Hydrogen/Deuterium Exchange Catalyzed by an Unusually Stable Mercury – Toluene Complex**

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The chemistry of mercury(II) salts, in particular the trifluoroacetate, with aromatic hydrocarbons is well developed with regard to electrophilic attack on aromatic compounds, that is, aromatic mercuration. Olah et al. have shown that arenemercurinium ion complexes are involved, in a fast exchange, as intermediate complexes in aromatic mercuration.[1] Extensive studies by Kochi and co-workers showed that the activation of the arene is related to a charge-transfer transition in the π complex.[2, 3] As part of this work they also isolated a η^6 complex of C_6Me_6 and $[Hg(O_2CCF_3)_2]$.[4] Crabtree and co-workers have demonstrated that photolysis of metallic mercury in the presence of aromatic compounds results in a variety of C–C bond-forming reactions and have proposed a π complex as a key intermediate.[5] Thus, the activation of aromatic compounds by mercury salts is well established. Our interest in this area was initially stimulated by the possibility of exploring the activation of small molecules by Lewis acids,[6, 7] in particular the use of Group 13 halides to enhance the Lewis acidity of other metal halides, for example, mercury.

The reaction of $HgCl_2$ with two molar equivalents of $GaCl_3$ in toluene yields an orange photosensitive solution from which yellow crystals may be obtained in high yield. The solubility in toluene suggests a simple Lewis acid base complex rather than a cation/anion pair. Although the EI mass spectrum and elemental analysis are consistent with the presence of toluene, solution ^1H and ^{13}C NMR spectroscopy do not allow an unambiguous characterization (see below). However, an X-ray crystallographic structure determination showed that the molecular formula was $[Hg(\eta^2\text{-}C_6H_5Me)_2(GaCl_4)_2]$ (**1**), and that the toluene ligands are π bound to the mercury center (Figure 1).[8, 9] Complex **1** represented only the second unsupported π-aryl complex of mercury to be structurally characterized, although a number of intramolecular π complexes have been structurally characterized.[10, 11] Arene complexes of mercury(II) with SbF_6^- and AsF_6^- ions have been proposed based upon NMR data, but no structural evidence was obtained,[12] however, based on the structure of **1** these assignments were undoubtedly correct.

Each toluene in **1** is bound in an asymmetric η^2 manner with the Hg(1)–C(4) bond *para* to the toluene methyl group (2.349(9) Å) being significantly shorter than the Hg(1)–C(3) bond in the *meta* position (2.71(1) Å). Noteworthy is that these values are either side of the values reported by Lau and Kochi for $[Hg_2(\mu\text{-}O_2CCF_3)_4(\eta^2\text{-}C_6Me_6)_2]$ (2.56 and 2.58 Å[2]) and significantly shorter than observed for the intramolecular coordination discussed above (ca. 3.2 Å[10, 11]). The relative Hg–C bond lengths would suggest that the methyl is *para* directing as would be expected from traditional Friedel–Craft chemistry. It is also worth noting that a typical Hg–C σ bond is 2.1–2.2 Å in length which is only slightly shorter than the $Hg-C_{para}$ interaction.[13] Although the Kochi complex was the first (and only) crystallographically characterized mercury–arene π complex prior to our work, several examples have been spectroscopically characterized.[14, 15] Of note is the isostructural relationship of **1** to the reported $[Ag(C_6H_4Me_2)_2(ClO_4)]$ complex,[16] in which the arene rings in the silver complex are also bound in an asymmetric η^2 manner. It was proposed that the perchlorate group played a significant role in stabilizing the Ag^I-aromatic complex and the $[GaCl_4]^-$ ion clearly performes a simmilar function with the mercury.

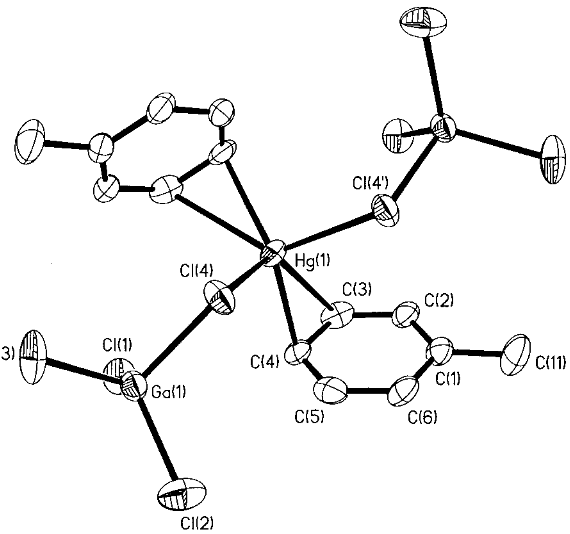

Figure 1. Molecular structure of **1**. Thermal ellipsoids are set at the 30% probability level and the hydrogen atoms are omitted for clarity.

