throughout all the modes, since the density of states increases. For instance, the only known example of selective bond breaking in a bimolecular reaction by vibrational mode selectivity is the reaction of H with HOD, where a local mode picture of the OH and OD bonds is warranted.[70,71] For larger molecules the local mode picture breaks down, and energy is transferred more efficiently. More work of the type presented here and elsewhere is needed to determine whether S_N2 reactions involving larger ions and molecules will also show nonstatistical behavior.

Acknowledgment. We thank the following people for helpful discussions: Mark Johnson, Susan Graul, Mike Bowers, Bill Hase, Don Truhlar, John Brauman, Michael Henchman, and Steven Buckner.

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Alkyl Substituent Effects in Cyclopentadienyl Metal Complexes: Trends in Gas-Phase Ionization and Electron Attachment Energetics of Alkylnickelocenes

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Abstract: Electron-transfer equilibrium (ETE) methods have been used to establish the gas-phase ionization and electron attachment energetics for nickelocene and several alkylated derivatives, (RCp)(R′Cp)Ni (R, R′ = H, Me, Et, *t*-Bu). The nickelocene derivatives were highly purified by reversed-phase HPLC, and ETE studies were performed on a Fourier transform ion cyclotron resonance mass spectrometer. The results are summarized as free energies of ionization ($\Delta G_\mathrm{i}^\circ$) and free energies of electron attachment ($\Delta G_\mathrm{a}^\circ$) at 350 K for the $(RCp)(R'Cp)Ni^{0/+}$ and $(RCp)(R'Cp)Ni^{0/-}$ couples, respectively. The order of ionization energies follows the expected trend, with more and larger alkyl substituents leading to decreasing values of $\Delta G_\mathrm{i}^\circ$. The $\Delta G_\mathrm{a}^\circ$ values become more endoergic as methyl groups are substituted, but larger alkyl groups lead to more exoergic electron attachment as the size of the alkyl substituents increases. Alkyl substituent effects cannot be described as uniformly "electron donating" in these redox processes and must be rationalized on the basis of more detailed models. As an example, a model based on a combination of inductive and polarization effects is used to analyze the data. Alternative single-parameter correlations with published substituent parameters are also considered. The average differential solvation free energy for the $Cp_2Ni^{+/0}$ and $Cp_2Ni^{0/-}$ couples in THF is estimated from the gas-phase data and the difference in the solution electrode potentials ($\Delta\Delta G_{\mathrm{solv,av}}^\circ = -39 \pm 3$ kcal mol^{-1}).

Introduction

Alkyl substituent effects have been studied extensively in organic chemistry with an emphasis on acidities, basicities, and reactivity in carbon compounds.[1] It has been recognized that *intrinsic* substituent effects are best determined in gas-phase experiments that remove the influence of solvation, which can significantly modify the intrinsic effects.[1,2] Relatively few gas-phase studies of alkyl substituent effects in the chemistry of metal complexes have appeared[3–5] and little is known about intrinsic alkyl effects in the thermochemistry of metal complex redox couples.

On the basis of the results of photoelectron[4,5] and electrochemical[6] studies, it is commonly assumed that alkyl groups on metal complex ligands are "electron-donating" in metal complex redox processes (i.e., stabilizing the oxidized form relative to the reduced form). In order to explore the nature of alkyl substituent effects in transition metal compounds further, we have used

