

# Communications

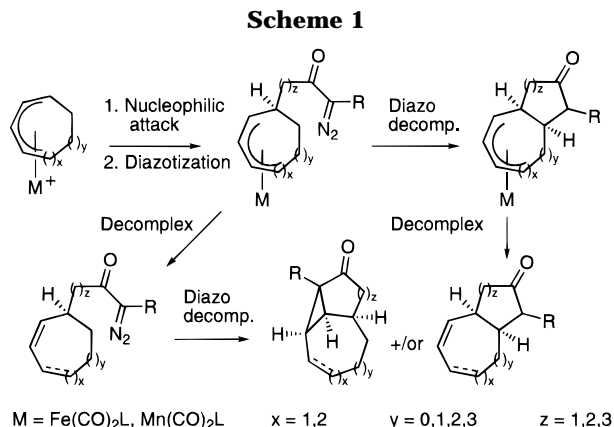
## Preparation and Diazodecomposition Reaction of an $\alpha$ -Diazocarbonyl-Tethered Tricarbonyl( $\eta^4$ -cyclohexadiene)iron Complex

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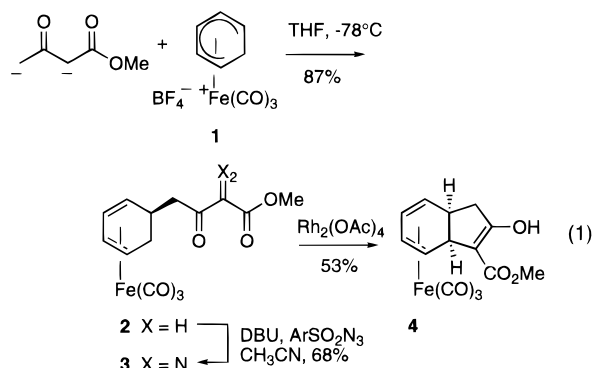
Received February 6, 1996

The use of transition metal complexes in organic synthesis has increased dramatically in the past 25 years, and the utilization of nucleophilic attack on transition metal  $\pi$ -complexes<sup>1</sup> in complex synthetic schemes has contributed significantly to this increase. Rhodium- and copper-initiated metallocarbenoid reactions<sup>2</sup> have also found acceptance among the practicing organic community as useful transformations that can be extremely valuable in organic synthesis. In each case, the ability to form carbon–carbon bonds selectively, often with both regio- and stereocontrol, has been examined in detail and demonstrated in a variety of systems. It appears, however, that the literature contains few examples<sup>3–5</sup> where the combination of these two valuable synthetic schemes has been demonstrated. Our approach to the merger of the chemistry of transition metal  $\pi$ -complexes and transition metal-mediated metallocarbenoid reactions involves the strategy outlined in Scheme 1. Thus, it is envisioned that utilization of the propensity of transition metal  $\pi$ -complexes to undergo nucleophilic



attack, combined with the ability of metallocarbenoids to form carbon–carbon bonds via intramolecular C–H insertion or cyclopropanation, will allow for the preparation of a variety of useful bicyclic and tricyclic substrates. We report here the first results of our examination of this approach employing the well-known chemistry of tricarbonyl( $\eta^5$ -cyclohexadienyl)iron complexes.<sup>6</sup>

In order to generate an iron  $\pi$ -complex that incorporates an  $\alpha$ -diazo carbonyl tether, nucleophilic attack on tricarbonyl( $\eta^5$ -cyclohexadienyl)iron cation **1** was examined. Reaction of iron cation **1** has been reported with a wide variety of nucleophiles, including ketone and ester enolates, Grignard and organolithium reagents, malonates and acetoacetates, amines, and alkoxides.<sup>6</sup> In this case, a two-step approach, with nucleophilic attack to provide the tether followed by elaboration of the tether to include the sensitive diazo functionality, proved to be the most effective route to the desired substrate. Reaction of tricarbonyl( $\eta^5$ -cyclohexadienyl)iron complex **1** with the dianion of methyl acetoacetate, followed by diazotization using the Davies reagent,<sup>7</sup> provided the desired complex **3** in 59% overall yield (eq 1). Complex **3** is



purified readily by chromatography on silica gel and is stable for extended periods of time if stored at 0 °C. Attempts to prepare complex **3** by reaction of the lithium enolate of methyl 2-diazoacetoacetate with iron complex **1** also provided complex **3**, but in only moderate yields. The <sup>1</sup>H nuclear magnetic resonance spectra of complexes

(6) For a recent review of this chemistry see: Pearson, A. J. *Iron Compounds in Organic Synthesis*; Academic Press: San Diego, 1994; Chapter 5.

(7) Davies, H. M. L.; Cantrell, W. R.; Romines, K. R.; Baum, J. S. *Org. Synth.* **1991**, 70, 93.

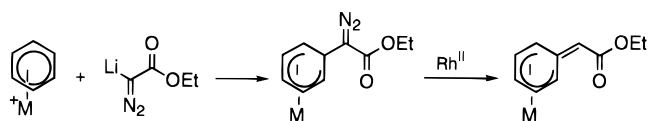
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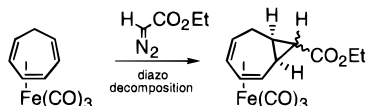
(1) See, for example: *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1994; Vol. 12, Chapters 6.1, 6.3, 8.2, and 9.1.

