Catalytic Iron-Mediated [4 + 1] Cycloaddition of Diallenes with Carbon Monoxide

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Abstract: Conjugated diallenes undergo stereoselective [4 + 1] cycloadditions in a variety of solvents. Accelerated thermal exchange of CO in $Fe(CO)_5$ is catalyzed by the diallene substrate, consistent with the previous kinetic analysis. The Eyring activation parameters were determined to be $\Delta H^{\ddagger} = 16.2$ (±0.7) kcal mol^{-1} and $\Delta S^{\ddagger} = -17.9$ (±2.3) cal mol^{-1} K^{-1}. The negative entropy of activation is consistent with rate determining associative coordination of diallene to form a diallene−iron complex. The effect of coordinating solvents on this cycloaddition reaction suggests that the synthetic utility of these transformations can now be expanded to include diallenes with functional groups that may only weakly coordinate to the iron. Only one sterically demanding substituent on the diallene termini is necessary to give good π-facial selectivity, which also expands the synthetic utility of these transformations.

Introduction

Many small molecule drugs contain five-membered carbocyclic rings, such as prostaglandins,[1,2] methylenomycin antibiotics, and claviridenone antineoplastics.[3] Transition-metal mediated assembly of five-membered carbocycles could prove to be an important methodology for the synthesis of these ring systems. Syntheses of carbocyclic rings has been accomplished by [3 + 2][4] and the Pauson−Khand[5] [2 + 2 + 1] cycloadditions. Adding to the scope of transition-metal mediated synthesis of five-membered rings was the discovery of catalytic iron-mediated [4 + 1] cycloaddition of diallenes with carbon monoxide to give 2,5-dialkylidenecyclopentenones.[6] These molecules have been important for the investigation of reactivity and electronic structure in planar cross-conjugated π-systems. The biological activity and material science applications of 2,5-dialkylidenecyclopentenones have yet to be fully investigated.[7]

Until recently iron carbonyls catalytically mediating carbon−carbon bond formation was unprecedented. Historically, carbon−carbon bond chemistry accomplished with iron carbonyls had been stoichiometric.[8] In addition, catalytic iron carbonyl [4 + 1] cycloaddition reactions did not appear to require the extremes of thermal and/or photochemical activation that usually accompany the use of $Fe(CO)_5$. Herein we report a more detailed study of these new cycloaddition reactions.
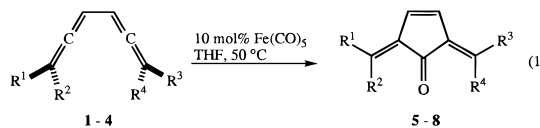
	R^1	R^2	R^3	R^4
1, 5	CH_3	CH_3	CH_3	CH_3
2, 6	$C(CH_3)_3$	CH_3	$C(CH_3)_3$	CH_3
3, 7	C_6H_5	CH_3	C_6H_5	CH_3
4, 8	$C(CH_3)_3$	CH_3	CH_3	$C(CH_3)_3$

The discovery of the [4 + 1] cycloaddition of diallenes with CO resulted from the treatment of **1** with stoichiometric amounts of $Fe_2(CO)_9$ to yield cycloaddition product **5** in less than 9 min. The catalytic [4 + 1] cycloaddition was achieved for **1**−**4** by treatment with $Fe(CO)_5$ (10 mol%, 17 mM CO) and gave highly stereoselective product formation and good yields (72−81%) of **5**−**8** (eq 1). Based on the previously published kinetic analysis (Table 1), differences in reactivity of the diallene

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

[**1**], mM	[Fe(CO)$_5$], mM	[CO], mM	k_{obs}, s^{-1}	k_{rel}
290	29	17	9.6×10^{-4}	1
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

Figure 1.   Effect of solvent on the [4 + 1] cycloaddition of **1** with CO.

diastereomers, and concomitant alkylidene stereochemistry of the cyclopentenone products, a mechanism was proposed as depicted in Scheme 1.

The first order dependence of the observed rate on the concentration of **1** and Fe(CO)$_5$ and inverse dependence on CO concentration is consistent with rate determining association of **1** and concomitant loss of carbon monoxide from Fe(CO)$_5$ to form **A**. The reactivity of **3** was observed to be significantly greater than **4**, apparently a consequence of the diallene symmetry. Meso diallenes **2** and **3** have an *s-cis* conformation (π-faces are different) where the steric hindrance on coordination of the metal can be minimized. The diallene diastereomer **4** has equivalent π-faces and C_2 symmetry for the s-cis conformation, necessitating coordination to a sterically hindered π-face. Because the two diastereomers give different and discrete products the cycloaddition must occur by a mechanism whereby the relative stereochemistry of the diallene is transfered to render the dialkylidenecyclopentenones stereospecifically. This symmetry-dependent outcome is consistent with η^4-coordination of the *s-cis* diallene and appears to rule out a mechanism whereby facial selectivity is determined by η^2-coordination.