Solid-state ^{199}Hg and ^{13}C MAS NMR (MAS = magic angle spinning) spectra for **1** are consistent with the X-ray structure.[17] In the ^{199}Hg NMR spectrum the chemical shift of the mercury center ($\delta = -1970$) is downfield to that reported for $HgCl_2$ ($\delta = -1497$[18]) and closer to that of Hg^{II} aquated salts ($\delta = -2253$ to -2361[19]) than simple Lewis base complexes, for example, $[HgCl_2\{P(nBu)_3\}_2]$ ($\delta = -404$[20]). The UV/Vis spectrum of **1** shows an intense absorption at 305 nm ($\varepsilon = 7000\,mol^{-1}cm^{-1}$). The band at 305 nm is likely that of the π-π* transition for the coordinated toluene,[21] however, it is also consistent with the toluene—Hg charge-transfer transitions observed for arene complexes of $[Hg_2(\mu\text{-}O_2CCF_3)_4]$.[2] However, two observations differentiate the present system from $[Hg_2(\mu\text{-}O_2CCF_3)_4(\eta^2\text{-arene})_2]$ complexes. First, the absorption for **1** is at significantly lower energy than those observed for $[Hg_2(\mu\text{-}O_2CCF_3)_4(\eta^2\text{-arene})_2]$ (288–315 nm[2]) or the toluene complexes of $HgCl_2$ (274 nm[15]). Second, whereas the absorption for $[Hg_2(\mu\text{-}O_2CCF_3)_4$-

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$(\eta^2\text{-arene})_2]$ is transient the absorption for **1** is sustained indefinately. Both of these observations suggest a stronger interaction between mercury and the aromatic group than previously observed. Exposure of **1** to ambient light results in rapid decomposition, however, sensitivity to O_2 and CO is negligible.

As was noted above, solution NMR spectra could not be obtained for $[Hg(\eta^2\text{-}C_6H_5Me)_2(GaCl_4)_2]$; dissolution in C_6D_6 results in the rapid (< 5 min, 25 °C), quantitative formation of C_6D_5Me and C_6D_5H, as confirmed by ^1H and ^{13}C NMR spectroscopy as well as GC/MS. When C_6H_5Me and C_6D_6 are mixed in the presence of < 0.1 mol% of **1** complete scrambling of the aromatic hydrogen/deuterium atoms occurs, indicating that the H/D exchange reaction is catalytic. Furthermore, H/D exchange is catalyzed for C_6D_6 and xylenes in the presence of < 0.1 mol% of $[Hg(\eta^2\text{-}C_6H_5Me)_2(GaCl_4)_2]$, suggesting that the identity of the initial aromatic is not vital in defining the catalytic exchange.

Hydrogen/deuterium exchange reactions for aromatic compounds are known to occur in the presence of strong acids or transition metals.[22] For example, addition of H_2SO_4 to a mixture of D_2O and C_6H_6 allows for the synthesis of C_6D_6.[23] Other suitable acid catalysts include HO_2CCF_3 and HBr. In all cases an acid with a suitable pK_a (< 0.2) is required. In the present system we propose that the acidity of the aromatic protons/deuteriums of the coordinated aromatic molecule (toluene or benzene) is increased from their uncomplexed values (pK_a (benzene) = 43[24]) through activation by the mercury/gallium complex. Initial ab initio calculations suggest that the coordination of benzene to a "$Hg(GaCl_4)_2$" moiety results in a threefold increase in negative charge at the carbon associated with the shortest Hg–C bond, that is, Hg(1)-C(4) in $[Hg(\eta^2\text{-}C_6H_5Me)_2(GaCl_4)_2]$.[25]

Experimental Section

Toluene (25 mL) was added to the solid mixture of anhydrous $HgCl_2$ (1.00 g, 3.68 mmol) and $GaCl_3$ (1.298 g, 7.37 mmol). The resulting orange solution was heated at approximately 100 °C while being vigorously stirred to allow all the $HgCl_2$ to dissolve. After about 15 min heating was stopped and the reaction flask was wrapped in aluminum foil to prevent the decomposition reaction caused by bright light. Large yellow crystals grew within 1 h at room temperature, yield: 90%; m.p. 78 °C.

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[8] X-ray structure analysis of $[Hg(\eta^2\text{-}C_6H_5Me)_2(GaCl_4)_2]$: space group *Pbcn*, $a = 13.477(3)$, $b = 12.659(3)$, $c = 14.370(3)$ Å, $V = 2451.6(8)$ Å^3, $\rho_{calcd} = 2.189\ g\,cm^{-3}$, $\mu = 9.30\ mm^{-1}$, 1782 unique reflections, 1439 observed $[I > 4\sigma(I)]$, computing = SHELXTL version 5, refinement method = full-matrix least squares on F^2, number of parameters = 115, $R = 0.0610$, $R_w = 0.1434$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151202. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] Selected bond lengths [Å] and angles [°]: Hg(1)-C(3) 2.71(1), Hg(1)-C(4) 2.349(9), Hg(1)-Cl(4) 2.652(2), Ga(1)-Cl(1) 2.166(3), Ga(1)-Cl(2) 2.147(3), Ga(1)-Cl(3) 2.144(3), Ga(1)-Cl(4) 2.239(2); Cl(4)-Hg(1)-Cl(4') 82.4(1), Hg(1)-Cl(4)-Ga(1) 110.2(1).

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[17] ^{13}C CPMAS NMR (50.32 MHz; CPMAS = cross polarization magic angle spinning): $\delta = 158.3$ (1-C), 142.2 (5-CH), 139.3 (3-CH), 136.5 (2-CH, 6-CH), 102.0 (4-CH), 23.9 (CH_3); ^{199}Hg MAS NMR (35.84 MHz): $\delta = -1970$.

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