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Competitive ligand losses in mono- and dicationic L′FeL$^{+/2+}$ complexes (L′, L = arene): structural insight and charge-state dependent reversals of branching ratios

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Abstract

The unimolecular decays of mass-selected mono- and dicationic iron complexes L′FeL$^{+/2+}$ with two arene ligands L′ and L are examined by means of sector-field mass spectrometry. Chemical ionization of $Fe(CO)_5$ in the presence of the arene ligands is used to generate the monocations L′FeL$^+$ which are mass selected and converted to the corresponding dications L′FeL^{2+} in high-energy collisions (charge stripping). For most of the mixed bisarene complexes, the FeL$^+$/FeL′$^+$ ratios evolving from the metastable ions reverse from mono- to dications. Thermochemical, kinetic, and structural arguments are used to rationalize the fragmentation patterns. Energy-resolved charge-stripping measurements are used to determine some vertical ionization energies, inter alia $IE_v[Fe(C_6H_6)^+] = 13.3 \pm 0.3$ eV and $IE_v[Fe(C_6H_6)_2^+] = 12.5 \pm 0.3$ eV. (Int J Mass Spectrom 212 (2001) 327–336) © 2001 Elsevier Science B.V.

Keywords: Charge stripping; Dications; Kinetic method; Metal-arene complexes

1. Introduction

In this contribution, two mass spectrometric techniques are used in whose developments R.G. Cooks played a major role, i.e. charge stripping [1] and the kinetic method [2]. In charge stripping (CS), ionization of mass-selected mono- to dications is brought about in high-energy collisions. Thus, CS allows the generation of new dications, the assessment of their energetics, and additionally, it can provide valuable structural insight [3,4]. The kinetic method [5] is based on the assumption that the branching ratio in the dissociation of an ion $AB^{+/-}$ to $A^{+/-}$+B as well as $A+B^{+/-}$ correlates with the intrinsic thermochemistry of the respective dissociation asymptotes in terms of the Gibbs-Helmholtz equation $\Delta G = -RT_{eff} \ln K_{eq}$, where T_{eff} is an effective temperature and the equilibrium constant is given as the ratio of the product intensities, i.e. $K_{eq} = I(A^{+/-})/I(B^{+/-})$. Although the physical foundations of the kinetic method are still under debate [6–9], it has found valuable applications in numerous fields of gas-phase ion chemistry [10]. Here, we combine both approaches in the examination of mono- and dicationic iron-arene

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Dedicated to Graham Cooks in recognition of his outstanding contributions to mass spectrometry on the occasion of his 60th birthday.

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complexes $L'FeL^{+/2+}$, which are generated by chemical ionization and charge stripping, respectively.

2. Experimental methods

The experiments were performed with a modified VG-ZAB/HF/AMD-604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) which has been described elsewhere [11]. Briefly, the $L'FeL^+$ monocations were generated by chemical ionization of mixtures of $Fe(CO)_5$ and the arene ligands L and L′. After acceleration to a kinetic energy of 8 keV, the B(1)/E(1) mass-selected monocations were characterized by metastable ion (MI) and collisional activation (CA) spectra; in the latter, oxygen was used as a collision gas which induces dissociation as well as charge stripping to the corresponding dications. For further examination, the doubly charged ions were selected by means of B(2) and their metastable ion (CS/MI) or collisional activation mass spectra (CS/CA) were recorded by scanning E(2). In this contribution, we focus on the MI data.

In the quantitative analysis of the monocation dissociations, only peak heights were considered. For the monocationic fragments formed upon Coulomb explosion of the dicationic species, the average heights of the low- and high-energy components were considered as a measure of relative abundance. Because the masses of the arene ligands examined do not differ largely, no further corrections were applied to account for mass discrimination effects, etc. Product branching ratios are reported as averages of at least two independent experiments. The uncertainties of the branching ratios amount to less than ±2% for the mono- and ±30% for the dications. As far as the effective temperature used in the kinetic method is concerned, it is certainly desirable to evaluate T_{eff} using some reference systems, however, such an attempt is obstacled by the error bars of the absolute binding energies available so far (see below). Therefore, the ion-source temperature is used as a pragmatic guess for the monocations, i.e. $T_{eff} = 473 \pm 200$ K [12,13]. Although this value of T_{eff} lacks a concise physical foundation, it turned out reasonable for a variety of metastable metal-ion complexes examined in our laboratory [12–15]. The choice of T_{eff} for the dicationic species is discussed below.

Because of the superior energy resolution of E(1), the energy-resolved CS experiments were conducted with B(1)-only mass-selected ions [16]. To this end, the mono- and dication signals in charge-stripping experiments were scanned at energy resolutions $E/\Delta E \geq 4000$, and the Q_{min} values were determined from the differences between the high-energy onsets of the mono- and the dication peaks [17]. As a reference for the kinetic energy scale, we applied charge stripping of the molecular ion of toluene, $C_7H_8^+ \rightarrow C_7H_8^{2+}$ with $Q_{min}(C_7H_8^+) = 15.7$ eV, using a multiplicative calibration scheme [4,18].

