Organometallics 1992, 11, 2006-2007

Generation and Trapping of $(\eta^3$-4,5-Dimethylenecyclopentenyl)$(\eta^5$-cyclopentadienyl)iron, the Parent Ferrocene-Based *o*-Quinodimethane[1]

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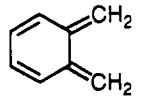
Received November 19, 1991

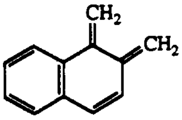
Summary: **The flash vacuum pyrolysis of the 1-amino-2-phenylaziridine hydrazone of 2-methylferrocenecarboxaldehyde (6) gives ferrocenocyclobutene (5), presumably by the formation of (2-methylferrocenyl)carbene (7), which rearranges to 5. Heating 5 in the presence of *N*-phenylmaleimide (NPMI) in phenyl ether at 200 °C for 30 h gives two stereoisomeric Diels–Alder adducts of NPMI and $(\eta^3$-4,5-dimethylenecyclopentenyl)$(\eta^5$-cyclopentadienyl)iron (4), the parent ferrocene-based *o*-quinodimethane.**

The reactive molecule *o*-xylylene (1) is the parent benzene-based member of the large and important class of reactive molecules called *o*-quinodimethanes (*o*-QDM's).



1

o-QDM's have been shown to be transient intermediates in many reactions[2,3] and have been used extensively as dienes in several organic syntheses.[2k,m–o,s,t,v,x,z] Many *o*-QDM's based on aromatic systems other than benzene are known. Examples of these are the *o*-QDM's which are derivatives of naphthalene (2)[4] and furan (3).[3b,5] In general, *o*-QDM's readily undergo reactions such as dimerizations and Diels–Alder reactions which generate the aromatic system on which they are based.[2–5]



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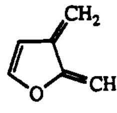

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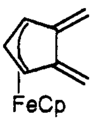
Although many *o*-QDM's have been prepared and studied, only a few organometallic *o*-QDM's are known. A number of *o*-xylylene derivatives with a metal coordinated to the exocyclic diene moiety have been synthesized,[6] but these compounds lack the high reactivity characteristic of free *o*-xylylenes. Kündig[7] and Butenschön[8] have recently reported the syntheses of substituted tricarbonylchromium–benzocyclobutene complexes which, when heated in the presence of a dienophile, exhibited chemical behavior similar to that of the uncomplexed analogs. Apparently the chromium-complexed substituted benzocyclobutenes undergo ring opening to give the corresponding complexed substituted *o*-xylylene, which reacts with the dienophile at a rate comparable to that of the uncomplexed species.[7,8] Also, Butenschön has recently reported the generation of a $(\eta^3$-4,5-dimethylenecyclopentenyl)cobalt complex that appears to exhibit *o*-QDM-like reactivity.[9] In this communication we present evidence for the generation of the parent ferrocene-based *o*-QDM (4) by the electrocyclic ring opening of ferrocenocyclobutene (5).



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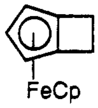

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Ferrocenocyclobutene (5)[10] was prepared by the flash vacuum pyrolysis (FVP)[12] of hydrazone 6,[13,14] which was

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(1) Based on work by J.M.F. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

