Mechanistic Aspects of the Reactions of Bis(tricarbonylchromium) Coordinated Biphenyl Dianions with Electrophiles and Their Subsequent Oxidation

Reuben D. Rieke,* Khushroo P. Daruwala, Louis D. Schulte,† and Steven M. Pankas

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Received June 21, 1991

Reaction of the (η^6:η^6-biphenyl)bis(tricarbonylchromium) dianion (2) with a wide variety of primary electrophiles results exclusively in an ipso addition. NMR data point out the formation of the endo isomer upon protonation. While a definitive answer is not possible for primary alkyl electrophiles, indirect evidence suggests either a carbanionic type S_N2 or a metal-assisted endo addition to the ipso position. Reaction with cyclopropylcarbinyl bromide as well as 6-bromo-1-hexene suggests an inner-sphere polar S_N2 mechanism for most of the primary electrophiles. However, easily reduced halides such as allylic and benzylic or those halides which have steric hindrance toward S_N2 processes may well proceed via an electron-transfer process or a combination of S_N2 and electron-transfer processes. 1,2-Aryl migration has been found to be the predominant pathway in the oxidative cleavage of the alkylated (η^6:η^6-4,4′-dimethylbiphenyl)bis(tricarbonylchromium) dianion (6), thereby indicating a cationic intermediate in the mechanism of this step. Alkylation followed by iodine oxidation of 4,4′-disubstituted biphenyls provides a short convenient approach to 2-alkyl-5,4′-disubstituted biphenyls.

Introduction

Since our initial report in 1975 on the electrochemical generation of stable arene metal tricarbonyl dianions,[1] we have been pursuing the chemistry of (arene)metal carbonyl complexes which undergo the reductive rearrangements. Initial studies carried out on the bis(tricarbonylchromium) complexes of biphenyl compounds showed that they reduced electrochemically by one electron per tricarbonyl chromium group to give dianions which were stable under anhydrous, oxygen-free conditions.[2] Recently, we reported our findings on the reactions of the dianion of the bis(tricarbonylchromium) complexes of biphenyl compounds with a wide variety of electrophiles.[3] Unexpectedly, the reaction with primary halides proceeded via an ipso attack to form the {6-(substituted)-6-[(η^6-phenyl)$Cr(CO)_3$-(1,5-η^5-cyclohexadienyl)$Cr(CO)_3$} anions (3) in a stereo- and regioselective manner. Oxidation of these alkylated species with iodine then yielded quantitatively the corresponding 2-alkylbiphenyls 4 after decomplexation of the chromium tricarbonyl groups (Scheme I).

The rather unusual reaction of the dianions with electrophiles, as well as their subsequent oxidation, raises several questions regarding the overall mechanism. Three major points need to be addressed. The first is whether attack of the dianion on the electrophile is a metal-assisted S_N2 process yielding an overall endo addition or whether it involves a direct carbanionic type S_N2 attack. Secondly, does the mechanism occur via an electron-transfer process and involve free radical and/or carbanionic type intermediates or is it an inner-sphere polar S_N2 type substitution process? Finally, in the subsequent oxidation of the alkylated complex to yield the uncomplexed 2-alkylbiphenyl, does the rearrangement proceed via a 1,2-alkyl or a 1,2-aryl shift?

Results and Discussion

Mode and Regioselectivity of the Alkylation Process. It has been well documented that the addition of electrophiles to chromium–tricarbonyl complexed benzylic anions proceeds by means of a direct carbanionic S_N2 type attack.[4] On the other hand, the number of metal-assisted endo additions leading to arene ring alkylations is limited.[5] Protonation of the (η^4-naphthalene)tricarbonylchromium dianion was suggested to occur via a metal-assisted endo mechanism on the basis of NMR data.[6] Kündig's acylation transfer to the (η^6-cyclohexadienyl)tricarbonylchromium anion also has been pointed out as being an endo process.[7] Recently, Cooper also has shown that protonation and carboxylation of activated benzene in $[Cr(\eta^4\text{-}C_6H_6)CO_3]^{2-}$ is a metal-assisted endo delivery.[8] As

† Los Alamos National Laboratory LA-UR-89-3428.

(1) Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R., Jr.; Polimer, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951.

(2) (a) Milligan, S. N.; Rieke, R. D. *Organometallics* **1983**, *2*, 171. (b) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699.

(3) (a) Schulte, L. D.; Rieke, R. D. *J. Org. Chem.* **1987**, *52*, 4827. (b) Schulte, L. D.; Rieke, R. D. *Tetrahedron Lett.* **1988**, 5483. (c) Rieke, R. D.; Schulte, L. D.; Dawson, B. T.; Yang, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 8388.

(4) (a) Trahanovsky, W. S.; Card, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 2897. (b) Jaouen, G.; Meyer, A. *Tetrahedron Lett.* **1976**, 3547. (c) Meyer, A.; Hofer, O. *J. Am. Chem. Soc.* **1980**, *102*, 4410. (d) Semmelhack, M. F.; Seufert, W.; Keller, L. *J. Am. Chem. Soc.* **1980**, *102*, 6586. (e) Brocard, J.; Lebibi, J.; Corturier, D. *J. Chem. Soc., Chem. Commun.* **1981**, 1264. (f) Brocard, J.; Lebibi, J.; Corturier, D. *Bull. Soc. Chim. Fr.* **1982**, *2*, 357. (g) Jaouen, G.; Top, S. *J. Am. Chem. Soc.* **1984**, *106*, 2207. (h) Jaouen, G. *Pure Appl. Chem.* **1986**, *58*, 597. (i) Brocard, J.; Lebibi, J. *J. Organomet. Chem.* **1986**, *310*, C63. (j) Dickens, P. J.; Gilday, J. P.; Negri, J. T.; Widdowson, D. A. *Pure Appl. Chem.* **1990**, *62*, 575.

(5) (a) Davies, S. G.; Felkin, H.; Watts, O. J. *J. Chem. Soc., Chem. Commun.* **1980**, 159. (b) Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2857. (c) Chung, Y. K.; Choi, H. S.; Sweigart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *104*, 4245. (d) Weber, L.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 498. (e) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638. (f) Brookhart, M.; Lukacs, A. *Organometallics* **1983**, *2*, 649. (g) Williams, G. M.; Rudisill, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 3357. (h) Rush, P. K.; Noh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745. (i) Brookhart, M.; Yoon, J.; Noh, S. K. *J. Am. Chem. Soc.* **1989**, *111*, 4117. (j) Padda, R. S.; Sheridan, J. S.; Chaffee, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1226. (k) Pike, R. D.; Ryan, W. J.; Lennhoff, N. S.; Van Epp, J.; Sweigart, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4798.

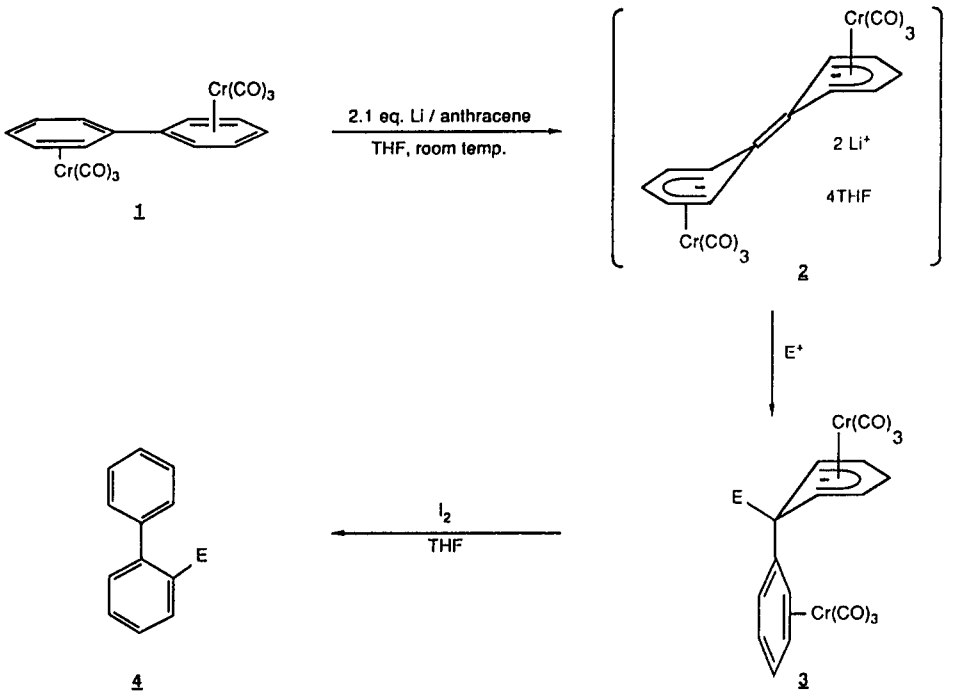
(6) (a) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6314. (b) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420.

(7) (a) Desobry, V.; Kündig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288. (b) Kündig, E. P.; Simmons, D. P. *Chem. Commun.* **1983**, 1320. (c) Kündig, E. P.; Desobry, V.; Simmons, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 6962. (d) Kündig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. (e) Kündig, E. P.; Desobry, V.; Simmons, D. P.; Wenger, E. *J. Am. Chem. Soc.* **1989**, *111*, 1804. (f) Kündig, E. P.; Cunningham, A. F., Jr.; Paglia, P.; Simmons, D. P.; Bernardinelli, G. *Helv. Chim. Acta* **1990**, *73*, 386.

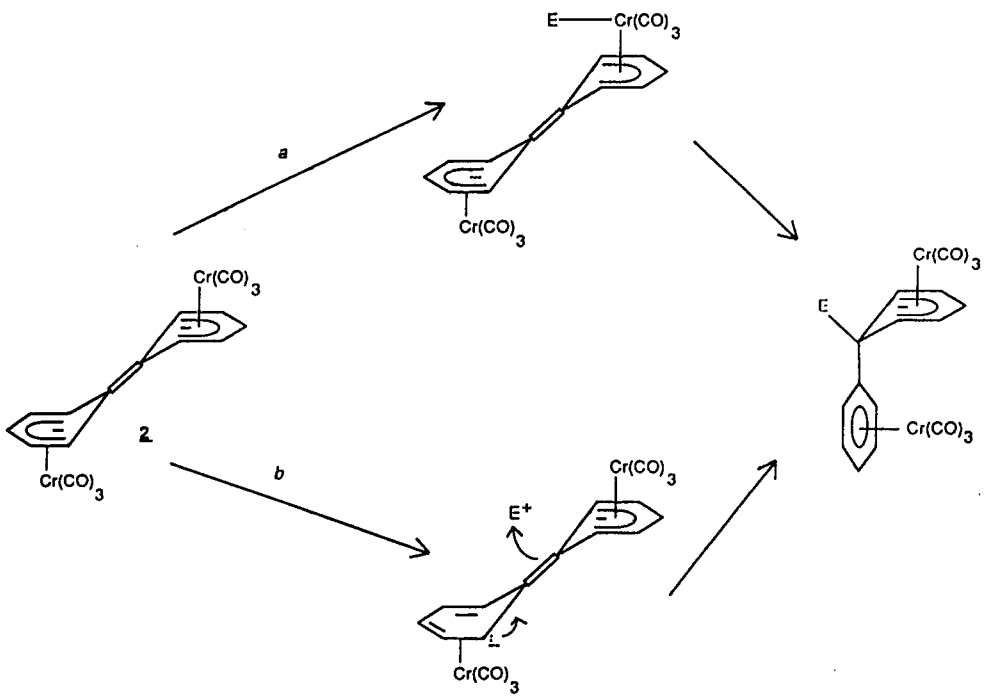
(8) (a) Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644. (b) Correla, J. A., II; Cooper, N. J. *J. Am. Chem. Soc.* **1990**, *112*, 2832.

0276-7333/92/2311-0284$03.00/0

Scheme I



Scheme II



discussed in our previous papers,[3a,c] protonation of the $(\eta^6{:}\eta^6$-biphenyl)bis(tricarbonylchromium) dianion (**2**) occurs in an endo manner. The protonation could occur either via a chromium–hydride species (pathway a) or by means of a direct attack of the ipso-carbon (pathway b) (Scheme II). On the other hand, reaction of dianion **2** with primary alkyl iodides and bromides may or may not follow the same pathway as protonation. Since NMR data were of no value in determining if the added electrophile was endo or exo with respect to the $-Cr(CO)_3$ group on the ring being alkylated, attempts were made to grow crystals of the anion **2**. However, all efforts to date have not yielded suitable crystals for X-ray analysis. Accordingly, we are left to speculate whether the pathways for both protonation and alkylation are metal-assisted endo processes.[9] However, it is possible that, for alkylation, a direct S_N2 type carbanionic attack, exo to one ring but endo to the phenyl ring being alkylated, is the mode of reaction (Scheme II).

It is likely that the factors determining the regiochemistry of direct alkylations would be quite different from a metal-assisted alkylation mechanism. In either case, one might anticipate that regioselectivity could be predicted by HUMO–LUMO coefficients. Nucleophilic and electrophilic substitution patterns of many $(\eta^6$-arene)tri-

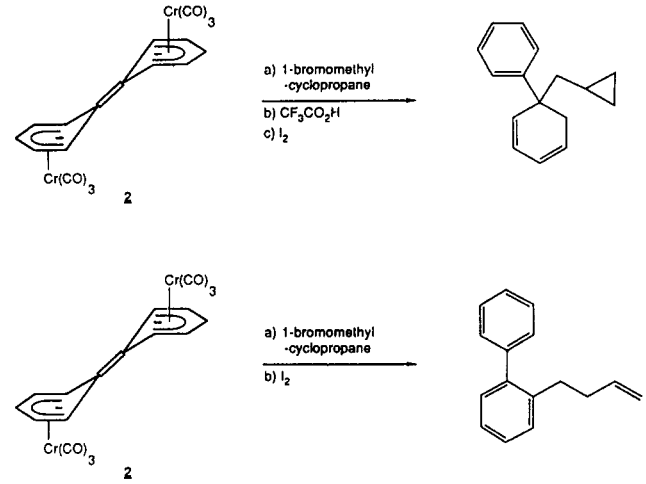
(9) A similar mechanism has been shown for the addition of methyl iodide to $(\eta^5\text{-}C_9H_7)(CO)_3Cr^-$ and $(\eta^5\text{-}C_{13}H_9)(CO)_3Cr^-$: Nesmeyanov, A. N.; Ustynyuk, N. A.; Makarova, L. G.; Andrae, S.; Ustynyuk, Y. A.; Novikova, L. N.; Luzikov, Y. N. *J. Organomet. Chem.* **1978**, *154*, 45.

carbonylchromium complexes have been shown to follow such considerations.[10] In some cases steric requirements of the chromium tricarbonyl moieties are the overriding factor.[11] Electrophilic substitution of uncomplexed biphenyl usually occurs in the 4-position for both electronic as well as steric reasons.[12] For the uncomplexed dianion, the Hückel HOMO coefficients are −0.35 (1-position), −0.30 (2-position), +0.14 (3-position), and +0.40 (4-position).[13] While these are admittedly Hückel coefficients and, accordingly, likely to be approximate, they do suggest little difference in the reactivity of the 1-, 2-, and 4-positions. NMR studies of products derived from primary bromides showed no sign of any isomers other than the product of ipso attack at the 1-position. Accordingly, this high regioselectivity does not seem explicable by these considerations.