Scheme I

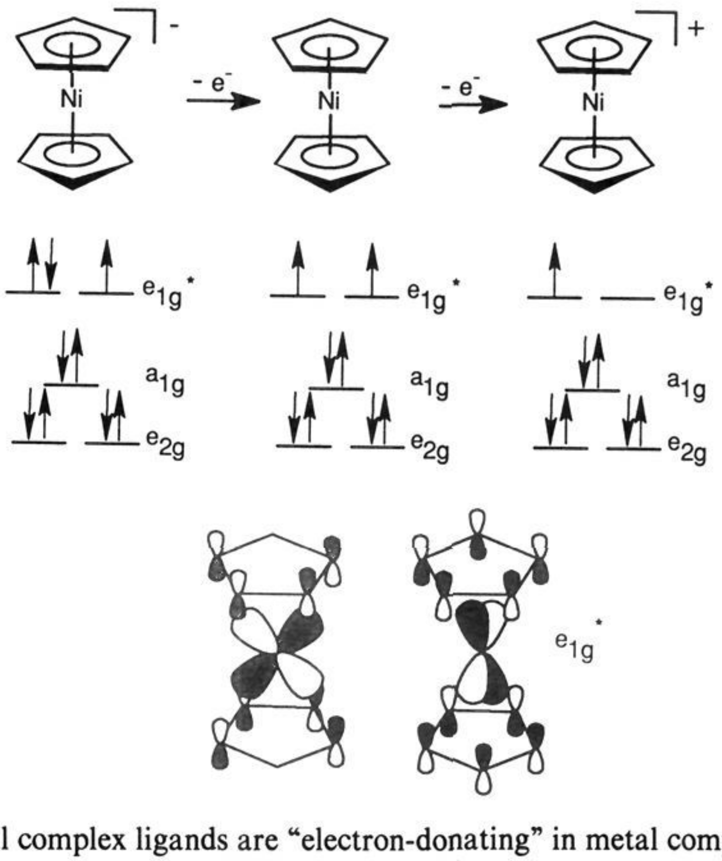

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Table I. Analysis of Free Energies of Ionization and Electron Attachment for Nickelocenes

L	L′	$\Delta G_i°$ [a,b]	$-\Delta G_a°$ [a,b]	$\Delta G_1°$ [a,c]	$\Delta G_2°$ [a,c]	$\Delta G_4°$	$\sum\sigma_I$	$\sum\sigma_\alpha$	$\sum I$ [a]	$\sum P$ [a]
Cp	Cp	143.8	19.7	0	0	0	0	0	0	0
MeCp	MeCp	139.6	19.0	−2.9	0.7	−3.6	−0.092	−0.70	1.8	1.1
EtCp	Cp	141.5	20.2	−2.3	−0.5	−1.8	−0.057	−0.49	1.4	0.9
EtCp	EtCp	138.2	20.3	−5.6	−0.6	−5.0	−0.114	−0.98	2.5	3.1
t-BuCp	*t*-BuCp	136.4	21.2	−7.4	−1.5	−5.9	−0.148	−1.5	3.0	4.4
C_5Me_5	C_5Me_5	121.3	(~ 16)[d]	−22.5	(~ 3.5)[d]	(−26)[d]	−0.46	−3.5		

[a] Units are kcal mol^{-1}. [b] Estimated error in absolute values ± 1.5 kcal mol^{-1}. [c] Estimated error in relative values ± 0.4 kcal mol^{-1}. [d] Estimated (see text).

gas-phase electron-transfer equilibrium (ETE) methods[7] to derive the free energies of ionization ($\Delta G_i°$) and electron attachment ($\Delta G_a°$) for a series of alkylnickelocenes. Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS)[8] has been used to determine electron-transfer equilibrium constants for these alkylnickelocenes and four reference compounds. The results show that, as in organic systems,[1,2] alkyl group substituent effects are not always "electron-donating" in organometallic redox processes and that other models, such as one that includes the polarizability of a substituent,[1,2] must be applied to rationalize the data.

Nickelocene is a useful parent compound for these studies since it forms gas-phase cations and anions.[3a,c,9] Furthermore, electron addition and removal involve the same e_{1g}^* molecular orbital (Scheme I).[10] A simple one-electron model suggests that shifts in the e_{1g}^* energy due to alkyl substitution on Cp would be reflected equally in the energetics of the ionization and electron attachment processes.[11] As shown below, however, a more flexible model must be used to rationalize the trends in the experimental data.

