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Radical Stabilizing Ability of the Ferrocenyl and Cyclobutadieneiron Tricarbonyl Groups

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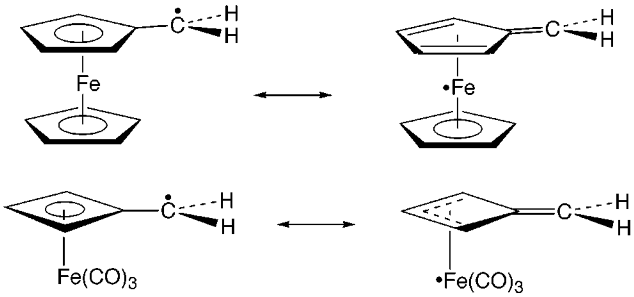
ABSTRACT

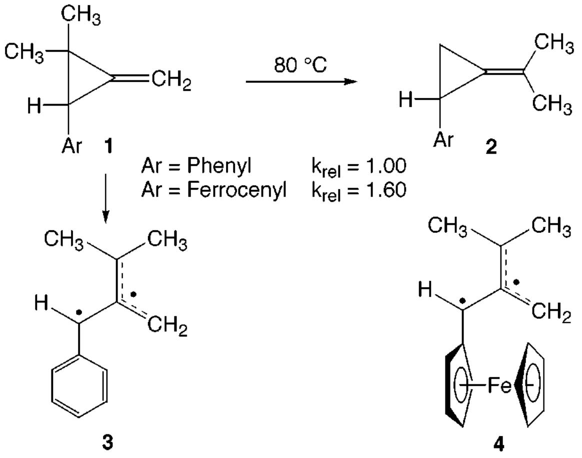


Computational studies indicate that ferrocenyl-substituted methyl radicals owe their stability to a spin delocalization mechanism involving Fe and a major contribution from an η^4 form. Cyclobutadieneiron tricarbonyl substituted methyl radicals are also calculated to be highly stabilized by spin delocalization onto Fe and a major contribution from an η^3 form.

This year represents the 100th anniversary of the Gomberg discovery of the triphenylmethyl radical, a species which owes its stability and persistence to spin delocalization involving the aromatic phenyl groups.[1] Next year will represent the 50th anniversary of the discovery of the aromatic organometallic compound ferrocene.[2] In light of these two pioneering discoveries, we would like to report our computational studies on the quantitative ability of the aromatic ferrocenyl group to stabilize free radicals. We would also like to report our calculations on the radical stabilizing ability of the aromatic cyclobutadieneiron tricarbonyl group.

We and others[3] have been interested in the quantitative ability of various groups to stabilize free radicals. Toward this end we have developed the experimental methylenecyclopropane rearrangement probe illustrated in Scheme 1. In

Scheme 1



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[1] Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757.
[2] Kealy, T. J,; Pauson, P. L. *Nature (London)* **1951**, *168*, 1039.
[3] For a recent summary and leading references, see: (a) Creary, X.; Engel, P. S.; Kavaluskas, N.; Pan, L.; Wolf, A. *J. Org. Chem.* **1999**, *64*, 5634. (b) Adam, W.; Harrer, H. M.; Kita, F.; Korth, H.-G.; Nau, W. M. *J. Org. Chem.* **1997**, *62*, 1419. (c) Adam, W.; Harrer, H. M.; Kita, F.; Nau, W. M. *Adv. Photochem.* **1998**, *24*, 205.