The regioselectively of electrophilic attack on (η^6-arene)$Cr(CO)_3$ complexes also has been related to the conformational preferences of the $Cr(CO)_3$ group. In several (η^6-arene)$Cr(CO)_3$ complexes, where it has been shown that the $Cr(CO)_3$ moiety adopts a highly preferred conformation, electrophilic attack has been found to take place on those carbon atoms which have the chromium hybrid orbitals pointed toward them. On the basis of known complexed cyclohexadienyl anions, the metal orbitals are expected to be strongly bonded to the 2-, 4-, and 6-positions and, therefore, one would expect primarily an ortho and para attack. However, proton and carbon-13 spectral data of the alkylated intermediates[3a,c] have clearly shown that alkylation does not take place at the 2 (ortho) and 4 (para) positions, but instead it takes place exclusively at the 1-position. If, however, the mechanism is one which involves a direct benzylic type S_N2 attack by the ipso-carbon, the high regioselectivity is readily explained. This fact alone provides strong support for this mode of attack.

Mechanism of Addition. The second question that must be addressed is whether the reactions with alkyl electrophiles proceed by an electron-transfer process or by an inner-sphere polar mechanism. The use of 6-halo-1-hexenes[14] and (halomethyl)cyclopropanes[15] as probes for evidence of a single-electron transfer (SET) mechanism has been well documented.[16] Reaction of **2** with 6-bromo-1-hexene resulted in clean alkylation at the phenyl-substituted position with no observable cyclization. Likewise, reaction of **2** with (1-bromomethyl)cyclopropane, followed by treatment with trifluoroacetic acid and iodine, led cleanly to the 5-alkyl-5-phenyl-1,3-cyclohexadiene without any ring opening of the cyclopropyl group. However, when the reaction of **2** with (1-bromomethyl)cyclopropane was worked up with iodine only, considerable ring opening of the methylcyclopropane ring was observed (Scheme III). The above results are consistent with an inner-sphere polar S_N2 process.

Scheme III



However, reaction of **2** with *tert*-butyl bromide, allyl and benzyl bromides, and secondary bromides and iodides generated a more complex reaction mixture and lower yields of the alkylated products. Workup of these reaction mixtures with trifluoroacetic acid (TFAA) followed by iodine oxidation generated mixtures of the 5-alkyl-5-phenyl-1,3-cyclohexadiene and 4-alkyl-1-phenyl-1,3-cyclohexadiene. Workup of these same reaction mixtures with iodine directly without any TFAA yielded not only the 2- and 4-substituted biphenyl but also traces of the 3-alkylbiphenyl isomer.[3c]

The above results indicate that electrophiles which have shown evidence of a competitive reaction pathway have certain common characteristics in that they may be reduced at potentials less negative than those of the electrophiles that react cleanly. In addition, several of these electrophiles inherently undergo S_N2 reactions more slowly due to steric hindrance. Evidence of a slower reaction was observed not only with secondary and tertiary bromides but also with primary bromides bearing additional functional substituents in the β position. It could, therefore, be postulated that as the electrophiles become more hindered and/or more easily reduced, outer-sphere electron-transfer processes become more predominant. In support of this postulate was the behavior observed for benzyl or allyl tosylates when compared to that observed for the corresponding bromides. Benzyl and allyl tosylate each reacted with the dianion to generate cleanly the {6-(substituted)-6-[(η^6-phenyl)$Cr(CO)_3$](1,5-η^5-cyclohexadienyl)-$Cr(CO)_3$}$_3$ anion, while benzyl or allyl bromide did not generate this intermediate cleanly, resulting instead in the formation of several isomers after workup.

These results suggest that there are two pathways available for the reaction of dianions of (η^6:η^6-biphenyl)-bis(tricarbonylchromium) systems with electrophiles. H_2O, D_2O, allyl and benzyl tosylate, methyl iodide and primary alkyl bromides, tosylates and sulfates were observed to react cleanly with ipso attack, suggesting an inner-sphere, polar S_N2 type of reaction. Conversely, secondary and tertiary halides and the more easily reduced alkyl halides are more likely to undergo reaction by an electron-transfer mechanism as opposed to an S_N2 attack.

Simple energetics qualitatively support these ideas. The reduction potential of **1** is −1.60 V, while the reduction potential of most primary bromides is −2.20 to −2.30 V,

(10) Semmelhack, M. F.; Clark, G. R.; Farina, R.; Saeman, M. *J. Am. Chem. Soc.* **1979**, *101*, 217 and references therein.

(11) (a) Saillard, J. Y.; Grandjean, D. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2285. (b) Van Meurs, F.; Van Konigsveld, H. *J. Organomet. Chem.* **1977**, *131*, 423. (c) Solladie-Cavallo, A.; Wipff, G. *Tetrahedron Lett.* **1980**, 3047. (d) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *19*, 3092. (e) Muetterties, E. Z.; Bleeke, J. R.; Wücherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (f) Schallkopf, K.; Stezowskii, J. J.; Effrenberger, F. *Organometallics* **1985**, *4*, 922. (g) Jackson, W. R.; Rae, I. D.; Wong, M. G. *Aust. J. Chem.* **1986**, *39*, 303. (h) Bitterwolf, T. E.; Herzog, R.; Rockswold, P. D. *J. Organomet. Chem.* **1987**, *320*, 197.

(12) Dabrowskii, R.; Witkiewicz, Z.; Kenig, K. *Mol. Cryst. Liq. Cryst.* **1980**, 251.

(13) Values of coefficients are given by: Coulson, A.; Streitweiser, A. *Dictionary of π Electron Calculations*; W. H. Freeman and Co.: San Francsico, 1965; p 91.

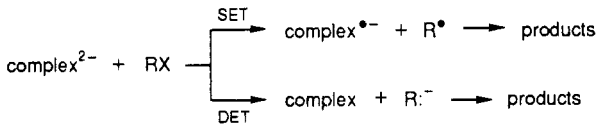
(14) (a) San Fillippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834. (b) Smith, J. G.; Irwin, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 2757.

(15) (a) Maillard, M.; Forest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1520. (b) Krusic, J. C.; Levisalles, J.; Normant, J.-M.; Rose, E. *J. Am. Chem. Soc.* **1977**, *99*, 250. (c) Matthews, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981.

(16) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8.

making outer-sphere electron transfer seem unlikely. In contrast, allyl bromides reduce at approximately −1.20 V, making outer-sphere electron transfer more likely. However, allyl tosylates which give clean ipso attack have reduction potentials of −2.10 to −2.20 V.

An additional variation on the electron-transfer reactions also must be addressed. In contrast to the majority of the electron-transfer reactions discussed in the literature, the reaction of the dianions with alkyl halides has the possibility of being a single-electron transfer (SET) process or a double-electron transfer (DET) process, as shown.

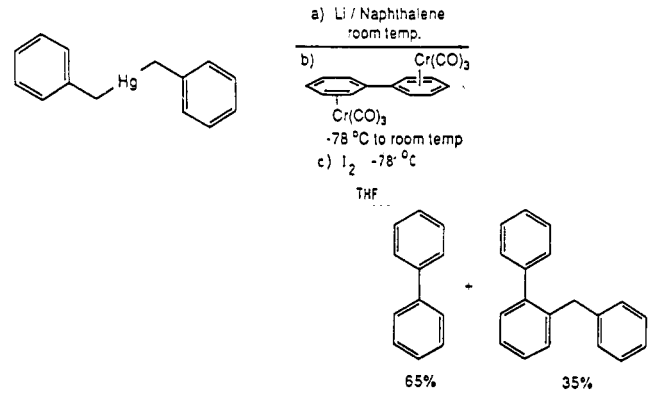


In fact, it would be expected that the DET process would be the one observed on the basis of simple thermodynamic considerations. The reduction potential for both electrons of **2** is −1.60 V, while, in the reductive cleavage of alkyl halides, the initial electron transfer requires the most energy and results in an almost instantaneous cleavage of the carbon–halogen bond. The resulting carbon radical is reduced more easily than the initial halide. Accordingly, it would appear that the second electron transfer could hardly be avoided.

The study of the additions of carbanions to $(\eta^6{:}\eta^6$-biphenyl)bis(tricarbonylchromium) (**1**) has, in fact, been investigated earlier in our laboratories.[17] Nitrile-stabilized primary anions were found to add to the 2-position only, while nitrile-stabilized secondary and tertiary anions were found to add to both the 2- and 4-positions of the $(\eta^6{:}\eta^6$-biphenyl)bis(tricarbonylchromium) complex (**1**). In contrast, unstabilized primary nucleophiles such as *n*-butyllithium gave only small amounts of addition to the 2- and 4-positions with essentially no ring metalation. The major product obtained in the case of reaction with unstabilized nucleophiles such as *n*-butyllithium was the unreacted biphenyl. This provides support that primary bromides, iodides, tosylates, and sulfates are reacting via a S_N2 process while the more easily reduced halides such as those of the allylic or benzylic type may be proceeding by a DET process and leading to addition at the 2- and 4-positions of the neutral bis complex **1**.

In fact, our studies of the reaction of dianion **2** with benzyl chloride, bromide, and iodide seem to support this thesis. The benzyl halides were reacted with **2** over a temperature range of −78 °C to room temperature. Aliquots periodically removed at several temperature intervals were quenched with benzoyl chloride. The product, 2-phenylacetophenone, that would have been formed by trapping any benzyl anion species with benzoyl chloride, was obtained along with biphenyl, starting benzyl halides, bibenzyl, and benzylated biphenyl. The results parallel the reduction potentials of the initial benzyl halides as well as the carbon–halogen bond strengths. Benzyl chloride did not start to react with **2** until approximately at −20 °C. The aliquot removed at room temperature gave after workup a product mixture of 20% benzylated biphenyl, 5% biphenyl, and 14% 2-phenylacetophenone. The reaction of **2** with benzyl bromide took place at −78 °C, and the quench removed at room temperature yielded 29% benzylated biphenyl, 33% bibenzyl, and 29% 2-phenylacetophenone. Benzyl iodide also reacted rapidly with **2** at −78 °C, and a room temperature quench yielded 10% benzylated biphenyl, 83% bibenzyl, and 2% 2-phenylacetophenone. These results clearly show that for the easily reduced benzyl halides, particularly the bromide and the iodide, electron-transfer processes are occurring. The presence of the benzyl phenyl ketone (obtained from trapping the benzyl anion with benzoyl chloride) in yields up to 29% supports a DET process.

If DET would be the mode of reaction, it would then mean that the benzyl anion, so generated by a double electron transfer of the dianion **2**, could now act as a nucleophile and attack the neutral $(\eta^6{:}\eta^6$-biphenyl)$[Cr(CO)_3]_2$ complex (**1**). On the basis of our previous work on addition of nucleophiles to $(\eta^6{:}\eta^6$-biphenyl)$[Cr(CO)_3]_2$,[17] such an attack would then result in addition of the primary benzyl anion in the 2-position of the biphenyl system to give the ortho-substituted product. In order to prove this point, the neutral complex **1** was reacted with benzyllithium, generated from the dissolved metal reduction of dibenzyl mercury.



Addition of the primary benzyl anion took place exclusively in the 2-position, resulting in the formation of 2-benzylbiphenyl in about 35% GC yield, after oxidative decomplexation of the chromium tricarbonyl moieties. The amount of the product obtained from this nucleophilic addition parallels that obtained in the reaction of the dianion **2** with benzyl bromide.[3c] Thus, while an absolute statement that the only electron-transfer process occurring is a DET process cannot be made, it is quite clear that in the reaction of **2** with benzyl iodide and bromide, electron-transfer processes are more likely the dominant mode of reaction.

Oxidative Decomplexation of the Organometallic Complex after Alkylation. The reaction of (arene)tricarbonylchromium compounds with iodine in THF has been widely used to liberate the coordinated arene from the chromium tricarbonyl unit.[18]

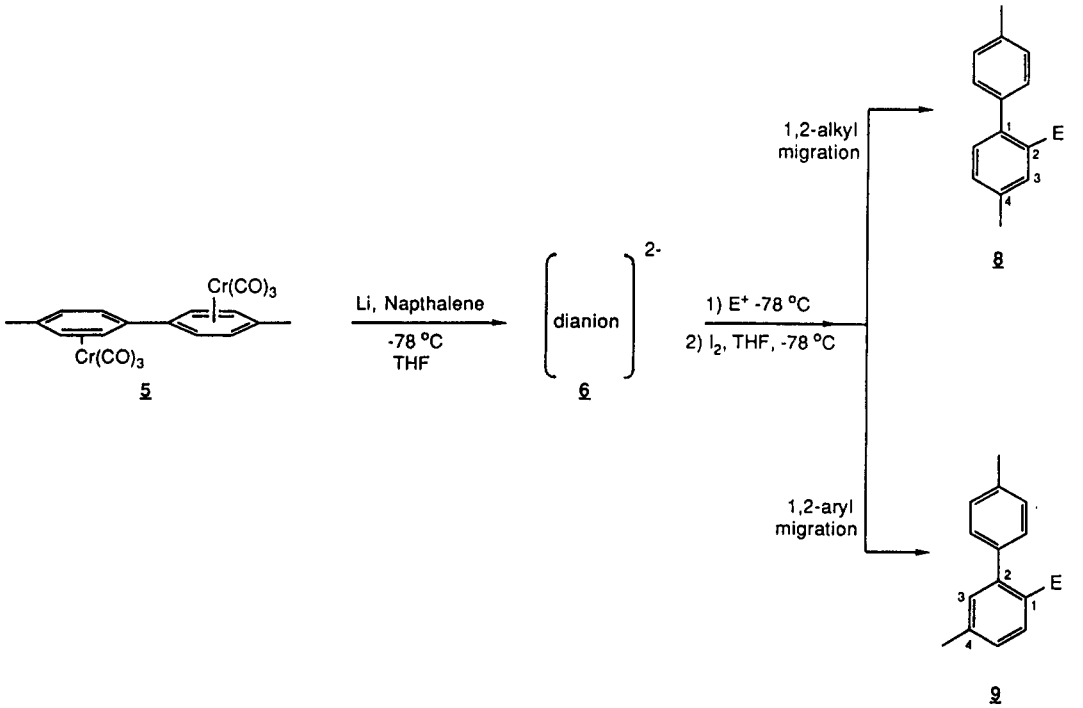
$$(\text{arene})Cr(CO)_3 + \tfrac{3}{2}I_2 \rightarrow \text{arene} + CrI_3 + 3CO$$

Semmelhack in his study of nucleophilic addition to $(\eta^6$-arene)$Cr(CO)_3$ has shown that the reaction of iodine with the alkylated η^5-cyclohexadienyl anionic complex, results in decomplexation of the $Cr(CO)_3$ moieties, with the loss of chromium as Cr(III) and the loss of hydrogen as a proton.[18c-e]

(17) Rieke, R. D.; Daruwala, K. P. *J. Org. Chem.* **1988**, *53*, 2073.

