MeOHT and ODT, respectively. We find values of ΔW_{adh} of 2 mJ m^{-2} for hexadecane, 9 mJ m^{-2} for acetonitrile, and 43 mJ m^{-2} for water. For water, this corresponds to an interaction free energy of ~5 kJ per mole of MeOHT.

Sum-frequency spectroscopy shows that specific microscopic interactions, dependent on the chemical structure of both the liquid and the monolayer, clearly exist at the solid–liquid interface. To understand the wettability of organic surfaces, changes in the structure of the surface must be considered, particularly when hydrogen bonding is possible.

Registry No. MeOHT, 115422-11-2; Au, 7440-57-5; hexane, 110-54-3; acetonitrile, 75-05-8.

The First Catalytic Iron-Mediated [4 + 1] Cyclopentenone Assembly: Stereoselective Synthesis of 2,5-Dialkylidenecyclo-3-pentenones

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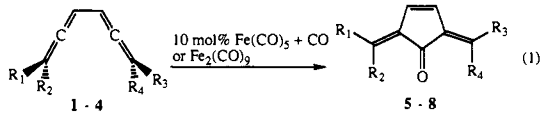
Herein is described the first transition metal catalyzed [4 + 1] cycloaddition reaction.[1] Conjugated diallenes react with CO under mild conditions in the presence of iron carbonyls to give the new ring structure of 2,5-dialkylidenecyclo-3-pentenones[2] in good yield. Several examples of [4 + 1] cycloadditions have been reported recently.[3] The assembly of 5-membered carbocyclic rings frequently involves [3 + 2][4] and Pauson-Khand[5] [2 + 2 + 1] cobalt-mediated cycloadditions. There is no precedent for iron carbonyls catalyzing [4 + 1] cycloaddition reactions.

Our discovery of this reaction came when diallene **1**[6] was treated with 1 equiv of $Fe_2(CO)_9$ at ambient temperature (eq 1), yielding **5** (79%) in less than 9 min! Surprisingly, the catalytic [4 + 1] reaction was achieved with $Fe(CO)_5$ (10 mol %, 17 mM CO).



1, **5** $R_1, R_3, R_2, R_4 = CH_3$

2, **6** $R_1, R_3 = C(CH_3)_3$, $R_2, R_4 = CH_3$

3, **7** $R_1, R_3 = C_6H_5$ $R_2, R_4 = CH_3$

4, **8** $R_1, R_4 = CH_3$ $R_2, R_3 = C(CH_3)_3$ and $R_2, R_3 = CH_3$ $R_1, R_4 = C(CH_3)_3$

Meso conjugated diallenes **2**[7] and **3**[8] gave a highly stereoselective reaction to form only **6** (72%) and **7** (81%), which would be difficult to prepare by other synthetic methods.

We also tested $Fe_3(CO)_{12}$ (10 mol %, 17 mM CO, THF) and found no detectable reaction. In contrast, $Fe_2(CO)_9$ (10 mol %, 17 mM CO) rapidly converted one turnover of **1** to **5**, with subsequent product formation occurring at a rate comparable to that observed for $Fe(CO)_5$ (Table I).

The catalytic reaction rate was measured at varying concentrations of **1**, $Fe(CO)_5$, and CO (Table I). It was found that the reaction was approximately inverse second order in CO and first order in **1** and $Fe(CO)_5$. These results are consistent with rate-determining coordination of monomeric iron to the diallene with concomitant loss of two CO groups.

The stereoselectivity of alkylidene bond formation provides information about the topology of this [4 + 1] reaction. Why was only one product formed in the case of the diallenes **2** and **3**? Since only one of the two symmetric products was formed using meso conjugated diallenes, the iron appears to exert a π-facial preference in binding or reaction with the diallene ligand. To probe reaction topology, a chiral (racemic) diallene diasteromer was studied. By fractional crystallization[6] pure diastereomer **2** was obtained as determined by X-ray crystallography.[6] A reaction of 4:6 mixture of diastereomers **2**(meso,C_s)/**4**(chiral,C_2) was stopped at 45% completion with 44% recovered starting material. NMR analysis revealed a symmetric product consistent with **6**[6] (89% based on recovered starting material) and confirmed by X-ray analysis (Figure 1). In addition, a minor unsymmetric isomeric product **8** was formed (7%). The recovered diallene showed a ratio of 14:86 for **2**/**4**, indicating that the meso isomer had reacted faster than the chiral (racemic) diastereomer.

Nevertheless, the formation of **8** requires stereospecific disrotatory movement of the sp diallene carbons of **4** during the cycloaddition. Since **2** was shown to give only **6**, the product **8** came from diastereomer **4**. One plausible mechanism to account for the assembly of **8** is shown in Scheme I. The kinetic data are consistent with rate-determining associative coordination of **4** to give **11** necessitating the formation of $Fe(CO)_5$ as part of the catalytic cycle. The reactivity of **2** is significantly greater than that of **4**, implying η^4-coordination to the s-cis diallene conformation as opposed to a mechanism whereby facial selectivity is determined by rate-determining η^2-coordination.