Results and Discussion

Electron-Transfer Equilibria. Samples of alkylnickelocenes prepared according to literature methods[12] were found to be impure by mass spectrometry; therefore, reversed-phase HPLC was used to purify the samples. The principal impurities were nickelocene derivatives with one or two unmodified Cp ligands. For ETE studies, the purified compounds were sublimed through a precision leak valve to yield a known partial pressure of the metallocene in the ion trap of the FTICR/MS.[8]

Free energy ladders for gas-phase equilibria studied in this work are shown in Figure 1. Derived values of $\Delta G_i°$ and $\Delta G_a°$ at ~350 K are also shown in Figure 1 and are given in Table I. The reference compounds for ionization equilibria are shown on the left of Figure 1a, and their $\Delta G_i°$ values have been discussed previously[3c] with the exception of that of (dibenzene)chromium(0/+). The $\Delta G_i°$ value for Bz_2Cr was based on the photoelectron spectrum,[4a,13] which has an exceptionally sharp first ionization at 5.47 eV (=IP_v, the vertical ionization potential). The $\Delta G_i°(Bz_2Cr)$ value (125.7 kcal mol^{-1}) was estimated by assuming that $\Delta H_i° = IP_v = 126.1$ kcal mol^{-1} and that $\Delta S_i°$ is determined only by the electronic entropy change associated with the formation of the ^2A cation (R ln 2).[14]

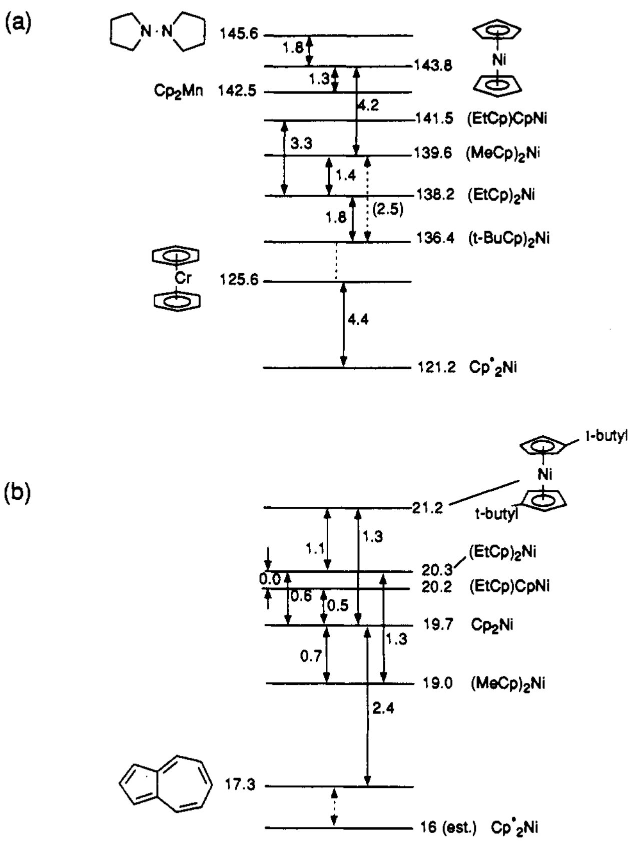

Figure 1. Electron–transfer equilibrium ladders showing gas-phase equilibria studied in this work. (a) Ionization ($L_2M \rightarrow L_2M^+ + e^-$). (b) Electron attachment ($L_2M + e^- \rightarrow L_2M^-$). Free energies of equilibria are shown adjacent to the arrows connecting compounds brought to equilibrium, and derived free energies of ionization ($\Delta G_i°$) and electron attachment ($-\Delta G_a°$) are shown next to compounds. The value for Cp^*_2Ni in part b is an estimate (see text).