3. Excursus: general features of the cationic iron-benzene complexes $Fe(C_6H_6)_n^{+/2+}$ (n = 1, 2)

In the gas phase, most singly charged metal ions easily form association complexes $M(L)_n^+$ with one or two arene ligands via radiative as well as collisional stabilization [19]; genuine metal-arene complexes with $n > 2$ have not been observed so far [20]. Gapeev and Dunbar have shown that a profound analysis of the reaction kinetics can be used to determine the relevant thermochemistry of ionic metal-arene complexes [21]. This approach has been complemented by applications of the kinetic method to mixed $L'ML^+$ complexes with different arene ligands L′ and L, allowing for the evaluation of relative metal-ion affinities for various arenes [12–15,22]. Several other methods have been applied as well, among which the results of the threshold collision-induced dissociation (CID) of $M(C_6H_6)^+$ and $M(C_6H_6)_2^+$ complexes by Meyer and coworkers [23] are most relevant here because the bond dissociation energies *BDE* (Fe^+-C_6H_6) = 2.15 ± 0.10 eV and *BDE*($C_6H_6Fe^+$-C_6H_6) = 1.94 ± 0.17 eV can be used as anchors in converting relative to absolute *BDEs*. Therefore, the benzene complexes $Fe(C_6H_6)_n^{+/2+}$ (n = 1, 2) are considered as prototypes.

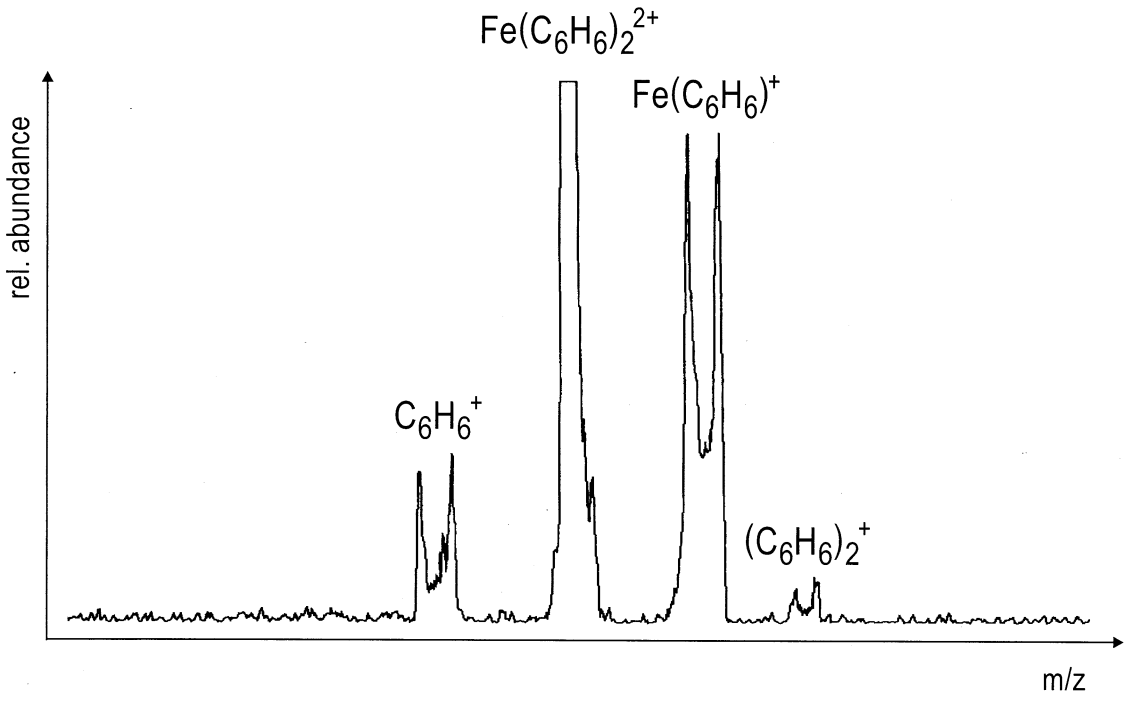


Fig. 1. CS/MI spectrum of B(2)-selected $Fe(C_6H_6)_2^{2+}$ dication generated by charge-stripping from the B(1)/E(1)-selected $Fe(C_6H_6)_2^+$ monocation at 8 keV kinetic energy. The spectrum was obtained by scanning E(2). Note that the dication precursor signal appears in the middle of the spectrum and is cutoff at 1/600 of its abundance.

