Journal of Organometallic Chemistry, 445 (1993) 143–145

JOM 23132

The reaction of iron-alkyls with triethyloxonium tetrafluoroborate: formation of iron ethoxycarbene complexes

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(Received April 1, 1992; in revised form August 3, 1992)

Abstract

At room temperature under an atmosphere of carbon monoxide the iron alkyls, $(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{–}R$ (R = CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH(CH_3)_2$, $CH_2CH_2C(CH_3)_3$) react with triethyloxonium tetrafluoroborate to provide the iron ethoxycarbenes, $(\eta^5\text{-}C_5H_5)(CO)_2Fe^+{=}C(OEt)(R)BF_4^-$ in moderate to very good yield.

1. Introduction

Heteroatom-stabilized iron carbene complexes are used as intermediates in the synthesis of more reactive secondary, nonheteroatom-stabilized carbene complexes [1]. These nonheteroatom-stabilized carbenes readily react with alkenes giving cyclopropanes [2], provide olefin complexes by hydride migration [3] or give bridgehead olefin complexes by alkyl migration [1d–e]. We report here a simple, efficient one pot synthesis of heteroatom-stabilized carbene complexes from the iron alkyl complexes.

2. Results and discussion

The reaction of Fp alkyls (**1**) with triethyloxonium tetrafluoroborate (**2**) in dichloromethane under an atmosphere of CO produces the corresponding ethoxycarbene complexes **3** (Scheme 1). The experimental results are summarized in Table 1. An excellent yield of carbene was observed when a 1 : 1 mole ratio of iron alkyls **1** and oxonium cation **2** were reacted for an extended period of time (compare run 3 with 4, 5). More carbene complex was formed when the mole ratio of **2** to **1** was 2 (compare run 1 with 2).

In general, the heteroatom-stabilized iron carbene complexes are synthesized by alkylation of an iron acyl complex [4*,5]. Our results describe a new way of preparing ethoxycarbene iron complexes via CO insertion/O-alkylation. The mechanism of the reaction is presently being investigated.

3. Experimental details

Infrared spectra were obtained using a Beckman IR4210 or a Nicolet MX-1 FTIR spectrometer. Proton NMR spectra were recorded on a Varian EM 390 or on a Bruker 250 MHz NMR spectrometer. Carbon-13 NMR spectra were recorded on an IBM NR-80 or on a Bruker 62.9 MHz NMR spectrometer.

All of the operations were performed under a nitrogen atmosphere using Schlenk tube techniques. Reagent grade diethyl ether, benzene and tetrahydrofuran were purifed by distillation under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane was distilled under nitrogen from phosphorus pentoxide. Technical grade pentane was purified by sequential stirring overnight with concentrated, sulfuric acid, distilling, stirring with a second batch of sulfuric acid, washing with water and distilling from phosphorus pentoxide. The purified pentane was stored over sodium ribbon and distilled from sodium under nitrogen immediately prior to use. Activity IV alumina was

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* Reference number with asterisk indicates a note in the list of references.

0022-328X/93/$6.00

TABLE 1. Isolated product yield from the reactions of $Fp(\eta^1\text{-}R)$ (1) and $Et_3O^+BF_4^-$ (2) in CH_2Cl_2 [a]

Run	Compound	R	Mole ratio 2:1	Time at 25°C	% Yield [b,c] of 3
1	**1a**	CH_2CH_3	2.00	24	64
2	**1a**	CH_2CH_3	1.00	24	47
3	**1b**	$CH_2CH_2CH_3$	1.00	25	62
4,5	**1b**	$CH_2CH_2CH_3$	1.00	4	19.5 ± 3.5
6,7	**1c**	$CH_2CH_2CH(CH_3)_2$	1.00	25	54.5 ± 2.5
8	**1d**	$CH_2CH_2C(CH_3)_3$	1.00	24	76

[a] Under CO at 1 atm unless otherwise indicated. Time in hours. [b] Isolated, unoptimized yield based on **1**. [c] The only other product isolated was the corresponding acyl complex, FpCOR.

