An Induced Barrier to Rotation About the η^6-Arene–Metal Bond in Centrally Bound *bent*-Terphenylenechromium Tricarbonyl: A Gauge for Aromatic Character and Bond Localization?

Mitchell Nambu and Jay S. Siegel*

Department of Chemistry, University of California
San Diego, La Jolla, California 92093

Received February 12, 1988

Due to the highly symmetric nature of an η^6-metal–arene bond one finds that the approximation of free rotation holds better for metal–arene dynamics than for ethane dynamics.[1] Select examples that violate this assumption have appeared[2] though few have been demonstrated rigorously.[3] No example of an unencumbered neutral arene complex with a restricted metal–arene rotor has been cited.

Theoretical work in this area has been pursued by Hoffmann and co-workers.[7] They looked at the effect of completely localizing the arene π system to one Kekulé resonance form (cyclohexatriene) on the metal–arene barrier to rotation. For the two extremes, alternate single/double-[$D_{3}h$] **1** versus delocalized-[$D_{6}h$] **2**, they found barriers of ca. 20 kcal/mol and ca. 0 kcal/mol, respectively. The ground-state conformation for the cyclohexatriene-like ligand has the carbonyls bisecting the single bonds (pseudooctahedral); the transition conformation has the carbonyls bisecting the double bonds (pseudotrigonalprismatic).[8]

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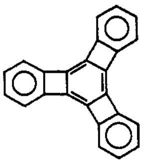
These extremes, though easy to attain by calculational techniques, are no small task for experimentalists. Thus motivated, we set out to test Hoffmann's prediction. We present here our findings of the first example of restricted rotation in metal–arene π complex due to localized π character of the bound arene.

Benzocyclobutane structures have been noted to show bond alternation in the arene geometry.[10] The bond alternation in simple benzocyclobutanes is rather slight. The greatest degree of bond alternation is seen in compound **3**. However, in designing a system to study tripod rotation, it is important to regulate the symmetry as well as the geometry of the system. Arenes of threefold symmetry such as **3** are useless because their symmetry masks the process one wishes to probe. Desymmetrization of **3**, either by removal of one ring (vide infra) or substitution of one of the rings, would then yield a desired system.



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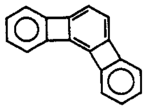

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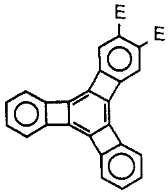

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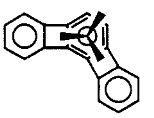
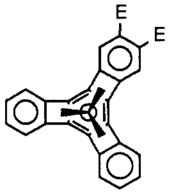
From the above considerations the ideal arene for our initial study is the bent terphenylene **4**. A synthesis of **4** has been presented by Diercks and Vollhardt.[12] We were able to repeat this procedure to produce **4** in quantity sufficient to run complexation studies. Treatment of **4** with $Cr(CO)_3(NH_3)_3$ in dry dioxane at reflux for 4–5 h yielded a mixture of regioisomers from which the centrally bound complex can be isolated by chromatography on silica gel with 10% ethyl acetate/hexane. From 100 mg of **4** about 10 mg of **4-Cr** can be isolated as orange-reddish needles.[13]



4-Cr



5-Cr

Variable temperature ^{13}C NMR experiments were run at 125 MHz in order to ascertain the barrier to tripod rotation. Decoalescence of the ^{13}C enriched carbonyl signals is seen at 195 K, sharpening to a 2:1 doublet ($\Delta\nu$ = 145 Hz) at 170 K. The major peak is found up field which is consistent with the calculated ground-state geometry of **1**[7] and the crystal structure of biphenylene chromium tricarbonyl.[9] The up field shift comes from the anisotropic shift of the "wing" arenes. By using the Gutowsky–Holm approximation,[14] a coalescence temperature of 200 ± 5 K, and a chemical shift difference of 145 Hz one can conclude that the barrier to rotation is 9.4 ± 0.5 kcal/mol.

Starting from Hoffmann's value of 19.4 kcal/mol for the barrier in a completely localized system we can estimate an expected value for **4-Cr**. The bond alternation in **4** is seen geometrically as an average single bond length of 1.45 Å and an average double bond length of 1.35 Å.[12] These lengths correspond to Pauling bond orders of 1.38 and 1.91, respectively.[15] Assuming, tenuous though it may be, that barrier height correlates linearly with bond order one would predict the barrier in **4** to be about 53% of that calculated by Hoffmann (i.e., ca. 10.3 kcal/mol). Considering the crude nature in which we arrived at this estimate there seems to be excellent agreement between theory and experiment.

In order to test our assumption that there exists a linear correlation between bond order and barrier to rotation it will be

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(1) Most barriers for tripod rotation are well below the 3 kcal/mol associated with C–C rotation in ethane. Early studies on these dynamics include the following: (a) Chiu, N.-S.; Schäfer, L.; Seip, R. *J. Org. Met. Chem.* **1975**, *101*, 331. (b) Price, J. T.; Sorensen, T. S. *Can. J. Chem.* **1968**, *46*, 515. (c) Delise, P.; Allegra, G.; Mognaschi, E. R.; Chieroico, A. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 207.

