Substituent Effects on the Bond-Dissociation Energies of Cationic Arene−Transition-Metal Complexes☆

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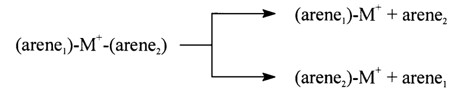
Received November 7, 1997

Keywords: Bond-dissociation energies / Arenes / Transition metals / Ionization energies / Gas-phase chemistry

The bond-dissociation energies (*BDE*s) of more than twenty arene−M$^+$ complexes (M = Cr, Fe, Co) have been studied by mass spectrometry, using the kinetic method. With minor exceptions, the same relative order of *BDE*s is found for the three metals and the series of substituted arenes: electron-donating substituents, like alkyl or amino groups, increase the arene−metal *BDE* whereas electron-withdrawing substituents, e.g. halogens, lower the *BDE* compared to the unsubstituted benzene complexes. Interestingly, inverse linear correlations of the arene−M$^+$ *BDE*s and the arenes' ionization energies (IEs) exist for particular classes of substituents. The present results may serve as a guide to predict *BDE*s of similar organometallic complexes based on the IEs of substituted arenes and vice versa.

Introduction

Since the discovery of ferrocene in 1951[1] and the first efficient synthesis of bis-benzene metal complexes in 1955,[2] organometallic "sandwich" compounds have been studied extensively by various experimental and theoretical approaches.[3] Quite helpful for our understanding of the bonding properties of these systems is the knowledge of their thermochemical data, especially the bond-dissociation energies (*BDE*s) of the aromatic ligands bound to the metal fragment. The gas phase represents an ideal environment to study the intrinsic interactions of arenes and metal ions, as counter ions, aggregate, solvation, and other complicating bulk effects do not exist. Therefore, experiments based on mass-spectrometric techniques, like collision-induced dissociation,[4a] photodissociation,[4b] equilibrium reactions,[4c][4d] and kinetic studies of the radiative association reactions,[4c][4d][4e][4f] have frequently been used to determine the absolute *BDE*s of cationic benzene−transition-metal complexes. In combination with theoretical results[5] these studies revealed that the *BDE*s of benzene−M$^+$ for late transition metals are of the order of 40−60 kcal/mol. At first glance, this value is surprisingly high for a non-polar ligand, compared for example to that of a strong dipolar ligand like water, that exhibits a *BDE*(H_2O-M^+) of only 30−40 kcal/mol for the same metal ions.[6] The strong binding of arenes to metal cations also shows up occasionally in the condensed phase. For example, metal ions can be extracted from an aqueous solution using polycyclic hydrocarbons that contain aromatic substituents.[7] Likewise, proteins in an aqueous environment in some cases use arene−cation interactions to stabilize their reactive centers or to bind cationic substrates.[8] Our interest in arene−metal complexes was stimulated by the observation that certain transition-metal cations induce the cyclization of unsaturated hydrocarbons to yield aromatic complexes.[9] To understand the effects of substituents on the reaction mechanism, knowledge of the dissociation energy of the resulting ligand−metal bond proved crucial. Here, we will describe the results obtained for the *BDE*s of arene−transition-metal complexes using the kinetic method.[10] The kinetic method, that was originally developed to determine proton affinities and later generalized to study the interaction of nearly any kind of charged species with a neutral, can also be applied to determine *BDE*s of ligands that are bound to a transition-metal cation. To measure the *BDE*s of arene−M$^+$ complexes we examined the rates of competitive dissociations of bis-ligated complexes by studying the unimolecular dissociations of mass-selected sandwich complexes to give the individual mono-arene compounds, as shown in equation (1).



For structurally related ligands, like two differently substituted arenes, the entropic effects associated with these fragmentations are, to a first approximation, almost identical for loss of either ligand, and if there are negligible reverse activation energies one obtains the approximate expression (2).[10b]

$$\ln\frac{[(arene_1)-M^+]}{[(arene_2)-M^+]}=\frac{\Delta BDE}{R\cdot T_{eff}} \qquad (2)$$

In equation 2 [(arene$_1$)−M$^+$] and [(arene$_2$)−M$^+$] are the abundances of the two mono-ligated fragments, Δ*BDE* denotes the bond-dissociation energy difference between the arenes bound to the metal cation, and T_{eff} is the effective temperature[10c] of the parent sandwich ions which is a

