Lithium and sodium cation binding of cyclopentadienyl anions: Electronic effects of cyclopentadienyl substitution

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A B S T R A C T

The Li^+ and Na^+ binding of substituted cyclopentadienyl (Cp) anions were investigated using computational techniques. The ring centroid-metal distances and the binding energies of the Cp-metal complexes correlate very well with the $\sum \sigma_m$ of the substituted Cp ring. These properties also correlate well with the Cp Θ_{zz} values. The trend in the correlations is the more electron-rich the Cp (negative $\sum \sigma_m$ and Θ_{zz} values values), the shorter the Cp-metal bond and the stronger the binding energy. The NBO metal charges correlate, though not very well in either case, with the Cp Θ_{zz} and $\sum \sigma_m$ values. However, there is a substantial increase in correlation when the sum of the absolute value of the Hammett σ_m ($\sum |\sigma_m|$) is employed. The significantly improved correlation when the $\sum |\sigma_m|$ values are employed leads us to propose a model for substituted Cp charge transfer upon Li^+ or Na^+ complexation, and it also informs us that the Hammett substituent constant σ_m contains information about substituent polarizabilities, at least in the case of Li^+- and Na^+-substituted Cp anions.

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1. Introduction

Since the discovery of ferrocene in the 1950s [1–3], metal complexes with cyclopentadienyl ligands (Cp) have been extensively investigated [4–6]. The nature of Cp-metal complexes has been widely probed via Cp–Li complexes, and to a lesser extent via Cp–Na complexes. For instance, the relative binding affinity of benzene and the Cp ring in ferrocene was recently reported [7], the ligand exchange properties of CpCaI complexes with lithium and sodium salts to form Cp–Li and Cp–Na complexes has been studied [8], and a significant number of Cp–Li and Cp–Na solid-state structures have been prepared over the past few decades [6,9]. The experimental work on Cp–Li and Cp–Na complexes almost entirely involves substituted Cp ligands and/or lithium/sodium atoms that are either solvated or complexed by other molecules. To gain a more basic understanding of Cp–Li and Cp–Na complexes numerous computational studies have been performed. Cp–Li complexes have been calculated to probe the aromaticity of Cp [10] and to aid in assessing IGLO chemical shift calculations [11]. Computational studies have included Cp–Li to help understand the fluorenyl-lithium complex [12], the pentabenzylcyclopentadienyl-lithium complex [13], and the effects of Li-coordinating ligands on Cp–Li complexes [14]. There have been numerous computational studies comparing Cp–Li and Cp–Na [15–17], and the Cp–Na complex has

been studied via calculations as part of larger work on sodocene [16,18]. While this is by no means a comprehensive overview of the computational studies involving Cp–Li and Cp–Na complexes, it illustrates the wide array of work done in the area.

Work on substituted Cp rings has generally focussed on the addition of sterically bulky groups and the recent review by Deck [4] nicely summarizes why electronic effects have not received the same attention. Namely, Cp rings are primarily prepared as ligands for catalytic systems and Cp rings substituted with sterically small electron-donating substituents (ie. OH, NH_2) and electron withdrawing groups (ie. CN, NO_2) either present challenges to the synthesis of Cp-metal catalysts or, if the catalyst is able to be prepared, the Cp substituent would render the catalyst less reactive or non-reactive [4]. Still, a search of the Cambridge Structural Database (CSD) shows that many such substituted Cp rings have been prepared. The aim of this study is to explore the electronic effects of Cp substitution on Cp-metal systems by computationally investigating Cp–Li and Cp–Na complexes. Small, sterically non-hindering Cp substituents were chosen based on the availability of the substituted Cp ring either via purchase or literature preparation.[1] The effects of substitution on the Cp-metal distances, binding energies and the charge on the metal center are discussed, and correlations between these properties and the quadrupole moment

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[1] All substituted Cp rings presented in this paper have crystal structures on the Cambridge Structural Database (CSD) and can either be purchased from Sigma-Aldrich or prepared via the literature preparation available from the CSD citation.

