Organometallics **2007,** *26,* 201−203

Investigation of the Reaction of Allyl(cyclopentadienyl)iron(II) Dicarbonyl with Iminium Salts: Synthesis of Ammonium Salts of Substituted Five-Membered-Ring Iron Complexes

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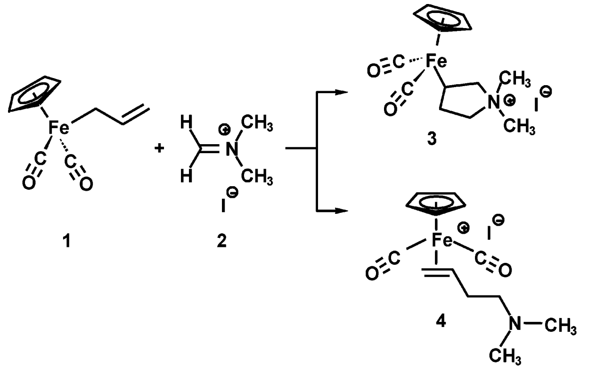
Received August 29, 2006

Series of quaternary ammonium salts of substituted five-membered-ring iron complexes were prepared by reaction of allyl(cyclopentadienyl)iron(II) dicarbonyl with iminium salts. Also, reactions of allyl(cyclopentadienyl)iron(II) dicarbonyl with in situ prepared iminium salts afford the same products in good to excellent isolated yields.

Cycloaddition reactions between transition-metal 2-alkynyl and η^1-allyl complexes and unsaturated electrophilic reagents have been studied in detail over the last 30 years.[1] The pioneering works in this area have been done by the groups of Rosenblum, Wojcicki, and Welker.[1c,d] The [3 + 2] cycloaddition reactions of η^1-allyl complexes have been shown to yield transition-metal-substituted heterocyclic as well as carbocyclic five-membered rings which offer alternative approaches to prepare these ring systems, when the metal moiety is subsequently removed from the ring.[2−4]The reaction of the lithium enolate of the pseudooctahedral complex (η^5-Cp)Fe(PPh$_3$)(CO)COCH$_3$ with Eschenmoser's iminium salt and the reactions of complex **1** with *N*-tosylimines, which are activated by Lewis acids such as BF$_3$·OEt$_2$, ZnCl$_2$, MgBr$_2$, SnCl$_4$, and TiCl$_4$, have been reported in the literature.[5,6] As a continuation of our research devoted to the reaction of nucleophiles with iminium salts,[7,8] especially in situ generation of iminium ions,[9] herein we report a new and practical entry to a series of interesting nitrogen-containing heterocyclic compounds (Scheme 1).

Scheme 1. Reaction of Complex 1 with Eschenmoser Salt



When the iron complex **1** was reacted with the Eschenmoser salt **2**, the expected olefin complex **4** was not formed, but surprisingly complex **3** was obtained in good yield. This transformation does not need extra activation by a Lewis acid. Mechanistically the above reaction is a formal [3 + 2] cycloaddition. In order to detect the possible intermediate, we followed the progress of the reaction by IR spectroscopy. Immediately after **1** was added to the solution of Eschenmoser salt **2**, an intermediate was formed. The IR spectrum of this intermediate showed two CO stretching bands at 2075 and 2035 cm^{-1}, which correspond to the olefin complex **4**. As the reaction proceeded, the above signals in the IR spectrum diminished and new CO absorption bands appeared at 2000 and 1940 cm^{-1}, which correspond to complex **3**. Obviously in a very fast tandem reaction, the tertiary amine present in the intermediate **4** adds to the activated double bond and gives rise to the complex **3**.

To optimize the reaction conditions, we examined different molar ratios of complex **1** and Eschenmoser salt **2** in THF as solvent. We found out that the best yields were obtained when we used the 1.5/1.0 ratio. Different solvents such as diethyl ether and CH$_2$Cl$_2$ were also examined. We found out that THF and CH$_2$Cl$_2$ are the best solvents for this reaction, but the yields are higher in CH$_2$Cl$_2$. To show the generality of the reaction, we carried out the reaction of **1** with different iminium salts of aldehydes and ketones, and we obtained good to excellent yields of the expected products **3** and **5a**−**g**. The results are summarized in Table 1.