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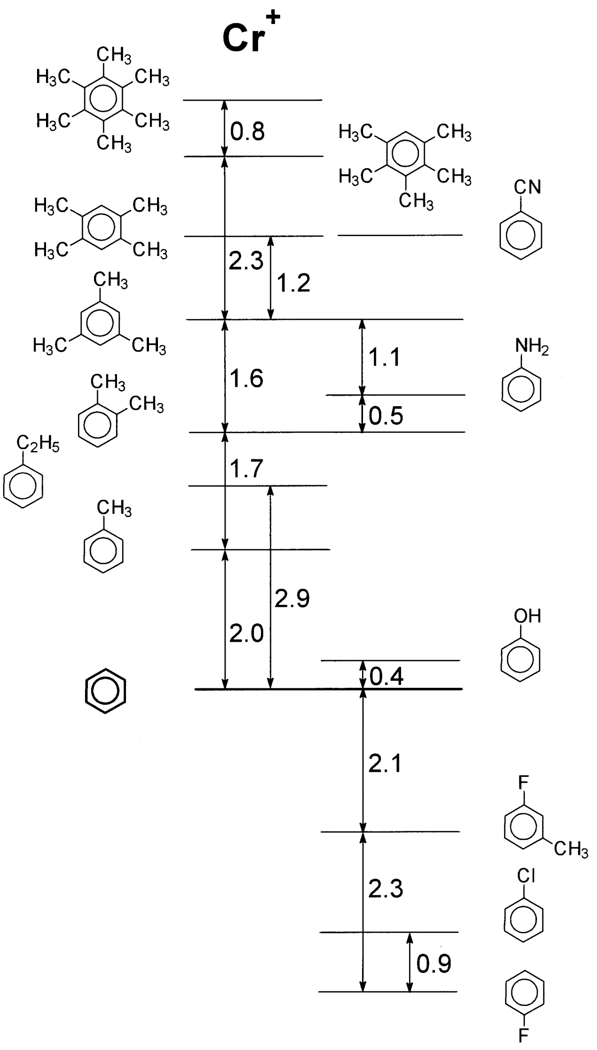
measure of their average internal energy.[10] By comparison with known values also absolute *BDE*s can be derived by this method.

Results and Discussion

Methyl-Substituted Arenes

An overview of the differences in *BDE*s for the studied arene$-$M$^+$ complexes (M = Cr, Fe, Co) is given in Schemes 1$-$3. We will first discuss the effects of methyl ligands on the *BDE*(arene$-$M$^+$). Adding a methyl group to the aromatic ring of benzene induces a distinct increase in *BDE*. For M = Cr ΔBDE (toluene/benzene) amounts to 2.0 kcal/mol, in agreement with a recent study of Dunbar and coworkers.[4e] Even slightly larger differences are observed for M = Fe (2.2 kcal/mol) and M = Co (2.3 kcal/mol), respectively. The investigation of complexes of isomeric xylenes revealed that the *BDE*s of the three regioisomers cannot be distinguished within the accuracy of the applied method. As a representative, in the Schemes we arbitrarily present the results of the *ortho* isomer. Not suprisingly, *o*-xylene forms a stronger bond to M$^+$ than toluene, though the effect of the second methyl group is less pronounced compared to the first one. We arrive at ΔBDE (*o*-xylene/toluene) = 1.7 kcal/mol for M = Cr[4e] and 1.8 kcal/mol for M = Fe, Co. Addition of the third methyl substituent further rises the *BDE* by 1.6 kcal/mol for M = Cr and Co and by 1.7 kcal/mol for M = Fe as compared to *BDE*(*o*-xylene$-$M$^+$). As for the xylenes, the *BDE*s of mesitylene, i.e. 1,3,5-trimethylbenzene, and its 1,2,4-trimethylbenzene isomer are also identical within experimental error. The higher methylated complexes follow the trend observed for the less substituted arenes, and the results for tetra-, penta-, and hexamethylbenzene may be extracted from Schemes 1$-$3 and Table 1. The completely methylated arene, i.e. hexamethylbenzene, represents the strongest bound ligand within this series. We note that the absolute *BDE*(hexamethylbenzene$-$Co$^+$) of 70.9 ± 3.0 kcal/mol is already in the range of covalent bonds. The results for the methylated arenes may be summarized in a qualitative way as follows: The *BDE*(arene$-$M$^+$) increases with growing number of methyl substituents; this can be attributed to the electron-donating properties of the methyl groups that enhance the electrostatic interaction between the ion and the neutral arene ligand. Also the fact that the incremental difference in bond energies decreases from $\geq$ 2 kcal/mol for the first methyl group to ca. 1 kcal/mol for the sixth substitution suggests the operation of a predominantly electrostatic effect. Further support for this explanation is gained from the results for ethylbenzene. As an ethyl group is a stronger electron donor than a methyl group, ethylbenzene should form a stronger bond to M$^+$ than toluene. This is indeed observed for all three metal cations examined. As side reactions prevent the direct comparison of both ligands using a mixed ethylbenzene/toluene complex, we investigated the competing losses of benzene and ethylbenzene. *BDE*(ethylbenzene$-$M$^+$) exceeds *BDE*(benzene$-$M$^+$) by 2.9 kcal/mol for M = Cr, by 3.3 kcal/mol for M = Fe, and by 3.1 kcal/mol for M = Co. As expected, these values lie between the ones obtained for toluene and *o*-xylene. In addition, the influence of methyl (alkyl) substitution on ΔBDE is also slightly dependent on the metal cation. The strongest effect is observed for M = Co and the differences are somewhat smaller with M = Fe and M = Cr. For example, ΔBDE (hexamethylbenzene/pentamethylbenzene) amounts to 1.2 for Co$^+$, and 0.8 kcal/mol for Cr$^+$. This behavior is in line with the known absolute *BDE*s which are 61.1 ± 2.5 kcal/mol, 49.6 ± 2.3 kcal/mol, and 40.6 ± 2.3 kcal/mol for the benzene complexes of Co$^+$, Fe$^+$, and Cr$^+$, respectively.[4a]

