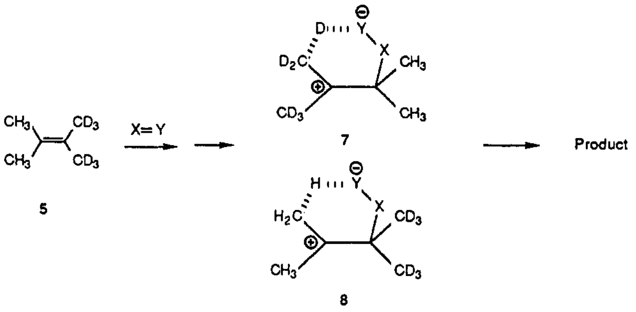
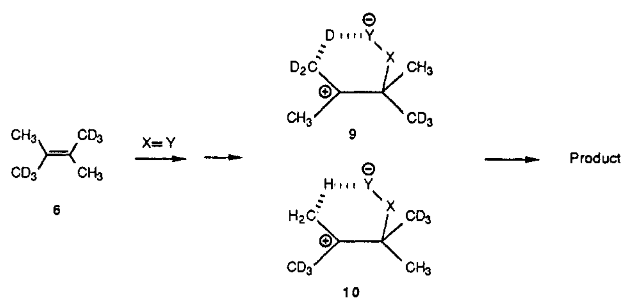
parently anomalous isotope effects.

The existence of such intermediates also can provide a framework for understanding of other interesting product isotope effects in ene reactions. The trans- and *gem*-substituted olefins **5** and **6** would be expected to give the same isotope effects in an ene reaction. In fact these compounds provide a ratio of $(k_H/k_D)_5/(k_H/k_D)_6$ of ca. 1.5 with a number of enophiles.[3,7] The actual isotope effect for hydrogen removal from **5** will be determined by the free energy difference in the transition structures **7** and **8**. The corresponding isotope effect from **6** will arise from the free energy difference between **9** and **10**. To the extent the charge can be considered localized in these structures the secondary isotope effect of the trideuteriomethyl group on the adjacent position will enhance the isotope effect for **5** and depress it for **6**.[10] While the magnitude of the effect is uncertain and would be modified by the partitioning noted above, this apparently anomolous effect is consistent with the partitioning of an intermediate between competitive transition structures in accord with precedented effects.





In summary, we provide a general scheme to explain a range of kinetic isotope effects in ene reactions, including those which have appeared anomalous. We emphasize the quantitative values chosen are illustrative only and further work will be needed to determine the viability of the proposed scheme. This work further demonstrates the advantage of combined kinetic and product isotope effects in mechanistic studies.

Acknowledgment. We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. 1, 1192-37-6; D_2, 7782-39-0; diethyl oxomalonate, 609-09-6.

---

[10] Saunders, M.; Jelkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *49*, 8070. For example two trideuteromethyl groups have an effect of 1.7 on the solvolysis of *tert*-butyl chloride. Shiner, V. J., Jr.; Murr, B. L.; Heinemann, G. *J. Am. Chem. Soc.* **1963**, *85*, 2413.

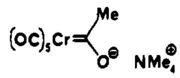
Zhiguo Song, Douglas R. Chrisope, Peter Beak*
Department of Chemistry
University of Illinois
Urbana, Illinois 61801

Received March 18, 1987

Cationic Iron Vinylidene Complexes in Bicyclic β-Lactam Synthesis

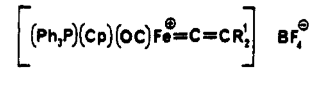
Summary: The iron vinylidene complex $[(Cp)[(MeO)_3P](CO)Fe{=}C{=}CMe_2]^+CF_3SO_3^-$ reacted in a stepwise manner with the imines PhCH=NMe, 2-thiazoline, ethyl 2-thiazoline-4-carboxylate, and methyl 5,5-dimethyl-2-thiazoline-4-carboxylate to produce the corresponding [2 + 2] azetidinylidene cycloadducts (66%, 82%, 72%, 51%).

Sir: Recently we reported that the chromium carbene complex **1**[1] and the cationic iron vinylidenes **2** (R^1 = H, Me)[2] are useful in the preparation of the azetidinylidene complexes **3a** (R^2 = aryl; 6–25%), **3b** (R^2 = Ph; 52%), and **4a** (R^1 = Me, R^2 = aryl, PhCH=CH; 31–52%). Subsequent oxidation of these materials gave the corresponding β-lactams **3c** (68–100%) and **4b** (R^1 = Me, R^2 = Ph; 19%).