(2) (a) Hu, X.; Duchowski, J.; Pomeroy, R. K. *J. Chem. Soc., Chem. Commun.* **1988**, in press. (b) Pomeroy, R. K.; Harrison, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 661. (c) Acampora, M.; Ceccon, A.; Dal Farra, M.; Giacometti, G.; Rigatti, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 483.

(3) A controversy over the barrier in hexaethylbenzenechromium tricarbonyl still exists.[4] McGlinchey and co-workers[5] believe the barrier to be as high as 11 kcal/mol; Mislow and co-workers[6] believe the barrier is unlikely to exceed ca. 5 kcal/mol.

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(5) (a) McGlinchey, M. J.; Fletcher, J. L.; Sayer, B. G.; Bougeard, P.; Faggiani, R.; Lock, C. J. L.; Bain, A. D.; Rodger, C.; Kündig, E. P.; Astruc, D.; Hamon, J.-R.; Le Maux, P.; Top, S.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1983**, 634. (b) McGlinchey, M. J.; Bougeard, P.; Sayer, B. G.; Hofer, R.; Lock, C. J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 789.

(6) (a) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. (b) Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 172.

(7) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(8) This is consistent with the crystallographic work of Albright on biphenylenechromium tricarbonyl.[9]

(9) Rogers, R. D.; Atwood, J. L.; Albright, T. A.; Lee, W. A.; Rausch, M. D. *Organometallics* **1984**, *3*, 263.

(10) (a) Giovannini, E.; Vuilleumier, H. *Helv. Chim. Acta* **1977**, *60*, 1452. (b) Thummel, R. P. *J. Am. Chem. Soc.* **1976**, *98*, 628. (c) Thummel, R. P.; Nutakul, W. *J. Org. Chem.* **1977**, *42*, 300.

(11) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150.

(12) Diercks, R.; Vollhardt, K. P. C. *Angew. Chem.* **1986**, *98*, 268.

(13) Experimental data: **4-Cr**, IR 1965, 1900 cm^{-1}; UV λ_{max} 400, 296, 262, 228 nm; ^1H NMR ($CDCl_3$ = δ 7.25) 7.04–7.00 (m, 4 H), 6.95 (dd, 2 H), 6.89 (dd, 2 H), 5.48 (s, 2 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$ = δ 76.9) 232.28, 148.93, 145.34, 129.71, 128.68, 119.85, 119.07, 109.94, 80.68; MS (high resolution), *m/e* 362.0019 (362.0035 calcd for $C_{21}H_{10}O_3Cr$).

(14) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(15) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: 1960; pp 239–240. Pauling derives the formula $D(n) = D_1 - 0.71$ Å $\log n$ for determining bond order from bond length. D_1 = 1.55 Å for a C–C single bond.

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necessary to have at least one other point along the curve. Such a system exists in the literature.[11] Compound **3** has bond lengths of 1.34 Å (av) and 1.49 Å (av)[11] which yields a difference in bond order of 77%[15] (i.e., ca. 15 kcal/mol barrier). A derivative of **3** with one ring substituted, **5**, is synthetically feasible, and we hope to gain information on the system, **5Cr**, in the near future.

This experiment corroborates the observation[11] that the central ring in *bent*-terphenylene is more cyclohexatriene-like than benzene-like. It also raises the question of whether one can use barriers to rotation around metal–arene bonds as a gauge for aromatic character in free arenes.

Presently we are probing this idea further by semiempirical calculational and crystallographic methods in order to present a more comprehensive picture of the cyclohexatriene fragment as a ligand.

Acknowledgment. We thank K.P.C. Vollhardt for helpful discussions. The VT-NMR work was done at UCLA thanks to F.A.L. Anet. Support for this work was provided by UCSD-Ac.Sen. Grant (RL208-G).

Registry No. 4, 65513-20-4; **4-CR**, 113779-29-6; $Cr(CO)_3(NH_3)_3$, 14974-11-9.

Evidence for a Chair Cyclohexane 1,4-Radical Cation Intermediate in the Single Electron Transfer Induced Cope Rearrangement of 2,5-Diaryl-1,5-hexadienes

