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[2+2] CYCLOADDITION REACTIONS OF CATIONIC IRON VINYLIDENE COMPLEXES

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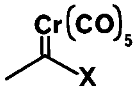
Summary: Complexes $(Ph_3P)(Cp)(OC)\overset{+}{Fe}=C=CR^1_2\overset{-}{BF_4}$ underwent [2+2] cycloaddition reactions with the imines $MeN=CHR^2$ to give the corresponding cationic iron (II) 2-azetinylidene adducts.

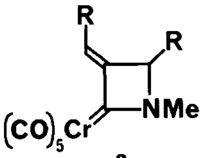
Recently we described the application of the chromium carbene complex **1a**[1] in β-lactam synthesis[2]. Thus reaction of the imines **2** with **1b** and toluene 4-sulfonyl chloride gave the derived azetidinylidene complexes **3**. Oxidation of these species smoothly provided the corresponding β-lactams **4**. It is possible that the carbene complexes **3** were produced via the formal [2+2] cycloaddition of the imines **2** with the reactive intermediate **5**[3] to produce **6** and subsequent C-3 functionalization. As part of our program on the cycloaddition chemistry of such species we examined the reactions of the known[4] cationic iron (II) vinylidene complexes **7** with imines. Herein we report our preliminary observations.



1

$RCH=NMe$

2



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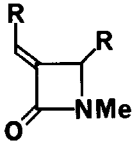


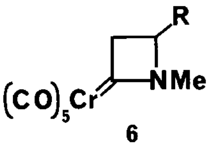
4

a X = OTs
b $X = O^{\ominus}\ N^{\oplus}Me_4$

a R = Ph
b $R = 4\text{-}Me\text{-}C_6H_4$
c $R = 3\text{-}Me\text{-}C_6H_4$

$CH_2=C=Cr(CO)_5$

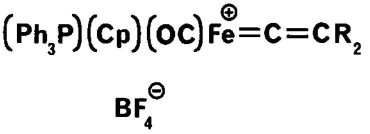
5



6

The cationic iron (II) vinylidenes **7a** and **7b** were respectively prepared from the corresponding iron acyls **8a** and **8b** by dehydration with tetrafluoroboric acid and trifluoromethanesulfonic anhydride according to the method of Hughes and coworkers[4]. The imine **2a** reacted with **7a** without solvent to produce an adduct tentatively assigned as **9** (52%). This was not fully purified and characterized but was directly oxidized using iodosobenzene in dichloromethane solution to produce the known[2] α-benzylidene-β-lactam **4a** (68%). Clearly the reaction of **2a** with **7a** closely parallels the corresponding chromium carbene chemistry[2].

In contrast the dimethyl analog **7b** reacted with the imines **2a-c** in dichloromethane solution at -78°C to 25°C to produce the corresponding azetidinylidene complexes **10a** (52%), **10b** (38%) and **10c** (31%). Each cycloadduct was produced as an inseparable mixture of diastereoisomers [**10a** (8:5), **10b** (4:3), **10c** (4:3)] and this prevented our obtaining crystalline samples. However these amorphous adducts were readily purified and fully characterized[5]. Additionally **10a** was oxidized with oxygen in dichloromethane to produce



$(Ph_3P)(Cp)(OC)\overset{\oplus}{Fe}{=}C{=}CR_2 \quad BF_4^{\ominus}$

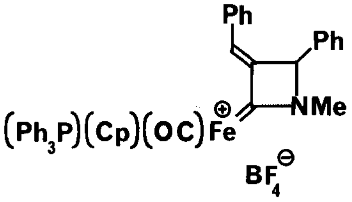
$(Ph_3P)(Cp)(OC)FeCOCHR_2$

7

a R=H

b R=Me

8



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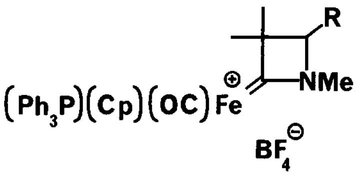


