Chemical Hermaphroditism: The Potential of the Cr(CO)$_3$ Moiety To Stabilize Transition States and Intermediates with Anionic, Cationic, or Radical Character at the Benzylic Position

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Abstract: It is known that *both* benzylic cations *and* anions are stabilized by Cr(CO)$_3$ complexation. This unusual characteristic of chromium arenes has been the subject of many synthetic, spectroscopic, and physical organic studies over the last four decades. The effect of Cr(CO)$_3$ on benzylic radicals has received comparatively little attention, however. In this report, cyclopropylcarbinyl anions, cations, and radicals substituted with both phenyl and Cr(CO)$_3$-phenyl groups are shown to rearrange via ring-opening to produce, selectively, Cr(CO)$_3$-stabilized benzylic anions, cations, and radicals, implying that the Cr(CO)$_3$ moiety is capable of stabilizing transition states with ionic or radical character at the benzylic position. The highest selectivity (>99:<1) was observed in the anionic reaction, slightly lesser selectivity (95:5) was observed in the cationic reaction, and only modest selectivity (2.5:1) was observed in the radical reaction. A parallel trend in ground-state stabilities of Cr(CO)$_3$-complexed benzyl anion, cation, and radical is predicted by density functional theory calculations. These calculations reveal that considerable structural distortions of both benzyl anion and cation occur upon complexation, but that little distortion occurs for benzyl radical. The connections between Cr(CO)$_3$ complexation and the stability of the complexed species are explained in terms of interactions between frontier molecular orbitals of the Cr(CO)$_3$ and benzyl fragments.

Introduction

The Cr(CO)$_3$ moiety has been described as "hermaphroditic" [1] because of its ability to stabilize *both* benzylic cations *and* anions. It has been shown that Cr(CO)$_3$ complexes of benzylic halides and alcohols solvolyze approximately 10^3-10^5 times faster than their noncomplexed counterparts.[2] pK_{R^+} values suggest that the Cr(CO)$_3$-complexed benzyl cation is nearly as stable as the benzhydryl cation and at least 5 pK units more stable than free benzyl cation.[2d] However, the Cr(CO)$_3$ moiety can also stabilize complexed anions. The pK_as of benzylic acids, anilines, and phenols are known to be lowered by several pK_a units upon complexation to Cr(CO)$_3$.[3] These large pK_a differences have been attributed to the net electron-withdrawing ability of the Cr(CO)$_3$ moiety. Since the ability of the Cr(CO)$_3$ moiety to stabilize conjugated ions is well-known and plays an important role in the formation of new bonds,[4] we were curious about the extent to which Cr(CO)$_3$ can interact with and stabilize neighboring radicals.

Despite sustained interest in Cr(CO)$_3$-complexed benzylic ions, little progress has been made in elucidating the effect of Cr(CO)$_3$ on the corresponding radical species. Several reports mention the possibility of interactions between chromium and benzylic radicals, yet no conclusive evidence has been offered concerning the stability of such species.[5] One report does suggest that Cr(CO)$_3$ complexation slightly destabilizes an intermediate with radical character at the benzylic position arising from a trimethylenemethane structure.[5i]

The detailed nature of the interactions between the Cr(CO)$_3$ moiety and complexed benzyl reactive intermediates remains to be firmly established. The key issues are how the free and chromium-complexed species differ in structure and whether the Cr(CO)$_3$ group interacts directly with the benzylic position of each reactive intermediate. Are the chromium complexes best represented as a Cr(CO)$_3$ group complexed to a phenyl ligand with a neighboring p-orbital (Scheme 1, structure **A**) or as a Cr(CO)$_3$ group complexed to a pentadienyl moiety with or without complexation to an exocyclic alkene (Scheme 1, structures **B** and **C**)? For the cation, the chromium may interact directly with the benzylic position and still maintain an 18-electron configuration at the metal, but maintenance of an 18-

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(4) See Davies, S. G.; Donohoe, T. J. *Synlett* **1993,** 323−332 and references therein.

(5) (a) Taniguchi, N.; Uemura, M. *Tetrahedron* **1998,** *54,* 12775−12788. (b) Taniguchi, N.; Uemura, M. *Tetrahedron Lett.* **1998,** *39,* 5385−5388. (c) Merlic C. A.; Walsh, J. C. *Tetrahedron Lett.* **1998,** *39,* 2083−2086. (d) Salazar, K. L.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997,** *119,* 9053−9054. (e) Taniguchi, N.; Uemura, M. *Tetrahedron Lett.* **1997,** *38,* 7199−7202. (f) Taniguchi, N.; Kaneta, N.; Uemura, M. *J. Org. Chem.* **1996,** *61,* 6088−6089. (g) Schmalz, H. G.; Siegel, S.; Schwartz, A. *Tetrahedron Lett.* **1996,** *37,* 2947−2950. (h) Schmalz, H.-G.; Siegel, S.; Bats, J. *Angew. Chem., Int. Ed. Engl.* **1995,** *34,* 2383−2385. (i) Creary, X.; Mehrshiekh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989,** *54,* 2904−2910.

Scheme 1

$(* = \oplus, \ominus \text{ or } \bullet)$
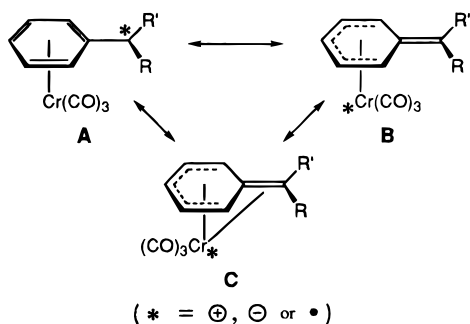
electron configuration in the anion would preclude such an interaction. In the case of the radical, the chromium may remain in an 18-electron configuration by interacting only with the phenyl ring (in **A**), become 17-electron by interacting with only the pentadienyl moiety (in **B**), or become 19-electron by interacting with both the pentadienyl moiety and the exocyclic alkene (in **C**). The best representation of each reactive intermediate remains to be determined.

Many synthetic endeavors have taken advantage of Cr(CO)₃-complexed arenes due to the ability of Cr(CO)₃ to facilitate formation of anionic and cationic benzylic intermediates and to direct the stereoselective formation of new bonds at the benzylic position.[4,6,7] Chromium arene complexes have also been prepared in enantiomerically pure form, allowing for the enantioselective synthesis of tetrahydronaphthalene-, tetrahydroisoquinoline-, tetrahydrobenzazepine-, and diphenylmethane-derived natural and biologically active products.[4,6a,c,7]

In addition, transition metal-templated radical reactions are providing new opportunities for radical chemistry and stereoselective synthesis.[5,8–11] Examples have been reported which demonstrate the remarkable ability of certain transition metals to provide complete control of stereoselectivity in carbon–

carbon bond formation by radical processes.[5] Although steric effects of the transition metal moiety are undoubtedly influencing the stereochemical outcome of these radical reactions, electronic interactions between the metal and the radical intermediates may also contribute. This issue has not been adequately addressed for arene or other complexes.

We now report experiments and theoretical calculations that demonstrate the ability of Cr(CO)₃ to stabilize both transition states and intermediates having ionic or radical character at the benzylic position. The origins of the "hermaphroditic" nature of the Cr(CO)₃ group are discussed.

Results

Competition Experiments. Previous work from one of our laboratories involved attempts to observe a stabilized chromium arene radical.[12] These attempts proved unsuccessful due to the sensitive nature of these radicals, so a competition experiment was designed to help elucidate the nature of such species. We envisioned formation of a cyclopropylcarbinyl radical with two different aryl substituents at the 2- and 3-positions of the cyclopropane (Scheme 2). The ratio of homoallylic radicals **E**

Scheme 2
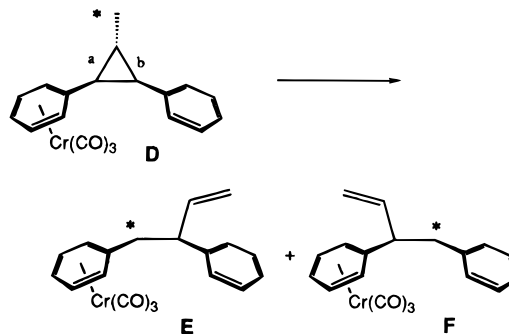
and **F**, produced by rearrangement of the cyclopropylcarbinyl radical, would be determined by the relative abilities of each arene to stabilize radical character at the benzylic position.[13] It has been demonstrated that cyclopropylcarbinyl ring-openings can show remarkable selectivities in the formation of regioisomeric ring-opened products despite early transition states.[13d] Enhanced stabilization of radical character by Cr(CO)₃ complexation would selectively weaken bond *a* of **D** (see Scheme 2) and increase the rate of formation of product **E**. Quenching of radicals **E** and **F** would then lead to 3,4-diaryl-1-butene products. The beauty of this internal competition is that a single experiment will yield the kinetic ratio of ring-opened radicals **E** and **F**.

