Cationic Iron Aminocarbene Complexes as Dienophiles in Diels-Alder Reaction with Cyclopentadiene

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The cationic iron (alkynyl)aminocarbene complexes $[Cp(CO)_2Fe(C(NHR)C{\equiv}CSiMe_3][PF_6]$, ($R = C_6H_5$, $p\text{-}CH_3C_6H_4$) **1** derived from aromatic amines smoothly react with cyclopentadiene in dichloromethane to yield the cycloadducts **2**. No reaction was observed for complexes derived from sterically demanding aliphatic amines, like L-alanine *tert*-butyl ester. For comparison, the alkynyl-substituted acyl iron compounds $Cp(CO)_2Fe(C{=}O)C{\equiv}CR$ ($R = SiMe_3$, C_6H_5) **3** were investigated, requiring $TiCl_4$ catalysis to undergo the cycloaddition reaction. The structures of the cycloadducts **4** were determined by X-ray crystallography.

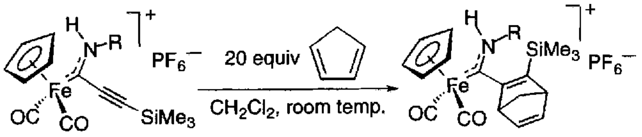
During the past two decades α,β-unsaturated Fischer-type carbene complexes of chromium and tungsten have proven to be useful reagents in organic synthesis, e.g. Diels-Alder reactions[1,2]. During recent years cycloaddition reactions with alkynylalkoxycarbene complexes of group-6 metals[3] and analogous tetracarbonyliron(0) complexes[4] have attracted the interest of organic chemists. In contrast, synthetic applications of aminocarbene complexes have been less extensively studied[5,6]. However, all attempts to use substituted (alkynyl)aminocarbene complexes in Diels-Alder reactions as dienophiles failed[7,8]. Only the acetylene complexes ($(CO)_5M[C(NMe_2)C{\equiv}CH]$, M = Cr, W) afforded the cycloadducts upon treatment with cyclopentadiene (neat) at room temperature. The corresponding TMS-substituted tungsten complex did not react even after prolonged reaction time (48 h), probably for steric reasons[8].

Being interested in the reactivity of $Cp(CO)_2Fe$-substituted aminocarbene complexes in comparison to chromium analogues, the application of **1** (Scheme 1) in Diels-Alder reactions with cyclopentadiene was examined.

The alkynyl-substituted aminocarbene complexes **1** were prepared as described in a previous paper[9]. Thus, **1a** and **1b** were allowed to react with cyclopentadiene (20 equiv.) at room temperature in dichloromethane (monitoring by IR spectroscopy) to yield the cycloadducts **2** (Scheme 1) in >90% yield. The reaction time varied from one to three hours. Compound **2a** crystallized directly from the reaction mixture, whereas **2b** was precipitated by addition of petroleum ether.

The structural and analytical characterization revealed the isolated cycloadducts to be formed exclusively. The NMR spectra show only one single isomer to be present in solution. In accordance with the starting materials **1a,b**, the *anti* isomer should be favored[10]. The ν(CO) absorptions

Scheme 1



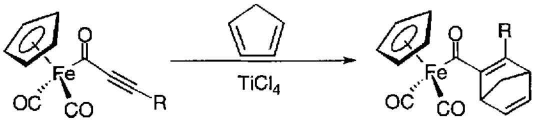
1	R
a	C_6H_5
b	$p\text{-}CH_3C_6H_4$
c	(*S*)-$CH(CH_3)C_6H_5$