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(1) For recent reviews of transition-metal-mediated [3 + 2] cycloaddition see: (a) Li, C. L.; Liu, R. S. *Chem. Rev.* **2000**, *100*, 3127−3161. (b) Chan, D. M. T.; Trost, B. M. *Comprehensive Organic Synthesis*; Pergamon: New York, 1991; p 271. (c) Welker, M. E. *Chem. Rev.* **1992**, *92*, 97. (d) Wojcicki, A. *Coord. Chem. Rev.* **1990**, *105*, 35. (e) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191.

(2) Chen, L. S.; Lichtenberg, D. W.; Robinson, P. W.; Yamamoto, Y.; Wojcicki, A. *Inorg. Chim. Acta* **1977**, *25*, 165.

(3) Ni, L. M.; Belot, J. A.; Welker, M. E. *Tetrahedron Lett.* **1992**, *33*, 177.

(4) Stokes, H. L.; Ni, L. M.; Belot, J. A.; Welker, M. E. *J. Organomet. Chem.* **1995**, *487*, 95−104.

(5) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189.

(6) Chen, T.; Jiang, S, Turos, E. *Tetrahedron Lett.* **1994**, *35*, 8325.

(7) (a) Saidi, M. R.; Roushenas, P. Proceedings of the 6th International Symposium on Carbanion Chemistry, Phillips University, Marburg, Germany, July 28−Aug 1, 2001. (b) Roushenas, P. M. Thesis, Sharif University of Technology, 2001.

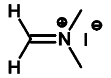
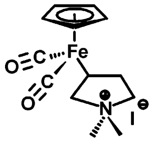
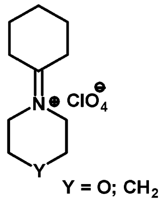
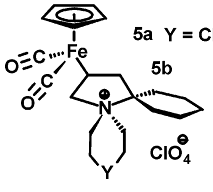
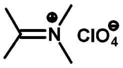
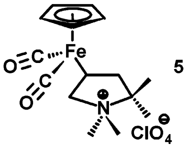
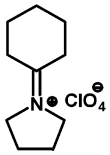
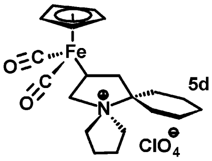
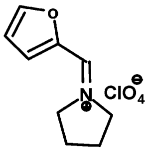
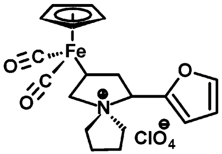
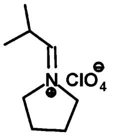
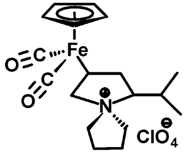
(8) (a) Ipaktschi, J.; Mohsseni-Ala, J.; Dulmer, A.; Loschen, C.; Frenking, G. *Organometallics* **2005**, *24*, 977. (b) Azizi, N.; Rajabi, F.; Saidi, M. R. *Tetrahedron Lett.* **2004**, *45*, 9233. (c) Yousefi, R.; Azizi, N.; Saidi, M. R. *J. Organomet. Chem.* **2005**, *690*, 76. (d) Azizi, N.; Saidi, M. R. *Tetrahedron* **2003**, *59*, 5329.

(9) (a) Saidi, M. R.; Khalaji, H. R.; Ipaktschi, J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1983. (b) Naimi-Jamal, M. R.; Mojtahedi, M. M.; Ipaktschi, J.; Saidi, M. R. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3709. (c) Naimi-Jamal, M. R.; Ipaktschi, J.; Saidi, M. R. *Eur. J. Org. Chem.* **2000**, 1735.

(10) (a) Jiang, S.; Turos, E. *Tetrahedron Lett.* **1994**, *35*, 7889. (b) Jiang, S.; Turos, E. *Tetrahedron Lett.* **1991**, *32*, 4639. (c) Agoston, G. E.; Cabal, M, P.; Turos, E. *Tetrahedron Lett.* **1991**, *32*, 3001. (d) Jiang, S.; Turos, E. *Organometallics* **1993**, *12*, 4280. (e) Jiang, S.; Agoston, G. E.; Chen, T.; Cabal, M.-P.; Turos, E. *Organometallics* **1995**, *14*, 4697.

