Journal of Organometallic Chemistry 748 (2013) 68–74

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Complex consequences: Substituent effects on metal···arylmethylium interactions

Rebecca L. Davis[1,3], Michael W. Lodewyk[3], Matthew R. Siebert[2,3], Dean J. Tantillo*

Department of Chemistry, University of California, Davis, One Shields Avenue Davis, CA 95616, USA

ARTICLE INFO

Article history:
Received 15 January 2013
Received in revised form
22 February 2013
Accepted 24 February 2013

Keywords:
Arene
Chromium tricarbonyl
Ferrocene
Cyclobutadiene
Reactive intermediate
Substituent effects

ABSTRACT

Metal complexation to aryl (Ph, Cp, cyclobutadienyl) methylium cations, radicals, and anions was investigated using hybrid density functional theory methods (B3LYP/LANL2DZ), with a focus on the effects of substituents. The results of these calculations, in which both geometric and energetic consequences of adding substituents were examined, indicate that metal–methylium interactions are most sensitive to substituent effects for complexed cations.

1. Introduction

Metal complexation to arylmethylium cations, radicals, and anions has garnered significant interest from experimental and theoretical chemists alike. For example, these complexes are used as chiral auxiliaries and have been widely applied in asymmetric synthesis [1]. Arene chromium tricarbonyl complexes have been used to control the configuration of a forming stereocenter at the benzylic position [2]. Similar reactivity and selectivity has been observed for reactive intermediates adjacent to ferrocenes [3], $Fe(CO)_3$-complexed cyclobutadienes [3h,4], $Fe(CO)_3$-complexed acyclic butadienes [5], and $Co_2(CO)_6$-complexed alkynes [6]. Additions to metal complexed π-systems with reactive intermediates near to but not in direct conjugation with the aryl ring have also exhibited stereoselectivity [5a,7]. Stereocontrol is thought to occur as a result of metal···reactive intermediate interactions that bias attack at the reactive center. This biasing is connected to geometric distortions of the benzylic system. For example, in the case of the $Cr(CO)_3$ complexed benzyl cation, the benzylic carbon bends toward the metal, while for the anionic system it bends away and for the radical it does not bend significantly (see Chart 1) [7c,8].

While the electronic and geometric properties of unsubstituted aryl methylium reactive intermediates have been thoroughly examined [7c,8], the effects of placing substituents on their aromatic rings have not been explored (to our knowledge). As many of the synthetic applications of metal–arene complexes involve highly substituted ring systems [2], we sought to explore the effects of substituents on the electronic and geometric properties of aryl methylium reactive intermediates. We hoped that by understanding the effects of substituents on the methylene unit, the selectivity and reactivity of these systems could be modulated via simple functional group interconversions (e.g., conversion of an NO_2 to NH_2 or an OR to an OAc group).

Herein we describe correlations between Hammett parameters [9] with geometric and electronic properties of the substituted arylmethylium species shown in Chart 2 ($* = +, \bullet$ or $-$), predicted using density functional theory calculations. The measures employed for assessing substituent effects are: (1) geometric changes (bond lengths, bending angles, etc.), and (2) changes to the barrier for methylene rotation (since direct interactions between

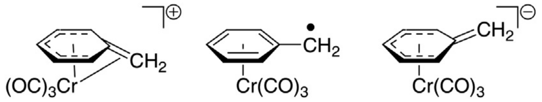

Chart 1. Chromium tricarbonyl-complexed benzyl cation, radical, and anion.

---

* Corresponding author.
E-mail address: djtantillo@ucdavis.edu (D.J. Tantillo).

[1] Current address: Center for Catalysis, Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark.

[2] Current address: Department of Chemistry, Missouri State University, 901 S National Ave., Springfield, MO 65897, USA.

[3] Authorship order is alphabetical; RLD, MWL and MRS contributed equally.

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.02.034

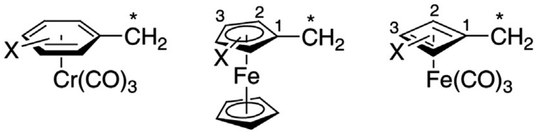

Chart 2. The organometallic systems examined.

carbocations, carbanions or radical centers at the arylic position with the complexed aryl ring must be sacrificed for rotation to occur). We found that all three systems exhibit similar substituent dependencies, so we focus our discussion on the Cr(CO)$_3$-complexes. A full description of the results for the ferrocenyl and Fe(CO)$_3$-cyclobutadienyl systems can be found in the Supplementary data. We do, however, include a brief discussion of the few significant differences between Cr(CO)$_3$-complexes and the other systems from Chart 2.