Nickelocene is expected to have the highest electron affinity of the first-row η^5-dicyclopentadienyl complexes since it has the least negative electrode potential of the $Cp_2M^{0/-}$ couples.[15] This expectation has been confirmed in our gas-phase studies in that

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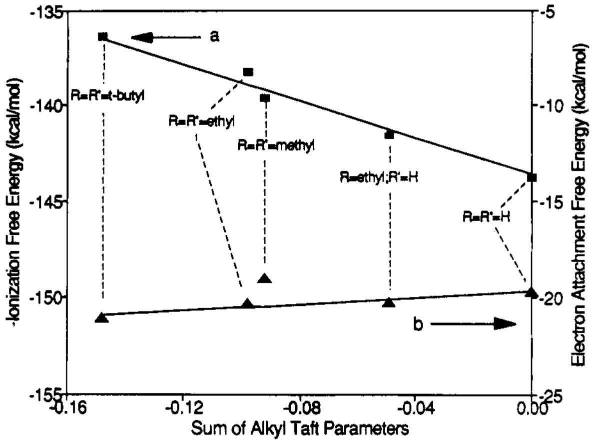


Figure 2. Plots of observed free energies of ionization and electron attachment vs sum of Taft σ_I parameters (ref 17a). (a) Ionization (plotted as $-\Delta G_i°$ for $L_2Ni \rightleftharpoons L_2Ni^+ + e^-$, left scale, squares). (b) Electron attachment (plotted as $\Delta G_a°$ for $L_2Ni + e^- \rightleftharpoons L_2Ni^-$, right scale, triangles).

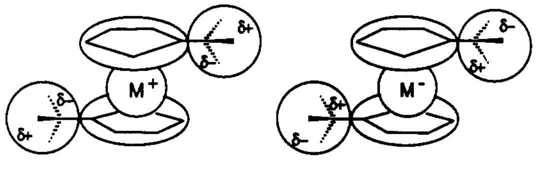
no other metallocene has been observed to form a negative ion by low-energy electron attachment or chemical ionization. Decamethylnickelocene ($Cp^*{}_2Ni$) could not be brought to equilibrium with any reference compound in negative ion ETE experiments, nor was it possible to form the negative ion by electron attachment or chemical ionization. An estimate of the $\Delta G_a°$ for $Cp^*{}_2Ni$ ($\sim$−16 kcal mol^{-1}) has been made from $\Delta G_a°((MeCp)_2Ni)$ by assuming that the effect of the methyl groups is additive (Table I). The estimated electron affinity for $Cp^*{}_2Ni$ puts it near the bottom of the ladder of compounds that have had their electron affinities estimated by the ETE method.[7a]

It is clear from the data in Table I that increasing the number and size of alkyl groups lowers the ionization free energy of alkylnickelocenes. In contrast to the ionization data, the trends for electron attachment free energies do not consistently reflect an "electron-donating" effect; indeed, the *ethyl and tert-butyl groups lead to a higher electron affinity* than does H on the Cp rings. Two methyl groups lower the electron affinity to a small extent compared to R = H. The shifts in $\Delta G_a°$ upon alkylation of nickelocene are rather small but appear to be significantly larger than the error estimated for the relative free energies derived from equilibrium experiments ($\sim$0.4 kcal mol^{-1}; note that absolute energies have a higher estimated error of ±1.5 kcal mol^{-1}).

An increase in electron affinity for larger alkyl substituents relative to R = Me is a well-known effect in organic systems.[16] For example, the electron affinities of alkoxy radicals, RO•, increase in the order R = Me < Et < *n*-Pr < *t*-Bu.[16a,b] For *p*-benzoquinone (BQ) derivatives, the electron affinity of 2,6-di-*tert*-butyl-BQ is $\sim$1 kcal mol^{-1} higher than that of 2,6-dimethyl-BQ.[16c] The lower electron affinity for $(MeCp)_2Ni$ relative to Cp_2Ni is in keeping with the usual destablization of anions by methyl substitution on sp^2 carbons.[7a,16c]

Alkyl Substituent Parameter Analysis. Various alkyl substituent parameter sets have been used to fit the present data to electrostatic models for substituent effects. Both single-parameter and two-parameter models based on previously published schemes[17-20] were used. All fits were to shifts in free energy data relative to R = H (values for $\Delta G_1°$, eq 1, and $\Delta G_2°$, eq 2, are given in Table I).