(2) (a) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 1701. (b) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266. (c) Cava, M. P.; Deana, A. A.; Muth, K. *J. Am. Chem. Soc.* **1959**, *81*, 6458. (d) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949. (e) Baudet, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 191. (f) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941. (g) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1973**, *95*, 5802. (h) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280. (i) Dolbier, W. R., Jr.; Kazumasa, M.; Michl, J.; Horák, D. V. *J. Am. Chem. Soc.* **1977**, *99*, 3876. (j) Michl, J.; Tseng, K. L. *J. Am. Chem. Soc.* **1977**, *99*, 4840. (k) Oppolzer, W. *Synthesis* **1978**, 793. (l) Roth, W. R.; Biermann, M.; Dekker, H.; Jochems, R.; Mosselman, C.; Hermann, H. *Chem. Ber.* **1978**, *111*, 3892. (m) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41. (n) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863. (o) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463. (p) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270. (q) Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1981**, *114*, 3741. (r) See also: Dolbier, W. R., Jr.; Dulcere, J.-P.; Sellers, S. F.; Koroniak, H.; Shatkin, B. T.; Clark, T. L. *J. Org. Chem.* **1982**, *47*, 2298. (s) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609. (t) Taub, D. In *The Total Synthesis of Natural Products*; ApSimon, J. W., Ed.; Wiley-Interscience: New York, 1984; Vol. 6, pp 17–37. (u) Kreile, J.; Munzel, N.; Schulz, R.; Schweig, A. *Chem. Phys. Lett.* **1984**, *108*, 609. (v) Ciganek, E. *Org. React.* **1984**, *32*, 72–374. (w) Trahanovsky, W. S.; Macias, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 6820. (x) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873. (y) Martin, N.; Seoane, C.; Hanack, M. *Org. Prep. Proced. Int.* **1991**, *23*, 329. (z) Hoey, M. D.; Dittmer, D. C. *J. Org. Chem.* **1991**, *56*, 1947.

(3) (a) Macias, J. R. Ph.D. Dissertation, Iowa State University, Ames, IA, 1987. (b) Huang, Y. J. Ph.D. Dissertation, Iowa State University, Ames, IA, 1987. (c) Fischer, D. R. Ph.D. Dissertation, Iowa State University, Ames, IA, 1990.

(4) Trahanovsky, W. S.; Chou, C.-H.; Fischer, D. R.; Gerstein, B. C. *J. Am. Chem. Soc.* **1988**, *110*, 6579.

(5) Chou, C.-H.; Trahanovsky, W. S. *J. Org. Chem.* **1986**, *51*, 4208 and references cited therein.

(6) (a) Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* **1967**, 2053–2058. (b) Johnson, B. F. G.; Lewis, J.; Thompson, D. J. *Tetrahedron Lett.* **1974**, 3789–3792. (c) Boschi, T.; Vogel, P.; Roulet, R. *J. Organomet. Chem.* **1977**, *133*, C36–C38. (d) Hersh, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 6992–6994. (e) Hull, J. W.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 1716–1718. (f) Grosselin, J.; Le Bozec, H.; Moinet, C.; Toupet, L.; Köhler, F.; Dixneuf, P. *Organometallics* **1988**, *7*, 88–98.

(7) Kündig, E. P.; Bernardinelli, G.; Leresche, J.; Romanens, P. *Angew. Chem.* **1990**, *102*, 421–423; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 407.

(8) Wey, H. G.; Butenschön, H. *Angew. Chem.* **1991**, *103*, 871; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 880.

(9) Butenschön, H. *Angew. Chem.* **1990**, *102*, 1058–1059; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1057.

(10) **5** (analysis by GC, GC/MS, and NMR methods confirmed the presence of small amounts of ferrocene (ca. 1.5%), methylferrocene (ca. 0.5%), 1,2-dimethylferrocene (ca. 0.9%), and an unidentified ferrocene derivative[11] (ca. 2%)): mp 51.1–59.7 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 3.99 (2 H, d, *J* = 2.1 Hz), 3.94 (5 H, s), 3.70 (1 H, t, *J* = 2.1 Hz), 2.93–2.83 (2 H, AA′BB′, m), 2.71–2.61 (2 H, AA′BB′, m); ^{13}C NMR (75 MHz, C_6D_6) δ 92.381, 70.114, 65.688, 61.976, 29.207; MS *m/z* (relative intensity) 212 (M^+, 100), 184 (6.1), 134 (37), 121 (72), 91 (14), 56 (53); HRMS *m/z* for $C_{12}H_{12}Fe$ (M^+) calcd 212.028 84, found 212.029 34.

(11) The impurity has a molecular weight of 225 and may be 1-cyano-2-methylferrocene.

(12) (a) Trahanovsky, W.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem.* **1971**, *36*, 3575. Commercial FVP apparatus is available from Kontes Scientific Glassware, Vineland, NJ 08360. (b) For a review, see: Brown, R. C. F. *Pyrolysis Methods in Organic Chemistry*; Academic: New York, 1980; Chapter 2.