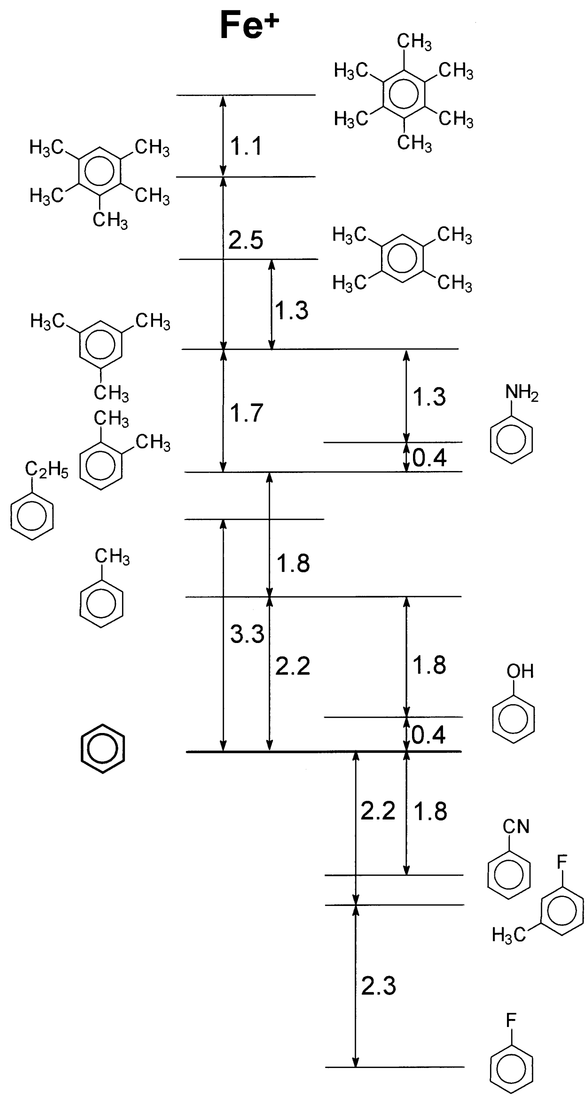
Scheme 1



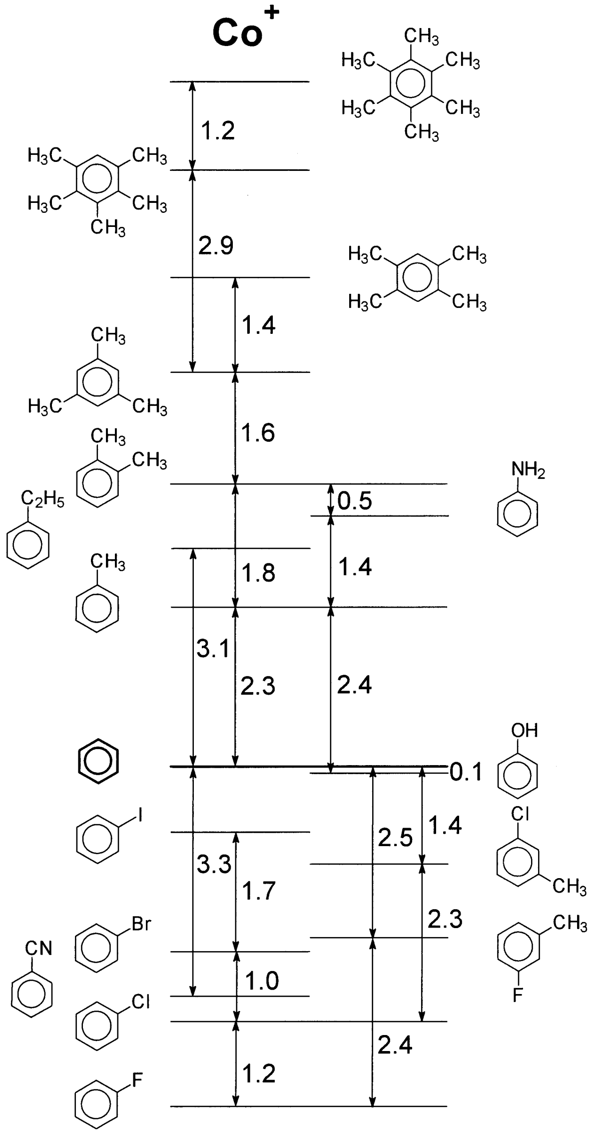
Heteroatom Substituents

Unfortunately, the systematic investigation of heteroatom-substituted arenes (see Table 2) is strongly limited by side reactions which prevent application of the kinetic method.[10] For example, in the MI spectra of (benzene)(C_6H_5X)M$^+$ (X = Cl, Br, I), loss of the intact ligands is barely observed; rather, elimination of HX accompanied by coupling of the ligands represents the domi-

Scheme 2



Scheme 3



nant process.[11] Only for X = F is this reaction negligible, but the fluorine substituent lowers the *BDE* so drastically, compared to benzene, that Δ*BDE* cannot be derived from a direct comparison.[12] As we have demonstrated above, methyl substituents increase the *BDE* of arene−M$^+$, so fluorotoluene is a reasonable candidate to bridge the gap between benzene and fluorobenzene. In principle, the different regioisomers of fluorotoluene could correspond to distinguishable *BDE*s, and indeed *o*-fluorotoluene appears to be the strongest bound isomer for the three metals. But the observed differences lie within experimental error if the *BDE*s of the isomeric fluorotoluenes are independently compared to benzene and fluorobenzene. On