$$Fe(C_6H_6)^+ \rightarrow Fe^+ + C_6H_6 \quad (1)$$

$$Fe(C_6H_6)_2^+ \rightarrow Fe(C_6H_6)^+ + C_6H_6 \quad (2)$$

The unimolecular and collision-induced dissociation behavior of $Fe(C_6H_6)^+$ and $Fe(C_6H_6)_2^+$ monocations has been described previously [23–26] and is not at all spectacular in that ligand losses according to reactions (1) and (2) largely prevail; activations of C–H and/or C–C bonds are minor and only occur at elevated energies. When oxygen is used as a collision gas for B(1)/E(1) mass-selected monocations at keV energies, charge-stripping affords dication signals corresponding to $Fe(C_6H_6)^{2+}$ and $Fe(C_6H_6)_2^{2+}$ with ~10% abundance relative to the losses of one benzene ligand according to reactions (1) and (2) which give rise to the respective base peaks. Mass-selection of the dication signals using B(2) enables to subsequently examine their unimolecular dissociation behavior by using the analyzer E(2) in CS/MI experiments. For both metastable dications, charge separations according to reactions

$$Fe(C_6H_6)^{2+} \rightarrow Fe^+ + C_6H_6^+ \quad (3)$$

$$Fe(C_6H_6)_2^{2+} \rightarrow Fe(C_6H_6)^+ + C_6H_6^+ \quad (4)$$

$$Fe(C_6H_6)_2^{2+} \rightarrow Fe^+ + C_{12}H_{12}^+ \quad (5)$$

are found to predominate.

Fig. 1 shows a representative CS/MI spectrum of $Fe(C_6H_6)_2^{2+}$. Charge separation of the dication according to reaction (4) gives rise to signals assigned to $Fe(C_6H_6)^+$ and $C_6H_6^+$ which both have characteristic peak shapes. Thus, instead of Gaussian-type signals, only the low- and high-energy components of the dissociation are detected in a sector field mass spectrometer. This effect is caused by the fact that once the Coulomb barrier for charge separation is surmounted, repulsion of the positively charged fragments gives rise to the release of a large amount of

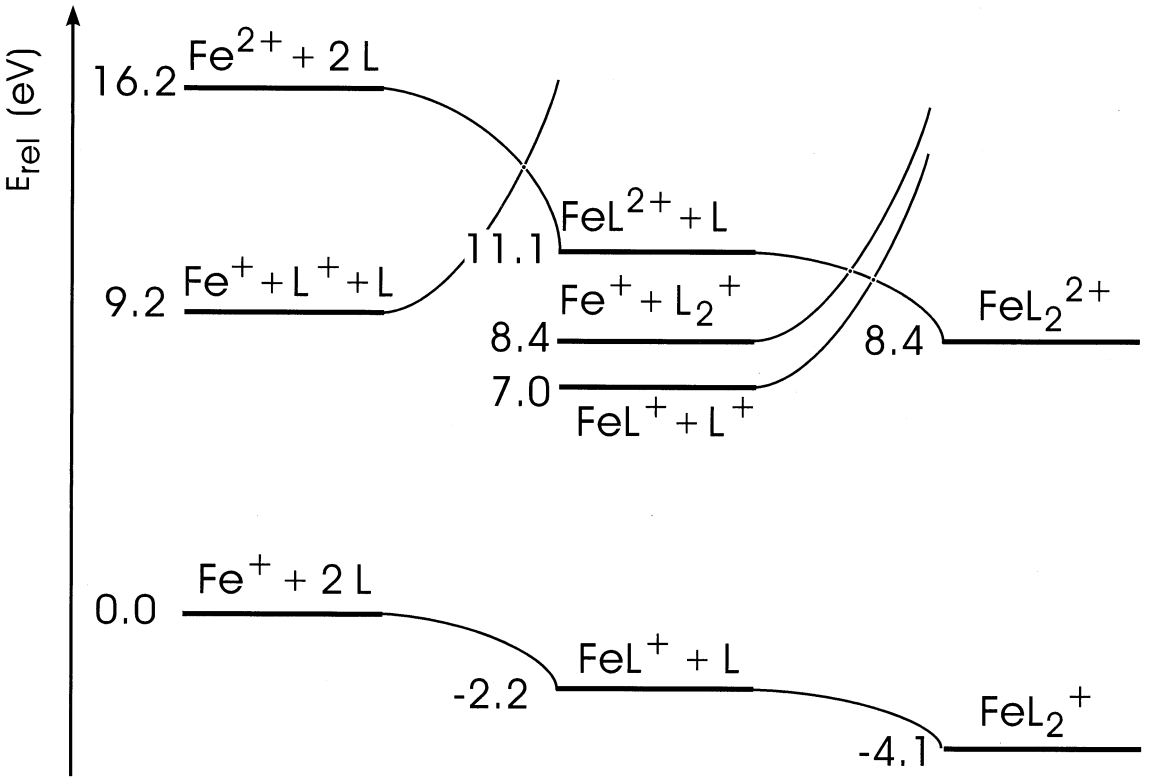


Fig. 2. Approximate energetics (in eV) of $FeL_n^{+/2+}$ (n = 1, 2 with L = C_6H_6) and of the relevant dissociation channels.

kinetic energy. Due to instrumental discrimination effects, only the forward and backward scattered ions are detected, giving rise to two sharp peaks centered around the *m/z* value of the monocation fragment. An additional reaction of $Fe(C_6H_6)_2^{2+}$ leads to the formation of a $C_{12}H_{12}^+$ cation — most probably the ionized dimer of benzene $(C_6H_6)_2^+$ [20] — concomitant with Fe^+ (reaction 5). Although this process is hardly visible for metastable $Fe(C_6H_6)_2^{2+}$, it gains in importance upon collisional activation of the dication (CS/CA, not shown) and is mentioned here, because ionized arene dimers are also formed from several of the mixed $LFeL'^{2+}$ dications (see below).