Scheme II



$$(RCp)(R'Cp)Ni + Cp_2Ni^+ \rightleftharpoons (RCp)(R'Cp)Ni^+ + Cp_2Ni \qquad (1)$$

$$(RCp)(R'Cp)Ni + Cp_2Ni^- \rightleftharpoons (RCp)(R'Cp)Ni^- + Cp_2Ni \qquad (2)$$

The free energies of ionization ($\Delta G_i°$) and electron attachment ($\Delta G_a°$) derived from ETE experiments are plotted against one set of σ_I parameters[17a] in Figure 2 to provide a correlation of the data with inductive alkyl substituent parameters. Additivity of the parameters is assumed. The σ_I parameters have been used previously to correlate organometallic ionization energy data for substituted (benzene)$Cr(CO)_3$ derivatives[18] and alkylferrocenes.[3c] The plots in Figure 2 clearly illustrate the much different effect of alkyl groups on electron attachment energies compared to ionization energies.

The ionization data ($\Delta G_1°$ values in Table I) can be fit with eq 3 (r = 0.997), where the coefficient ρ_I (=49.9) reflects the sensitivity of the free energy of ionization to the parameter σ_I. This value of ρ_I is comparable to that obtained from a fit of $\Delta G_i°$ data for alkylferrocenes (57 kcal mol^{-1}).[3c] On the other hand,

$$\Delta G_1°((RCp)(R'Cp)Ni^{0/+}) = \rho_I(\sigma_I(R) + \sigma_I(R')) + c = [49.9(\sigma_I(R) + \sigma_I(R')) + 0.45] \text{ kcal mol}^{-1} \qquad (3)$$

the same parameters provide an unacceptable fit of the electron attachment data in Table I (r = 0.51).

Hehre et al.[19] devised a σ_α substituent scale that accounts for the polarizability effect of an R group and used the parameters to successfully fit gas-phase data for the proton-transfer acidities of various cationic and neutral acids. Fits to the alkylnickelocene ionization and electron attachment values ($\Delta G_1°$ and $\Delta G_2°$) result in a good correlation of ionization data (r = 0.994) but, again, only poor correlation with electron attachment energies (r = 0.63). Thus, unlike the organic acids analyzed by Hehre et al.,[19] it appears that a single-parameter scale is not adequate to fit the alkyl substituent effects in the present case. The failure to fit the electron attachment data with either single-parameter model can be traced partly to the observed opposite effects of Me vs Et and *t*-Bu, since both σ_I and σ_α predict the same direction of effect for all three types of R groups.

The trends in the data require a more complex model for interpreting alkyl substituent effects than one based only on a single parameter. A simple alternative model combines the effect of the polarizability of alkyl groups with inductive effects. A quantitative model has been used by Taft et al.[20] to separate polarizability and inductive effects for gas-phase proton-transfer equilibria involving a number of alcohols (ROH) and their conjugate bases (RO^-) and acids (ROH_2^+). The successful σ_α fit to the same data led Hehre et al.[19] to assert that such an approach is invalid, but we have applied the method for comparison to the single-parameter fits above. The polarizability and inductive effects relative to R = H are separated by analyzing the free energies of the hypothetical gas-phase equilibria described by eq 4, where nickelocene (R = H) is used as the reference compound ($\Delta G_4° = \Delta G_1° - \Delta G_2°$). It is assumed that the polarization effect

$$(RCp)(R'Cp)_2Ni^- + Cp_2Ni^+ \rightleftharpoons (RCp)(R'Cp)_2Ni^+ + Cp_2Ni^- \qquad (4)$$

("P") of a substituent R relative to H is the same in both L_2Ni^- and L_2Ni^+, and thus the $\Delta G_4°$ values of eq 4 depend only on the inductive effect ("I").[20] With I and P positive, the model[20] requires $-\Delta G_1° = P + I$, $-\Delta G_2° = P - I$, and $-\Delta G_4° = 2I$.

