

Organometallic Chemistry of Main Group Elements in the Gas Phase: Formation and Reactions of Gaseous $[\text{AsI}_2 \cdot \text{arene}]^+$ Complexes[†]

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Abstract: The reactions of AsI_3^{*+} in the gas phase with arenes or n-donor substrates efficiently yield the complexes $[\text{AsI}_2 \cdot \text{arene}]^+$ (**3**) and $[\text{AsI}_2 \cdot \text{n-donor}]^+$ (**5**), respectively, by substitution of one iodine atom. This reaction was studied by FT-ICR spectrometry preparing AsI_3^{*+} by electron impact in an external ion source and reacting AsI_3^{*+} with an excess of the neutral ligand in the FT-ICR cell. The complexes **3** and **5** exchange the π - or n-donor ligand by a ligand with a larger AsI_2^+ affinity, ΔG_{AsI_2} , with reaction efficiencies >50%. This fast ligand exchange is reversible, and measurements of the ligand exchange equilibrium were used to establish quantitatively the relative AsI_2^+ affinity, $\delta \Delta G_{\text{AsI}_2}$, of π - and n-donor ligands. For both types of ligands, $\delta \Delta G_{\text{AsI}_2}$ is related to the ligand proton affinity by a single correlation line with a slope of 0.6, showing that the As–ligand bond is less sensitive to substituent effects. The bond dissociation energy (BDE) of the As–ligand bond in the benzene complex **3a** and the acetone complex **5c** was determined by energy-resolved collision-induced decomposition (CID), yielding $\text{BDE}(\mathbf{3a}) = 77 \pm 19$ kJ/mol and $\text{BDE}(\mathbf{5c}) = 106 \pm 19$ kJ/mol. The collisional activation (CA) mass spectra of the arene complexes **3** show back-dissociation into AsI_2^+ and the arene and hydride abstraction from methyl-substituted benzenes by the leaving AsI_2^+ as the main fragmentations indicating an intact AsI_2 group in the complexes. The combined experimental results agree with a structure of the arene complexes **3** which corresponds to an AsI_2^+ fragment weakly bonded to the arene either in a σ -complex (**I**) or an electrostatically bonded π -complex (**II**), but not with structures **III** and **IV** which result from an insertion of the carbenic AsI_2^+ into C–C bonds of the arene.

Introduction

It has been known for a long time that halogenides EX_3 of various main group metalloids (E = As, Sb) and main group metals (E = Al, Ga, In, Bi) dissolve in aromatic solvents forming brightly colored solutions.¹ Elucidation of the structures of some of these solvates was achieved recently by Schmidbaur and Frank.² In most cases a fairly symmetrical η^6 coordination of a polymethyl-substituted arene ligand to the main group element center was observed in the solid state. It is reasonable to assume electrostatic forces and crystal packing effects to be responsible for this particular coordination mode in which the fragment EX_3 with C_{3v} symmetry aligns on the rotation axis of the arene. In contrast, in cyclopentadienide compounds of the p-block elements bonding between the main group element center and the hydrocarbon π -system is best described by semipolar covalent bonds. Various coordination modes are

possible ranging from η^1 to η^3 as is observed, for example,³ η^1 in $(\text{H}_5\text{C}_5)\text{AsMe}_2$ or η^2 , η^3 in $(\text{Me}_5\text{C}_5)_2\text{As}^+$. Interestingly, the energy difference between both coordination modes is very small according to quantum mechanical calculations.⁴

The interactions between arenes and cationic fragments EX_2^+ of group-15 elements are of special interest since these fragments are isolobal to carbenes. In the case of NF_2^+ ions, which are isoelectronic and isolobal to CF_2 , this relationship is clearly seen in the insertion reaction with methane.⁵ However, until now these reactions have not been demonstrated for the heavier element based ions. Phosphenium ions, R_2P^+ , give [4 + 1] cycloadducts with dienes.⁶ This [4 + 1] reactivity in solution is typical for singlet carbene analogues of the heavier main group elements and has been observed also by Burford et al.⁷ in reactions of N- or S-substituted arsenium ions, R_2As^+ . However, no discrete $[\text{EX}_2 \cdot \text{arene}]^+$ complexes (E = As, Sb, Bi; X = F, Cl, Br, I) are known. All compounds reported in the literature so far exhibit significant interactions with the counter

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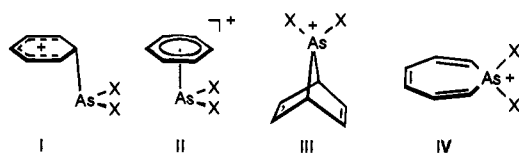
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anion (AlCl_4^- in most cases). Thus, the η^6 -bonded complex of a 1-phosphazonium salt, $\text{R}-\text{N}=\text{P}^+ \text{AlCl}_4^-$, to benzene shows two P-Cl contacts between the phosphorus center and the AlCl_4^- anion in the solid state.⁸ The difficulty in studying the chemistry of *isolated* $[\text{EX}_2\text{arene}]^+$ complexes in the condensed phase is elegantly circumvented by the modern techniques of gas phase chemistry like Fourier-transform ion-cyclotron-resonance (FT-ICR) spectrometry.

In marked contrast to the extensively studied gas phase chemistry of transition metal ions and ionic fragments containing transition metals,⁹ little is known about the ionic gas phase chemistry of p-block element based ions.¹⁰ The former investigations show that a wealth of valuable thermochemical data and kinetic data about organometallics is obtained by gas phase reactivity studies using modern mass spectrometric techniques. In view of the need for reliable thermochemical and reactivity data of heavy elementorganic species, the elucidation of their intrinsic properties is of particular interest. The most direct approach to these properties is the study of ion/molecule reactions in the gas phase. Most of the gas phase studies of ionized p-block elements deal with the reactions of the ions of bare elements or of ionic clusters. For example, the gas phase reactions of Pb^+ and P^+ with benzene were studied,^{11,12} and in the latter case, insertion of P^+ into a C-C bond and ring expansion to a phosphatropylium ion was suggested.¹²

In explanatory experiments, we have observed¹³ that ionized molecules and ionic fragments containing heavy group-15 elements exhibit a rich ion/molecule chemistry with many organic substrates under the condition of chemical ionization (CI), indicating addition or even bond insertion reactivity of heavy element based ions. The possibility that these reactions were induced by $[\text{EX}_2]^+$ cations was especially intriguing in view of the isolobal analogy with neutral carbenes. In particular, an efficient production of adducts $[\text{EX}_2\text{C}_6\text{H}_6]^+$ ($\text{E} = \text{As}, \text{Sb}, \text{Bi}; \text{X} = \text{Br}, \text{I}$) was observed by electron impact ionization of $\text{EX}_3/\text{C}_6\text{H}_6$ mixtures in a CI ion source. Weakly bonded σ - or π -adducts **I** and **II**, 1,4-addition products **III**, and the products **IV** formed by C-C or C-H bond insertion are possible structures for these ionic $[\text{EX}_2\text{C}_6\text{H}_6]^+$ adducts.



