istry of arsenic. Functionalities such as phosphonium methanides and amino groups as well as oxygen are tolerated in the ring closure reaction between the sulfonium ylide complex 1 and the corresponding bis(arsine).

Six-membered ylide–chelate complexes are also accessible by this synthetic route when 1,2-ethylenebis(-phosphines) and -bis(arsines) are employed.

These results deserve additional attention because the ligands generated here in a template reaction are still unknown as free molecules.

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Registry No. 1, 58751-37-4; **2b**, 95531-55-8; **2c**, 50964-61-9; **2d**, 2215-16-9; **2e**, 3134-95-0; **3a**, 83746-96-7; **3b**, 95531-57-0; **3c**, 95531-58-1; **3d**, 95531-59-2; **3e**, 95531-60-5; **4b**, 95531-61-6; **4c**, 95531-62-7; **4d**, 95531-63-8; **4e**, 95531-64-9; **5d**, 95552-52-6; **5e**, 95552-53-7; **7a**, 1663-45-2; **7b**, 23936-60-9; **7c**, 23582-06-1; **7d**, 4431-24-7; **8a**, 95552-54-8; **8b**, 95531-65-0; **8c**, 95531-66-1; **8d**, 95531-67-2; **9a**, 29890-04-8; **9b**, 40544-95-4; **9c**, 40545-10-6; H_2S, 7783-06-4; $Cr(CO)_6$, 13007-92-6; $(CO)_5Cr(C_8H_{14})$, 95531-68-3; chlorodiphenylarsine, 712-48-1; triphenylphosphonium methylide, 19493-09-5; tetracarbonyl(norbornadiene)chromium, 12146-36-0; (*Z*)-cyclooctene, 931-88-4.

A ^{199}Hg FT-NMR and X-ray Structural Study of the Interaction of MeHg^{II} with Pyridines. The Effect of Solvent and Steric Interactions

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A ^{199}Hg FT-NMR study on the extent of complexation of methylmercury with a series of pyridines is described. The formation constants decrease as the steric hindrance around the nitrogen increases in both methylene chloride and nitromethane solvents. However, in methanol solvent one sees a reversal of trends in that the K_f increases on going from pyridine to 2-methylpyridine and levels off with the more hindered 2,6-dimethylpyridine. The increase in complexation is attributed to a ground-state solvation effect on the pyridines. The decrease in hydrogen bonding of the more hindered nitrogenous bases increases their Lewis basicity. An X-ray structural study on the complex of 2-methylpyridine with methylmercury(II) trifluoroacetate shows that the C–Hg–N is nearly linear with trifluoroacetate anion being weakly bound to two mercury atoms forming a losely associated dimeric complex with Hg–O bridging distances of 2.668 (9) and 2.805 (8) Å.

Introduction

The sulfhydryl group has been established to be among the most important binding sites for MeHg^{II} in biological systems.[1] Recently, it has been demonstrated that the imidazole functionality also has a high affinity for methylmercury.[2] This is of particular interest since the imidazole moiety is an integral part of many proteins, and this provides yet another pathway to methylmercury poisoning. Davidson[3] initially showed that DNA was denatured by methylmercury. Subsequently, it was found that MeHg^{II} causes chromosomal damage leading to its mutagenicity.[4] Consequently the interaction of methylmercury and various nitrogenous bases has assumed increased importance.[5,6] Attempts have been made to quantitatively measure the extent of binding of various metal ions with nucleosides and nucleotides.[7] Notable among these are

Table I. Rate Constant Data for Methylation of Pyridines with CH_3I

pyridine	10^5k (25 °C) nitrobenzene[a]	10^4k (60 °C) nitromethane[b]
pyridine	34.3	62.5
2-methylpyridine	16.2	31.3
2,6-dimethylpyridine	1.45	3.36
2-ethylpyridine	7.64	17.1
2-methoxypyridine		NR
2-*tert*-butylpyridine	0.008[c]	

[a] Reference 11. [b] Reference 12. [c] Estimated.

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Table II. Variation of ^1H–^{199}Hg J and log K_f for MeHg$^+$-Pyridine

ligand	^1H–^{199}Hg J, Hz	log K_f
pyridine	229.6	3.8
2-methylpyridine	227.9	4.14
2,6-dimethylpyridine	225.2	4.61

[a] Calculated from the relationship[16b] log K_f = 48.92 – 0.1965 × ^2J.

the pioneering UV spectral studies of Simpson[8] and the Raman studies by Tobias.[9]

As part of a study on the kinetics of the cleavage of disulfides with MeHg^{II},[10a] we recently reported the quantitative measurement of equilibrium constants for complexation of MeHg^{II} with a series of sulfides and disulfides.[10b] Our method is a highly sensitive one that utilizes ^{199}Hg NMR and is readily adaptable to the measurement of relatively small formation constants. We now wish to utilize this methodology to probe the solvation and steric effects involved in the complexation of MeHg^{II} with nitrogenous bases. Conceivably, the quantitative aspects of complexation of MeHg^{II} with model systems can be extrapolated to their binding with comparable protein functional groups. We chose a series of substituted pyridines as model substrates in this study since the effect of steric interactions and solvation phenomena for these aromatic bases have been previously reported.[11,12] A comparison of the reversible protonation of pyridines with their reaction with alkyl halides in the Menschutkin reaction provided an analysis of the effect of steric interactions on chemical behavior.