By reference to the thresholds of charge stripping (Q_{min} values), the energetics of $Fe(C_6H_6)_n^{+/2+}$ (n = 1, 2) can be estimated. Energy-resolved experiments yield $Q_{min}[Fe(C_6H_6)^+]$ = 13.3 ± 0.3 eV and Q_{min} $[Fe(C_6H_6)_2^+]$ = 12.5 ± 0.3 eV, respectively. Although energy transfer in rovibrational modes may well play a role [17,27], the Q_{min} values correspond to the vertical ionization energies (IE_v) of the monocations in a first approximation [3,4]. Further, we deliberately neglect the differences between vertical and adiabatic *IEs*. This, admittedly crude assumption— to be discussed further below— is mandatory in order to gain at least a rough insight into the redox energetics (Fig. 2). At first, the fact that the Q_{min} values of $Fe(C_6H_6)^{2+}$ and $Fe(C_6H_6)_2^{2+}$ are considerably lower than $IE(Fe^+)$ = 16.19 eV [28] indicates a substantial stabilization of the iron dication upon ligation [18], i.e. the ligated metal is easier to ionize than the bare atom. The same trend is reflected in the binding energies of the mono- and dications: $BDE(Fe^+-C_6H_6)$ = 2.15 ± 0.10 eV and BDE $(C_6H_6Fe^+-C_6H_6)$ = 1.94 ± 0.17 eV [23] compared to $BDE(Fe^{2+}-C_6H_6)$ = 5.04 ± 0.32 eV and BDE $(C_6H_6Fe^{2+}-C_6H_6)$ = 2.74 ± 0.34 eV derived from the CS measurements. Nevertheless, inspection of

Table 1
Relative abundances of FeL^+ and FeL'^+ fragments in the unimolecular fragmentations of mixed $L'FeL^{+/2+}$ complexes and thermochemical quantities (in meV) derived thereof. Column (7) indicates formation of the ionized arene dimers $L'L^+$ concomitant with loss of Fe^+ from the dications; For the sake of simplicity, the arene ligands are encoded as: Ben = benzene, Py = pyridine, Tol = toluene, Pic = 4-picoline, PhF = fluorobenzene, and PhCl = chlorobenzene

L/L′	Monocations			Dications					
	FeL^+	FeL'^+	ΔBDE[a]	FeL^+	FeL'^+	$L'L^+$	ΔG[b]	ΔCSA[c]	$\Delta\Delta$[d]
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Ben[e]/Py	100	68	−16[f]	6	100	25	485	1	484
Ben/Tol	11	100	90	100	15	<3[g]	−327	−326	−1
Ben/Pic	10	100	94	7	100	25	458	−110	568
Py/Tol	10	100	94	100	8	10	−435	−338	−97
Py/Pic	9	100	98	100	60	40	−88	−122	34
Tol/Pic[h]	90	100	4	20	100	6	277	216	61
Ben/PhF	100	1	−188	<3[g]	100	6	604	−231	835
Ben/PhCl[i]	0.9	0.4	−33	<10[g]	100	<10[g]	516	−207	723

[a]Difference of the bond dissociation energies calculated from the FeL^+/FeL'^+ ratio according to the kinetic method using T_{eff} = 473 K, see experimental section.
[b]Difference of the charge-separation asymptotes calculated from the FeL^+/FeL'^+ ratio according to the kinetic method using T_{eff} = 2000 K, see text.
[c]Calculated as: $\Delta CSA = IE(L) - \Delta BDE - IE(L')$; all *IEs* of the arene ligands were taken from [31], also see Table 2.
[d]Defined as $\Delta\Delta = \Delta G - \Delta CSA$.
[e]In order to avoid mass overlaps, C_6D_6 was used.
[f]For the unlabeled ion $(C_6H_6)Fe(C_6H_5N)^+$, a ratio of a $Fe(C_6H_6)^+/Fe(C_6H_5N)^+ = 1.25$ and hence $\Delta BDE = -9$ meV was found [15].
[g]Upper limit given by the noise level.
[h]In order to avoid mass overlaps, 4-[D_3-methyl]-pyridine was used.
[i]The dissociation of metastable $(C_6H_6)Fe(C_6H_5Cl)^+$ gives rise to loss of HCl (100%) as the base peak.

Fig. 2 suggests that $Fe(C_6H_6)^{2+}$ and $Fe(C_6H_6)_2^{2+}$ are both metastable dications in that the charge separations according to reactions (3) and (4) are exothermic by 1.9 and 1.4 eV, respectively; reaction (5) is almost thermoneutral. Even though consideration of the adiabatic properties would lower these exothermicities, the differences between IE_v and IE_a appear unlikely to render the $Fe(C_6H_6)_n^{2+}$ dications thermochemically stable (see below).