(18) (a) Hieber, W.; Romberg, E. *Z. Anorg. Allg. Chem.* **1935**, *221*, 321. (b) Natta, G.; Ercoli, R.; Calderazzo, F.; Santambrogio, E. *Chim. Ind. (Milano)* **1958**, *40*, 1003. (c) Semmelhack, M. F. In *Journal of Organometallic Chemistry Library*; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; Vol. 1, pp 361–395. (d) Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535. (e) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957. (f) Hoff, C. D. *J. Organomet. Chem.* **1983**, *246*, C53. (g) Harrison, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1487.

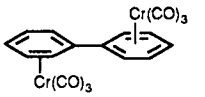
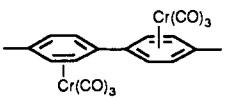
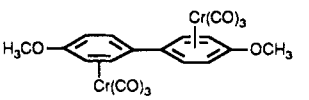
Scheme IV



In our study, as shown in the preceding section, the dianion obtained from the reduction of (η^6:η^6-biphenyl)bis(tricarbonylchromium) (1) reacted stereo- and regioselectively with primary electrophiles in the 1-position.[3] Oxidative workup of these alkylated intermediates with iodine resulted in the formation of 2-alkylbiphenyls after loss of the chromium tricarbonyl group. It was clear that these alkylated intermediates were undergoing a 1,2 rearrangement. But it was still uncertain whether the migrating species was the aryl ring or the alkyl group. For 1 the point is ambigous, since migration of either group results in formation of the same 2-alkylbiphenyl. In order to determine whether the phenyl or the alkyl group migrates in the rearrangement and also to gain further mechanistic information, a substituted biphenyl system, 4,4′-dimethylbiphenyl was selected. Alkylation of the dianion of (η^6:η^6-4,4′-dimethylbiphenyl)bis(tricarbonylchromium), followed by oxidation with iodine would then lead to 2-alkyl-4,4′-dimethylbiphenyl (8), if 1,2-alkyl migration had occurred, or 2-alkyl-5,4′-dimethylbiphenyl (9), if 1,2-aryl migration had taken place (Scheme IV).

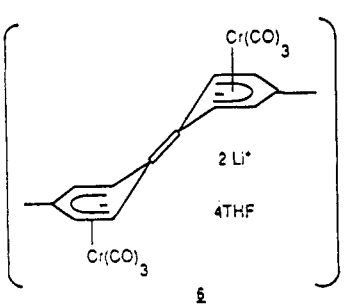
The preparation of (η^6:η^6-4,4′-dimethylbiphenyl)bis(tricarbonylchromium) (5) was carried out by standard methods.[19] Polarographic and cyclic voltammetric studies of 5 have shown that it exhibits reductive characteristics very similar to those of 1 (Table I). The features of electrochemical reduction such as $E_{3/4} - E_{1/4}$ indicate that the reduction process involves a total of two electrons, one electron per chromium tricarbonyl group. The more negative reduction potential ($E_{1/2}$ = −1.70 V compared to $E_{1/2}$ = −1.61 V for the biphenyl complex 1) is due to the presence of two electron-releasing methyl groups. Table I further indicates that introduction of two powerful electron-releasing methoxy groups instead of methyl groups in the 4,4′-positions, results in a much more negative potential ($E_{1/2}$ = −1.95 V) for the (η^6:η^6-4,4′-dimethoxybiphenyl)bis(tricarbonylchromium) complex.[3b] The cyclic voltammograms for 5 were found to be reversible,

Table I. Electrochemical Results

compd[a]	$E_{1/2}$,[b] V	$E_{3/4} - E_{1/4}$,[c] mV	I_d, mA
 1	−1.606	30	2.60
 5	−1.700	32	2.30
	−1.950	41	4.80

[a] Approximately 3 mmol in propylene carbonate, 0.2 M TEAP, 0 °C, on the DME. [b] Vs the Ag/AgCl, saturated NaCl (aq) reference electrode, ±0.005 V. [c] Values for $E_{3/4} - E_{1/4}$ on the order of 30 mV are indicative of a two-electron process.

demonstrating that the resulting dianion was persistent on that time scale. Coulometric examinations carried out at low temperatures, confirmed the two-electron reduction. The mechanism postulated for the reduction of 5 is thus identical to the ECE process proposed before for the (η^6:η^6-biphenyl)[Cr(CO)$_3$]$_2$ system. The structure of the resultant dianion 6 obtained from electrochemical reduction would be similar to that of the biphenyl dianion 2 reported previously.[3a,c]



6

(19) (a) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1979**, *182*, 381. (b) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.

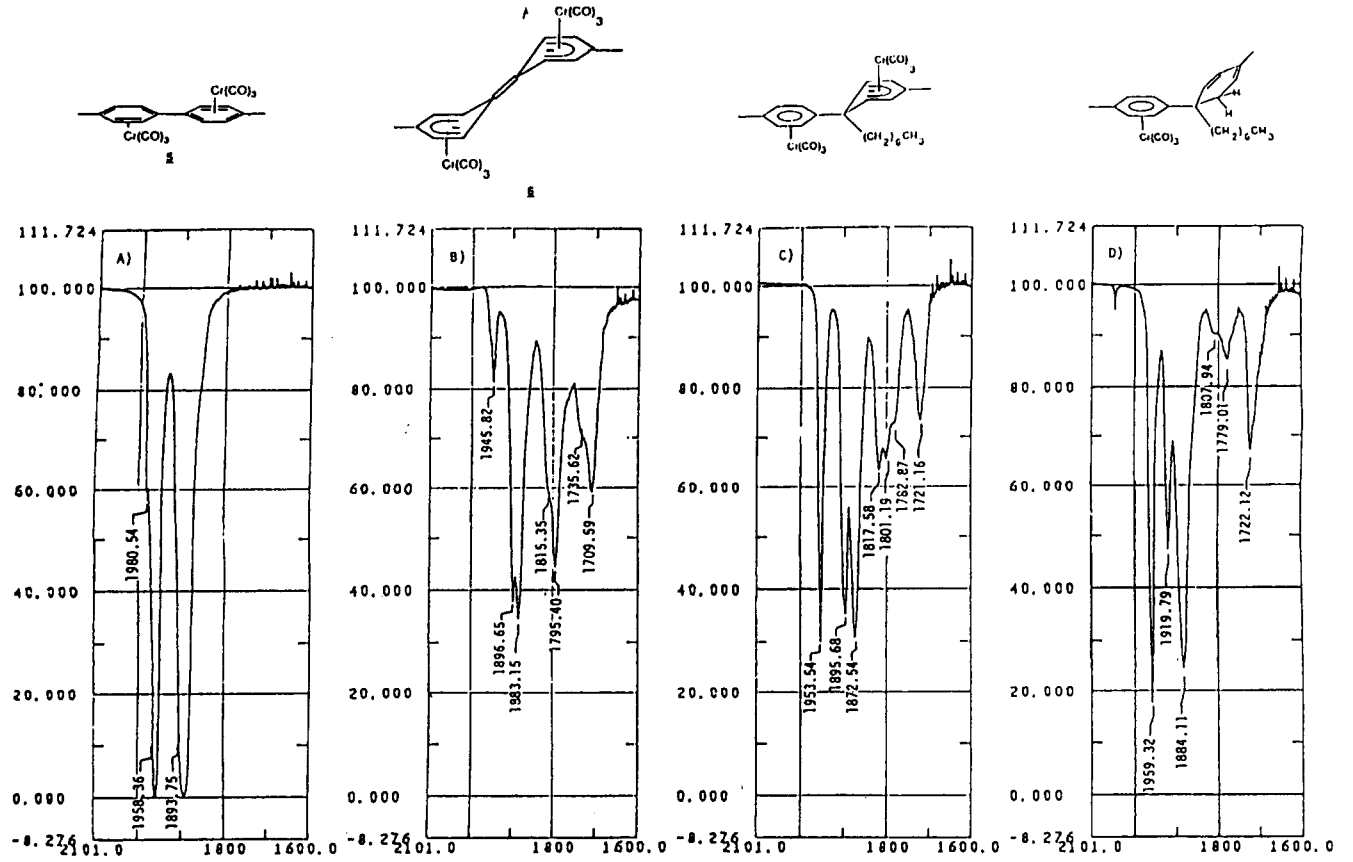
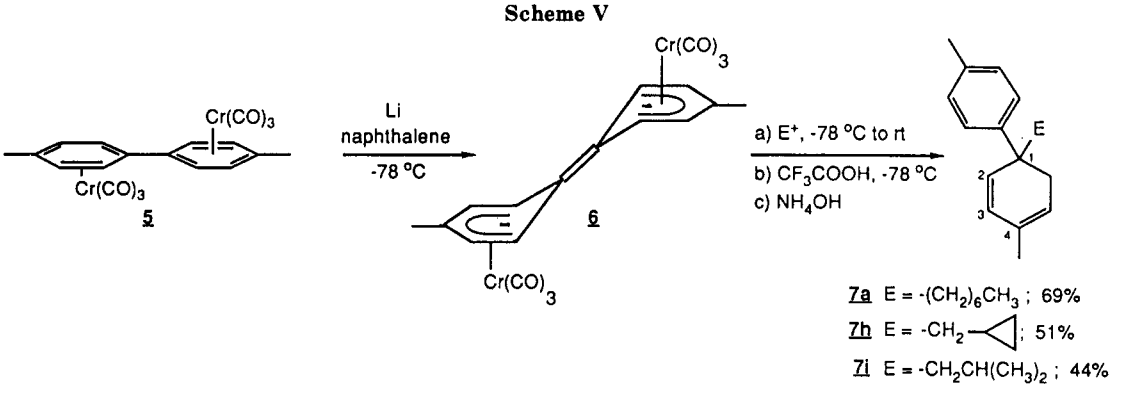


Figure 1. Infrared carbonyl stretching bands (cm^{-1}) for $(\eta^6{:}\eta^6$-4,4′-dimethylbiphenyl)bis(tricarbonylchromium) in THF: (A) before reduction; (B) after reduction with lithium naphthalenide; (C) after alkylation of the reduced species with 1 equiv of heptyl iodide; (D) after protonation of the alkylated species with 1 equiv of trifluoroacetic acid.

Scheme V



7a E = $-(CH_2)_6CH_3$; 69%

7h E = $-CH_2$-cyclopropyl ; 51%

7i E = $-CH_2CH(CH_3)_2$; 44%

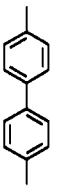
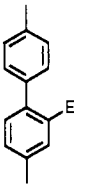
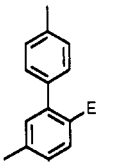
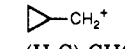
Reduction of **5** with lithium naphthalenide in THF resulted in an instantaneous color change from pale yellow to dark brown. However, unlike the case of the $(\eta^5{:}\eta^5$-biphenyl)$[Cr(CO)_3]$ dianion (**2**), no solid precipitate corresponding to dianion **6** was isolated. At −78 °C, a slight precipitate of dianion **6** was observed. However, attempts to precipitate and isolate this dianion on a medium Schlenkware frit failed.

The first thing, therefore, to be determined was whether the initial alkylation did, in fact, occur in the 1-position. The progress of the above reaction was monitored by performing an infrared study of the carbonyl stretching bands (see Figure 1). As observed before for other $(\eta^6$-arene)tricarbonylchromium complex,[2] $(\eta^6{:}\eta^6$-4,4′-dimethylbiphenyl)bis(tricarbonylchromium) (**5**) displayed two sharp carbonyl bands in THF at 1958 and 1894 cm^{-1} (spectrum A). These bands disappeared upon reduction with lithium naphthalenide, while new bands appeared at 1896, 1883, 1795, and 1709 cm^{-1} (spectrum B). The observed new frequencies are consistent with the proposed structure **6**, since a shift in carbonyl stretching frequencies to lower wavenumbers, along with an increase in the number of IR-active bands, suggests a lowering of symmetry at the chromium atoms and a change in the $-Cr(CO)_3$ bonding going from η^6 to η^5.[20,21] Addition of heptyl

(20) For a theoretical discussion of η^5-cyclohexadienyl complexes, see: (a) Hoffmann, R.; Hoffmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598. (b) Paquette, L. A.; Daniels, R. G.; Gleiter, R. *Organometallics* **1984**, *3*, 560.

