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Arene−Mercury Complexes Stabilized by Aluminum and Gallium Chloride: Catalysts for H/D Exchange of Aromatic Compounds

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Abstract: Dissolution of $Hg(arene)_2(MCl_4)_2$ [arene = C_6H_5Me, C_6H_5Et, o-$C_6H_4Me_2$, C_6H_3-1,2,3-Me_3; M = Al, Ga] in C_6D_6 results in a rapid H/D exchange and the formation of the appropriate d_n-arene and C_6D_5H. H/D exchange is also observed between C_6D_6 and the liquid clathrate ionic complexes, $[Hg(arene)_2(MCl_4)][MCl_4]$, formed by dissolution of $HgCl_2$ and MCl_3 in C_6H_6, m-$C_6H_4Me_2$, or p-$C_6H_4Me_2$. The H/D exchange reaction is found to be catalytic with respect to $Hg(arene)_2(MCl_4)_2$ and independent of the initial arene ligand. Reaction of a 1:1 ratio of C_6H_5Me and C_6D_6 with <0.1 mol % $Hg(C_6H_5Me)_2(MCl_4)_2$ results in an equilibrium mixture of all isotopic isomers: $C_6H_{5-x}D_xMe$ and $C_6D_{6-x}H_x$ ($x = 0-5$). DFT calculations on the model system, $Hg(C_6H_6)_2(AlCl_4)_2$ and $[Hg(C_6H_6)_2(AlCl_4)]^+$, show that the charge on the carbon and proton associated with the shortest Hg···C interactions is significantly higher than that on uncomplexed benzene or $HgCl_2(C_6H_6)_2$. The protonation of benzene by either $Hg(C_6H_6)_2(AlCl_4)_2$ or $[Hg(C_6H_6)_2(AlCl_4)]^+$ was calculated to be thermodynamically favored in comparison to protonation of benzene by HO_2CCF_3, a known catalyst for arene H/D exchange. Arene exchange and intramolecular hydrogen transfer reactions are also investigated by DFT calculations.

Introduction

Electrophilic aromatic substitution is a well-understood reaction in organic chemistry, and hydrogen exchange is perhaps the simplest of this type of reaction.[1] In general, the reaction involves the addition of a strong protic acid (HA) to an aromatic (ArH). For a quantitative study of the reaction, dedeuteriation (i.e., eq 1) has a number of advantages including (a) the determination of the rate of reactivity of specific positions and (b) the susceptibility of the rate of hydrogen exchange to substitution effects but not steric effects. The majority of H/D exchange reactions are carried out under acid-catalyzed conditions. The addition of water or a mineral acid can significantly enhance the rate of exchange between C_6D_6 and HO_2CCF_3,[2] whereas the addition of an aprotic Lewis acid reduces the rate of exchange.[3] H/D exchange reactions for aromatic compounds are also known to occur in the presence of transition metal catalysts. For example, H/D exchange between heavy water and aromatic hydrocarbons is homogeneously catalyzed by $[PtCl_4]^{2-}$ salts.[4] Recently Calderazzo et al.[5] have reported H/D exchange of the ring protons between C_6D_6 and $C_6H_{6-n}Me_n$ promoted by titanium(IV)−arene complexes. Gaseous deuterium can be exchanged with C_6H_6 if tantalum (Cp_2TaH_3) or iridium $[(PhEt_2P)_2IrH_5]$ hydrides are used as catalysts.[6]

$$ArD + HA \rightleftharpoons ArH + DA \qquad (1)$$

As was reported previously,[7,8] the ^1H and ^{13}C NMR for $Hg(arene)_2(MCl_4)_2$ (M = Al, Ga) could not be obtained in C_6D_6 solution due to a facile H/D exchange reaction of the aromatic protons with the deuterium of the solvent. The rates of these exchange reactions are faster than would be expected given the conditions of the reaction: *aprotic solvent and without a strong protic acid*. In this regard the reaction of $Hg(arene)_2(MCl_4)_2$ with C_6D_6 is unusual. This observation prompted the following question: Do the coordinated arenes behave as strong protic acids?

We report, herein, the catalytic activity of $Hg(arene)_2(MCl_4)_2$ toward H/D exchange between C_6D_6 and a variety of aromatic substrates, as well as a DFT study on the possible reaction intermediates.

