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Catalytic Iron-Mediated Carbon-Oxygen and Carbon-Carbon Bond Formation in [4 + 1] Assembly of Alkylidenebutenolides

Matthew S. Sigman, Charles E. Kerr, and Bruce E. Eaton*

Department of Chemistry
Washington State University
Pullman, Washington 99164

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Herein is described the first iron-mediated catalytic [4 + 1] cycloaddition involving both carbon–carbon and carbon–oxygen bond formation. Transition-metal-mediated synthesis of 5-membered carbocyclic rings has been accomplished by [3 + 2],[1] Pauson–Khand [2 + 2 + 1],[2] and [4 + 1][3] cycloaddition. Transition-metal-mediated synthesis of α-methylene-γ-butyrolactones has been demonstrated previously.[4] Assembly of furans[5] and pyrones[6] has been accomplished by transition-metal-mediated carbon–oxygen bond formation. However, iron carbonyls are not known to facilitate catalytic carbon–oxygen bond formation,[7] and aldehyde oxygens are typically viewed as σ-donor ligands. Our discovery of this new [4 + 1] cycloaddition came when **1** was treated with 10 mol % $Fe(CO)_5$ and 64 mM CO in THF (eq 1)[8] under *fluorescent light*, affording **7** in high yield.[9] Typically, reactions of $Fe(CO)_5$ require elevated temperatures or UV photochemical activation. It is surprising that **1–6** react under such mild conditions. Benzene, acetonitrile, and CH_2Cl_2 could also be used as solvent in the cyclization. Both allenyl ketones and aldehydes react cleanly under these conditions to give the alkylidene-γ-butenolides as the only products. In analogy to our previous work on diallenes,[3a] these reactions show selectivity in alkylidene bond formation consistent with a π-facial preference of iron coordination. Good selectivity (83/17 *E*/*Z*) of alkylidene bond isomers can be achieved for both ketones and aldehydes when the terminal allene substituents are *tert*-butyl and methyl groups (**1–3**). These molecules would be difficult to prepare by other synthetic methods.

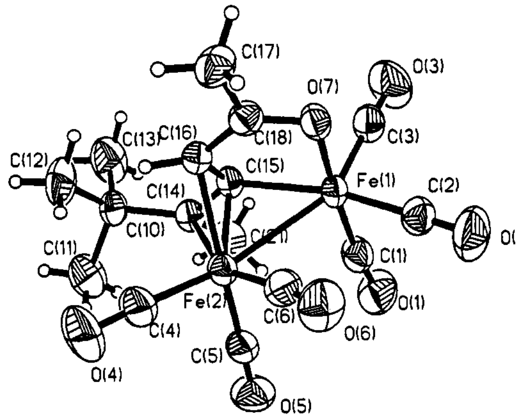
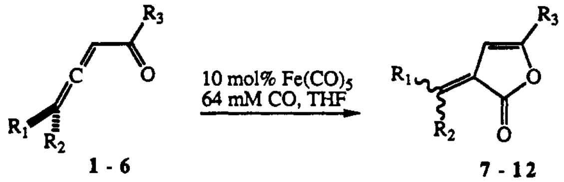


Figure 1. X-ray crystal structure analysis ORTEP view of **13**. Selected bond distances (Å): Fe1–Fe2 2.615, Fe1–C15 2.024, Fe1–O7 1.993, Fe2–C16 2.117, Fe2–C15 1.958, Fe2–C14 3.367, C18–O7 1.259, C16–C18 1.426, C15–C16 1.459, C14–C15 1.409.



1 - 6 **7 - 12** (1)

		%Yield	*E*/*Z*
1, 7	$R_1 = C(CH_3)_3$, $R_2 = CH_3$, $R_3 = CH_3$	89	83/17
2, 8	$R_1 = C(CH_3)_3$, $R_2 = CH_3$, $R_3 = H$	62	84/16
3, 9	$R_1 = C(CH_3)_3$, $R_2 = CH_3$, $R_3 = C_6H_5$	76	86/14
4, 10	R_1, $R_2 = CH_3$ $R_3 = H$	54	
5, 11	R_1, R_2, $R_3 = CH_3$	76	
6, 12	R_1, $R_2 = CH_3$ $R_3 = C_6H_5$	64	

Iron clusters do not facilitate this [4 + 1] cycloaddition reaction. Treatment of **1** with $Fe_2(CO)_9$ in pentane gave an excellent yield (90%) of the air-stable dinuclear cluster **13**[9] (ORTEP diagram, Figure 1). It will be noted that only one of the two possible alkylidene bond isomers was isolated, again consistent with coordination of iron showing selectivity in binding. Exposure of **13** to the reaction conditions outline by eq 1 failed to produce **7**, eliminating **13** from consideration as the active cycloaddition mediator. On treatment of **1** with $Fe_3(CO)_{12}$ (10 mol %), **13** (7%) was formed slowly with a concomitant equivalent of the active catalyst $Fe(CO)_5$, resulting in slow formation of **7**. As was seen for diallenes, these results are consistent with mononuclear iron acting as the catalyst.[10] No butenolide formation was observed after 36 h in the dark at 60 °C.

