

From these studies we concluded (a) that deconjugation of the  $\Delta^2$ -isomer **3**, under kinetic control leads to the 2-epi isomer **2** exclusively, and (b) that partial isomerization, **2**  $\rightarrow$  **1**, can be achieved, but only in a *protic medium* and only if the polarity of the molecule is appropriate. Furthermore, an important Corollary of our studies is that 3,4-alkenes, such as **6a** and **6b**, must be regarded as unreliable synthons for the "southern" oxahydrindene moiety of these molecules.

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**Supplementary Material Available:** <sup>1</sup>H NMR spectra, 300 MHz, of pure specimens of **1Ab**, **2Ab**, and **3Ab**, spectra of admixtures of isomers and of the crude product from a deconjugation experiment, and experimental conditions for the deconjugation and chromatographic isolation (9 pages). Ordering information is given on any current masthead page.

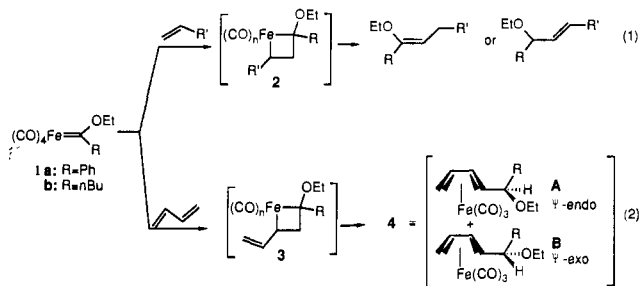
### Coupling of 1,3-Dienes with (Carbene)iron Complexes To Give Substituted (1,3-Diene)Fe(CO)<sub>3</sub> Derivatives

M. F. Semmelhack\* and Jaiwook Park

Department of Chemistry, Princeton University  
Princeton, New Jersey 08544

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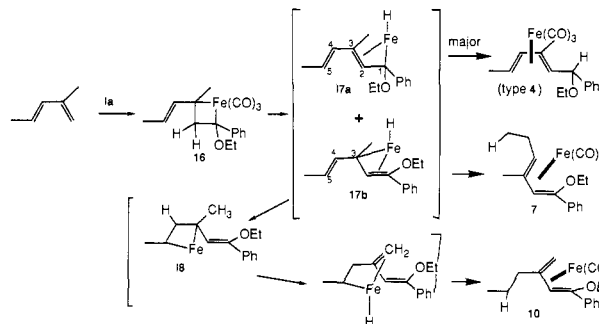
Fischer-type carbene complexes of chromium react with alkenes by several pathways but the processes are not very general and no useful synthesis methodology has appeared.<sup>1</sup> Recent studies of simple iron analogues (i.e., **1**) demonstrated a one-carbon homologation process, according to eq 1. A ferracyclobutane



intermediate (**2**) was suggested.<sup>2</sup> Following the same pathway, conjugated dienes would lead to an intermediate (**3**) with new opportunities for further reaction involving the additional double bond. In this paper we describe the first examples of coupling **1a** with 1,3-dienes, which results in a new preparation of (η<sup>4</sup>-1,3-diene)Fe(CO)<sub>3</sub> complexes **4** bearing an allylic ethoxy group, as shown for 1,3-butadiene in eq 2.

(1) For a review, see: (a) Dötz, K.-H. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983; pp 204 ff. (b) Fischer, E. O.; Kiener, V. *Adv. Organomet. Chem.* **1976**, *14*, 1-32. (c) Cardin, D. J.; Cetinkaya, B.; Doyle, M. T.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545-574. (d) Brown, F. J. *Prog. Inorg. Chem.* **1981**, *27*, 1-122. (e) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651.

(2) (a) For reactions of **1** with simple alkenes, see: Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6730. (b) For preparation of **1**, see: Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099.



**Figure 1.** Suggested mechanism illustrated with **1a** and 2-methyl-1,3-pentadiene. CO ligands are deleted to simplify the intermediates.