Tsutomu Miyashi,* Akinori Konno, and Yasutake Takahashi

Department of Chemistry, Faculty of Science
Tohoku University, Sendai 980, Japan

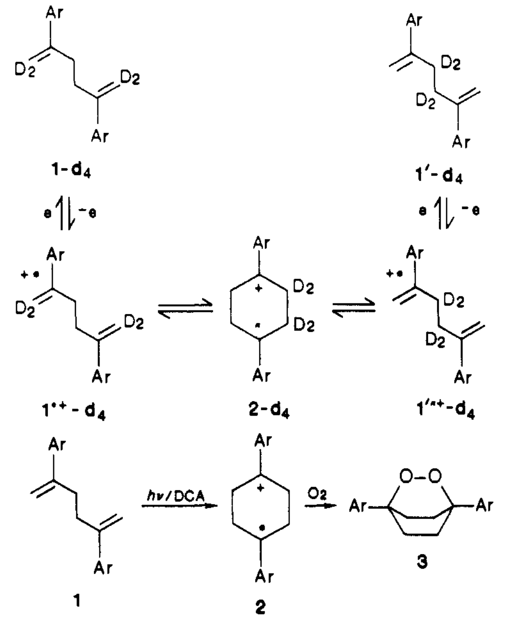
Received November 13, 1987

The possible intermediacy of cyclohexa-1,4-diyl in the Cope rearrangement, suggested by Grob[1] and Doering,[2] was supported by theoretical considerations.[3] However, kinetic experiments[4] rather suggest that cyclohexa-1,4-diyl is not a discrete intermediate in the thermal rearrangement pathway.[5]

Our interest was an intermediacy of a radical cation counterpart on the radical cation energy surface.[7] If generated as a stable intermediate, it can be captured by molecular oxygen as trimethylenemethane radical cation is captured.[8] Although the photoassisted, zeolite-catalyzed Cope rearrangement of 1,3,4-triphenyl-1,5-hexadiene was reported and is proposed as the first example of a single electron acceptor (hole)-catalyzed Cope rearrangement,[9] no experimental information was available for an intermediacy in the radical cation rearrangement pathway.

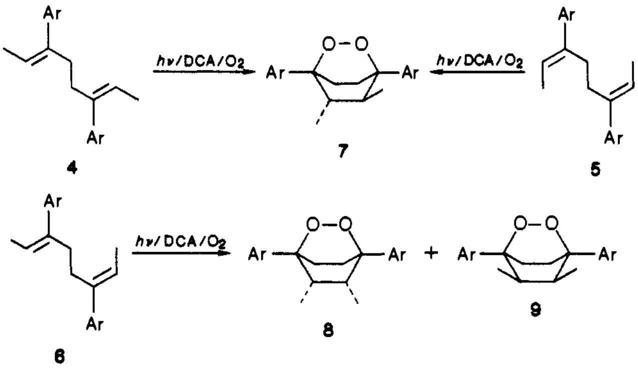
We thus investigated the photoinduced electron-transfer reactions of 2,5-diaryl-1,5-hexadienes (**1a,b**) and three isomers of 3,6-bis(*p*-methoxyphenyl)-2,6-octadienes (**4–6**), in which cyclohexane–1,4-radical cations would be most likely expected to be generated. Herein we, for the first time, demonstrate that the chair cyclohexane–1,4-radical cation serves as an intermediate in a single electron transfer induced Cope rearrangement of 2,5-diaryl-1,5-hexadienes.

Scheme I



a; Ar = C_6H_5. **b**; Ar = *p*-$MeOC_6H_4$

Scheme II



(Ar = *p*-$MeOC_6H_4$)

The fluorescence of 9,10-dicyanoanthracene (DCA) was quenched either by **1a** ($E_{1/2}^{ox}$ = 1.70 V versus SCE) or **1b** ($E_{1/2}^{ox}$ = 1.22 V versus SCE), giving Stern–Volmer slopes, $k_q\tau$ = 164 and 273 M^{-1} in acetonitrile, respectively, which indicate that **1a** and **1b** are effective quenchers of the DCA singlet. Upon irradiation (>390 nm) of a solution of DCA (0.5 mM) and 2,5-diphenyl-1,5-hexadiene-*1,1,6,6*-d_4 (**1a**-d_4) (0.1 M) in dichloromethane-d_2 or chloroform-*d* under argon, the degenerate Cope rearrangement to give a 1:1 photostationary mixture of **1a**-d_4 and 2,5-diphenyl-1,5-hexadiene-*3,3,4,4*-d^4 (**1a′**-d_4) was observed. Similar irradiation of **1b**-d_4 resulted in the formation of a 1:1 mixture of **1b**-d_4 and **1b′**-d_4.

The degenerate rearrangement can be most likely explained by a sequential cyclization–cleavage mechanism through $\mathbf{1}^{\bullet+}$-d_4 and **2**-d_4.[10] In support of the key intermediacy of **2** was the photooxygenations of **1** leading to 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octanes (**3**). Thus, upon irradiation in oxygen-saturated

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(5) A 1,4-cyclohexene-1,4-diyl as a metastable intermediate was also excluded in the Cope rearrangement of 1-hexen-5-yne.[6]

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(9) Lorenz, K.; Bauld, N. L. *J. Catal.* **1983**, *95*, 613.

(10) The initial cyclization of 1,5-hexadiene radical cation to cyclohexane-1,4-radical cation is supported by theoretical calculation[7] and is recently confirmed by Williams.[11] However, it cannot be ruled out that a direct precursor of the degenerate rearrangement of **1** is 1,4-diarylcyclohexane-1,4-diyl which can be generated by the back electron transfer of $DCA^{\bullet-}$ to **2**.