The Claisen Rearrangement of Iron Allyloxy Carbene Complexes

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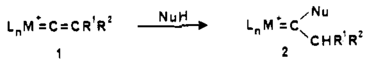
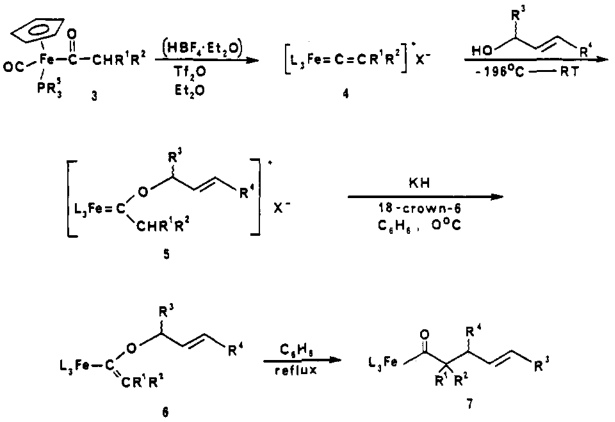
Summary: Several cationic iron(II) allyloxy carbene complexes have been prepared from the corresponding iron vinylidenes $\{Fe(\eta^5\text{-}C_5H_5)(CO)[P(OCH_3)_3](C{=}CR^1R^2\}^+X^-$ ($X = BF_4$, OSO_2CF_3). These compounds have been deprotonated with KH and 18-crown-6 and thermally rearranged in situ to give the corresponding γ,δ-unsaturated iron acyl complexes in moderate yields.

Scheme I



Scheme II



Metal vinylidene complexes have been the subject of considerable recent investigations.[1,2] Mononuclear vinylidene complexes such as **1** undergo reactions which include deprotonation at the β-carbon (to give the σ-bonded acetylide)[3,4] and dimerization.[4,5] However, the key characteristic of these complexes is the extremely electrophilic α-carbon (^{13}C NMR δ 320–380).[2] In most cases, the addition of nucleophiles to this center occurs with ease, resulting in formation of the corresponding carbene complexes **2** (Scheme I).[6,7] Since the metal moiety in **2** can be oxidatively cleaved[8] to give the corresponding carbonyl compound, vinylidene complexes can be envisioned as organometallic ketene surrogates. The chemistry of transition-metal acyl complexes is complementary in that oxidative demetalation can be used to produce the corresponding carboxylic acid, ester, or amide.[9] Metal acyls have found widespread use in organic synthetic methodology since electrophilic functionalization of the derived enolate anions can be used to readily produce extended carbon frameworks. Such acyl anion chemistry is particularly useful in that spectacular stereochemical control can be observed when the metal center is asymmetric.[10] In contrast, the use of vinylidene intermediates to stereoselectively elaborate organic molecules has been completely neglected. Indeed even the application of metal vinylidenes in synthetic methodology has remained relatively unexplored. However recent research efforts in this laboratory have demonstrated that vinylidene complexes are especially useful in the synthesis of β-lactams.[8] Herein we report the reaction of cationic iron(II) vinylidenes with allylic alcohols and the subsequent deprotonation and Claisen rearrangement[11] of the resulting allyloxy carbene complexes. The synthetic sequence leading to the rearrangement products **7** is illustrated with the unsubstituted vinylidene complex **4b** ($R^1 = R^2 = H$, $R^5 = OCH_3$, $X = BF_4$; Scheme II). This compound was prepared from the corresponding iron acyl complex **3b**[12] by dehydration with tetrafluoroboric acid (2.5 equiv) and trifluoromethanesulfonic anhydride (3 equiv) according to the general procedure of Boland-Lussier and Hughes.[7] The vinylidene, although characterized by ^1H NMR [($CDCl_3$, 90 MHz) δ 3.64 (d, 9 H, J = 12 Hz), 5.33 (s, 5 H), 5.37 (d, 2 H, J = 3 Hz)], was not isolated but instead was condensed directly with allyl alcohol by using standard Schlenk techniques[13] to give the cationic allyloxy carbene complex **5b** [^1H NMR ($CDCl_3$, 90 MHz)δ 3.05 (s, 3 H), 3.78 (d, 9 H, J = 12 Hz), 5.10 (s, 5 H), 5.18 (s, 2 H), 5.39–5.70 (m, 2 H), 5.92–6.32 (m, 1 H)]. Deprotonation of **5b** with KH and 18-crown-6[14] gave the neutral iron vinyl allyl ether **6b**,[15] which was thermally rearranged in situ in refluxing benzene to give the desired γ,δ-unsaturated acyl complex **7b**[16] [^1H NMR ($CDCl_3$, 400 MHz) δ 2.14 (m, 2 H), 2.93 (m, 2 H), 3.63 (d,