Results and Discussion

Dissolution of $Hg(arene)_2(MCl_4)_2$ (M = Al, Ga) in C_6D_6 results in the rapid (<5 min at 25 °C) quantitative formation of

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d_n-arene and C_6D_5H (eq 2, where M = Al, Ga and arene = C_6H_5Me, C_6H_5Et, o-$C_6H_4Me_2$, C_6H_3-1,2,3-Me_3). The identity

$$Hg(arene)_2(MCl_4)_2 + nC_6D_6 \rightarrow Hg(d_n\text{-arene})_2(MCl_4)_2 + nC_6D_5H \quad (2)$$

of the deuterated products is confirmed by ^1H and ^{13}C NMR spectroscopy as well as GC/MS. Deuteration is limited to the aromatic C*H* groups, with no exchange occurring for the alkyl substituents (i.e., Me and Et groups). Exchange is not limited to the use of C_6D_6 as a deuterium source, but is also observed with $C_6D_5CD_3$, in which case $C_6D_{5-x}H_xCD_3$ is formed along with the appropriate d_n-arene. If a 1:1 ratio of C_6H_5Me and C_6D_6 is mixed with $Hg(C_6H_5Me)_2(MCl_4)_2$ as a catalyst, then an equilibrium mixture of all isotopic isomers is observed. For example, the exchange between C_6H_5Me with 1 equiv of C_6D_6 yields $C_6H_{5-x}D_xMe$ and $C_6D_{6-x}H_x$ ($x = 0-5$).

We have reported that liquid clathrates are formed by dissolution of $HgCl_2$ and MCl_3 in C_6H_6, m-$C_6H_4Me_2$, or p-$C_6H_4Me_2$.[8] The upper (neutral) layer contains $Hg(arene)_2(MCl_4)_2$ while the lower (ionic) layer contains $[Hg(arene)_2(MCl_4)][MCl_4]$. The layers may be physically separated and H/D exchange is observed independently for both layers with the addition of C_6D_6. The rate of exchange for the upper (neutral) layer is slower than that for the lower (ionic) layer. Although the difference in reactivity could be a function of the relative concentrations of mercury/Group 13 complex in each layer, DFT calculations suggest that the rationale for this difference is more complex (see below).[9]

Quantitative exchange, for example, formation of C_6D_5Me and C_6D_5H, from C_6H_5Me and 5 molar equiv of C_6D_6, requires at least 10 H/D exchange reactions per mercury center, indicating that the reaction is catalytic. If C_6H_5Me and C_6D_6 (excess) are mixed in the presence of <0.1 mol % of $Hg(C_6H_5Me)_2(MCl_4)_2$ (per C_6H_5Me) complete scrambling of the aromatic hydrogen/deuteriums occurs, confirming the catalytic nature of the H/D exchange reaction. Each of the isolable arene complexes[7,8] will catalyze the exchange between C_6D_6 and the appropriate arene. Furthermore, the mercury complex does not have to contain the particular arene for it to catalyze that arene's H/D exchange. Thus, H/D exchange is catalyzed for C_6D_6 and xylenes in the presence of <0.1 mol % of $Hg(C_6H_5Me)_2(MCl_4)_2$. This would suggest there must be an exchange between coordinated and "free" arenes, and that the identity of the aromatic initially bonded to mercury does not affect the overall reaction.[10]

The observation of separate resonances for each of the potential isomers in the ^1H NMR of an equilibrium mixture of C_6H_5Me and C_6D_5Me catalyzed by $Hg(C_6H_5Me)_2(MCl_4)_2$ (i.e., $C_6H_{5-x}D_xMe$) indicates that the lifetime of each species is greater than that of the NMR experiment (10^{-5} s). Thus, the rate of H/D exchange is $\leq 10^{-5}$ s^{-1} at 25 °C. By using 0.065 mol % of $Hg(C_6H_5Me)_2(MCl_4)_2$ in a 1:10 solution of C_6H_5Me and C_6D_6, an H/D turnover rate is determined to be ca. 3.3 min^{-1} at room temperature; however, a rate of ca. 33 min^{-1} is calculated for all exchanges including degenerate D/D and H/H exchange.[11] These rates are increased with temperature such that at 80 °C the total turnover rate approaches 4000 min^{-1}, while the "H/D-only" turnover rate under these conditions is 400 min^{-1}.

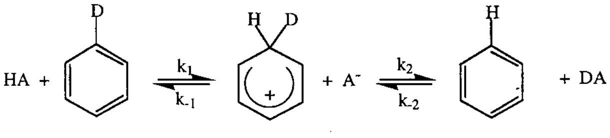
No degradation of the catalyst is observed with time. The addition of further quantities of either C_6D_6 or arene results in continued H/D exchange demonstrating that the $Hg(arene)_2(MCl_4)_2$ is a living catalyst. Furthermore, the catalyst solutions may be stored (in the absence of light[12]) indefinitely and maintain their catalytic activity.

There appears to be a slightly greater rate of H/D exchange when using aluminum as opposed to gallium as may be expected from the greater Lewis acidity of the former.[13] This small difference is consistent with the greater effect of $AlCl_3$ that $GaCl_3$ on the arene as measured from the UV−visible spectra.[8] The Group 13 anion (i.e., $[MCl_4]^-$) clearly affects the activation of the mercury since Damude et al.[14] reported that the mercury···arene complexes formed with the hexafluoride anions of arsenic and antimony showed well-characterized ^1H and ^{13}C NMR with no evidence for H/D exchange. Furthermore, we note that the copper(I) complex, $Cu(C_6H_6)(AlCl_4)$, has been structurally characterized,[15] but no H/D exchange was reported.