To gain further insight into this reaction, the influences of CO pressure, solvent polarity/coordination (Figure 2), and temperature were studied. In the π-ligand solvent C_6D_6, CO pressure had a negligible impact on the initial rates of reaction. The observed depression in the rate of formation of **7** at lower CO pressure was due to slow formation of the catalytically inactive complex **13**. Polarity of the solvent had a greater effect. CD_3CN as solvent caused a significant decrease in the rate of reaction, possibly due to its ability to serve as a σ-donor ligand. No formation of **13** was observed in CD_3CN. The relatively noncoordinating solvent CD_2Cl_2 caused a decrease of ca. 4-fold

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[1] (a) Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* **1992**, *57*, 6094. (b) Trost, B. M.; Matelich, M. C. *J. Am. Chem. Soc.* **1991**, *113*, 9007. (c) Trost, B. M.; Grese, T. A.; Chan, D. M. T. *J. Am. Chem. Soc.* **1991**, *113*, 7350. (d) Boivin, J.; Tailhan, C.; Zard, S. Z. *J. Am. Chem. Soc.* **1991**, *113*, 5874. (e) Rathjen, H.-J.; Margaretha, P.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 3904. (f) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, (g) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. (h) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61.

[2] (a) Pearson, A. J.; Shivly, R. J., Jr.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096. (b) Pauson, P. L. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer-Verlag: Berlin, 1987; p 234. (c) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (d) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855. (e) Billington, D. C.; Pauson, P. L. *Organometallics* **1982**, *1*, 1560.

[3] (a) Eaton, B. E.; Rollman, B.; Kaduk, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 6245. (b) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025.

[4] (a) Mori, M.; Washioka, Y.; Urayama, T.; Yoshiura, K.; Chiba, K.; Ban, Y. *J. Org. Chem.* **1983**, *48*, 4058. (b) Trost, B. M.; Coppola, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 6879. (c) Murray, T. F.; Samsel, E. G.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520. (d) Semmelhack, M. F.; Brickner, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3945. (e) Cowell, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4193. (f) Matsuda, I. *Chem. Lett.* **1978**, 773. (g) Corey, E. J.; Hegedus, L. *J. Am. Chem. Soc.* **1969**, *91*, 1233.

[5] (a) Padwa, A.; Kassir, J. M.; Xu, S. L. *J. Org. Chem.* **1991**, *56*, 6971. (b) Davies, H. M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343. (c) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520. (d) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550.

[6] (a) Cho, S. H.; Liebeskind, L. S. *J. Org. Chem.* **1987**, *52*, 2631. (b) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363. (c) Mitsudo, T.; Ogino, Y.; Komiya, Y.; Watanabe, H.; Watanabe, Y. *Organometallics* **1983**, *2*, 1202.

[7] (a) Alper, H. In *Organic Syntheses via Metal Carbonyls*; Wender, P., Ed.; Wiley: New York, 1977; Vol. 2, pp 545–593. (b) Trifonov, L. S.; Orahovats, A. S.; Linden, A.; Heimgartner, H. *Helv. Chim. Acta* **1992**, *75*, 1872.

[8] The isolated yields for the reactions shown by eq 1 are not optimized.

[9] The supplementary material contains synthetic details, X-ray crystallographic analysis, and analytical data.

[10] Control experiments under identical reaction conditions in the absence of $Fe(CO)_5$ gave no reaction.

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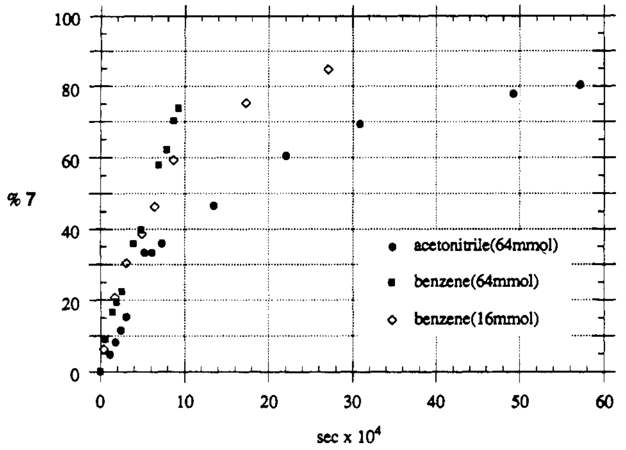


Figure 2. Effect of solvation and CO concentration on the rate of [4 + 1] cycloaddition of **1** under continuous irradiation.