Table I displays the results with a series of simple 1,3-dienes, following a standard procedure.<sup>3</sup> Coupling of **1a** with dienes which bear one monosubstituted olefin unit (entries 1-6) occurs at 25 °C to give high yields of coupled products as 5-ethoxy 1,3-diene complexes **4**. In one case (entry 1), the ligand is partially detached (20% yield) from the iron during the coupling and/or isolation process, but generally the coupled product appears as a mixture of diastereomeric iron complexes (**4A/B** in eq 2), in a ratio of 2:1 to 4:1. The major isomer can be tentatively assigned configuration **4B**, based on consistent chromatographic elution behavior and closely related examples in the literature.<sup>4</sup> The diastereomeric complexes are readily separated by preparative TLC, and the yields are based on weighed amounts of the separated isomers. The 1-ethoxy 1,3-diene double bond positional isomer can be a significant byproduct, either as the free ligand (**5** and **6**; Table I) or as the Fe(CO)<sub>3</sub> complex (**7** and **8**). Further rearrangement occurred to a minor extent in two cases (**9** and **10**, Table I).

Complexes of 1,3-dienes with Fe(CO)<sub>3</sub> provide starting points for useful synthesis methodology via direct nucleophile addition<sup>5</sup> and by conversion to (η<sup>5</sup>-pentadienyl)Fe(CO)<sub>3</sub> cationic complexes

(3) General procedure: a sample of complex **1** (1.5 mmol) and the diene (6-10 mmol) in 25 mL of *n*-hexane was allowed to stir under argon at 60-70 °C for 0.5-10.0 h. The mixture was concentrated at reduced pressure, and the residue was purified by preparative TLC on silica gel. Elution with hexane/ether 8:1 provided complete separation of the isomeric adducts. All structures of type **4** listed in Table I show satisfactory IR, <sup>1</sup>H NMR, and low-resolution MS data. In addition, evidence for composition (high-resolution MS or combustion analysis) has been obtained for at least one member of each diastereomeric pair **4**. The minor product **5** is a mixture of geometrical isomers (<sup>1</sup>H NMR), while **6** is homogeneous by chromatographic and spectral analysis; the *cis*-ethoxy configuration shown is based on the special chemical shift of "inner" proton at C-4, δ 2.0-2.1. In the absence of the *cis*-ethoxy, the "inner" proton appears near δ 1.0. Complexes **9**, **12**, and **14** were characterized primarily by spectral data, while spectral and composition data have been obtained for complexes **7**, **8**, **10**, **11**, **13**, and **15**. Representative characterization data from Table I, entry 3. Eluted first was the minor diastereoisomer, 117 mg, 18% yield, as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.4-7.2 (m, 5 H, Ar H), 5.06 (d, *J* = 8.4 Hz, 1 H), 3.96 (d, *J* = 7.5 Hz, 1 H), 3.40-3.20 (m, 2 H), 2.06 (s, 3 H), 1.38 (d, *J* = 6.3 Hz, 3 H), 1.18 (t, *J* = 7.0 Hz), 1.04 (q, *J* = 6.3 Hz, 1 H), 0.98 (dd, *J* = 8.4, 7.5 Hz, 1 H). IR (neat): 2980 (m), 2880 (m), 2040 (s), 1965 (s), 1450 (m), 1390 (m) cm<sup>-1</sup>. Mass spectrum (EI): *m/e* 356 (parent, 13% of base), 328 (15), 300 (32), 272 (29), 228 (100), 226 (91), 174 (45), 95 (59). Eluted next was the major diastereomer, 353 mg, 54% yield as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.4-7.2 (m, 5 H, Ar H), 5.06 (d, *J* = 8 Hz, 1 H, H at C-3), 3.96 (d, *J* = 7.5 Hz, 1 H, H at C-1), 3.4-3.2 (m, 2 H), 2.06 (s, 3 H, C-9 Me), 1.38 (d, *J* = 6.3 Hz, 3 H, C-6 Me), 1.18 (t, *J* = 7.0 Hz, 3 H, C-8 Me), 1.04 (q, *J* = 6.3 Hz, 1 H, H at C-5), 0.98 (dd, *J* = 8.4, 7.5 Hz, 1 H, H at C-2). IR (neat): 2980 (m), 2880 (m), 2040 (s), 1965 (vs), 1450 (m), 1390 (m) cm<sup>-1</sup>. Mass spectrum (EI): *m/e* 356 (parent, 8% of base), 338 (9), 300 (24), 272 (15), 228 (83), 226 (72), 170 (87), 155 (80), 143 (61), 115 (44), 91 (100). Anal. Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>Fe: C, 60.70; H, 5.66; Fe 15.68. Found: C, 60.80; H, 5.48; Fe 15.90.