Cobalt η^4-bisketene[9] and iron vinylallene[10] complexes isoelectronic to **A** have been isolated and characterized by X-ray crystallography. Conversion of **A** to the metallacyclopentene **B** may be proposed in analogy to the isolobal cobalt,[11] molybdenum,[12] and zirconium[13] diene complexes. Due to the highly stereoselective cycloaddition of **4**, the mechanism proposed in Scheme 1 requires synchronous disrotatory movement of both distal diallene carbons. Following a CO insertion step, reductive elimination[14] of **C** could form **8** and regenerate the catalyst.

Many unanswered questions remain concerning how this iron catalyzed reaction occurs under such mild conditions. For example, a dissociative reaction to form the Fe(CO)$_3$–η^4-butadiene complex from Fe(CO)$_5$, a complex isoelectronic to **A**, required prolonged heating at 140 °C.[15] Clearly the diallene substrate plays an important role in the iron-mediated [4 + 1] cycloaddition. Specifically, the preliminary data suggested an unprecedented associative mechanism as the rate determining step, which needed to be explored in greater detail. In addition, the effect of solvent and nonsymmetric diallenes on the product

distribution were of interest. The experiments described herein were designed to address these unanswered questions.

Results and Discussion

Solvent Effects. From the previous results it was not clear if coordinating solvents assist the coordination of the diallene to the iron or impede the reaction progress by competitively binding the iron. Previously reported kinetic experiments were only performed in THF-d_8. To determine the effect of solvent on the rate of the [4 + 1] cycloaddition of diallenes, the relative rates were measured in THF-d_8, C$_6$D$_6$, CD$_2$Cl$_2$, and CD$_3$CN (Figure 1). The poorly coordinating solvent, CD$_2$Cl$_2$, and the π-ligand solvent, C$_6$D$_6$, gave the fastest rates, while the σ-donor solvent, THF-d_8, gave slower rates. The strong σ-donor solvent, CD$_3$CN, gave significantly slower rates with only 2% conversion after 60 h under standard reaction conditions. These results are consistent with a mechanism where coordination of the diallene to the iron is slowed by use of a competitive solvent ligand, possibly involved in a nonproductive equilibrium. It remains to be shown that iron solvent complexes are not produced in the rate determining step in these coordinating solvents.

Selectivity of the [4 + 1] Cycloaddition. The highly stereoselective cycloaddition for diallenes containing two *tert*-butyls (or phenyls) made it important to test a diallene containing only one sterically demanding substituent. As discussed in the introduction, the iron putatively binds the diallene by η^4-coordination, and, thereby, **4** gives only one product that results from synchronous disrotatory movement of both terminal diallene carbons. It was unclear whether the stereoselectivity of alkylidene bond formation would be observed for a nonsymmetric diallene that did not contain two bulky groups on the diallene termini. The possibility existed that in the absence of two bulky substituents to dictate the π-face of iron coordination that alternative fluctional processes could yield a mixture of bisalkylidene-cyclopentenone products.

Compound **12** was prepared to test the effect of a nonsymmetric diallene in the [4 + 1] cycloaddition. Bromoallene **9**

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(10) (a) Alcock, N. W.; Richards, D. J.; Thomas, S. E. *Organometallics* **1991**, *10*, 231. (b) Kerr, C. E.; Eaton, B. E.; Kaduk, J. A. *Organometallics* **1995**, *14*, 269.
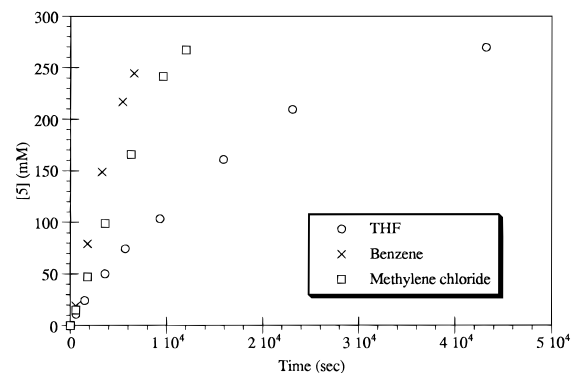
(11) Eaton, B. E.; King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359.