average, the fluorotoluenes are by 2.4 kcal/mol stronger bound than fluorobenzene for M = Cr, Co and by 2.6 kcal/mol for M = Fe and weaker bound than benzene by 2.0 kcal/mol for M = Cr, Fe and 2.4 kcal/mol for M = Co. The overall effect of the fluorine atom thus amounts to a decrease of the *BDE*(benzene−M$^+$) by ca. 4.5 kcal/mol, depending slightly on the metal ion. For M = Cr, a comparison of fluorobenzene with chlorobenzene reveals that the latter is stronger bound by 0.9 kcal/mol. Due to interfering reactions, for M = Fe, the *BDE* of chlorobenzene could not be determined as well as the *BDE*s of the bromo- and iodo-substi-

Table 1. Absolute bond dissociation energy of methyl-substituted arene−M$^+$ complexes

ligand	*BDE* in kcal/mol Cr$^+$	 Fe$^+$	 Co$^+$
benzene	40.6 ± 2.3	49.6 ± 2.3	61.1 ± 2.5
toluene	42.6 ± 2.4	51.8 ± 2.4	63.4 ± 2.6
ethylbenzene	43.5 ± 2.4	52.9 ± 2.4	64.2 ± 2.6
o-xylene	44.3 ± 2.5	53.6 ± 2.5	65.2 ± 2.7
m-xylene	44.3 ± 2.5	53.9 ± 2.5	65.3 ± 2.7
p-xylene	44.3 ± 2.5	53.8 ± 2.5	65.3 ± 2.7
mesitylene	45.9 ± 2.6	55.2 ± 2.6	66.8 ± 2.8
1,2,4-trimethylbenzene	45.7 ± 2.6	55.3 ± 2.6	66.9 ± 2.8
durene	47.1 ± 2.7	56.6 ± 2.7	68.2 ± 2.9
pentamethylbenzene	48.2 ± 2.7	57.8 ± 2.7	69.7 ± 2.9
hexamethylbenzene	49.0 ± 2.8	58.9 ± 2.8	70.9 ± 3.0