The Menschutkin reaction involves the direct attack of an amine upon an alkyl halide. Brown[11] and Clarke[12] have used this S_N2 displacement reaction to evaluate the steric and electronic factors involved in the addition of pyridine to methyl iodide. They found that the rate of addition of MeI to pyridine was strongly influenced by steric encumbrance around the nucleophilic nitrogen. The rate of nucleophilic displacement decreases steadily in the series of pyridine, picoline (2-methylpyridine), and lutidine (2,6-dimethylpyridine), and the rate constant is $\sim 10^3$ smaller for the very hindered 2-*tert*-butylpyridine. This obviously is due to a steric retardation of the attack of the nucleophile on the electrophilic center of MeI. Thus, the substitution rate declines sharply as the number and size of the 2 substituents on the pyridine ring increases (Table I). It would appear that a 2-methoxy substituent is anomalous, and this may conceivably be due to an electronic perturbation of the nucleophilic nitrogen as a consequence of the electron-withdrawing oxygen substituent.[13] The resonance interaction of the π-type oxygen lone pair with the aromatic ring cannot increase the basicity at nitrogen since the orbitals are mutually orthogonal.

The above study in dipolar aprotic solvent is consistent with the basic trends anticipated for the steric retardation of S_N2 reactions. In this regard we were particularly intrigued by a series of papers by Canty[14] that reported the ^{199}Hg–^1H coupling constants for complexes of $MeHgNO_3$ with pyridines measured in CD_3OD to decrease within the series pyridine, 2-methylpyridine, and 2,6-dimethylpyridine.

A decrease in the coupling constant (Table II) for MeHgX compounds is usually indicative of an increase in bond order of the MeHg–X bond[15,16] and an attending increase in the log K_f. The coupling interaction between ^{199}Hg and the ^1H has been attributed to a Fermi contact interaction,[17] wherein the coupling constant decreases with a decreasing contribution of the mercury 6s orbital to the ligand–mercury bond. Since a linear relationship between ^{199}Hg–^1H coupling constant and K_f has been established,[15,16] we were able to estimate the K_f for these complexes from the relationship[16b] log K = 48.92 – 0.1965 × $^2J_{^1H-^{199}Hg}$. The results given in Table II strongly suggest that MeHg(II) complexation with pyridines *increases* with increasing ortho-substitution on the pyridine. We now report that this is indeed the case in protic solvent but that the complexation is impeded by steric interactions in nonpolar and polar aprotic solvents.

Experimental Section

All liquid pyridines were distilled from potassium hydroxide. Bipyridyl was used as received from Aldrich Chemical Co. Methanol for spectral measurements was distilled from magnesium activated with iodine and stored under argon. All other solvents were of spectroscopic grade. 2-Ethylpyridine was a generous gift form Riley Tar and Chemical Corp. Indianapolis, IN.

Measurement of ^{199}Hg Spectra.[18] The ^{199}Hg spectra for all methylmercury compounds were measured by using a Nicolet NT-300 spectrometer equipped with a Nicolet 1180 data system using a NTCFT-1180 software package. All spectra were measured at a frequency of 53.712 282 MHz, with a 20-μs pulse width and a 250-ms post-acquisition delay using a ±35 714.2 Hz spectral width and quadrature phase detection. Data points (8K) were accumulated and zero filled to 32 K. A trapezoidal multiplication was used to reduce base line artifacts. An exponential multiplication yielding 15-Hz line broadening was also applied to the free induction decay before Fourier transformation. Ten millimeter sample tubes were used with a 0.10 M solution of CH_3HgX in 50% $CDCl_3$ or CH_3OD as an internal lock solvent. The spectra represent 4096 scans with a ^1H-decoupling frequency of 300.058 421 MHz.

Neat $(CH_3)_2Hg$ in a concentric capillary tube was used as an external standard. All ^{199}Hg chemical shifts are reported in parts per million relative to $(Me)_2Hg$. A negative sign for the chemical shift denotes resonances to higher field or lower frequency.[18] No bulk susceptibility corrections were made.

Methylmercuric Iodide. With use of a modification of the procedure of Marvel,[19] methylmercuric iodide was prepared by the addition of HgI_2 to MeMgI. The preparation of this compound

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Table III. Experimental Parameters from the X-ray Diffraction Study of the Methylmercury(II) Trifluoroacetate-Picoline Complex

Crystal Data

mol formula	$C_9H_{10}NO_2F_3$	mol wt	421.8
cell dimens		cryst size	0.12 × 0.25 × 0.25 mm³
a, Å	8.697 (1)		
b, Å	10.218 (1)	cryst system	triclinic
c, Å	7.471 (1)	space group	$P\bar{1}$
α, deg	104.60 (1)	V, Å³	549.0 (2)
β, deg	111.65 (1)	Z	2
γ, deg	90.04 (1)	D(calcd), g/cm³	2.34