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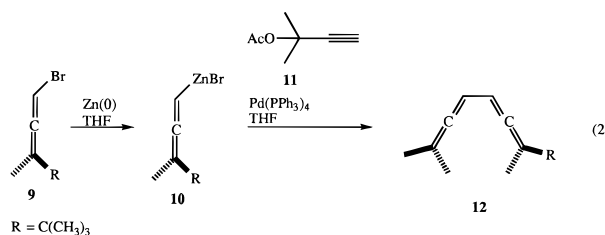
was prepared by methods previously reported.[16] Treatment of **9** with granular zinc afforded **10** which was treated *in situ* with **11** in the presence of a catalytic amount of $Pd(PPh_3)_4$ (1 mol%) to give the conjugated diallene **12** (eq 2).[17] It should be noted that in contrast to the symmetric diallenes studied previously that **12** is formed as a racemic mixture and that the cycloaddition experiment may be viewed as probing the ability of the iron to coordinate preferentially to the enantiotopic *re* or *si* faces of **12**.
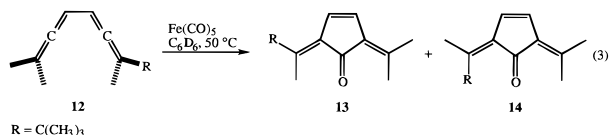
The diallene was treated with 10 mol% of $Fe(CO)_5$ and allowed to react at 50 °C (eq 3). The reaction was quenched with silica gel/triethylamine. Analysis by ^1H NMR showed only 2,5-dialkylidenecyclopentenone products **13** and **14** together with starting diallene **12**. Ratios of **13**:**14** were calculated to be 86:14 by ^1H NMR. GCMS analysis of the same mixture gave an identical product ratio. With only one sterically demanding substituent on the terminal diallene carbons, $Fe(CO)_5$ exhibits good π-facial selectivity. The diastereoselectivity is similar to that observed in the photochemical $Fe(CO)_5$ catalyzed [4 + 1] cycloadditions of allenyl imines,[18] allenyl ketones, and aldehydes.[19] Allenyl ketones were recently shown to undergo thermal cycloaddition with CO in 2-methyl-THF subsequent to photochemical activation of $Fe(CO)_5$ to give $Fe(CO)_4S$ (S = 2-methyl-THF).[20] However, the diallene cycloaddition reaction proceeds by a purely thermal mechanism and the stereoselectivity of alkylidene bond formation may be only superficially related.

$Fe(CO)_5$ Carbon Monoxide Exchange Studies. The kinetic data of Table 1 suggests that $Fe(CO)_5$ associatively equilibrates with **A**. Scheme 1 requires that the diallene catalyze CO exchange via **A** converting to $Fe(CO)_5$, which increases with CO pressure. Because $Fe(CO)_5$ is the resting state of the catalyst, a rate determining equilibrium could be ruled out if the diallene could not be shown to give any enhancement of the CO exchange in the iron carbonyl. It is important to note that the thermal exchange of CO from a pure sample of $Fe(CO)_5$ is very slow ($T_{1/2} > 4$ yr).[21]

It was of interest to determine if the diallene promoted exchange of CO in $Fe(CO)_5$. An experiment was performed under standard conditions for [4 + 1] cycloaddition using diallene **1** (290 mM), $Fe(CO)_5$ (29 mM, 10 mol%), and ^{13}CO (99.3% ^{13}C) at 64 mM in THF-d_8. The $Fe(CO)_5$ was carefully purified by repeated bulb-to-bulb distillation. Carbon monoxide exchange in $Fe(CO)_5$ was monitored in separate experiments by ^{13}C NMR and IR. At time zero, the ^{13}C NMR resonance for $Fe(CO)_5$ was observed at 211 ppm. The NMR tube was then placed in a constant temperature bath at 50 °C, and several data points were obtained (Figure 2). After reaction completion (96% conversion measured by ^1H NMR), the intensity of the $Fe(CO)_5$ peak in the ^{13}C NMR increased by 1.6 times relative

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(17) Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermee, P. *Tetrahedron Lett.* **1981**, *22*, 1451.
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(20) Sigman, M. S.; Eaton, B. E.; Heise, J. D.; Kubiak, C. P. *Organometallics* **1996**, *15*, 2829.
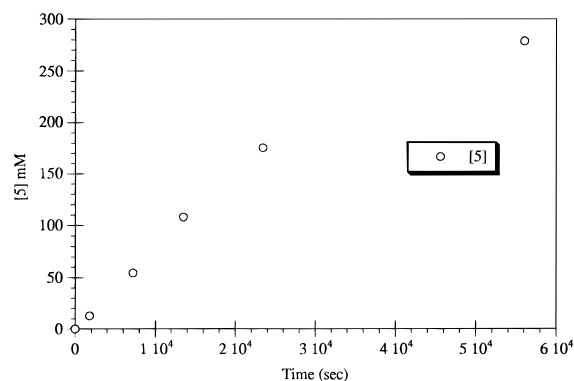(21) Keeley, D. F.; Johnson, R. E. *J. Inorg. Nucl. Chem.* **1959**, *11*, 33.

