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Exo-Selective Diels–Alder Reactions of α,β-Unsaturated Hexacarbonyl–Diiron Bridging Acyl Complexes

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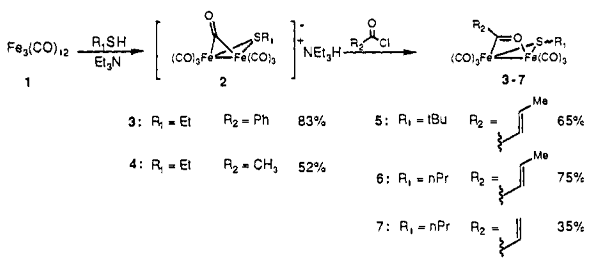
In the last 20 years, organic synthetic methodology has seen considerable growth in the use of stoichiometric transition-metal organometallic reagents. There are a number of reasons for this growth. In many cases, organometallic reagents offer increased reactivity over traditional organic moieties. Another advantage is that organometallic reagents allow access to reaction manifolds one does not see in traditional organic chemistry. Reductive elimination, oxidative addition, and carbon monoxide insertion are specific examples of transformations not usually utilized in organic chemistry. In 1985, Seyferth reported a facile route to iron acyl complexes of type **3** and **4**.[1] These complexes appear potentially useful for organic synthesis. First, the bridging acyl carbonyl in each of these complexes is polarized by the bond between the oxygen and second iron atom. One might think of this iron as an internal Lewis acid. This should make the carbonyl of these complexes electron deficient and therefore more reactive than simple organic esters. Second, the structure of the chiral iron moiety is such that one might expect to see diastereoselective reaction at either the "activated" carbonyl or groups attached to it. As a probe of these two features, we have investigated the reactivity and stereoselectivity of the Diels–Alder reaction of α,β-unsaturated complexes of this type with 1,3-dienes.

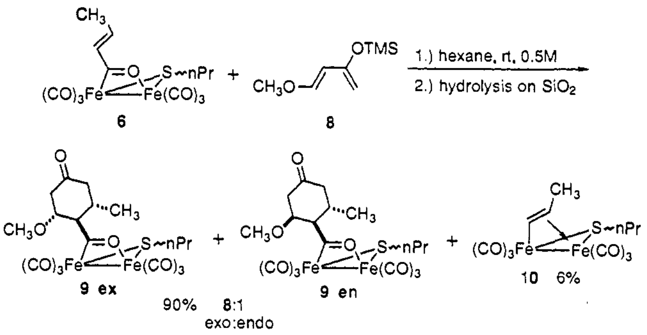
The synthesis of the dienophile **6** is effected by Seyferth's standard procedure, addition of *n*-propanethiol and triethylamine gives intermediate **2**, which is converted to the bridging acyl complex by addition of crotonyl chloride in 75% yield as a 2:1 ratio of isomers at sulfur (Scheme I).[1a] The air-stable complex was purified by silica gel chromatography. Reaction of the diastereomeric mixture **6** with Danishefsky's diene yielded four Diels–Alder adducts **9**, endo and exo products, each a 2:1 ratio of epimers at sulfur (90%), and another compound resulting from the deinsertion of the acyl carbonyl **10** (6%), (Scheme II).[1d,2] The formation of only four products, exo and endo, each epimeric at sulfur, is significant in that it indicates that the reaction takes place on only one face of the dienophile.

The ability of these complexes to undergo the Diels–Alder reaction at room temperature demonstrates that these complexes react as though they are electron deficient. Methyl crotonate requires, at the same concentration, 30 h at 120 °C to give an 86% yield of the Diels–Alder adduct with a 2:1 exo:endo ratio.[3,4] It has been reported that the monoiron acyl complexes, studied by Davies and others, do not undergo the Diels–Alder reaction without the influence of a Lewis acid.[5] This is an indication that the chemistry of the diiron complexes will be complementary to the chemistry of the monoiron cyclopentadiene complexes.

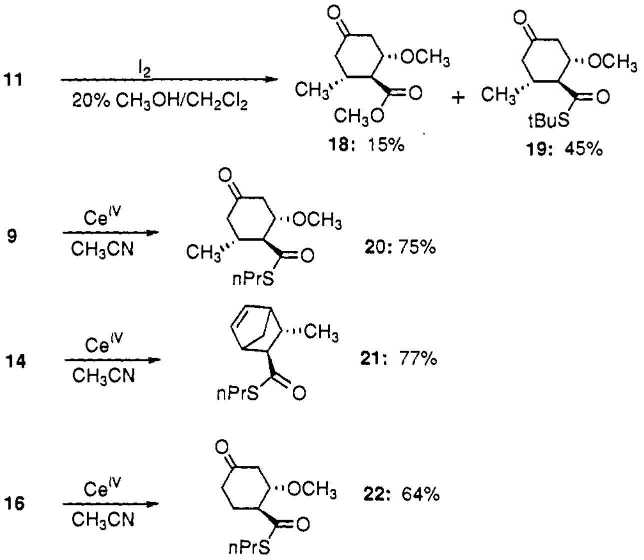
Scheme I



Scheme II



Scheme III. Oxidative Removal of the Metal



In addition to the increase in reactivity over the corresponding ester, we have also observed that the diiron system exhibits greater exo selectivity with acyclic dienes than the simple methyl ester.[6] The exo stereochemistry of the Diels–Alder adducts has been established by NMR and in the case of **20** by an X-ray crystal structure.[7] We have found that the selectivity of the reaction is dependent on the size of the alkyl group on the bridging sulfur. The ratio is 18:1 when R is *tert*-butyl (**5**), dropping to 8:1 when R is *n*-propyl (**6**) in the reaction with Danishefsky's diene (Table I). We believe the exo stereochemical preference of the reaction is due to the large steric nature of the diiron group. At the present time, we cannot determine whether the dienophile reacts in an

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(1) (a) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398. (b) Hoke, J. B.; Dewan, J. C.; Seyferth, D. *Organometallics* **1987**, *6*, 1816. (c) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430. (d) Seyferth, D.; Archer, C. M.; Ruschke, D. P. *Organometallics* **1991**, *10*, 3363.