(4) The separation and identification of isomers referred to as ψ-endo (**4A**) and ψ-exo (**4B**) have been studied carefully in closely related systems: (a) Gresham, D. G.; Lillya, C. P.; Uden, P. C.; Walters, F. H. *J. Organomet. Chem.* **1977**, *142*, 123. (b) Clinton, N. A.; Lillya, C. P. *J. Am. Chem. Soc.* **1970**, *92*, 3058. (c) Kahn, D. E.; Lillya, C. P. *Ibid.* **1972**, *94*, 1682.

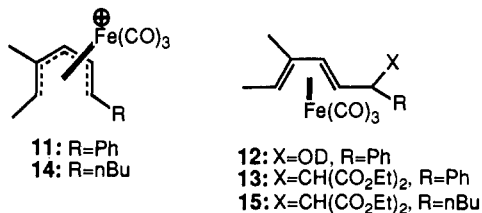
(5) (a) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363. (b) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497. (c) Semmelhack, M. F.; Herndon, J. W.; Liu, J. K. *Organometallics* **1983**, *2*, 1885.

**Table I.** Coupling of 1,3-Dienes with Complexes **1a** and **1b**

entry	complex	1,3-diene	products yield (diastereomer ratio)	byproducts (yield)
1.	<b>1a</b>		 68% <sup>a</sup> (3:1)	 5 (5%) <sup>b</sup>
2.	<b>1a</b>		 90% (2:1)	 6 (10%) <sup>c</sup>
3.	<b>1a</b>		 72% (3:1)	---
4.	<b>1b</b>		 68% (4:1)	---
5.	<b>1a</b>		 87% (3:1)	---
6.	<b>1a</b>		 83% (2:1)	---
7.	<b>1a</b>		 42% (-)	 9 (22%)  7 (10%)  10 (7%)
8.	<b>1a</b>		 23% (2:1) <sup>e</sup>	 7 (10%)  10 (7%)
9.	<b>1a</b>		 0%	 8 (19%)

<sup>a</sup>This yield includes a 20% yield of the uncomplexed diene. <sup>b</sup>A mixture of geometrical isomers was obtained. <sup>c</sup>A single isomer was obtained but the configuration has not been established. <sup>d</sup>Only one isomer was isolated. <sup>e</sup>The major isomer could not be obtained pure; the structure assignment is tentative.

which are powerful electrophiles.<sup>6</sup> The 5-ethoxy substituent is particularly convenient for conversion to the activated  $\eta^5$ -pentaadienyl system. When the major adduct from 4-methyl-1,3-pentadiene (entry 3) was allowed to react with perchloric acid (70%) in acetic anhydride at 0 °C, the salt **11** was produced as orange crystals in 99% yield.<sup>7</sup> Reaction of **11** with D<sub>2</sub>O in an NMR tube



produced the alcohol **12** in high yield, as a single diastereomer.<sup>8</sup>

(6) Formation of ( $\eta^5$ -cyclohexadienyl)Fe(CO)<sub>3</sub> cations by hydride abstraction from ( $\eta^4$ -1,3-cyclohexadiene)Fe(CO)<sub>3</sub> complexes is a general technique which has been developed as the first stage of the synthesis methodology for coupling nucleophiles with cyclohexadienyl ligands. For a review, see: Birch, A. J. *J. Organomet. Chem.* **1985**, *285*, 267.