Garnett et al. have reported[16] that $AlCl_3$ will catalyze the H/D exchange between C_6D_6 and toluene. They suggested that traces of dissolved water were likely involved in the proton transfer. This proposal was recently supported by Gaines and Beall with regard to the $AlCl_3$-catalyzed H/D exchange between $B_{10}H_{14}$ and C_6D_6.[17] Using ^1H NMR, we have determined that the rate of H/D exchange for $Hg(C_6H_5Me)_2(AlCl_4)_2$ is approximately 1.5 times faster (per Al) than that observed for $AlCl_3$.

DFT Calculations. Hydrogen/deuterium exchange reactions for aromatic compounds are known to occur in the presence of strong acids. 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.[1] Other suitable acid catalysts include HO_2CCF_3 and HBr. In all cases an acid with a suitable pK_a (<0.2) is required.[18]

The acid-catalyzed reaction takes place through an A-S_E2 mechanism (eq 3), consisting of a bimolecular reaction between an acid HA and the aromatic ring, resulting from the transfer of a hydrogen cation from the former to the latter.[13] The Wheland intermediate (**I**) then loses a hydrogen cation to A^-. The reaction is reversible, and the energy profile must be



(3)

(**I**)

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[9] Further kinetic studies and site selectivity studies will be reported elsewhere.

[10] The observation of a single set of resonances in the ^1H NMR spectrum of $Hg(C_6H_5Me)_2(AlCl_4)_2$ dissolved in C_6H_5Me suggests that the rate of arene exchange is greater than 10^{-5} s^{-1}, see ref 8.

(11) It should be noted that precautions were taken to ensure that no hydrolysis of the catalyst occurred when measuring H/D exchange reactions.

(12) Solutions of $Hg(arene)_2(MCl_4)_2$ are light sensitive, see refs 7 and 8.

(13) We are presently undertaking detailed kinetic studies of the H/D exchange reaction in concert with ligand exchange. The results of these investigations will be published elsewhere: Branch, C. S.; Bott, S. G.; Barron, A. R., 57th Southwest Region ACS Meeting, San Antonio Texas, 2001.

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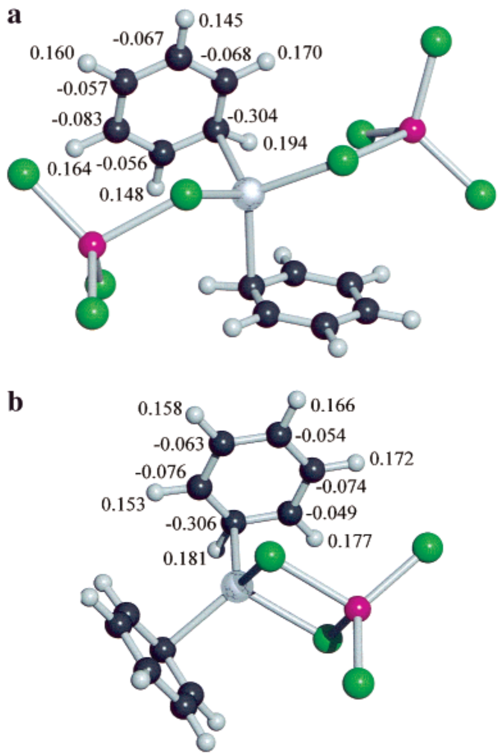

Figure 1. Calculated charge distribution on the aromatic C and H atoms in (a) $Hg(C_6H_6)_2(AlCl_4)_2$ and (b) $[Hg(C_6H_6)_2(AlCl_4)]^+$.

symmetrical about the intermediate **I**, except for a small isotope effect. An intramolecular exchange of the proton between positions of equal proton affinity on the same carbonium ion (**I**) has also been proposed. Brichall and Gillespie concluded, however, that the reaction shown in eq 3 was the most important.[19]

If such a mechanism is valid in the present system, the acidity of the aromatic protons (deuteriums) of the coordinated arene would be expected to be increased from their uncomplexed values [pK_a (benzene) $= 43$][20] through activation by the mercury/Group 13 chloride complex. To investigate this possibility we have performed DFT calculations at the B3LYP level using the 6-31G** basis set for C and H and the Stuttgart RLC ECP basis set for Hg, Cl, and Al. We have previously calculated the structures for $Hg(C_6H_6)_2(AlCl_4)_2$ and $[Hg(C_6H_6)_2(AlCl_4)]^+$.[8]

The charge distribution on the aromatic C and H atoms in $Hg(C_6H_6)_2(AlCl_4)_2$ is shown in Figure 1a; the equivalent values for uncomplexed C_6H_6 are C (-0.0804) and H ($+0.084$). It may be clearly seen that the charge on the proton associated with the shortest Hg⋯C interaction ($+0.194$) is significantly higher than that on free benzene. Similarly, the carbon associated with the short Hg⋯C contact has over a 3-fold increase in negative charge (-0.304) as compared to free benzene. It should also be noted that this effect is present, albeit reduced, on the C and H atoms ortho to the short Hg⋯C interaction.