Data Collection

radiatn: Mo Kα(λ = 0.710 69 Å)
monochromator: graphite
reflctns measd: $+h,\pm k,\pm l$; 2θ range = 4–55°
scan type: θ–2θ; moving crystal-moving counter
scan speed: 2.0–5.0 °/min.
scan width: [2θ(Mo Kα_1) – 1.0] to [2θ(Mo Kα_2) + 1.0]
bkgd measurement: stationary crystal-stationary counter at beginning and end of 2θ; each for one-fourth the time taken for the 2θ scan
std reflctns: 3($\bar{1}30$; $22\bar{3}$; $\bar{1}\bar{1}\bar{1}$) measd every 97 reflctns; no significant deviation from the mean was obsd
unique data: 3040 (total measd)
unique data with $F_o^2 \geq 3.0\sigma(F_o^2)$ = 2094
abs coeff: 129.77 cm⁻¹
$F(000)$ = 388
R_F = 0.047; R_w = 0.056
NV = 145
max residual electron density: 3.0 e/Å³, 1.01 Å away from Hg
max shift/error = 0.019 77
goodness of fit = 1.60

and the methylmercury derivatives that follow have been described in detail in ref 20.

Methylmercuric Trifluoroacetate. Addition of MeHgI to $AgOCOCF_3$ according to a modification of the procedure of Evans[21] gave methylmercuric trifluoroacetate in excellent yields.[20]

Methylmercuric Nitrate. Methylmercuric nitrate was prepared by a modification of the procedure of Canty,[22] from MeHgI and $AgNO_3$.[20]

Methylmercuric Acetate. Using an adaptation of the procedure of Sneed,[23] MeHgI (17.13 g, 0.05 mol) was added to a well-stirred slurry of silver acetate (8.5 g, 0.051 mol) in absolute ethanol (300 mL), and the mixture was stirred overnight. The yellow precipitate was filtered, and the filtrate was diluted with water (100 mL) and filtered again. The residue was washed with ethanol (50 mL), and the combined filtrates were carefully concentrated under reduced pressure at 50–60 °C, to give 10.3 g (75%) of white crystalline solid, mp 127.5–128 °C (lit.[23] mp 128 °C). The solid was recrystallized from absolute ethanol: IR (KBr) 1570 (s), 1400 (s) cm⁻¹; ^{1}H NMR ($CDCl_3$) δ 1.105 ($^2J_{H-^{199}Hg}$ = 210.97 Hz), 2.013.

Methylmercuric Trifluoroacetate–Picoline Complex. To a solution of methylmercuric trifluoroacetate (0.442 g, 2 mmol) in acetone (1 mL) was added distilled picoline (0.4 mL, 4.6 mmol). A crystalline solid resulted immediately. The solid was washed with hexane (4 × 0.5 mL), dissolved in a minimum amount of acetone (~2 mL), and allowed to crystallize slowly. The resulting white crystalline solid had the following: mp 108–109 °C; IR (KBr) 1160 (s), 1440 (w), 1390 (w), 1220 (s) 840 (m), 810 (m), 720 (m) cm⁻¹; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 3 H, ^{199}Hg–^{1}H J = 226 Hz), 2.76 (s, 3 H), 7.33–8.0 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 2.01, 24.50, 32.23, 121.50, 124.29, 137.55, 149.31, 158.02, 171.53. Anal. Calcd for $C_{29}H_{10}O_2NF_3Hg$: C, 25.63; H, 2.39. Found: C, 25.58; H, 2.49.

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Table IV. Atomic Coordinates for Methylmercury(II) Trifluoroacetate-Picoline Complex

atom	x	y	z
Hg	0.29291 (6)	0.09482 (4)	0.08835 (7)
N	0.3105 (11)	0.2445 (8)	−0.0618 (12)
C(1)	0.3717 (17)	0.2122 (11)	−0.2059 (19)
C(2)	0.3881 (18)	0.3019 (12)	−0.3074 (18)
C(3)	0.3379 (17)	0.4268 (12)	−0.2644 (19)
C(4)	0.2786 (16)	0.4621 (11)	−0.1141 (18)
C(5)	0.2655 (14)	0.3693 (11)	−0.0128 (16)
C(6)	0.2076 (19)	0.4046 (14)	0.1562 (21)
C(7)	0.2327 (24)	−0.0402 (16)	0.2254 (28)
O(1)	0.6212 (11)	0.0967 (7)	0.1921 (13)
C(8)	0.6757 (13)	0.2024 (10)	0.3247 (16)
O(2)	0.5989 (11)	0.2861 (8)	0.3966 (13)
C(9)	0.8640 (16)	0.2308 (12)	0.4170 (20)
F(1)	0.9252 (15)	0.2989 (22)	0.3510 (37)
F(2)	0.9409 (14)	0.1261 (13)	0.4246 (26)
F(3)	0.9190 (16)	0.2915 (19)	0.6034 (22)

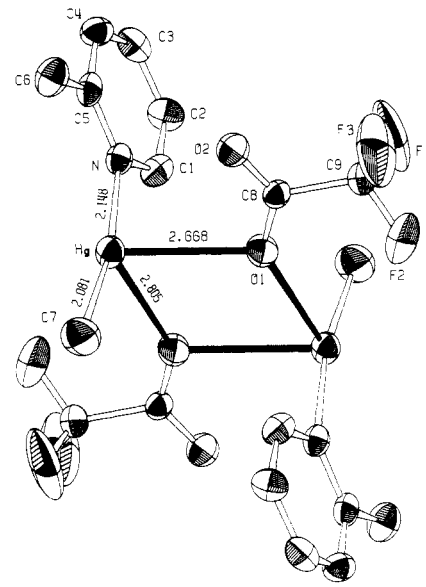

Figure 1. An ORTEP diagram of the methylmercury(II) trifluoroacetate–picoline complex with the atoms labeled. The atoms are represented by 50% thermal elipsoids.