10.1021/om060783i CCC: $37.00

Table 1. Reaction of Iminium Salts with Allyliron Complex 1

Iminium salt	Product	yield[a]
 2	 3	95 (88)[b]
	 5a Y = CH_2 5b Y = O	95 (87)[b] 70
	 5c	85
	 5d	87
	 5e	94
	 5f	89

[a] Isolated yield in CH_2Cl_2. [b] Isolated yield in THF.

We also have extended our investigation to reaction of **1** with in situ generated iminium salts. For this purpose, the iminium salts were prepared by reaction of an aldehyde (1 mmol) with a secondary amine (1 mmol) in lithium perchlorate dispersed (3 mmol) in CH_2Cl_2. Addition of compound **1** to this mixture gave compounds **6a**−**c** as the only products in excellent yields as yellow to brownish salts (Scheme 2). In this transformation we did not observe a direct addition of allyl complex **1** to the carbonyl group of the aldehyde.

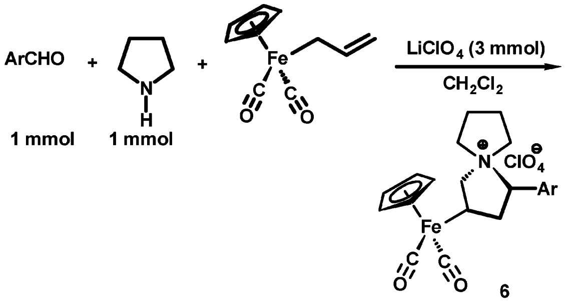
The oxidative demetalation reaction of complex **3** to give the methyl ester **7** was carried out in the presence of methanol with different oxidation reagents such as cerium ammonium nitrate and $CuCl_2$. We found that $CuCl_2$ and cerium ammonium nitrate are suitable reagents for the demetalation reaction (Scheme 3). However, during workup, the purification process for cerium ammonium nitrate is more difficult than that for $CuCl_2$.

In conclusion, we have detailed a new [3 + 2] cycloaddition reaction of allyl(cyclopentadienyl)iron(II) dicarbonyl with iminium salts to prepare new series of five-membered rings of ammonium salts substituted with an iron complex in good to excellent yield.

Experimental Section

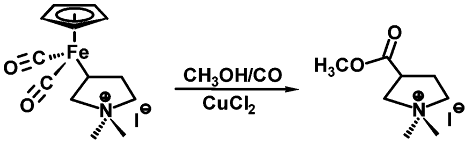
General Considerations. All reactions were carried out under an argon atmosphere (99.99%, by Messer-Griesheim) with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare the iminium salts, and the allyl(cyclopentadienyl)iron(II) dicarbonyl complex was commercially available. NMR spectra were obtained on Bruker AM 400 and AC 200 spectrometers. Proton chemical shifts are referenced to TMS. IR spectra were recorded on a Bruker FT-IR IFS 85 instrument. Microanalyses were done on a Carlo Erba 1104 elemental analyzer.

Scheme 2. Reaction of in Situ Generated Iminium Salt with Complex 1



Ar	yield	
Phenyl	90%	6a
4-Chlorphenyl	76%	6b
4-Nitrophenyl	80%	6c

Scheme 3. Oxidative Demetalation Reaction of Complex 3



3 7

General Procedure. To a solution of the iminium salt (1 mmol) in CH_2Cl_2 (25 mL) at 0 °C under an argon atmosphere was added the allyliron reagent **1** (1.5 mmol) in CH_2Cl_2 (5 mL). The temperature was raised to room temperature, and stirring was continued for an additional 16−20 h. When the reaction was completed, the solvent was evaporated and the residue was treated with hot ether to form a light yellow powdery precipitate (in some cases, refluxing of the ether solution was carried out for $^1/_2$ h to get the solid product). Filtering using a Buchner funnel and then washing the solid with hot ether (two to three times) gave the product as a powdery yellow solid.