Similar effects are observed for the cationic complexes, e.g., $[Hg(C_6H_6)_2(AlCl_4)]^+$, see Figure 1b. The greater charge effects on the cationic complexes are consistent with the H/D exchange activity of the lower 1:1 electrolyte layers of the clathrates,[7,8] suggesting that concentration is not the only factor in determining the relative rate of the lower and upper clathrate layers.

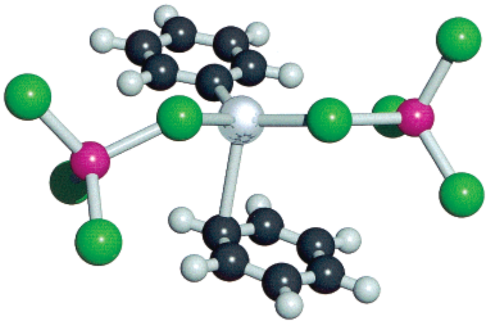

Figure 2. Calculated structure for the $[HgPh(C_6H_6)(AlCl_4)_2]^-$ anion showing both λ^1-phenyl and η^1-benzene ligands.

The magnitude of the increase in relative charges on the C and H atoms of the coordinated arene in $Hg(C_6H_6)_2(AlCl_4)_2$ is significantly larger than that calculated for $HgCl_2(C_6H_6)_2$ (-0.188 on C and 0.145 on H).[8] This is in accord with the experimental observation that no H/D exchange is observed by the addition of $HgCl_2$ to a mixture of C_6D_6 and C_6H_5Me. Thus, it would appear that the influence of the Group 13 halides is to activate the mercury by dramatically increasing the Lewis acidity of the latter.

The increased "acidity" of the arene proton associated with the Hg⋯C interaction suggests that it may be possible for the coordinated arene to "protonate" a second arene molecule in a manner similar to that observed for H/D exchange with mineral acids. To investigate the potential of such a reaction we have determined the structure and stability of the species formed from the deprotonation of one of the arene rings in $Hg(C_6H_6)_2(AlCl_4)_2$, i.e., eq 4.

$$Hg(C_6H_6)_2(AlCl_4)_2 + C_6H_6 \rightarrow [HgPh(C_6H_6)(AlCl_4)_2]^- + [C_6H_7]^+ \quad (4)$$

The optimized geometry for the $[HgPh(C_6H_6)(AlCl_4)_2]^-$ anion is shown in Figure 2; selected structural features are given in Table 1 along with those of $Hg(C_6H_6)_2(AlCl_4)_2$ for comparison. The most notable feature of the calculated structure for the $[HgPh(C_6H_6)(AlCl_4)_2]^-$ anion is that the phenyl group, formed from deprotonation of one benzene, is σ-bound to mercury. The calculated Hg−C σ-bond distance (2.079 Å) is comparable to that in $HgPh_2$ [2.085(7) Å] as determined by X-ray crystallography.[21] A second feature of note is that the closest Hg⋯C(p) distance in the $[HgPh(C_6H_6)(AlCl_4)_2]^-$ anion (2.873 Å) is significantly longer than the comparable interaction calculated for the neutral complex, $Hg(C_6H_6)_2(AlCl_4)_2$ (2.402 Å). A consequence of the weaker Hg⋯arene interaction is the distortion of the mercury away from tetrahedral to trigonal planar. This partial dissociation of the second arene ligand suggests a possible route for arene exchange to occur during the H/D exchange reaction.

The total energies of the model compounds, along with C_6H_6 and $[C_6H_7]^+$, were determined at the B3LYP/Stuttgart RLCECP for Hg, Cl, and Al, and the 6-31G** for C and H. From these values the enthalpy of reaction ($\Delta H = 427$ kJ·mol^{-1}) may be

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Table 1. Calculated Bond Lengths (Å) and Angles (deg) in Mercury−Arene Complexes

	$Hg(C_6H_6)_2(AlCl_4)_2$[a]	$[HgPh(C_6H_6)(AlCl_4)_2]^-$	$[Hg(C_6H_6)_2(AlCl_4)]^{+}$[a]	$HgPh(C_6H_6)(AlCl_4)$	$[HgPh(AlCl_4)_2]^-$	$[HgPh_2H(AlCl_4)]^-$
Hg−C (p)	2.402	2.873	2.371	2.816		2.267
Hg−C (s)		2.079		2.069	2.068	
Hg−Cl	2.463	2.509, 2.599	2.466	2.519, 2.646	2.508	2.522
$Al-Cl_{br}$	2.393	2.324, 2.339	2.364	2.341, 2.314	2.352	2.343
$Al-Cl_{ter}$	2.200−2.245	2.222−2.242	2.181	2.195, 2.203	2.217, 2.230	2.193
$C-H_{br}$						1.476
C−Hg−C	109.37	105.01	110.06	105.78	134.60	80.79
Cl−Hg−Cl	95.94	90.95	85.24	81.67	90.79	84.37
Hg−Cl−Al	119.43	121.78, 124.56	92.49	91.30, 93.92	116.19	91.52