Crystal and Molecular Structure of Methylmercury(II) Trifluoroacetate–Picoline Complex. The crystal and molecular structure of methylmercury trifluoroacetate–picoline complex was determined by using single-crystal X-ray diffraction techniques with data collected by counter methods on a Syntex $P2_1$ diffractometer. The experimental parameters, cell dimensions, and conditions for data collection are listed in Table III.

Solution and Refinement of the Structure. The centric space group $P\bar{1}$ was assumed[24a] and gave satisfactory refinement throughout. Solution of the three-dimensional Patterson functions gave the position of the mercury atom. All other non-hydrogen atoms were located from a series of Fourier maps. Gaussian integration absorption corrections[25] were applied (μ = 129.765 cm⁻¹). The correction factors ranged from 3.966 to 11.920. Position and temperature factors of all non-hydrogen atoms were refined by a least-squares technique. Hydrogen atoms were placed in calculated positions and were adjusted after every second least-squares cycle. All parameters associated with hydrogen were held fixed throughout the refinement. Full-matrix least squares of the function $w(|F_o| - |F_c|)^2$ using the weighting scheme $w = 1/\sigma^2(F_o)^2$ yielded residual indices of R_F = 0.047 and R_{wF} = 0.056. The largest peak on the final difference map represented 3.0 e/Å

(24) (a) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1969; Vol. 1. (b) 1974, Vol. 4, p 150.
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Table V. Selected Interatomic Distances and Angles for $MeHgOCOCF_3$-Picoline Complex

atoms	dist, Å	atoms	angles, deg
Hg-N	2.148 (9)	N-Hg-O(1)	85.6 (3)
Hg-O(1)	2.668 (9)	O(1)-Hg-O(7)	104.5 (6)
Hg-O(1′)	2.805 (8)	N-Hg-C(7)	69.6 (5)
Hg-C(7)	2.081 (15)	N-Hg-O(1′)	88.6 (3)
Hg-O(2)	2.067 (9)	O(1)-Hg-O(1′)	67.5 (3)
Hg-O(2′)	4.957 (8)	C(7)-Hg-O(1′)	97.3 (5)
		Hg-O(1)-C(8)	103.0 (7)
		Hg-O(1)-Hg′	112.5 (3)

and was located 1.01 Å away from the mercury atom. Neutral-atom scattering factors[26] were used, and those for Hg were corrected[24b] for anomalous dispersion. The errors were estimated by the variance–covariance method. Lattice errors were not included. Table IV lists the atomic coordinates for the non-hydrogen atoms. A complete listing of interatomic distances and angles (S-1), anisotropic thermal factors (S-2), equations of planes (S-3), hydrogen atom positional parameters (S-4), observed and calculated structure factors (S-5) and a packing diagram are available.[27]

Discussion of Structure

Figure 1 gives a view of two symmetry-related units with the atoms labeled. The space group $P\bar{1}$ requires that the two halves of the bridged dimer are related by a center of inversion. The coordination sphere around the mercury atom consists of four atoms, the methyl carbon atom, the picoline nitrogen, and two oxygens from CF_3COO^- groups. The second oxygen atom is further removed 3.067 Å from the mercury. The structure may be viewed as consisting of two nearly linear methylmercury picoline cations (N–Hg–C angle = 169.5°) bridged by an oxygen atom from each of the two trifluoroacetate groups. The two mercury atoms and the bridging oxygen atoms must be planar from symmetry considerations. This plane is nearly perpendiular to the plane described by the N, O(1), C(7), and Hg. A further point of interest is that the Hg atom may be described as being in a trigonal plane described by N, C(7), and O(1) with the O(1) atom nearly on the perpendicular above the mercury. The opposite side of the trigonal plane is vacant leaving the mercury atom exposed along the Hg–O axis. The distortion of the N–Hg–C unit from linearity and the unsymmetrical placement of the bonding O atoms most likely results from the many steric interactions present between the trifluoroacetate group and the other moieties in the system. The pertinent bond angles and distances are summarized in Table V.