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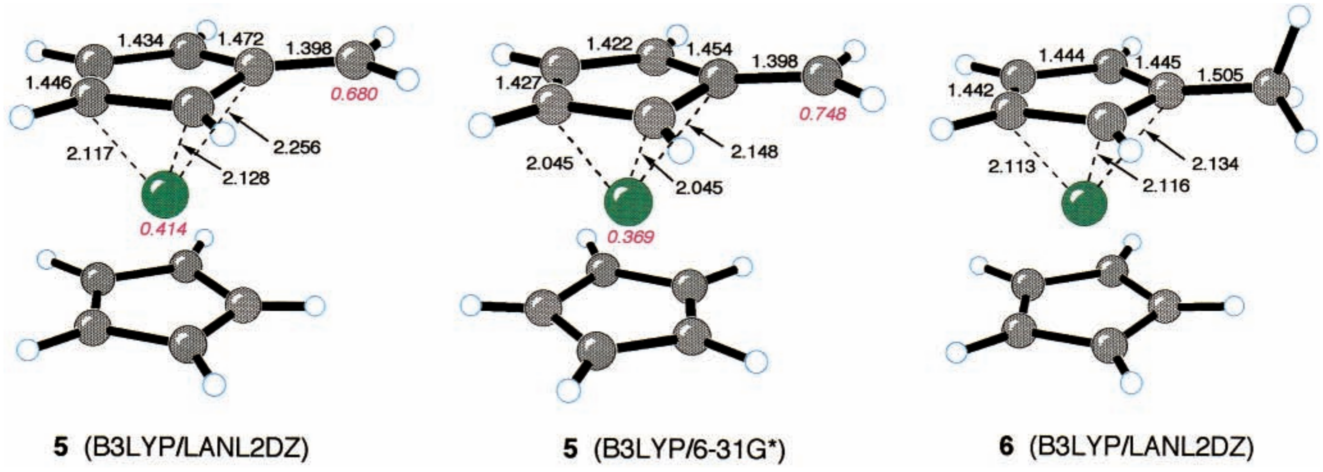


5 (B3LYP/LANL2DZ) **5** (B3LYP/6-31G*) **6** (B3LYP/LANL2DZ)

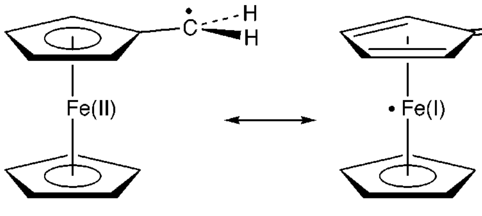
Figure 1.

this reaction, aromatic radical stabilizing groups increase the rate of this rearrangement. Among the aromatic groups that we have investigated is the ferrocenyl group which also accelerates the rearrangement of **1**.[4] The γ. value of 0.20 for ferrocenyl suggests that the intermediate biradical **4** is slightly more stable than **3**. However, the origin of this radical stabilizing ability of the ferrocenyl group was unknown. Our computational study now sheds light on this radical stabilizing effect.

Density functional theory has recently been used by us[3a] and others[5] to evaluate radical stabilizing effects. Calculations on ferrocene have also been carried out using DFT.[6] The chromium tricarbonyl complex of the benzyl radical, cation, and anion have recently been evaluated at the B3LYP/LANL2DZ level.[7] Calculations have now been carried out using this method[8] on the ferrocenyl radical **5** and methylferrocene **6**, and structures are shown in Figure 1. The LANL2DZ basis set results in an eclipsed conformation of the C_p rings. The conformations of **5** and **6** with staggered C_p rings are 0.49 and 0.64 kcal/mol higher in energy with one imaginary frequency and are hence transition states. However, the staggered conformations of **5** and **6** are energy minima at the 6-31G* level.

Comparison of the B3LYP/LANL2DZ bond lengths in radical **5** with those of methylferrocene **6** is informative. The exocyclic $C_1{-}C_2$ bond length in radical **5** (1.398 Å) is significantly shorter than that in **6** (1.505 Å) and is indicative of a substantial interaction of the radical center with the directly attached Cp ring. Also of interest are the bond lengths of Fe to the carbons of this ring. The $Fe{-}C_2$ distance of 2.256 Å is longer than the distances to the other ring carbons, which are 2.128 and 2.117 Å. This increase in bond length indicates that the interaction of iron with C_2 of this Cp ring is decreased.

The bond lengths in radical **5** are consistent with stabilization of this radical by spin delocalization as represented by **5b**. Form **5b** is an η^4 complex, where the iron is formally a 17-electron system in the +1 oxidation state. Major contributions from this form account for the decreased exocyclic $C_1{-}C_2$ bond length, the increased $Fe{-}C_2$ bond length, and the other bond lengths in this η^4 ligand.



5a **5b**

Calculated spin densities are also in line with this interpretation. The B3LYP/LANL2DZ calculated spin density on C_1 of radical **5** is only 0.680. The corresponding spin density on the benzylic carbon of benzyl radical **10** is 0.811. The spin density on the Fe atom in **5** is 0.414. Therefore, spin is substantially delocalized away from the methylene carbon and the delocalization mainly involves the Fe atom, i.e., the η^4 form **5b** is a major contributor to structure of this radical.