Complexes of AsF_2^+ with n-donors in the gas phase are known,¹⁴ but the addition to a delocalized π -system is a new

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process and is of interest with respect to related EX_3/arene complexes in the condensed phase.² Extending our preliminary report,¹⁵ we present here the results of a detailed study of the formation and reactions of the complexes $[\text{AsI}_2\text{arene}]^+$ and $[\text{AsI}_2\text{n-donor}]^+$ in the gas phase by FT-ICR spectrometry. In particular, the kinetics and the equilibria of an exchange of π - and n-donor ligands were studied. These results provide *inter alia* relative bond dissociation energies of the ligands of the ionized AsI_2^+ fragment. In addition, the absolute bond dissociation energies of benzene and acetone, respectively, of this fragment have been determined by energy-resolved collision-induced decomposition (energy-resolved CID) of the adducts using FT-ICR spectrometry.

Experimental Section

A Bruker CMS 47X FT-ICR spectrometer with an external CI ion source¹⁶ was used for this study. Equilibrium measurements involving arenes were recorded with the standard cylindrical cell while n-donor ligand exchange reactions and all CID spectra were measured using the Bruker Spectrospin Infinity cell.^{17,18} The standard vacuum system was improved by exchanging the 50 L s^{-1} by a 270 L s^{-1} turbo pump in the transfer region, maintaining a background pressure $< 3 \times 10^{-9}$ mbar and allowing a better pressure control of ion/neutral collisions during energy-resolved CID experiments even under CI conditions in the external source.

All spectra were recorded in broad band mode (rf chirp excitation). The time domain signal was apodized by a suitable Gaussian multiplication before Fourier transformation, achieving the same shape of all peaks in the magnitude spectrum. The pressure readings from the ion gauge of the ICR cell were first calibrated with the reaction $\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$ ($k = 1.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)¹⁹ to account for the different positioning of the ion gauge and pumping system and were subsequently corrected to the different sensitivities toward the neutral molecules.²⁰ The temperature of the gas and the ions within the ICR cell was at room temperature, and all derived thermodynamic properties refer to 298 K.

All organic chemicals were checked by GC and were purified if necessary. Prior to use, the compounds were subjected to several freeze-pump-thaw cycles. AsI_3 (**1**) was prepared from As_2O_3 and KI in HCl and was recrystallized from diethyl ether.²¹ The formation of complexes $[\text{AsI}_2\text{benzene}]^+$ (**3a**) from AsI_3^{+} (**1**⁺) and benzene (**2a**) has been described before.¹⁵ Similarly, the direct substitution of I⁺ in AsI_3^{+} by ethanol or acetone was achieved by generating the ion AsI_3^{+} externally by low-energy ($< 20 \text{ eV}$) electron impact ionization in the ICR cell. The neutral molecules were present in the cell at a pressure of 1.0×10^{-8} mbar (ethanol) and of 5.0×10^{-8} mbar (acetone), respectively. After broad band (rf chip excitation) ejection of all ions with $m/z < 350$, an Ar pulse is applied to cool the ions. Finally, all remaining ions besides the educt were ejected by “single shots” (rf pulses) of low accelerating voltage ($V_{p-p} \leq 14 \text{ V}$) to avoid excitation of the reacting ions. The pseudo-first-order rate constant $k_{\text{obs}} = k_{\text{bi}}[\text{neutral}]$ was determined from the exponential decay of $[\text{AsI}_3^{+}]$ and was transformed into the second-order rate constant k_{bi} by dividing k_{obs} by the number density of the neutral molecules in the ICR cell.

Equilibrium Measurements. $[\text{AsI}_2\text{benzene}]^+$ (**3a**) was formed in the external CI ion source from AsI_3 and benzene (**2a**) under CI conditions. After transfer into the ICR cell **3a** reacted with a mixture of the neutral molecules under investigation by ligand exchange. The

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Table 1: Rate Constants, k_{bi} , and Reaction Efficiencies of the arene Exchange Reaction (II)

reaction	$p(2i)^a$	k_{bi}^b	$k_c^{b,c}$	eff (%)
3a + 2b → 3b + 2a	7.0	6.0	9.5	61
3a + 2e → 3e + 2a	7.8	5.2	9.6	54
3a + 2f → 3f + 2a	7.1	5.4	9.5	57
3a + 2g → 3g + 2a	6.3	5.9	1.1	55
3a + 2h → 3h + 2a	5.1	7.6	1.0	76

^a $\times 10^{-8}$ mbar. ^b $\times 10^{-10}$ [cm³ molecule⁻¹ s⁻¹]. ^c Reference 29.

molar ratio of both neutral molecules was controlled by introducing the minor component first, and after reading the ion gauge, the major component was added to adjust the total pressure in the ICR cell to 10^{-8} – 10^{-6} mbar. After a sufficient time to convert **3a** into the complexes of reaction III, all ions besides one of the complexes (**3i** or **3j**) and its isotopomers were removed by a combination of broad band and single shot ejection. Subsequently, the relaxation of the system into the equilibrium state was measured. Starting with the initial ejection of **3j** ($I(\mathbf{3j}) = 0\%$, $I(\mathbf{3i}) = 100\%$), the bimolecular rate constants of the forward ligand exchange reaction, k_{ij} , the backward exchange reaction, k_{ji} , and the equilibrium constants, K_{ij} (reaction III), were extracted from the relaxation data in the following way: the pseudo-first-order rate constants ($k_{ij}[\mathbf{2j}]$) and ($k_{ji}[\mathbf{2i}]$) were determined by curve fitting²² of the decay (k_{ij}) and of the increase (k_{ji}) of the intensity of **3i** and **3j**, respectively, by eq 1.²³

$$I(\mathbf{3i})_t = \frac{100}{k_{ij}[\mathbf{2j}] + k_{ji}[\mathbf{2i}]} (k_{ji}[\mathbf{2i}] + k_{ij}[\mathbf{2j}] e^{-(k_{ij}[\mathbf{2j}] + k_{ji}[\mathbf{2i}])t})$$

$$I(\mathbf{3i})_t = \frac{100k_{ij}[\mathbf{2j}]}{k_{ij}[\mathbf{2j}] + k_{ji}[\mathbf{2i}]} (1 - e^{-(k_{ij}[\mathbf{2j}] + k_{ji}[\mathbf{2i}])t}) \quad (1)$$

The equilibrium constants $K_{ij} = k_{ij}/k_{ji}$ were calculated from the ratio of the pseudo-first-order rate constants ($k_{ij}[\mathbf{2j}]/k_{ji}[\mathbf{2i}]$) by multiplying with the molar ratio $[\mathbf{2i}]/[\mathbf{2j}]$, which is obtained from the partial pressures readings corrected for the relative sensitivities of the ion gauge toward the respective neutral molecules.²⁰

The individual bimolecular rate constants k_{ij} were calculated from the pseudo-first-order rate constants derived from eq 1 by dividing with the number density of **[2i]** and **[2j]**, respectively, using the corrected partial pressures. For this purpose the calibration of the ion gauge at the FT-ICR cell was achieved by the bimolecular rate constant $k_{\text{benzene,toluene}}$ of the direct ligand exchange reaction of the benzene complex **3a** with toluene **2b**. The value of $(6.0 \pm 1.5) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ of $k_{\text{benzene,toluene}}$ (Table 1) has been determined before by a series of independent measurements.¹⁵ In some cases the equilibrium constant was determined additionally from the ratio of intensities after the equilibrium state was reached ($t = \infty$, eq 2). In each case the results obtained by the two methods were identical within the limits of error.

$$K_{ij} = \frac{I(\mathbf{3j})_{t=\infty}[\mathbf{2i}]}{I(\mathbf{3i})_{t=\infty}[\mathbf{2j}]} \quad (2)$$

The equilibrium constants of n-donor ligand exchange reactions were determined analogously.