The formation of the structure as a dimer is supported by the relatively short Hg–O distances of 2.668 (9) Å and 2.805 (8) Å when compared to the corresponding Hg–O distances of 3.16 Å in the ionic nitrate complex $[MeHg(py)]NO_3$[28c] and the Hg–O distances of 2.77 (2) and 2.82 (1) Å in the trifluoroacetate group of the (3-oxo-2-butyl)(pyridine)mercury(II) cation.[28a]

Measurement of Equilibrium Constants

In our previous report,[10b] we described a sensitive analytical probe that accurately measured the extent of aggregation of MeHgOAc with a variety of ligands. The sensitivity of the ^{199}Hg nucleus to both its primary ligands and the immediate solvation shell surrounding the metal is reflected in a range of chemical shift differences that span over 4000 ppm.[18] Consequently, even relatively small formation constants, K_f, can be measured by a least-squares fit of ^{199}Hg NMR data. The application of ^{199}Hg NMR to this problem has been amply demonstrated by several groups.[29]

For the equilibrium involving the interaction of MeHgX with added ligand L to form complex X, it follows that

$$\mathrm{MeHgX} + \mathrm{L} \overset{K}{\rightleftharpoons} \mathrm{MeHgX{\cdot}L}$$

$$(a - x)\,(b - x) = (x)$$

if one assumes no prior dissociation or association of the reactants. Since equilibrium is attained rapidly on the NMR time scale, only one mercury resonance is observed. In these experiments the initial concentration of MeHgX (a) remains constant while the concentration of the ligand (b) is varied. The concentration of the complex (x) may be expressed in terms of (x/a), the molar ratio of the complex to initial concentration of MeHgX. When an equilibrium involved is such that $b >> a$ and/or K_f is very small, then the reciprocal of the ligand induced change in ^{199}Hg chemical shift, $\Delta\delta^{-1}$, is linearly related to the reciprocal of the ligand concentration, b^{-1}, such that

$$\Delta\delta^{-1} = K_f^{-1}\,(\delta_x - \delta_0)^{-1}b^{-1} + (\delta_x - \delta_0)^{-1} \qquad (1)$$

When the formation constants are relatively large and a large excess of ligand b cannot be attained, then a quadratic expression in terms of ($a - x/a$) as described initially by Popov[30] may be utilized as follows

$$\delta_{obsd} = \Delta\delta + \delta_0 = \frac{1}{2Ka}(-(\mathrm{D})^{1/2} + (D + 4Ka))^{1/2}(\delta_0 - \delta_x) + \delta_x \qquad (2)$$

where $D = (Kb - Ka + 1)^2$.

The procedure employed in the evaluation of K_f is to substitute the experimental parameters $\Delta\delta$, δ_0 (the initial chemical shift of a), a, and b and vary the two adjustable parameters K_f and δ_x (the chemical shift of fully complexed a) until the calculated chemical shifts correspond to the experimental $\Delta\delta$ values within given error limits.[31] The general non linear curve fitting program KINFIT-4[32] was used with the appropriate equations given here and elsewhere.[10b]

The series of complexes involving heterocyclic ligands that were isolated and characterized by Canty[33] utilized $MeHgNO_3$ as the electrophile. We therefore focussed our initial attempts on measuring the formation constant with this relatively ionic mercurial. However, an immediate precipitation of the complex resulted upon addition of pyridine to a solution of $MeHgNO_3$ in either $CDCl_3$ or CH_2Cl_2 solvent. In methanol, the linewidths were so large that no signal was observed until a 1:1 stoichiometry of the mercurial and the ligand was attained. These phe-

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nomena are attributable to an exchange reaction involving methylmercury cation. This exchange process is presumably altered upon complete displacement of the nitrate anion with a more nucleophilic ligand.[16c]

In an effort to alleviate this problem we utilized $MeHgOCOCF_3$ which is less ionic than $MeHgNO_3$. One measure of the nucleophilicity of the anion is the pK_a of the conjugate acid of the ligand. The lower acidity of trifluoroacetic acid is indicative of the fact that the trifluoroacetate anion is more strongly bound to the metal center than NO_3^-. By this criterion, MeHgOAc should be essentially unionized in both $CDCl_3$ and methanol at the concentration used in this study (i.e., 0.10 M). In contrast, $MgHgOCOCF_3$ should be highly ionized in methanol but only slightly dissociated in $CDCl_3$, a less polar solvent. As can be seen from the data in Table VI, the formation constants estimated from the linear relationship that exists between $^{199}Hg-^1H$ coupling contants and K_f[16b] are consistent with this treatment.

Methanol and CH_2Cl_2 were chosen as the polar protic and nonpolar solvents for this study. Nitromethane was included as the polar-aprotic solvent, since it has a dielectric constant[34] (ϵ = 35.87), which is similar to that of methanol (ϵ = 32.7). This is a relatively nonnucleophilic solvent and should not compete with the pyridine bases for the electrophilic center on the MeHgX.

Kiefer[35] and Canty[36] have proposed the existence of weak intramolecular π-coordination of aromatic rings to alkylmercury compounds. Sens[18b] has demonstrated that the ^{199}Hg chemical shifts for Me_2Hg show a remarkable solvent dependence. In order to separate any such aromatic ring induced anisotropy shifts due to the pyridine π-system, we first measured the formation constants for MeHg(II) with benzene. However, we were unable to measure any appreciable association with $MeHgOCOCF_3$ in CH_2Cl_2, and the K_f has a value of only 0.12 in CH_3OH which is small compared to the K_f of the pyridines in the same solvent. Thus we feel that aromatic anisotropy effects are too small to account for the chemical shift changes noted in our study. We also examined the sensitivity of the ^{199}Hg chemical shift to small changes in temperature. We found the $\Delta\delta$ for $MeHgOCOCF_3$ in CH_2Cl_2 from 15 to 35 °C to be negligible but did observe a 0.8 ppm shift in CH_3OH solvent. This relatively small change in chemical shift may be due to the fact that the frequencies of both $MeHgOCOCF_3$ and $(Me)_2Hg$, the external standard, are changing in the same direction with the change in temperature.