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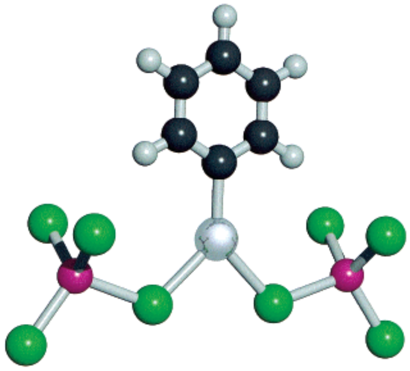


Figure 3. Calculated structure for the $[HgPh(AlCl_4)_2]^-$ anion showing the trigonal planar coordination of the mercury.

calculated for the model reaction shown in eq 4. While this number is open to interpretation due to the lack of solvation effects being taken into account, it is ca. 44% of the value calculated for the self-ionization of benzene (ΔH = 970 kJ·mol^{-1}), eq 5. More importantly, the calculated ΔH for eq 4

$$2C_6H_6 \rightarrow [C_6H_5]^- + [C_6H_7]^+ \qquad (5)$$

should be compared to the calculated value for the protonation of benzene by trifluoroacetic acid (ΔH = 634 kJ·mol^{-1}), an acid that is known to catalyze H/D exchange (eq 6).[22] It is

$$HO_2CCF_3 + C_6H_6 \rightarrow [O_2CCF_3]^- + [C_6H_7]^+ \qquad (6)$$

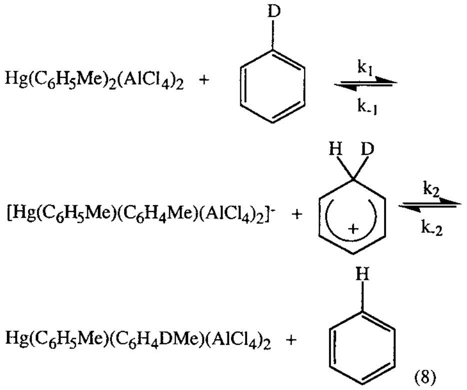
important to note that these calculated values do not take into account the activation barrier for these reactions or solvation effects; however, the trend is consistent with the higher rate observed for $Hg(C_6H_5Me)_2(AlCl_4)_2$ as compared to HO_2CCF_3 in the H/D exchange between C_6H_5Me and C_6D_6.

The structure of the product that would be formed from deprotonation of the cation $[Hg(C_6H_6)_2(AlCl_4)]^+$, i.e., the neutral complex $HgPh(C_6H_6)(AlCl_4)$, was also optimized and its total energy determined. The energy (ΔH = 164 kJ·mol^{-1}) for protonation of benzene by $[Hg(C_6H_6)_2(AlCl_4)]^+$ (eq 7) is significantly lower than that for the reaction shown in eq 4. It

$$[Hg(C_6H_6)_2(AlCl_4)]^+ + C_6H_6 \rightarrow HgPh(C_6H_6)(AlCl_4)_2 + [C_6H_7]^+ \qquad (7)$$

is important to note that this relative trend is in good agreement with both (a) the higher exchange rate experimentally observed for the ionic layer versus neutral layer of the liquid clathrates formed with benzene and *m*- and *p*-xylene and (b) the greater charge effects on the benzene ligands in $[Hg(C_6H_6)_2(AlCl_4)]^+$ in comparison to those in $Hg(C_6H_6)_2(AlCl_4)_2$, see Figure 1.

In comparison to a reaction known to occur during acid-catalyzed H/D exchange (i.e., eq 6), a mechanism by which the Hg···arene complex protonates free C_6H_6 (eqs 4 and 7) is not thermodynamically unreasonable.[14] Furthermore, our proposal that complexation of the arene to the "activated" $HgCl_2$ results in a dramatic increase in the acidity of the aromatic protons is plausible. Based upon the foregoing, we may propose that the H/D exchange between $Hg(C_6H_5Me)_2(AlCl_4)_2$ and C_6D_6, for example, occurs in a manner similar to that observed for protic acids, i.e., eq 8.



Arene Exchange and Intramolecular H-Transfer. As noted above, the benzene ligand in the anionic model complex $[HgPh(C_6H_6)(AlCl_4)_2]^-$ is only weakly associated. On the basis of the optimized structure of $[HgPh(AlCl_4)_2]^-$ (Figure 3 and Table 1) and its total energy, the bond dissociation energy for the neutral benzene (eq 9) is calculated to be 7.7 kJ·mol^{-1}. A dissociation energy of 12.7 kJ·mol^{-1} was similarly obtained for $HgPh(C_6H_6)(AlCl_4)$, eq 10. The related arene dissociation for

$$[HgPh(C_6H_6)(AlCl_4)_2]^- \rightarrow [HgPh(AlCl_4)_2]^- + C_6H_6 \quad (9)$$

$$HgPh(C_6H_6)(AlCl_4) \rightarrow HgPh(AlCl_4) + C_6H_6 \qquad (10)$$

the neutral complex (eq 11) is calculated to be an exothermic process (−7.6 kJ·mol^{-1}), in the absence of solvation affects. Clearly the stability of mercury−arene complexes in solution is determined by the excess of arene solvent present. An

$$Hg(C_6H_6)_2(AlCl_4)_2 \rightarrow Hg(C_6H_6)(AlCl_4)_2 + C_6H_6 \quad (11)$$

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(22) We note that solvation effects are likely to be important in the reactions shown in eqs 4 and 6.

