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Journal of Organometallic Chemistry 617–618 (2001) 329–333

Journal of Organo metallic Chemistry

Reaction of iron aminocarbene complexes with electronically deficient alkenes

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Received 17 July 2000; accepted 26 September 2000

Abstract

Thermal reaction of iron aminocarbene complexes bearing aromatic substituent $(CO)_4Fe{=}C(Ar)N(CH_3)_2$ with methyl acrylate, acrylonitrile and methyl vinyl ketone furnishes 1,4-dicarbonyl compounds — formal products of Michael addition of an acyl anion and the alkene. Nonactivated, di- and trisubstituted alkenes are unreactive under the same conditions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Acyl anion equivalent; Aminocarbene; C–H insertion

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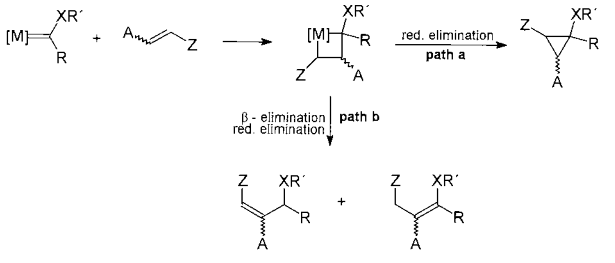
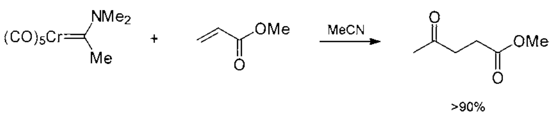
1. Introduction

Alkoxycarbene complexes of Group 6 elements are known to form cyclopropanes via metallacyclobutane intermediate [1] (Scheme 1, path a). These products are often accompanied with derivatives arising from the olefinic C–H insertion reaction (Scheme 1, path b).



Scheme 1.



Scheme 2.

Alkoxycarbenes of Group 6 elements usually form cyclopropanes as the main product in a reaction with electron deficient alkenes. Aminocarbene complexes have been studied to a much lesser extent in this regard. It was demonstrated that aminocarbenes of Group 6 elements form cyclopropanes only in the intramolecular manner [2]. Intermolecular reactions give different products. Thus, thermal reaction of *N*-arylamino-substituted Fischer chromium carbenes having a pendant 2-(1-alkenyl) substituent at the benzene ring affords either substituted indoles or quinolines, depending on the starting material [3]. Pentacarbonyl[(*N*,*N*-dimethylamino)methylene]chromium forms products of formal [2 + 2 + 1] cycloaddition, [4 + 1] cycloaddition or C–H insertion [4], which depends on the substrate structure. Reaction of $(CO)_5Cr{=}C(CH_3)N(CH_3)_2$ (**1**) with methyl acrylate has been reported to afford 1,4-dicarbonyl substituted compounds (formal Michael addition products of an acyl anion and the alkene) as a result of C–H insertion and subsequent hydrolysis (Scheme 2) [4]. Recently it has been shown that the same reaction of analogous aryl-substituted chromium aminocarbenes is catalyzed by $Pd(OAc)_2$, presumably via an unstable palladium carbene intermediate [5]. Thermal and photolytic reactions of lithium- [6] or tetramethylammonium pentacarbonyl(1-oxidoalkylidene)chromate(0) [7] salts with various electron-deficient alkenes also give products of formal Michael addition.

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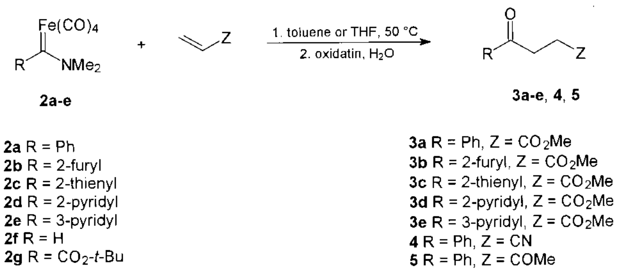
PII: S0022-328X(00)00707-5



Scheme 3.