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(1) The first transition-metal vinylidene complex, containing a bridging vinylidene ligand in a diiron complex, was obtained in 1966: Mills, O. S.; Redhouse, A. D. *J. Chem. Soc., Chem. Commun.* **1966**, 444; *J. Chem. Soc. A* **1968**, 1282.

(2) For an excellent review of vinylidene (and propadienylidene) metal complexes, see: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

(3) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763. Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203.

(4) Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1978**, *155*, C8.

(5) Boland-Lussier, B. E.; Hughes, R. P. *Organometallics* **1982**, *1*, 635.

(6) For examples see: Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455. Berke, H. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 86. Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7232. Bruce, M. I.; Wallis, R. C. *J. Organomet. Chem.* **1978**, *161*, C1. Bruce, M. I.; Swincer, A. G.; Wallis, R. C. *J. Organomet. Chem.* **1979**, *171*, C5. Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471. Selegue, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 119.

(7) Boland-Lussier, B. E.; Hughes, R. P. *Organometallics* **1982**, *1*, 628.

(8) Barrett, A. G. M.; Sturgess, M. A. *Tetrahedron Lett.* **1986**, *27*, 3811; *J. Org. Chem.* **1987**, *52*, 3940.

(9) Aktogu, N.; Felkin, H.; Baird, G. J.; Davies, S. G.; Watts, O. *J. Organomet. Chem.* **1984**, *262*, 49.

(10) For examples see: Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250. Liebeskind, L. L.; Welker, M. E.; Fengl, R. W. *Ibid* **1986**, *108*, 6328 and references therein. Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P.; Jones, R. H.; Prout, K. *J. Organomet. Chem.* **1985**, *285*, 213. Rusik, C. A.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 4652.

(11) For recent reviews on the Claisen rearrangement, see: Rhoads, S. J.; Raulins, N. R. *Org. React.* (*N.Y.*) **1975**, *22*, 1. Bennett, G. B. *Synthesis* **1977**, 589. Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.

(12) Wilkinson, G.; Piper, T. S. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104. Green, M.; Westlake, D. J. *J. Chem. Soc.* A **1971**, 367.

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(15) For examples of related iron vinyl complexes see: Reger, D. L.; Belmore, K. A. *Organometallics* **1985**, *4*, 305. Reger, D. L.; Swift, C. A. *Organometallics* **1984**, *3*, 876. Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940. Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligot, P. J. *Organometallics* **1984**, *3*, 134. Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics* **1986**, *5*, 1072. Grötsch, G.; Malisch, W. *J. Organomet. Chem.* **1983**, *246*, C42, C49. Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. Grötsch, G.; Malisch, W. *J. Organomet. Chem.* **1984**, *262*, C38.

(16) All rearrangement products were fully authenticated by spectral data and microanalyses or high-resolution mass ion measurements.

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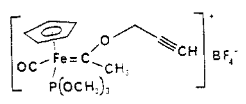
Table I. Summary of Rearrangement Results

entry	carbene complex	solv	temp, °C	time, h	product (%)[a]
1	$R^1 = R^2 = R^3 = R^4 = H$, $R^5 = Ph$, $X = BF^4$ (**5a**)	C_6H_6	68	120	**7a** (10)[b]
2	$R^1 = R^2 = R^3 = R^4 = H$, $R^5 = OCH_3$, $X = BF^4$ (**5b**)	xylenes	118–120	24	**7b** (33)
3	$R^1 = R^2 = R^3 = H$, $R^4 = CH_3$, $R^5 = OCH_3$, $X = BF_4$ (**5c**)	PhMe	114	25	**7c** (22)[c]
4	$R^1 = R^2 = R^4 = H$, $R^3 = CH_3$, $R^5 = OCH_3$, $X = BF_4$ (**5d**)	C_6H_6	reflux	26	**7d** (60)[d]
5	$R^1 = R^3 = R^4 = H$, $R^2 = CH_3$, $R^5 = OCH_3$, $X = BF_4$ (**5e**)	C_6H_6	76–78	26	**7e** (13)[e]
6	$R^1 = R^3 = H$, $R^2 = R^4 = CH_3$, $R^5 = OCH_3$, $X = BF_4$ (**5f**)	C_6H_6	reflux	26	**7f** (34)[f]
7	$R^3 = R^4 = H$, $R^1 = R^2 = CH_3$, $R^5 = OCH_3$, $X = OSO_2CF_3$ (**5g**)	C_6H_6	reflux	21	**7g** (21)
8	**8**	C_6H_6	reflux	20	**9** (28)

