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A new method for the synthesis of iron azadiene and diene complexes. Reaction of (η^2-RCHCHCOR′)Fe(CO)$_4$ with aniline and ylide

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Abstract

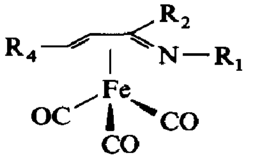
The reactions of (η^2-RCH=CHCOR′)Fe(CO)$_4$ (R = Ph, R′ = H; R = H, R′ = H and R = H, R′ = CH$_3$) with aniline or its derivative afforded η^4-azadiene complexes **1**, **2** and **3** in various yields. The azadiene ligands in **2** and **3** are too reactive to isolate at ambient temperature, but **2** and **3** are stable up to ca 110 ° C. Treatment of (η^2-CH$_2$=CHCHO)Fe(CO)$_4$ with Ph$_3$PCHCOOMe gave a η^2-diene complex **4** which was converted to (η^4-CH$_2$=CHCH=CHCOOMe)Fe(CO)$_3$ on heating, or reacting with (CH$_3$)$_3$NO.

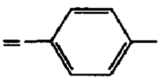
Introduction

Iron carbonyl complexes bearing a conjugated diene or a azadiene moiety constitute two important classes of organometallic iron complexes [1]. Synthetic methods available for those types of species are limited nearly to direct substitution reaction of these ligands with iron carbonyls [1]. Our interests in the chemistry of iron diene compounds [2] led us to explore new routes for the preparation of diene complexes. In this paper, we describe the reactions of η^2-α,β-unsaturated carbonyl compounds with an amine or ylide. The reactions give a new way for making iron diene or azadiene compounds. In particular, the reactions with amine provide the only method to date for preparing iron-stabilized 1-azadiene species.

Results and discussion

The reaction of (η^2-PhCH=CHCHO)Fe(CO)$_4$ with aniline at room temperature leads to the formation of an azadiene complex (η^4-PhCHCHCHNPh)Fe(CO)$_3$ (**1**) as well as PhCHCHCHNPh and $Fe(CO)_5$. The mixture can be separated on silica gel and **1** was isolated as crystalline material in approximately 50% yield. This η^4-1-azadiene species [3] was identified by comparing its spectroscopic data with those of an authentic sample prepared from a direct reaction of the azadiene ligand with $Fe_2(CO)_9$ [4]. It is noteworthy that the present synthetic method gave a much better yield of **1** than that reported previously [3a]. In an earlier paper [5], the reaction of $(PhCH{=}CHCHO)Fe(CO)_4$ with BF_3 and subsequently with aniline leading ultimately to the formation of **1** was described. However, no isolation of the complex was reported.

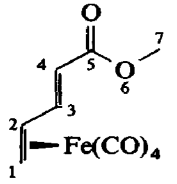


1 $R_1 = Ph, R_2 = H, R_4 = Ph$
2 $R_1 = Ph, R_2 = H, R_4 = H$
3 $R_1 =$  $-OCH_3, R_2 = CH_3, R_4 = H$

In a similar manner, $(CH_2{=}CHCHO)Fe(CO)_4$ and $(\eta^2\text{-}CH_2{=}CHCOCH_3)Fe(CO)_4$ also react with aniline or a substituted aniline to yield the corresponding 1-azadiene(tricarbonyl) iron (**2** and **3**) albeit in lower yields. Based on the NMR, IR and mass spectral data of these complexes, it is clear that the azadiene ligands are π-bonded to the iron center resembling the coordination of PhCH=CHCHNPh in **1**. Notable here is that attempts to prepare the corresponding 1-azadiene of acrolein and methyl vinyl ketone from direct reaction with aniline result in only the formation of unidentified products, possibly, polymers. No 1-azadiene was isolated from the reaction solution. To the best of our knowledge, there is no exiting method for the synthesis of these azadienes. In spite of the difficulty in making these ligands, **2** and **3** are air stable at room temperature. Significant decomposition occurs only at temperature above 110 °C. Consequently, these ligands appear to be stabilized on coordination to the iron center. In summary, the reaction of η^2-α,β-unsaturated carbonyl ligands with aniline may be expressed according to the equation

$$(\eta^2\text{-}RCH{=}CHCOR')Fe(CO)_4 + PhNH_2 \rightarrow \left[(\eta^2\text{-}RCH{=}CHCR'NPh)Fe(CO)_4\right] + H_2O \rightarrow (\eta^4\text{-}RCH{=}CHCR'NPh)Fe(CO)_3 + CO \quad (1)$$