4. Results for the mixed bisarene-iron complexes $L'FeL^{+/2+}$

From the excursus to $Fe(C_6H_6)_n^{+/2+}$ (n = 1, 2) we conclude that unimolecular ligand losses prevail for mono- and dicationic $L'FeL^{+/2+}$ complexes of arene ligands L′ and L, unless metal-mediated bond activations occur. Although competitive formation of the monocationic fragments FeL^+ and FeL'^+ is expected in both cases, the $L'FeL^+$ monocations afford neutral losses, whereas the $L'FeL^{2+}$ dications, via Coulomb explosion, lead to ionized ligands. Loss of neutral arene ligands from the dications is unlikely, because $IE(FeL^+)$ exceeds $IE(L)$ by several eV (see below).

The metastable ion and CS/MI data of the $L'FeL^{+/2+}$ complexes examined in this work are summarized in Table 1. For the monocations, application of the kinetic method provides a clean set of relative *BDEs*. Thus, the Fe^+-affinities of benzene (Ben) and pyridine (Py) are almost identical and the same applies for their mono-methyl derivatives, toluene (Tol) and 4-picoline (Pic). Notable is the internal consistency of the data. For example, the directly measured difference of 98 meV for Py/Pic matches perfectly with the value obtained from the couples Ben/Pic, Ben/Tol, and Py/Tol (i.e. 94 − 90 + 94 = 98). The present data are in qualitative agreement with a previous study of Ma and coworkers using the kinetic method [22] as well as the recent determination of $BDE(Fe^+ - C_5H_5N) = 2.32 \pm 0.09$ eV by

Rodgers et al. using threshold CID [29]. Nevertheless, some quantitative differences remain, and a detailed comparison of these results, including several other heteroarene ligands [15], will be published elsewhere [30]. For reasons that will become obvious further below, also L′ = fluoro- and chlorobenzene are included here.

Interestingly, most FeL^+/FeL'^+ ratios reverse for the metastable $L'FeL^{2+}$ dications in comparison to the monocations. For example, the benzene ligand is lost primarily in the unimolecular dissociation of $(C_6H_6)Fe(C_6H_5CH_3)^+$, whereas $Fe(C_6H_6)^+$ is preferentially formed from the dicationic counterpart. The effect is most pronounced for the couple benzene/fluorobenzene where the branching ratio of 100:1 in favor of $Fe(C_6H_6)^+$ formation from the monocation changes to 1:>33 for the dicationic species. In fact, only for the couples Ben/Pic and Tol/Pic, the base peaks coincide for mono- and dications (Table 1).

One obvious reason for these reversals in branching ratios is the associated thermochemistry. Thus, charge separation of $(C_6H_6)Fe(C_6H_5CH_3)^{2+}$ to yield $Fe(C_6H_6)^+$ and $C_6H_5CH_3^+$ is favored over $Fe(C_6H_5CH_3)^+ + C_6H_6^+$ because the difference of *IE*(toluene) = 8.828 eV [31] and *IE*(benzene) = 9.2438 eV [31] compensates the larger Fe^+-affinity of toluene compared to benzene (0.09 eV, Table 1). Hence, the difference of the charge-separation asymptotes (*CSA*) amounts to $\Delta CSA = 0.326$ eV [Fig. 3(a)]. It is obvious from the other data, however, that the thermochemistry of the charge-separation asymptotes cannot be the only decisive parameter in the dissociation of the bisligated dications. Thus, formation of $Fe(C_5H_5N)^+ + C_6D_6^+$ clearly prevails in the Coulomb explosion of the $(C_6D_6)Fe(C_5H_5N)^{2+}$ dication, whereas the energetics of the two competing processes are identical: $IE(C_6D_6) = 9.245$ eV [31], IE(pyridine) = 9.26 eV [31], and $\Delta BDE = 0.016$ eV (Table 1) lead to $\Delta CSA = 0.001$ eV (Fig. 3(b)). Even the value $\Delta BDE = 0.17 \pm 0.14$ eV derived from the absolute binding energies [23,29] cannot account for the observed behavior. An attempt to rationalize the dissociation behavior of the dications is presented in the next section.

An interesting chemical aspect evolves with the benzene/chlorobenzene couple. For the monocation, ligand losses are almost completely suppressed by Fe^+-mediated dehydrochlorination to afford $Fe(C_{12}H_{10})^+$ - probably biphenyl/Fe^+ [32]. In the CS/MI mass spectrum of the dication, however, loss of HCl is not observed at all. This observation indicates that Fe^{2+}, although much more electron withdrawing, is chemically less reactive than Fe^+ with regard to bond activations. This conclusion finds an analogy in the low reactivities of various substrates with the monocations Mn^+ and FeX^+ (X = Cl, Br, I, etc.) [33,34] which are formally isoelectronic with Fe^{2+}.