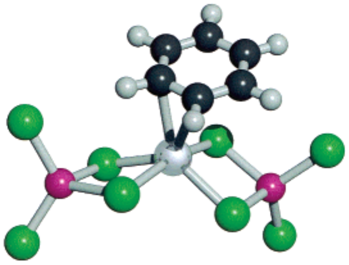

Figure 4. Calculated structure for the $Hg(C_6H_6)(AlCl_4)_2$ showing the λ^2-coordination of the "$AlCl_4$" ligands to mercury.

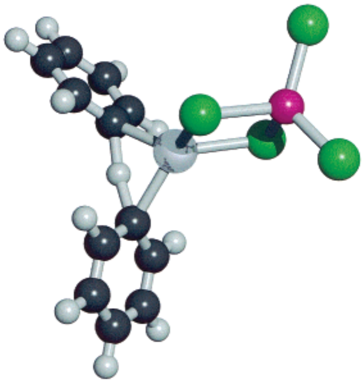

Figure 5. Calculated structure for the $[HgPh_2H(AlCl_4)]^-$ anion; a possible intramolecular hydrogen transfer transition state.

interesting feature of mono-benzene complex $Hg(C_6H_6)(AlCl_4)_2$ (Figure 4 and Table 1) is that two $AlCl_4$ moieties are bound λ^2 to the mercury, rather than λ^1 as observed for both anionic and nondissociated complexes (cf., Figure 1), and thus account for the exothermic nature of the benzene dissociation. Thus, the dissociation of benzene from $Hg(C_6H_6)(AlCl_4)_2$ can be considered as an intramolecular S_N2 substitution of benzene by a terminal chlorine atom of the $[AlCl_4]^-$ anionic ligand. Constraining angles of "$AlCl_4$" groups in their approach to mercury center, the approximate activation energy for the dissociation of benzene from neutral complex can be calculated (60 $kJ\cdot mol^{-1}$).

If arene exchange (eq 12) is a highly facile reaction[10] then the possibility of an intramolecular H/D exchange reaction may be considered. Once the phenyl derivative is formed (eq 4), arene

$$[HgPh(C_6H_6)(AlCl_4)_2]^- + C_6D_6 \rightleftharpoons [HgPh(C_6D_6)(AlCl_4)_2]^- + C_6H_6 \quad (12)$$

exchange may occur more rapidly than intermolecular proton transfer (eq 8), allowing for H/D exchange to occur by way of a intramolecular H/D exchange reaction in which hydrogen transfer from the neutral arene to the phenyl group would be necessary (eq 13). We have calculated the possible transition

$$[Hg(C_6D_6)(C_6H_5)(AlCl_4)_2]^- \rightleftharpoons [Hg(C_6D_5)(C_6H_5D)(AlCl_4)_2]^- \quad (13)$$

state with the corresponding activation energy (233.7 $kJ\cdot mol^{-1}$) for such a reaction, i.e., $[HgPh_2H(AlCl_4)_2]^-$. The molecular symmetry turned out to be C_{2v} as shown in Figure 5 and Table 1.

Two possible mechanisms for H/D exchange may be proposed: intermolecular (eq 8) and intramolecular (eq 13). Intermolecular exchange is based on the protonation of C_6D_6 by the mercury–arene complex followed by the recombination of the resulting $[C_6D_6H]^+$ and mercury–arene anion with 50% probability for the successful H/D exchange (eq 8). This would be expected to follow the same kinetic and site selectivity trends as a traditional mechanism involving a Wheland intermediate.[14] In contrast, the intramolecular exchange would require that the deprotonated mercury–phenyl species be sufficiently long-lived to allow for an intramolecular deuterium shift. Although plausible, the latter mechanism would be more susceptible to steric limitations and as such we propose that such a mechanism is less likely.

Conclusions

Group 13 chloride-stabilized arene–mercury complexes are highly active catalysts for aromatic H/D exchange. The rate of these exchange reactions is unexpectedly fast, given that they are carried out in an aprotic solvent and without a Brönsted acid. Most importantly, it should be noted that ordinarily the addition of aprotic Lewis acid reduces the rate of H/D exchange.[1,3] Thus, the catalytic activity of $Hg(arene)_2(AlCl_4)_2$ and $[Hg(arene)_2(AlCl_4)]^+$ for H/D exchange is highly unusual.