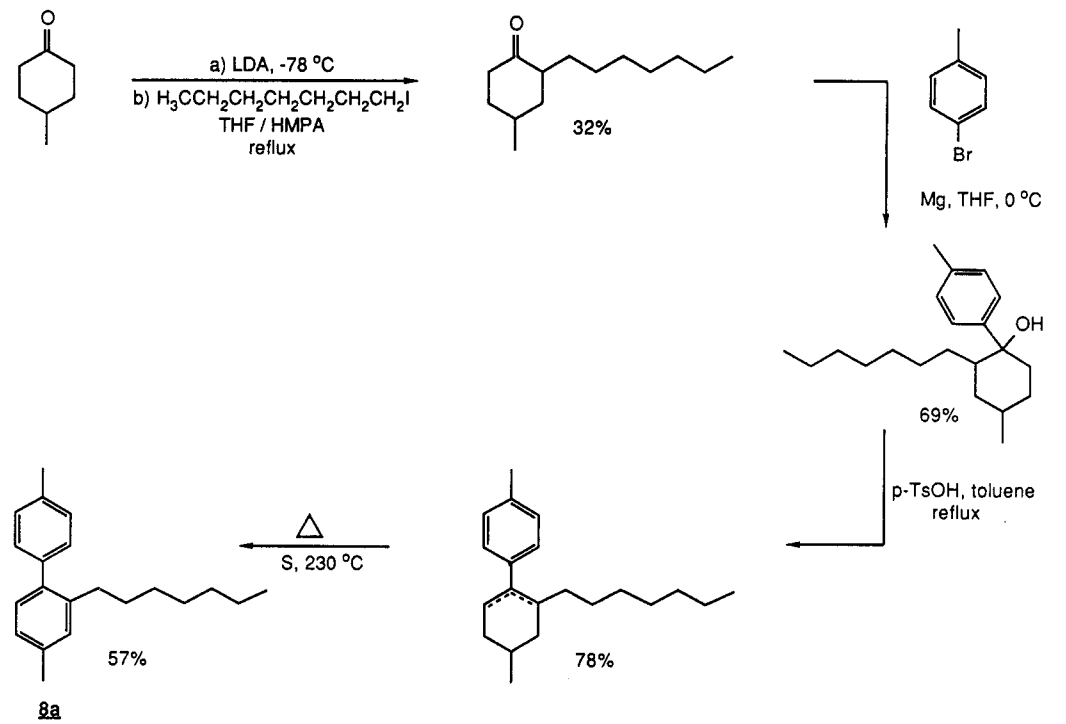
(21) For some $(\eta^5$-cyclohexadienyl)metal–tricarbonyl complexes and their spectra see: (a) Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2479. (b) Fischer, E. O.; Schmidt, M. W. *Chem. Ber.* **1967**, *100*, 3782. (c) Churchill, M. F.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950. (d) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024. (e) Walker, P. J. C.; Mawby, R. *Inorg. Chim. Acta* **1973**, *7*, 621. (f) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1976**, *15*, 874. (g) Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2069. (h) Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207. (i) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1980**, *102*, 3490. (j) Sievert, A. C.; Muetterties, E. Z. *Inorg. Chem.* **1981**, *20*, 2276. (k) Chung, Y. K.; Wilhard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053. (l) Ceccon, A.; Gambaro, A.; Romanin, A. M.; Venzo, A. *J. Organomet. Chem.* **1983**, *254*, 199. (m) Werner, R.; Werner, H.; Burschka, C. *Chem. Ber.* **1984**, *117*, 142, 152, 161.

Table II. Reduction of (η^6:η^6-4,4′-Dimethylbiphenyl)bis(tricarbonylchromium) with Lithium Naphthalenide, Followed by Reaction with 1 Equiv of Electrophiles and Oxidation with Iodine

			% product distrib[a]		ratio of alkylated products[b]	
						
entry	electrophile	reagent		alkylated products 8 + 9	8 1,2-alkyl shift	9 1,2-aryl shift
a	$H_3CCH_2CH_2CH_2CH_2CH_2CH_2^+$	$H_3CCH_2CH_2CH_2CH_2CH_2CH_2Br$	20	66	28	72
		$H_3CCH_2CH_2CH_2CH_2CH_2CH_2I$	17	83	32	68
b	$H_3CCH_2CH_2CH_2^+$	$H_3CCH_2CH_2CH_2Br$	10	64	30	70
		$H_3CCH_2CH_2CH_2I$	8	85	31	69
c	$H_3CCH_2^+$	H_3CCH_2Br	11	62	30	70
d	$H_2C{=}CHCH_2^+$	$H_2C{=}CHCH_2OTs$	44	17	100	00
e	$HC{\equiv}C{-}CH_2^+$	$HC{\equiv}C{-}CH_2OTs$	67	33	74	26
f	$H_2C{=}CHCH_2CH_2CH_2CH_2^+$	$H_2C{=}CHCH_2CH_2CH_2CH_2Br$	21	79	28	72
g	$H_2C{=}CHCH_2CH_2^+$	$H_2C{=}CHCH_2CH_2Br$	71	28	26	74
h			73	27	86 of **8g**	14
i	$(H_3C)_2CHCH_2^+$	$(H_3C)_2CHCH_2Br$	14	86	21	79

[a] Determined by GC. [b] Determined from ^1H NMR spectrum, by integrating the signals of the methyl group in the alkylated ring.

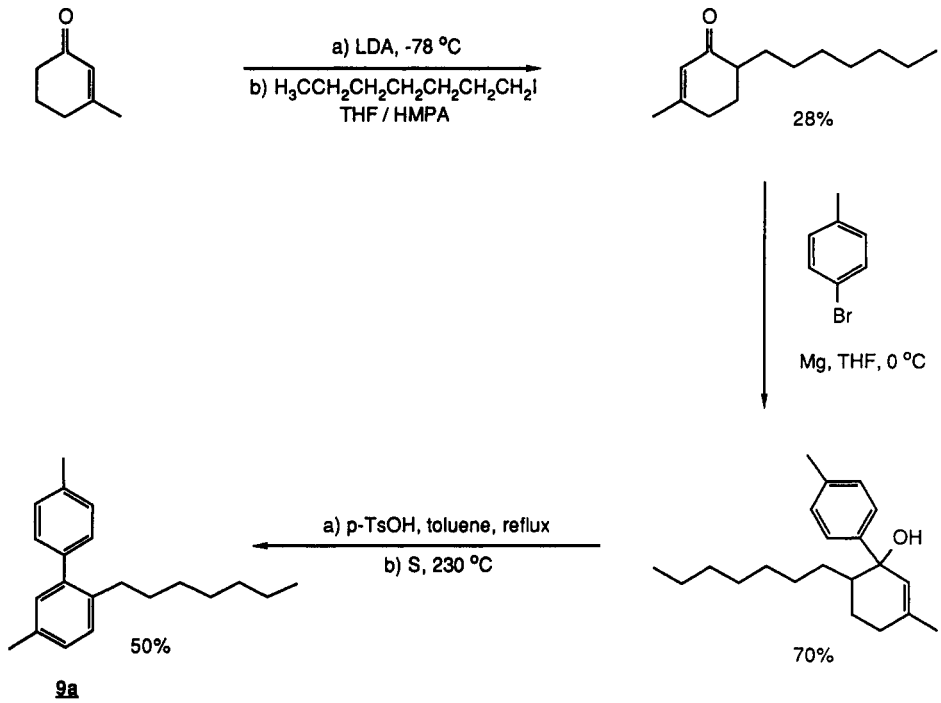
Scheme VI



iodide resulted in a reemergence of bands at higher wavenumbers, along with ones at lower wavenumbers (spectrum C). Such an increase in the number of bands is consistent with the formation of a monoanion and is in agreement with our previous work on the biphenyl system.[2,3] In spectrum C, the bands observed at 1954 and 1896 cm^{-1} point out the presence of a $-Cr(CO)_3$ group η^6-coordinated to a phenyl ring, while the bands at 1873, 1818, and 1801 cm^{-1} are due to the other $-Cr(CO)_3$, η^5-coordinated to a cyclohexadienyl anion, substituted by the heptyl group in the 1-position. Protonation of the alkylated monoanion with 1 equiv of trifluoroacetic acid, resulted in an increase in intensity of the two bands at 1959 and 1884 cm^{-1} and a nearly complete disappearance of the lower wavenumber bands (spectrum D). Such a change upon trifluoroacetic acid addition is indicative of the loss of a $Cr(CO)_3$ group, generating a diene species. The less labile $Cr(CO)_3$ group, which is η^6-coordinated to the other phenyl ring, then is cleaved by exposure to air and sunlight, to give the product **7a**. The formation of compound **7a** clearly shows that, as in the case of the biphenyl dianion, the capture of the electrophile does take place exclusively in the 1-position. Scheme V further shows the results of alkylation with various electrophiles followed by protonation with trifluoroacetic acid.

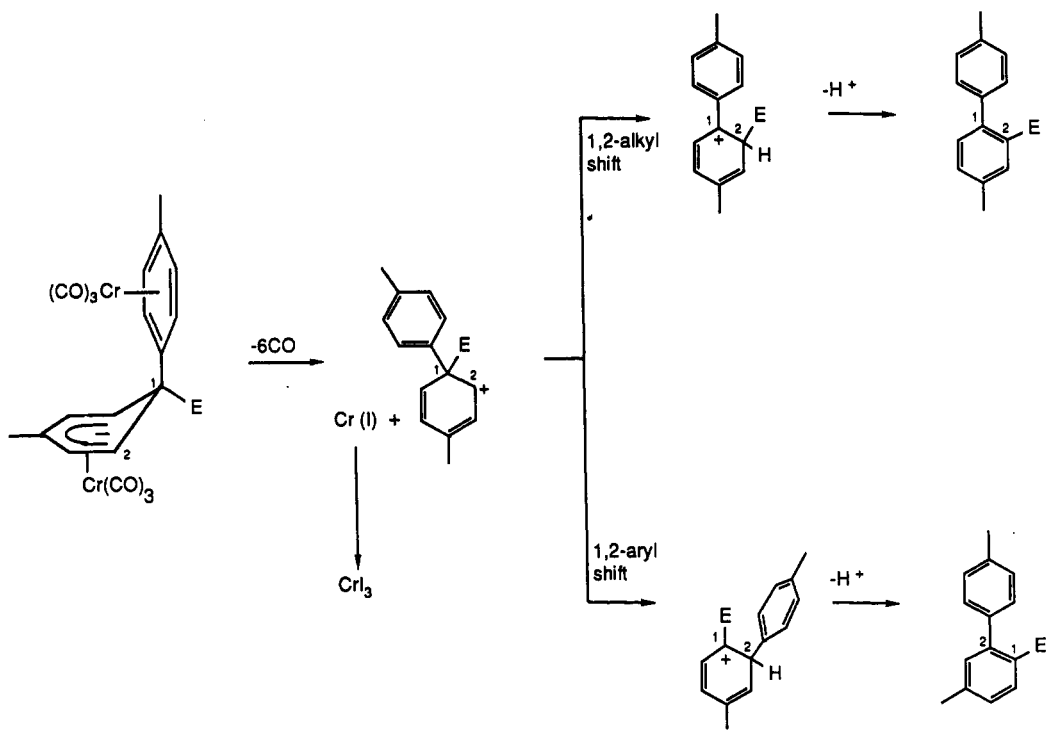
The results of the reaction of dianion **6** with various alkyl halides, followed by oxidation with iodine to yield the two rearranged product isomers **8** and **9**, are shown in Table

Scheme VII



9a

Scheme VIII

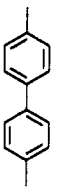
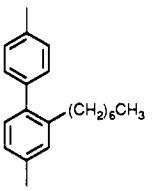
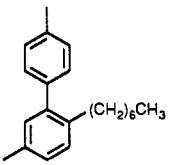
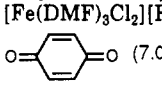


II. Nearly all entries show a 2.60:1.00 preference for aryl migration over alkyl migration. For all cases, the two isomers obtained from rearrangement could not be separated by any means of chromatography. In order to compare the two isomers obtained after rearrangement, an independent synthesis of each of the two isomers for the heptyl-substituted case was carried out (Schemes VI and VII). Using these two isomers as model systems, the ratio of the two isomers in all cases (Table II) was determined by integrating the ^1H NMR signals of the methyl groups in the alkylated ring.

With the exception of allyl tosylate (entry d), propargyl tosylate (entry e), and 1-(bromomethyl)cyclopropane (entry h), virtually all entries displayed a consistent ratio for the migratory preference of the aryl ring over the alkyl substituent. Even when oxidative cleavage of the $Cr(CO)_3$ moieties was carried out with different oxidizing agents (Table III), migratory ratios of aryl to alkyl did not fluctuate drastically. It has been shown that migrating substituents such as aryl, vinyl, and acyl groups, which possess an sp^2-hybridized carbon atom bonded to the atom serving as the origin of the migration, generally migrate more readily than alkyl groups.[22-24] Phenyl migration has been

(22) For competition between aryl and alkyl migration see: (a) House, H. O.; Grubbs, E. J.; Gannon, W. F. *J. Am. Chem. Soc.* **1960**, *82*, 4099. (b) Gremand, J.; Laurent, A. *Bull. Soc. Chim. Fr.* **1967**, 3599.

Table III. Oxidation of the Reaction Mixture Obtained after Reduction of 5 with Lithium Naphthalenide and Alkylation with 1 Equiv of Heptyl Iodide

			% product distrib[a]		ratio of alkylated products[b]	
						
entry	oxidizing agents (no. of equivs)	solvent		alkylated products 8a + 9a	8a 1,2-alkyl shift	9a 1,2-aryl shift
a	$(NH_4)_2Ce(NO_3)_6$ (7.0)	H_3CCN	24	47	29	71
b	anhydrous $FeCl_3$ (12.0)	THF	18	82	43	57
c	anhydrous $CuCl_2$ (12.0)	DMF	16	46	43	57
d	$[Fe(DMF)_3Cl_2][FeCl_4]$ (7.2) (Fe-DMF complex)	THF	14	82	46	54
e	 (7.0)	THF	56	44	42	58
f	O_2 (excess)		16	62	31	69

[a] Determined by GC. [b] Determined from ^1H NMR spectrum, by integrating the signals of the methyl group in the alkylated ring.

observed in the oxidative cleavage (halogenation) of 2-phenethyl-iron bonds,[25] as well as in the cupric chloride induced cleavage of β-phenethyl-palladium bonds.[26]

The mechanism of 1,2 rearrangement could then be explained as follows (Scheme VIII).[27] The oxidative loss of both $-Cr(CO)_3$ groups generates an unstable secondary carbocation which undergoes a 1,2 shift to a more stable tertiary carbocation. The latter then loses a proton, yielding the aromatized product. In our study it is uncertain whether oxidation leads to rearrangement after the removal of the labile η^5-$Cr(CO)_3$ group or whether the η^5-$Cr(CO)_3$ loss is anchimerically assisted by the migrating species. The rather close isomer ratio obtained for different electrophiles and from the use of different oxidizing agents (Table III) suggests that these intramolecular 1,2 shifts may be proceeding through a cationic transition state analogous to the one observed in the dienone–phenol and Wagner–Meerwein rearrangements.[28,29]

An interesting point to note is the reaction with 1-(bromomethyl)cyclopropane (entry h). Oxidation with iodine gave 86% of the 1,2-alkyl shift product **8g**, with the cyclopropyl ring being opened to the 3-butenyl group (entry h). No cyclopropyl ring opening was observed for the minor isomer **9h** (14%) obtained from 1,2-aryl (*p*-tolyl) migration. (This was indicated by the presence of cyclopropane ring peaks in the ^1H and ^{13}C NMR spectra of the purified product.)[30] The formation of compound **8g** in the reaction with 1-(bromomethyl)cyclopropane (entry h) indicates that cyclopropyl ring cleavage occurs in the oxidation–rearrangement step, rather than in the addition step.