In analogy to the cyclopropylcarbinyl radical rearrangement, cyclopropylcarbinyl anions and cations also rearrange to homallylic anions and cations. While rearrangements in anionic

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Scheme 3
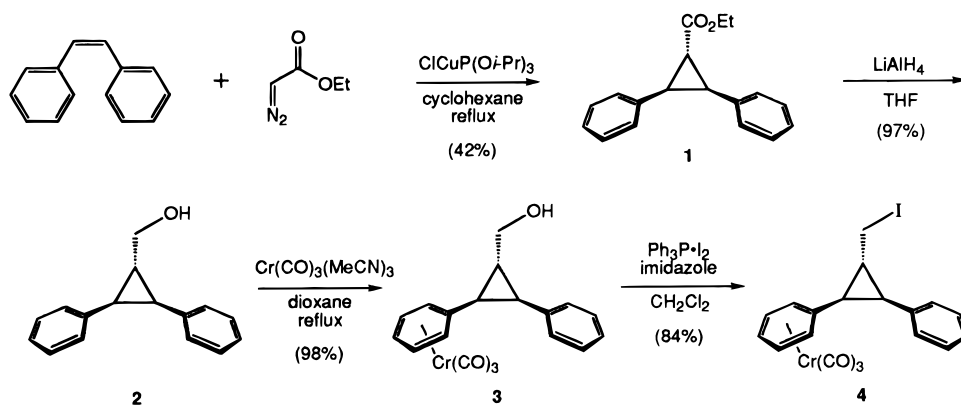
systems are relatively facile,[14] those in cationic systems are more complex. In fact, the structure of cyclopropylcarbinyl cations and their potential equilibria with not only homoallylic cations but also cyclobutyl (or nonclassical bicyclobutonium) cations has received much attention over the past half century.[15] However, aryl substitution at the 2- and 3-positions of the cyclopropane is expected to greatly stabilize the homallylic cation resulting from ring-opening relative to the cyclopropyl-carbinyl cation precursor. In addition, the pseudosymmetry of the cyclopropylcarbinyl ions and radicals in our design should result in product distributions upon rearrangement that reflect the relative influence of phenyl and $Cr(CO)_3$-phenyl on ring-opening transition states. The fact that the ionic and radical reactions utilize identical substrates and lead to identical products upon quenching simplifies characterization and allows for facile comparison of all three reaction types.

Synthesis of the rearrangement substrate **4** was straightforward (Scheme 3). Cyclopropanation of *cis*-stilbene with ethyl diazoacetate utilizing a copper(I) triisopropyl phosphite catalyst[16] in refluxing cyclohexane afforded the 2,3-*cis*-diphenyl-1-*trans*-carboethoxycyclopropane (**1**) in 42% yield after recrystallization. The ester was reduced with lithium aluminum hydride to give the cyclopropane alcohol **2**. Metalation of the alcohol with Cr-$(CO)_3(MeCN)_3$[17] smoothly afforded the cyclopropane chromium arene complex **3** in 98% yield. Interestingly, the ortho and meta positions of the metalated ring are diastereotopic, so five separate signals for those aryl protons are observed in the ^1H NMR. Analogously, six resonances are observed for the complexed arene ring in the ^{13}C NMR. Conversion of the alcohol to the corresponding iodide was accomplished in 84% yield using freshly recrystallized $Ph_3P\cdot I_2$ and imidazole in dichloromethane; other methods resulted in low yields of mixtures of products and demetalated material.

With cyclopropyl iodide chromium arene adduct **4** in hand, we then tested it under ionic and radical reaction conditions in

order to explore the rearrangement selectivities. When **4** was reacted with *t*-BuLi at −78 °C in THF and then quenched with dilute HCl, alkene **5** was isolated as a single isomer arising from rearrangement to the chromium-stabilized benzylic anion; no competing product **6** was detected (Scheme 4). When cyclo-

Scheme 4

t-BuLi, -78 °C; H_2O	>99	:	<1
$AgBF_4$, Et_3SiH	95	:	5
SmI_2, HMPA, *t*-BuOH	2.5	:	1
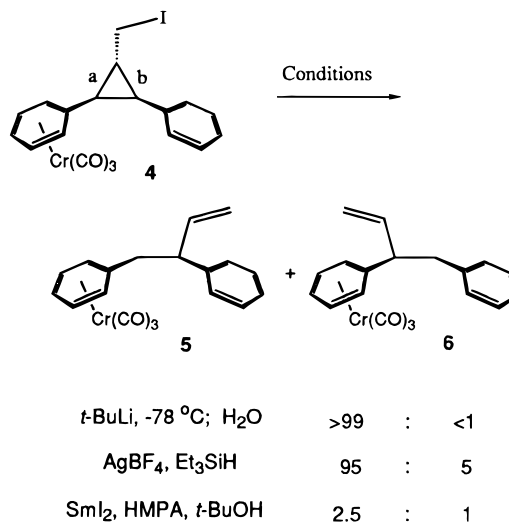
propyl iodide **4** was treated with $AgBF_4$ and Et_3SiH in dichloromethane, alkenes **5** and **6** were formed in a 95:5 ratio, again favoring ring-opening on the chromium-bound side, but via the cation. When iodide **4** was subjected to radical-forming conditions using SmI_2/HMPA[18] and *t*-BuOH in THF, products **5** and **6** were produced in a ratio of 2.5:1, only modestly favoring the product arising from the benzylic radical of the $Cr(CO)_3$-complexed arene.

The excellent selectivity of the anionic ring-opening is in agreement with previous reports on the strong stabilizing effect of $Cr(CO)_3$ on complexed anions.[3] In examining the ring-opening of the cyclopropyl carbocation, we were somewhat surprised by the 95:5 ratio of ring-opened products. Indeed, the major product arises from enhanced stabilization of cationic character by the $Cr(CO)_3$ moiety, but it appears that this stabilization is not at great as that in the anionic case. More surprising, however, was the modest selectivity exhibited in the radical rearrangement.

It is known that the 2-phenylcyclopropylcarbinyl radical rearranges with a rate constant of 3×10^{11} s^{-1},[13j] which is 10^3

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times faster than the rearrangement of the parent cyclopropyl-carbinyl radical.[19] This rate enhancement is due to stabilization of radical character in the transition state by the conjugated aromatic ring. Because there is an enhancement in the ring-opening rate of **D** leading to the benzylic radical that is conjugated to the Cr(CO)₃-complexed arene, it can be concluded that the Cr(CO)₃ group does, indeed, stabilize radical character in the transition state. However, the ring-opening of cyclopropylcarbinyl radical **D** does not demonstrate the same selectivity as seen in the corresponding ionic rearrangements. It can therefore be concluded that, although the Cr(CO)₃ moiety stabilizes the benzylic radical, the extent of stabilization is not nearly as great as that in the anionic and cationic cases. Computational studies were undertaken to provide a better understanding of the nature of the interactions between the metal fragment and the benzylic reactive intermediates.

Computed Structures of Free and Cr(CO)₃-Complexed Benzyl Species. (i) Cation. A wealth of implicit structural information on Cr(CO)₃-complexed benzylic cations is available. It was observed in the 1960s that Cr(CO)₃ complexation of a benzylic halide or alcohol led to increased rates of solvolysis.[2e,20] It was also observed that such substitution reactions proceed with retention of stereochemistry at the benzylic position,[4] due to stereocontrol in the three fundamental reaction steps. First, ionization proceeds with the leaving group anti to chromium. Second, the Cr(CO)₃ group protects the back side of the cation and increases the barrier to rotation around the exocyclic carbon—carbon bond. Third, attack on the benzylic cation occurs anti to the bulky Cr(CO)₃ group, preserving the stereochemistry of the starting material. ^{1}H and ^{13}C NMR experiments demonstrated hindered rotation about the exocyclic carbon—carbon bond in 1-*p*-tolylethyl- and di-*p*-tolylmethyltricarbonylchromium cations.[21a,b] Hindered rotation can arise from an increase in double bond character of the exocyclic bond or direct interaction between the chromium and the benzylic carbon. Such an interaction could also provide anchimeric assistance to departure of benzylic leaving groups. The involvement of similar factors has also been suggested in reactions of ferrocenyl cations.[22] Attempts to isolate Cr(CO)₃ complexes of simple benzylic cations led to decomposition via loss of carbon monoxide.[2e] This observation suggests that the Cr—CO bonds were made more labile by complexation—an effect that should manifest itself spectroscopically and in increased Cr—CO and decreased C—O bond lengths relative to those in normal Cr(CO)₃-arene complexes. In fact, increased CO stretching frequencies in IR experiments[2c] and altered chemical shifts in NMR experiments[2c,21] have been observed for Cr(CO)₃-complexed cations relative to those of related neutral species, indicating decreased back-donation of chromium electron density to the CO ligands and a corresponding shift in positive charge from the benzyl ligand to the chromium.