We have previously shown[23] that Group 13 Lewis acids, such as AlR_3, can increase the proton acidity, as measured by a decrease in the pK_a, by at least 7 units. A maximum decrease of 30 units is estimated from the activation of amines. If we compare the pK_a of benzene (43) with those of H_2SO_4 (ca. −2) and HO_2CCF_3 (>2),[13] then a significant decrease in the pK_a of an aromatic hydrogen would be required for H/D exchange to occur. On the basis of DFT calculations, it appears that the coordination of the arene to the mercury/Group 13 complex results in a significant increase in the acidity of the aromatic hydrogens. It is particularly important to note the activation from the mercury/Group 13 complex is significantly greater than that for $HgCl_2$ itself. Thus, the Lewis acidity of the normally weakly acidic mercury is enhanced by the presence of the two strong Lewis acids. This indirect activation is sufficient to cause the coordinated arene to act as the acid in a typical electrophilic aromatic substitution reaction. Using DFT calculations we have shown that the protonation of "free" benzene by the acidic coordinated arene is thermodynamically favored in comparison with the known reaction of benzene with HO_2CCF_3.

Experimental Section

NMR spectra were obtained on Bruker AC-250 and Avance 200, 400, and 500 spectrometers. Chemical shifts are reported relative to internal solvent resonances. NMR tubes are cleaned in basic solution, followed by acetone wash. The tubes are dried and stored in an oven prior to use, from which they are taken directly to the port on the drybox which is immediately evacuated. The C_6D_6 is predried and stored in the drybox over molecular sieves. GC/MS analyses were carried out with use of a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra and equipped with a Hewlett-Packard 5890 series II gas chromatograph using a DB5 30 m × 0.25 mm i.d. column with a 0.25 mm coating of DB-5 stationary phase and injector and transfer line temperatures of 180 and 250 °C, respectively. The column was started at 35 °C for 2 min, then heated at 25 $°C\cdot min^{-1}$ for 6 min and maintained at 185 °C for 1 min. Isotope patterns for all deuterium containing species were matched with

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calculated distributions. The synthesis of Hg(arene)$_2$(MCl$_4$)$_2$ (arene = C_6H_5Me, C_6H_5Et, *o*-$C_6H_4Me_2$, and C_6H_3-1,2,3-Me_3; M = Al, Ga) was as reported previously.[7,8] Solvents and all arenes were distilled and degassed prior to use.

Reaction of Hg(arene)$_2$(MCl$_4$)$_2$ with C_6D_6. In a 5 mm NMR tube containing Hg(arene)$_2$(MCl$_4$)$_2$ (0.10 mmol) was added C_6D_6 (0.5 mL). If necessary, the resulting solution can be heated to allow all the catalyst to dissolve. Usually the formation of a benzene clathrate layer is observed on the bottom of the NMR tube. ^{1}H and ^{13}C NMR spectra were obtained immediately. Then, the NMR tube solution was quenched with water and analyzed by GC/mass spectroscopy.

C_6D_5Me: GS/MS (EI, %) *m*/*z* 97 (M$^+$, 100). ^{1}H NMR (C_6D_6) δ 2.10 (3H, s, C*H*$_3$). ^{13}C NMR (C_6D_6) δ 139.3 (s, *C*-CH$_3$), 129.5 [t, *J*(C−D) = 23.8 Hz, *o*-*C*D], 128.5 [t, *J*(C−D) = ca. 24 Hz, *m*-*C*D], 124.7 [t, *J*(C−D) = 24.4 Hz, *p*-*C*D], 21.5 (s, *C*H$_3$).

C_6D_5Et: GS/MS (EI, %) *m*/*z* 111 (M$^+$, 45), 96 (M$^+$ − Me, 100). ^{1}H NMR (C_6D_6) δ 7.16 (5H, s, C_6D_5*H*), 2.44 [2H, q, *J*(H−H) = 7.6 Hz, C*H*$_2$], 1.07 [3H, t, *J*(H−H) = 7.6 Hz, C*H*$_3$]. ^{13}C NMR (C_6D_6) δ 145.5 (s, *C*-CH$_3$), 128.5 [t, *J*(C−D) = 24 Hz, *o*,*m*-*C*D], 124.9 [t, *J*(C−D) = 25.0 Hz, *p*-*C*D], 29.4 (s, *C*H$_2$), 16.1 (s, *C*H$_3$).

***o*-$C_6D_4Me_2$**: GS/MS (EI, %) *m*/*z* 110 (M$^+$, 100), 95 (M$^+$ − Me, 90). ^{1}H NMR (C_6D_6) δ 7.16 (4H, s, C_6D_5*H*), 1.98 (6H, s, C*H*$_3$). ^{13}C NMR (C_6D_6) δ 141.3 (s, *C*-CH$_3$), 131.3 [t, *J*(C−D) = 24.2 Hz, *o*-*C*D], 124.5 [t, *J*(C−D) = 24.1 Hz, *m*-*C*D], 20.2 (s, *C*H$_3$).