The method for the preparation of azadiene complexes can also be applied to the synthesis of iron dienes. Thus, the reaction of $(\eta^2\text{-}CH_2CHCHO)Fe(CO)_4$ with a Witig reagent $Ph_3PCHCOOMe$ leads to the formation of an intermediate **4**. The regio chemistry of **4** was established based on the large coupling constant of 15 Hz between the two protons at C-2 and C-3 [6]. While no elemental analysis was performed for this species due to its instability at room temperature, precise mass



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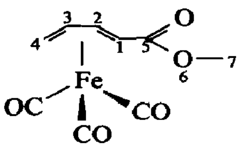

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data are in agreement with the proposed formula. In addition, the IR and ^{1}H NMR data strongly support that only the terminal carbon–carbon double bond is coordinated to the iron center. The conversion of **4** to **5** may be achieved by heating the solution of **4**. Alternatively, **5** can be obtained by reaction of **4** with trimethylamine oxide. The oxide selectively transfers its oxygen to one of the CO groups in **4** to CO_2. Further reaction with the CO groups in **5** is relatively slow at room temperature. The *exo* structure of **5** was assigned by comparing its spectral data with those reported for the structure previously [7] and is consistent with the observed regio chemistry of the intermediate **4**.

Experimental

^{1}H NMR spectra were recorded on a JEOL FX-90Q, while IR spectra were obtained on a Perkin–Elmer Infrared Spectrometer 283. Melting points were measured at an electrothermal melting apparatus. Acrolein and cinnamaldehyde (Aldrich) were used as purchased.

$(CH_2{=}CHCHO)Fe(CO)_4$ and $(PhCH{=}CHCHO)Fe(CO)_4$ were synthesized after the literature methods [6]. However, $(CH_2{=}CHCHO)Fe(CO)_4$ was purified by passing through a silica gel column using a 1 : 1 mixture of hexanes and benzene as the eluent, followed by removal of the solvent in the last step. Poor yield was obtained if sublimation method as reported in the literature was used in the last step.

Synthesis of 1 from cinnamaldehyde(tetracarbonyl)iron and aniline

To 0.467 g (1.55 mmol) of $(\eta^2\text{-}PhCH{=}CHCHO)Fe(CO)_4$ in 10 ml of THF was added 0.30 ml (3.30 mmol) of aniline via a syringe drop-by-drop. The solution was stirred for 2.5 h at room temperature. The mixture was filtered through silica gel, concentrated and separated on silica gel using 1 : 1 hexane/benzene as the eluent. Subsequent evaporation gave 0.290 g (54%) of the desired product, of which the spectral data are identical to those of an authentic sample prepared by a reported method [4a].

Synthesis of 2 from acrolein(tetracarbonyl)iron and aniline

Method I. To 1.83 ml of acrolein in 20 ml of benzene was added 10.0 g of $Fe_2(CO)_9$. The mixture was stirred at 53 °C for 0.5 h. Aniline (5.0 ml) was then added via a syringe drop-by-drop to the solution with stirring. The solution was further heated for 1.0 h at the same temperature. The mixture, filtered through silica gel, was evaporated on a rotary evaporator and was chromatographed on silica gel. Elution with benzene and subsequent evaporation gave 0.99 g (13%) of the product as red crystalline material. M.p. 56–57 °C. Found: C, 53.05; H, 3.46; N, 5.01; Fe, 20.42. $C_{12}H_9FeNO_3$ calcd.: C, 53.17; H, 3.35; N, 5.17; Fe, 20.60%. ^{1}H NMR($CDCl_3$): δ1.58 (d, 9 Hz, 1 H, H-4′), 2.09 (d, 7 Hz, 1 H, H-4), 5.22 (ddd, 9, 7, 2 Hz, 1 H, H-3), 6.09 (m, 4 H, H-2 and Ph *m*-H and *p*-H), 7.12 (d, 7 Hz, 2 H, Ph *o*-H). IR ($CDCl_3$): 2042(s), 1987(s), 1972(s), 1595(m), 1480(m), 1442(m), 1300(b). MS: 271 (M^+), 243, 215, 187, 131.

Method II. To 1.05 g of $(\eta^2\text{-}CH_2CHCHO)(CO)_4Fe$ in 30 ml of benzene was added 0.53 ml of aniline drop-by-drop via a syringe at room temperature and the solution was left at room temperature for 22 h. The mixture was oven-dried $MgSO_4$, filtered and the solvent was removed. Separation on silica gel using a 2 : 1 mixture of benzene and hexane as eluent gave 0.33 g of the product (26%) after solvent removal.