tuted species for M = Cr, Fe. However, the complete series of monohalogenated arenes was studied for M = Co where loss of hydrogen halides is only a side reaction. The results are visualized in Scheme 3. Chlorobenzene binds stronger than fluorobenzene by 1.2 kcal/mol, bromobenzene adds another 1.0 kcal/mol, and iodobenzene is the strongest bound monohalogenated arene, being 1.7 kcal/mol stronger bound than bromobenzene. However, all halogenated arenes are less strongly bound to Co^+ than benzene itself. Comparison of chlorobenzene with chlorotoluene again shows that for an arene$-Co^+$ complex a single methyl substitution raises the *BDE* by 2.3 kcal/mol.[13] As for the methyl substituents, electrostatic effects can explain the systematic change of the *BDE*s from fluorobenzene to iodobenzene. Replacing one hydrogen atom in benzene by an electron-withdrawing halogen atom leads to reduction of the electron density of the aromatic ring, thus lowering the *BDE*(arene$-M^+$). Obviously, fluorine, the element with the highest electronegativity, causes the strongest effect on the *BDE*. With decreasing electronegativity of the halogens, the *BDE*s of the corresponding arene$-M^+$ complexes become larger. In analogy to halogen substitution, the cyano group, a pseudohalogen, should exhibit a similar behavior. Indeed, the *BDE* of (benzonitrile$-M^+$) is lowered by 1.8 kcal/mol for M = Fe and by 3.3 kcal/mol for M = Co as compared to benzene. However, an unexpected result is obtained for M = Cr, where benzonitrile forms a distinctly *stronger* complex than the parent compound benzene itself. Most likely, Cr^+ does not form a π-complex with the aromatic ring of benzonitrile but is rather attached to the lone pair of the cyano group. To support this idea we also included acetonitrile as the simplest organic nitrile for comparison. In line with the above reasoning, *BDE*(acetonitrile$-Cr^+$) exceeds *BDE*(benzene$-Cr^+$) by ca. 3.0 kcal/mol, thus explaining the unusual behavior of the *BDE*(benzonitrile$-Cr^+$) within the series of arene$-Cr^+$ complexes. In contrast to the halogenated arenes and benzonitrile, *BDE*(phenol$-M^+$) is almost equal to *BDE*(benzene$-M^+$). For M = Cr, Fe, phenol binds stronger than benzene by 0.4 kcal/mol, but it is by 0.1 kcal/mol less bound for M = Co. Obviously, the electronegativity of the hydroxy group is canceled by the interaction of the aromatic π system with the lone pairs of the oxygen atom. Thus, there is almost no net effect on the bond energy in the arene$-M^+$ complex when a hydrogen atom is replaced by a hydroxy group. However, substitution by an amino group drastically raises the *BDE* of the corresponding arene$-M^+$ bond. For Cr^+ and Fe^+, aniline is even stronger bound than *o*-xylene by 0.5 kcal/mol and 0.4 kcal/mol, respectively. As in the phenol case, the relative *BDE* of aniline compared to benzene is lower for Co^+, but aniline still binds stronger than toluene by 1.4 kcal/mol. The overall effect on replacing a hydrogen by an amino group thus amounts to 3.7−4.4 kcal/mol.