Attention was next turned to the cyclobutadiene $Fe(CO)_3$ complexed radical **7**. Although this group is a good car-

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(4) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989**, *54*, 2904.

(5) Wu, Y.-D.; Wong, C.-L.; Chan, K. W. K.; Ji, G.-Z.; Jiang, X.-K. *J. Org. Chem.* **1996**, *61*, 746.

(6) (a) Koch, H.; Jorgensen, P.; Helgakar, T. *J. Chem. Phys.* **1996**, *104*, 9528. (b) Mayor-Lopez, M. J.; Weber, *Chem. Phys. Lett.* **1997**, *281*, 226.

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

(8) Frisch, M, J.; Trucks, G. W.; Schlegel, Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I. Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.

bocation stabilizer,[9] we are aware of no studies on the ability of cyclobutadiene iron tricarbonyl group to stabilize radicals. Shown in Figure 2 are two views of the B3LYP/LANL2DZ-optimized structure of radical **7**. Immediately apparent is the short C_1-C_2 bond length of 1.361 Å, suggesting that this is essentially a double bond. The corresponding C_1-C_2 bond length in methylcyclobutadieneiron tricarbonyl, **8**, is 1.497 Å. The C_2-C_3 and C_2-C_5 bonds in **7** are 1.518 Å, suggesting that these are essentially single bonds. The cyclobutadiene ring is not planar, and the distance between C_2 and the Fe atom is significantly longer (2.303 Å) than those to the other three carbons in the ring (2.122 and 2.176 Å). Calculated spin densities indicate a highly Fe-centered radical. The spin density on Fe is 0.908, while the spin on C_1 is only 0.388. This represents the smallest spin density that we have calculated to date at C_1 (benzylic position) of a radical of type $ArCH_2$.

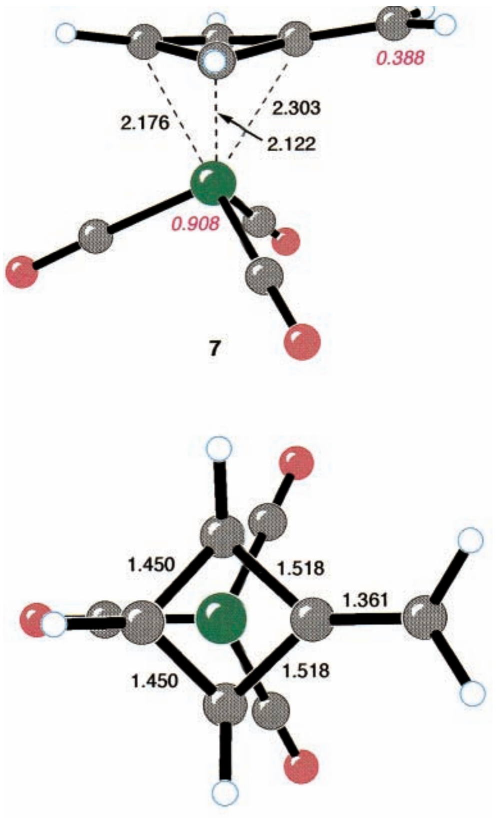
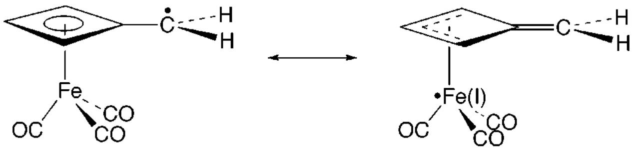


Figure 2.

These bond lengths and spin densities are in line with a large stabilization of radical **7** by a delocalization mechanism. In valence bond terms, radical **7** is best represented as a hybrid of forms **7a** and **7b**, with **7b** being the major contributor. The form **7b** is an η^3 system, where Fe is formally in the +1 oxidation state with the allylic portion of **7b** acting as a 4-electron donor. The bonding of Fe to C_2 is minimal. This valence bond picture of **7** is in good agreement with calculated bond lengths as well as spin densities.