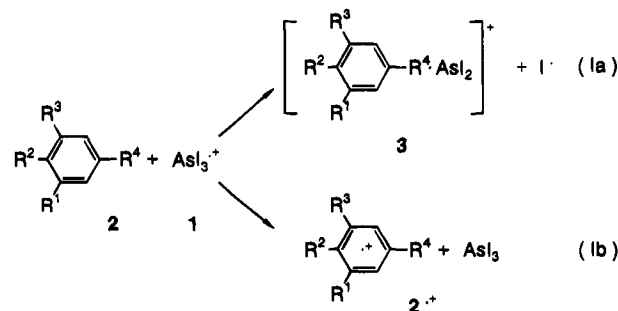
CID Spectra of [AsI₂arene]⁺. Ions **3b–f** were prepared by reaction of externally generated **3a** with **2b–f** added via a pulsed valve into the ICR cell. The neutral reagent was pumped off, the parent ion was isolated as usual, and Ar was added via a second pulsed valve with a "peak pressure" of $p_{\text{max}} \approx 2 \times 10^{-6}$ mbar. Any daughter ions formed were ejected again by single shots, and following a delay of 2 s, the parent ion was accelerated by a single pulse of 30 μ s length and a

voltage $V_{p-p} = 105$ V. The center-of-mass energy E_{cm} ranges from 6 eV for **3a** to 5 eV for **3f**.¹⁸ The Ar pressure during the collision delay time was approximately 8×10^{-8} mbar, and the CID spectra were recorded after 20 ms postcollision delay time.

Energy-Resolved CID. The principles of the method of energy-resolved CID have been discussed before,²⁴ and the method has already been used with a similar instrument.^{24b} A detailed discussion of the adoption of this technique to the new Infinity cell by a determination of the geometry factor ($\beta = 0.90$) will be presented elsewhere.¹⁸ Briefly, the procedure used was as follows: the ions **3a** and **5c** were formed under CI conditions in the external source with **2a** and **4c** as CI gases and introduction of AsI₃ by the solid sample probe. A constant target gas (Ar) pressure of $(3-5) \times 10^{-8}$ mbar was used in the ICR cell. Single collision conditions are attained if the product of pressure and reaction delay is below 7×10^{-7} mbar \times ms.^{24b} The parent ion was isolated by broad band ejection and cooled as usual (total cooling delay time of about 10 s). Any ions still appearing in the expected m/z region of the daughter ions are ejected (no signal above noise level), and the parent ions were cooled by a supplementary delay time (typically 2 s). Eventually, the parent ion was translationally excited by a rf pulse with constant peak-to-peak voltage. After a postcollision delay time (postexcitation delay), the CID spectrum was obtained by the broad band detection. The kinetic energy of the parent ion was varied by changing the rf pulse length. From the set of energy-resolved CID spectra thus obtained, a plot of daughter ion yield vs E_{cm} was constructed. Assuming a linear increase of the reaction cross section above the threshold and accounting for the random thermal motion of the target gas (Doppler broadening), the appearance energy of AsI₂⁺ (AE(AsI₂⁺)) was derived by fitting²² the data to a function (eq 31, in ref 25) developed by Chantry.²⁵ As a test, the AE(C₇H₈⁺) = 0.74 eV and AE(C₇H₇⁺) = 1.50 eV from *n*-butylbenzene radical cations were measured with this energy-resolved CID procedure. The results agree fairly well with the literature values of 0.78 and 1.40 eV from PEPICO measurements,²⁶ indicating an accuracy of better than ± 0.2 eV for our measurements.

Results

Formation and Ligand Exchange Reactions of Gaseous [AsI₂arene]⁺ **3.** In the diluted gas phase, AsI₃⁺ generated by electron impact ionization reacts efficiently with neutral arenes **2** by substitution of one I ligand by an arene ligand¹⁵ (reaction Ia). In addition, charge exchange (reaction Ib) occurs depending on the difference of the ionization energy (IE) of the arene and AsI₃ (IE = 9.00 eV²⁷). Thus, no charge exchange is observed during the reactions with benzene (**2a**, IE = 9.22 eV²⁷) if AsI₃⁺ is carefully thermalized in the FT-ICR cell by collision with Ar. In the case of toluene (**2b**, IE = 8.79 eV²⁷) charge transfer competes extensively and becomes by far the most important reaction in the case of xylenes (**2c–e**, IE = 8.44–8.55 eV²⁷). A collision complex or adduct ion [AsI₃arene]⁺ stabilized by third body collisions or emission of radiation was never observed.



In the case of benzene (**2a**) a quantitative and exclusive conversion of AsI₃⁺ into the complex [AsI₂C₆H₆]⁺ (**3a**) is observed with a bimolecular rate constant $k_{bi} = (5.5 \pm 1.5) \times 10^{-10}$ cm³ molecules⁻¹ s⁻¹. The efficiency $100k_{bi}/k_c = 60\%$

(22) ORIGIN 3.0, MicroCal Software Inc., Northampton, MA, 1993. This software package provides nonlinear least-square fits by customizing the Levenberg–Marquardt algorithm.

(23) The relaxation is pseudo-1st order in both directions. Therefore, the kinetics of the simple reversible reaction $\mathbf{A} \rightleftharpoons \mathbf{B}$ is utilized. See: Steinfeld, J. I.; Francisco, J. S.; Hase, W. J. *Chemical Kinetics and Dynamics*; Prentice Hall: Englewood Cliffs, 1989; p 23.

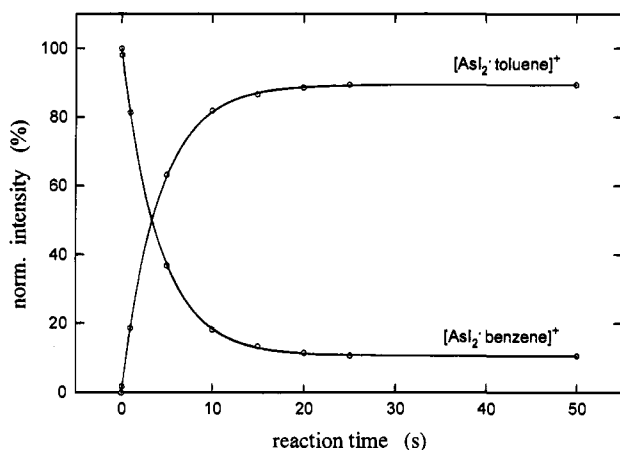
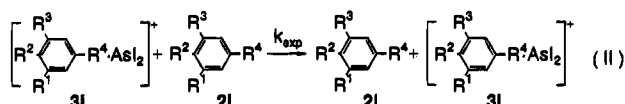


Figure 1. Experimental kinetic curves for the arene exchange reaction (II) of the benzene complex **3a** with toluene (**2b**).