Figure 2. Kinetics of the [4 + 1] cycloaddition of **1** with ^{13}CO in THF-d_8.
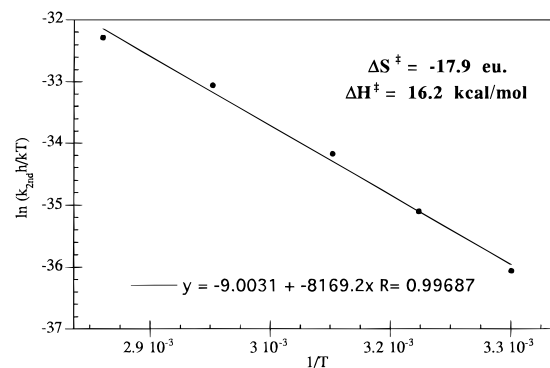

Figure 3. Activation parameters of the $Fe(CO)_5$ catalyzed [4 + 1] cycloaddition of **1** with CO.

to the solvent internal standard, which is consistent with incorporation of ^{13}CO into the $Fe(CO)_5$. No change was observed for the ^{13}C NMR CO resonance of $Fe(CO)_5$ without the diallene substrate under identical conditions.

IR experiments in THF at time zero showed bands assigned to the CO stretching frequencies of $Fe(CO)_5$ at 1993 cm^{-1} (E) and 2018 cm^{-1} (A$_2$). After cycloaddition completion a new IR band was observed at 1967 cm^{-1} (with unresolved shoulders) which is consistent with the expected isotopic shift for iron pentacarbonyl containing ^{13}CO. In addition, mass spectral analysis of the resulting cycloaddition product **5** showed two isotopic peaks for the molecular ions with an increase in ^{13}C abundance of ~30%. These results are consistent with a diallene promoted exchange of CO in $Fe(CO)_5$. The rate enhancement by **1** observed for ^{13}CO exchange in $Fe(CO)_5$ cannot be accurately determined from these experiments because rates of diffusion of CO in the absence of mixing could be rate limiting.

Activation Parameters. All of the data thus far supports rate determining association of the diallene to form **A** with concomitant loss of 2 CO's from $Fe(CO)_5$. The production of iron carbonyl complexes usually proceeds by either high temperature or photochemical-promoted dissociation of one or two carbon monoxide ligands.[8a] In order to probe the transition state of this unusual reaction for $Fe(CO)_5$, the activation parameters were determined in C_6D_6 using a temperature range from 30 °C to 80 °C (Figure 3). Kinetic data were collected in triplicate to at least 80% conversion for five temperatures. Using Eyring transition state theory, $\Delta H^\ddagger$ was calculated to be 16.2 ($\pm$ 0.7) kcal mol^{-1}, and $\Delta S^\ddagger$ was calculated to be -17.9 ($\pm$ 2.3) cal mol^{-1} K^{-1}. The large negative value for $\Delta S^\ddagger$ is consistent with an ordered transition state as would be expected for an associative coordination of diallene to $Fe(CO)_5$ as depicted in Scheme 1.

Scheme 1
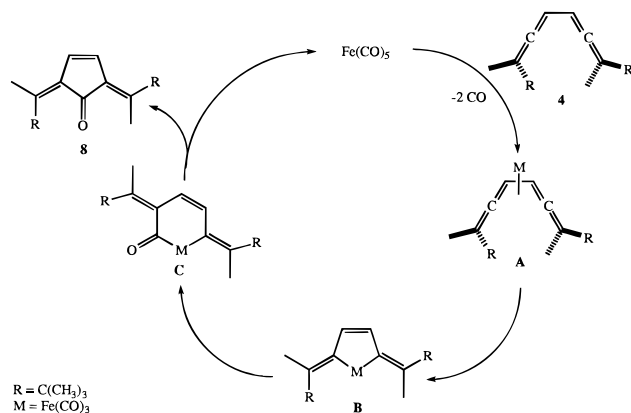
Scheme 2
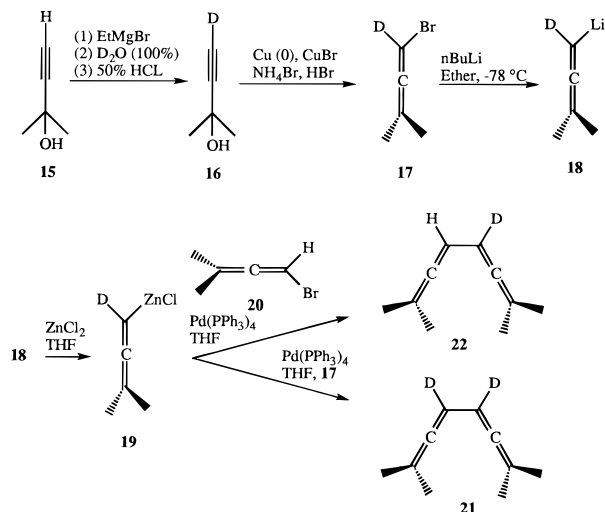
From Benson[22] table calculations it is clear that diallenes are high energy molecules relative to other conjugated systems such as dienes. It might be expected that the Hammond postulate would be manifested in the coordination of the diallene to the iron and that the low value of $\Delta H^{\ddagger}$ determined is consistent with significant stabilization in **1** proceeding to **A**.[23] However, it may be expected that such stabilization in forming **A** would be accompanied by a significant change in the hybridization of the diallene π-system on coordination to the iron. It remained unclear to what degree the diallene π-system had been affected at the transition state in coordination to the iron.