1,2,3-$C_6D_3Me_3$: GS/MS (EI, %) *m*/*z* 123 (M$^+$, 80), 108 (M$^+$ − Me, 100). ^{1}H NMR (C_6D_6) δ 7.16 (3H, s, C_6D_5*H*), 2.09 (6H, s, C*H*$_3$), 1.91 (3H, s, C*H*$_3$). ^{13}C NMR (C_6D_6) δ 139.3 (s, 1,3-*C*-CH$_3$), 137.6 (s, 2-*C*-CH$_3$), 127.1 [t, *J*(C−D) = 23.8 Hz, 4,6-*C*D], 125.4 [t, *J*(C−D) = 24.6 Hz, 5-*C*D], 21.0 (s, 1,3-*C*H$_3$), 15.7 (s, 2-*C*H$_3$).

Reaction of C_6D_6 with Clathrates. In a 5 mm NMR tube containing a clathrate bottom layer (50 mg) was added C_6D_6 (0.5 mL). ^{1}H and ^{13}C NMR spectra were obtained immediately. Then, the NMR tube solution was run through silica gel to kill the catalyst. The resulting colorless mixture of d$_n$-arenes was analyzed by GC/mass spectroscopy. If the top clathrate layer is used the heating of the sample is necessary to complete the exchange reaction.

***m*-$C_6D_4Me_2$**: GS/MS (EI, %) *m*/*z* 110 (M$^+$, 90), 95 (M$^+$ − Me, 100). ^{1}H NMR (C_6D_6) δ 7.16 (4H, s, C_6D_5*H*), 2.14 (6H, s, C*H*$_3$). ^{13}C NMR (C_6D_6) δ 152.0 (s, *C*-CH$_3$), 134.9 [t, *J*(C−D) = 24.5 Hz, 2-*C*D], 132.9 [t, *J*(C−D) = 24.9 Hz, 5-*C*D], 119.9 [t, *J*(C−D) = 24.7 Hz, 4,6-*C*D], 22.4 (s, *C*H$_3$).

***p*-$C_6D_4Me_2$**: GS/MS (EI, %) *m*/*z* 110 (M$^+$, 100), 95 (M$^+$ − Me, 85). ^{1}H NMR (C_6D_6) δ 7.16 (4H, s, C_6D_5*H*), 2.10 (6H, s, C*H*$_3$). ^{13}C NMR (C_6D_6) δ 136.9 (s, *C*-CH$_3$), 129.4 [t, *J*(C−D) = 24.1 Hz, *C*D], 21.2 (s, *C*H$_3$).

Catalytic H/D Exchange. In a 5 mm NMR tube containing Hg(C_6H_5Me)$_2$(AlCl$_4$)$_2$ (5 mg, 0.007 mmol) were added C_6D_6 (0.710 g, 8.452 mmol) and C_6H_5Me (85 mg, 0.924 mmol). When the catalyst was completely dissolved the ^{1}H NMR spectra were recorded at 1.5 h intervals. After the first 1.5 h, the integration of C_6D_5H and $C_6D_{5-x}H_x$ reveals that 40% of toluene protons have exchanged, given the average turnover rate of 3 min^{-1} per Hg. The same experiment was performed at elevated temperature. The NMR tube was heated at 80 °C for 30 s. The ^{1}H NMR spectrum was recorded shortly afterward showing that 30% of toluene have exchanged, given the average turnover rate of 400 min^{-1} per Hg. Using a 1:1 ratio of toluene and C_6D_6 results in a mixture of all isotopic isomers, for example, three well-resolved peaks for *C*H$_3$, as well as 3 peaks for *C*-CH$_3$, are observed in ^{13}C NMR. All other resonances are hard to describe and consist of overlapping triplets and singlets.

In a 5 mm NMR tube containing Hg(C_6H_5Me)$_2$(AlCl$_4$)$_2$ (20 mg, 0.028 mmol) were added C_6D_6 (0.500 g, 8.452 mmol) and $C_6H_4Me_2$ (80 mg, 0.755 mmol). The NMR tube was heated at 80 °C for 1 min. The ^{1}H NMR spectrum was recorded shortly afterward showing the complete H/D exchange between $C_6H_4Me_2$ and C_6D_6.

In a 5 mm NMR tube containing either Hg(C_6H_5Me)$_2$(AlCl$_4$)$_2$ (6.9×10^{-6} mol) or AlCl$_3$ (1.4×10^{-5} mol) were added C_6D_6 (0.500 g, 8.452 mmol) and C_6H_5Me (0.500 mg, 0.543 mmol). The NMR tube was heated at 30 °C for 100 min. The ^{1}H NMR spectrum was recorded to determine the relative extent of the H/D exchange between C_6H_5Me and C_6D_6.

Computational Methods. All density functional calculations were carried out using a Gaussian-98 suite.[24] Complete geometry optimizations were performed at the B3LYP[25] level using the 6-31G** basis set for C and H only and Stuttgart RLC ECP basis set for Hg, Cl, and Al. C_2 and C_s symmetries were imposed on neutral and cationic molecules, respectively. Vibrational frequencies were then evaluated for benzene complexes to verify the existence of the true potential minimum and to determine zero-point energies.

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Supporting Information Available: Structural parameters and energies for optimized structures from DFT calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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