum. This gave a purple sublimate. Anal. Calcd for $C_{32}H_{16}N_8AlCl$: C, 66.85; H, 2.81; Al, 4.69; Cl, 6.17. Found: C, 66.56; H, 2.69; Al, 4.99; Cl, 5.94.

A modification of this procedure was found to be better. In this modified procedure a mixture of phthalonitrile (20 g), aluminum trichloride (5.0 g), and quinoline (distilled twice and then deoxygenated with nitrogen, 100 mL) was refluxed for 30 min. The reaction mixture then was cooled to approximately 0 °C and filtered. The solid thus isolated was washed with benzene, carbon tetrachloride, and acetone and dried at $\sim$110 °C (10.7 g).

For some of the work the compound was recrystallized twice from 1-chloronaphthalene.

AlPcF.[17] A mixture of AlPcCl (2.5 g), concentrated ammonium hydroxide (50 mL), and pyridine (25 mL) was refluxed for 7 h. The resulting solid was filtered, and the filter cake was washed with pyridine, concentrated ammonium hydroxide, and hot water. It was then dried at 110 °C (2.3 g).

A portion of this product, $AlPcOH\cdot H_2O$[3] (2.1 g), was evaporated to dryness on a steam bath with two separate portions of 48% hydrofluoric acid ($\sim$18 mL each time). The resulting solid was washed with water, methanol, pyridine, and acetone and dried at 110 °C (1.9 g). A portion of this was heated to 540 °C under vacuum. The product

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(1) Most of this work was presented at the 162nd National Meeting of the American Chemical Society: Paul, T. R.; Linsky, J. P.; Kenney, M. E. "Abstracts of Papers", 162nd National Meeting of the American Chemical Society, Washington, DC, Sept 1971; American Chemical Society: Washington, DC, 1971; INOR 22.

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