Selected Spectroscopic Data. 3: IR (ν, cm^{-1}) 1999, 1937; ^{1}H NMR δ 1.8 (m, 2H), 2.4 (m, 2H), 2.8 (1H, m), 3.2 (1H, m), 3.3 (3H, s), 3.5 (3H, s), 4.2 (1H, m), 5.1 (5H, s, cp). Anal. Calcd for $C_{13}H_{18}NO_2FeI$: C, 38.90; H, 4.48; N, 3.49. Found: C, 38.86; H, 4.25; N, 2.90.

5a: IR (ν, cm^{-1}) 2013, 1955; ^{1}H NMR δ 1.1−2.1 (14H, m), 2.3 (1H, m), 2.8−3.4 (6H, br), 3.7 (2H, m), 4.1 (2H, br), 5.0 (5H, s, cp). Anal. Calcd for $C_{21}H_{30}NO_6FeCl$: C, 52.19; H, 6.20; N, 2.89. Found: C, 52.22; H, 6.43; N, 2.92.

5e: IR (ν, cm^{-1}) 2001, 1943; ^{1}H NMR δ 1.2−2.3 (7H, m), 2.7 (2H, m), 3.1−4.1 (4H, m), 4.8 (1H, t), 5.0 (5H, s, cp), 6.4 (1H, m), 6.7 (1H, m), 7.6 (1H, m). Anal. Calcd for $C_{19}H_{22}NO_7FeCl$: C, 48.70; H, 4.70; N, 2.99. Found: C, 48.49; H, 4.48; N, 3.02.

General Method for Preparation of the Product with in Situ Prepared Iminium Salt. To a solution of benzaldehyde (1 mmol) in CH_2Cl_2 (25 mL) at 0 °C were added $LiClO_4$ (4 mmol) and pyrrolidine (1.2 mmol), and the mixture was stirred for 20 min. Then, freshly prepared allyliron reagent (1.5 mmol) in CH_2Cl_2 (5 mL) was added under an argon atmosphere. The mixture was stirred at room temperature for 20 h. Evaporation of the solvent and then treatment with ether and refluxing the solution for 30 min provided a precipitate. Filtration of the precipitate and washing the solid with ether (two to three times) gave the product as a brownish yellow solid.

Selected Spectroscopic Data. 6a: IR ($\tilde{\nu}$, cm^{-1}) 2007, 1946; ^{1}H NMR δ 1.7−2.3 (6H, m), 2.6−3.1 (3H, m), 3.1−3.8 (3H, m), 3.9 (1H, br), 4.8 (1H, t), 5.0 (5H, s, cp), 7.2−7.4 (5H, m, Ph). Anal. Calcd for $C_{21}H_{24}NO_6FeCl$: C, 52.77; H, 5.03; N, 2.93. Found: C, 52.88; H, 5.02; N, 2.88.

General Method for Replacement of Metal Complex by Carboxylic Ester. A suspention of $CuCl_2$ (8 mmol, 1.1 g) in methanol (15 mL) was added to a solution of compound **3** (201 mg, 0.5 mmol) in methanol (25 mL) and CH_2Cl_2 (5 mL), which was saturated with CO gas. The color of the mixture was changed from yellow to black. The mixture was stirred for 5 h under CO, and the reaction was monitored by IR spectroscopy. After completion of the reaction, the solvent was evaporated and the product was extracted with CH_2Cl_2. By evaporation of the solvent, dissolution of the residue in water, filtration of this solution, and evaporation of the water, the white precipitate of compound **7** was obtained in 20% yield.

Spectroscopic data of 7: IR (ν, cm^{-1}) 1745; ^{1}H NMR δ 3.8 (3H, s), 3.7 (3H, s), 3.5 (1H, m), 3.3 (3H, s), 2.4−2.7 (3H, m), 1.9−2.2 (3H, m).

Acknowledgment. We thank the Volkswagen-Stiftung (Grant No. I/78849) of the Federal Republic of Germany for financial support toward the purchase of equipment and chemicals. A.Z.H. gratefully acknowledges receipt of a grant for a study visit from Volkswagen-Stiftung.

Supporting Information Available: Text giving general experimental procedures and figures giving ^{1}H NMR and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060783I