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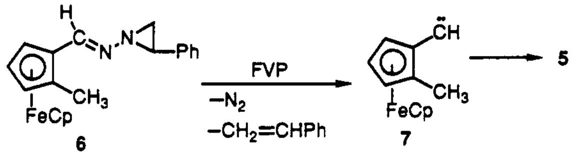
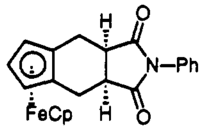
prepared from 2-methylferrocenecarboxaldehyde[15] and 1-amino-2-phenylaziridine[16] by the method of Eschenmoser et al.[16] It has been proposed that carbenes can be conveniently and efficiently generated by the decomposition of 1-amino-2-phenylaziridine hydrazones.[17] FVP of **6** presumably gives molecular nitrogen, styrene, and (2-methylferrocenyl)carbene (**7**), which rearranges to **5** by C–H insertion. Compound **5** was obtained in relatively high purity (>95%; the rest of the material was ferrocene, methylferrocene, 1,2-dimethylferrocene, and an unidentified ferrocene derivative[11]) but in only fair yields (30–35%). No vinylferrocene was detected, which indicates that the ferrocenylcarbene **7** does not readily undergo the analogous series of rearrangements which converts *o*-tolylcarbene to styrene in the gas phase.[18]



Evidence for ring opening of **5** to *o*-QDM **4** was obtained from a trapping experiment analogous to the one used to provide evidence for the production of *o*-xylylene by the ring opening of benzocyclobutene.[2c,19] Compound **5** was heated in the presence of *N*-phenylmaleimide (NPMI) in phenyl ether at 200 °C for 30 h. Compounds **8** and **9**, the Diels–Alder adducts of **4** and NPMI, were formed in an 11:1 ratio as determined by NMR spectroscopy. Compound **8** was separated from this mixture in pure form in 13% yield; **9** was not isolated in pure form.[20] Production of these adducts provides strong evidence for the conversion of **5** to **4** under these conditions. Notice that the



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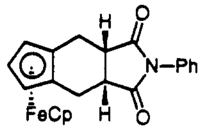

9

$$5 \rightleftharpoons 4 \xrightarrow{\text{NPMI}} 8 + 9$$

conversion of **5** to **4** is an example of a ring-slippage reaction,[22] with the hapticity of the reacting ligand changing from η^5 to η^3. Possibly a solvent molecule coordinates with the iron atom of **4** to retain the inert-gas electronic configuration, or possibly the coordinatively unsaturated **4** remains intact long enough to react with NPMI. Reaction of **4** with NPMI to produce **8** and **9** involves changing the hapticity of the reacting ligand from η^3 to η^5.

Acknowledgment. We thank Maitland Jones, Jr., for helpful suggestions and the National Science Foundation for generous financial support of this research (Grant CHE8710712).

Supplementary Material Available: Experimental details, including additional spectral data, for 2-methylferrocenecarboxaldehyde, 1-phthalimido-2-phenylaziridine, 1-amino-2-phenylaziridine, **5**, **6**, **8**, and **9** (5 pages). Ordering information is given on any current masthead page.

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(13) FVP (sample head, 65–95 °C; pyrolysis tube, 380 °C; 6 × 10^{-5} Torr; 4–6 h) of ca. 75 mg (0.22 mmol) of **6**[14] gave two products in the cold trap. The lower white band (styrene) was dissolved in CS_2 and removed. The yellow-orange upper band was concentrated and chromatographed on neutral alumina with hexanes. The first major fraction was **5** (30–35% yield).

(14) 1-Amino-2-phenylaziridine (0.192 g, 1.43 mmol) was added to 2-methylferrocenecarboxaldehyde (0.150 g, 0.66 mmol) in 15 mL of benzene. After 30 h, chromatography on neutral alumina with 8% EtOAc in hexanes gave 0.157 g (0.46 mmol, 70%) of a dark red oil (**6**) as a pair of diastereomers: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.55, 8.54 (1 H, two s), 7.51–7.31 (5 H, m), 4.56 (1 H, m), 4.31 (1 H, m), 4.26 (1 H, t, J = 2.4 Hz), 4.14, 4.13 (5 H, two s), 3.07–3.01 (1 H, two dd), 2.51–2.47 (1 H, two dd), 2.40–2.37 (1 H, two dd), 2.15, 2.14 (3 H, two s).