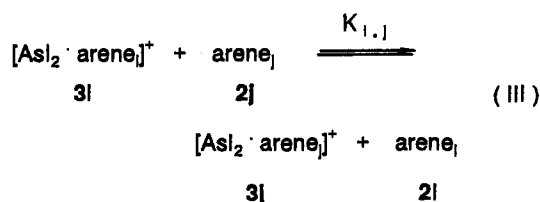
of the process is calculated from the collision rate constant k_c by the method of Su and Chesnavich²⁸ showing that gas phase AsI_3^{++} exchanges efficiently one iodo ligand by a neutral C_6H_6 .

The exchange of a second iodo ligand of the complex $[\text{AsI}_2\cdot\text{arene}]^+$ is never observed. However, the complexes **3** exchange easily the arene ligand by a more basic one in a fast ion/molecule reaction¹⁵ with efficiencies > 50% (reaction II; Table 1). Figure 1 shows the experimental kinetic curves of the ligand exchange reaction of $[\text{AsI}_2\cdot\text{C}_6\text{H}_6]^+$ **3a** with toluene (**2b**). An exchange starting with **3a** is the most convenient synthesis of other complexes **3b–3f** containing alkylated benzenes **2b–2f** of lower IE since no side reactions occur.



R ¹	R ²	R ³	R ⁴		
H	H	H	H	2a	3a
CH ₃	H	H	H	2b	3b
H	CH ₃	H	CH ₃	2c	3c
CH ₃	CH ₃	H	H	2d	3d
CH ₃	H	CH ₃	H	2e	3e
CH ₃	H	CH ₃	CH ₃	2f	3f
(CH ₃) ₃ C	H	H	H	2g	3g
(CH ₃) ₃ C	H	(CH ₃) ₃ C	CH ₃	2h	3h

In principle, the arene ligand exchange is reversible (reaction III) and results in an equilibrium mixture if two or more different arenes are present in the gas phase. The equilibrium constant



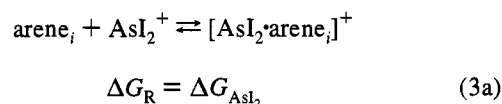
$K_{i,j}$ of reaction III reflects the competition of arene_i and arene_j

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for AsI_2^+ and gives information about substituent effects at the arene on the binding energy of the fragment AsI_2^+ . For a quantitative description of these effects the *free AsI₂ cation affinity*, ΔG_{AsI_2} , of ligands toward AsI_2^+ is defined in eq 3.



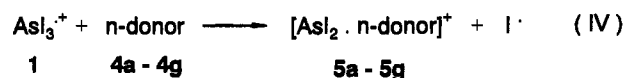
$$\delta\Delta G_{\text{AsI}_2} = \Delta G_{\text{AsI}_2}(\text{benzene}) - \Delta G_{\text{AsI}_2}(\text{arene}_j) \quad (\text{3b})$$

$$\delta\Delta G_{\text{AsI}_2} = -RT \ln K_{\text{benzene},j}$$

By measurements of the ligand exchange equilibrium reaction III only *relative* affinities, $\delta\Delta G_{\text{AsI}_2}$, are accessible, and benzene was chosen as the reference ligand (arene_i = benzene). A direct determination of an exchange equilibrium of $[\text{AsI}_2\cdot\text{C}_6\text{H}_6]^+$ **3a** with every alkylbenzene is not possible because the values of the equilibrium constants $K_{\text{benzene},j}$ span several orders of magnitude, and because the dynamic range for accurate relative intensity measurements of the FT-ICR spectrometer is limited to less than 10^4 . However, the exchange equilibria for arenes **2i** and **2j** of similar ΔG_{AsI_2} are observed easily by injecting ion source-generated **3a** into a known mixture of gaseous arenes **2i** and **2j** in the FT-ICR cell. The identical equilibrium state is achieved within a few seconds by ejecting initially either $[\text{AsI}_2\cdot\text{arene}_i]^+$ (**3i**) or $[\text{AsI}_2\cdot\text{arene}_j]^+$ (**3j**). The very small amount of **2a** released in the first transfer step does not interfere with the exchange equilibrium. Figure 2 shows the experimental intensity curves of the ligand exchange equilibrium involving *m*-xylene (**2d**) and mesitylene (**2f**). A “ladder” of equilibrium constants $K_{i,j}$ is obtained in this way, and the $K_{i,j}$ are converted eventually to $K_{\text{benzene},i}$ and $\delta\Delta G_{\text{AsI}_2}$ (Table 2).

The bimolecular rate constants $k_{i,j}$ and the equilibrium constants $K_{i,j}$ of the ligand exchange reactions can also be extracted from the relaxation kinetics using eq 1. The bimolecular rate constants thus obtained are listed in Table 2. As expected, the efficiencies of exoergic arene exchanges are between 50% and 100%, while the efficiencies of the endoergic exchanges are distinctly below 1%.

Formation and Ligand Exchange Reactions of $[\text{AsI}_2\cdot\text{n-donor}]^+$ **5.** Additional information about the $[\text{AsI}_2\cdot\text{arene}]^+$ complexes **3** is obtained by a comparison with complexes $[\text{AsI}_2\cdot\text{n-donor}]^+$ (**5a–g**) of the cationic fragment $(\text{AsI}_2)^+$ with n-donor substrates **4a–g**. These latter complexes are formed in the reaction IV of AsI_3^{++} with suitable substrates, but for most of the n-donors studied, other reactions compete with substitution of I in AsI_3^{++} . Thus, the rate constants of reaction IV were only determined for the reaction of ethanol (**4a**, $k_{\text{bi}} = (5.3 \pm 1.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and acetone (**4c**, $k_{\text{bi}} = (1.3 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). For these two n-donors the formation of $[\text{AsI}_2\cdot\text{C}_2\text{H}_5\text{OH}]^+$ or $[\text{AsI}_2\cdot\text{CH}_3\text{COCH}_3]^+$ is by far the main reaction and efficiencies of 35% and 62% indicate substitution reactions near the collision limit.