But only very little is known about reactivity of iron carbene complexes toward alkenes. Alkoxycarbene complexes of iron are known to afford products of C–H insertion exclusively in the reaction with alkenes [8] and dienes [9]. However, nothing is known about aminocarbenes. Therefore we aimed our studies at this class of compounds, and herein we wish to report the results of our study of the reaction of iron aminocarbenes bearing aromatic substituent with electron deficient alkenes. Since iron alkyl substituted aminocarbenes are not accessible directly from tertiary amides [10] and alkoxy–amine exchange is reported to give very poor results with iron alkoxycarbene complexes [11], these compounds were not included in the study.

2. Results and discussion

Reaction of [(*N*,*N*-dimethylamino)phenylmethylene]-tetracarbonyliron(0) (**2a**) with excess methyl acrylate in THF at 50°C furnished methyl-4-oxo-4-phenylbutanoate (**3a**) [12] as the single organic product. The structure of this compound was established unambiguously by ^{1}H-NMR spectrum (see Section 3), which was identical with that reported in the literature [13]. This is a difference from the reaction of iron alkoxycarbenes with alkenes, where only formation of alkoxyalkenes was reported [8].

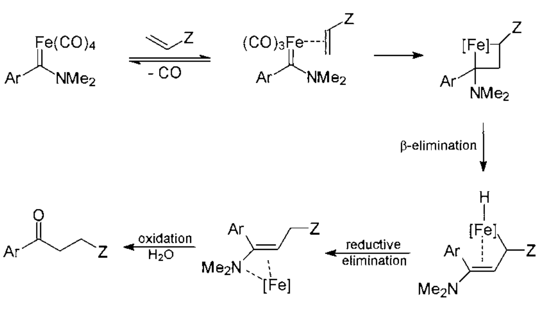
Further experiments showed that while reaction at 50°C in THF or toluene was completed in 48 h, reaction in 1,2-dichloromethane and in acetonitrile did not reach completion even in 80 h. Increasing the temperature resulted in formation of inseparable mixtures of products. Therefore THF and toluene at 50°C were used for the next experiments. While the reaction itself was very smooth and clean, work-up proved difficult, since iron is very efficiently complexed by the product. Many attempts to oxidize iron compounds (Fe^{III} and Ce^{IV} salts, organic peroxides, aminooxides, molecular oxygen in aqueous and non-aqueous solutions) have been tried without success. Finally simple exposure of the dilute ethereal solution of the reaction mixture to light (sunlight gave the best results) in the presence of $FeCl_3 \cdot 6H_2O$ on air, followed by filtration of the precipitated iron oxides and chromatography, gave the best results. However, this process is very slow and complete precipitation of the iron oxides takes about 2 weeks.

Other typical Michael acceptors — acrylonitrile and methyl vinyl ketone also react with **2a**, giving the corresponding 1,4-dicarbonyl compounds **4** and **5**, respectively (Scheme 3, Table 1). Substrates with di- or trisubstituted double bonds (methyl crotonate, methyl cinnamate, methyl methacrylate, cinnamaldehyde, crotonaldehyde, mesityl oxide and maleic anhydride) were unreactive, probably due to steric reasons. Iron aminocarbene complexes **2b**–**e**, bearing heteroaromatic substituents, reacted in a similar manner, giving the corresponding 4-substituted 4-oxobutanoates **3b**–**e** in acceptable yields (Scheme 3, Table 1). In most cases reaction in toluene gave better results compared to THF. The only exceptions were the reactions of 2-thienylcarbene (**2c**) and 3-pyridylcarbene (**2e**), which gave slightly better results when THF was used as the solvent. 2-Pyridyl complex **2d**, for reasons that are unclear, reacted with methyl acrylate only in toluene. Complexes $(CO)_4Fe{=}C(H)N(CH_3)_2$ (**2f**) and $(CO)_4Fe{=}C(CO_2\text{-}t\text{-}Bu)N(CH_3)_2$ (**2g**) gave only inseparable mixtures of products under identical conditions.