Geometry optimizations on the free and Cr(CO)₃-complexed benzyl cations (B3LYP/LANL2DZ, see Methods section) were performed in an effort to rationalize these experimental results. Fully optimized structures are shown in Figure 1b. The differences between the free and complexed structures reflect the changes in physical properties observed upon complexation. An increase in the Cr—CO and a decrease in the C—O bond lengths in the complexed cation relative to those in the Cr(CO)₃-toluene complex are predicted, consistent with the spectroscopic information described above and the tendency of cationic complexes to decompose through loss of CO. The expected redistribution of positive charge from the benzyl ligand to the Cr(CO)₃ moiety is reflected in computed Mulliken atomic charges (B3LYP/LANL2DZ level, not shown) and can be seen clearly in the electrostatic potential surfaces shown in Figure 2.

The structure of the cationic benzyl ligand in the Cr(CO)₃ complex is also highly distorted from the planar structure of the free ligand. The complexed species can be thought of as a pentadienyl cation fragment and an exocyclic double bond, which serve as 4- and 2-electron ligands, respectively, for the chromium. As such, the exocyclic carbon—carbon bond is inclined toward the chromium (Figure 1b, i and ii), and the chromium is not centered below the centroid of the phenyl ring (Figure 1b, iii) as it is in neutral Cr(CO)₃-arene complexes such as Cr(CO)₃-toluene (Figure 1a, iii). An earlier study utilizing semiempirical INDO calculations noted a similar distortion but suggested that specific bond formation between chromium and the benzylic center was not involved.[23]

(ii) Anion. Less experimental information on the structure of Cr(CO)₃-complexed benzylic anions is available. It was shown around 1970 that base-catalyzed hydrogen—deuterium exchange of benzylic protons in Cr(CO)₃-indan complexes was stereoselective; only the benzylic protons anti to the metal were exchanged (in a solution of 0.5 M potassium *tert*-butoxide in DMSO).[24] It was proposed that this selectivity arose from anchimeric assistance by the chromium, although a steric effect could not be excluded.[24] IR, ^{1}H NMR, and ^{13}C NMR spectroscopy of the bis(tricarbonylchromium)diphenylmethyl and free diphenylmethyl carbanions indicated that the benzylic center was most likely sp[2]-hybridized and that electron density from the benzyl ligand was redistributed through the chromium onto the carbonyl ligands, but also that there was no direct interaction between the chromium and the benzylic carbon.[1]

Geometry optimizations on the free and Cr(CO)₃-complexed benzyl anions (B3LYP/LANL2DZ, see Methods section) were performed in order to rationalize these experimental results, and the fully optimized structures are shown in Figure 1c. A decrease in the Cr—CO and an increase in the C—O bond lengths in the complexed anion relative to those in the toluene complex are predicted, consistent with the spectroscopic observations described above. In addition, negative charge is clearly redistributed from the benzyl framework onto the carbonyl ligands, as shown in the electrostatic potential surfaces displayed in Figure 2 (and this is reflected in Mulliken atomic charges computed at the B3LYP/LANL2DZ level, not shown). A significant increase in bond order for the exocyclic carbon—carbon bond and an increase in bond length alternation/localization in the complexed anion relative to those in the free system are also predicted.

The anionic benzyl ligand is distorted toward a pentadienyl moiety plus an exocyclic double bond to an even larger extent than in the case of the cation. Since the chromium is most stable as an 18-electron species, and a pentadienyl anion is a 6-electron

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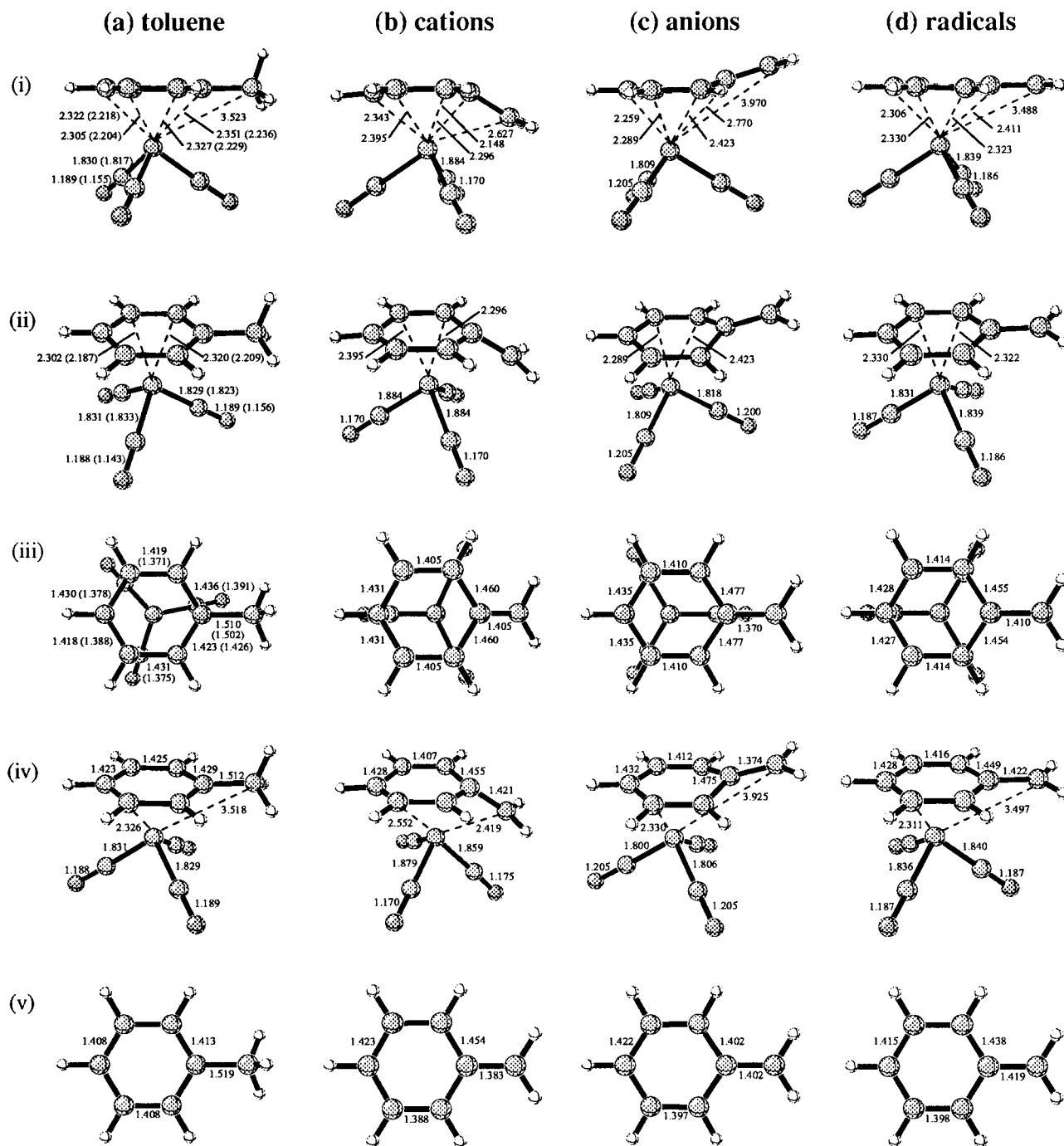
Figure 1. (U)B3LYP/LANL2DZ-optimized geometries of free and Cr(CO)$_3$-complexed toluene, benzyl cation, benzyl anion, and benzyl radical. Selected bond lengths are in angstroms. Values in parentheses are from the X-ray structure of Cr(CO)$_3$-toluene.[26,39] (i) Side view of preferred rotamers of Cr(CO)$_3$ complexes. (ii) Elevated view of complexes in (i). (iii) Top view of complexes in (i). (iv) Elevated view of disfavored rotamers of Cr(CO)$_3$ complexes. (v) Free toluene and benzyl species.

ligand, the exocyclic double bond tilts away from the chromium (Figure 1c, i and ii), and the chromium moves closer to the pentadienyl fragment (Figure 1c, iii). Thus, the Cr(CO)$_3$ fragment again moves away from the centroid of the phenyl ring, but in a direction opposite to that observed in the cationic system. As predicted by experiment,[1] there is no direct interaction between the chromium and the benzylic carbon. The relative increase in kinetic acidity of the benzylic protons anti to the Cr(CO)$_3$ group is, therefore, likely a result of steric blocking of the endo face of the exocyclic double bond by the CO ligands of the Cr(CO)$_3$ fragment.