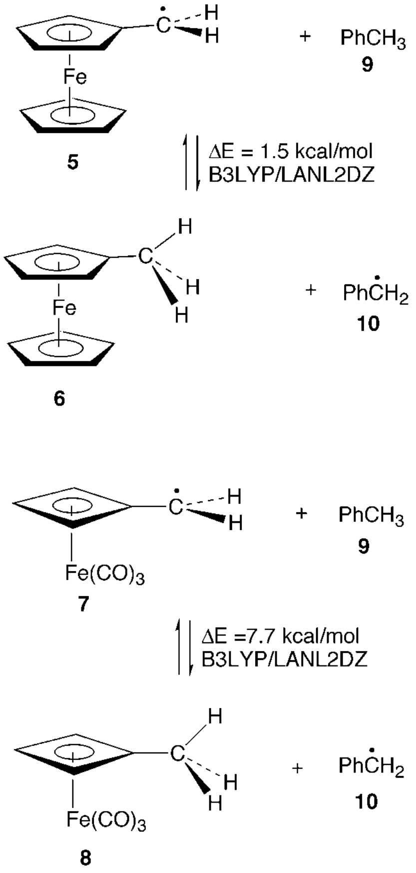


7a

7b

Also of interest are the relative energies of radicals **5** and **7**. We have found that rearrangement rates of a number of aryl-substituted methylenecyclopropanes **1** correlate with radical stabilization energies, as determined by the value of ΔE for the isodesmic reaction of the radical $ArCH_2$ with $PhCH_3$.[3a] Density functional computational methods can therefore give quantitative insights into radical stability. The isodesmic reactions shown in Scheme 2 were used to evaluate radicals **5** and **7** at the B3LYP/LANL2DZ level. As indicated by these calculations, the ferrocenyl radical **5** is somewhat

Scheme 2



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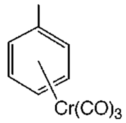
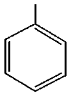
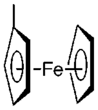
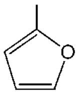
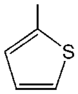
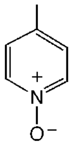
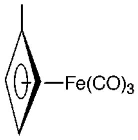
[9] (a) Davis, R. E.; Simpson, H. D.; Grice, N.; Petit, R. *J. Am. Chem. Soc.* **1971**, *93*, 6688. (b) Eschbach, C. S.; Seyferth, D.; Reeves, P. C. *J. Organomet. Chem.* **1976**, *104*, 363.

Table 1. ΔE Values (B3LYP/LANL2DZ) for the Isodesmic Reaction in Scheme 2 and Related Rearrangement Rates of **1**

Aryl	ΔE (kcal/mol)	k_{rel}
	-1.3[7]	0.33
	0.0	1.0
	1.5	1.6
	2.9	44
	4.1	50
	6.7	75
	7.7	??[a]

[a] Predicted value = 400

stabilized (1.5 kcal/mol) relative to the benzyl radical. This is in line with our methylenecyclopropane rearrangement probe where the aromatic ferrocene group is rate enhancing relative to phenyl.

Table 1 shows calculated ΔE values for a series of radical stabilizing aromatic groups for which rearrangement rates of 1 have been measured.[4] There is a fair correlation ($r = 0.92$) in a plot of log k_{rel} vs ΔE values for the first six entries. The value of ΔE for radical **7** is 7.7 kcal/mol and is one of the largest values for radical stabilization that we have calculated. Stabilization by the $C_4H_3Fe(CO)_3$ group appears to exceed that of the 4-pyridyl *N*-oxide group, which is one of the best radical stabilizers experimentally[4] and computationally[3a] ($\Delta E = 6.7$ kcal/mol at the B3LYP/LANL2DZ level).

In summary, computational studies show that the ferrocenyl group stabilizes radicals by a delocalization mechanism where significant spin is placed on the Fe atom, i.e., there is major contribution from an η^4 form. The cyclobutadieneiron tricarbonyl group is predicted to be one of the best radical stabilizing groups by an analogous spin delocalization mechanism involving an η^3 contribution, placing spin largely on the Fe atom. Studies are underway in an attempt to experimentally verify the predicted large radical stabilizing ability of the aromatic $C_4H_3Fe(CO)_3$ group.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Supporting Information Available: Energies and zero point corrections for **5**−**8**, as well as bond lengths and atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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