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The model above assumes that polarization effects are equally efficient in stabilizing negative or positive charge remote from the substituent. A polarizable group will stabilize both positive and negative charge concentrated at the remote metal center upon ionization and electron attachment, respectively, as illustrated in Scheme II for R = *t*-Bu. In the case of nickelocenes, since the same molecular orbital is both donor and acceptor orbital for ionization and electron attachment, the assumption that the stabilization due to polarization is the same in both cases seems justified. It is also assumed that any structural changes that accompany oxidation or reduction are consistent throughout the series.

A fit of $\Delta G_4°$ to the sum of σ_I parameters yields a good correlation ($r = 0.992$). The resulting *P*/*I* analysis summarized in Table I leads to the conclusion that the contributions of polarizability and inductive effects to shifts in $\Delta G_i°$ and $\Delta G_a°$ for alkylnickelocenes are similar in magnitude. The derived *P* and *I* values in kilocalories/mole are H, $P = I = 0$ (defined); Me, $P = 0.55$, $I = 0.9$; Et, $P = 1.2$, $I = 1.3$; and *t*-Bu, $P = 2.2$, $I = 1.5$. The rather small changes in $\Delta G_a°$ for various alkyl-substituted nickelocenes (Table I) relative to Cp_2Ni can be viewed as the difference between two effects of comparable size ($P - I$), but in the case of $\Delta G_i°$ the two effects are additive ($P + I$) and lead to the larger overall sensitivity to alkyl substitution.

In contrast to the results for alkylnickelocenes, the separation of polarization and inductive effects for acid and base equilibria of gas-phase alkyl alcohols leads to the conclusion that the polarization effect is several times more important than the inductive effect in determining the relative gas-phase acidities and basicities of ROH.[20] According to Hehre et al.,[19] the separation in the latter cases may not be valid since σ_α provides an acceptable fit alone. However, it may be necessary to use a two-parameter fit when the magnitude of polarization and inductive effects is comparable, as appears to be the case here.

Any of the above correlation schemes suggests that the effect of alkyl group polarizability is smaller than the effects of the same groups on the electron affinities of $RO^•$ radicals.[16a,b] The much smaller contribution of polarizability in the alkylnickelocenes is easily rationalized by the increased distance between the charge center and the R group (~3.3 Å from the metal center to the Cp-bound alkyl carbon) in comparison to RO^-. The polarizability effect has a $1/r^4$ distance dependence, which can be compared to the $1/r^2$ dependence of inductive effects,[19] and a rapid falloff in polarizability effect (*P*) relative to inductive effect (*I*) with increasing distance is consistent with the present data.

Solvation Energetics. The $E°$ values for oxidation or reduction of a compound can be related to gas-phase free energies of ionization or electron attachment by thermochemical cycles that include the effect of differential solvation energies[21] for the two members of the couple. In the following we estimate the average differential solvation free energies for the $Cp_2Ni^{+/0}$ and $Cp_2Ni^{0/-}$ couples.

Nickelocene has an electrochemically reversible one-electron oxidation in many nonaqueous solvents, but the one-electron reduction is only quasireversible in DMF and THF at low temperature.[15] We have repeated the earlier electrochemical studies and find that the cathodic peak potential for the $Cp_2Ni^{0/-}$ couple is relatively insensitive to temperature. The estimated $\Delta E_{1/2}$ from $E_{1/2,\mathrm{ox}}$ and $E_{1/2,\mathrm{red}}$ is ~2.0 ± 0.1 V in THF. From the gas-phase (Table I) and solution data for the $Cp_2Ni^{+/0}$ and $Cp_2Ni^{0/-}$ couples it is possible to extract the average differential solvation energy, $\Delta\Delta G_{\mathrm{solv,av}}°$, by using eq 5.[22] Note that an estimate of the average solvation free energy by eq 5 *does not require knowledge of the absolute potential of the reference electrode.* A $\Delta\Delta G_{\mathrm{solv,av}}°$ value of −39 ± 3 kcal mol^{-1} is obtained with the THF data, and this value is equal within error limits to the value of $\Delta\Delta G_{\mathrm{solv}}°(Cp_2Ni^{+/0})$ estimated previously[3c] from an estimate for the absolute electrode potential of the $Cp_2Ni^{+/0}$ couple in acetonitrile (−38 ± 5 kcal mol^{-1}). Thus, it appears that the differential solvation free energies are essentially the same for both cationic and anionic couples of nickelocenes, and the energies are predicted well by the Born dielectric continuum model.[3c,23] Electrochemical studies of alkylnickelocenes are underway to assess the combined influences of intrinsic substituent effects and solvation energetics on observed electrode potentials.

