

## Insights into the Effects of Through-Space and Through-Bond Interactions of Super Phanes

Quinetta Shelby

Literature Seminar

March 1, 1994

There has been much recent interest in the chemistry of phanes, which are molecules that contain two parallel  $\pi$ -systems held in close proximity by bridging chains. The large intramolecular cavities of these molecules can be designed to accommodate specific guests. Presently, several issues related to super phanes are being investigated, including the distribution of strain, the reactivities due to strain, and the effects of through-bond and through-space orbital interactions on the chemistry [1].

Dewar's proposal that diphenylhydrazine rearranges in the presence of acid via an intermediate possessing a  $\pi$ -stack interaction sparked the interest in phane formation [2]. Hence, the theory that one  $\pi$ -system donates electrons to the other during reactions was developed [3-7]. The concept that through-space interactions of two subunits affects the overall  $\pi$ -basicity of the new  $\pi$ -system is supported by trends found as a function of bridge length. Comparison of the  $\pi$ -basicities of  $[M_2](1,4)$ cyclophane (where  $M=2,4,6$ ) supports this theory that  $\pi$ -basicity decreases as bridge length increases. However, unusual trends are observed for bridges containing an odd number of carbons since  $[3_2](1,4)$ cyclophane does not follow this trend [3,4]. It proves to be the best  $\pi$ -base in the series.

Cyclic diacetylenes can be considered as super phanes. However, differences in reactivity are seen depending on whether the bridges that connect the two acetylene units have an even or odd number of carbon atoms [8,9]. When the bridges have an even number of carbons, these cyclic diynes react with  $CpCo(CO)_2$  to give an intramolecular 1:1 tricyclic adduct. However, when the bridges have an odd number of carbons, new caged super phanes ( $\eta^4:\eta^4$ - $[M_4]$ cyclobutadienophane)bis( $\eta^5$ -cyclopentadienyl)cobalt (where  $M=3,5,7$ ) are also formed [9-14].

1,6-cycloundecadiyne which has a three-membered and a four-membered bridge, reacts directly with  $CpCo(CO)_2$  to give the intramolecular product. No super phane is formed [8]. A stepwise synthetic pathway for these cobalt cyclobutadienosuperphane complexes where a cycloalkynol is the precursor was used to form the lopsided  $[3_2][4_2]$ super phane cobalt complex [8]. These results suggest additional interactions in the phane.

Assignments of the photoelectron spectrum and molecular orbital calculations indicate that the in-plane and out-of-plane  $\pi$ -orbitals in the diyne interact with the  $\sigma$ -orbitals of the bridging carbons (Figure 1). The antibonding in-plane  $\pi$ -orbitals are strongly destabilized by interactions with  $\sigma$ -antibonding orbitals of their adjacent carbon bridges when the attached bridge has an odd number of carbons in its chain [8,9].

The destabilizing interaction raises the energy of the HOMO and thus increases the  $\pi$ -basicity of the in-plane p-orbitals of the diyne. This type of destabilization is not observed when the bridges contain an even number of carbons. These diynes have in-plane  $\pi$ -orbitals that are relatively low in energy. Hence, no dimeric superphane product is formed when these diynes are added to  $CpCo(CO)_2$ . This observation may explain the trends of the cyclophanes mentioned above.