(2) See, for example: *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1994; Vol. 12, Chapters 5.1 and 5.2.

(3) The reaction of ethyl lithiodiazoacetate with both [(arene)Cp]iron complexes and tricarbonyl( $\eta^6$ -arene)manganese has been reported to give the expected addition products. In this case, however, diazo decomposition to form the metallocarbenes initiates a 1,2-hydrogen migration (see below). See: (a) Motallebi, S.; Muller, P. *Organometallics* **1993**, 12, 4668. (b) Reau, R.; Reed, R. W.; Dahan, F.; Bertrand, G. *Organometallics* **1993**, 12, 1501.



(4) The decomposition of ethyl diazoacetoacetate in the presence of tricarbonyl( $\eta^4$ -cycloheptatriene)iron has been reported to provide the cyclopropanation product as is shown below. See: (a) Goldschmidt, Z.; Antebi, S.; Goldberg, I. *J. Organomet. Chem.* **1984**, 260, 105. (b) See also: Taylor, G. A. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1716.



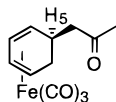
(5) Franck-Neumann and co-workers recently have reported the preparation and reactions of several tricarbonyl iron  $\pi$ -complexes bearing a free diazo group. See: Franck-Neumann, M.; Geoffroy, P.; Winling, A. *Tetrahedron Lett.* **1995**, 36, 8213.

**2** and **3** provide evidence for the expected *exo* nature of the nucleophilic attack. Thus, the chemical shifts of  $H_{5endo}$  at  $\delta$  2.3–2.5 in both complexes **2** and **3**, respectively, correspond well to values reported for a variety of 5-*exo*-substituted tricarbonyl( $\eta^4$ -cyclohexadiene)iron complexes.<sup>8</sup>

Reaction of complex **3** with rhodium(II)acetate in refluxing dichloromethane generates a new ( $\eta^4$ -diene)-iron complex, whose  $^1H$  NMR,  $^{13}C$  NMR, and IR spectra fit that expected for C–H insertion<sup>2,9</sup> product **4**. In particular, the  $^1H$  NMR signal corresponding to the *exo* methylene hydrogen ( $H_{6exo}$ ) in complex **3**, which appears as a broad doublet at  $\delta$  1.04 ( $J = 15.5$  Hz), is absent from the spectrum of complex **4**, as is the diazo absorption in the infrared spectrum. Single-crystal X-ray data collected for complex **4** confirms the cis ring fusion and the proposed enol tautomer (Figure 1).<sup>12</sup> It appears therefore that the iron moiety not only functions to induce nucleophilic attack, allowing attachment of the desired tether, but also acts as a protecting group,<sup>10</sup> preventing the metallocarbenoid species from cyclopropanating the unsaturated portion of the cyclohexadiene.<sup>11</sup>

This overall transformation demonstrates the potential

(8) The iron complex resulting from the reaction of acetone with iron cation **1** provides a good comparison for these compounds. The 5-*endo* hydrogen in this complex comes at 2.4 ppm. See: Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882.



(9) For specific examples of rhodium(II)-catalyzed diazodecomposition reactions leading to C–H insertion see: (a) Taber, D. F.; Petty, E. H.; Raman, K. *J. Am. Chem. Soc.* **1985**, *107*, 196. (b) Taber, D. F.; Ruckle, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7686. (c) Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagheri, V.; Pearson, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 958.

(10) For a review of the use of ( $\eta^4$ -diene)iron complexes as protecting groups for 1,3-dienes see: Donaldson, W. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1994; Vol. 12, Chapter 6.2.

(11) Intramolecular cyclopropanation of conjugated dienes has been demonstrated. See: Hudlicky, T. et al. *Tetrahedron* **1987**, *43*, 5685.

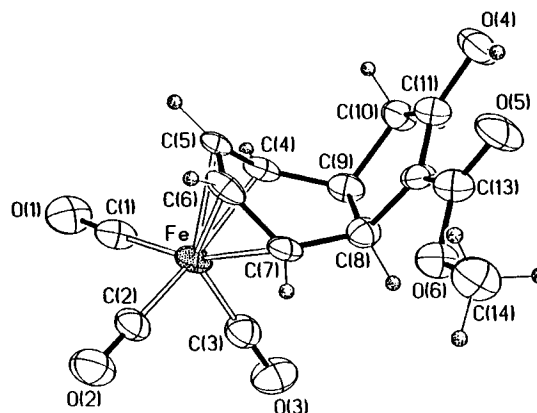


Figure 1. X-ray structure of complex **4**.

of the combination of the chemistry of transition metal  $\pi$ -complexes with diazodecomposition reactions of  $\alpha$ -diazo carbonyl species for the facile preparation of functionalized bicyclic skeletons. Continued investigation of this transformation, including examination of the effect of diazodecomposition catalyst choice, transition metal complex ring size and hapticity, and diazo tether length and substitution currently is in progress.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (K.F.M., No. 26608-AC1, and M.C.M., No. 28135-G) and to the Ohio University Research Challenge Program for support of this research.

**Supporting Information Available:** Experimental procedures and characterization data for compounds **2–4** (3 pages).

JO960229Q

(12) The author has deposited atomic coordinates for **4** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.