Analogous formation of 1,4-dicarbonyl compounds has been reported recently from the reaction of aryl substituted chromium aminocarbenes with methyl acrylate and acrylonitrile catalyzed with $Pd(OAc)_2$ in the

Table 1

Carbene complex	Alkene	Product	Yield (%)	
			Reaction in toluene	Reaction in THF
2a	Methyl acrylate	**3a**	77	30
2a	Acrylonitrile	**4**	33	29
2a	Methyl vinyl ketone	**5**	46	34
2b	Methyl acrylate	**3b**	48	26
2c	Methyl acrylate	**3c**	56	61
2d	Methylacrylate	**3d**	44	No reaction
2e	Methyl acrylate	**3e**	27	32



Scheme 4.

presence of triethylamine. A non-catalyzed reaction afforded only a low yield of 1,4-dicarbonyl product after prolonged reaction time [5]. In our case, however, the reaction of iron carbene **2a** with methyl acrylate was not influenced by the presence of a palladium catalyst ($Pd(OAc)_2$ or $Pd(PPh_3)_4$) under the conditions described in the Ref. [5]. The chromium aminocarbene $(CO)_5Cr{=}C(Ph)N(CH_3)_2$ did not react with Michael acceptors under the above conditions used for its iron analogue **2a**.

We suppose that the mechanism of this reaction is the same as was suggested previously for similar reactions of chromiun carbenes [1,4]. This involves formation of a metallacyclobutane with subsequent β-elimination and reductive elimination followed by hydrolysis during work-up (Scheme 4).

In conclusion, reaction of iron aminocarbene complexes with non-hindered electron deficient alkenes proceeds with olefinic C–H insertion under formation of 1,4-dicarbonyl compounds. This is the first example of iron carbenes giving such a type of product. The reaction is limited in scope (only aromatic iron aminocarbenes can be used) and the isolation of the product is time consuming. However, since this reaction proceeds under very mild and neutral conditions, we believe that in some cases iron aminocarbene complexes can be used as synthetic equivalents of an acyl anion.

3. Experimental

^{1}H-NMR spectral data were recorded on a Varian Gemini spectrometer at 300 MHz in $CDCl_3$, and chemical shifts are referenced to TMS. IR spectra were recorded on a Nicolet 750FT-IR spectrometer. Tetrahydrofuran was distilled from benzophenone ketyl under argon prior to use. Toluene was distilled from sodium. Non-dried diethyl ether was used for work-up of reaction mixtures. Michael acceptors were obtained from Aldrich and Fluka and used as purchased. Iron aminocarbene complexes were prepared according to published procedures [10]. For the purification of crude reaction mixtures, radial-layer chromatography (Chromatotron model 8924 and Merck silica gel 60 PF) was used. Neutral aluminum oxide (activity II–III) was obtained from Merck. All prepared 1,4-dicarbonyl compounds are known compounds.

3.1. [(N,N-Dimethylamino)-2-thienylmethylene]-tetracarbonyliron(0) ***(2c)***

Iron pentacarbonyl (1.4 ml, 10 mmol) was added at −78°C via syringe to a suspension of C_8K [14], prepared from potassium (1.06 g, 27 mmol) and graphite (2.49 g, 207 mmol) in THF (40 ml). The resulting mixture was stirred for 10 min at −78°C, then a solution of *N*,*N*-dimethylthiophene-2-carboxamide (1.11 g, 8 mmol) in THF (10 ml) was added via syringe, and stirring was continued at this temperature for another 10 min. The reaction vessel was then transferred to a cooling bath adjusted to −45°C, and stirring was continued at this temperature. (At higher temperature, insoluble and therefore unreactive solvate of $K_2Fe(CO)_4$ precipitates! [10]) After 20 min, the mixture was cooled again to −78°C and chlorotrimethylsilane (2.5 ml, 20 mmol) was added. Stirring was continued for 20 min at −78°C, and the mixture was allowed to warm to 10°C. Alumina (8 g) was added, THF was evaporated at diminished pressure (bath temperature < 30°C), and the residue was dried under high vacuum for several hours. Light petroleum (50 ml) was added, and the mixture was stirred vigorously for several minutes under argon atmosphere. The suspension formed was then transferred onto a column filled with neutral alumina (60 g). Elution with light petroleum–dichloromethane 5:1 and crystallization from *n*-heptane–dichloromethane furnished 0.785 g (45%) of pure carbene complex: M.p. (dec.) 82°C; ^{1}H-NMR δ 3.23 (s, 3H, *anti*-NCH_3), 4.00 (s, 3H, *syn*-NCH_3), 6.58 (m, 1H, Ar*H*), 6.98 (m, 1H, Ar*H*), 7.45 (m, 1H, Ar*H*); IR ($CHCl_3$) $\nu = 2043$ (s), 1968 (m), 1940 (s), 1919 (s) cm^{-1}. *Anal.* Calc. for $C_{11}H_9FeNO_4S$: C, 43.02; H, 2.95; N, 4.56. Found: C, 42.99; H, 3.16; N, 4.53%.