In the case of reaction with allyl tosylate, a single isomer resulting from migration of the allyl group was obtained. Similarly, reaction with propargyl tosylate resulted in two isomers, the major being the one where the propargyl group had undergone the 1,2 shift. A possibility does exist, that the alkylated intermediate obtained after the addition of these two electrophiles could also undergo a Cope type rearrangement. However, spectral analysis of the products obtained in both cases ruled out the formation of those isomers that could have been formed from such rearrangements (a complete absence of any allene type structure was observed in the case of reaction with propargyl tosylate).

Conclusion

The reaction of (η^6:η^6-biphenyl)bis(tricarbonylchromium) dianions with a wide variety of primary electrophiles results in an exclusive ipso attack. NMR data showed that protonation of the dianion resulted in the endo isomer. Although it is not unequivocal, evidence suggests that primary alkyl electrophiles react by a direct carbanionic S_N2 attack of the ipso-carbon, to yield a product of overall endo addition. The results of reaction with cyclopropylcarbinyl bromide as well as 6-bromo-1-hexene strongly suggest the operation of an inner-sphere polar S_N2 process for most primary electrophiles. However, easily reduced halides such as allylic and benzylic or those halides which have a steric hindrance toward S_N2 processes may well proceed via an electron-transfer process or a combination of S_N2 and electron-transfer processes. These systems are characterized by both reduced yields and, more impor-

(23) For migratory abilities of various aryl groups see: Bachmann, W. E.; Ferguson, J. W. *J. Am. Chem. Soc.* **1934**, *56*, 2081.

(24) Studies of 1,2 rearrangements involving electron-deficient carbon atoms that differ from the trend aryl > alkyl groups, both in the arrangement of groups and in the order of magnitude of differences between them, have also been reported. (a) Freiss, S. L.; Farnham, N. *J. Am. Chem. Soc.* **1950**, *72*, 5519. (b) Hawthorne, M. F.; Emmons, W. D.; McCallum, K. S. *Ibid.* **1958**, *80*, 6393. (c) Hawthorne, M. F.; Emmons, W. D. *Ibid.* **1958**, *80*, 6398.

(25) (a) Flood, T. C.; Disanti, F. J. *J. Chem. Soc., Chem. Commun.* **1975**, 8. (b) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539.

(26) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 393.

(27) For a comparative study on the electrochemical oxidation of (η^6-arene)$Cr(CO)_3$ complexes, see: (a) Degrand, C.; Radecki-Sudre, A.; Besancon, J. *Organometallics* **1982**, *1*, 1311. (b) Doxsee, K. M.; Grubbs, R. H.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819. (c) Ikeshoji, T.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1985**, *B39*, 797. (d) Zoski, C. G.; Sweigert, D. A.; Stone, N. J.; Reiger, P. H.; Mocellin, E.; Mann, T. F.; Mann, D. R.; Gosser, D. K.; Doeff, M. M.; Bond, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 2109.

(28) Molecular orbital calculations have clearly indicated the unfavorable nature of 1,2-alkyl radical migrations. For 1,2-alkyl shifts, the energy difference between the rearranged radical and the half-migrated state has been calculated by LCAO-MO methods to be an unfavorable +0.41β. Zimmerman, H. E. In *Molecular Rearrangements*; DeMayo, P., Ed.; Interscience: New York, 1963; Vol. I, pp 394–399.

(29) Attempts to observe a vicinal 1,2 shift of an alkyl group by a radical pathway in solution have been made, but they are essentially unknown. (a) Walling, C. In *Molecular Rearrangements*; DeMayo, P., Ed.; Interscience: New York, 1963; Vol. I, pp 416–423. (b) Friedlina, R. Kh. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Academic Press: New York, 1965; Vol. I, pp 263–267.

(30) The ratios of the alkylated products in this case were determined by integrating the signals of the methyl group in the alkylated ring as well as the benzylic methylenes, in the ^1H NMR spectrum of the reaction mixture. The ratio obtained from integrating both types of protons was found to be the same.

tantly, by attack of the electrophiles at all four positions of the aromatic ring. Finally, 1,2-aryl migration has been found to be the major mode of rearrangement in the oxidation of the alkylated dianion of $(\eta^6:\eta^6$-4,4′-dimethylbiphenyl)bis(tricarbonylchromium) (5). Alkylation followed by iodine oxidation of 4,4′-disubstituted biphenyls provides a short convenient approach to 2-alkyl-5,4′-disubstituted biphenyls.

Experimental Section

General Procedures. ^{1}H NMR and ^{13}C NMR spectra were obtained on 360-MHz Nicolet NMC-360 and 50-MHz VXR-200 superconducting NMR spectrometers, respectively. For ^{1}H NMR analysis all peaks were referenced to tetramethylsilane. Double-intensity peaks in ^{13}C NMR spectra are referred to as 2×. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer, neat between NaCl plates or as KBr disks. High-resolution mass spectra were obtained at the Midwest Regional Center for Mass Spectrometry, University of Nebraska—Lincoln, Lincoln, NE. Elemental analyses were performed by Oneida Research Services Inc., Whitesboro, NY.

GC analyses were done on a Hewlett-Packard 5890A gas chromatograph (interfaced with a Perkin-Elmer LC-100 integrator) equipped with a 14 ft × $^1/_8$ in. column of GP 10% SP 2100 on 100–120 Supelcoport. Preparative GC work was done on a Varian 920 gas chromatograph equipped with a 12 ft × $^1/_4$ in. column of GP 10% SP 2100 on 100–120 Supelcoport. Purification of the crude reaction mixture was carried out by means of either (i) column chromatography using hexane as the eluant and silica gel (E. Merck, Cat. No. 7734, 70–230-μm mesh size) as the stationary phase or (ii) preparative thick-layer chromatography using hexane as the eluant and 20 cm × 20 cm silica gel GF plates of 1000-μm thickness (Analtech, Cat. No. 02013) or 2000-μm thickness (Analtech, Cat. No. 02015). More difficult separations for purification were performed either (i) on a Harrison Research Model 7924 T 25 chromatotron using hexane as the eluant and 1 mm thick rotors of silica gel 60PF-254 containing gypsum (E. Merck, Cat. No. 7740) as the stationary phase or (ii) by preparative reversed-phase thick-layer chromatography using 10% H_2O in H_3CCN as the eluant and 20 cm × 20 cm PLKC-18F linear K plates of 1000-μm thickness (Whatman, Cat. No. 4800-840).

All manipulations were carried out on a dual manifold providing vacuum and dry argon. Linde prepurified grade argon was further purified by passing it through a 150 °C catalyst column (BASF R3-11) and then through a column of phosphorus pentoxide followed by a column of granular potassium hydroxide. Tetrahydrofuran (THF), *n*-butyl ether, and toluene were freshly distilled under argon from sodium/potassium alloy. Lithium cut into small pieces and naphthalene were weighed in a Vacuum Atmosphere Co. argon drybox.

Electrochemistry Experiments. All electrochemistry experiments were performed using a PAR Model 173 potentiostat/galvanostat equipped with *iR* feedback compensation in conjunction with a PAR Model 174 polarographic analyzer, a PAR Model 175 universal programmer, and a PAR Model 179 digital coulometer. Electrochemical data were recorded on a Hewlett-Packard Model 7004B X-Y plotter.

All electrochemical experiments were performed in anhydrous solvents under an argon atmosphere in a jacketed electrochemical cell. The working electrode for cyclic voltammetry was a hanging-mercury-dropping electrode (HMDE), which was equipped with a micrometer device which produced an electrode area of 1.38 ± 0.05 mm^2 for every two divisions. A dropping-mercury electrode (DME), with a drop knock of 1 drop/s was employed for polarographic studies. The reference electrode used was Ag/AgCl, saturated NaCl(aq) (±0.042 V from saturated calomel electrode), separated from the bulk electrochemical solution by means of a glass frit. The auxiliary electrode was a platinum screen, similarly buffered with a frit. The electrolyte salts, tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP), were dried under vacuum at 100 °C for 10 h prior to use. Propylene carbonate (PC) was vacuum-distilled using a spinning band distillation apparatus and stored over molecular sieves, until needed.

Reaction of the $(\eta^5:\eta^5$-Biphenyl)bis(tricarbonylchromium) Dianion (2) with Benzyl Halides. Trapping Experiment To Determine the Nature of the Reaction Mechanism. The preparation of the $(\eta^5:\eta^5$-biphenyl)bis(tricarbonylchromium) dianion (2) was carried out as before,[2b] by reducing $(\eta^6:\eta^6$-biphenyl)bis(tricarbonylchromium) (1) with lithium anthracenide in THF at room temperature. The dark brown dianion powder which precipitated out after the reduction was collected under argon on a medium Schlenkware frit, washed with THF, blown dry under argon, and removed to the drybox where it was stored in a freezer at −35 °C. The $(\eta^5:\eta^5$-biphenyl)bis(tricarbonylchromium) dianion (2) weighed in the drybox to a constant weight (0.5 mmol) was loaded into a two-necked round-bottomed flask. After the flask was brought out and connected to the double manifold, 12 mL of THF was injected into it. The internal standard *n*-decane was syringed in, and after the flask was cooled to −78 °C, the benzyl halide was syringed into the stirred brown suspension. After 1 h of stirring at −78 °C, an aliquot (1.0 mL) was transferred by means of a cannula to a test tube under argon at −78 °C. The trapping reagent benzoyl chloride (1.0 mmol) was added to the removed aliquot in the test tube. After the test tube was shaken for 10 min, the aliquot was diluted with diethyl ether and quenched with 1.0 mL of 3.5 mmol of ammonium cerium(IV) nitrate solution in H_3CCN. The quenched aliquot was washed, respectively, with saturated $Na_2S_2O_3$ solution, water, and saturated NaCl solution and then dried over $MgSO_4$. The dried aliquots were analyzed by gas chromatography, using a 12 ft × $^1/_8$ in. column of 3% OV17 on 100–120 mesh size Chromasorb G-AW. Subsequent quenches were removed at −40, −20, and 0 °C and at room temperature and were likewise quenched, worked up, and analyzed by GC. The crude reaction mixture was purified by preparative thick-layer chromatography using 10% diethyl ether in hexane as the solvent system. The identity of the product of trapping, viz., 2-phenylacetophenone, was confirmed by infrared, ^{1}H NMR, and GC mass spectrometry.

Reaction of Benzyllithium[31] with $(\eta^6:\eta^6$-Biphenyl)bis(tricarbonylchromium) (1). Lithium (5.9 mg, 0.86 mmol) and naphthalene (14.0 mg, 1.10 mmol) were stirred in 7 mL of THF at ambient temperature for a period of 2 h, during which time all the lithium pieces were consumed. To the dark green lithium naphthalenide solution under argon was transferred a solution of dibenzylmercury (150.0 mg, 0.40 mmol) in 5 mL of THF. The reaction mixture was stirred at room temperature for 90 min, during which time it turned yellowish gray. This solution was allowed to stand under argon for an additional 30 min, during which time a gray solid mass precipitated out of solution. The supernatant solution was transferred by a cannula to a septum-capped centrifuge tube and centrifuged for 10 min. The transparent amber benzyllithium solution was transferred back to a round-bottomed flask and cooled to −78 °C. The orange solution of $(\eta^6:\eta^6$-biphenyl)$[Cr(CO)_3]_2$ (334.0 mg, 0.78 mmol) in THF (7 mL) was added to the benzyllithium solution. The resultant bright red solution was stirred at −78 °C for 5 min, at 0 °C for 25 min and at room temperature for 2 h. The reaction flask then was cooled to −78 °C and the contents quenched with a solution of iodine (1.4 g, 5.5 mmol) in THF (10 mL). The resulting black solution was stirred overnight as it warmed to room temperature. The GC internal standard *n*-decane (112.0 mg, 0.78 mmol) was then syringed into the reaction mixture. This reaction mixture was diluted with ether, and the ether solution was washed three times with saturated $Na_2S_2O_3$ solution, twice with water, and once with saturated NaCl solution and dried over $MgSO_4$. About 2.0 mL of this solution was kept aside for GC analyses. Rotary evaporation of the solvent ether, followed by purification by preparative TLC, gave 31.0 mg of a colorless oil which was characterized as the product 2-(1-phenylmethyl)biphenyl.

2-(1-Phenylmethyl)biphenyl. ^{1}H NMR ($CDCl_3$): δ 7.13–7.37 (m, 12 H), 6.97 (d, 2 H), 3.95 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 142.24,

(31) The preparation of benzyllithium by stirring lithium pieces and dibenzylmercury in THF (according to the procedure of: Waack, R.; Doran, M. A.; Baker, E. B.; Olah, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 1272) failed to give any significant amounts of benzyllithium. Even after sonication of the two reagents in THF for 10 h, a poor yield of the benzyl anion was obtained. On the other hand carrying out the reduction of dibenzylmercury with a prepared solution of lithium naphthalenide in THF resulted in a quantitative conversion of the organomercurial to benzyllithium.

141.63, 141.43, 138.22, 130.27, 130.09, 129.27, 128.83, 128.20, 128.01, 127.43, 126.86, 126.13, 125.74, 39.02. IR (neat): 3058, 3024, 2952, 2920, 2850, 1599, 1495, 1477, 1452, 1437, 1072, 1009, 750, 700 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 244 (M^+, 100), 167 (M - C_6H_5, 26), 165 (80), 91 (16). High-resolution mass spectrum calcd for $C_{19}H_{16}$: 244.1252. Found: 244.1245.

Preparation of (η^6:η^6-4,4'-Dimethylbiphenyl)bis(tricarbonylchromium) (5). A mixture of THF (35 mL) and *n*-butyl ether (315 mL) was added to a 500-mL round-bottomed flask containing 4,4'-dimethylbiphenyl (4.0 g, 40.8 mmol) and chromium hexacarbonyl (13.6 g, 61.8 mmol) under an argon atmosphere. The mixture was refluxed with stirring for a period of 7 days, during which time it became yellow. It was cooled to 0 °C and suction-filtered to remove the precipitated yellow solid. Sublimation at 55 °C (0.3 mm) resulted in removal of 1.60 g of $Cr(CO)_6$. Increasing the temperature to 110 °C resulted in removal of (η^6-4,4'-dimethylbiphenyl)tricarbonylchromium to leave 6.77 g (36%) of pure yellow crystals of **5**. ^1H NMR ($CDCl_3$): δ 5.68 (d, 4 H, J = 6.54 Hz), 5.25 (d, 4 H, J = 6.51 Hz), 2.22 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 232.35 (*C*=O), 109.28, 102.26, 93.00, 91.85, (Ar *C*), 20.43 (CH_3). IR (THF): 1981, 1958, 1893, 663, 624 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 454 (M^+, 25), 370 (M - 3CO, 17), 342 (M - 4CO, 19), 314 (M - 5CO, 36), 234 (M - $Cr(CO)_6$, 100), 182 (M - $Cr_2(CO)_6$, 16). High-resolution mass spectrum calcd for $C_{20}H_{14}O_6Cr_2$: 453.9601. Found: 453.9605. Anal. Calcd for $C_{20}H_{14}Cr_2O_6$: C, 52.87; H, 3.11; Cr, 22.91; O (by difference), 21.14. Found: C, 53.04; H, 3.15; Cr, 23.34; O (by difference), 20.47.