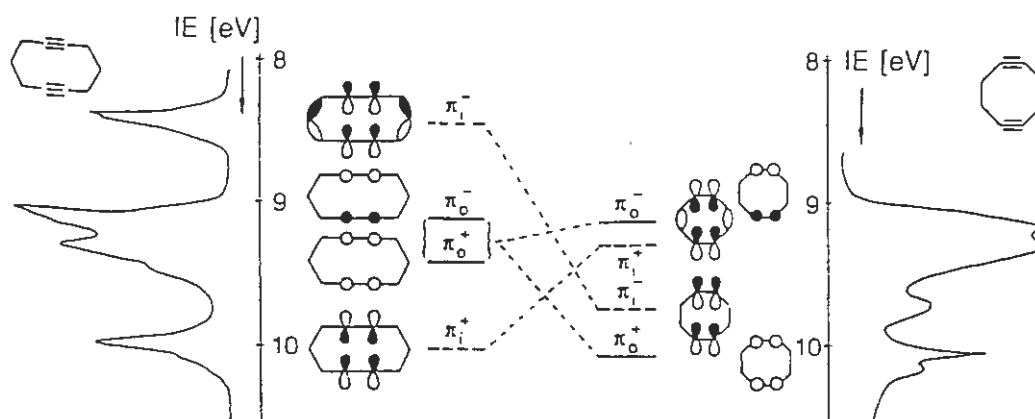


Figure 1. Comparison of the first bands of the PE spectra of 1,6-cyclodecadiyne and 1,5-cyclooctadiyne.

Attempts to prepare ferrocene-based superphanes have been unsuccessful with trimethylene [15-20] or pentamethylene bridges [16,17,21,22] but successful with tetramethylene bridges [16,17,23,24]. Spectroscopic and structural characterization of [4]superferrocenophane sheds light on other bond effects. The X-ray crystal structure of this super phane shows that the Cp  $\alpha$ -carbons are displaced from the plane of the Cp rings (Figure 2). The high energy (403 nm) of the d-d\* transition in the UV-vis spectrum indicates that the d-p orbital overlap is enhanced due to a decrease in  $\pi$ - $\pi$  distances and to the inductive effects of the electron-donating bridges.

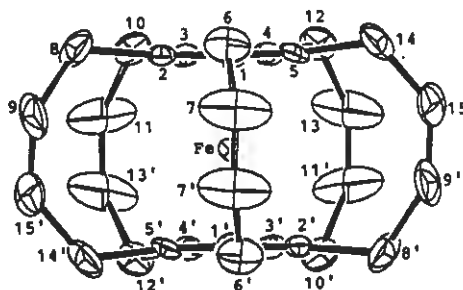


Figure 2. X-Ray crystal structure of [4]Superferrocenophane.

Complete hydrogenation of the cyclopentadienyl rings in [4]superferrocenophane [24] has not yet been achieved, but could give a caged metal prismane. Chemical oxidators and photolyses of cobalt cyclobutadienosuperphane complexes generate bishomoprismene and prismane products [8,25].

## References

1. Odashima, K.; Koga, K., In "Cyclophanes, Vol 2." (P. M. Keehn and S. M. Rosenfeld, eds.) Chap 11. Academic Press, New York, 1983. 1945, 156, 784.
2. Dewar, M. J. S., "Mechanism of the Banzidine and Related Rearrangements," *Nature* 1945, 156, 784.
3. Cram, D. J.; Allinger, N. L.; Steinberg, H., "Macro Rings. VII. The Spectral Consequences of Bridging Two Benzene Rings Face to Face," *J. Am. Chem. Soc.* 1954, 76, 6132.
4. Kovac, B.; Mohraz, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H., "Photoelectron Spectra of the Cyclophanes," *J. Am. Chem. Soc.* 1980, 102, 4314-4324.
5. Cram, D. J.; Wilkinson, D. L., "Macro Rings. XXIII. Carbonylchromium Complexes of Paracyclophanes and Model Compounds," *J. Am. Chem. Soc.* 1960, 82, 5721-5723.
6. Sheehan, M.; Cram, D. J., "Macro Rings. XL. Transannular Interactions in the Tetracyanoethylene Complexes of [3.3]Paracyclophane and Derivatives," *J. Am. Chem. Soc.* 1969, 91, 3553-3558.
7. Cram, D. J.; Steinberg, H., "Macro Rings. I. Preparation and Spectra of the Paracyclophanes," *J. Am. Chem. Soc.* 1950, 72, 5691-5704.
8. Gleiter, R., "Cycloalkadiynes-From Bent Triple Bonds to Strained Cage Compounds," *Angew. Chem. Int. Ed. Engl.* 1992, 31, 27-44.
9. Gleiter, R.; Merger, R.; Nuber, B., "Skipped Cyclic Ene- and Dienediynes. I. Synthesis, Spectroscopic Properties, and Reactions of a New Hydrocarbon Ring Family," *J. Am. Chem. Soc.* 1992, 114, 8921-8927.
10. Gleiter, R.; Kratz, D., "Isolation of a Donor-Acceptor Superphane with a Quinone and a CpCoCyclobutadiene Unit," *Tetrahedron Lett.* 1990, 31, 5893-5896.
11. Gleiter, R.; Karcher, M.; Ziegler, M. J.; Nuber, B., "A Superphane of Cyclobutadiene Capped by Cyclopentadienylcobalt," *Tetrahedron Lett.* 1987, 28, 195-198.
12. Gleiter, R.; Treptow, B.; Kratz, D.; Nuber, B., "A One Step Synthesis of a Pentamethylene-bridge Superphane of a CpCo-Stabilized Cyclobutadiene Complex," *Tetrahedron Lett.* 1992, 33, 1733-1736.
13. Gleiter, R.; Pfästerer, G.; Nuber, B., "A Heptamethylene Bridged Superphane of a Co(C<sub>5</sub>H<sub>5</sub>)-Stabilized Cyclobutadiene Complex," *J. Chem. Soc. Chem. Commun.* 1993, 454-456.
14. Gleiter, R.; Schäfer, W., "Interactions between Nonconjugated  $\pi$ -Systems," *Acc. Chem. Res.* 1990, 23, 369-375.
15. Brown, A. D. Jr.; Winstead, J. A., "[m][n]Ferrocenophanes. Derivatives Containing Tri-, Tetra-, and Pentamethylene Bridging Groups," *J. Org. Chem.* 1971, 36, 2832-2835.