(iii) Radical. Very little is known about the structure and reactivity of Cr(CO)$_3$-complexed benzylic radicals other than

that reactions of such radicals occur anti to the Cr(CO)$_3$ moiety.[5] To obtain detailed structural information on such species, geometry optimizations on the free and Cr(CO)$_3$-complexed benzyl radicals (UB3LYP/LANL2DZ, see Methods section) were performed. Fully optimized structures are shown in Figure 1d. Unlike the cationic and anionic species, the benzyl radical experiences little distortion upon complexation. The chromium remains centered beneath the ring, which remains nearly planar (Figure 1d, i−iii). The benzylic methylene group does bend slightly away from the chromium, suggesting that the metal center does not interact with all seven electrons of the benzyl ligand (which would make it a 19-electron species) but rather interacts solely with the phenyl moiety as a 6-electron ligand.
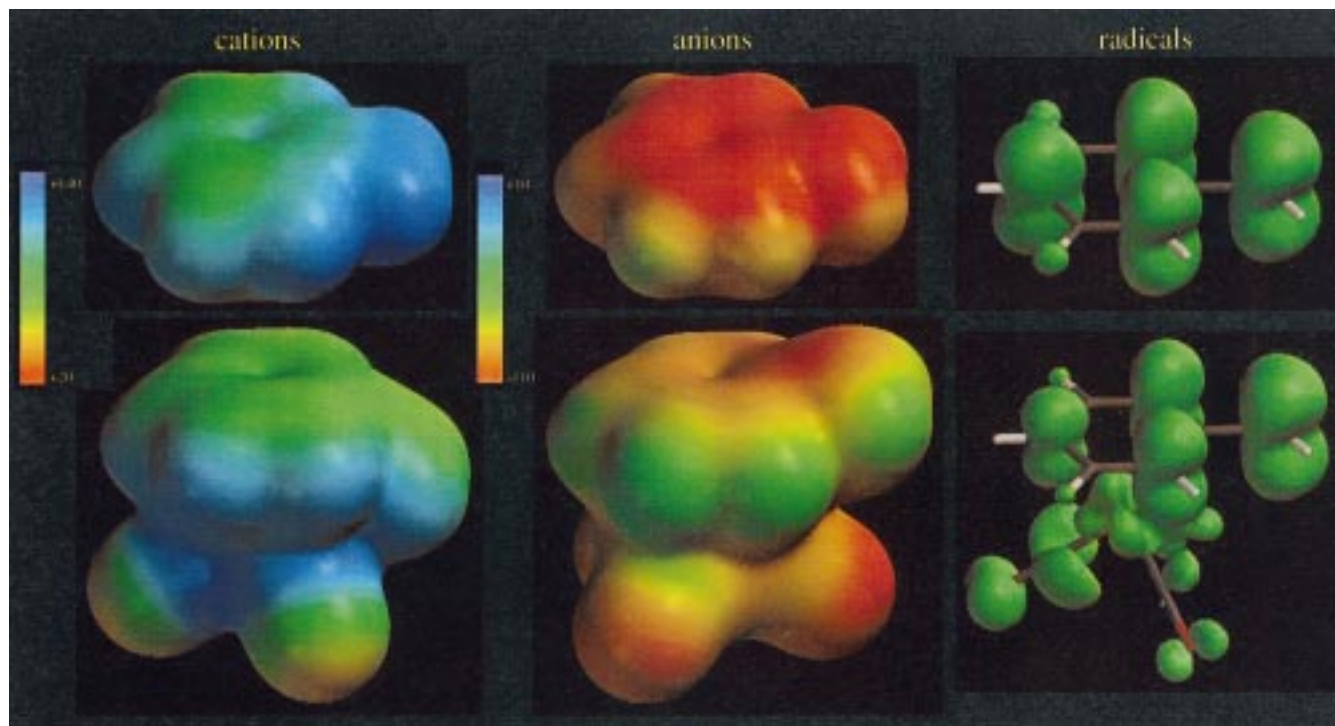
Figure 2. Electrostatic potential surfaces of free and Cr(CO)$_3$-complexed benzyl ions and constant spin density surfaces of free and Cr(CO)$_3$-complexed benzyl radicals. The electrostatic potential is graphed over the ranges shown, in units of kcal/mol. See Methods section for details.

As shown in Figure 2, the unpaired spin density in the Cr-(CO)$_3$-complexed benzyl radical remains mostly on the benzyl ligand. Computed Mulliken atomic spin densities (UB3LYP/LANL2DZ) suggest that the spin density that resides on the benzylic carbon in the free species ($+0.81$) decreases only slightly upon complexation ($+0.73$ for the benzylic carbon, $+0.31$ for the chromium). Although some spin density is delocalized onto the chromium, the complexed ligand is predicted to behave similarly to an uncomplexed benzyl radical from an electronic standpoint.

(iv) Rotamers. Rotation of the Cr(CO)$_3$ moiety relative to the arene ligand in chromium arene complexes is known to occur. As previously explained on the basis of orbital considerations,[25] complexes with electron-donating substituents on the aromatic ring tend to prefer syn-eclipsed conformations (in which a carbonyl ligand eclipses the ring-substituent bond when viewed down the axis between the metal and the ring center), while those with electron-withdrawing substituents tend to prefer anti-eclipsed conformations (in which a carbonyl ligand is anti to the ring-substituent bond). In the case of toluene, for example, the syn-eclipsed conformation is preferred so that vacant metal hybrid orbitals can interact with the ortho and para positions of the aromatic ring positions that bear larger orbital coefficients than the meta and ipso positions, respectively, in the toluene HOMO (see Figure 3).

Various rotamers of the Cr(CO)$_3$-benzyl species described above were examined, and the expected preferences were observed. First, unconstrained optimizations (B3LYP/LANL2DZ) on the Cr(CO)$_3$-toluene complex led to a slightly distorted syn-eclipsed conformer (Figure 1a, i−iii). This conformer is similar to that observed in the X-ray structure of Cr(CO)$_3$-toluene.[26] A pure syn-eclipsed conformer is most likely disfavored by small steric interactions with the methyl group. Constraining the complex to be anti-eclipsed led to a structure which was only 0.6

kcal/mol less stable than the fully optimized structure (Figure 1a, iv), suggesting that the rotational potential is relatively shallow for the toluene complex, consistent with the fact that a methyl group is only slightly electron-donating. Fully optimized structures ((U)B3LYP/LANL2DZ) for all syn- and anti-eclipsed rotamers of the Cr(CO)$_3$-complexed benzyl cation, anion, and radical are shown in Figure 1b−d (iv). The following conformational preferences are predicted: the cation prefers to be anti-eclipsed by 11.7 kcal/mol,[27] the anion prefers to be syn-eclipsed by 6.3 kcal/mol, and the radical prefers to be anti-eclipsed by 2.8 kcal/mol. These preferences are predicted by orbital analysis, since these conformations involve maximum bonding between metal orbitals and those of the benzyl fragments (see below). The considerable difference in the magnitude of the energetic preferences of the cation and radical is most likely due to the direct interaction of chromium with the exocyclic bond of the benzyl cation. Since the benzylic methylene is brought close to the chromium in this case, unfavorable steric interactions with the carbonyl groups in the syn-eclipsed rotamer are amplified, as are favorable orbital interactions in the anti-eclipsed rotamer (see below).

Computed Stabilization Energies of Cr(CO)$_3$ Complexes. The gas-phase hydride affinity, proton affinity, and bond dissociation energy of toluene are lower than those of methane by approximately 80, 40, and 20 kcal/mol, respectively.[28] It is also known that the Cr(CO)$_3$ moiety can provide additional stabilization in the case of complexed benzylic anions, cations, and related transition states.[1−4] Our experiments support these observations and provide evidence that the Cr(CO)$_3$ group can also provide minor stabilization of a benzylic radical. Although the "hermaphroditic" nature of Cr(CO)$_3$-complexed arenes was revealed by the early experiments, the details of how this group provides stabilization were not clearly defined. In an effort to