Secondary Isotope Effects. The activation parameters and kinetic analysis indicate that formation of the η^4-complex **A** is rate determining. X-ray analysis of a $Fe(CO)_3$−vinylallene complex electronically related to intermediate **A** showed very little change in hybridization of the internal allenic sp^2 carbons.[10b] It was appreciated at the outset of designing this experiment that the secondary isotope effects would only be observable for large changes in hybridization of the internal diallene carbons at the transition state and that if the transition state resembled **A** it was unlikely to give significantly different rates for the deuteriodiallenes. Dideuteriodiallenes appropriately labeled would be expected to be most sensitive ($\{k_D/k_H\}^2$) in this regard when compared to **1** if rate determining η^4-coordination was occurring and resulted in changes in hybridization of the π-system.

(22) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

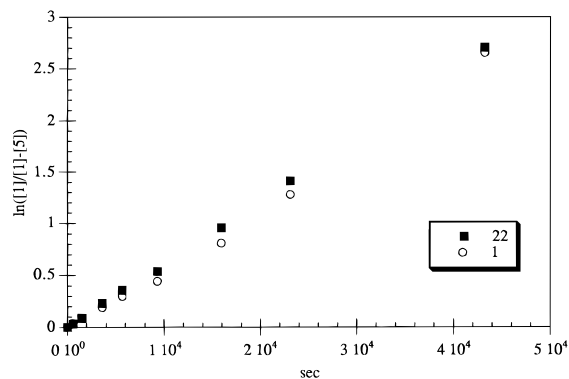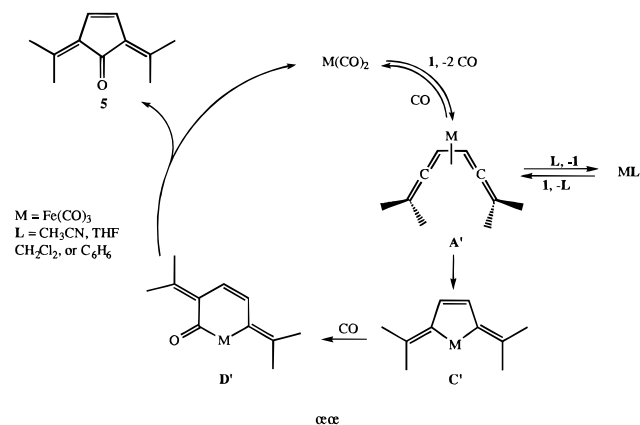(23) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

**Figure 4.** Relative rates for the iron-mediated cycloaddition of **1** and **22**.

Scheme 3

Isotopically labeled diallenes **21** and **22** were synthesized as shown in Scheme 2. Deprotonation of the acetylide proton of **15** with CH_3CH_2MgBr and quenching with D_2O gave **16**.[24] The allenyl bromide **17** was made by standard conditions[16] with no loss of deuterium incorporation. Allenyl zinc reagent **19** was prepared *in situ* by treatment of **18** with $ZnCl_2$. Deuteriodiallenes were assembled by a palladium catalyzed coupling of allenyl zinc reagent **19** with either bromoallene **17** or **20** with no loss of deuterium incorporation.[17]

Under standard conditions for cycloaddition (290 mM diallene, 29 mM $Fe(CO)_5$), the reaction was monitored for >3 half-lives but showed no observable difference in rates between diallene **1** and **22** (Figure 4). With the more sensitive diallene **21** there was also no rate difference measured. These data are consistent with either of three possibilities; first, only minimal changes in hybridization at the internal sp^2 diallene carbons are occurring in the transition state leading to **A**, second, diallene coordination proceeds directly to **B**, where the internal diallene carbons are not significantly affected, and third these results do not rule out the possibility of rate determining coordination of the iron to the terminal π-bonds of the diallene followed by rapid isomerization to the internal π-bonds.