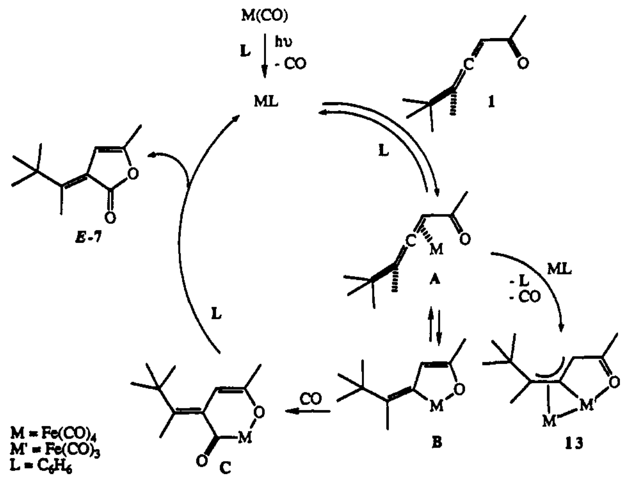
in the rate. Cooling the reaction vessel to –78 °C (toluene-d_8) slowed the reaction of **1** considerably, suggesting that a thermal step subsequent to photochemical activation can be made rate determining.

We studied the effect of more intense UV/vis sources on this reaction.[9] Iron pentacarbonyl has a weak UV/vis absorption (λ = 350 nm, ϵ = 209). When the reaction solution [$Fe(CO)_5$ 10 mol %, 16 mM CO] containing **5** was irradiated at 350 nm, **5** was converted to **11** (86%) in 10 min, consistent with photochemical excitation being important in the cycloaddition mechanism. Surprisingly, irradiation of **5** at higher energy (254 nm) gave incomplete conversion to **11** (50%) and considerable decomposition after prolonged irradiation. Because this reaction may be promoted by ambient fluorescent light to give excellent yields, it was of interest to investigate the relative quantum yield at 350 nm.[9] Employing an actinometer in an identical NMR tube, concentration and solvent (C_6D_6) initial rates of reaction gave a quantum yield > 1, consistent with a photochemical chain reaction. This result explains why these reactions can be facilitated by ambient fluorescent light.

Solvation/coordination has a significant effect on the rate of reaction. Only in benzene is the observed chemistry due to a photochemically initiated chain reaction. A proposed mechanism in benzene solvent that is consistent with the results discussed above and published photochemistry[11] of $Fe(CO)_5$ is given by Scheme I.

Photochemical activation of $Fe(CO)_5$ gives substitution of CO with solvent to form **ML**. In the presence of the allene substrate (e.g., **1**), **L** is displaced to give the η^2-complex **A** that is in equilibrium with the metallocycle **B**. These proposed intermediates have precedent in the closely related vinyl ketone,[12] vinyl amide,[13] and allenyl ester[14] iron carbonyl complexes. The lack of CO dependence for the reaction in benzene rules out rate-determining formation of coordinatively unsaturated intermediates. Step **B** to **C** cannot be rate determining because it would be aided by CO. Consistent with Scheme I, the coordinating solvent CH_3CN stabilizes **ML**, reducing its catalytic efficiency, perhaps requiring photochemical activation to allow substitution by the allene substrate.[11] Similarly, CH_2Cl_2 may not bind to the iron competitively relative to CO, resulting in formation of $Fe(CO)_5$ concomitant with product formation. Higher energy irradiation (254 nm) would produce a greater concentration of **ML** that could attack **A** or its isomer **B** to give the catalytically inactive **13** (Scheme I).

Scheme I



In summary, we have found that allenyl ketones and aldehydes can undergo iron-catalyzed [4 + 1] cycloaddition with carbon monoxide to give α-alkylidenebutenolides. Good control of alkylidene bond stereochemistry was achieved when the terminal allene substituents were methyl and *tert*-butyl groups. Reactions could be performed in a wide variety of solvents, lending to the flexibility of the method. The fastest reaction rates were observed in benzene, and relative quantum yield experiments suggest a photochemically initiated catalytic [4 + 1] cycloaddition reaction in this solvent. To avoid formation of the catalytically inactive dinuclear cluster **13**, lower energy irradiation was preferred, giving significantly higher yields of cycloaddition products.

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Supplementary Material Available: Experimental and analytical data; X-ray crystal structure determination of **13** including solution and refinement, atomic coordinates, bond lengths, bond angles, isotropic and anisotropic displacement coefficients, and stereo ORTEP plots (13 pages). Ordering information is given on any current masthead page.

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(11) Poliakoff, M. *Chem. Soc. Rev.* **1978**, *7*, 527 and references cited therein.

(12) (a) Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1987**, 226. (b) Thomas, S. E.; Tustin, G. J.; Ibbotson, A. *Tetrahedron* **1992**, *48*, 7629.

(13) Pouilhes, A.; Thomas, S. E. *Tetrahedron Lett.* **1989**, *30*, 2285.

(14) Trifonov, L. S.; Orahovats, A. S. Heimgartener, H. *Helv. Chim. Acta* **1990**, *73*, 1734.