Similar to the synthesis of the arene complexes **3** the generation of the complexes **5** by ligand exchange with a stronger n-donor (reaction V) is also much more convenient if the exchange is not hindered sterically. Ligand exchange by

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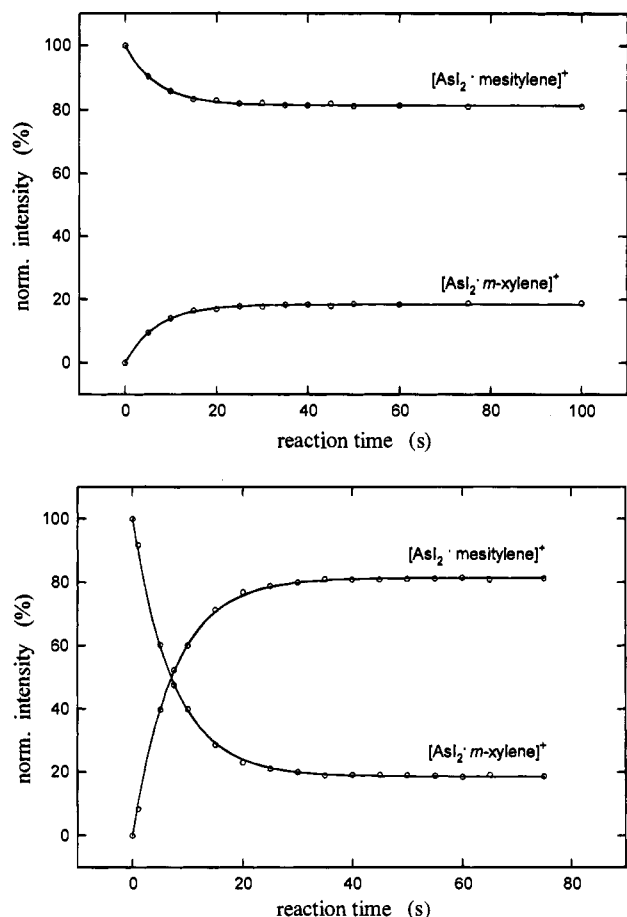
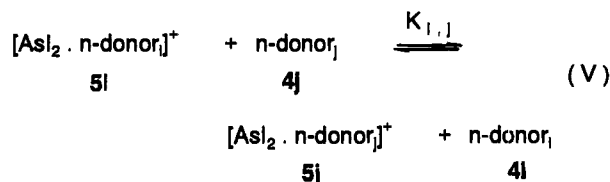


Figure 2. Experimental kinetic curves for the arene exchange equilibrium (III) of *m*-xylene (**2d**) and mesitylene (**2f**); (a, top) Initial ejection of the *m*-xylene complex **3d**; (b, bottom) initial ejection of the mesitylene complex **3f**.

an *n*-donor is observed for the arene complex **3a** as well, thus **3a** was used preferably to prepare **5**. Again the ligand exchange is reversible, and an investigation of the equilibria of the ligand exchanges has been used to establish the free AsI_2 cation affinity $\delta\Delta G_{\text{AsI}_2}$ of *n*-donor substrates relative to benzene by the methods discussed in the previous section. The corresponding data are collected in Table 3.



- equ. Va : **3a** + ethanol (**4a**)
 equ. Vb : **5a** + 1,4-dioxane (**4b**)
 equ. Vc : **5a** + acetone (**4c**)
 equ. Vd : **5b** + acetone (**4c**)
 equ. Ve : **5c** + diethylether (**4d**)
 equ. Vf : **5b** + ammonia (**4e**)
 equ. Vg : **5d** + di-*n*-butylether (**4f**)
 equ. Vh : **5e** + acetophenone (**4g**)

Collision-Induced Decomposition of $[\text{AsI}_2\text{arene}]^+$ **3.** Information about the structure and the bonding of the arene complexes **3** was obtained by collision-induced decomposition (CID) with low-energy collisions and by energy-resolved CID with Ar in the FT-ICR instrument under single collision

conditions for the ions. The results are shown in Table 4. An abundant fragmentation of the arene complexes **3** is always the dissociation into AsI_2^+ and the neutral arene, indicating a weak bond of AsI_2^+ to the arene. With increasing methyl substitution at the arene, the formation of $[\text{arene-H}]^+$ ions starts to compete effectively with dissociation into the components of the complex. It is not known whether the ions $[\text{arene-H}]^+$ correspond to benzyl cations or to tropylium ions. However, both structures are stabilized by methyl substituents so that the formation of these ions is energetically more favorable in **3c-f** containing polymethyl-substituted benzenes. *A priori* there are two routes to generate the ions $[\text{arene-H}]^+$ from **3**. First, the complex **3** may dissociate by loss of an AsI_2 radical, yielding the molecular ion of the respective arene ligand which decomposes subsequently by loss of an H atom. Methyl substitution decreases the IE of the arene; therefore, charge transfer to the ligand will be more favored in complexes of the polymethylbenzenes. However, the EI mass spectra of the xylenes **2c-e** and in particular of mesitylene **2f** show predominant fragmentation of the molecular ions by loss of a CH_3 radical instead of loss of a H atom.²⁹ Thus, to explain these differences in the fragmentations, the arene molecular ions must have been generated in a very specific state during the CID of **3**. This is not very likely, and although small peaks of the molecular ions of the arenes are observed in the CID spectra, they cannot be the precursors of the ions $[\text{arene-H}]^+$. Second, formation of the ions $[\text{arene-H}]^+$ can occur by hydride abstraction of the AsI_2^+ fragment from the ligand during the dissociation of the complex **3**. This mechanism gives a simple explanation for the large intensity of the ions $[\text{arene-H}]^+$ without observing the other known fragment ions of the ionized ligands. As will be shown elsewhere the hydride comes indeed specifically from the α -position of an alkyl substituent of the arene ligand of **3**.³⁰ Note, however, that it is not possible to decide by the experiments performed whether hydride abstraction occurs during the CID by the leaving AsI_2^+ or has happened before CID in the complex by insertion of AsI_2^+ into the C-H bond of a methyl substituent.

By controlling the kinetic energy of the colliding ions in the FT-ICR cell by varying the length of the cyclotron excitation rf pulse at constant pulse height, it is possible to measure the threshold energy for the dissociation of ions and to determine the absolute *bond dissociation energy* (BDE) of a particular bond.²⁴ However, meaningful data are obtained only if the ion decomposes by a single reaction path and if CID of the ion occurs by a single collision. For a certain constant background pressure of the collision gas, the dominant occurrence of single collisions depends on the delay time between kinetic excitation and detection of the ions. The CID spectrum of **3a** (Table 4) of the benzene complex **3a** contains >95% AsI_2^+ , and Figure 3a shows the dependence of the AsI_2^+ intensity on the collision energy E_{cm} of **3a**.

From the curves measured at short delay times an appearance energy $\text{AE}(\text{AsI}_2^+)$ of 0.8 ± 0.2 eV which corresponds to a BDE- $(\text{AsI}_2^+ - \text{benzene}) = \text{AE}(\text{AsI}_2^+) + \Delta nRT = 0.8 \pm 0.2$ eV (77 ± 19 kJ/mol) was obtained.