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(27) This is in contrast to earlier semiempirical INDO calculations that suggested that the relative energies of the syn- and anti-eclipsed rotamers of the cation are similar and that a staggered conformation is actually preferred by approximately 6 kcal/mol.[23]
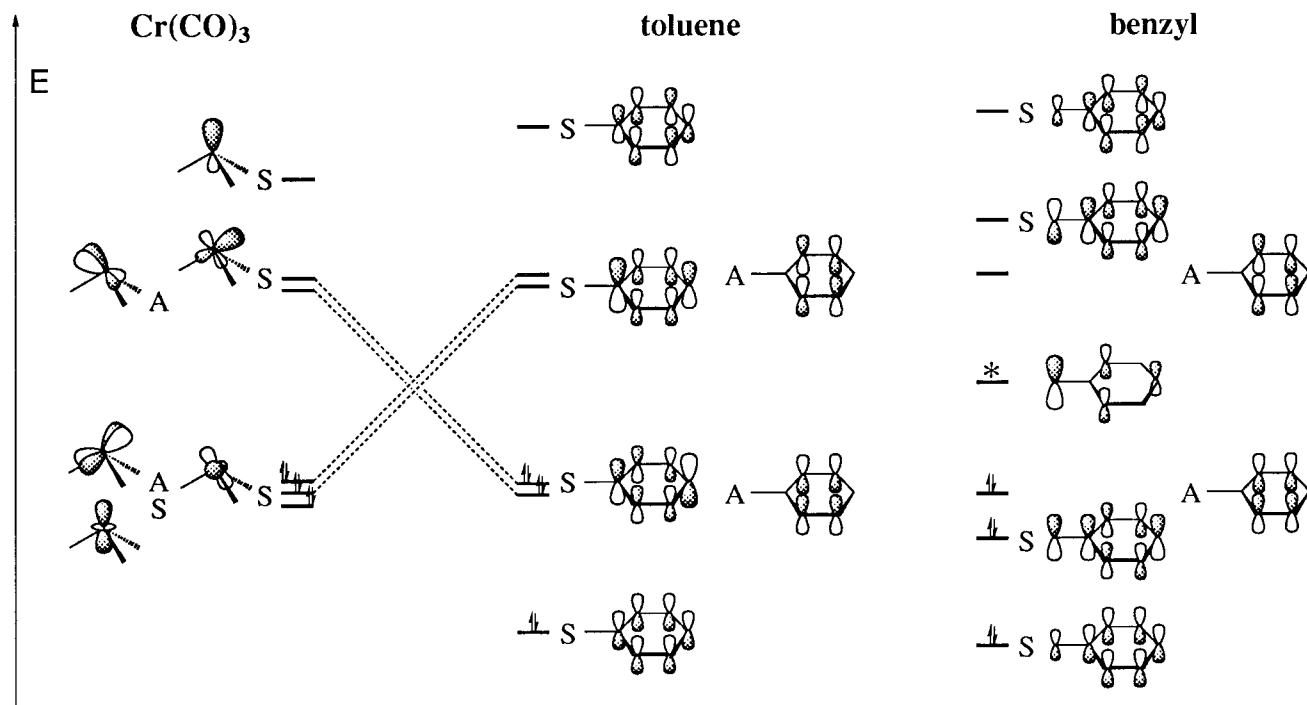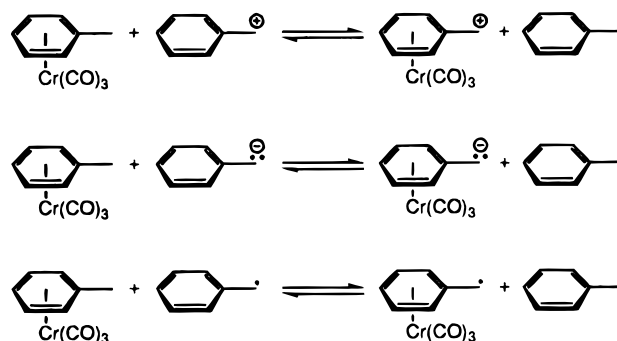
Figure 3. (a) Hybrid fragment orbitals of Cr(CO)₃. (b) π molecular orbitals of toluene. Frontier orbitals that are of appropriate symmetry to interact, and whose interactions constitute the key features of chromium-arene bonding, are connected by dashed lines. (c) π molecular orbitals of benzyl. The asterisk indicates that this orbital may contain zero, one, or two electrons, depending on the reactive intermediate in question. "S" and "A" indicate whether the orbitals are symmetric or antisymmetric with respect to the plane of symmetry of the complexes.

assess the relative energetic influence of the Cr(CO)₃ moiety on different benzylic reactive intermediates, the enthalpies for several homodesmotic equations (these represent the enthalpy differences between the gas phase hydride affinities of free and complexed benzyl cation, proton affinities of free and complexed benzyl anions, and bond dissociation energies of free and complexed benzyl radicals; see Scheme 5 and Table 1) were calculated using a hybrid HF-DFT method. (U)B3LYP/ LANL2DZ-optimized geometries were used, and single-point energies were calculated at the (U)B3LYP/LANL2DZ and (U)- B3LYP/DZVP2+ levels (see Table 1 and Methods section). These calculations predict, in accord with experiment, that both the anion and cation should be strongly stabilized by the Cr- (CO)₃ moiety (Table 1) but that the Cr(CO)₃ group should have little effect on the stability of the radical.

The hydride affinity of the benzyl cation is reduced by approximately 4−12 kcal/mol upon Cr(CO)₃ complexation, while the proton affinity of the benzyl anion is decreased by approximately 30−40 kcal/mol (Table 1). The lesser stabiliza- tion of the cation is reflected experimentally in the fact that a significant amount (5%) of the competing product is detected

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Scheme 5

Table 1. ΔE (kcal/mol) for the Homodesmotic Reactions Shown in Scheme 5 Based on (U)B3LYP/LANL2DZ Geometries and Single-Point Energies at the Levels Shown Below
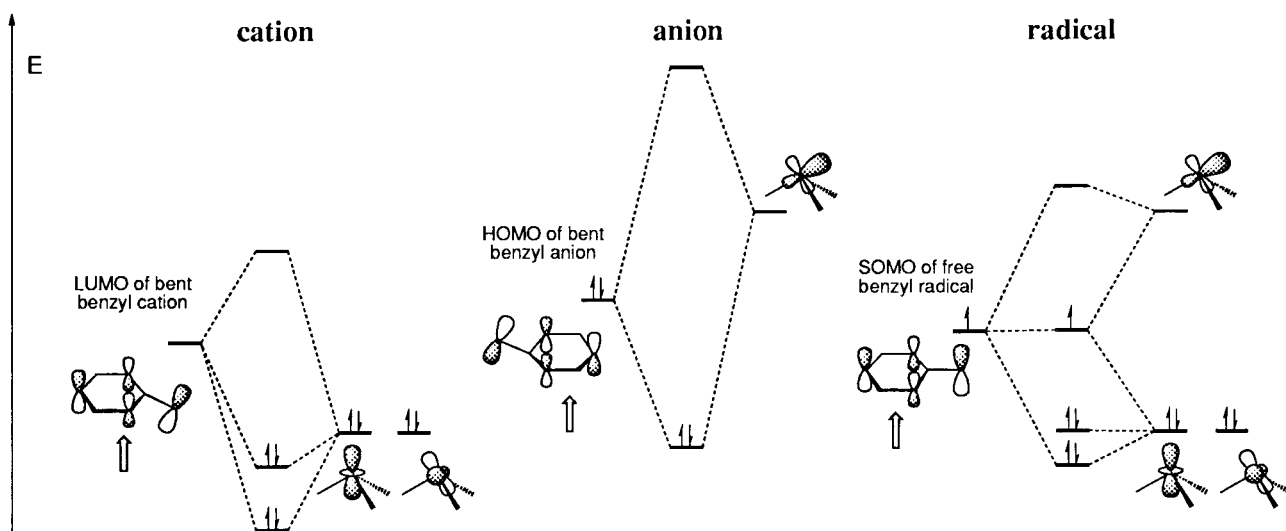
level of theory	cationic	anionic	radical
(U)B3LYP/LANL2DZ	−4.3	−41.3	1.3 (0.784, 0.780)[a]
(U)B3LYP/DZVP2+	−11.7	−34.0	1.0 (0.782, 0.777)

[a] S^2 values for free and complexed radicals, respectively, are given in parentheses.

for the cationic ring-opening of substrate **4** described above, while no competing product is observed for the analogous anionic ring-opening reaction (Scheme 4).

In the radical ring-opening reaction, a 2.5:1 ratio of products **5** and **6** is observed, corresponding to a ΔΔG‡ of approximately 0.5 kcal/mol. This result also agrees (within experimental and computational error) with the small difference in bond dissocia- tion energies (approximately 1 kcal/mol, but favoring the uncomplexed species) predicted by the calculations for the free and complexed radical species. Several caveats should be noted at this point. First, the competition experiments reflect kinetic

Figure 4. Selected stabilizing orbital interactions between $Cr(CO)_3$ and benzyl species. The position of the $Cr(CO)_3$ fragment, deduced from geometry optimizations, is indicated by an arrow for each case.

ratios while the calculations predict thermodynamic values; nonetheless, the stabilization of the reactive intermediates should be reflected in transition-state energies. Second, calculations were performed only on the parent benzyl system; substitutions at the benzylic position and on the aromatic ring are likely to alter the magnitude of the $Cr(CO)_3$-induced stabilization.[2b,d]

Discussion

The large stabilization of anionic and cationic, and almost negligible stabilization of radical-like, transition states and intermediates, demonstrated by our experiments and computations, can be rationalized in terms of changes in orbital interactions between the benzylic species and $Cr(CO)_3$ relative to those in typical $Cr(CO)_3$-complexed arenes such as $Cr(CO)_3$-toluene. Symmetry-allowed interactions between the π molecular orbitals of toluene and the hybrid fragment orbitals[25] of $Cr(CO)_3$ are shown schematically in Figure 3. The three occupied and three vacant hybrid orbitals of the $Cr(CO)_3$ fragment are shown, along with the π orbitals of toluene. All are labeled according to their symmetry with respect to the plane of symmetry of the complex (S, symmetric, and A, antisymmetric, correspond to A′ and A″ in the C_s point group). The dashed lines represent stabilizing interactions between filled and vacant orbitals of the two fragments. There is strong complementarity between the HOMOs and LUMOs of the two systems. The small syn-eclipsed preference of toluene can be attributed to the more favorable interactions of the S HOMO and LUMO of the metal with the S LUMO and HOMO of toluene. The methyl group enhances the para orbital coefficient in the S HOMO and the ipso orbital coefficient in the S LUMO of toluene, and the $Cr(CO)_3$ fragment aligns to maximize interaction with these sites.