Synthesis of 3 from 3-butenone(tetracarbonyl)iron and anisidine

A mixture of 15 g of $Fe_2(CO)_9$ and 3.5 ml of 3-butenone in 50 ml was stirred under argon at 46° C for 1 h. The solution was evaporated on a rotary evaporater to remove $Fe(CO)_5$ produced. To the residue was added 10.0 g of *p*-anisidine, 30 ml of benzene and 15 g of molecular sieve 4 Å, the mixture was stirred at 53 ± 2° C for 2 days and was then filtered through Celite. Evaporation of the solvent, followed by separation on silica gel using benzene as eluent gave 1.13 g of the product (8.7%). The compound decomposes above 112° C. Found: C, 53.54; H, 4.24; N, 4.54; Fe, 17.49. $C_{14}H_{13}FeNO_4$ calcd.: C, 53.39; H, 4.16; N, 4.45; Fe, 17.73%. ^1H NMR ($CDCl_3$): δ 1.39 (d, 9 Hz, 1 H, H-4′), 1.92 (d, 6 Hz, 1 H, H-4), 2.28 (s, 3 H, H-5), 3.74 (s, 3 H, H-6), 4.97 (dd, 9, 6 Hz, 1 H, H-3), 6.67 (m, AA′BB′ splitting, 4 H, Ph H). IR ($CDCl_3$), 2040(s), 1970(s and b), 1495(m), 1385(m), 1234(m) cm^{-1}. MS: 315 (M^+), 287, 259, 231, 175, 160, 148, 92, 77.

Synthesis of 4 from acrolein(tetracarbonyl)iron and methyl (triphenylphosphoranylidene)acetate, $PPh_3CHCOOMe$

(η^2-$CH_2CHCHO)Fe(CO)_4$ (0.789 g, 3.52 mmol) in 20 ml THF was added with stirring to $PPh_3CHCOOMe$ (1.26 g, 3.78 mmol) at 24° C. The reaction mixture was stirred at the same temperature for 10 h. Evaporation of the solvent, followed by extraction with ether gave a yellow-brown solution which was filtered through a short column of silica gel and was washed with ether. Concentration of the filtrate, further extraction with hexanes and evaporation of the solvent gave 0.72 g (73.0%) of a yellow oil which solidified on storage at −20° C. The structure of the product was characterized based on the following data. ^1H NMR ($CDCl_3$): δ 2.65 (m, 2 H, H-1, H-1′), 3.72 (s, 3 H, H-7), 3.92 (m, 1 H, H-2), 5.94 (d, 15 Hz, 1 H, H-4), 6.75 (dd, 15 and 10 Hz, 1 H, H-3). IR ($CDCl_3$): 2090(s), 2015(s), 1990(s) ν(CO)), 1703(m) (ν(C=O)), 1625(m) (ν(C=C)), 1270, 1195, 1146 cm^{-1}. MS, 280 (M^+), 252 ($M^+ -$ CO), 224 ($M^+ -$ 2CO), 196 ($M^+ -$ 3CO), 168 ($M^+ -$ 4CO). Precise mass measurement: Found, 279.9661, $C_{10}H_8FeO_6$ calcd.: 279.9670.

Synthesis of 5 from acrolein(tetracarbonyl)iron and methyl (triphenylphosphoranylidine)acetate

Method I. (η^2-$CH_2CHCHO)Fe(CO)_4$ (0.503 g, 2.24 mmol) in 20 ml of ether was added to $PPh_3CHCOOMe$ (0.800 g, 2.37 mmol). The mixture was stirred at room temperature for one day and then was heated at 43° C for 21 h. The solution was filtered, concentrated and chromatographed on silica gel. Elution with a mixture of 1 : 6 ratio of ether and hexane and subsequent evaporation of the solvent gave an orange oil. Addition of hexane, followed by storage at −20° C afforded orange crystals (0.292 g, 51.6%); m.p., 48–49° C. ^1H NMR ($CDCl_3$): δ 0.57 (ddd, 10, 3, 1 Hz, 1 H, H-4′), 0.96 (dd, 8, 1 Hz, 1 H, H-1), 1.95 (ddd, 6, 3, 1 Hz, 1 H, H-4), 3.67 (s, 3 H, H-7), 5.38 (m, 1 H, H-3), 5.93 (m, 1 H, H-2). IR ($CDCl_3$): 2055(s), 1990(s), 1705(m), 1315(m), 1175(m).

Method II. (η^2-$CH_2CHCHO)Fe(CO)_4$ (1.01 g, 4.50 mmol) in 30 ml of THF was added to $PPh_3CHCOOMe$ (1.70 g, 5.08 mmol) at room temperature with stirring.

After all the ylide was dissolved, 0.65 g (5.86 mmol) of $(CH_3)_3NO \cdot 2H_2O$ was added to the solution, and the mixture was stirred at room temperature for 2 h. Compoud was isolated according to the procedures shown in Method I in 51% yield.

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