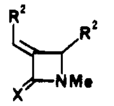
$(OC)_5Cr{=}C(Me)O^- \; NMe_4^+$

1

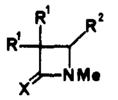


$[(Ph_3P)(Cp)(OC)Fe^+{=}C{=}CR^1_2]\ BF_4^-$

2



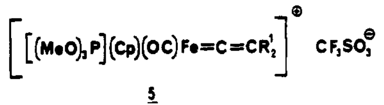
3



4

3
a X = $Cr(CO)_5$
b X = $Fe^+(Cp)(CO)(PPh_3)\ BF_4^-$
c X = O
d X = $Fe^+(Cp)(CO)[P(OMe)_3]\ CF_3SO_3^-$

4
a X = $Fe^+(Cp)(CO)(PPh_3)\ BF_4^-$
b X = O



$[[(MeO)_3P](Cp)(OC)Fe{=}C{=}CR'_2]^+\ CF_3SO_3^-$

5
a R' = H
b R' = Me

In principle the complexes **3a**, **3b**, and **4a** may have arisen via formal [2 + 2] cycloaddition reactions with the intermediacy of $(OC)_5Cr{=}C{=}CH_2$[3] in the chromium case. In order to improve the synthetic versatility of this ketene surrogate chemistry, we have examined several alternative cationic vinylidene systems.[4] Herein we report a preliminary account of the preparation and reactions of complexes **5a** and **5b**. Vinylidene **5b** is especially useful for the preparation of bicyclic azetidinylidene complexes in high yield.

The preparation of **6b** via double methylation of **6a** was inefficient due to competitive Cp lithiation.[5] However, reaction of $Cp(CO)_2Fe$-*i*-Pr[6] with trimethyl phosphite[7]

---

[1] Barrett, A. G. M.; Brock, C. P.; Sturgess, M. A. *Organometallics* **1985**, *4*, 1903.

[2] Barrett, A. G. M.; Sturgess, M. A. *Tetrahedron Lett.* **1986**, *27*, 3811.

[3] For a reference to this possible intermediate, see: Weiss, K.; Fischer, E. O.; Müller, J. *Chem. Ber.* **1974**, *107*, 3548.

[4] For a review on metal vinylidene complexes, see: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

[5] For a related Cp methylation, see: Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185.

[6] Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58.

[7] For a reference on related transformations, see: Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1971**, 367.

0022-3263/87/1952-3940$01.50/0

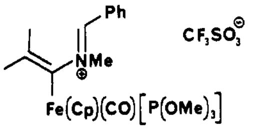
provided the corresponding acyl **6b**[8] (93%). Dehydration of **6a** and **6b** according to the Hughes procedure using

$[(MeO)_3P](Cp)(OC)FeCOCHR^1_2$

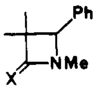
6

a $R^1 = H$
b $R^1 = Me$

trifluoromethanesulfonic anhydride[9] gave the cationic iron vinylidenes **5a** (used directly in situ) and **5b** (85%) as yellow and peach colored solids, respectively. Vinylidene **5a** reacted with the imine PhCH=NMe[10] in dichloromethane at room temperature over 24 h to give the complex **3d** (R^2 = Ph; 14% from **6a**). Alternatively PhCH=NMe reacted with **5b** rapidly in dichloromethane solution at −78 °C to produce the acyclic adduct **7**. This material was slowly converted into the azetidinylene complex **8a** on standing (NMR) or preferably by brief reflux in 1,2-dichloroethane in the presence of anhydrous Amberlyst A21 resin. Thus, addition of PhCH=NMe to a 1,2-dichloroethane solution of **5b** at room temperature followed by refluxing for 3 h gave **8a** in good yield (66%) as a mixture of diastereoisomers (1.5:1). Recrystallization from methanol gave the *R*(*S*),*R*(*S*) diastereoisomer.[11] Oxidation of **8a** with iodosobenzene in ethanol solution gave the corresponding β-lactam **8b** (36%).[12]



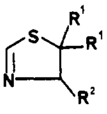
7



8

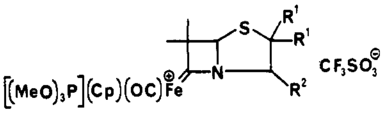
a X = $Fe^{+}(Cp)(CO)[P(OMe)_3]$ $CF_3SO_3^-$
b X = O