(2) A number of conditions were investigated to prevent the formation of **10**. Running the reaction under 14 psi of carbon monoxide had no effect on the Diels–Alder deinsertion partition. Running the reaction at a higher concentration increased the yield of the Diels–Alder adduct slightly. Seyferth has reported that there appears to be no requirement of prior dissociation of carbon monoxide before the deinsertion takes place in α,β-unsaturated complexes.[1d]

(3) Danishefsky, S.; Kitahara, T.; Yan, C. F.; Morris, J. *J. Am. Chem. Soc.* **1979**, *101*, 6996.

(4) Vorndam, P. E. *J. Org. Chem.* **1990**, *55*, 3693.

(5) Herndon, J. W. *J. Org. Chem.* **1986**, *51*, 2853.

(6) W. D. Wulff has recently reported that aminocarbene complexes give exo products selectively. Anderson B. J.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10785.

(7) The stereochemical analysis of the diiron Diels–Alder adducts is complicated by the additional stereochemistry at the sulfur. It was therefore necessary to carry out the stereochemical analysis of the Diels–Alder selectivity on the corresponding thioesters. We have isolated both the exo and endo isomers of **9** and have found that they are converted to the thioester without isomerization or elimination.

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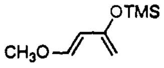
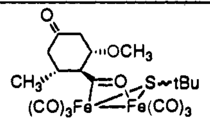
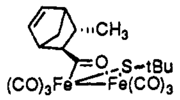
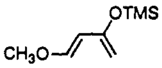
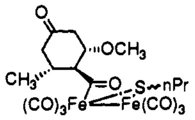
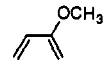
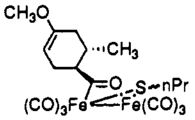
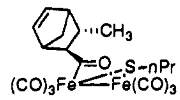
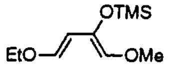
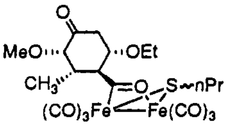
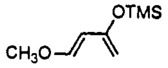
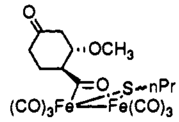
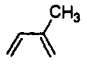
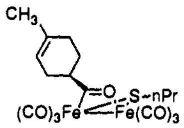
Table I. Diels–Alder Reactions

complex	diene	yield of D–A adduct (%)	exo:endo[a] (conditions)[b]	yield of deinsertion product (%)	product	
5		66[c]	18:1 (neat, 36 h)	32	11	
5		80	1:1 (neat, 18 h)	9	12	
6		90[c]	8:1 (0.5 M, 48 h, 3 equiv of diene)	6	9	
6		23	(neat, 3 days)	70	13	
6		89	1:1 (neat, 12 h)	5	14	
6		87[c]	14:1 (1.0 M, 8 h, 3 equiv of diene)	9	15	
7		86[c]	2.3:1 (neat, 12 h)	2	16	
7		73	(neat, 12 h)	2	17	

[a] The endo:exo ratios were determined by GC after conversion to the thioester.[10] [b] All reactions were run at room temperature. [c] The silyl enol ether product was hydrolyzed to the corresponding ketone during column chromatography on silica gel.

s-trans or s-cis conformation. Once these complexes are resolved, we should be able to address this issue.

The reaction of the crotonyl complex **6** is high yielding and exo selective for 2-siloxy-substituted dienes. Unfortunately, with less active dienes, the compound from deinsertion of the acyl carbonyl is the major product. The acrylate complex **7**, however, is sufficiently reactive to give **17** in a 73% yield in the reaction with isoprene. Addition of Lewis acids, $BF_3 \cdot Et_2O$, $SnCl_4$, or BBr_3, had no effect on the reactivity of the crotonyl complex **6** with isoprene or 1-methoxybutadiene. We have also attempted to replace one of the carbon monoxide ligands on the crotonyl complex with nitrosyl to increase the electron-deficient nature of the dienophile. To date, no Diels–Alder adducts have been observed by using that approach.

In order for these complexes to be use in organic synthesis, it is necessary to remove the acyl group from the iron in a clean and productive manner. Oxidation of **11** with iodine in the presence of methanol gave the expected methyl ester **18** in 15% yield along with a 45% yield of the thioester **19** (Scheme III).[8-10] Running the reaction with Ce^{IV} as the oxidant and without methanol present gives the thioester as the major product.

We are currently working on the resolution of these complexes to perform asymmetric Diels–Alder reactions. The exo selectivity and the fact that we observe only four iron complexes in the Diels–Alder reaction bodes well for the possibility of performing asymmetric Diels–Alder chemistry with these complexes.

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Supplementary Material Available: Experimental procedures, spectral data, and assignments of Diels–Alder adduct stereochemistry (7 pages). Ordering information is given on any current masthead page.

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(8) (a) Davies, S. G. *Chem. Br.* **1989**, 268. (b) Davies, S. G. *Aldrichim. Acta* **1990**, *23*(2), 31.

(9) (a) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194. (b) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (c) Liebeskind, L. S.; Welker, M. E. *Tetrahedron Lett.* **1984**, *25*, 4341.

(10) (a) Wong, P. K.; Madhavarao, M.; Marten, D. F.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2823. (b) Berryhill, S. R.; Rosenblum, M. *J. Org. Chem.* **1980**, *45*, 1984.