Cobalt η^4-bisketene[9] and iron vinylallene[10] complexes isoelectronic to **11** have been characterized by X-ray crystallography. In analogy to isolobal cobalt,[11] molybdenum[12] and zirconium[13] diene complexes **11** may convert to the metallacyclopentene **12**, necessitating synchronous movement of methyl (and *tert*-butyl) on *both* terminal diallene carbons. Insertion of CO to give **13**

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Table I. Relative Rate Dependence of $Fe(CO)_5$-Catalyzed [4 + 1] Cycloaddition at 50 °C in THF[a]

[**1**], mM	[M], mM	[CO], mM	k_{obsd}, s^{-1}	k_{rel}
290	29	17	9.6×10^{-4}	1.00
70	29	17	1.8×10^{-4}	0.19
290	10	17	3.9×10^{-4}	0.41
290	29	64	7.8×10^{-5}	0.08

[a] Each entry represents the average of five kinetic experiments monitored to at least 80% completion by ^1H NMR (200 MHz). M = $Fe(CO)_5$.

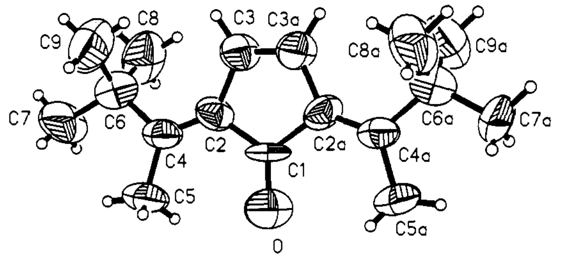
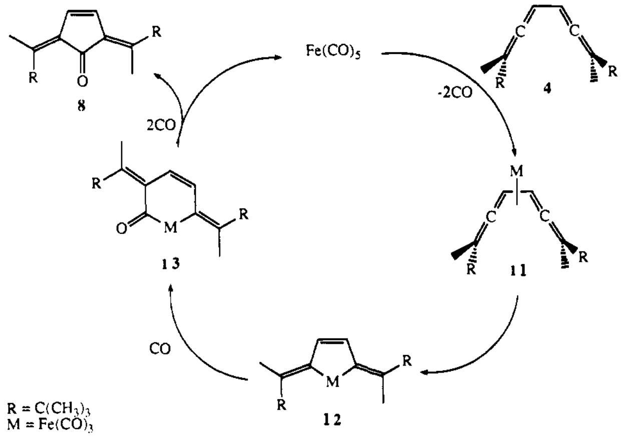


Figure 1. X-ray crystal structure analysis ORTEP view of **6**. Selected bond distances (Å): O–C1 1.232; C1–C2 1.508; C2–C3 1.467; C2–C4 1.319; C3–C3A 1.315; C4–C5 1.473; C4–C6 1.573.

Scheme I



and subsequent reductive elimination could form **8**[14] and regenerate the catalyst.

In summary, conjugated diallenes undergo stereoselective [4+1] cycloaddition with CO in the presence of $Fe(CO)_5$ or $Fe_2(CO)_9$ under preparatively useful conditions. Consistent with the first step being rate-limiting coordination of iron to the diallene, CO was found to be inhibitory. Facial selectivity of iron coordination may account for why meso diastereomers **2** and **3** yield only **6** and **7**. Surprisingly, sterically demanding diallene **4** gave some of **8** indicative of a stereospecific mechanism.

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Supplementary Material Available: Details of the X-ray crystal structure determination of **2** and **6** including solution and refinement, atomic coordinates, bond lengths, bond angles, isotropic and anisotropic displacement coefficients, and stereo ORTEP plots, together with experimental and analytical data (16 pages); tables of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Ring-Opening Polymerization of Strained, Ring-Tilted Ferrocenophanes: A Route to High Molecular Weight Poly(ferrocenylsilanes)[†]

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The development of new synthetic routes to macromolecules which contain inorganic elements or organometallic units is of considerable interest as a means of preparing materials with unusual and potentially useful properties.[1-5] Ring-opening polymerization represents an important, well-established route to organic polymers[6] and an increasingly successful method for the synthesis of inorganic macromolecules.[3-5] Ring-opening methods may also prove of great utility in the preparation of organometallic polymers, however, very few attempts to investigate this approach have been reported.[7] In this paper, we report the discovery of a novel, ring-opening route to organometallic polymers which provides access to the first examples of high molecular weight poly(ferrocenylsilanes).[8] These macromolecules possess a highly unusual main chain comprising ferrocene units and silicon atoms. Significantly, the synthetic route described is of potentially broad applicability as a similar methodology might also be successful with other strained organometallic monomers with related structures.[9,10]

[†] Dedicated to Beverley John Morris.

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