In the context of substituent effects on arene reactivity, a comparison of the *BDE* dependence with the rates of electrophilic aromatic substitution reactions is expected to be informative. Roughly speaking, substituents that strengthen the arene$-M^+$ bond, as alkyl or amino groups, also increase the arene's reactivity towards electrophiles. The rate constants for the electrophilic aromatic substitution[14] as well as the *BDE* of the respective arene$-M^+$ complex both grow with increasing number of methyl substituents on the ring. In fact, hexamethylbenzene is the most reactive arene and forms the strongest arene$-M^+$ bond among the examined methylated arenes. In analogy, substituents that lower the arene$-M^+$ bond strength, like halogen atoms or the cyano group, also deactivate the rings towards electrophiles. Thus, the rate constants for aromatic substitution reactions are, in a first approximation, expected to correlate with the *BDE* of the corresponding arene$-M^+$ bond compared to the benzene$-M^+$ complex. However, this agreement holds true at best only qualitatively and fails completely for the hydroxy group which strongly activates phenol in electrophilic substitution as compared to benzene but leaves the corresponding *BDE*s almost unchanged. Comparison with Hammett substituent constants suggests that inductive effects are much more relevant than resonance effects in the binding of the metal cation,[15] which accounts for the deviation from the substitution rates. In fact, a much better − and almost quantitative − correlation of the *BDE*s with the arenes' polarizabilities perpendicular to the ring plane is likely to exist, considering the nature of the arene$-M^+$ bond, which is mostly due to ion-induced dipole and ion-quadrupole interactions,[5] and neglecting the contribution of orbital interactions.[16] However, these data are presently not available in the literature. Even the experimentally determined average polarizabilities are only known for a few of the compounds included in this study.[17] However, we discovered that a surprisingly good inverse correlation ($R^2 \geq 0.98$) exists between the *BDE*s (arene$-M^+$) and the ionization energy (IE) of the respective free arene.[18] As depicted in Figure 1 for the methylated arenes, the absolute *BDE* of the arene$-M^+$ bond linearly decreases with increasing IE of the arene.

In agreement with the almost identical effects of methyl substitution for the three metals (see above) the slope of the line is slightly steeper for M = Co (−6.4) than for M = Fe (−6.3) and M = Cr (−5.9). Most remarkably, the data of

Table 2. Absolute bond dissociation energies of heteroatom-substituted arene$-M^+$ complexes

ligand	*BDE* in kcal/mol Cr^+	Fe^+	Co^+
phenol	41.0 ± 2.5	50.0 ± 2.5	61.0 ± 2.7
fluorobenzene	36.2 ± 2.7	45.1 ± 2.7	56.2 ± 2.9
chlorobenzene	37.1 ± 2.9	[a]	57.4 ± 2.9
bromobenzene	[a]	[a]	58.4 ± 3.1
iodobenzene	[a]	[a]	60.1 ± 3.3
o-fluorotoluene	38.8 ± 2.5	47.8 ± 2.5	58.8 ± 2.7
m-fluorotoluene	38.5 ± 2.5	47.4 ± 2.5	58.6 ± 2.7
p-fluorotoluene	38.5 ± 2.5	47.7 ± 2.5	58.6 ± 2.7
o-chlorotoluene	[a]	[a]	59.7 ± 2.7
m-chlorotoluene	[a]	[a]	59.6 ± 2.7
p-chlorotoluene	[a]	[a]	59.6 ± 2.7
aniline	44.8± 2.9	54.0 ± 2.9	64.8 ± 2.9
benzonitrile	47.0 ± 3.2	47.8 ± 2.5	57.8 ± 2.7

[a] *BDE* could not be determined due to interfering reactions.

Figure 1. Relationship of *BDE*(arene−M^+) and IE(arene) for methylated arenes (M = Cr, Fe, Co);[18] correlation coefficients are R^2 = 0.98 for all metals; numbers on the data points correspond to the number of the arene's methyl groups; for reasons of clarity, the data for *m*- and *p*-xylene are omitted (see text); **3a** corresponds to mesitylene, **3b** to 1,2,4-trimethylbenzene, and **4** to durene; ethylbenzene is denoted by **1′**