(7) The open ( $\eta^5$ -pentaadienyl)Fe(CO)<sub>3</sub> cationic complexes have been much less developed compared to the  $\eta^5$ -cyclohexadienyl analogues, partly for lack of general methods of preparation. However, for examples and leading references, see: (a) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans.* **1976**, 954. (b) Bonner, T. G.; Holder, K. A.; Powell, P. *J. Organomet. Chem.* **1974**, *77*, C37. The protonolysis method of formation used here is adapted from: Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955.

Addition of diethyl sodiomalonate at 25 °C converted **11** into adduct **13**, in 81% yield, again as a single diastereomer. Similarly, the major diene complex in the table, entry 4 (from the *n*-butylcarbene complex **1b** and 4-methyl-1,3-pentadiene) was converted to the salt **14** (brown oil, 83%). Reaction of **14** with diethyl sodiomalonate gave a mixture of products from which isomer **15** could be obtained in 25% yield.

A mechanism for the (carbene)iron/diene coupling is postulated in Figure 1 by using as an example 2-methyl-1,3-pentadiene because the substrate leads to all three product types: the major product of type **4**, the diene positional isomer **7**, and the further rearrangement product **10** (Table I, entry 8). The first step is likely to be dissociation of CO and  $\eta^2$ -coordination of the less substituted double bond of the 1,3-diene, although we have not probed for direct evidence on this point. The failure of more highly alkyl substituted dienes is consistent with poor coordination of such species to low-valent iron. Formation of a vinyl-substituted ferracyclobutane (**16**) is proposed, which can undergo  $\beta$ -H elimination to give Fe(II) hydride complexes **17a** and **17b** or their  $\eta^3$ -allyl equivalent. Reductive-elimination from **17a** gives the product of type **4**, usually the major product, while the same process from **17b** produces the simple diene positional isomer **7**.<sup>9</sup> Alternatively, the iron-hydride unit can add across C-4/C-5 in **17b** to produce a new ferracyclobutane, **18**. Now  $\beta$ -H elimination followed by reductive elimination gives **10**. We imagine that a substituent at C-3 in **17a** disfavors reductive elimination to the product type **4** due to the formation of a highly substituted 1,3-diene ligand, while formation of **7** or **10** is favored by an electronic effect of the phenyl and/or ethoxy groups. Further characterization of the pathway and full elaboration of the coupling process is under way.

**Acknowledgment** is made to the National Science Foundation and the National Institutes of Health for generous support of our programs. We thank Dr. D. Little for collecting the mass spectral data.

(8) Nucleophile addition to  $\eta^5$ -pentaadienyl ligands is known to be highly stereoselective for the  $\psi$ -exo isomer. For examples, see ref 4. See also: Maglio, G.; Musco, A.; Palumbo, R. *J. Organomet. Chem.* **1971**, *32*, 127.

(9) The overall cycloaddition of olefins with carbene ligands followed by  $\beta$ -hydrogen elimination and reductive elimination is rare; for a discussion and leading references, consult ref 2a. However, each step is well precedented.

## Dehydrogenation and Cracking of *n*-Butane with Gas-Phase Ni<sub>n</sub><sup>+</sup>, Pd<sub>n</sub><sup>+</sup>, and Pt<sub>n</sub><sup>+</sup> Cluster Ions

Thomas F. Magnera, Donald E. David, and Josef Michl\*

Department of Chemistry, University of Utah  
Salt Lake City, Utah 84112

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The reactivity of small transition-metal particles as a function of their size has been of considerable interest in bridging the gap between homogeneous and heterogeneous catalysis.<sup>1</sup> An obvious approach is to investigate the reactivity of transition-metal clusters or cluster ions<sup>2</sup> as a function of size. Although some reports of such work with neutral clusters have appeared,<sup>3</sup> progress with cluster ions has been hampered by the poor availability of intense sources. Sputtering by kiloelectronvolt atoms or ions promises to be such a source.<sup>4</sup> We now report an extension of our previous

\* Present address: Department of Chemistry, University of Texas at Austin, Austin, TX 78712-1167.

(1) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981.

(2) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(3) For instance, Geusic, M. E.; Morse, M. D.; Smalley, R. E. *J. Chem. Phys.* **1985**, *82*, 590.