$$\Delta\Delta G_{\mathrm{solv,av}}° = -\tfrac{1}{2}[-F(E°_{\mathrm{ox}} - E°_{\mathrm{red}}) + (\Delta G_a° + \Delta G_i°)] \qquad (5)$$

Conclusions. The alkylnickelocenes have allowed the first survey of alkyl substituent effects for electron attachment and ionization energetics in which the same molecular orbital can be considered both the acceptor and donor orbital. The present work and studies of ruthenium β-diketonate complexes[3a,b,c] show that the gas-phase electron affinity of metal complexes can be *increased* by larger alkyl substituents. It is clear from these observations that alkyl groups are not intrinsically "electron-donating" with respect to the gas-phase redox thermochemistry of these metal complexes (only in the sense that they do not always result in lower electron affinities and lower ionization energies). An electrostatic model for the alkyl effects incorporating both inductive and polarization contributions successfully rationalizes the gas-phase trends. An analysis of the solvation energetics for the one-electron oxidation and reduction couples of nickelocene shows that both couples have the same differential solvation energy (ca. −39 ± 3 kcal mol^{-1}).

Experimental Section

Positive and negative ion ETE studies were performed on a Fourier transform ion cyclotron resonance mass spectrometer as described previously.[3,7b,c] The system used in this work employed a 3-T magnetic field and an Ionspec data station. The temperature of the ion trap was 350 ± 10 K as determined by a RTD sensor mounted on the cell. Near thermal ion temperatures were assured by following the approach to equilibrium for at least 5–10 s, during which ions underwent >100 collisions with the neutrals, which were at a total pressure of ~10^{-6} Torr or higher.[24] Cyclic voltammetry studies were performed with a PAR system (Models 173/175). A platinum button working electrode and a Ag/AgCl reference electrode were used. THF for electrochemical studies was distilled after drying and stored over molecular sieves.

Alkylnickelocenes were prepared according to literature methods.[12] A Dynamax 60 column (C-18, 4.6 mm × 25 cm) on a Rainin system was used with acetonitrile (HPLC grade) as the mobile phase to purify the samples prior to the ETE studies. All separations were done under an inert atmosphere, and fractions were collected by using a multireceiver Schlenk-ware adapter, also under an inert atmosphere. The solvent was removed from the fractions on a vacuum line, and the metallocene samples were introduced into the FTICR via a precision leak valve.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE9008663), and K.A.M. was supported by a Research Experiences for Undergraduates supplement to that grant.

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(21) Richardson, D. E. *Inorg. Chem.* **1990**, *29*, 3213.

(22) (a) Parker, V. *J. Am. Chem. Soc.* **1976**, *98*, 98. (b) Note that the sign convention of eq 5 results in negative values of $\Delta\Delta G_{\mathrm{solv}}°$ for both +/0 and 0/− couples. The value of $\Delta\Delta G_{\mathrm{solv}}°$ represents the additional stabilization of the ionic member of the couple relative to the neutral member due to solvation.

(23) (a) Born, M. *Z. Phys.* **1920**, *1*, 45. (b) Roux, B.; Yu, H.-A.; Karplus, M. *J. Phys. Chem.* **1990**, *94*, 4683.

(24) Long reaction times allow collisional cooling of ions, which is particularly efficient with polyatomic neutrals as the background gas. Ion/molecule reaction rate studies as a function of system temperature indicate that even monoatomic buffer gases can cool the ion population to quasiequilibrium with neutrals (see: Bruce, J. E.; Eyler, J. R. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 727.