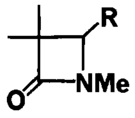
10

a R=Ph

b R=4-Me-C_6H_4

c R=3-Me-C_6H_4

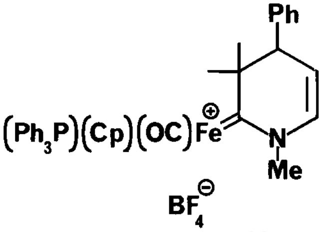
d R=CH=CHPh



11

a R=Ph

b R=CH=CHPh



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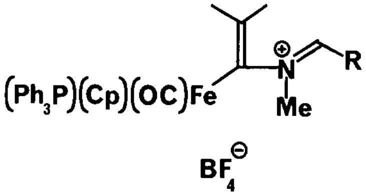

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11a[6] (19% based on **7b**, unoptimized). The imine **2** (R=E-PhCH=CH) also reacted with **7b** to produce **10d** (33%) with a diastereoselectivity of 3:1. Formulation of the product as the [2+2] cycloadduct **10d** rather than the isomer **12** was consistent with spectroscopic data[7] and subsequent oxidation (O_2) to produce **11b**[8]. It is probable that the cationic azetidinylidene complexes **10** were produced via **13** and subsequent cyclization[9]. Such a mechanism is fully consistent with the known reactions of **7b** with simple nucleophiles[4].

Clearly iron vinylidene complexes are potentially useful in β-lactams synthesis. This novel methodology complements the synthesis of β-lactams from the oxidative cyclization of β-amino-iron acyls previously described by Rosenblum[10], Liebeskind[11], Davies[12] and Ojima[13].

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References and Notes

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[3] For a review of metal vinylidenes see M.I. Bruce and A.G. Swincer, Adv. Organometallic Chem., **1983**, 22, 59.

[4] B.E. Boland-Lussier, M.R. Churchill, R.P. Hughes, and A.L. Rheingold, *Organometallics*, **1982**, *1*, 628.

[5] For example **10c** exhibited the following data: IR ($CDCl_3$) ν max 1960, 1440, 1270, 1050 cm^{-1}; UV (CH_2Cl_2) 236 nm (ε 1.6 x 10^4), 264 (1.0 x 10^4), 322 sh (2.7 x 10^3); ^1H NMR ($CDCl_3$) δ 7.9-6.9 (m, aryl-H), 6.43, 6.34, (m, 1H, aryl-H), 5.30*, 5.15 (2s, 1H, CH-N), 4.96, 4.90* (2s, 5H, Cp), 3.28, 3.20* (2s, 3H, NMe), 2.31 (s, 3H, aryl-Me), 1.36*, 1.00, 0.67*, 0.52 (4s, 6H, CMe_2) (* Peaks due to the major diastereoisomer); ^{13}C NMR ($CDCl_3$) *inter alia* δ 278.9 ($C=Fe^+$), 218.4 (CO) 85.4, 85.0, (Cp), 65.9, 62.0 (NMe), 24.9, 22.4, 21.5, 19.7 (CMe_2); mass spectrum *m/e* (FAB) 598 (M^+), 570 (M^+ -CO), 383 (M^+ -CO-Me_2C·CH(aryl)NMeC), 336 (M^+ -Ph_3P), 308, 254, 162, 121. Anal. calc for $C_{37}H_{37}FeNOP^+BF_4^-$; C, 64.82; H, 5.45; N, 2.04. Found: C, 64.76; H, 5.33; N, 1.68%.

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[7] Adduct **10d** exhibited the following data: IR ($CDCl_3$) 1960, 1435, 1050, 690 cm^{-1}; UV (CH_2Cl_2) 236 nm (ε 1.45 x 10^4), 257 (1.53 x 10^4), 327 (4.0 x 10^3); ^1H NMR ($CDCl_3$) δ 7.7-7.1 (m, aryl-H), 6.58 (m, 1H, aryl-H), 5.63 (m, 1H, CH-N), 4.95 (s, 5H, Cp), 3.1*, 2.75 (2s, 3H, NMe), 1.27*, 0.98, 0.87, 0.75* (4s, 6H, CMe_2) (* peaks due to major diastereoisomer); mass spectrum *m/e* (FAB) 610 (M^+), 582 (M^+ -CO), 383 (M^+ -CO - Me_2C-CH(CH=CHPh)NMeC), 320, 279, 201, 183, 162. High resolution FAB mass spectrum calc for $C_{38}H_{37}FeNOP^+$: M^+, 610.1961. Found: M^+, 610.1937.

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