In addition, the Q_{min} values for FeL^+ complexes with L = benzene, pyridine, toluene, and picoline as well as for the homodimers $Fe(C_6H_6)_2^+$ and $Fe(C_5H_5N)_2^+$ were determined (Table 2). Not surprisingly, the Q_{min} values of the monoligated metal-arene complexes are quite similar (12.7–13.3 eV) and within experimental uncertainty. Nevertheless, the slight trend of decreasing Q_{min} values from benzene to picoline appears reasonable as the ligands become better donors and are thus more capable to stabilize the metal dication. In marked contrast to the monoligated species, the Q_{min} values for the bisligated ions $Fe(C_6H_6)_2^+$ and $Fe(C_5H_5N)_2^+$ differ by as much as 1.2 eV which is clearly significant with respect to the error margins of the experiment. We shall return further below to this aspect.

5. Analysis of the dications' dissociation behavior

The picture for the monocation fragmentations of the $L'FeL^+$ species is internally consistent and not analyzed in any more detail here [30]. However, the dissociation behavior of the $L'FeL^{2+}$ dications requires further consideration. As a first approach, let us assume that the branching ratios in the dications' dissociations are determined by the energy demands of the corresponding charge-separation asymptotes. Hence, the apparent ΔG values derived using the kinetic method would correspond to ΔCSA. Of course, the thermochemistry of the asymptotes cannot fully contribute to the situations in the transition structures (TSs) associated with the competing charge-separa-

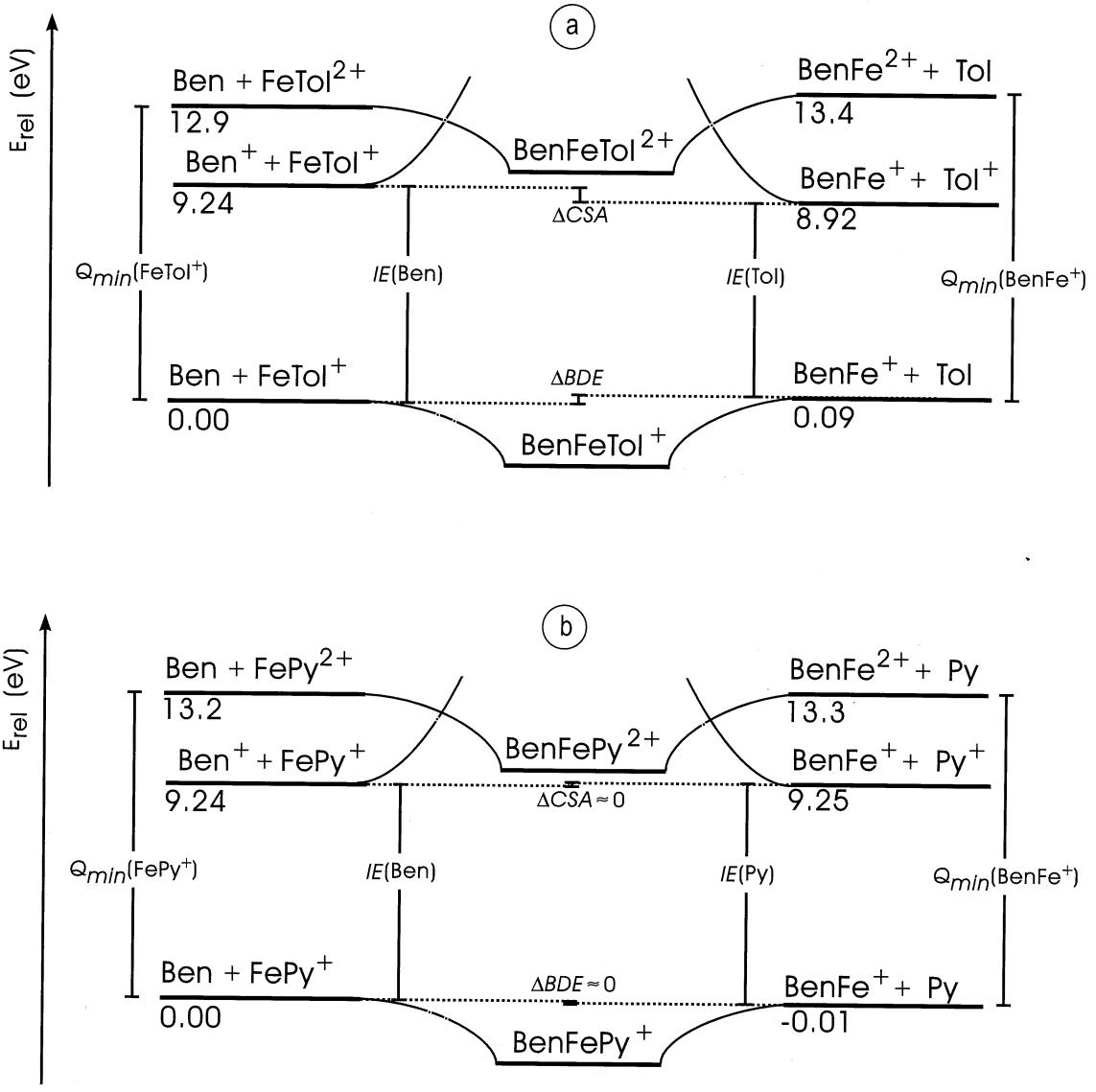


Fig. 3. Schematic energetics (in eV) in the dissociation of L′FeL^{2+} for (a) L′ = benzene and L = toluene and (b) L′ = benzene and L = pyridine.