By an analogous experiment (Figure 3b) using the acetone complex **5c**, the BDE(acetone- AsI_2^+) = 1.1 ± 0.2 eV (106 ± 19 kJ/mol) was determined. From the absolute BDE of these two ligands, a ΔBDE of 29 kJ/mol is obtained. Assuming that there is no activation barrier for the association reaction and neglecting the change in entropy for the equilibrium reaction,

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Table 2: Rate constants,^a k , Reaction Efficiencies, Equilibrium Constants,^a K , and AsI_2^+ Affinities, ΔG_{AsI_2} , of the Arene Exchange Reaction (III)

equilibrium	k_1^b	eff (%) ^c	k_2^d	eff (%) ^c	K_{ij}	$\Delta G_{\text{AsI}_2}^e$	$\delta\Delta G_{\text{AsI}_2}^e$	GB ^{e,f}
3a + 2b \rightleftharpoons 2a + 3b	6.0	60	1.0	0.12	580	-15.8(\pm 0.3)	-15.8(\pm 0.3)	761
3b + 2c \rightleftharpoons 2b + 3c	5.5	58	5.4	0.55	103	-11.5(\pm 0.3)	-27.3(\pm 0.4)	772
3b + 2d \rightleftharpoons 2b + 3d	5.2	50	4.3	0.44	121	-11.9(\pm 0.3)	-27.7(\pm 0.5)	779
3b + 2e \rightleftharpoons 2b + 3e	8.3	84	0.12 ^g	0.012	6670 ^g	-21.8(\pm 0.9)	-37.6(\pm 1.0)	787
3e + 2f \rightleftharpoons 2e + 3f	9.8	104	2.7	0.28	363	-14.6(\pm 0.3)	-52.2(\pm 1.3)	810

^a Error of relative rate constants = 10%, resulting in an error of the equilibrium constants $K_{ij} = 15\%$. ^b $\times 10^{-10}$ [cm³ molecule⁻¹ s⁻¹]. ^c Using capture rates k_c ; ref 25. ^d $\times 10^{-12}$ [cm³ molecule⁻¹ s⁻¹]. ^e [kJ mol⁻¹]. ^f Reference 30, GB(benzene) = 730.5 kJ mol⁻¹. ^g The error of k_2 for this reaction is 33%, leading to an error of 36% of the corresponding equilibrium constant.

Table 3: Equilibrium Constants, K , and AsI_2^+ Affinities, ΔG_{AsI_2} , of the n-Donor Exchange Reaction (V)

equilibrium	K_{ij}	$\Delta G_{\text{AsI}_2}^a$	$\delta\Delta G_{\text{AsI}_2}^{a,b}$	$\delta\Delta G_{\text{AsI}_2}^a$	GB ^{a,d}
3a + 4a \rightleftharpoons 2a + 5a	1792	-18.6(\pm 0.3)		-18.6(\pm 0.3)	754
5a + 4b \rightleftharpoons 4a + 5b	123	-11.9(\pm 0.3)		-30.5(\pm 0.4)	778
5a + 4c \rightleftharpoons 4a + 5c	1071	-17.3(\pm 0.3)	-35.9(\pm 0.5)	-36.6(\pm 0.4) ^c	790
5b + 4c \rightleftharpoons 4b + 5c	15.8	-6.8(\pm 0.4)	-37.3(\pm 0.7)		
5c + 4d \rightleftharpoons 4c + 5d	4.5	-3.7(\pm 1.0)	-39.6(\pm 1.1)	-40.3(\pm 1.6) ^c	805
			-41.0(\pm 1.2)		
5b + 4e \rightleftharpoons 4b + 5e	84	-11.0(\pm 1.5)	-50.6(\pm 1.9)	-51.3(\pm 2.8) ^c	818
			-52.0(\pm 1.9)		
5d + 4f \rightleftharpoons 4d + 5f	94.9	-11.3(\pm 0.3)	-50.9(\pm 1.1)	-51.6(\pm 1.6) ^c	820
			-52.3(\pm 1.2)		
5e + 4g \rightleftharpoons 4e + 5g	76.8	-10.8(\pm 0.3)	-61.3(\pm 1.9)	-62.1(\pm 2.7) ^c	826
			-62.8(\pm 1.9)		

^a [kJ mol⁻¹]. ^b The two values correspond to the different successive combination of K_{ij} . ^c $\delta\Delta G_i$ is the mean of the two independent $\delta\Delta G_i$. ^d Reference 30, GB(benzene) = 730.5 kJ mol⁻¹.

Table 4: CA Mass Spectra^a of the Complexes $[\text{AsI}_2\text{arene}]^+$

fragment ion	3a	3b	3c	3d	3e	3f
arene ⁺	1.1	<1	5.8	<2	<1	4.2
[arene-H] ⁺	<1	1.1	36.3	4.6	1.9	19.1
AsI_2^+	95.2	88.2	53.4	84.3	88.4	64.7
AsI^+	3.2	9.3	3.9	6.7	3.8	2.7
[arene-H]AsI ⁺	<.5	<1	<1	4.4	4.8	6.5

^a % intensity relative to total fragment ion intensity.

this ΔBDE can be compared to $\delta\Delta G_{\text{AsI}_2}(\text{acetone}) = 36.6$ kJ/mol (Table 3) from equilibrium measurements. Thus, the difference of the absolute BDE measured by energy-resolved CID is in reasonable agreement with the relative bond energy reflected by the $\delta\Delta G_{\text{AsI}_2}$ obtained from measurements of the equilibria of ligand exchange reactions.

Discussion

The formation of complexes $[\text{AsI}_2\text{arene}]^+$ by reaction I is the first example of the bonding of a simple carbene analogue AsR_2^+ fragment to an arene in the gas phase. Reaction I exchanges effectively an iodine atom of a AsI_3^{2+} radical cation by benzene or a methyl-substituted benzene, thus converting this radical cation into an even-electron cation (3) with a structure of I–IV.

The large efficiency of reaction I is only in accord with an exothermic ion/molecule reaction. The appearance energy (AE) of AsI_2^+ in the mass spectrum of AsI_3 is 9.5 ± 0.5 eV,²⁷ and from this value and the $\text{IE}(\text{AsI}_3) = 9.00$ eV,²⁷ a lower limit of the $\text{BDE}(\text{AsI}_2^+ - \text{benzene}) > 0.5$ eV is obtained by postulating an exothermic reaction I. Furthermore, the substitution of I* in AsI_3^{2+} must occur without a large intrinsic barrier of the chemical reaction within the collision complex because otherwise the ion/molecule reaction would again be inefficient. Similarly, the fast exoergic arene ligand exchange reaction (II) indicates the absence of any remarkable intrinsic activation barrier also for this reaction. This would agree with a loose electrostatic attachment of AsI_2^+ to the arene ligand or a weakly bound π -complex (structure II). For As complexes in con-