2. Methods

All calculations were performed with *GAUSSIAN03* [10]. Structures were optimized without symmetry constraints at the B3LYP/LANL2DZ level of theory [11,12]. The B3LYP density functional, despite its reputed downfalls [13], has found a great deal of utility in geometric and energetic computations on organometallic systems such as those discussed herein. The LANL2DZ basis set and associated pseudopotential has also been employed to successfully describe the geometric and energetic features of organometallic systems. For select Cr(CO)$_3$-complexes, optimizations with the B3LYP density functional and the all-electron DZVP2+ basis set were carried out [14,15]; we found no noteworthy geometric changes using this larger basis set. Frequency analyses were used to characterize each stationary point as a minimum or transition state structure. Reported energies from B3LYP/LANL2DZ calculations are electronic energies with unscaled zero-point energy corrections added, except where noted. Energies calculated at the B3LYP/DZVP2+//B3LYP/LANL2DZ level of theory do not include zero-point energy corrections. This method has been used previously to describe a variety of organometallic systems, including Cr(CO)$_3$-complexed benzylic reactive intermediates [5a,7a–c,8a,16,17]. We refer to energies throughout the text by the basis set used (i.e., “LANL2DZ” is used to refer to B3LYP/LANL2DZ energies, while “DZVP2+” is used to refer to B3LYP/DZVP2+//B3LYP/LANL2DZ energies). In certain instances, intrinsic reaction coordinate (IRC) calculations were used to characterize transition state structures [18]. Stability tests on wavefunctions were also performed, and when restricted wavefunctions were found to be unstable with respect to unrestricted alternatives, reoptimization with uB3LYP was carried out (see below). Plots were generated with *GNUPlot* [19]. Structural drawings were produced using *Ball & Stick* [20].

3. Results and discussion

3.1. Revisiting unsubstituted Cr(CO)$_3$-complexes

Chromium arene complexes have been the subject of numerous theoretical and experimental studies designed to explore structure and fundamental reactivity [2,7,8,21]. The observed tendency for stronger interaction with both the cation and anion relative to the radical [7b,7c,8] has been previously described as “chemical hermaphroditism” [8a]. The geometric perturbations associated with benzyl···Cr interactions are evident in the structures ($\mathbf{1}^*$) shown in Fig. 1.

In addition to increased stability, interaction with the metal is expected to increase the barrier to rotation of the methylene group [5b,6b,8b] while blocking one face of the organic fragment. The transition state structures for methylene rotation ($\mathbf{2}^*$) exhibit a roughly coplanar arrangement of the ring and methylene carbon for all oxidation states (Fig. 1). The transition state structure for methylene rotation in the anion ($\mathbf{2}-$) is not C_s symmetric due to pyramidalization of the exocyclic methylene carbon (sum of angles = 338°; note that a perfect tetrahedral [pyramidal] geometry is described by a sum of angles of 328.5° [3 × 109.5°], while a trigonal planar geometry is described by a sum of angles of 360°). The barriers for methylene rotation in the cation, radical, and anion are approximately 43–48, 13–14, and 41–46 kcal/mol, respectively. These values are consistent with strong stabilization of benzyl cation and anion by complexation and a much smaller benefit for benzyl radical [22], i.e., chemical hermaphroditism [8a].

3.2. Substituent effects on metal–methylene distances

As stated above, we expected that the metal–methylium interactions would be modulated by the presence of donor and acceptor groups at various positions around the arene. In order to assess the magnitudes of these effects, the structures and energies of metal–arylmethylium complexes with a variety of electron-withdrawing and electron-donating groups were determined. Substituents (S$^-$, NMe$_2$, OMe, SiMe$_3$, CF$_3$, H, CN, NO$_2$, SO$_2$CN, N$_2^+$) were chosen to provide the greatest variation in Hammett parameter (σ_p) [9b,23]. The extremes are the highly electron donating S$^-$ ($\sigma_p = -1.21$) and the highly electron withdrawing N$_2^+$ ($\sigma_p = 1.91$). Plots of Hammett parameters versus metal···CH$_2$ distances in Cr(CO)$_3$ complexes with *para* (Fig. 2a) and *meta* (Fig. 2b) substituents are shown in Fig. 2.

The positive slope for the cationic systems with *para* substituents (Fig. 2a) indicates that as electron-donating character of the substituent increases, the metal···methylene distance decreases. As the electron-donating character of the substituent increases, so does the contribution from the resonance forms shown in Chart 3 (**I** and **II**). In response, the metal positions itself for optimal interaction with an η^5-pentadienyl ligand and the exocyclic methylene. Fig. 3 shows extreme examples of this behavior for S$^-$-substituted systems, emphasizing the maximum structural distortions expected for systems with electron-donating substituents (compare with structure $\mathbf{1}^+$ in Fig. 1).

The radical systems display only a slightly positive slope while the anionic systems appear to be essentially insensitive to substituents (Fig. 2). Not surprisingly, the metal···CH$_2$ distances for cationic systems are most sensitive to substituents, since in these systems the methylene group interacts directly with the metal.

3.3. Substituent effects on methylene rotation barriers

The effects of substitution on the barriers to methylene rotation for Cr(CO)$_3$ complexes were also investigated and the computed results are shown in Fig. 4. Analysis of this data is complicated by the fact that many of the transition state structures for methylene rotation in the cationic and anionic structures display RHF → UHF instabilities; full unrestricted optimization of these structures results in inconsistent changes in both energies and geometries. The data from the restricted calculations are discussed below first, followed by the data from the unrestricted calculations.

Fig. 4a shows the effect of substitution on the barriers to methylene rotation for the *para*-substituted Cr(CO)$_3$ complexes using restricted B3LYP calculations. For the cationic systems, it is evident that the barrier to rotation increases with increasing electron-donating ability of substituents in the *para* position, consistent with resonance form **II** ($* = +$, Chart 3) increasing in relative importance as electron density is released into the benzyl