The equilibrium constants measured for the interaction of the various pyridines with MeHgOAc and $MeHgOCOCF_3$ in the three solvents are summarized in Table VII.

An examination of these data reveal several interesting trends. The equilibrium constants for MeHgOAc decrease on going from pyridine to the more hindered lutidine in CH_2Cl_2 solvent. The K_f for $MeHgOCOCF_3(CH_2Cl_2)$ also shows a similar trend as the number of methyl groups on the pyridine is increased. There is a slight increase for picoline which is attributable to an inductive stabilization of the complex. However, the K_f decreases for 2,6-dimethyl and 2,6-di-*tert*-butyl compounds where there is a greater steric encumbrance around the nitrogen. The formation

Table VI. Formation Constants and % Dissociation of MeHgX in Aprotic and Polar Protic Solvents

	$CDCl_3$			CH_3OH		
X	^2J[b]	K_f[a]	% dissociated	^2J[b]	K_f[a]	% dissociated
OAc	212	1.82×10^7	0.07	228	1.31×10^4	2.7
$OCOCF_3$	227	2.06×10^4	2.18	246	3.81	77.26
NO_3	237	2.24×10^2	19.03	252	0.25	97.60

[a] Calculated from the relationship[16b] $\log K_f = 48.92 - 0.1965 \times {}^2J$. [b] J values in hertz.

Table VII. Formation Constants and Changes in ^{199}Hg Chemical Shifts for Pyridines with $MeHgOCOCH_3$ and $MeHgOCOCF_3$

	$CH_3HgOCOCH_3$				$CH_3HgOCOCF_3$							
	CH_2Cl_2		CH_3OH		CH_2Cl_2		CH_3NO_2		CH_3OH			
ligand	K_f	$\Delta\delta$, ppm (eq)[a]	K_f	$\Delta\delta$, ppm (eq)[a]	K_f	$\Delta\delta$, ppm (eq)[a]	K_f	$\Delta\delta$, ppm (eq)[a]	K_f	$\Delta\delta$, ppm (eq)[a]
pyridine	0.44 ± 0.03	18.94 (8)	0.34 ± 0.04	17.35 (8)	12.95 ± 0.53	137.8 (10)	13.60 ± 0.96	154.2 (10)	40.50 ± 0.55	42.60 (10)
2-methylpyridine	0.19 ± 0.06	10.32 (8)	1.41 ± 0.16	18.52 (8)	13.5 ± 0.20	178.9 (10)	16.9 ± 0.60	195.8 (10)	87.3 ± 0.30	87.2 (10)
2,6-dimethylpyridine	0.04 ± 0.004	8.68 (8)	1.57 ± 0.13	14.87 (8)	7.5 ± 0.20	210.8 (10)	10.2 ± 0.40	233.9 (10)	87.7 ± 4.4	131.2 (10)
2,6-di-*tert*-butylpyridine	*b*	0.1 (9)	*b*	0.82 (9)	0.07 ± 0.005	5.66 (5)	...		0.30 ± 0.11	9.1 (10)
2-methoxypyridine	*b*	...	1.77 ± 0.08	10.77 (8)	...		...		63.3 ± 6.3	97.6 (10)
2-ethylpyridine	0.12 ± 0.005	7.93 (8)	1.1 ± 0.1	17.44 (8)	...		...		...	
2,6-dimethoxypyridine	*b*		0.13 ± 0.01	5.11 (8)	...		...		...	
2,2'-bipyridyl	0.45 ± 0.004	4.79 (8)	*c*		*c*		*c*		*c*	
benzene	*b*	0.02 (10)	0.12 ± 0.03	3.13 (8)	*b*		0.5 (10)	...	...	

[a] = number of equivalents of added ligand. [b] $\Delta\delta$ is too small to measure K_f accurately. [c] Signal could not be observed due to exchange and line broadening.

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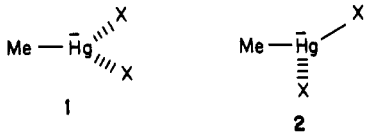
constants in nitromethane, the polar aprotic solvent, also show a similar trend in that the K_f increases from pyridine to picoline and becomes smaller for lutidine. In methanol solvent however, one sees a reversal of trends in that *the K_f increases from pyridine to picoline* and the K_f levels off with the bulkier lutidine with both MeHgOAc and $MeHgOCOCF_3$.