3.2. [(N,N-Dimethylamino)-2-pyridylmethylene]-tetracarbonyliron(0) ***(2d)***

The same procedure as above starting with *N*,*N*-dimethyl-2-pyridylcarboxamide (1.20 g, 8 mmol), after chromatography (light petroleum–dichloromethane 3:2) and crystallization from *n*-heptane–dichloromethane, afforded 0.95 g (39%) of yellow solid. ^{1}H-NMR δ 3.09 (s, 3H, *anti*-NCH_3), 4.01(s, 3H, *syn*-NCH_3), 7.08 (m, 2H, Ar*H*), 7.73 (m, 1H, Ar*H*), 8.57 (m, 1H, Ar*H*); IR ($CHCl_3$): $\nu = 2045$ (m), 1969 (m), 1941 (s), 1923 (s) cm^{-1}. *Anal.* Calc. for $C_{12}H_{11}FeN_2O_4$: C, 47.68; H, 3.34; N, 9.27. Found: C, 47.57; H, 3.55; N, 9.33%.

3.3. General procedure for the reaction of iron aminocarbenes with electron deficient alkenes

Carbene complex (0.5 mmol) and unsaturated substrate (5 mmol) were dissolved in THF or toluene (2 ml) and the mixture was heated to 50°C under argon atmosphere for 48 h. The reaction mixture was than diluted with diethylether, $FeCl_3 \cdot 6H_2O$ (0.032 g, 0.1 mmol) was added and the solution was allowed to sit in sunlight until all iron compounds precipitated and a clear solution was formed (usually 2 weeks were required). The solids were then filtered off, the solvents were evaporated and the crude product was purified by chromatography. Reaction products were characterized by comparison of their ^{1}H-NMR spectra with that reported in the literature.

3.4. Methyl 4-oxo-4-phenylbutanoate (**3a**) [12]

Reaction in toluene, after chromatography (light petroleum–diethyl ether–acetone, 80:10:10) furnished 0.074 g (77%) of the product. The yield in THF was 0.029 g (30%). ^{1}H-NMR [13] δ 2.75 (t, $J = 13.2$ Hz, 2H, CH_2), 3.30 (t, $J = 13.2$ Hz, 2H, CH_2), 3.68 (s, 3H, $COOCH_3$), 7.44 (t, $J = 15.9$ Hz, 2H, Ar*H*), 7.55 (t, $J = 14.8$ Hz, 1H, Ar*H*), 7.97 (d, $J = 8.7$ Hz, 2H, Ar*H*).

3.5. 4-Oxo-4-phenylbutyronitrile (**4**) [15]

Reaction in toluene, after chromatography (light petroleum–diethyl ether–acetone, 80:10:10) afforded 0.027 g (33%) of the product. The yield in THF was 0.023 g (29%). ^{1}H-NMR [16] δ 2.78 (t, $J = 7.1$ Hz, 2H, CH_2), 3.39 (t, $J = 7.2$ Hz, 2H, CH_2), 7.50 (t, $J = 15.4$ Hz, 2H, Ar*H*), 7.61 (t, $J = 14.3$ Hz, 1H, Ar*H*), 7.97 (d, $J = 8.2$ Hz, 2H, Ar*H*).