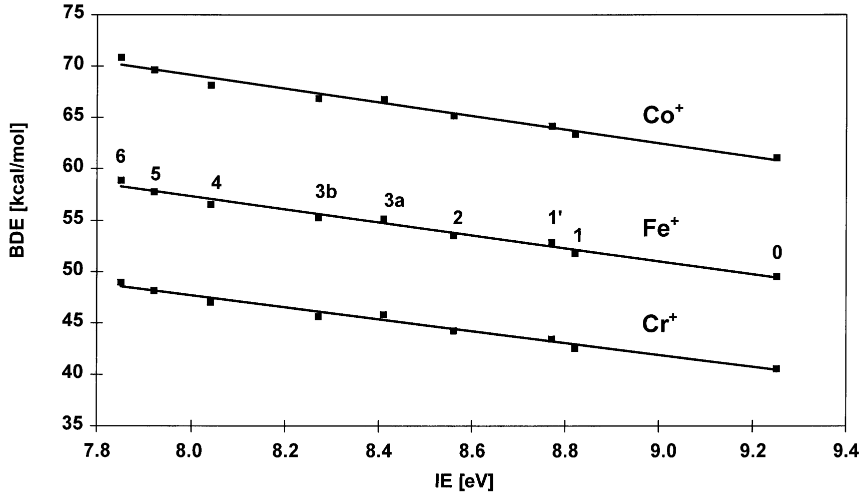
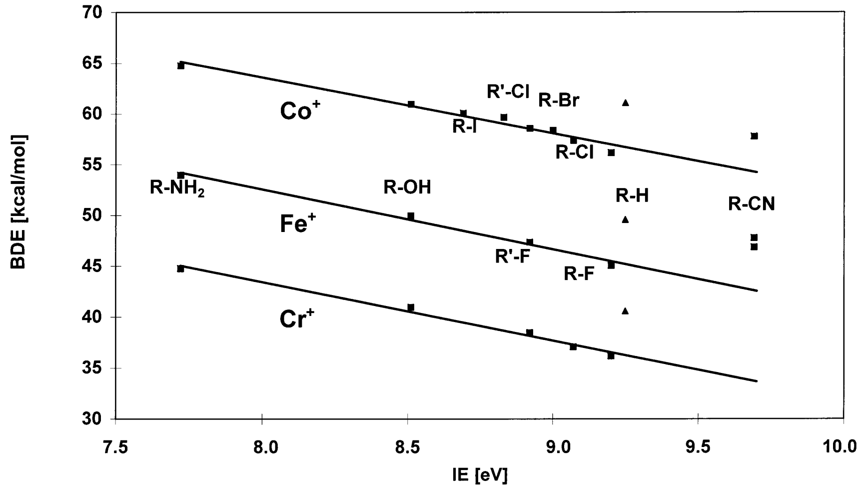


Figure 2. Relationship of *BDE*(arene−M^+) and IE(arene) for heteroatom-substituted arenes (M = Cr, Fe, Co);[18] R = C_6H_5−, R′ = $CH_3C_6H_4$−; correlation coefficients, not including the data of benzonitrile and benzene, are R^2 = 0.99 for M = Cr, Fe and R^2 = 0.97 for M = Co; for comparison, benzene is also included and labeled by a triangle



the particular ligands deviate from an perfect linear correlation in exactly the same way for all metals. A similar linear relationship exists for the heteroatom substituted arenes and the corresponding complexes of Cr^+, Fe^+, and Co^+ (see Figure 2). The correlation of *BDE*s and IEs is excellent for the halogenated arenes and is also applicable for phenol and aniline. Only for benzonitrile the correlation fails. As pointed out before, the benzonitrile−Cr^+ complex corresponds to a σ-bound species rather than a π complex with the arene, thus explaining the drastic deviation from the linear behavior. Also for M = Fe and Co exist remarkable deviations, and one might reason that the interaction of the C−N triple bond with the aromatic ring is responsible for that. While, with the exception of benzonitrile, the heteroatom-substituted arenes obey a similar *BDE*-IE relationship as observed for the methylated ones the combined correlation of both series is not possible. For example, benzene possesses about the same IE as fluorobenzene (ca. 9.2 eV) but forms a distinctly stronger bond to the metal cation. Obviously, the relationship between *BDE* and IE is not general but limited to a certain kind of substituted arenes.