It is important to know the nature of the complex formed by MeHg^{II} with the nucleophilic species in solution. Goggin[29b] has examined the Raman and IR spectral changes for the complexation of X^- with MeHgX. He was able to observe only one Hg–X stretching vibration in the region of the Hg–X bond. If the complex were to be a symmetric trigonal species such as 1, one should observe



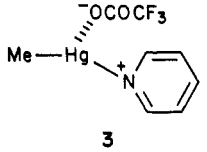
1

2

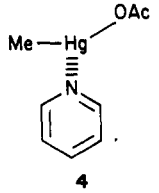
a symmetric and an antisymmetric stretching vibration. Goggin also observed a single absorption in the far-IR which he assigned to a weak polar Hg–X bond. On the basis of these observations and the small changes in the Hg–X Raman frequency, he has suggested that 2 more closely reflects the structure of $MgHgX_2^-$, with the C–Hg–X bond angle deviating slightly from linearity and the second ligand being held by a comparatively weak polar bond.

Our X-ray study on the complex of 2-methylpyridine with $MeHgOCOCF_3$ is consistent with this bonding scheme. The stronger ligand in this case is the pyridine base, and the trifluoroacetate anion is weakly bound to the metal center. An examination of other X-ray data available for MeHgX compounds also reveals that in the absence of secondary interactions, the C–Hg–X bond is essentially linear. Deviations from linearity do occur when there is a secondary intramolecular interaction[28c] present in the molecule. For seven prior X-ray structures of pyridine bases with $MeHgNO_3$,[14c,28c,33,36] C–Hg–N bond angles of 150–172° have been reported for the four complexes involving intramolecular Hg···N interaction.[14c,33,36c,d]

We note that in all of these structures the basic nitrogen is along the principle sp bond axis of the mercury as indicated in 3. In contrast we suggest that the more covalently bound MeHgOAc has structure 4 in nonpolar solvents where the acetate anion is not dissociated from the metal center. However, in a polar solvent where the acetate anion would be more highly solvated, one would expect a structure resembling 3 since the log K value for pyridine interacting with CH_3Hg^{II} is higher than acetate ion in an aqueous medium.[8,38]



3



4

In view of the apparent differences in the structures of the complexes, it is interesting to note that in a given solvent, the trends for the formation constants with a series of pyridines parallel one another for the two mercurials. This is indicative of a ground-state solvation effect on the pyridines rather than on the mercurials. Since the dielectric constants of the solvents methanol and nitromethane are similar, the major differences in their properties is the hydrogen bonding ability of methanol. Thus, it is likely that the observed differences in the complexation ability may be due to the differences in the solvation of the pyridines. Consistent with such a proposition is the observation of Johnson,[37] who noted a lack of substituent induced rate variation of the Menschutkin reaction in methanol.

The variation in the rates of S_N2 reactions (such as the Menschutkin reaction) observed on changing the solvent from a polar aprotic to an aprotic solvent have been explained on the basis of a desolvation of the nucleophile in the latter solvent which decreases the energy gap between the reactant and the transition state. Alternatively, this may be an effect of the increased solvation of the transition state in the polar aprotic solvent. A combination of both is also conceivable. A similar reasoning can be invoked for the equilibria between the pyridines and the methylmercury electrophile under consideration. For the $MeHgOCOCF_3$ interaction with the series of pyridines, the solvent effect is constant for the electrophile in the given solvent. Arnett[39a] has shown that for S_N2 rate studies, one can determine the difference in the enthalpies of activation of a reaction in a pair of solvents ($\delta\Delta H'$) and compare them to the enthalpies of transfer of reactants from one solvent to the other ($\delta\Delta H_s$). Haberfield,[39b] in a study of the solvent effects on the Menschutkin reaction, has shown that the enthalpy of transfer of pyridine from DMF to methanol is −0.86 kcal/mol and this stabilization is due to a hydrogen-bonding solvation of the pyridine in methanol. The ground-state hydrogen bonding of the pyridine in methanol provides a plausible explanation for the observed extent of complexation of the pyridines with MeHg(II). Pyridine is much better solvated by methanol than the more hindered 2,6-lutidine. Implicit in such a comparison is the assumption that the complexes for the same mercurial have similar structures in both solvents. One should bear in mind that there is the possibility for an inductive stabilization of the complex that can increase with alkyl substitution.

Condon[40a] has observed steric hindrance to solvation of nitrogenous bases and has attributed the difference in the calculated and measured basicity of di-*tert*-butylpyridine to a decreased solvation by the protic solvent. McDaniel and Ozcan[40b] suggested that the base-weakening effect of the ortho di-*tert*-butyl groups was indeed due to a steric inhibition of solvation, since they noted that the pK_a was strongly dependent upon the structure of the alcohol. Brown,[11c] however, attributed the variation in pK_a to a steric hindrance toward the proton.

In nitromethane, one notes that the difference in the solvation of the pyridine bases is of a much smaller magnitude. In this polar aprotic solvent, where there can be no hydrogen bonding solvation of the base, the K_f is dependent upon the steric requirements for the interaction of the nucleophile with methylmercury. Consequently, the K_f decreases as the substitution around the nucleophilic center is increased. Such an effect is clearly seen in the rate of the S_N2 reaction measured in nitromethane (see Table I). The rate decreases by a factor of 6 on introducing one methyl group and by a factor of ~250 upon intro-

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duction of a second methyl group.