Reduction of (η^6:η^6-4,4'-Dimethylbiphenyl)[$Cr(CO)_3$]$_2$ (5) with Lithium Naphthalenide, Followed by Reaction with Heptyl Iodide. IR Experiment To Study the Change of Bonding of the $Cr(CO)_3$ Group. The experiment was performed using a 0.025-mm NaCl solvent cell, and the infrared spectra were determined on a Analect RFX-65 FTIR spectrometer interfaced with a Analect ATC-652 286 FTIR data system. Background scans were run on the empty cell and on THF. The backgrounds were then automatically deleted from all the spectra taken. Approximately 100 mg (0.22 mmol) of **5** was stirred under argon in 3 mL of THF for 10 min. A small amount was transferred by cannula into the solvent cell sealed by septa at both ends. The IR spectrum (spectrum A) was determined, and the cell then was cleaned. The reaction flask was cooled to -78 °C, and the solution of **5** was reduced with lithium naphthalenide (obtained by stirring lithium (3.8 mg, 0.55 mmol) and naphthalene (84.6 mg, 0.66 mmol) in THF, at ambient temperatures for 2 h). A small amount of the dark brown reaction mixture obtained after reduction was transferred to the IR cell and the spectrum determined (spectrum B). Heptyl iodide (36 μL, 0.22 mmol) was syringed in neat at -78 °C into the reaction mixture. The reaction mixture was stirred at -78 °C for 10 min and at room temperature for 20 min. A small amount of the resultant brown solution was transferred under argon to the clean IR cell, and the spectrum was taken (spectrum C). The reaction flask was once again cooled to -78 °C and the contents quenched with trifluoroacetic acid (16 μL, 0.22 mmol). After stirring at -78 °C for 10 min and at room temperature for 40 min, a small amount of the solution was transferred into the clean IR cell in order to obtain the spectrum of the protonated species (spectrum D). All spectra were stored on disk and after processing were plotted on a Analect FXO-641 digital plotter.

General Procedure for the Reduction of (η^6:η^6-4,4'-Dimethylbiphenyl)bis(tricarbonylchromium) (5), Followed by Reaction with Electrophiles and Protonation with Trifluoroacetic Acid. Lithium (11.2 mg, 1.62 mmol) and naphthalene (247 mg, 1.93 mmol) were stirred in THF (10 mL) at ambient temperature for a period of 2 h, during which time all the lithium pieces were consumed. The dark green solution was transferred to a stirred yellow solution of **5** (350 mg, 0.77 mmol) in THF (10 mL) at -78 °C. After about 7 min of stirring at -78 °C, the electrophile (0.77 mmol) was syringed neat into the reaction mixture. The reaction mixture was stirred at -78 °C for 10 min, at 0 °C for 40 min, and at room temperature for 60 min. The reaction mixture was once again cooled to -78 °C, and CF_3CO_2H (527.3 mg, 4.62 mmol) was syringed into it. The dark orange solution was continually stirred at -78 °C for 60 min, after which it was poured into 30 mL of NH_4OH. The resultant pale orange solution was suction-filtered to remove the precipitated solids. The organic solution was extracted with ether. The ether extracts were washed once with saturated NaCl solution, dried over $MgSO_4$, and left at room temperature for 3 days, during which time the solution became colorless. Filtration followed by rotary evaporation of the solvent gave the crude product which was purified by preparative thick-layer chromatography.

5-Heptyl-2-methyl-5-(4-methylphenyl)-1,3-cyclohexadiene (7a). Isolated yield: 69%. ^1H NMR (acetone-d_6): δ 7.23 (d, 2 H, J = 8.00 Hz), 7.07 (d, 2 H, J = 7.93 Hz), 5.97 (d, 1 H, J = 9.73 Hz), 5.88 (d, 1 H, J = 9.73 Hz), 5.41 (broad s, 1 H), 2.47 (d, 1 H, J = 17.16, 2.04 Hz), 2.36 (m, 1 H), 2.26 (s, 3 H), 1.79 (m, 1 H), 1.71 (m, 1 H), 1.66 (s, 3 H), 1.20 (broad s, 8 H), 1.09 (m, 2 H), 0.84 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 144.70, 135.01, 134.57, 130.52, 128.68 (2×), 127.33, 126.29 (2×), 119.66, 41.34, 40.79, 37.13, 31.87, 30.38, 29.16, 24.66, 22.62, 20.85, 14.00. IR (neat): 3040, 2950, 2890, 1550, 825 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 282 (M^+, 9), 183 (M - C_7H_{15}, 100). High-resolution mass spectrum calcd for $C_{21}H_{30}$: 282.2347. Found: 282.2342.

2-Methyl-5-(1-cyclopropylmethyl)-5-(4-methylphenyl)-1,3-cyclohexadiene (7h). Isolated yield: 51%. ^1H NMR ($CDCl_3$): δ 7.28 (d, 2 H, J = 8.17 Hz), 7.11 (d, 2 H, J = 7.98 Hz), 6.08 (d, 1 H, J = 9.71 Hz), 5.89 (d, 1 H, J = 9.68 Hz), 5.43 (broad s, 1 H), 2.54 (dd, 2 H, J = 4.22, 2.01 Hz), 2.32 (s, 3 H), 1.77 (dd, 1 H, J = 13.81, 5.77 Hz), 1.71 (d, 3 H, J = 1.57 Hz), 1.61 (dd, 1 H, J = 13.84, 7.05 Hz), 0.42–0.50 (m, 1 H), 0.31–0.39 (m, 2 H), +0.02 to -0.02 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 144.49, 135.07, 130.59, 129.09, 128.60 (2×), 127.23, 126.32 (2×), 119.67, 45.79, 42.17, 36.14, 20.89, 6.99, 5.46, 4.46. IR (neat): 3080, 3010, 2910, 2850, 1510, 1435, 990, 810 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 238 (M^+, 2), 236 (M - H_2, 3), 195 (M - C_3H_7, 11), 183 (M - C_4H_7, 100). High-resolution mass spectrum calcd for $C_{18}H_{22}$: 238.1721. Found: 238.1716.

2-Methyl-5-(4-methylphenyl)-5-(2-methylpropyl)-1,3-cyclohexadiene (7i). Isolated yield: 44%. ^1H NMR ($CDCl_3$): δ 7.23 (d, 2 H, J = 8.23 Hz), 7.07 (d, 2 H, J = 8.04 Hz), 5.99 (d, 1 H, J = 7.94 Hz), 5.85 (dd, 1 H, J = 9.75, 1.42 Hz), 5.40 (broad s, 1 H), 2.49 (dd, 2 H, J = 17.04, 1.85 Hz), 2.30 (s, 3 H), 1.79 (dd, 1 H, J = 13.82, 5.72 Hz), 1.69 (d, 3 H, J = 1.76 Hz), 1.63 (dd, 1 H, J = 13.83, 5.60 Hz), 1.54 (septet, 1 H), 0.75 (d, 3 H, J = 6.58 Hz), 0.74 (d, 3 H, J = 6.60 Hz). ^{13}C NMR ($CDCl_3$): δ 144.74, 135.11, 134.99, 130.60, 128.56, 127.06, 126.29, 119.67, 49.16, 41.58, 37.30, 24.98, 24.75, 24.66, 20.92, 20.88. IR (neat): 3022, 2952, 2922, 2866, 1512, 1466, 1450, 1383, 1365, 812, 750 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 240 (M^+, 9), 238 (M - H_2, 13), 195 (M - C_3H_7, 30), 180 (M - C_4H_9, 100). High-resolution mass spectrum calcd for $C_{18}H_{24}$: 240.1878. Found: 240.1875.

General Procedure for the Reduction of (η^6:η^6-4,4'-Dimethylbiphenyl)bis(tricarbonylchromium) (5), Followed by Reaction with Electrophiles and Oxidation with Iodine. Lithium (8.0 mg, 1.15 mmol) and naphthalene (176 mg, 1.38 mmol) were stirred under argon in THF (7 mL) until all the lithium pieces were consumed (about 2 h). This dark green solution was then transferred by cannula to a yellow stirred solution of (η^6:η^6-4,4'-dimethylbiphenyl)[$Cr(CO)_3$]$_2$ (**5**) (250 mg, 0.55 mmol) in THF (10 mL) at -78 °C. An instantaneous color change from pale yellow to a dark brown was observed. After stirring for an additional 10 min at -78 °C, the electrophile (0.55 mmol) was syringed neat into the reaction mixture. Stirring was maintained at -78 °C for 20 min and continued at 0 °C for 60 min and then at room temperature for an additional 60 min. The dark solution became pale in color as it warmed to room temperature. The reaction mixture was once again cooled to -78 °C and quenched with a solution of iodine (979 mg, 3.85 mmol) in THF (20 mL). The resultant black solution was stirred overnight as it warmed to room temperature. The reaction mixture was then partitioned between ether (20 mL) and saturated $Na_2S_2O_3$ solution (50 mL). The ether layer was washed twice with saturated $Na_2S_2O_3$ solution, twice with water, and once with saturated NaCl solution and dried over $MgSO_4$. GC analysis of the product mixture was performed by injecting the internal standard *n*-decane (78.3 mg, 0.55 mmol) into the reaction mixture prior to the workup.

2-Heptyl-4,4'-dimethylbiphenyl (8a)/2-Heptyl-5,4'-dimethylbiphenyl (9a). ^1H NMR ($CDCl_3$): δ 7.18 (s, 4 H), 7.16 (d, 1 H, J = 7.93 Hz), 7.08 (d, 1 H, J = 7.46 Hz), 7.01 (s, 1 H), 2.52 (t, 2 H), 2.39 (s, 3 H), 2.36 (s, 3 H of minor isomer **8a**), 2.33 (s, 3 H of major isomer **9a**), 1.44 (m, 2 H), 1.17–1.25 (m, 8 H), 0.84 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 141.62, 140.29, 139.24, 139.09,

138.94, 137.38, 136.63, 136.11, 136.03, 134.82, 130.82, 130.03, 129.90, 129.22, 129.09 (2×), 128.63 (2×), 127.84, 126.25, 32.98, 31.71, 31.61, 31.48, 29.73, 29.46, 29.39, 28.99, 22.64, 21.15, 20.91, 14.12, 14.08. IR (neat): 3010, 2930, 2860, 1610, 1500, 1470, 1105, 815 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 280 (M^+, 61), 195 (M − C_6H_{13}, 100), 165 (16). High-resolution mass spectrum calcd for $C_{21}H_{28}$: 280.2191. Found: 280.2190.

2-Butyl-4,4′-dimethylbiphenyl (8b)/2-Butyl-5,4′-dimethylbiphenyl (9b). ^1H NMR ($CDCl_3$): δ 7.18 (s, 5 H), 7.07 (d, 1 H, J = 6.28 Hz), 7.00 (s, 1 H), 2.53 (t, 2 H), 2.39 (s, 3 H), 2.36 (s, 3 H of minor isomer **8b**), 2.33 (s, 3 H of major isomer **9b**), 1.43 (two overlapping quintets, 2 H), 1.22 (two overlapping multiplets, 2 H), 0.79 (two overlapping triplets, 3 H). ^{13}C NMR ($CDCl_3$): δ 141.63, 139.23, 137.32, 136.65, 136.15, 134.85, 130.85, 130.05, 129.91, 129.23, 129.10 (2×), 128.64 (2×), 127.85, 33.72, 32.68, 32.27, 22.60, 22.52, 21.20, 20.93, 13.89. IR (neat): 3020, 2930, 1620, 1495, 1450, 810 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 238 (M^+, 50), 195 (M − C_3H_7, 100), 180 (23), 165 (24). High-resolution mass spectrum calcd for $C_{18}H_{22}$: 238.1721. Found: 238.1721. Anal. Calcd for $C_{18}H_{22}$: C, 90.76; H, 9.24. Found: C, 90.02, H. 9.44.

2-Ethyl-4,4′-dimethylbiphenyl (8c)/2-Ethyl-5,4′-dimethylbiphenyl (9c). ^1H NMR ($CDCl_3$): δ 7.19 (s, 4 H), 7.10 (d, 1 H, J = 7.47 Hz), 7.09 (d, 1 H, J = 7.42 Hz), 7.01 (s, 1 H), 2.57 and 2.56 (two overlapping quartets, 2 H), 2.39 (s, 3 H), 2.37 (s, 3 H of minor isomer **8c**), 2.33 (s, 3 H of major isomer **9c**), 1.09 and 1.08 (two overlapping triplets, 3 H). ^{13}C NMR ($CDCl_3$): δ 141.48, 141.40, 139.13, 138.99, 138.72, 138.62, 136.84, 136.20, 136.12, 134.89, 130.77, 129.99, 129.25, 129.17 (2×), 129.03 (2×), 128.65 (2×), 128.45, 127.99, 126.27, 26.06, 25.69, 21.15 (2×), 20.89, 15.77, 15.69. IR (neat): 3010, 2960, 2920, 1610, 1490, 1005, 810, 790 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 210 (M^+, 60), 195 (M − CH_3, 72), 180 (26), 91 (93), 57 (100). High-resolution mass spectrum calcd for $C_{16}H_{18}$: 210.1408. Found: 210.1408.

4,4′-Dimethyl-2-(2-propenyl)biphenyl (9d). ^1H NMR ($CDCl_3$): δ 7.19 (s, 4 H), 7.13 (d, 1 H, J = 7.77 Hz), 7.09 (s, 1 H), 7.06 (d, 1 H, J = 7.71 Hz), 5.34–5.94 (m, 1 H, C proton of ABC pattern), 4.91–5.03 (ddd, 2 H, AB protons of ABC pattern), 3.31 (d, 2 H, J = 6.35 Hz), 2.39 (s, 3 H), 2.37 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 138.66, 137.94, 137.05, 136.83, 136.28, 130.28, 130.05, 129.42, 129.20, 128.68, 126.82, 115.59, 37.45, 21.16, 21.11. IR (neat): 3080, 3010, 2920, 2860, 1900, 1640, 1610, 1490, 1010, 910 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 222 (M^+, 76), 207 (M − CH_3, 100), 192 (M − $2CH_3$, 65), 182 (67), 181 (M − C_3H_5, 17). High-resolution mass spectrum calcd for $C_{17}H_{18}$: 222.1408. Found: 222.1406.