At first glance, it would be tempting to explain the correlation of *BDE*s and IEs by a contribution of charge transfer from the arene ligand to the metal cation. Thus, the lower the IE of the ligand, the more effectively the charge can be delocalized over the complex resulting in an enhanced stabilization. However, the IEs of the neutral metal atoms (Cr = 6.8 eV, Fe, Co = 7.9 eV)[18] are distinctly lower than the IEs of most arenes examined here. Thus, net charge will probably only to a minor extent be transferred to the aromatic ligand. Moreover, the concept of a significant contribution of charge transfer to the arene−metal bonding completely fails to explain the different *BDE*s of benzene and fluorobenzene. Thus, it is more likely that both the *BDE*s of the complexes and the IEs of the aromatic ligands, depend on a common third property, rather than being directly correlated. The IEs of the arenes are determined by the energy of their highest occupied molecular orbitals (HOMOs). A simple MO scheme of arene−transition-metal complexes reveals that a major contribution to the overall binding results from the interaction of the arenes′ HOMO with empty metal orbitals of appropriate symmetry and energy.[5][12] The closer the overlapping orbitals are in energy the stronger the resulting bond. A lower IE implies a HOMO of higher energy and therefore a stronger interaction with the metal center. Thus, neglecting the symmetry of the HOMO, the extent of the metals′ orbitals interaction with the HOMO is primarily determined by its energy which explains the correlation of ligand−metal *BDE*s and IEs. This line of reasoning has some bearing on the difference between the methylated and the heteroatom-substituted arenes. Replacing a hydrogen atom of benzene by a methyl group does not drastically perturb the symmetry of the HOMO so that the interaction with the metal cation is mostly determined by its energy, i.e. the IE. In contrast, a heteroatom, e.g. fluorine, represents a major perturbation to the benzene orbitals′ symmetry. Accordingly, the different *BDE*s cannot be attributed to energetic differences of the corresponding HOMOs alone, and the correlation of benzene (or the methylated arenes) with heteroatom-substituted arenes fails. If, however, the perturbation is kept constant within a series of compounds, as for the singly heteroatom-substituted arenes, their trend in relative *BDE*s to transition-metal cations can again be correlated with their respective IEs. The values for fluoro- and chlorotoluene also fall on the same line as for the heteroatom-substituted ones; this also supports the reasoning that the methyl group′s influence on the HOMO mostly affects its energy whereas its symmetry remains nearly undisturbed. Of course, this model is far from describing the true nature of the arene−M^+ bond as all other, except the HOMO′s, interactions with the metal center are neglected. Nevertheless, it serves as a reasonable explanation for the experimental finding that a linear correlation exists between the IEs of certain types of substituted arenes and the *BDE*s of the respective arene−M^+ complexes. In summary, the results presented in this paper may be used to predict *BDE*s of similar organometallic complexes not only in a qualitative but also in a semi-quatitaive way based on the knowledge of the corresponding IEs.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for continuous financial support and thank *Jeremy Harvey*, Ph. D. for critically reading the manuscript.

Experimental Section

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 sectors), which has been described elsewhere.[19] Cationic sandwich complexes were generated by chemical ionization (CI) of appropriate precursor mixtures by electrons having 50−100 eV kinetic energy using $Cr(CO)_6$, $Fe(CO)_5$, and $Co(NO)(CO)_3$ as metal sources and carbon monoxide as the ionization gas. After acceleration to 8 keV kinetic energy, $(arene_1)(arene_2)M^+$ ions were mass-selected using $B(1)E(1)$ at a resolution of $m/\Delta m \geq 4000$, which is sufficient to resolve most isobaric ions. Unimolecular dissociations of metastable ions (MI) in the field-free region preceding $B(2)$ were monitored by scanning this sector. To further check the purity of the ion beam, collision-activation (CA) spectra were recorded routinely, by using helium as a target gas (80% transmission, T) in the field-free region preceding $B(2)$. The resulting fragment ions were monitored by scanning $B(2)$. These CA results will not be reported here but are available upon request. All spectra were accumulated (5 to 30 scans) and processed on-line with the AMD/Intectra data system. The relative *BDE*s of the aromatic ligands were derived from the mass-corrected intensities[20] of the MI spectra using as an effective temperature T_{eff} = 473 K. This value has recently been derived by Schröder and Schwarz[21] using the same experimental setup in a study of bisligated cationic iron complexes.[22] For each reported value, the intensity ratios of at least three independently recorded spectra were averaged. The maximum error introduced by the spectra averaging corresponds to ± 0.1 kcal/mol in the relative *BDE*s of the methyl-substituted and to ± 0.2 kcal/mol for the heteroatom-substituted arenes. Cross-checking experiments, where the *BDE*s of three ligands were independently compared to each other, verify this value as an upper limit. For example, comparisons of benzene, toluene, and phenol for Fe^+ yield ΔBDE (toluene/benzene) = 2.2 kcal, ΔBDE(toluene/phenol) = 1.8 kcal, and ΔBDE(phenol/benzene) = 0.4 kcal, in excellent agreement. The relative values obtained are converted to absolute *BDE*s using the experimentally determined *BDE*s (benzene−M^+) of Armentrout and coworkers as anchor points.[4a]

☆ Dedicated to Professor *Klaus Hafner* on the occasion of his 70th birthday.

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