Additional support for the hydrogen bonding solvation effects comes from trends in the relative nucleophilicities of halide ions in protic and polar aprotic solvents. In methanol, the order of nucleophilicities is $I^- > Br^- > C^-$, but in dimethylformamide the order is reversed.[41] This is due to hydrogen bonding, which is important for small anions. Similarly, the rate of reaction of N_3^- with MeI increases by $\sim 10^4$ on going from methanol to DMF, where N_3^- is not as effectively solvated.[41]

The lower formation constant for 2-methoxypyridine with $MeHgOCOCF_3$ (compared to picoline) could in part be due to secondary interactions of the more ionic mercurial with the $-OCH_3$ group. An inductive effect in the σ framework due to the electronegative oxygen is most likely responsible for its diminished basicity. 2,2′-Bipyridyl was also examined to evaluate the equilibrium constant in what could potentially be a two coordinated MeHg(II) species. 2,2′-Bipyridyl has a small K_f (with MeHgOAc) in methylene chloride solvent. The attempted measurement in methanol was unsuccessful due to extensive line broadening of the mercury signal.

Conclusions

The data presented demonstrate the importance of hydrogen bonding and steric effects on complexation equilibria. The steric inhibition to hydrogen bonding in methanol solvent causes a reversal of the expected trend in the formation constants. Further, we feel that the coupling constants measured by Canty in CD_3OD (Table II), which show an increased complexation with increased substitution, can best be understood on the basis of the above explanation of an encumbrance to solvation. These data further suggest that complexation of heavy metals with bioorganic substrates in aqueous media may exhibit similar behavior and the metal may bind preferentially with a more hindered site.

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Registry No. MeHgI, 143-36-2; $MeHgOCOCF_3$, 21502-74-9; $MeHgNO_3$, 2374-27-8; MeHgOAc, 108-07-6; MeHg(py), 94750-89-7; MeHg(B)OAc (B = 2-methylpyridine), 94750-90-0; MeHg(B)OAc (B = 2,6-dimethylpyridine), 94750-91-1; MeHg(B)OAc (B = 2,6-di-*tert*-butylpyridine), 94750-93-3; MeHg(B)OAc (B = 2-methoxypyridine), 94750-95-5; MeHg(B)OAc (B = 2-ethylpyridine), 94750-96-6; MeHg(B)OAc (B = 2,6-dimethoxypyridine), 94750-98-8; MeHg(B)OAc (B = 2,2′-bipyridyl), 94750-99-9; $MeHg(py)OCOCF_3$, 94751-00-5; $[MeHg(B)OCOCF_3]_2$ (B = picoline), 94780-99-1; $MeHg(B)OCOCF_3$ (B = 2,6-dimethylpyridine), 94751-01-6; $MeHg(B)OCOCF_3$ (B = 2,6-di-*tert*-butylpyridine), 94751-02-7; $MeHg(B)OCOCF_3$ (B = 2-methoxypyridine), 94751-03-8; py, 110-86-1; 2-methylpyridine, 109-06-8; 2,6-dimethylpyridine, 108-48-5; 2,6-di-*tert*-butylpyridine, 585-48-8; 2-methoxypyridine, 1628-89-3; 2-ethylpyridine, 100-71-0; 2,6-dimethoxypyridine, 6231-18-1; 2,2′-bipyridine, 366-18-7; benzene, 71-43-2; silver acetate, 563-63-3; $MeHg(B)OCOCF_3$ (B = picoline), 94751-04-9.

Supplementary Material Available: Tables containing complete listing of interatomic distances and angles, anisotropic thermal parameters, equations of planes, hydrogen atom positional parameters, observed and calculated structure factors and a packing diagram (17 pages). Ordering information is given on any current masthead page.

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Structure of $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(Ph_2PCH_2PPh_2)_2][ClO_4]\cdot 0.866CH_2Cl_2$: An "A-Frame" Compound Containing a σ,π-Acetylido Group

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Received July 26, 1984

The structure of $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(DPM)_2][ClO_4]$ has been determined. It is found to have an "A-frame" geometry in which the acetylide moiety is σ-bound to one metal and π-bound to the other. Owing to steric interactions between the *tert*-butyl group and the DPM phenyl groups the acetylide moiety is involved in only a weak π interaction with the second metal. This compound crystallizes with 0.866 (7) equiv of CH_2Cl_2 in the space group $P\bar{1}$ (a = 13.011 (4) Å, b = 20.765 (5) Å, c = 12.559 (2) Å, α = 90.73 (2)°, β = 117.45 (2)°, γ = 71.89 (2)°, and Z = 2). The structure was refined to R = 0.052 and R_w = 0.072 based on 332 parameters varied and 6596 unique observed reflections.

Introduction

The acetylide group ($:C{\equiv}CR^-$) is quasi-isoelectronic with the ubiquitous carbonyl ligand and consequently is found to parallel the latter somewhat in its binding modes. In polynuclear complexes, for example, the ligand can adopt the terminal binding mode[1] or it can bridge two or more metals in several ways.[1-6] Even in the simplest polynuclear case, in which the acetylide ligand is involved with only two metals, two bridging modes are observed; either it can

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