The π molecular orbitals of the benzyl ligands (Figure 3) involve a p-orbital at the benzylic position mixing with the π molecular orbitals of the phenyl group; doing so results in a new frontier molecular orbital (FMO). Due to electron−electron repulsion, this orbital is higher in energy for the anion than for the radical and is higher in energy for the radical than for the cation. The result is a new low-lying LUMO for the benzyl cation, a new high-lying HOMO for the benzyl anion, and a SOMO for the benzyl radical of intermediate energy.

Interactions of the antisymmetric benzyl orbitals with the $Cr(CO)_3$ fragment are expected to be of comparable magnitude to the analogous interactions involving the antisymmetric toluene

orbitals, since these orbitals are of the wrong symmetry to interact with the benzylic p-orbital. In addition, symmetry-allowed interactions between $Cr(CO)_3$ orbitals and π orbitals of toluene and benzyl are very similar, except for the new interactions involving the benzyl cation LUMO, anion HOMO, and radical SOMO. These interactions are shown schematically in Figure 4 for the preferred rotamers of the benzyl complexes and are described below. The position of the chromium in each complex is indicated in Figure 4 on the benzyl orbitals by arrows and is related to the degree of spatial overlap between the metal and ligand orbitals.[29]

In the case of the cation, the low-lying LUMO of the benzyl fragment interacts more strongly with the occupied symmetric hybrid metal orbitals than does the lowest unoccupied symmetric toluene π orbital (Figure 4). Distortion of the benzyl ligand away from planarity and shifting of the chromium away from the center of the aromatic ring increase the spatial overlap between the metal and ligand orbitals (in particular, with the d_{z^2}-like metal orbital) and leads to further stabilization. In fact, single-point energy calculations (B3LYP/LANL2DZ and B3LYP/DZVP2+) on a cationic species constrained to the planar geometry of the radical complex predict that planarization of the benzyl cation increases the energy of the complex by 9−15 kcal/mol. The direct interaction of the chromium with the exocyclic carbon−carbon bond accompanying ligand distortion is, therefore, essential for stabilization.

In the case of the anion, the high-lying HOMO of the free benzyl fragment interacts more strongly with the vacant symmetric hybrid metal orbital shown than does the highest occupied symmetric toluene orbital, again leading to enhanced stabilization through a two-electron interaction (Figure 4). In this case, distortion of the benzyl ligand away from planarity and shifting of the chromium away from the center of the aromatic ring also lead to improved overlap and increased stabilization. Single-point energy calculations (B3LYP/LANL2DZ and B3LYP/DZVP2+) on an anionic species constrained to the planar geometry of the radical complex predict that planarization of the benzyl anion increases the energy of the complex by approximately 14−17 kcal/mol. Ligand distortion is clearly essential for maximum stabilization.

(29) In this treatment, we make the simplifying approximation that the different benzyl orbitals of the cation, anion, and radical will be mixed with identical $Cr(CO)_3$ fragment orbitals.

In the case of the radical, the SOMO of the free benzyl fragment interacts with the occupied and vacant symmetric hybrid metal orbitals shown in Figure 4. Little stabilization is expected from these odd-electron interactions due to decreased orbital overlap and decreased matching of orbital energies relative to the ionic cases. Distortion of the benzyl fragment to increase overlap or to allow for additional interactions with the benzylic center does not provide enough additional stabilization to compensate for the energy required for distortion. Single-point energy calculations (UB3LYP/LANL2DZ and UB3LYP/DZVP2+) on radical species constrained to the nonplanar geometries of either the cationic or anionic complexes predict that distortion in either direction will lead to destabilization, by approximately 18−20 kcal/mol in the cation geometry (despite increased delocalization of spin density) and approximately 15−22 kcal/mol in the anion geometry. Being an odd-electron species dooms the radical to a planar existence.

These experiments and computations also have important implications for the use of metal-complexed benzylic radicals in synthesis and physical organic studies. First, the high stereoselectivities observed, to date, in radical reactions of Cr-(CO)$_3$-complexed arenes[5] must be attributed to the steric effect of the Cr(CO)$_3$ moiety rather than to a direct bonding interaction beween chromium and the radical center. Second, the results of the cyclopropylcarbinyl radical ring-opening reactions suggest that metal arene complexes may provide faster radical clocks.[13i] The parent cyclopropylcarbinyl radical rearranges with a rate constant of 1.2×10^8 s^{-1},[19] but the 2-phenylcyclopropylcarbinyl radical rearranges with a rate constant of 3×10^{11} s^{-1}.[13j] Based on the work of Castellino and Bruice,[30] it can be estimated that the 2,3-diphenylcyclopropylcarbinyl radical rearranges with a rate constant close to 3×10^{11} s^{-1}. Therefore, based on the 2.5:1 ratio of ring-opened products described above, we can estimate that the rate constant for rearrangement of the Cr(CO)$_3$-complexed 2,3-diphenylcyclopropylcarbinyl radical is approximately $(7-8) \times 10^{11}$ s^{-1}. Thus, incorporation of transition metal complexes into rearrangement substrates may lead to faster radical clocks. Furthermore, the large difference in regioselectivities observed for the ionic and radical ring-opening reactions of substrate **4** suggests that systems of this type may find application as probes for the intermediacy of radical vs ionic intermediates.[31]

Conclusions

Cyclopropylcarbinyl ring-opening competition experiments demonstrate that transition states bearing anionic, cationic, or radical character at the benzylic position are stabilized to a greater extent by phenyl-Cr(CO)$_3$ than by phenyl alone. The magnitude of this stabilization is greatest for the anionic case and least in the case of the radical. This hierarchy of transition-state stabilization energies is mirrored by computed ground-state stabilization energies for Cr(CO)$_3$-complexed benzyl anion, cation, and radical.

The factors leading to stabilization of benzylic transition states and intermediates by Cr(CO)$_3$ can be summarized as follows. Improved matching of orbital energies, coupled with geometric changes such as bending of the benzyl framework and shifting of the Cr(CO)$_3$ moiety, lead to strengthened orbital interactions in the ions, which are accompanied by delocalization of charge

Chart 1
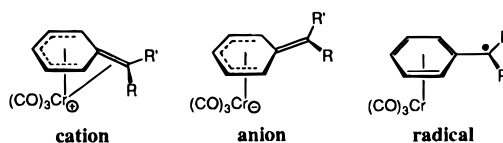
from the benzyl ligands to the Cr(CO)$_3$ fragment. Since geometric changes or delocalization of the unpaired electron of a benzylic radical upon complexation would lead to 17- or 19-electron species, enhanced orbital interactions and extensive spin delocalization are not possible, and little stabilization is therefore observed.

Computed structures of the various benzyl species demonstrate that direct interaction between chromium and the benzylic position is present in cationic complexes but not in the corresponding complexes of anions and radicals. The structural representations shown in Chart 1 capture the essential features of the computed structures. Further experiments and computations on chromium-complexed benzylic ions and radicals are underway in our laboratories.

