

From these studies we concluded (a) that deconjugation of the Δ^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: ¹H 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.

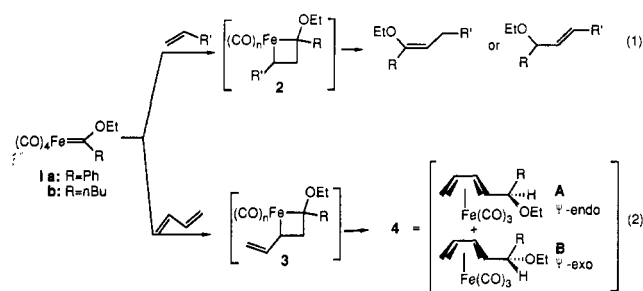
Coupling of 1,3-Dienes with (Carbene)iron Complexes To Give Substituted (1,3-Diene)Fe(CO)₃ Derivatives

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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.¹ 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.² 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^4 -1,3-diene)Fe(CO)₃ 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.

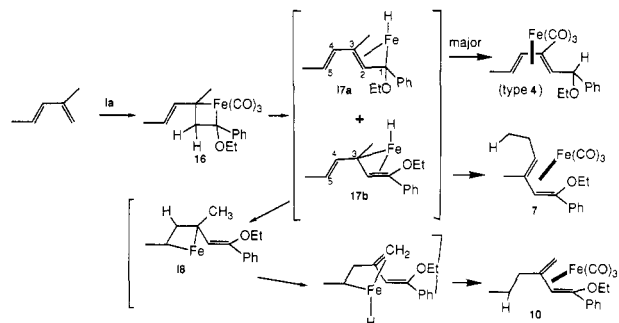


Figure 1. Suggested mechanism illustrated with **1a** and 2-methyl-1,3-pentadiene. CO ligands are deleted to simplify the intermediates.

Table I displays the results with a series of simple 1,3-dienes, following a standard procedure.³ 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.⁴ 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)₃ 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)₃ provide starting points for useful synthesis methodology via direct nucleophile addition⁵ and by conversion to (η^5 -pentadienyl)Fe(CO)₃ 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, ¹H 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 (¹H 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. ¹H NMR (CDCl₃, 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⁻¹. 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. ¹H NMR (CDCl₃, 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⁻¹. 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 C₁₈H₂₀O₄Fe: 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.

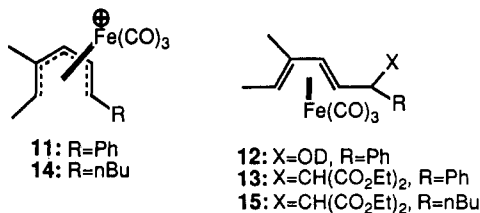
(5) (a) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363. (b) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497. (c) Semmelhack, M. F.; Herndon, J. W.; Liu, J. K. *Organometallics* **1983**, *2*, 1885.

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

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

^aThis yield includes a 20% yield of the uncomplexed diene. ^bA mixture of geometrical isomers was obtained. ^cA single isomer was obtained but the configuration has not been established. ^dOnly one isomer was isolated. ^eThe major isomer could not be obtained pure; the structure assignment is tentative.

which are powerful electrophiles.⁶ The 5-ethoxy substituent is particularly convenient for conversion to the activated η^5 -penta-1,3-dienyl 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.⁷ Reaction of **11** with D₂O in an NMR tube



produced the alcohol **12** in high yield, as a single diastereomer.⁸

(6) Formation of (η^5 -cyclohexadienyl)Fe(CO)₃ cations by hydride abstraction from (η^4 -1,3-cyclohexadiene)Fe(CO)₃ 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 (η^5 -penta-1,3-dienyl)Fe(CO)₃ cationic complexes have been much less developed compared to the η^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 η^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 β -H elimination to give Fe(II) hydride complexes **17a** and **17b** or their η^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**.⁹ Alternatively, the iron-hydride unit can add across C-4/C-5 in **17b** to produce a new ferracyclobutane, **18**. Now β -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.

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(8) Nucleophile addition to η^5 -penta-1,3-dienyl ligands is known to be highly stereoselective for the ψ -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 β -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_n⁺, Pd_n⁺, and Pt_n⁺ Cluster Ions

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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.¹ An obvious approach is to investigate the reactivity of transition-metal clusters or cluster ions² as a function of size. Although some reports of such work with neutral clusters have appeared,³ 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.⁴ We now report an extension of our previous

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(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.