16. Hisatome, M.; Hillman, M., "Bridged Ferrocenes VII. Synthesis of Di- and Tri-bridged Ferrocenes with Pentamethylene Chains," *J. Organomet. Chem.* **1981**, 212, 217-231.
17. Hisatome, M.; Watanabe, J.; Yamakawa, K.; Iitaka, Y., "[4<sub>5</sub>](1,2,3,4,5)Ferrocenophane: Superferrocenophane," *J. Am. Chem. Soc.* **1986**, 108, 1333-1334.
18. Hisatome, M.; Watanabe, J.; Yamakawa, K., "Organometallic Compounds XXXVIII. Condensed-Ring Ferrocenophanes Containing Two Bridges," *J. Organomet. Chem.* **1984**, 266, 159-171.
19. Hisatome, M.; Watanabe, N.; Sakamoto, T.; Yamakawa, K., "Organometallic Compounds XXIII. Formation of Novel Di- and Tri-bridged Ferrocenophanes," *J. Organomet. Chem.* **1977**, 125, 79-93.
20. Bublitz, D. E.; Rinehart, K. L. Jr., "1,1'; 3,3';4,5;4',5'-Tetrakis-(Trimethylene) Ferrocene," *Tetrahedron Lett.* **1964**, 827-833.
21. Hisatome, M.; Watanabe, J.; Kawajiri, Y.; Yamakawa, K., "Synthesis and Molecular Structure of [4<sub>5</sub>](1,2,3,4,5)Ferrocenophane ([4]Superferrocenophane)," *Organometallics*, **1990**, 9, 497-503.
22. Hisatome, M.; Yamashita, R.; Watanabe, J.; Yamakawa, K.; Iitaka, Y., "Synthesis and X-Ray Crystal Structure of [5<sub>4</sub>](1,2,3,4)Ferrocenophane," *Bull. Chem. Soc. Jpn.* **1988**, 61, 1687-1694.
23. Spaulding, L. D.; Hillman, M.; Williams, G. J. B., "Bridged Ferrocenes," *J. Organomet. Chem.* **1978**, 155, 109-116.
24. Rinehart, K. L. Jr.; Bublitz, D. E.; Gustafson, D. H., "Organic Chemistry of Ferrocene. VI. Acetylation of Mono-, Di-, and Tri-bridged Ferrocenes," *J. Am. Chem. Soc.* **1963**, 85, 970-981.
25. Gleiter, R.; Karcher, M., "Synthesis and Properties of a Bridged *syn*-Tricyclo-[4.2.0.0<sup>2,5</sup>]octa-3,7-diene: Formation of Propella[34]prismane," *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 840-841.