(Θ_{zz}) or the sum of the Hammett constants σ_p and σ_m ($\sum\sigma_p$ and $\sum\sigma_m$) of the substituted Cp rings are explored.

2. Computational methods

All substituted Cp anions were optimized and characterized via frequency calculations at the RHF/6-311++G** level of theory for the purpose of determining the quadrupole moments, Θ_{zz}. The RHF/6-311G** level of theory was chosen because it gives excellent agreement between the calculated and experimental Θ_{zz} values of benzene (calculated: -8.76 DÅ [19,20]; experimental: -8.7 ± 0.5 DÅ [21]) and hexafluorobenzene (calculated: $+10.06$ DÅ [19,20]; experimental: $+9.5 \pm 0.5$ DÅ [21]). We employed the 6-311++G** basis set for this work because a proper description of the electron density of anions requires diffuse functions. Of course, the molecular quadrupole moment is a 3 X 3 tensor and the calculations gave the diagonal quadrupole moment tensor components Θ_{ii} ($i = x, y$ or z) and the off-diagonal tensor components Θ_{ij} ($i = x, y$ or z; $j = x, y, z; i \neq j$). The Θ_{zz} values were determined from the equation $\Theta_{zz} = \Theta_{zz} - 0.5(\Theta_{xx} + \Theta_{yy})$. For the planar Cp rings the off-diagonal tensor components are all zero and the equation requires no approximations. For the Cp anions with substituents that extend above and below the plane of the ring the off-diagonal tensor components are non-zero, however, their magnitudes range from 0.1% to 10% of the value of the diagonal tensor components and therefore the equation is an excellent approximation of the Θ_{zz} value.

The Cp–Li and Cp–Na complexes were optimized, characterized and binding energies were calculated at the MP2(full)/6-311++G** level of theory, and the counterpoise method was subsequently employed to account for basis set superposition error (BSSE) [22]. This level of theory was chosen for binding energy calculations because the MP2(full)/6-311G** calculated Na$^+$-benzene binding energy gives excellent agreement with experiment; the calculated ΔH_{298} is -24.51 kcal/mol and the gas-phase experimental value is -22.13 ± 1.39 kcal/mol [23]. As was the case with the Θ_{zz} calculations, we incorporated diffuse functions to describe the anionic character of Cp. Metal charges were determined using the NBO method [24]. Hammett σ_m and σ_p constants were taken from standard references [25].

The Cp and Cp-cation geometries conformed to the highest level of symmetry, however, at the MP2(full)/6-311++G** level of theory the frequency calculation for certain Cp anions had one or more imaginary frequencies, indicating the optimized structure was not a minimum (details can be found in Supplementary material). These curious imaginary frequencies disappeared for methods other than MP2, and they were also absent when diffuse functions were omitted from the basis set. Similar results have been recently documented for aromatic compounds optimized at the MP2, MP3, CISD, and CCSD levels of theory, and explained as arising from a two-electron basis set incompleteness error (BSIE) where distortion from planarity improves the ability of the basis sets to recover σ–π electron correlation to which correlated wave functions such as MP2 are susceptible [26]. To account for the anionic nature of the Cp ring, all binding energies are reported at the MP2(full)/6-311++G** level of theory. For the Cp rings that were not minima at the MP2(full)/6-311++G** level of theory, the minimum character was assured by the absence of imaginary frequencies when the optimizations were done at the RHF/6-311++G** theoretical level. For the Cp-cation complexes that were not minima at the MP2(full)/6-311++G** level of theory, the minimum character was assured by the absence of imaginary frequencies when the optimizations were done at the MP2(full)/6-311G** theoretical level. All calculations were performed using the GAUSSIAN03 suite of programs [27].