3.6. 1-Phenylpentane-1,4-dione (**5**) [17]

Reaction in toluene and chromatography (light petroleum–diethyl ether–acetone, 80:10:10) furnished 0.041 g (46%) of the product. The yield in THF was 0.03 g (34%). ^{1}H-NMR [18] δ 2.26 (s, 3H, CH_3), 2.89 (t, $J = 6.3$ Hz, 2H, CH_2), 3.28 (t, $J = 6.3$ Hz, 2H, CH_2), 7.45 (m, 3H, Ar*H*), 8.00 (d, $J = 7.1$ Hz, 2H, Ar*H*).

3.7. Methyl-4-(2-furyl)-4-oxobutanoate (**3b**) [19]

Reaction in toluene and chromatography (light petroleum–diethyl ether–acetone–methanol, 50:30:17:3) furnished 0.044 g (48%) of the product. The yield in THF was 0.024 g (26%). ^{1}H-NMR δ 2.74 (t, $J = 13.2$ Hz, 2H, CH_2), 3.17 (t, $J = 13.7$ Hz, 2H, CH_2), 3.69 (s, 3H, $COOCH_3$), 5.63 (m, 1H, Ar*H*), 7.22 (d, $J = 3.8$ Hz, 1H, Ar*H*), 7.58 (d, $J = 1.1$ Hz, 1H, Ar*H*).

3.8. Methyl-4-oxo-4-(2-thienyl)butanoate (**3c**) [20]

Reaction in toluene, after chromatography (light petroleum–diethyl ether–acetone–methanol, 50:30:17:3) furnished 0.057 g (56%) of the product. The yield in THF was 0.06 g (61%). ^{1}H-NMR [21] δ 2.76 (t, $J = 13.7$ Hz, 2H, CH_2), 3.26 (t, $J = 13.7$ Hz, 2H, CH_2), 3.70 (s, 3H, $COOCH_3$), 7.13 (m, 1H, Ar*H*), 7.63 (d, $J = 4.9$ Hz, 1H, Ar*H*), 7.76 (d, $J = 3.8$ Hz, 1H, Ar*H*).

3.9. Methyl-4-oxo-4-(2-pyridyl)butanoate (**3d**) [22]

Reaction in THF and after chromatography (light petroleum–diethyl ether–acetone–methanol, 50:30:17:3) 0.042 g (44%) of the product. No product was isolated from the reaction in toluene. ^{1}H-NMR δ 2.76 (t, $J = 13.2$ Hz, 2H, CH_2), 3.59 (t, $J = 17.0$ Hz, 2H, CH_2), 3.69 (s, 3H, $COOCH_3$), 7.47 (t, $J = 12.1$ Hz, 1H, Ar*H*) 7.83 (t, $J = 14.8$ Hz, 1H, Ar*H*), 8.03 (d, $J = 7.7$ Hz, 1H, Ar*H*), 8.68 (d, $J = 3.9$ Hz, 1H, Ar*H*).

3.10. Methyl-4-oxo-4-(3-pyridyl)butanoate (**3e**) [23]

Reaction in toluene, after chromatography (light petroleum–diethyl ether–acetone–methanol, 50:30:17:3) furnished 0.026 g (27%) of the product. The yield in THF was 0.03 g (32%). ^{1}H-NMR δ 2.79 (t, $J = 13.2$ Hz, 2H, CH_2), 3.32 (t, $J = 13.2$ Hz, 2H, CH_2), 3.71 (s, 3H, $COOCH_3$), 7.44 (q, $J = 16.5$ Hz, 1H, Ar*H*), 8.25 (dt, $J = 12.1$ Hz, 1H, Ar*H*), 8.79 (d, $J = 6.0$ Hz, 1H, Ar*H*), 9.20 (d, $J = 1.6$ Hz, 1H, Ar*H*).

Acknowledgements

Support of this research under Grants 203/95/0160 and 203/00/1240 from the Czech Grant Agency is gratefully acknowledged.

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