The results of this investigation have failed to rule out the mechanism proposed previously. New insight into the mechanism of iron carbonyl catalyzed [4 + 1] cycloaddition of diallenes with carbon monoxide has been revealed, however, and Scheme 3 depicts the additional features of this chemistry that we now propose. Consistent with the previously reported kinetic results and the accelerated carbon monoxide exchange in $Fe(CO)_5$ facilitated by the diallene reported here, it now seems reasonable to propose an equilibrium in the rate determining

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Scheme 4

M = Fe(CO)$_3$
R = (CH$_3$)$_3$C
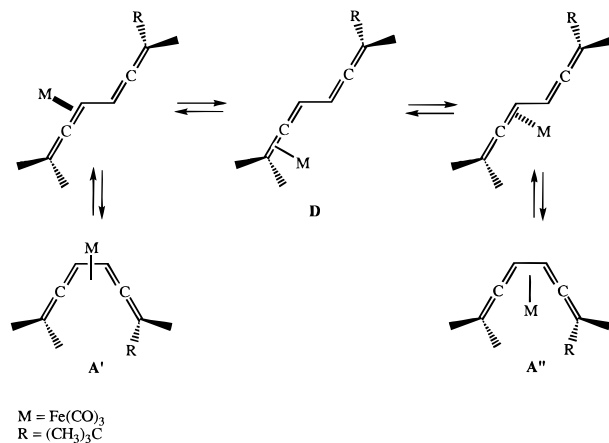
step, where the back reaction (Scheme 3) of **A′** to Fe(CO)$_5$ and **1** is competitive with cycloaddition. The solvent effects on the reaction appear to correlate with the σ-donor ability of the solvent and may be explained by a nonproductive equilibrium that diminishes the steady-state concentration of **A′**. No solvent complexes **ML** could be detected by ^{1}H NMR analysis in the solvent that resulted in the slowest rate of cycloaddition (CD$_3$CN 99.5% D).

Cycloaddition with the nonsymmetric diallene **12** gave a significant decrease in the stereoselectivity of alkylidene bond formation as compared to its symmetric counterpart **2**, which may be attributed to either decreased π-facial selectivity in forming **A′** or isomerization between the two possible η^4-diallene iron diastereomers **A′** and **A″** (Scheme 4). The rapid isomerization of η^2-allene−iron complexes has been reported previously.[25] Bulky groups on the diallene termini may impede the formation of complexes related to **D** and thereby slow the rate of equilibration between diastereomers.

Conclusions. It is now clear that conjugated diallenes undergo stereoselective [4 + 1] cycloaddition in a variety of solvents. Coordinating solvents slowed the rates of cyclo-addition, probably due to competitive binding to the metal center. No CO exchange in Fe(CO)$_5$ is observed in the absence of diallene under standard conditions for cycloaddition. Consistent with rate determining associative coordination of diallene to form complex **A**, a large negative entropy of activation was determined. The synthetic utility of these transformations can now be expanded to include diallenes with functional groups that may only weakly coordinate to the iron. Only one sterically demanding substituent on the diallene termini is necessary to give good π-facial selectivity, which also expands the synthetic utility of these transformations. The application of [4 + 1] cycloaddition to the synthesis of 2,5-dialkylidenecyclopenten-ones with biological activity and new material science applications is currently in progress.

Experimental Section

General Procedures. All reactions and manipulations were conducted under a dry argon atmosphere either using an inert atmosphere glovebox or standard Schlenk techniques. All NMR data were recorded on a Bruker AMX (300 MHz ^{1}H). NMR splitting patterns are reported as follows: s = singlet, d = doublet, q = quartet, h = heptet, sep = septet. IR were recorded on a Perkin Elmer 1600 FTIR. Mass spectral data were obtained from the departmental facility at Washington State University. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Tetrakistriphenylphosphinepalladium was prepared

by a literature method.[26] THF-d_8 and benzene-d_6 (Aldrich Chemical Co.) were distilled from benzophenone/potassium. Acetonitrile-d_3 and methylene chloride-d_2 (Aldrich Chemical Co.) were distilled form CaH$_2$. Isotopic ^{13}CO (99.3% ^{13}C) was purchased from Isotec Inc. Fe(CO)$_5$ (Strem Chemicals Inc.) was vacuum distilled and stored at −30 °C in the dark.