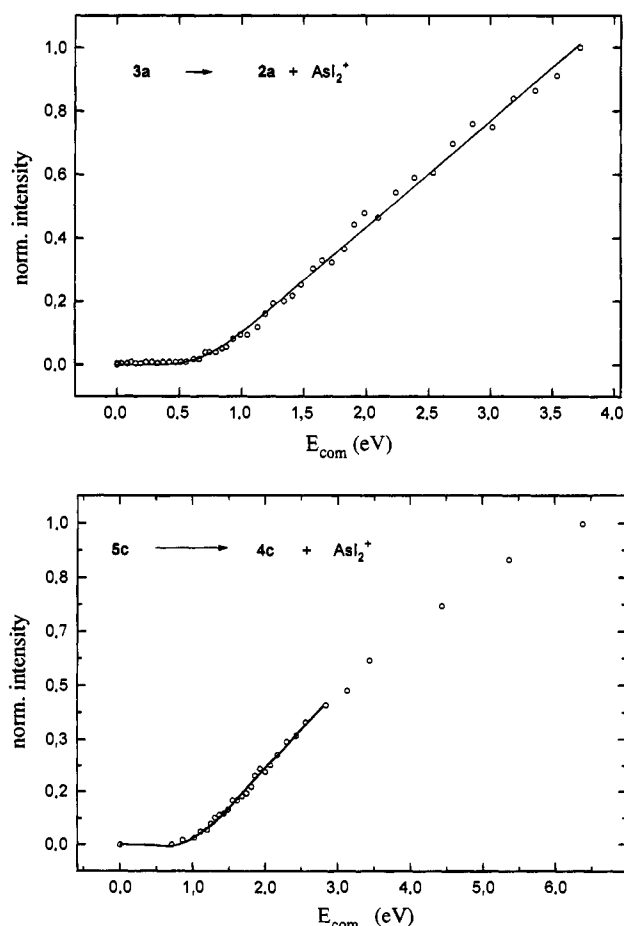


Figure 3. Experimental AsI_2^+ intensity curves for energy-resolved CID of (a, top) the benzene complex 3a (b, bottom) the acetone complex 5c.

densed phase in which mainly an electrostatic interaction between the arene and the As is assumed, a distance of As to the center of a π - or n-donor ligand of approximately 3 Å is

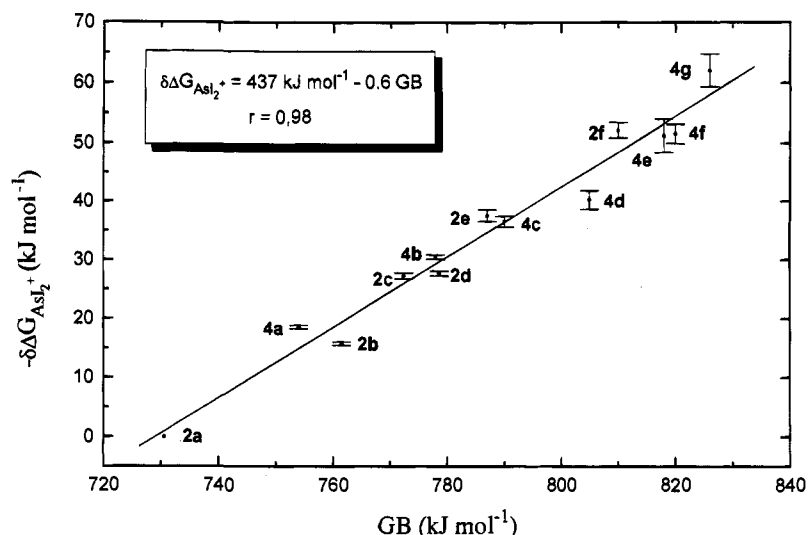


Figure 4. Correlation of the relative AsI_2^+ affinity, ΔG_{AsI_2} , of arene (2) and n-donor (4) ligands in complexes 3 and 5 with ligand proton affinity.

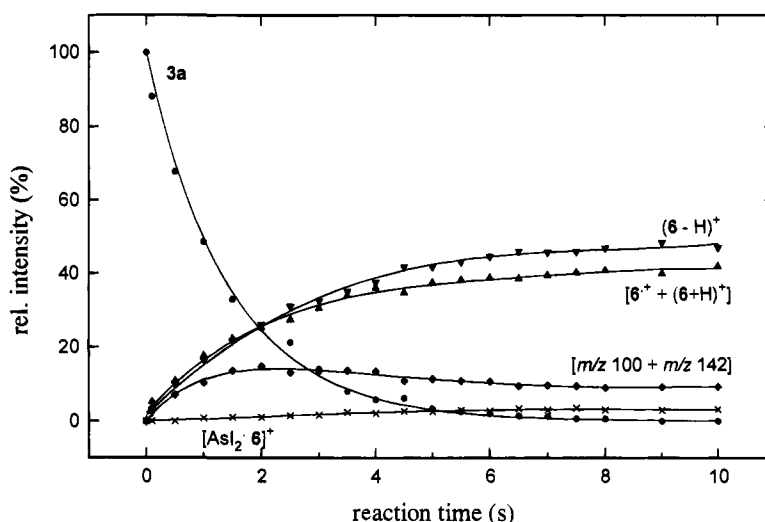


Figure 5. Experimental kinetic curves for the gas phase reaction of benzene complex 3a with tri-*n*-butylamine (6).

observed.^{2b} Assuming AsI_2^+ as a point charge at this distance for complex 3a, the calculation of the electrostatic interaction by the ADO potential³¹ results in an energy value of the “purely electrostatic” bond of 80 kJ/mol. However, in the case of a simple electrostatic attachment of the AsI_2^+ cation in structure II, the relative interaction energy expressed by the relative AsI_2^+ affinity $\delta\Delta G_{\text{AsI}_2}$ should follow the dipole moment and polarizability of the respective ligand. This is not observed experimentally, but this model of electrostatic bonding may be insufficient.

Figure 4 shows that $\delta\Delta G_{\text{AsI}_2}$ correlates linearly with the gas phase basicity (GB) of the ligand. The relationship $\delta\Delta G_{\text{AsI}_2} = 437 \text{ kJ/mol} - 0.6\text{GB}$ (correlation coefficient 0.98) extends over a GB difference of $\sim 100 \text{ kJ/mol}$ and includes arene ligands as well as n-donor ligands. Clearly the proton is bound by a σ -bond to all of the ligands of Figure 4, in particular a σ -complex is formed with the arenes. Similarly, n-donor ligands add to the electrophilic AsI_2^+ by donating two lone pair electrons into the vacant p-orbital and thus generating a dative σ -bond.³² Therefore, the observation of a single correlation line for $\delta\Delta G_{\text{AsI}_2}$ of arenes and of n-donor ligands is a strong indication that AsI_2^+ forms the σ -complex (structure I) with arenes. The

slope of 0.6 in Figure 4 demonstrates that the bond of AsI_2^+ to the ligand is less sensitive to a variation of the electron-donating properties of the ligand than the bonding of a proton. This is expected for a weak ($\text{AsI}_2\text{-C}$) σ -bond.