tion channels. Nevertheless, the Hammond postulate suggests that Δ*CSA* is reflected in the TSs, and the role of Δ*CSA* in the kinetic method can be tuned by variation of T_{eff}. Note that this approach effectively uses T_{eff} as a parameter rather than any "temperature." Column 8 of Table 1 gives the Δ*G* values derived from this approach with T_{eff} = 2000 K; the latter value is obtained by assuming Δ*G* = Δ*CSA* for the Ben/Tol system. With regard to the crudeness of the underlying assumptions as well as the experimental errors, also the couples Py/Tol, Py/Pic, and Tol/Pic agree reasonably well with this approximation within ± 0.1 eV. Compared to the competitive dissociation of mixed L'FeL$^+$ monocations, however, the related analysis of the dication dissociations via the kinetic method provides a less direct, less accurate,

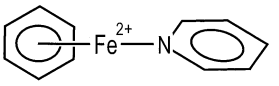
Table 2
Ligand ionization energies[a] *IE* and Q_{min} values[b] of FeL^+ ions (in eV) determined by energy-resolved charge stripping of mass-selected $Fe(L)_n^+$ monocations (n = 1, 2) to the corresponding dications

	benzene	pyridine	toluene	4-picoline
IE(L)[b]	9.2438	9.26	8.828	9.04
$Q_{min}(FeL^+)$	13.3 ± 0.3	13.2 ± 0.3	12.9 ± 0.3	12.7 ± 0.3[c]
$Q_{min}(FeL_2^+)$	12.5 ± 0.3	11.3 ± 0.3		

[a]Taken from [31].
[b]A multiplicative calibration scheme is employed, also see [18].
[c]Due to the vicinity of the mass of picoline to that of toluene used as the calibrant, also 4-[D_3-methyl]-pyridine was examined; the Q_{min} values of D_0- and D_3-picoline/Fe^+ were found to agree within the experimental error.

and experimentally much more demanding way to determine ΔBDEs of the monocationic FeL^+ species. Quite interesting and revealing are the exceptions, however. Thus, with T_{eff} = 2000 K, the 6:100 branching ratio in favor of $Fe(C_5H_5N)^+$ obtained for $(C_6D_6)Fe(C_5H_5N)^{2+}$ leads to ΔG = 0.5 eV, whereas Δ*CSA* is much smaller (0.001 eV according to Table 1 and 0.17 ± 0.14 eV using the absolute *BDEs*, see previous). Quite obviously, the dissociation of $(C_6D_6)Fe(C_5H_5N)^{2+}$ does not correlate with the thermochemistry of the exit channels, and the question remains why the system behaves in this manner. For some reason, coordination of pyridine to the $(C_6D_6)Fe^{2+}$ fragment must be "tighter" or "stronger" than that of benzene to $Fe(C_5H_5N)^{2+}$. Consideration of the dications' dissociation asymptotes gives no clue for this behavior, because the Q_{min} values of benzene/Fe^+ and pyridine/Fe^+ are within experimental error (Table 2 and Fig. 3).

In order to further pursue this aspect, some structural and electronic aspects of the bisligated complexes are considered. Pandey and coworkers [35] as well as Rodgers et al. [29] have reported some exploratory computational studies of metal-benzene and -pyridine complexes using density functional theory. However, neither spin multiplicities nor energetics were discussed specifically and uncertainties are considerable. For example, Pandey and coworkers note differences of >1 eV between experiment and theory [35], whereas Rodgers et al. [29] even refrain from reporting the calculated binding energies. Formally, $Fe(C_6H_6)_2^{2+}$ is an 18-electron complex isoelectronic with the well-known bisbenzene chromium. However, previous ab initio studies predict a quartet ground state for $Fe(C_6H_6)^+$ [36,37]; accordingly, $Fe(C_6H_6)_2^+$ may exhibit a quartet ground state as well. If so, the vertical transition to the dication upon charge stripping cannot yield the perfect pairing singlet state of the 18-electron complex, but a high-spin variant. Moreover, even if $Fe(C_6H_6)_2^+$ were a doublet [35], the triplet dication may be formed preferentially upon vertical electron transfer in the charge stripping experiment. The possibility that $Fe(C_6H_6)_2^{2+}$ does not have a singlet ground state further suggests a deviation from η^6-coordination of both arene ligands to lower coordination numbers, e.g. η^4/η^6 or η^5/η^5. For mixed $L'FeL^{2+}$ species, there might therefore exist a tendency for dissimilar coordination modes of the arene ligands. In the particular case of $(C_6H_6)Fe(C_5H_5N)^{2+}$, this could result in a binding situation with η^6-coordination of the benzene concomitant with coordination of the pyridine ligand via the lone pair of nitrogen, lying in the plane of the aromatic ring; such a structure, also indicated by the computational results of Rodgers et al. [29], is depicted in Scheme 1.