4,4′-Dimethyl-2-(2-propynyl)biphenyl (8e)/5,4′-Dimethyl-2-(2-propynyl)biphenyl (9e). ^1H NMR ($CDCl_3$): δ 7.42–7.50 (m, 1 H), 7.21 (broad s, 4 H), 7.05–7.12 (m, 2 H), 3.46 (d, 2 H of major isomer **8e**, $^4J_{HH}$ = 2.70 Hz), 3.45 (d, 2 H of minor isomer **9e**, $^4J_{HH}$ = 2.72 Hz), 2.40 (broad s, 6 H), 2.37 (s, 3 H), 2.14 (t, 1 H of major isomer **8e**, $^4J_{HH}$ = 2.72 Hz), 2.12 (t, 1 H of minor isomer **9e**, $^4J_{HH}$ = 2.73 Hz). ^{13}C NMR ($CDCl_3$): δ 141.16, 138.49, 137.94, 137.27, 136.71, 136.62, 136.36, 133.47, 130.75, 129.96, 129.40, 129.10 (2×), 128.91 (2×), 128.78, 128.26, 127.56, 126.78, 82.94, 70.15, 70.03, 22.94, 22.61, 21.14, 21.11, 20.95. IR (neat): 3300, 3020, 2920, 2850, 2100, 1610, 1490, 1005, 810 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 220 (M^+, 80), 205 (M − CH_3, 100). High-resolution mass spectrum calcd for $C_{17}H_{16}$: 220.1252. Found: 220.1244.

2-(5-Hexenyl)-4,4′-dimethylbiphenyl (8f)/2-(5-Hexenyl)-5,4′-dimethylbiphenyl (9f). ^1H NMR ($CDCl_3$): δ 7.18 (broad s, 4 H), 7.15 (d, 1 H, J = 7.74 Hz), 7.07 (d, 1 H, J = 7.54 Hz), 7.00 (broad s, 1 H), 5.65–5.76 (m, 1 H, C proton of ABC pattern), 4.86–4.94 (m, 2 H, AB protons of ABC pattern), 2.53 (two overlapping triplets, 2 H), 2.39 (s, 3 H), 2.34 (s, 3 H of minor isomer **8f**), 2.32 (s, 3 H of major isomer **9f**), 1.93 (m, 2 H), 1.42–1.52 (m, 2 H), 1.25–1.32 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 141.63, 140.00, 139.18, 139.03, 138.94, 138.87, 137.09, 136.66, 136.16, 136.07, 134.90, 130.84, 130.04, 129.87, 129.20, 129.07 (2×), 128.64 (2 ×), 129.86, 126.31, 114.19, 33.45, 32.79, 32.37, 31.29, 30.91, 29.71, 28.70, 28.62, 21.15, 20.90. IR (neat): 3010, 2920, 2850, 1645, 1490, 910, 820 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 264 (M^+, 78), 195 (M − C_5H_9, 100), 180 (47), 165 (44). High-resolution mass spectrum calcd for $C_{20}H_{24}$: 264.1878. Found: 264.1871. Anal. Calcd for $C_{20}H_{24}$: C, 90.91; H, 9.09. Found: C, 90.34; H, 9.35.

2-(3-Butenyl)-4,4′-dimethylbiphenyl (8g)/2-(3-Butenyl)-5,4′-dimethylbiphenyl (9g). ^1H NMR ($CDCl_3$): δ 7.19 (broad s, 4 H), 7.01–7.16 (m, 3 H), 5.68–5.77 (m, 1 H, C proton of ABC pattern), 4.85–4.93 (m, 2 H, AB protons of ABC pattern), 2.64 (t, 2 H), 2.39 (s, 3 H), 2.37 (s, 3 H of minor isomer **8g**), 2.33 (s, 3 H of major isomer **9g**), 2.16–2.23 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 141.72, 139.03, 138.33, 136.74, 136.28, 136.23, 135.17, 130.93, 130.12, 129.91, 129.17, 129.12, 129.03 (2×), 128.72 (2×), 127.89, 126.54, 35.43, 35.32, 32.55, 32.15, 29.72, 29.38, 22.71, 21.17, 21.08, 21.02, 20.94. IR (neat): 3080, 3025, 2920, 2850, 1640, 1610, 1495, 1450, 1110, 910, 810 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 236 (M^+, 14), 195 (M − C_3H_5, 100), 180 (35), 165 (25). High-resolution mass spectrum calcd for $C_{18}H_{20}$: 236.1565. Found: 236.1554.

2-(3-Butenyl)-4,4′-dimethylbiphenyl (8g)/2-(1-Cyclopropylmethyl)-5,4′-dimethylbiphenyl (9h) (from the Reaction with (1-Bromomethyl)cyclopropane). ^1H NMR ($CDCl_3$): δ 7.18 (broad s, 4 H), 7.02–7.10 (m, 3 H), 5.65–5.78 (m, 1 H, of major isomer **8g**, C proton of ABC pattern), 4.85–4.95 (m, 2 H, of major isomer **8g**, AB protons of ABC pattern), 2.65 (t, 2 H of major isomer **8g**), 2.47 (d, 2 H of minor isomer **9h**, J = 6.80 Hz), 2.39 (s, 3 H), 2.37 (s, 3 H of major isomer **8g**), 2.33 (s, 3 H of minor isomer **9h**), 2.17–2.24 (m, 2 H), 0.81–0.88 (m, 1 H of minor isomer **9h**), 0.41–0.44 (m, 2 H of minor isomer **9h**), 0.04–0.08 (m, 2 H of minor isomer **9h**). ^{13}C NMR ($CDCl_3$): δ 139.14, 139.04, 138.90, 138.29, 136.71, 136.18, 130.11, 129.90, 129.64, 129.31, 129.16 (2×), 128.71 (2×), 126.52, 126.46, 37.49, 35.28, 32.56, 29.70, 21.25, 21.14, 21.05, 11.90, 4.83, 0.50. IR (neat): 3060, 3010, 2920, 2860, 1650, 1615, 1490, 1010, 910, 810 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 236 (M^+, 27), 195 (M − C_3H_5, 100), 180 (33), 165 (24). High-resolution mass spectrum calcd for $C_{18}H_{20}$: 236.1565. Found: 236.1559.

4,4′-Dimethyl-2-(2-methylpropyl)biphenyl (8i)/5,4′-Dimethyl-2-(2-methylpropyl)biphenyl (9i). ^1H NMR ($CDCl_3$): δ 7.16 (broad s, 4 H), 7.12 (d, 1 H, J = 7.78 Hz), 7.06 (d, 1 H, J = 7.48 Hz), 7.00 (broad s, 1 H), 2.46 (d, 2 H of minor isomer **8i**, J = 7.07 Hz), 2.44 (d, 2 H of major isomer **9i**, J = 7.23 Hz), 2.38 (s, 3 H), 2.36 (s, 3 H of minor isomer **8i**), 2.32 (s, 3 H of major isomer **9i**), 1.65 (septet, 1 H), 0.76 (d, 6 H, J = 6.61 Hz). ^{13}C NMR ($CDCl_3$): δ 142.10, 139.45, 139.30, 139.02, 136.33, 136.11, 136.00, 135.92, 134.84, 130.88, 130.55, 130.06, 129.79, 129.36, 129.21 (2×), 128.57 (2×), 127.60, 126.26, 42.03, 41.69, 29.65, 22.41 (2×), 21.16, 20.91. IR (neat): 3018, 2952, 2922, 2866, 1610, 1516, 1495, 1464, 1383, 1365, 1109, 823, 806 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 238 (M^+, 50), 195 (M − C_3H_7, 100), 180 (M − C_4H_{10}, 28), 165 (M − C_5H_{13}, 21). High-resolution mass spectrum calcd for $C_{18}H_{22}$: 238.1721. Found: 238.1710.

Procedures for Oxidation with Other Oxidizing Reagents. All reactions employed 0.3 g (0.66 mmol) of $(\eta^6:\eta^6$-4,4′-dimethylbiphenyl$)[Cr(CO)_3]_2$, and the procedure adopted was exactly the same as described above, up to the addition of the oxidizing agent. The internal standard n-decane (0.66 mmol) was added to each of these reactions, 1 h prior to the workup.

(a) Oxidation with Ammonium Cerium(IV) Nitrate. About 2.53 g (4.62 mmol) of the oxidant in H_3CCN (10 mL) was transferred to the reaction mixture at −78 °C. The reaction mixture, after being allowed to stir overnight, during which time it warmed to room temperature, was diluted with ether. The ether solution was washed once with dilute HCl, twice with water, and once with saturated NaCl solution, dried over $MgSO_4$, and purified as before.

(b) Oxidation with Anhydrous Ferric Chloride. Anhydrous ferric chloride (1.29 g, 7.93 mmol) dissolved in THF (10 mL) was transferred to the reaction mixture at −78 °C. The dirty yellow solution was stirred at −78 °C for 1 h and then overnight at room temperature for 12 h. The brownish black solution was diluted with ether, washed once with saturated $Na_2S_2O_3$ solution, twice with saturated NH_4Cl solution, twice with water, once with saturated $NaHCO_3$ solution, and once with saturated NaCl solution, dried over $MgSO_4$, and purified as before.

(c) Oxidation with Anhydrous Cupric Chloride. Anhydrous cupric chloride (1.06 g, 7.93 mmol) in DMF (10 mL) was transferred to the reaction mixture at −78 °C. The dark-colored solution was stirred at −78 °C for 90 min, after which stirring was continued at room temperature for 12 h. The dark blue reaction mixture was diluted with ether and the ether solution washed twice

with NH_4OH–NH_4Cl solution, twice with water, and once with saturated NaCl solution, dried over $MgSO_4$, and purified as before.

(d) Oxidation with Tris(*N*,*N*-dimethylformamide)dichloroferric Tetrachloroferrate (Fe–DMF Complex). The preparation of this reagent was made according to the literature procedure.[32] The Fe–DMF complex (2.60 g, 4.78 mmol) in THF (12 mL) was transferred to the reaction mixture at −78 °C. An instantaneous dark blue-black coloration was observed. After stirring at −78 °C for 40 min, the reaction mixture was stirred at room temperature for 18 h. The dark solution was diluted with ether and washed twice with saturated NH_4Cl solution, twice with water, once with saturated $NaHCO_3$ solution, and once with saturated NaCl solution, dried over $MgSO_4$, and purified as before.

(e) Oxidation with *p*-Benzoquinone. *p*-Benzoquinone (0.5 g, 4.63 mmol) in THF (10 mL) was transferred to the reaction mixture at −78 °C. The dark black solution was stirred overnight, during which time it warmed to room temperature. The solution was diluted with ether and washed once with saturated $Na_2S_2O_3$ solution, once with diluted HCl solution, twice with water, once with saturated $NaHCO_3$ solution, and once with saturated NaCl solution, dried over $MgSO_4$, and purified as before.

(f) Oxidation with Molecular Oxygen. After the brown alkylated reaction mixture was stirred at room temperature for 90 min, the reaction flask was cooled to −78 °C. Dry oxygen was then bubbled into the reaction mixture by means of a syringe needle. During 30 min of bubbling at −78 °C, the reaction mixture turned dark in color. Oxygen addition was maintained for 2 h at 0 °C. The dark gray reaction mixture was diluted with ether and filtered through a 1.5-in. column of Florisil (in air), in order to remove the precipitated black solids. The orange solution was then washed once with saturated NH_4Cl solution, twice with water, once with saturated $NaHCO_3$ solution, and once with saturated NaCl solution, dried over $MgSO_4$, and purified as before.

Preparation of 2-Heptyl-4,4′-dimethylbiphenyl (8a) by an Independent Synthesis. (a) Preparation of 2-Heptyl-4-methylcyclohexanone. Lithium diisopropylamide was generated from *tert*-butyllithium (5.2 mL of 1.7 M solution in hexane, 9.0 mmol) and diisopropylamine (1.37 mL, 9.81 mmol) in THF (15 mL) by mixing the reagents at −78 °C under argon and stirring at 0 °C for 20 min. The colorless solution was cooled to −78 °C and 4-methylcyclohexanone (1.0 g, 8.91 mmol) in THF (7 mL) was added. The reaction mixture was stirred at 0 °C for 20 min and at room temperature for 10 min, after which it was once again cooled to −78 °C and HMPA (2 mL) was added, followed by heptyl iodide (1.46 mL, 8.91 mmol). After 30 min at 0 °C, 60 min at room temperature, and 2 h at reflux, the reaction flask was cooled and its contents quenched with saturated NH_4Cl solution. The quenched solution was extracted twice with ether, and the combined ether layers were washed twice with saturated $NaHCO_3$ solution and once with saturated NaCl solution and dried over $MgSO_4$. Filtration followed by rotary evaporation of solvent gave 1.61 g of a yellow oil. Purification by column chromatography (5% ethylacetate in hexane) gave 32% of pure 2-heptyl-4-methylcyclohexanone. ^1H NMR ($CDCl_3$): δ 2.25–2.40 (m, 3 H), 1.90–2.12 (m, 3 H), 1.20–1.40 (broad s, 12 H), 1.05–1.20 (m, 2 H), 1.00 (d, 3 H, J = 6.47 Hz), 0.90 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 212.86, 49.64, 42.41, 41.59, 36.01, 32.19, 31.83, 29.78, 29.18, 29.03, 27.14, 22.60, 21.28, 13.97. IR (neat): 2970, 2930, 2860, 1720, 1465, 1380, 1130 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 210 (M^+, 58), 138 (9), 125 (34), 112 (100), 97 (17), 55 (49). High-resolution mass spectrum calcd for $C_{14}H_{26}O$: 210.1984. Found: 210.1978.

(b) Preparation of 2-Heptyl-4-methyl-1-(4-methylphenyl)-1-cyclohexanol. A mixture of Mg (83 mg, 3.42 mmol), THF (5 mL), 4-bromotoluene (150 μL), and 1,2-dibromoethene (100 μL) was allowed to react. Further 4-bromotoluene (a total of 0.56 g, 3.26 mmol) was added until all the Mg dissolved. The reacton flask was then cooled to 0 °C, and 2-heptyl-4-methylcyclohexanone (0.327 g, 1.55 mmol) in THF (7 mL) was added. After 15 min of stirring at 0 °C, the reaction mixture was stirred at room temperature for 1 h. The reaction was then cooled to 0 °C, quenched with the saturated NH_4Cl solution, and extracted twice with diethyl ether. The combined ether extracts were washed twice with saturated $NaHCO_3$ solution and once with saturated NaCl solution and dried over $MgSO_4$. Filtration followed by rotary evaporation of the solvent gave 0.446 g of a viscous oily compound. Purification by column chromatography (5% ethyl acetate in hexane) gave 0.324 g (69%) of the pure 2-heptyl-4-methyl-1-(4-methylphenyl)-1-cyclohexanol. ^1H NMR ($CDCl_3$): δ 7.30 (d, 2 H, J = 7.84 Hz), 7.14 (d, 2 H, J = 7.94 Hz), 2.33 (s, 3 H), 1.70–1.80 (m, 4 H), 1.50–1.62 (m, 3 H), 1.32–1.44 (m, 1 H), 1.12–1.60 (m, 13 H), 0.97 (d, 3 H, J = 6.12 Hz), 0.83 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 145.59, 135.53, 128.74 (2×), 124.66 (2×), 75.92, 44.81, 41.92, 36.27, 32.58, 31.79, 30.80, 29.60 (2×), 29.13, 27.46, 22.62, 22.57, 20.88, 14.01. IR (neat): 3500, 2940, 2860, 1540, 1460, 1020, 810 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 302 (M^+, 10), 186 (7), 147 (100), 112 (27). High-resolution mass spectrum calcd for $C_{21}H_{34}O$: 302.2610. Found: 302.2615.