3. Results and discussion

The quadrupole moments of the parent and substituted Cp anions, calculated at the RHF/6-311++G** level of theory, are shown in Table 1. The MP2(full)/6-311++G** Cp–Li and Cp–Na ring centroid-metal distances (dCp–Li, dCp–Na), binding energies ($E_{bind,Li}$, $E_{bind,Na}$), and the NBO calculated metal charges (q_{Li}, q_{Na}) are also collected in Table 1. The general structure of the complexes is shown in Fig. 1.

3.1. Effects of substitution on Cp-metal distance

The values calculated for the Cp–Li and Cp–Na ring centroid-metal distances are in agreement with results obtained by previous computational work [15]. The calculated distances of 1.72 Å for Cp–Li and 2.22 Å for Cp–Na are significantly shorter than the Cp–Li and Cp–Na distances found in the solid-state. The solid-state literature is rich with examples of Cp–Li and Cp–Na complexes with differently substituted Cp rings and/or different solvent conditions [6] and these complexes have ring centroid-metal distances about 0.2–0.3 Å longer than the calculated values presented here. For instance, the crystal structure of a Cp–Li complex where the Li$^+$ metal is solvated by TMEDA has a ring centroid-metal distance of 1.92 Å and a Cp–Na complex where the Na$^+$ metal is solvated by three pyridine molecules has a solid-state Cp–Na distance of 2.40 Å [6]. As has previously been discussed, the primary reason for the discrepancy between the calculated values and the solid-state values is due to solvent coordination in the latter [15]. As shown in Fig. 2, the correlation between Cp–Li bond distances and the Cp Θ_{zz} values for the entire set of 30 substituted Cp rings is bad ($R^2 = 0.24$). The greatest outlier from the line of best fit is the amide (–NHC-OCH$_3$) substituted Cp (27) with a Cp–Li distance of 1.83 Å. This is the only substituted Cp where the substituent chelates to the metal and the calculated structure is shown in Fig. 3. This essentially mimics what is observed in the solid-state; chelation of Li$^+$ either by solvent or other complexing agents results in a longer Cp–Li ring centroid-metal distance. Removing the chelating Cp (27) from the analysis substantially improves the correlation with the Cp Θ_{zz} values, however, the R^2 of 0.55 is still not very good (Fig. 2). Although none of the other substituents chelate to the Li$^+$, the other major deviations from the line of best fit generally belong to Cp rings with substitution patterns that are likely to cause steric interactions between the Cp substituents and the lithium cation. Thus, if we omit the Cp rings with substituents that contain three or more linearly bonded atoms (15, 16, 21, 22, 24, 25 and 27), along with those containing four or more methyl groups (17, 18 and 20) we see a marked improvement for the correlation between the Cp–Li distance and the Cp Θ_{zz} values ($R^2 = 0.93$, Fig. 2).

Extending this analysis to the correlation between the Cp–Li distance and the $\sum\sigma_p$ values of the Cp rings shows slightly different results (Fig. 2). For all Cp rings, the correlation is significantly better ($R^2 = 0.45$) than it was with the Θ_{zz} values, and when Cp (27) is omitted the correlation is decent ($R^2 = 0.74$). However, for the Cp rings with the 20 sterically least hindering substitution patterns the correlation with the Cp $\sum\sigma_p$ values is much worse ($R^2 = 0.68$) than it was for Θ_{zz} values (Fig. 2). We next looked at the correlation between the Cp–Li distance and the Cp $\sum\sigma_m$ values and found significant improvement. For all 30 substituted Cp rings the line of best fit has an R^2 value of 0.53, and when Cp (27) is omitted the correlation improves to near-unity ($R^2 = 0.95$, Fig. 2). Omitting the Cp rings with sterically hindering substitution patterns does not improve the correlation ($R^2 = 0.95$, Fig. 2). Thus, the $\sum\sigma_m$ values of the substituted Cp rings allow us to discuss trends in Cp–Li ring centroid-metal distances without discarding certain substituents or substitution patterns based on the somewhat arbitrary definitions of steric hindrance we introduced above.