Methods

Computations. All calculations were performed with the Gaussian 94 program.[32] Geometry optimizations employed the hybrid HF-DFT B3LYP method[33] with the LANL2DZ basis set.[34] Density functional theory has been used effectively in modeling various organometallic systems,[35,36] including various chromium-containing species such as chromium carbonyls,[36e,k] Fischer carbenes,[36b−d,h,j] and chromium oxides and halides.[36a,f−h] It has also been used to model organometallic radical species.[35f−h] The LANL2DZ basis set is of double-ζ quality and utilizes an effective core potential (ECP) for chromium.[34] Many DFT calculations on organometallic species have utilized ECP basis sets.[35a,b,d,e,g,36f,h,j] (U)B3LYP/LANL2DZ bond lengths and angles for free toluene and benzyl species are comparable in both relative and absolute magnitudes with those calculated previously by (U)HF and (U)MP2 methods with

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double-ζ and triple-ζ basis sets (on average, the (U)B3LYP carbon−carbon bond lengths are approximately 0.01−0.03 Å longer than those computed with (U)HF or (U)MP2 methods)[28f,37] and with those observed in the recently published X-ray structure of the cumyl cation.[38] In addition, geometries of $Cr(CO)_6$ and the $Cr(CO)_3$ complex of toluene were calculated as test cases (see Figure 1). Computed CO bond lengths are overestimated relative to those observed in X-ray and neutron diffraction structures (by approximately 0.03−0.05 Å),[26,39] while Cr−CO bond lengths appear to be reproduced very precisely (± approximately 0.01 Å); Cr−C(ring) distances are overestimated systematically by approximately 0.1 Å. Single-point energies were also calculated for selected stationary points using an all-electron basis set (the B3LYP/DZVP2+ level).[35f,40] Electrostatic potential surfaces (contoured at 0.002 electrons/au³) and constant spin density surfaces (contoured at 0.004 electrons/au³) were calculated from (U)HF/3-21G single-point calculations on (U)B3LYP/LANL2DZ-optimized geometries using SPARTAN V5.0.[41]

General Experimental Procedures. All reactions were carried out in flame-dried glassware in an inert atmosphere of Ar. Reaction solvents were distilled from the indicated drying agents: THF (Na, benzophenone), Et₂O (Na, benzophenone), dioxane (Na, benzophenone), cyclohexane (CaH₂), and dichloromethane (CaH₂). All reagents were purified before use according to literature procedures. Samarium metal was purchased from Aldrich and was kept in a drybox under N₂ atmosphere. Samarium diiodide was generated by the procedure given by Wipf et al.[18b] The SmI₂ solution was concentrated to dryness and kept in a drybox under N₂ atmosphere. HMPA and Et₃SiH were distilled from CaH₂. CuCl was recrystallized from concentrated HCl. Ph₃P·I₂ was recrystallized from dried, degassed dichloromethane under Ar and kept in a drybox under N₂ atmosphere. Solvents for extractions and chromatography were not distilled. Flash column chromatography was performed by the method of Still et al.,[42] using 32−63-μm silica gel (ICN). ¹H NMR and ¹³C NMR spectra were recorded at either 400 or 500 MHz using CDCl₃ (δ 7.26 ppm for ¹H, δ 77.0 ppm for ¹³C), C₃D₆O (δ 2.05 ppm for ¹H, δ 29.92 and δ 206.68 ppm for ¹³C), and C₆D₆ (δ 7.16 ppm for ¹H, δ 128.39 ppm for ¹³C) as solvents and reference standards. Chemical shifts are given in ppm (δ); multiplicites are indicted by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broadened). Coupling constants, *J*, are reported in hertz. Infrared spectra (IR) were recorded on a Nicolet 510P spectrometer, and signals are reported in cm⁻¹. High-resolution electron impact (EI) mass spectra were obtained with an ionization voltage of 70 eV. Data are reported in the form of *m/z* (intensity relative to base peak = 100).

***cis*-2,3-Diphenyl-*trans*-1-carboethoxycyclopropane (1).** A solution of *cis*-stilbene (968 mg, 5.37 mmol), triethyl phosphite copper(I)

(37) (a) Adamo, C.; Subra, R.; di Matteo, A.; Barone, V. *J. Chem. Phys.* **1998**, *109*, 10244−10254. (b) Jones, J.; Bacskay, G. B.; Mackie, J. C. *J. Phys. Chem. A* **1997**, *101*, 7105−7113. (c) Eiden, G. C.; Lu, K.-T.; Badenhoop, J.; Weinhold, F.; Weisshaar, J. C. *J. Chem. Phys.* **1996**, *104*, 8886−8895. (d) Arnaud, R.; Postlethwaite, H.; Barone, V. *J. Phys. Chem.* **1994**, *98*, 5913−5919. (e) Amyes, T. L.; Richard, J. P.; Novak, M. *J. Am. Chem. Soc.* **1992**, *114*, 8032−8041. (f) Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942−6948. (g) Rice, J. E.; Handy, N. C.; Knowles, P. J. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 1643−1649.

(38) Laube, T.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.* **1997**, *119*, 3087−3092.

(39) (a) Rees, B.; Mitschler, A. *J. Am. Chem. Soc.* **1976**, *98*, 7918−7924. (b) Jost, A.; Rees, B.; Yelon, W. B. *Acta Crystallogr.* **1975**, *B31*, 2649−2658. (c) Whitaker, A.; Jeffery, J. W. *Acta Crystallogr.* **1967**, *23*, 977−984.

(40) The DZVP2 basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0 (http://www.emsl.pnl.gov:2080/forms/basisform.html), as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information. The basis set was augmented as described in ref 35f.

(41) *SPARTAN V5.0*; Wavefunction, Inc.: 18401 Von Karman Ave., #370, Irvine, CA 92612; 1997.

(42) Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923−2925.

chloride[16] (126 mg, 0.54 mmol), and distilled cyclohexane (1 mL) was heated to a gentle reflux. Ethyl diazoacetate (2.3 mL, 21.5 mmol) was added as a solution in cyclohexane (3 mL) to the refluxing solution at a rate of 0.2 mL h⁻¹. After the addition was complete, the reaction mixture was cooled to room temperature and filtered through a pad of alumina using Et₂O. The solution was evaporated to dryness, taken up in hot hexanes, decolorized with charcoal, and filtered. The resulting solution was evaporated to dryness, and the residue was recrystalized from hexanes to afford 600 mg (42%) of the cyclopropane **1** as white needles: ¹H NMR (500 MHz, CDCl₃) δ 1.39 (3H, t, *J* = 7.1 Hz), 2.60 (1H, t, *J* = 5.3 Hz), 3.11 (2H, d, *J* = 5.3 Hz), 4.28 (2H, q, *J* = 7.1 Hz), 6.99−7.01 (4H, m), 7.15−7.20 (6H, m); ¹³C NMR (125 MHz, CDCl₃) δ 14.19, 27.16, 33.16, 60.87, 126.32, 127.83, 128.78, 135.49, 173.24; IR (KBr) 3155, 3030, 1717, 1433, 1304, 1182, 908, 733, 650 cm⁻¹; MS (70 eV) 266 (M⁺, 30), 221 (20), 193 (100), 178 (30), 115 (85), 91 (35); HRMS (EI) calcd for C₁₈H₁₈O₂ 266.1307, found 266.1303.

***cis*-2,3-Diphenyl-*trans*-1-hydroxymethylcyclopropane (2).** A solution of cyclopropane ester **1** (780 mg, 2.93 mmol), THF (20 mL), and lithium aluminum hydride (111 mg, 2.93 mmol) was stirred overnight. The reaction was cooled to 0 °C and quenched by adding water (110 μL), followed by 15% aqueous NaOH (110 μL), followed by water (330 μL). The resulting mixture was warmed to room temperature, MgSO₄ was added, and the slurry was filtered. The solvent was removed in vacuo to give 638 mg (97%) of **2** as a white solid: ¹H NMR (400 MHz, CDCl₃) δ 1.56 (1H, t, *J* = 4.9 Hz), 2.10 (1H, pent, *J* = 5.9 Hz), 2.42 (2H, d, *J* = 5.7 Hz), 3.86 (2H, t, *J* = 6.1 Hz), 6.93−6.94 (4H, m), 7.04−7.13 (6H, m); ¹³C NMR (100 MHz, CDCl₃) δ 27.78, 29.60, 66.35, 125.88, 127.81, 128.95, 137.31; IR (KBr) 3359, 1603, 1496, 1446, 1030, 696 cm⁻¹; MS (70 eV) 224 (M⁺, 45), 206 (30), 193 (100), 151 (50), 91 (25); HRMS (EI) calcd for C₁₆H₁₆O 224.1201, found 224.1206.

***cis*-2-(Phenyltricarbonylchromium)-3-phenyl-*trans*-1-hydroxymethylcyclopropane (3).** A mixture of cyclopropyl alcohol **2** (104 mg, 0.46 mmol) and tris(acetonitrile)tricarbonylchromium (160 mg, 1.34 mmol) was diluted with dioxane (15 mL) and immersed in a preheated oil bath at 140 °C for approximately 3 min. The reaction was cooled to room temperature, filtered through a pad of silica gel, washed with EtOAc, and absorbed onto Celite. The arene complex was isolated by chromatography using 20% Et₂O/hexanes, followed by 50% Et₂O/hexanes as the eluent, to afford 162 mg (98%) of **3** as a yellow solid: ¹H NMR (500 MHz, C₃D₆O) δ 2.15−2.22 (2H, m), 2.67 (1H, dd, *J* = 9.4, 6.1 Hz), 3.60 (1H, t, *J* = 6.6 Hz), 4.04 (2H, dd, *J* = 11.0, 3.6 Hz), 5.00 (1H, d, *J* = 6.7 Hz), 5.28 (1H, t, *J* = 6.3 Hz), 5.44 (1H, t, *J* = 6.5 Hz), 5.51 (1H, d, *J* = 6.6 Hz), 5.57 (1H, t, *J* = 5.9 Hz), 7.14−7.22 (5H, m); ¹³C NMR (125 MHz, C₃D₆O) δ 26.19, 26.66, 31.26, 62.18, 90.96, 91.85, 94.39, 94.46, 95.05, 112.58, 126.10, 127.86, 129.51, 136.51, 233.94; IR (KBr) 3406, 1954, 1857, 665 cm⁻¹; MS (70 eV) 360 (M⁺, 50), 276 (50), 206 (50), 193 (100), 115 (55), 91 (40); HRMS (EI) calcd for C₁₉H₁₆CrO₄ 360.0454, found 360.0454.