(c) Preparation of 2-Heptyl-4-methyl-1-(4-methylphenyl)-1-cyclohexene and 6-Heptyl-4-methyl-1-(4-methylphenyl)-1-cyclohexene. A round-bottomed flask equipped with a condenser was charged with 0.190 g (0.63 mmol) of the above prepared alcohol and 12 mg (0.63 mmol) of *p*-toluenesulfonic acid in toluene (7 mL). The contents were brought to a reflux for 3 h. The flask was cooled, and the contents were diluted with ether. The ether solution was washed twice with saturated $NaHCO_3$ solution and once with saturated NaCl solution and dried over $MgSO_4$. Filtration followed by rotary evaporation of the solvent gave 0.17 g of a yellow liquid. Purification by column chromatography (5% ethyl acetate in hexane) gave 0.140 g (78%) of the isomeric alkenes. A small amount of the mixture was separated by means of preparative GC for characterization of the structures.

2-Heptyl-4-methyl-1-(4-methylphenyl)-1-cyclohexene. ^1H NMR ($CDCl_3$): δ 7.10 (d, 2 H, J = 7.72 Hz), 6.98 (d, 2 H, J = 7.88 Hz), 2.33 (s, 3 H), 2.20–2.30 (m, 2 H), 2.05–2.15, (m, 1 H), 1.70–1.95 (m, 5 H), 1.10–1.40 (m, 11 H), 1.00 (d, 3 H, J = 5.64 Hz), 0.85 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 141.66, 135.16, 132.62, 132.23, 128.63 (2×), 128.27 (2×), 37.63, 34.12, 32.70, 31.80 (2×), 29.48, 29.13, 29.04, 28.38, 22.64, 21.79, 21.05, 14.00. IR (neat): 2930, 2860, 1510, 1460, 1380, 810 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 284 (M^+, 72), 199 (M − C_6H_{13}, 59), 186 (M − C_7H_{14}, 30), 157 (38), 143 (100), 128 (30), 105 (75). High-resolution mass spectrum calcd for $C_{21}H_{32}$: 284.2504. Found: 284.2514.

6-Heptyl-4-methyl-1-(4-methylphenyl)-1-cyclohexene. ^1H NMR ($CDCl_3$): δ 7.20 (d, 2 H, J = 8.03 Hz), 7.08 (d, 2 H, J = 7.94 Hz), 5.74–5.83 (m, 1 H), 2.65 (m, 1 H), 2.33 (s, 3 H), 2.17–2.23 (m, 1 H), 1.68–1.80 (m, 4 H), 1.10–1.28 (m, 12 H), 0.99 (d, 3 H, J = 5.67 Hz), 0.85 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 142.03, 135.95, 128.87, 128.66, 126.47, 126.16, 126.11, 124.28, 38.59, 37.23, 36.21, 35.13, 35.05, 34.94, 34.35, 33.42, 31.88, 31.82, 29.72, 29.64, 29.27, 28.98, 28.03, 26.04, 23.53, 22.65, 22.23, 22.06, 21.03, 20.99. IR (neat): 3020, 2930, 2860, 1515, 1455, 800 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 284 (M^+, 13), 199 (M − C_6H_{13}, 7), 186 (M − C_7H_{14}, 100). High-resolution mass spectrum calcd for $C_{21}H_{32}$: 284.2504. Found: 284.2513.

(d) Preparation of 2-Heptyl-4,4′-dimethylbiphenyl (8a). The mixture of the two isomeric alkenes (82 mg, 0.29 mmol) in a few drops of diethyl ether was introduced into an ampule, along with elemental sulfur (27 mg, 0.87 mmol). The ampule was sealed under vacuum after removal of the ether. The sealed ampule was then placed in a muffle furnace maintained at 230 °C, for 15 min, after which it was removed and cut open in a hood so as to vent the H_2S vapors. The contents of the broken ampule were rinsed with hexane. Filtration followed by rotary evaporation of the solvent then resulted in 56 mg of a yellow oil which was purified by column chromatography (hexane) to give 46 mg (57%) of pure **8a**. ^1H NMR ($CDCl_3$): δ 7.18 (s, 4 H), 7.08 (d, 2 H), 7.02 (d, 1 H, J = 7.68 Hz), 2.53 (t, 2 H), 2.39 (s, 3 H), 2.37 (s, 3 H), 1.46 (m, 2 H), 1.18 (broad s, 8 H), 0.85 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 140.33, 139.23, 139.05, 136.61, 136.04, 130.04, 129.91, 129.26 (2×), 128.64 (2×), 126.25, 33.03, 31.71, 31.41, 29.45, 28.97, 22.61, 21.10 (2×), 13.99. IR (neat): 3050, 2930, 2860, 1610, 1490, 1460, 1010, 810 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 280 (M^+, 79), 195 (M − C_6H_{13}, 100), 180 (26), 165 (25). High-resolution mass spectrum calcd for $C_{21}H_{28}$: 280.2191. Found: 280.2191.

Preparation of 2-Heptyl-5,4′-dimethylbiphenyl (9a) by an Independent Synthesis. (a) Preparation of 6-Heptyl-3-methylcyclohex-2-en-1-one. Lithium diisopropylamide was generated from *n*-butyllithium (3.8 mL of 2.5 M solution in hexane,

(32) Tobinaga, S.; Kotani, E. *J. Am. Chem. Soc.* **1972**, *94*, 309.

9.5 mmol) and diisopropylamine (1.33 mL, 9.5 mmol) in THF (15 mL) by mixing the reagents under argon at −78 °C and stirring them at 0 °C for 30 min. The colorless solution was cooled to −78 °C, and HMPA (2 mL) was syringed in. After 10 min of stirring at −78 °C, 3-methylcyclohex-2-en-1-one (0.75 g, 6.8 mmol) in THF (2 mL) was added and the resultant yellow solution was stirred at −78 °C for 30 min. Heptyl iodide (2.80 mL, 17.0 mmol) in THF (1 mL) was then gradually dripped into the reaction mixture at −78 °C. After 30 min at −78 °C, 60 min at 0 °C and 120 min at room temperature, the reaction flask was cooled to 0 °C and the contents quenched with a saturated solution of NH_4Cl. The quenched solution was extracted twice with ether. The combined ether extracts were washed twice with saturated $NaHCO_3$ solution and once with saturated NaCl solution and dried over $MgSO_4$. Filtration, followed by rotary evaporation of the solvent, gave 2.53 g of an orange viscous oil. Purification by preparative TLC (5% ethyl acetate in hexane) yielded 0.39 g (28%) of 6-heptyl-3-methylcyclohex-2-en-1-one. ^1H NMR ($CDCl_3$): δ 5.82 (s, 1 H), 2.30 (t, 2 H), 2.16 (m, 1 H), 2.09 (m, 1 H), 1.93 (s, 3 H), 1.80 (m, 1 H), 1.72 (m, 1 H), 1.28 (broad m, 11 H), 0.87 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 201.46, 160.58, 126.40, 45.45, 31.82, 30.11, 29.67, 29.24, 29.16, 27.65, 27.07, 23.92, 22.59, 13.96. IR (neat): 2915, 2860, 1675, 1380, 1200 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 208 (M^+, 3), 110 (M − C_7H_{14}, 100), 82 (21). High-resolution mass spectrum calcd for $C_{14}H_{24}O$: 208.1827. Found: 208.1835.

(b) Preparation of 6-Heptyl-3-methyl-1-(4-methylphenyl)cyclohex-2-en-1-ol. A mixture of Mg (65 mg, 2.71 mmol), THF (5 mL), 4-bromotoluene (150 μL), and 1,2-dibromoethane (100 μL) was allowed to react. Further 4-bromotoluene (a total of 0.43 g, 2.5 mmol) was added until all the Mg dissolved. The reaction flask was then cooled to 0 °C, and 6-heptyl-3-methylcyclohex-2-en-1-one in THF (3 mL) was added. After 15 min at 0 °C and 60 min at room temperature, the reaction mixture was quenched with a saturated solution of NH_4Cl at 0 °C. The quenched solution was extracted twice with ether. The combined ether extracts were washed twice with saturated $NaHCO_3$ solution and once with saturated NaCl solution and dried over $MgSO_4$. Filtration followed by rotary evaporation of the solvent gave 0.53 g of a yellow liquid. Purification by column chromatography (5% ethyl acetate in hexane) yielded 0.21 g (70%) of pure 6-heptyl-3-methyl-1-(4-methylphenyl)cyclohex-2-en-1-ol. ^1H NMR ($CDCl_3$): δ 7.27 (d, 2 H, J = 8.12 Hz), 7.11 (d, 2 H, J = 8.04 Hz), 5.38 (s, 1 H), 2.33 (s, 3 H), 2.04 (m, 2 H), 1.80 (m, 1 H), 1.72 (s, 3 H), 1.64 (s, 1 H), 1.60 (m, 4 H), 1.28 (m, 2 H), 1.00–1.22 (broad m, 8 H), 0.83 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 144.66, 137.71, 135.63, 128.90, 128.43 (2×), 125.64 (2×), 74.63, 44.86, 31.80, 30.75, 29.61, 29.13, 28.10, 27.54, 23.85, 23.48, 22.61, 20.95, 14.05. IR (neat): 3450, 3050, 2940, 2860, 1660, 1515, 820 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 282 (M − H_2O, 23), 197 (11), 105 (17). High-resolution mass spectrum, M^+ ion not observed, however calcd for $C_{21}H_{30}$ (i.e. M − H_2O): 282.2347. Found: 282.2357.

(c) Preparation of 2-Heptyl-5,4′-dimethylbiphenyl (9a). A round-bottomed flask equipped with a condenser was charged with 0.134 g (0.45 mmol) of the above prepared alcohol and 25 mg (0.13 mmol) of *p*-toluenesulfonic acid in toluene (5 mL). The reaction mixture was brought to a reflux for 2 h, after which the flask was cooled and the contents quenched with saturated NH_4Cl solution. The quenched solution was extracted twice with diethyl ether. The combined ether extracts were washed twice with saturated $NaHCO_3$ solution and once with saturated NaCl solution and finally dried over $MgSO_4$. Filtration followed by rotary evaporation of the solvent gave 0.136 g of a dark yellow compound. Purification by column chromatography using hexane as an eluant gave 72 mg of an unknown compound and 18 mg of the biphenyl **9a**. About 55 mg of the unknown yellow compound, dissolved in a few drops of diethyl ether was introduced along with elemental sulfur (12 mg, 0.4 mmol) in an ampule. The ampule was sealed under vacuum after removal of the ether. The sealed ampule was placed in a muffle furnace maintained at 230 °C for 10 min. After removal from the furnace, the ampule was cooled and cut open in a hood, so as to evacuate the H_2S vapors. The contents of the broken ampule was rinsed with CCl_4. Filtration, followed by rotary evaporation of the solvent gave 49 mg of a yellow oil which was purified by column chromatography (hexane) to give the pure biphenyl **9a**. ^1H NMR ($CDCl_3$): δ 7.19 (broad s, 4 H), 7.16 (d, 1 H, J = 7.91 Hz), 7.08 (d, 1 H, J = 7.86 Hz), 7.00 (s, 1 H), 2.52 (t, 2 H), 2.40 (s, 3 H), 2.33 (s, 3 H), 1.44 (m, 2 H), 1.17 (broad s, 8 H), 0.84 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 141.59, 139.21, 137.38, 136.14, 134.83, 130.82, 129.07 (2×), 128.62 (2×), 127.83, 32.54, 31.69, 31.46, 29.38, 28.98, 22.63, 21.16, 20.92, 14.07. IR (neat): 3050, 2920, 2850, 1620, 1495, 1460, 820 cm^{-1}. Mass spectrum, m/e (ion, relative intensity): 280 (M^+, 44), 195 (M − C_6H_{13}, 100), 180 (21), 165 (18). High-resolution mass spectrum calcd for $C_{21}H_{28}$: 280.2191. Found: 280.2199.

Acknowledgment. The financial support provided by the National Science Foundation (Grant CHE-8719728) is gratefully acknowledged. We also thank Dr. Richard K. Shoemaker for able assistance during the IR study on the FTIR instrument.

Registry No. 1, 33010-84-3; 2, 136827-41-3; 5, 136892-75-6; 6, 136827-42-4; 7a, 136827-17-3; 7h, 136827-18-4; 7i, 136827-19-5; 8a, 136827-20-8; 8b, 136827-21-9; 8c, 136827-22-0; 8e, 136827-23-1; 8f, 136827-24-2; 8g, 136827-25-3; 8i, 136827-26-4; 9a, 136827-27-5; 9b, 136827-28-6; 9c, 136827-29-7; 9d, 136827-30-0; 9e, 136827-31-1; 9f, 136827-32-2; 9g, 136827-33-3; 9h, 136827-34-4; 9i, 136827-35-5; $(\eta^6:\eta^6$-4,4′-dimethoxybiphenyl)bis(tricarbonylchromium), 122619-75-4; 2-(phenylmethyl)biphenyl, 606-97-3; 2-heptyl-4-methylcyclohexanone, 3313-60-8; 2-heptyl-4-methyl-1-(4-methylphenyl)-1-cyclohexanol, 136827-36-6; 2-heptyl-4-methyl-1-(4-methylphenyl)cyclohex-1-ene, 136827-37-7; 6-heptyl-4-methyl-1-(4-methylphenyl)-1-cyclohexene, 136827-38-8; 6-heptyl-3-methylcyclohex-2-en-1-one, 136827-39-9; 6-heptyl-3-methyl-1-(4-methylphenyl)cyclohex-2-en-1-ol, 136827-40-2; 4-methylcyclohexanone, 589-92-4; 3-methylcyclohex-2-en-1-one, 1193-18-6.