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Attenuating and Supplanting Nonclassical Stabilization: $Cr(CO)_3$-Complexed Benzonorbornenyl Cations

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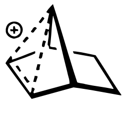
The structures of corner-protonated cyclopropanes such as the norbornenyl (**1**) and norbornyl (**2**) cations were the subject of one of the most ferocious debates in the history of physical organic chemistry.[1] These species, now generally accepted to be true nonclassical cations, boast hypervalent carbon atoms and homoaromatic bonding arrays.[2,3] Elegant experiments have revealed that the extent of the stabilization provided to classical cations through interaction with nonadjacent π-bonds—thereby leading to nonclassical structures—can be modulated through conjugating substituents that affect the electron donating ability of the π-system in question.[4] Metal complexation, however, provides another means to alter the electronic properties of such π-systems.[5]



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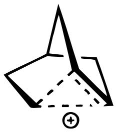

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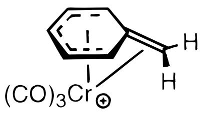

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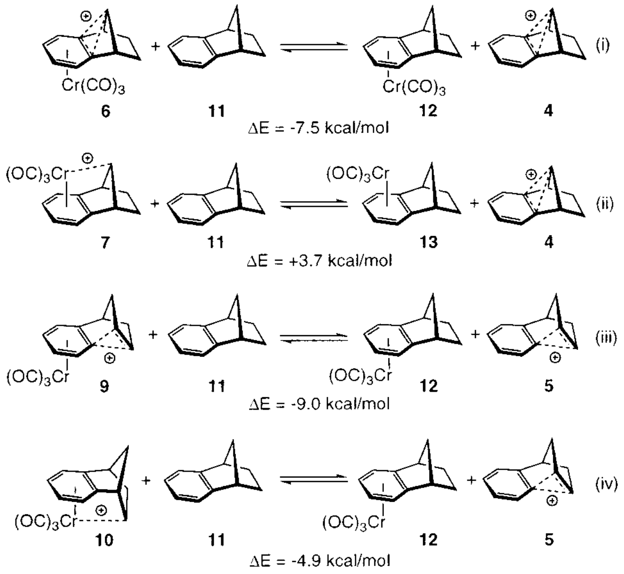
Our laboratories have recently explored the stabilization of benzylic cations by $Cr(CO)_3$ complexation.[6] The geometries of such cations are consistent with significant direct coordination of an exocyclic carbon−carbon double bond with the metal (**3**). The discovery of this direct Cr−C interaction led us to consider the possibility that chromium might also stabilize other types of carbocations.[7] The effect of $Cr(CO)_3$ complexation on the structures and stabilities of nonclassical benzonorbornenyl cations **4** and **5** (Scheme 1) is of particular interest. Structures of chromium complexes of **4** and **5** both with and without direct Cr−C interactions have been proposed,[8] but the issue of which type of structure predominates has not yet been resolved. We now report computations on these systems using density functional methods (B3LYP/LANL2DZ geometry optimizations and B3LYP/DZVP2+ single point energies)[9] which clarify the structural and energetic effects of $Cr(CO)_3$ complexation on benzonorbornenyl cations.

Scheme 1



The first cations to be studied were the benzannulated versions of **1** and **2**: benzonorbornenyl cations **4** and **5** (Scheme 1).[10] Calculations show that each of these exhibits nonclassical behavior. In compound **4**, the one-carbon bridge is inclined toward the arene ring to facilitate interaction of the cationic center with the π-system (Figure 1). This carbon is 1.980 Å from each of the interacting aryl carbons, compared to 1.883 Å[11] for the analogous distance in **1**,[12] consistent with the aromatic ring in **4** being a poorer π-donor than the alkene in **1**. In compound **5**, it is primarily the electrons of the adjacent σ bond that interact with the positive charge (Figure 1).[14] The cation has C_s symmetry, and the two partial single bonds in **5** are each 1.681 Å, compared to a distance of 1.936 Å[11] in the parent norbornyl cation **2**.[3,13]

We postulated that $Cr(CO)_3$ complexation to one face of the arene ring of **4** would lead to a direct Cr−C interaction, while complexation on the opposite face would not. Indeed, we found that complex **6**, in which the metal is anti to the cationic center, closely resembles the nonmetalated cation **4**, but complex **7**, in

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(1) For leading references, see: (a) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426−431. (b) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432−440. (c) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440−448. (d) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448−454. (e) Brown, H. C. (with comments by Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum: New York, 1977.

(2) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106−117.

(3) The exact nature of the bonding interactions in such cations is still a source of some discussion. See, for example: Werstiuk, N. H.; Muchall, H. M. *J. Mol. Struct. (THEOCHEM)* **1999**, *463*, 225−229 and references therein.

(4) For leading references, see: Prakash, G. K. S.; Iyer, P. S. *Rev. Chem. Intermed.* **1988**, *9*, 65−116.