Synthesis of 12. In a flame dried 50 mL flask, zinc (547 mg, 7.8 mmol) and 10 mL of freshly distilled THF (K/benzophenone) were combined. To this flask, 1-bromo-3,4,4-trimethylpentadi-2,3-ene (**9**) (1 mL, 6.0 mmol) was added and allowed to stir at ambient temperature for 3 h until a gray color persisted. The gray solution was then added via canula to a mixture of tetrakistriphenylphosphinepalladium (69 mg, 1 mol%) and 2-(2-methyl-3-butynyl)acetate (**11**) (795 mg, 6.3 mmol) in 20 mL of THF. After 30 min, the reaction was quenched with MeOH (1 mL) and silica gel (1 g). The solvent was removed, and the resulting residue was washed with 100 mL of pentane through a short pad of silica. Column chromatography of the resulting oil followed by vacuum distillation (35 °C, 1 mm) yielded 572 mg (54%) of **12** as a colorless oil. ^{1}H (300 MHz, C$_6$D$_6$) δ 1.01 (s, 9H), 1.56 (d, J = 2.7 Hz, 6H), 1.62 (d, J = 2.6 Hz, 3H), 5.70 (dsep, J = 2.7, 10.0 Hz, 1H), 5.78 (dq, J = 2.6, 10.0 Hz, 1H); ^{13}C{^{1}H} (75 MHz, C$_6$D$_6$) δ 15.10, 20.62, 29.23, 33.97, 89.69, 89.83, 91.16, 96.62, 203.01, 204.14; IR (CH$_2$Cl$_2$) 1960 cm^{-1}; HRMS m/z for C$_{13}$H$_{20}$ calcd 176.1565, found 176.1542.

Cycloaddition of 12. To a low pressure 5 mm NMR tube were combined **12** (48 mg, 0.284 mmol) and Fe(CO)$_5$ (4 μL, 10 mol%) in C$_6$D$_6$, and the tube charged with 10 psi CO. The reaction was allowed to heat for 60 h at 50 °C, and NMR analysis showed partial conversion to product. The reaction was quenched with silica gel/triethylamine, and the solvent was removed by a rotary evaporator. The crude product was washed with CH$_2$Cl$_2$, the solvent was removed by a rotary evaporator, and the residue was loaded onto a prep-silica gel plate. The plate was eluted with 15% CH$_2$Cl$_2$/hexane, and two small bands were isolated together. NMR analysis of the bands showed a mixture of products with a 86/14 isomeric ratio of *E/Z*. GCMS of the same sample gave identical results for the isomeric ratio and confirmation of the correct molecular weight.

13. 43% ^{1}H (300 MHz, C$_6$D$_6$) δ 1.04 (s, 9H), 1.53 (s, 3H), 2.30 (s, 3H), 2.47 (s, 3H), 6.45 (d, J = 7.3 Hz, 1H), 6.88 (d, J = 7.3 Hz, 1H); ^{13}C{^{1}H} (75 MHz, C$_6$D$_6$) δ 16.03, 20.11, 22.98, 30.35, 38.15, 127.77, 129.79, 132.92, 133.32, 141.93, 155.52, 195.72; IR (CH$_2$Cl$_2$) 1693 cm^{-1}; HRMS m/z for C$_{14}$H$_{20}$O calcd 204.1514, found 204.1512.

14. 8% ^{1}H (300 MHz, C$_6$D$_6$) δ 1.43 (s, 9H), 1.57 (s, 3H), 1.76 (s, 3H), 2.31 (s, 3H), 6.53 (d, J = 7.2 Hz, 1H), 6.62 (d, J = 7.2 Hz, 1H); ^{13}C{^{1}H} (75 MHz, C$_6$D$_6$) δ 20.08, 20.10, 23.01, 28.95, 37.24, 127.88, 131.19, 134.49, 135.56, 142.02, 155.80, 192.65; IR (CH$_2$Cl$_2$) 1697 cm^{-1}; MS m/z 204.

16. In a three necked 500 mL flask equipped with a reflux condenser and an addition funnel, 80 mL of a 3 M (238 mmol) solution of ethyl magnesium bromide in diethyl ether and 200 mL of freshly distilled diethyl ether (NaK/benzophenone) were combined at room temperature. The addition funnel was charged with 2-methyl-3-butyn-2-ol (**15**) (5.0 g, 59 mmol) and 20 mL of diethyl ether. This solution was added slowly with vigorous stirring, the resulting mixture was refluxed for 90 min, and the solution was then cooled to ambient temperature. The reaction was quenched by slow addition of a solution of D$_2$O (99.96%, 559 mmol, 10 mL in 70 mL of THF). The resulting mixture was vigorously stirred for 12 h and followed by addition of 50% HCl (10 mL). The salts were filtered and washed with diethyl ether (3×, 30 mL), and the resulting solution was washed with H$_2$O (4×, 50 mL) and brine (1×, 50 mL) and dried over MgSO$_4$. After filtration, the diethyl ether was removed by a rotary evaporator, and the crude oil was fractionally distilled (97 °C, uncorrected) to yield 2.73 g of a colorless oil (54%) with >95% deuterium incorporation by NMR. ^{1}H [300 MHz, CDCl$_3$] δ 2.40 (s, 0.05H), 2.08 (s, 1H), 1.51 (s, 6H).