Scheme 1.

As a consequence, the dissociation dynamics associated with losses of either ligands could differ that much that the neglect of the role of frequency factors in the kinetic method is not justified any longer. Three pieces of evidence support this conjecture. At first, significant differences between Δ*G* and Δ*CSA* also occur with fluoro- and chlorobenzene, which were chosen because the halogen atoms can serve as coordinating ligands for the metal [38]. Further, the significantly lower Q_{min} value of $Fe(C_5H_5N)_2^+$ compared to $Fe(C_6H_6)_2^+$ finds a rationale by involving N-coordination by one of the pyridine ligands. Finally, the fact that the Q_{min} value of $Fe(C_6H_6)_2^+$ is not

much lower than that of $Fe(C_6H_6)^+$ indicates that the metal center in $Fe(C_6H_6)_2^{2+}$ dication cannot fully benefit from the ligation of both arene ligands.

6. Recursus

The structural discussion at the end of the previous section has severe implications with respect to the properties of mono- and dicationic iron-arene complexes outlined in the excursus. As charge stripping at keV energies can safely be assumed a vertical process, the difference of the Q_{min} values of $Fe(C_6H_6)_2^+$ and $Fe(C_5H_5N)_2^+$ suggest that already the bisligated monocations experience some asymmetry in the binding of both arene ligands. Thus, if the coordination modes of the $Fe(C_6H_6)_2^+$ and $Fe(C_5H_5N)_2^+$ monocations were the same, the similarity of the Q_{min} values of the monoligated ions would imply that also those of the bisarene complexes do not differ greatly; however, a difference of 1.2 eV is observed in the experiment. Accordingly, the neglect of the dissociation dynamics in application of the kinetic method may already be inappropriate for the monocations when comparing aromatic hydrocarbons with heteroarenes or heteroatom-substituted arenes as ligands. The alternative coordination sites offered by heteroatoms - whether or not these are involved in the binding of the most stable coordination modes - contribute to the density of states upon dissociation and may hence affect the branching ratios via the frequency factors. Accordingly, whereas the derived Fe^+-affinities of the arene ligands discussed here are well reproducible and internally consistent, they may be subject to systematic errors. For example, despite the significant error margins, the values $BDE(Fe^+-C_6H_6) = 2.15 \pm 0.10$ eV [23] and $BDE(Fe^+-C_5H_5N) = 2.32 \pm 0.09$ eV [29] determined by threshold CID clearly suggest that pyridine is more strongly bound to Fe^+ than benzene. The preferential loss of pyridine from metastable $(C_6H_6)Fe(C_5H_5N)^+$ leads to the opposite conclusion, however. In turn, similar arguments question the analysis of the threshold CID because essentially the same models were used to analyze the data of the benzene and pyridine complexes [23,29].

As far as the dication energetics are concerned, the same line of reasoning suggests that the differences between IE_v and IE_a may in fact be larger than anticipated, when not only bond lengths and angles, but also coordination modes and spin couplings differ between mono- and dications. Adequate computational studies of the structures and spin states of $FeL_n^{+/2+}$ (n = 1, 2) might provide valuable insight in this respect. Notwithstanding, the present results provide an experimental indication that the coordination modes of benzene and pyridine differ in quality.

7. Conclusions

Application of the kinetic method to $L'FeL^+$ monocations provides an internally consistent order of the relative Fe^+-affinities for the arenes under study. The present results agree reasonably well with previous data [22,23,29], yet some quantitative differences remain. Consideration of the corresponding $L'FeL^{2+}$ dications formed via charge stripping resembles, however, the opening of Pandora's box. Not only are the dissociations of the dications dependent on several, yet unknown properties (spin states, coordination modes, etc.), the results also question the appropriateness of applying the kinetic method to the competitive arene ligand losses from some monocationic species. A future, more detailed analysis of this issue would very much benefit from more precise determinations of the absolute BDEs of FeL^+ for various arene ligands. A problem is, however, that the Fe^+-arene binding energies are relatively large (>2 eV), whereas their differences are small, thereby limiting the accuracy of this kind of approach. With respect to the specific problem of benzene and pyridine coordination, a detailed examination of the competitive dissociation of $(C_6H_6)Fe(C_5H_5N)^+$ as a function of internal energy might be particularly insightful. Notwithstanding these imponderabilities, the present results demonstrate that systematic examination of the dissociation patterns of mixed bisligand complexes - being they singly or doubly charged - can provide

profound insight into thermochemical, structural, and kinetic properties of these species; for a recent, elegant application to dinuclear metal dications, see [39].

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