(5) For leading references, see: (a) Bly, R. S.; Ni, E. K.; Tse, A. K. K.; Wallace, E. *J. Org. Chem.* **1980**, *45*, 1362−1366. (b) Zwick, J.-C.; Gabioud, R.; Vogel, P. *Helv. Chim. Acta* **1987**, *70*, 1079−1094. (c) Simion, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **1996**, *118*, 7345−7352. (d) Schleyer, P. v. R.; Kiran, B.; Simion, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **2000**, *122*, 510−515.

(6) Merlic, C. A.; Walsh, J. C.; Tantillo, D. J.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 3596−3606.

(7) Related systems will be reported: Merlic, C. A.; Miller, M. M.; Hietbrink, B. N.; Houk, K. N. Manuscript submitted for publication.

(8) (a) Bly, R. S.; Maier, T. L. *J. Org. Chem.* **1978**, *43*, 614−621. (b) Bly, R. S.; Strickland, R. C. *J. Am. Chem. Soc.* **1970**, *92*, 7459−7461. (c) Wells, D. K.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1970**, *92*, 7461−7463.

(9) See ref 6 and references therein. Energies reported in the text are from the B3LYP/DZVP2+ single point calculations and include zero point energy corrections (unscaled) from frequency calculations at the B3LYP/LANL2DZ level. The absolute energies for structures **4**−**7** and **9**−**13**, computed at both the B3LYP/LANL2DZ and B3LYP/DZVP2+ levels, are included in the Supporting Information.

(10) (a) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240−1246. (b) Tanida, H. *Acc. Chem. Res.* **1968**, *1*, 239−245 and references therein. (c) Wilt, J. W.; Chenier, P. J. *J. Org. Chem.* **1970**, *35*, 1571−1576 and references therein. (d) Volz, H.; Shin, J.-H.; Miess, R. *J. Chem. Soc., Chem. Commun.* **1993**, 543−544 and references therein.

(11) This distance is from our optimization at the B3LYP/LANL2DZ level; previous calculations have predicted similar distances for the same molecule.[3,12,13]

(12) Computations on norbornenyl cations: Bremer, M.; Schötz, K.; Schleyer, P. v. R.; Fleischer, U.; Schindler, M.; Kutzelnigg, W.; Koch, W.; Pulay, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1042−1044.

(13) Computations on norbornyl cations: (a) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 7849−7850. (b) Schreiner, P. R.; Severance, D. L.; Jorgensen, W. L.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 2663−2664. (c) Schleyer, P. v. R.; Sieber, S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1606−1608 and references therein.

(14) This structure may also be thought of as a phenonium ion; the geometry of **5** is, in fact, quite similar to that computed previously for the parent phenonium ion: Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987−6988. Structures of this type are perhaps best represented by a hybrid between two resonance structures: one a π-complex of a phenyl cation and the other having a cyclohexadienyl cation substructure (implying that the π-system is involved to some extent in cation stabilization).

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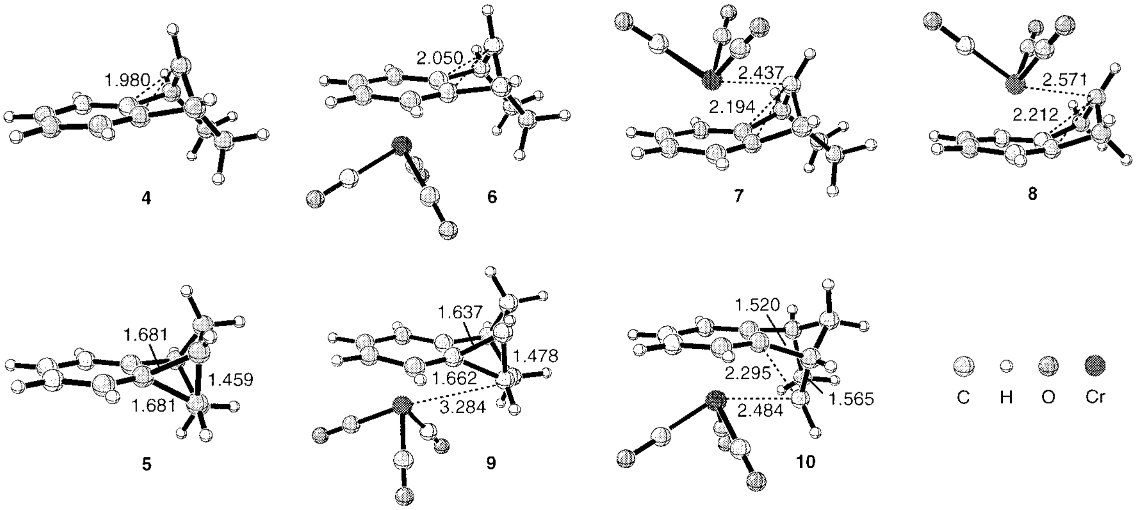

Figure 1. B3LYP/LANL2DZ optimized geometries of free and $Cr(CO)_3$-complexed benzonorbornenyl and indanyl cations. Selected bond lengths are in Å.

which the metal is syn to the cationic center, exhibits a strong chromium−carbon interaction (2.437 Å, Figure 1). In anti complex **6**, the p-like orbital at the cationic carbon interacts with the π-system of the arene ring; in syn complex **7**, however, the p-like orbital of the cation is redirected toward the $Cr(CO)_3$ moiety. We could not locate a minimum corresponding to the syn analogue of **6** (i.e. displaying direct arene−cation interactions).