The stepwise cycloaddition methodology was extended to the 2-thiazoline derivatives **9a–c**[13-15] to provide the corresponding complexes **10a** (82%), **10b** (72%), and **10c** (51%). Again these materials were obtained as mixtures of two diastereoisomers [**10a** (15:1), **10b** (8:1), and **10c** (6:1)]. While we have not unambiguously identified the stereochemistries of the principal adducts, it is reasonable to assume that their azetidinylidene ligands have the exo stereochemistry.[16] This is consistent with the known chemistry of 2-thiazolines.[14] Additional support for this contention was obtained when oxidation of **10b** with iodosobenzene in ethanol gave **11** (52%). The stereochemistry of this material was assigned as the exo configuration since treatment with catalytic base caused no epimerization.



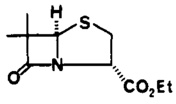
9

a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = CO_2Et$
c $R^1 = Me$, $R^2 = CO_2Me$



10

a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = CO_2Et$
c $R^1 = Me$, $R^2 = CO_2Me$



11

Clearly the phosphite cationic iron vinylidenes are efficient reagents for the synthesis of both monocyclic and bicyclic β-lactams with the penicillin framework from simple imines. The methodology complements the synthesis of β-lactams from the oxidative cyclization of β-amino acyl compounds previously reported by Rosenblum,[17] Liebeskind,[18] Davies,[19] and Ojima.[20]

Acknowledgment. We thank the National Science Foundation (CHE-8500890) for the generous support of this program, the Midwest Center for Mass Spectrometry, an NSF Regional Instrument Facility (CHE-8211164), for obtaining mass spectral data, and both the NIH (RR-01672) and the NSF (CHE-8300958) for providing the Enraf-Nonius CAD_4 single-crystal diffractomer.

---

(8) All new compounds were fully authenticated by spectral data and microanalyses or FAB high resolution mass spectra except for the vinylidenes **7a** and **7b**, which were characterized by NMR and IR spectra only.

(9) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628.

(10) Cromwell, N. H.; Babson, R. D.; Harris, C. E. *J. Am. Chem. Soc.* **1943**, *65*, 312.

(11) X-ray crystallographic structure: Sabat, M. unpublished results. Assignment of configuration was based on the following order of priority; $P(OMe)_3 > CO >$ carbene > Cp.

(12) Rogalska, E.; Belzecki, C. *J. Org. Chem.* **1984**, *49*, 1397.

(13) Ito, Y.; Inubushi, Y.; Zenbayashi, M.; Tomita, S.; Saegusa, T. *J. Am. Chem. Soc.* **1973**, *95*, 4447.

(14) Bose, A. K.; Manhas, M. S.; Chib, J. S.; Chawla, H. P. S.; Dayal, B. *J. Org. Chem.* **1974**, *39*, 2877.

(15) Bell, M. R.; Carlson, J. A.; Oesterlin, R. *J. Org. Chem.* **1972**, *37*, 2733.

(16) Exo refers to the stereochemistry of the alkoxycarbonyl group on the 4-thia-1-azabicyclo[3.2.0]heptylene ligand.

(17) Wong, P. K.; Modhavarao, M.; Marten, D. F.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2823.

(18) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *Ibid*, **1986**, *108*, 6328.

(19) Broadley, K.; Davies, S. G. *Tetrahedron Lett.* **1984**, *25*, 1743. Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Walker, J. C.; Jones, R. H.; Prout, K. *Tetrahedron* **1986**, *42*, 5123.

(20) Ojima, I.; Kwon, H. B. *Chem. Lett.* **1985**, 1327.

Anthony G. M. Barrett,* Michael A. Sturgess
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Received March 6, 1987

Dynamic NMR Study of Dimethyl Trithiocarbonate[1]

Summary: Low-temperature proton NMR spectra of dimethyl trithiocarbonate show that the populations of the *E,Z* and *E,E* conformations are 0.52 and 0.48, with free energy barriers to interconversion at −138 °C of 6.9_4 and 6.9_7 kcal/mol.

Sir: Although dialkyl carbonates and the various possible sulfur-substituted derivatives comprise a large class of compounds, no successful[2] dynamic NMR studies of these

---

(1) (a) This work was supported by the National Institutes of Health (Grant No. S06RR08047). (b) Presented at the 192nd National Meeting of the American Chemical Society, Anaheim, Ca, September 12, 1986.

(2) Methyl *tert*-butyl carbonate was reported[3] to exist as a mixture of conformations, but the slow-exchange spectrum was not observed, and the evidence for the conformational equilibrium is not conclusive.