prepared from Fischer certified, neutral alumina (Brockman activity I), 80–200 mesh by adding 6.6% water by weight as directed by the manufacturer. Triethyloxonium tetrafluoroborate was prepared by the method of Meerwein [6]. A dichloromethane solution of triethyloxonium tetrafluoroborate and cyclopentadienyliron dicarbonyl dimer were obtained from Aldrich Chemical Co. The compound $FpCH_2CH_3$ (**1a**) was prepared by the method of Piper and Wilkinson [7]; $FpCH_2CH_2CH_3$ (**1b**) was prepared by the method of Green and Nagy [7b]; $FpCH_2CH_2CH(CH_3)_2$ (**1c**) [8] was prepared in 80% yield from the corresponding alkyl bromide or brosylate and $FpCH_2CH_2C(CH_3)_3$ (**1d**) was prepared from the corresponding alkyl brosylate in 40% yield by the literature procedure [8,9].

3.1. Reaction of $FpCH_2CH_3$ (1a) with 2

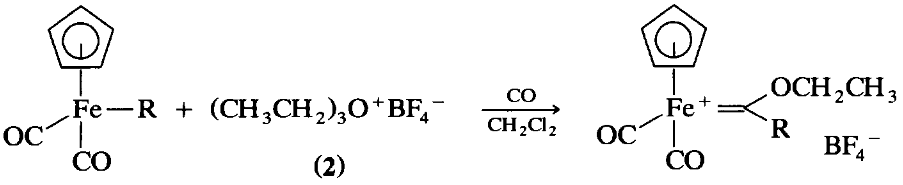
Procedure A. A 0.561 g (2.72 mmol) sample of **1a** was dissolved in 10 ml of dichloromethane. The solution was degassed and blanketed with carbon monoxide. A 5.60 mmol sample of triethyloxonium salt **2** in dichloromethane was added to **1a** at ambient temperature and the mixture was stirred for 24 h. About two-thirds of the solvent was removed by vacuum evaporation. The concentrate was cooled to −78°C and combined with 10 ml of diethyl ether. A precipitate formed immediately. Five recrystallizations from 1:1 ether/dichloromethane and two from 1:1 pentane/dichloromethane gave 0.606 g (64%) of the light yellow solid carbene **3a** with the following spectral properties: IR (CH_2Cl_2): 2062, 2016 cm^{-1}. ^1H NMR($CDCl_3$): δ 5.36 (s, 5H, Cp); 5.05 (m, 2H, $-OCH_2-$); 3.47 (q, J = 7.5 Hz, 2H, $-CH_2-$); 1.72 (t, J = 7.5 Hz, $-CH_3$); 1.23 (t, J = 7.5 Hz, $-CH_3$).

The solvent was removed from the filtrate by vacuum evaporation. The residual paste was dissolved in 5 ml of 10% ether/pentane and chromatographed on activity IV alumina to give 0.137 g (22%) of acyl complex, $FpCOCH_2CH_3$ [10].

Procedure B. This reaction was carried out as described in procedure A using 0.389 g (1.89 mmol) of **1a** and 1.90 mmol of **2** in a side-arm flask in 15 ml of dichloromethane. The solution was stirred for 24 h at ambient temperature. Product isolation from the reaction mixture as before gave 0.308 g (47%) of carbene complex **3a** and 0.064 g (14%) of acyl complex, $FpCOCH_2CH_3$ [10].

3.2. Reaction of $FpCH_2CH_2CH_3$ (1b) with 2

Procedure A. This reaction was carried out as described for compound **1a** (procedure A) using 0.210 g (0.95 mmol) of **1b** and 0.96 mmol of **2**. The solution was stirred for 25 h at ambient temperature. Product isolation from the reaction mixture as before gave 0.210 g (62%) of the carbene complex **3b** with the following spectral properties: IR (CH_2Cl_2): 2070, 2025 cm^{-1}. ^1H NMR(CD_2Cl_2): δ 5.36 (s, 5H, Cp); 5.05 (q, J = 7.5 Hz, 2H, $-OCH_2-$); 3.46 (t, J = 7.5 Hz, 2H, $-CH_2-$); 190–140 (m, 5H, $-CH_3$, $-CH_2-$); 1.0 (t, J = 7.5 Hz, 3H, $-CH_3$), ^{13}C NMR(CD_2Cl_2): δ 336.8, 209.2, 88.5, 82.5, 19.9, 15.3, 14.1. The resonance of the carbon next to the carbene carbon was not observed at ambient temperature. At −18°C it appears as two resonances at 68.7 and 58.7 ppm, respectively. Isolation also gave 12% of acyl complex, $FpCOCH_2CH_2CH_3$ [8].