Homodesmotic[15] eqs i and ii (Scheme 1) provide insight into the effect of the $Cr(CO)_3$ group on the stabilities of these cations. Equation i is exothermic by 7.5 kcal/mol. This indicates that, in **6**, chromium complexation anti to the cation decreases the stabilization conferred upon the cation through nonclassical interactions with the arene π-system. The $Cr(CO)_3$ fragment is an electron-withdrawing substituent, reducing the ability of the arene to donate electron density to the cation. In contrast, equation ii is endothermic by 3.7 kcal/mol, indicating that direct interaction with the metal center provides significant stabilization beyond that which nonclassical interactions could provide. This is also reflected in the fact that syn complex **7** is 15.0 kcal/mol more stable than anti complex **6**.

The essence of the comparison between **6** and **7** is captured by a consideration of the related $Cr(CO)_3$ complexed 2-indanyl cation **8** (Figure 1). Structures in which the cationic carbon interacts with the arene π-system (as in **6**), and in which the cationic carbon interacts directly with the metal center (as in **7**), are both possible for this cation. We were unable, however, to locate a minimum in which the cation is stabilized by the arene π-system; every attempt to do so ultimately converged to geometry **8** (Figure 1), with a distance of 2.571 Å between the chromium and the cationic carbon. This indicates that the direct Cr−C interaction overwhelms the nonclassical interaction in this system.

The structures and stabilities of chromium complexes of benzonorbornenyl cation **5** are also altered by metal complexation. The two π-faces of cation **5** are equivalent, so there is no distinction between syn and anti complexation, yet we were able to find two distinct complexes (**9** and **10**, Scheme 1 and Figure 1). Compound **9** is simply the π-complex between a chromium tricarbonyl fragment and nonclassical cation **5**. The symmetry of the three-membered ring is broken by the presence of the metal, but the partial single bonds differ in length by less than 0.03 Å. At 1.637 and 1.662 Å, these bonds are shorter than the analogous bonds in **5** (1.681 Å). This is consistent with destabilization, by the electron-withdrawing $Cr(CO)_3$ fragment, of resonance structures that place the positive charge on an arene carbon. Compound **10**, on the other hand, involves a direct interaction of the chromium center with a classical cation, as in syn complex **7**. The charged carbon does not interact with the arene, as demonstrated by relatively long C−C (2.295 Å) and short Cr−C distances (2.484 Å), and by the rehybridization of the carbocation center (seen in the C−H bond tilt).

Again, $Cr(CO)_3$ complexation has significant energetic consequences. Compound **10** is more stable than compound **9** by 4.2 kcal/mol as a result of its strong Cr−C interaction. Equations iii and iv (Scheme 1) make the comparison to nonclassical cation **5**. Equation iii is exothermic by 9.0 kcal/mol, showing that, as with **6**, the electron-withdrawing ability of the $Cr(CO)_3$ moiety decreases the strength of the nonclassical interaction. Equation iv is also exothermic, by 4.9 kcal/mol, showing that the direct interaction in **10** does not compensate for the loss of the nonclassical stabilization in **5**. Upon complexation, cation **5** requires significant geometric reorganization to enjoy through-space stabilization by the metal, unlike **4** which merely requires rehybridization of the cationic carbon. In effect, compound **4** is "preorganized" for chromium−carbon interaction and **5** is not.

The effects of metal complexation should also be manifested in the transition states for S_N1 solvolysis of suitable cation precursors. In fact, Bly and Trahanovsky have examined the solvolyses of brosylate and mesylate precursors of **6**, **7**, **9**, and **10**.[8] In each of these cases, syn complexes, which allow for direct Cr−C interaction in the resultant cation, do indeed solvolyze faster than the corresponding anti cases.

It is clear that $Cr(CO)_3$ complexation of nonclassical cations such as **4** and **5** has significant effects on their structures and stabilities, and the nature of these effects has now been revealed. When the $Cr(CO)_3$ moiety is geometrically confined away from the cationic center, it behaves as an inductively electron-withdrawing group, attenuating the nonclassical stabilization provided by the aromatic ring. However, when the chromium atom and the cationic carbon are in close proximity, filled d-orbitals on the metal can interact directly with the vacant p-orbital on carbon. This interaction can overwhelm and supplant the traditional nonclassical stabilization and also result in changes in chemical reactivity.[7]

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Supporting Information Available: Full structural data, absolute energies (both B3LYP/LANL2DZ and B3LYP/DZVP2+), and zero point energy corrections (B3LYP/LANL2DZ) for structures **4**−**7** and **9**−**13** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121−129.