(15) Sokolov, V. I.; Troitskaya, L. L.; Reutor, O. A. *J. Organomet. Chem.* **1979**, *182*, 537–546.

(16) (a) Eschenmoser, A.; Felix, D.; Müller, R.; Horn, U.; Joos, R.; Schreiber, J. *Helv. Chim. Acta* **1972**, *51*, 1276–1319. (b) Müller, R. K.; Joos, R.; Felix, D.; Schreiber, J.; Wintner, C.; Eschenmoser, A. In *Organic Syntheses*; Noland, W. E., Ed.; Wiley: New York, 1973; Collect. Vol. VI, pp 56–61.

(17) (a) Chen, N.; Jones, M., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 305–308. (b) White, W. R.; Platz, M. S.; Chen, N.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 7794–7796. (c) Chen, N.; Jones, M., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981–4992.

(18) (a) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. 1, Chapter 3. (b) Jones, W. M. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 3. (c) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. 1, Chapter 4. (d) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173–251. (e) Vander Stouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 1655–1661. (f) Baron, W. J.; Jones, M.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739–4740. (g) Hedaya, E.; Kent, M. E. *J. Am. Chem. Soc.* **1971**, *93*, 3283–3285. (h) Jones, W. M.; Joines, R. C.; Myers, J. A.; Mitsuhashi, T.; Krajca, K. E.; Waali, E. E.; Davis, T. L.; Turner, A. B. *J. Am. Chem. Soc.* **1973**, *95*, 826–835. (i) Gleiter, R.; Rettig, W.; Wentrup, C. *Helv. Chim. Acta* **1974**, *57*, 2111–2124.

(19) Jensen, F. R.; Coleman, W. E.; Berlin, A. J. *Tetrahedron Lett.* **1962**, 15–18.

(20) Compound **5** (8.9 mg, 0.042 mmol), NPMI (15.1 mg, 0.087 mmol), and 0.5 mL of phenyl ether were heated to 200 °C for 30 h in a sealed tube. An orange precipitate in an orange solution was obtained; analysis by ^{1}H NMR spectroscopy indicates that the precipitate was a mixture of two products in an 11:1 ratio. The solution from the tube was chromatographed on neutral alumina with hexanes and then acetone to give an orange powder. This was combined with the precipitate, and the mixture was recrystallized from toluene/hexane to give 2.1 mg (0.0055 mmol, 13%) of orange needles, which turn dark at 185 °C. The ^{1}H NMR spectrum of this material shows it to be the major component of the 11:1 mixture. The NMR signals of the tertiary protons of the major product are 0.32 ppm downfield from those of the minor product, and therefore the major isomer was assigned structure **8**;[21] the other product was assigned structure **9**. **8**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.53–7.43 (2 H, m), 7.43–7.37 (1 H, m), 7.21–7.17 (2 H, m) 4.15 (2 H, d, J = 2.4 Hz), 4.14 (5 H, s), 4.03 (1 H, t, J = 2.4 Hz), 3.59–3.49 (2 H, ABC m), 3.03–2.95 (2 H, ABC m), 2.57–2.49 (2 H, ABC m); ^{13}C NMR (75 MHz, C_6H_6) δ 178.912, 132.556, 129.358, 128.864, 127.008, 83.183, 69.263, 66.545, 65.464, 41.028, 24.170; MS m/z (relative intensity) 385 (M^+, 100), 172 (15), 121 (6.9), 121 (6.1), 113 (37), 103 (3.7), 101 (5.6), 56 (5.6); HRMS m/z for $C_{22}H_{19}FeNO_2$ (M^+) calcd 385.07648, found 385.07654. **9**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ (phenyl and ferrocenyl proton signals are obscured by the absorptions of **8**) 3.34–3.28 (m), 3.30–2.95 (m), 2.57–2.49 (m).

(21) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1981**, *215*, 77–86.

(22) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307–318.