***cis*-2-(Phenyltricarbonylchromium)-3-phenyl-*trans*-1-iodomethylcyclopropane (4).** Cyclopropane **3** (80 mg, 0.36 mmol) was added to a solution of Ph₃P·I₂ (184 mg, 0.36 mmol), imidazole (24 mg, 0.36 mmol), and CH₂Cl₂ (3 mL) at 0 °C. The reaction mixture turned color from yellow to white. The reaction was stirred for 40 min. The triphenylphosphine oxide was removed by filtration using Et₂O to rinse, and the solute was absorbed onto Celite. The arene complex was isolated by chromatography using hexane as the eluent to afford 134 mg (84%) of **4** as a yellow oil: ¹H NMR (400 MHz, C₃D₆O) δ 2.37 (1H, dd, *J* = 9.5, 6.2 Hz), 2.45 (1H, dddd, *J* = 9.5, 6.1, 2.9, 5.4 Hz), 2.64 (1H, dd, *J* = 9.4, 6.1 Hz), 3.38 (1H, t, *J* = 9.5 Hz), 3.75 (1H, dd, *J* = 9.8, 5.9 Hz), 5.05 (1H, d, *J* = 6.5 Hz), 5.30 (1H, t, *J* = 6.2 Hz), 5.42 (1H, t, *J* = 6.4 Hz), 5.46 (1H, d, *J* = 6.5 Hz), 5.55 (1H, t, *J* = 6.3 Hz), 7.16−7.24 (5H, m); ¹³C NMR (100 MHz, CDCl₃) δ 9.35, 30.18, 34.94, 37.37, 89.89, 90.36, 92.85, 93.29, 93.59, 109.80, 127.07, 128.42, 129.60, 135.13, 233.08; IR (KBr) 1956, 1863, 1601, 1410, 1296, 1172, 1147, 704, 630, 619 cm⁻¹; MS (FAB, Cs) 470 (M⁺, 75), 386 (95), 307 (100), 289 (40), 207 (40); HRMS (FAB) calcd for C₁₉H₁₅ICrO₃ 469.9467, found 469.9471.

Anionic Rearrangement: 4-(Phenyltricarbonylchromium)-3-phenyl-1-butene (5) via *t*-BuLi. To a solution of iodide **4** (100 mg, 0.21 mmol) and THF (5 mL) at −78 °C was added *t*-BuLi (1.7 M, 313

μL, 0.53 mmol), and the reaction was stirred for 10 min. The reaction mixture was poured onto dilute HCl and extracted with Et$_2$O (3×). The combined organic layers were dried over MgSO$_4$, filtered, and absorbed onto Celite. The residue was chromatographed, using 5% Et$_2$O/hexanes as the eluent, to afford 54 mg (74%) of alkene **5** as a yellow oil. ^{1}H NMR analysis indicated a >99:<1 ratio of products **5** and **6**, respectively.[43] **5**: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 2.32 (1H, dd, *J* = 13.5, 8.31 Hz), 2.41 (1H, dd, *J* = 13.5, 6.8 Hz), 3.04 (1H, q, *J* = 7.4 Hz), 4.10 (1H, d, *J* = 6.4 Hz), 4.20 (1H, t, *J* = 6.3 Hz), 4.32−4.34 (2H, m), 4.49 (1H, t, *J* = 6.3 Hz), 4.81 (1H, d, *J* = 17.1 Hz), 4.89 (1H, d, *J* = 10.3 Hz), 5.70 (1H, ddd, *J* = 17.4, 10.2, 7.4 Hz), 6.82 (2H, d, *J* = 7.1 Hz), 7.00−7.10 (3H, m); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 41.91, 52.65, 90.49, 93.54, 93.67, 93.84, 93.97, 111.40, 115.56, 127.34, 128.43, 129.16, 140.91, 142.65, 234.04; IR (KBr) 3235, 2280, 1968, 1892, 1618, 1454, 1331, 1163, 812 cm^{-1}; MS (70 eV) 344 (M$^+$, 40), 260 (100), 208 (15), 169 (10), 117 (60); HRMS (EI) calcd for C$_{19}$H$_{16}$CrO$_3$ 344.0505, found 344.0508.

Cationic Rearrangement: 4-(Phenyltricarbonylchromium)-3-phenyl-1-butene (5) and 3-(Phenyltricarbonylchromium)-4-phenyl-1-butene (6) via AgBF$_4$. To a 50-mL two-neck round-bottom flask containing iodide **4** (60 mg, 0.13 mmol), Et$_3$SiH (102 μL, 0.64 mmol), and CH$_2$Cl$_2$ (5 mL) was added AgBF$_4$ (25 mg, 0.13 mmol) via a solid addition funnel, causing the reaction mixture to turn a dark brown color. The reaction stirred for 1 h, whereby the color of the reaction dissipated to a clear yellow. H$_2$O (500 μL) was added, and the reaction was filtered through a pad of Celite using Et$_2$O to rinse. The solvent was absorbed onto Celite, and the crude reaction mixture was chromatographed, using 5% Et$_2$O/hexanes as the eluent, to afford 36 mg (82%) of alkenes **5** and **6** a yellow oil. ^{1}H NMR analysis indicated a 95:5 ratio of products **5** and **6**, respectively.[43] **6**: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 2.56 (1H, dd, *J* = 13.2, 8.5 Hz), 2.61 (1H, dd, *J* = 13.2, 6.2 Hz), 2.94 (1H, q, *J* = 7.8 Hz), 4.31−4.38 (3H, m), 4.44 (1H, t, *J* = 6.4 Hz), 4.55 (1H, d, *J*

= 6.4 Hz), 4.85 (1H, d, *J* = 6.6 Hz), 4.86−4.89 (1H, m) 5.64 (1H, dd, *J* = 13.5, 8.31 Hz), 6.88 (2H, d, *J* = 7.4 Hz), 7.02−7.09 (3H, m); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 42.01, 49.70, 91.53, 92.04, 92.13, 92.62, 93.10, 93.40, 115.05, 117.27, 127.00, 128.88, 130.01, 139.10, 233.91; IR (KBr, mixture) 3235, 2280, 1968, 1892, 1618, 1454, 1331, 1163, 812 cm^{-1}; MS (70 eV, mixture) 344 (M$^+$, 40), 260 (100), 208 (15), 169 (10), 117 (60); HRMS (EI, mixture) calcd for C$_{19}$H$_{16}$CrO$_3$ 344.0505, found 344.0508.

Radical Rearrangement: 4-(Phenyltricarbonylchromium)-3-phenyl-1-butene (5) and 3-(Phenyltricarbonylchromium)-4-phenyl-1-butene (6) via SmI$_2$. To a solution of SmI$_2$ in THF (0.04 M, 0.38 mmol) and HMPA (190 μL, 1.14 mmol) was added a degassed solution of iodide **5** (60 mg, 0.13 mmol) and *t*-BuOH (19 μL, 0.26 mmol) in THF (10 mL) via cannula. A white precipitate formed, and the reaction was allowed to stir at room temperature for 1 h. The reaction mixture was then poured onto dilute HCl and extracted with Et$_2$O (3×). The combined organic layers were dried over MgSO$_4$, filtered, and absorbed onto Celite. The residue was chromatographed, using 2.5% Et$_2$O/hexanes as the eluent, to afford 40 mg (89%) of alkenes **5** and **6** as a yellow oil. ^{1}H NMR analysis indicated a 2.5:1 ratio of products **5** and **6**, respectively.[43]

Note Added in Proof. A related paper, which arrives at similar conclusions, has just been published: Pfletschinger, A.; Dargel, T. K.; Bats, J. W.; Schmalz, H.-G.; Koch, W. *Chem. Eur. J.* **1999**, *5*, 537−545.

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(43) It is possible that a haptotropic shift of the Cr(CO)$_3$ moiety from one phenyl group to the other in the reactive intermediates could affect the observed product ratios. However, we are not aware of precedent for this, and the experimental results are fully in accord with literature precedent$^{1-7}$ and our computational results.