[a] Yield calculated from the starting saturated iron acyl complex 3, unless otherwise noted. [b] Yield calculated from the allyloxy carbene complex 5. [c] Product obtained as a 3:1 mixture of diastereomers. [d] Product obtained exclusively as the *E* isomer. [e] Product obtained as a 1:1 mixture of diastereomers. [f] Product obtained as a complex mixture of diastereomers.

9 H, J = 12 Hz), 4.63 (s, 5 H), 4.87 (d, 1 H, J = 9.2 Hz), 4.94 (dd, 1 H, J = 16.8, 1.6 Hz), 5.75 (m, 1 H)]. Further results are summarized in Table I. It is clear from these examples that a range of simple allylic alcohols (and propargyl alcohol, entry 8) indeed reacted with the cationic iron vinylidenes **4** to produce the desired carbene complexes, and these in turn gave the corresponding rearrangement products **7**. The overall yields from the starting acyl **3** were modest (10–60%).[17] However the method is clearly useful for the preparation of diverse systems including the sterically encumbered product **7g** (entry 7) and the allene **9** (entry 8). The allene **9** readily isomerized to produce the corresponding diene acyl complex **10**. In principle these γ,δ-unsaturated iron acyls **7** should be available from direct allylation of the enolate derived from **3**. Indeed this method has been efficiently used to prepare **7a**,[9] but attempts to apply this strategy to the preparation of the trimethyl phosphite substituted iron acyls failed due to competitive metalation of the cyclopentadienyl ring.[18,19] Thus the Claisen rearrangement provides a valuable route to the γ,δ-unsaturated iron acyls when the alternate alkylation route presents a problem.



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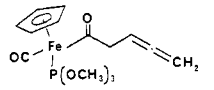

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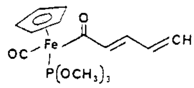

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In conclusion, these results demonstrate that iron allyloxy carbene complexes, on deprotonation, undergo a [3,3] sigmatropic rearrangement to give the corresponding γ,δ-unsaturated acyl complexes. Further studies are in progress to confirm the intramolecular nature of the rearrangement and to optimize the yield and diastereoselectivity of the transformation. Absolute stereochemical control of the Claisen rearrangement via organometallic intermediates would be a reaction of considerable synthetic importance.

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Supplementary Material Available: Spectroscopic and microanalytical data characterizing vinylidenes, carbenes, and acyls described in this paper (6 pages). Ordering information is given on any current masthead page.

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[17] Approximately 5–30% of the starting saturated acyl complex 3 was typically recovered.

[18] Sturgess, M. A., unpublished results.

[19] Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1185.

Thermal Rearrangement of (*S*,*S*)-1-Naphthylphenylmethyl(1-chloroethyl)silane and (*S*)-(1-Chloroethyl)phenyldimethylsilane

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Summary: (*S*,*S*)-1-Naphthylphenylmethyl(1-chloroethyl)silane (**1**) and (*S*)-(1-chloroethyl)phenyldimethylsilane (**2**) were prepared and employed in a study of the stereochemistry of their thermal rearrangements. Although the stereochemistry at silicon could not be determined due to racemization, the stereochemistry at carbon was found to be inversion with a high degree of stereospecificity. The stereochemistry at carbon is preserved in a subsequent oxidative cleavage of the Si–C bond providing an interesting silicon-mediated preparation of (*S*)-1-phenylethanol and (*S*)-1-(1-naphthyl)ethanol.

The rearrangement of α-haloorganosilanes has been shown to take place under thermal,[2] Lewis acid catalyzed,[3]

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[1] (a) University of Puerto Rico and Petrarch Systems. (b) University of Puerto Rico. (c) Louisiana State University. Taken in part from the Ph.D. Thesis of R.K., UPR, Rio Piedras, P.R., 1987.

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