A σ -complex (I) generated by attachment of an electrophile to benzene should be deprotonated in the gas phase by reaction with a strong base. The result of an attempt to deprotonate $[\text{AsI}_2\text{benzene}]^+$ (3a) by the strong base tri-*n*-butylamine (6) ($\text{GB} = 950 \text{ kJ/mol}$ ³³) is shown in Figure 5. The formation of protonated 6 is observed but can be pursued unequivocally to a secondary ion/molecule reaction of the molecular ions 6^+ with neutral 6. Besides some fragmentations of 6^+ yielding ions with $m/z = 142$, the other important reaction of 3a is hydride abstraction from the amine yielding ions with $m/z = 184$. Thus, a deprotonation of 3a by the amine 6 was not successful, but difficulties for deprotonation are known for other σ -complexes of cationic fragments containing a central heavy element.³⁴ Interestingly, the ligand exchange of 3a by the sterically hindered 6 is unusually slow.

Similar to that of the facile ligand exchange reaction of complexes 3, the CID of these ions reveal a weak bond of AsI_2^+

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to the arene by the preferred dissociation to AsI_2^+ and the arene. Further, this process shows that the AsI_2^+ fragment remains intact in **3**, and even the elimination of HI from **3** occurs only to a very small amount in the CID spectra. These observations disagree with a *carbenic* insertion of AsI_2^+ into a C–C bond or a C–H bond of the arene ligand and the presence of covalent As–C bonds as in structures **III** and **IV**. The abstraction of a hydride by AsI_2^+ and the abundant formation of [arene–H]⁺ ions especially in the CID spectra of **3e** and **3f** could be taken as an indication of AsI_2^+ insertion into a benzylic C–H bond of the polymethylbenzene ligands. However, hydride abstraction by a leaving carbenium ion is a well-known process during the unimolecular decomposition of gaseous σ -complexes of alkylbenzenes.³⁵ Thus, the CID spectra agree only with a structure of either a σ -complex (**I**) with a rather weak bond of carbon to AsI_2^+ in **3** or with an electrostatically bonded ion/neutral complex related to structure **II**.

The determination of the absolute bond dissociation energy of the complex **3a** by energy-resolved CID shows indeed a very weak bond between benzene and AsI_2^+ and a BDE of only 77 ± 19 kJ/mol. To our knowledge no other bond energy of a cationic As species is known. BDEs of 122 kJ/mol and 125 kJ/mol, respectively, are reported for the σ -complexes of $(\text{CH}_3)_3\text{Si}^+$ and $(\text{CH}_3)_3\text{Sn}^+$ with *o*-xylene.^{34a,36} For the analogous complex $[\text{AsI}_2^+\text{-xylene}]^+$, the BDE is 105 kJ/mol (estimated from $\delta\Delta G_{\text{AsI}_2}$, Table 3). In the case of the association of $(\text{CH}_3)_3\text{Si}^+$ and $(\text{CH}_3)_3\text{Sn}^+$ to acetone (BDE = 188 kJ/mol^{34a} and 156.5 kJ/mol,³⁶ respectively) the difference to the BDE(AsI_2^+ –acetone) = 106 ± 19 kJ/mol is distinctly larger for unknown reason. However, the small BDE of AsI_2^+ to arenes as well as to n-donors explains the high reactivity of the complexes **3** and **5** in ligand exchange reactions. Preliminary semiempirical PM3 calculation show only a σ -complex (**I**) between AsI_2^+ and benzene but not a π -complex (**II**) as a stable structure. In the calculated structure of **I**, a position nearly perpendicular above one ring C atom is occupied by the As atom with the two iodo ligands pointing away from the benzene ring and with a dihedral angle C–As–I of ca. 90°. Although these calculations have to be confirmed by *ab initio* methods, a σ -complex of this structure explains the experimental results since the As center is especially exposed to nucleophilic attack. Thus, this structure would explain the failure to deprotonate **3a** by the strong but sterically demanding base **6**, which can approach easily only the exposed As of **3a**. Therefore, the base reacts preferably as a nucleophile at the As center by breaking the weak As–C bond and substituting the benzene ligand but not by abstraction of a proton. The expected different reactivity of a σ -complex (H⁺ transfer) and a π -complex (AsI_2^+ transfer) are not detected.

Conclusion

The radical cations AsI_3^{2+} react easily in the gas phase of an FT-ICR spectrometer with arenes and n-donors by exchange of one iodo atom and formation of the complexes $[\text{AsI}_2^+\text{arene}]^+$

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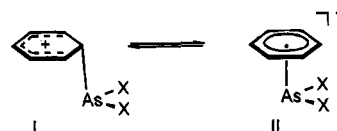


Figure 6.

3 and $[\text{AsI}_2^+\text{-n-donor}]^+$ **5**. In particular, the reaction of AsI_2^+ with benzene is fast, complete, and gives the benzene complex **3a** as the exclusive reaction product. Both type of complexes **3** and **5** exchange efficiently the π - or n-donor ligand by another ligand, but not a second iodo atom. Starting from the easily accessible benzene complex (**3a**), this exchange reaction is the most convenient method for preparing other gaseous **3** or **5**. The fast ligand exchange reaction of **3** and **5** as well as the absence of any further substitution of **I** shows that these complexes have to be pictured as an intact AsI_2^+ fragment bonded to a π - or a n-donor ligand. This is confirmed by the CA mass spectra of **3** which show mainly back-dissociation into AsI_2^+ or hydride abstraction by the leaving AsI_2^+ from methyl-substituted ligands.

The group AsI_2^+ is isolobal to carbenes, and the bonding of AsI_2^+ is of particular interest. The ligand exchange reaction is reversible and results in an equilibrium mixture if two ligands are present in the gas phase. From equilibrium constants a relative AsI_2 cation affinity, $\delta\Delta G_{\text{AsI}_2}$, is defined using benzene as a reference ligand, reflecting the competition of benzene and another ligand for the AsI_2^+ fragment. The experimental results show that $\delta\Delta G_{\text{AsI}_2}$ displays a linear correlation to the proton affinity (PA) of both π - and n-donor ligands with a slope of 0.6. Thus, the AsI_2^+ –ligand bond is less sensitive to substituents than the bond of the proton to the ligand. This is expected for a weak As–donor bond. No evidence for the insertion of AsI_2^+ into C–C bonds is obtained in contrast to the bonds formed by reaction of P^+ with arenes.¹² The BDE of the AsI_2^+ –ligand bond of the benzene complex **3a** and the acetone complex **5c** were determined by energy-resolved CID using FT-ICR spectrometry, yielding 77 ± 19 kJ/mol and 106 ± 19 kJ/mol, respectively. The difference of these two BDEs is in reasonable agreement with $\delta\Delta G_{\text{AsI}_2} = 36.6$ kJ/mol for both ligands. From these data and in particular with the observation of a single correlation line of $\delta\Delta G_{\text{AsI}_2}$ with the PA of all ligands studied, it can be concluded that AsI_2^+ adds in an electrophilic fashion to arenes by formation of a σ -complex (structure **I**). However, deprotonation of **3a** by a strong base in the gas phase was not successful. Approximately 80 kJ/mol was estimated by the ADO potential for a purely electrostatic attraction between AsI_2^+ and benzene at a distance of 3 Å in structure **II**. This value is near to the experimental BDE and it is possible that the σ -complex structure **I** is easily converted into a loose ion/neutral complex or π -complex **II** in the collision complex of an ion/molecule reaction (Figure 6).

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