17. In a 25 mL round bottom flask, a mixture of cuprous bromide (1.39 g, 9.67 mmol), ammonium bromide (1.10 g, 11.25 mmol), copper powder (135 mg, 2.12 mmol) and concentrated hydrobromic acid (48% w/w, 6.6 mL, 58 mmol) were sparged with argon for 10 min. 3-Deuterio-2-methyl-3-butyn-2-ol (**16**) (2.25 g, 26.48 mmol) was added to the mixture and allowed to stir for 30 min at room temperature. The

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(26) Coulson, D. R. *Inorg. Syn.* **1972**, *13*, 121.

mixture was put into a separatory funnel where the aqueous layer was extracted with pentane (4×, 5 mL). The pentane extracts were combined, filtered, washed with HBr (3×, 4 mL), washed with saturated NaHCO$_3$ (2×, 5 mL) and dried with MgSO$_4$. The pentane was removed by a rotary evaporator and the resulting oil was vacuumed distilled (25 °C, 20 mmHg) to yield 2.59 g of a colorless oil (66%) with >93% deuterium incorporation by NMR. ^{1}H (300 MHz, CDCl$_3$) 5.80 (h, J = 2 Hz, 0.07 H), 1.82 (s, 6H).

21. In a 100 mL round bottom flask 2.5 M n-butyllithium (1.5 mL, 3.74 mmol) was slowly added to a solution of 1-bromo-1-deuterio-3-methylbuta-1,2-diene (553 mg, 3.74 mmol) in 35 mL of freshly distilled diethyl ether (K/benzophenone) at −78 °C. The solution was allowed to stir for 2 h at −78 °C and then slowly added via canula into a cooled flask containing zinc chloride (510 mg, 3.74 mmol) and 5 mL of diethyl ether. The resulting mixture was allowed to warm to ambient temperature over 90 min where the solution turned gray. After stirring for 30 min at ambient temperature, the mixture was added via canula into a 250 mL flask containing tetrakistriphenylphosphinepalladium (22 mg, 18.7 μmol), 1-bromo-1-deuterio-3-methylbuta-1,2-diene (**17**) (570 mg, 3.85 mmol), and 100 mL of THF. The mixture was allowed to stir for 30 min at ambient temperature, and the solvent was then removed by a rotary evaporator. The residue was placed on a silica gel pad (30 mL, 20 g), the pad was eluted with pentane (125 mL), and the solvent was removed by a rotary evaporator. Column chromatography on flash silica gel (hexane) yielded a white solid 234 mg (46%). ^{1}H [300 MHz, CDCl$_3$] δ 5.42 (s, 0.14H), 1.69 (s, 12H); MS m/z 136.

22. Identical to method used for **21** except coupled with **20** 40% yield of a white solid. ^{1}H (300 MHz, CDCl$_3$) δ 5.42 (s, 1.07H), 1.69 (s, 12H). MS m/z 135.

CO Exchange Study. To a silanized Wilmad 522-PP 5 mm high pressure NMR tube, a solution of 290 mM **1** and 29 mM Fe(CO)$_5$ in THF-d_8 was added. The tube was freeze−pumped−thawed three cycles and then charged with 40 psi ^{13}CO (64 mM). An initial ^{13}C NMR was taken, and the tube was placed into a constant temperature water bath at 50 °C. The reaction was monitored by ^{1}H and ^{13}C NMR until 96% conversion. The tube was then freeze−pumped−thawed four cycles to remove the CO, and samples were prepared for FTIR and MS.

Solvent Effect Kinetics. To a silanized low pressure NMR tube equipped with a J. Young valve, **1** (20 mg, 0.149 mM), 510 μL of solvent, and Fe(CO)$_5$ (1.9 μL, 10 mol%) were combined. The tube was charged with 10 psi CO (16 mM) and placed into a 50 °C constant temperature bath and monitored by ^{1}H NMR using the residual solvent resonance as an internal standard. The tube was repressurized with CO after collecting each data point.

Activation Parameters. For each temperature, the reaction was run in triplicate. To three silanized low pressure NMR tubes equipped with J. Young valves was added 500 μL of a solution containing 290 mM of **1** (290 mM) and Fe(CO)$_5$ (29 mM) in C$_6$D$_6$. The tubes were pressurized with 10 psi CO (16 mM) and placed into a constant temperature bath. The reactions were monitored by ^{1}H NMR until at least 80% conversion using the residual benzene resonance as an internal standard. The tube was repressurized with CO after collecting each data point.

Secondary Isotope Effects. To silanized NMR tubes were added Fe(CO)$_5$ (29 mM) and diallene (**1**, **21**, or **22**, 290 mM) in THF-d_8. The tubes were pressurized with 16 mM CO and placed into a constant temperature bath at 50 °C. The reactions were monitored by ^{1}H NMR until at least 80% conversion using the residual THF resonance as an internal standard. The tubes were repressurized with CO after collecting each data point.