(2)

(3a–d)

1a, R = CH_2CH_3
1b, R = $CH_2CH_2CH_3$
1c, R = $CH_2CH_2CH(CH_3)_2$
1d, R = $CH_2CH_2C(CH_3)_3$

Scheme 1.

Procedure B. This reaction was carried out using 0.207 g (0.94 mmol) of **1b** and 0.94 mmol of **2** in 15 ml of dichloromethane under a carbon monoxide atmosphere. The reaction mixture was stirred for 4 h at ambient temperature. Isolation as before gave 23% of carbene complex **3b** and 66% of acyl complex, $FpCOCH_2CH_2CH_3$ [8].

Another run under comparable conditions using 0.40 g (1.80 mmol) sample of **1b** and 1.8 mmol of **2** gave 16% of carbene complex **3c** and 65% of acyl complex, $FpCOCH_2CH_2CH_3$ [8].

3.3. Reaction of $FpCH_2CH_2CH(CH_3)_2$ (1c) with 2

This reaction was carried out as described earlier for **1a** (procedure A) with 0.240 g (1.09 mmol) of **1c** and 1.05 mmol of **2** in 15 ml of dichloromethane under a CO atmosphere. The reaction mixture was stirred for 25 h at ambient temperature. Work up as before gave 0.191 g (52%) of **3c** with the following spectral properties: IR (CH_2Cl_2): 2070, 2025 cm^{-1}. ^1H NMR($CDCl_3$): δ 5.40 (s, 5H, Cp); 5.10 (q, $J = 7.5$ Hz, 2H, $-OCH_2-$); 3.46 (t, $J = 7.5$ Hz, 2H, $-CH_2-$); 1.70 (t, $J = 7.5$ Hz, 3H, $-CH_3$); 1.70–1.30 (m, 3H, $-CH_2CH<$); 0.93 (d, $J = 7.5$ Hz, 6H, $-CH_3$). ^{13}C NMR(CD_2Cl_2): δ 336.6, 208.0, 88.2, 81.2, 34.0, 27.9, 21.9, 14.25. The resonance of the carbon next to the carbene carbon was not observed at ambient temperature. At −25°C it appears as two resonances at 65.3 and 55.9 ppm, respectively. Isolation also gave 0.038 g (14%) of acyl complex, $FpCOCH_2CH_2CH(CH_3)_2$ [8].

Another run under comparable conditions provided 57% of carbene complex **3c** and 10% of the acyl complex, $FpCOCH_2CH_2CH(CH_3)_2$ [8].

3.4. Reaction of $FpCH_2CH_2C(CH_3)_3$ (1d) with 2

This reaction was carried out in the same manner as done for **1a** (procedure A) with 0.180 g (0.69 mmol) of **1d** and 0.68 mmol of **2**. The reaction mixture was stirred for 25 h at ambient temperature under a CO atmosphere. Isolation gave 0.210 g (76%) of carbene **3d** with the following spectral characteristics: IR(CH_2Cl_2): 2060, 2020 cm^{-1}. ^1H NMR($CDCl_3$): δ 5.40 (s, 5H, Cp); 5.10 (q, $J = 7.5$ Hz, 2H, $-OCH_2-$); 3.50 (m, 2H, $-CH_2-$); 1.70 (t, $J = 7.5$ Hz, 3H, $-CH_3$); 1.45 (m, 2H, $-CH_2-$); 0.93 (s, 9H, $-CH_3$). ^{13}C NMR (CD_2Cl_2): δ 337.4, 209.4, 88.8, 81.4, 39.2, 31.1, 28.9, 14.6. At −40°C the carbon next to the carbene carbon shows two resonances at 62.2 and 53.3 ppm, respectively.

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