2	R
a	C_6H_5
b	$p\text{-}CH_3C_6H_4$

observed at about 2045 and 2000 cm^{-1}, the $\delta(Fe{-}C_{Carbene})$ shifts in the ^{13}C-NMR spectra and the ν(C=N) stretching frequencies are at positions noted previously for aminocarbene complexes derived from aromatic amines[10]. With the cationic $[Cp(CO)_2Fe]$ fragment compared to the $(CO)_5Cr$ group a sterically less demanding moiety is introduced, which increases the electrophilicity of the carbene carbon and thereby the polarization of the alkyne substituent. However, when the aminocarbene complex **1c** was used, obtained from (*S*)-(1-phenylethyl)amine, only starting material was isolated (Scheme 1). In addition, neither complex $[Cp(CO)_2Fe(C(L\text{-}NHCH(CH_3)CO_2tBu)C{\equiv}CPh^+]$-$[PF_6^-]$[10] nor the trimethylsilyl-substituted compound $[Cp(CO)_2Fe(C(L\text{-}NHCH(CH_3)CO_2tBu)C{\equiv}CSiMe_3^+]$-$[PF_6^-]$[10] did react with cyclopentadiene by applying analogous experimental conditions. After addition of a catalytic amount of $TiCl_4$ (0.2 equiv., 1 M solution in CH_2Cl_2) to **1c** and cyclopentadiene, the cycloaddition did not occur either. Probably, the difference in reactivity observed for *N*-alky- and *N*-aryl-substituted aminocarbene complexes **1** is caused solely by steric hindrance, due to the bulkiness of the chiral aliphatic amines employed.

In comparison to the cationic aminocarbene complexes **1a,b** the neutral alkynyl-substituted iron acyl complexes **3** proved to be less reactive[11]. Thus, when **3a** was treated with an excess of cyclopentadiene (20–80 equiv.) at –10 °C or at room temperature in dichloromethane or benzene no reaction was observed (TLC monitoring). Fortunately, Lewis acid catalysis with $TiCl_4$ (1 equiv.) provided access to the cycloadduct **4a**, which could be isolated in moderate yield (40%) after aqueous work-up and column chromatography on silica gel.

Scheme 2

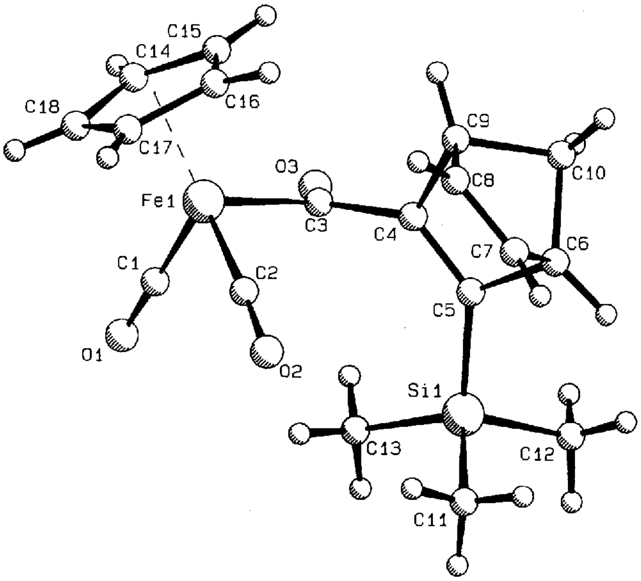


3

4	R	yield
a	$SiMe_3$	40 %
b	Ph	77 %

The use of 0.2 equiv. of $TiCl_4$ at room temperature in dichloromethane proved to be sufficient to effect clean conversion to the cycloadducts **4a** and **4b** (Scheme 2). A sample of **4a** was recrystallized from petroleum ether/ether (23%) for X-ray structure analysis. Similar structural features and data were observed for **4a** (Figure 1) and **4b**, except for the torsion angle O3–C3–C4–C5 [**4a**: –76.3(5); **4b**: –96.5(4)][14].

Figure 1. Crystal structure of **4a**[a]



[a] Selected bond lengths [Å] and angles [°]: Fe–C1 1.749(5), Fe–C2 1.750(5), Fe–C3 1.979(4), C1–O1 1.155(6), C3–O3 1.208(5), C3–C4 1.490(5), C4–C5 1.339(5), C8–C7 1.309(7); Fe–C3–O3 121.8(3), Fe–C3–C4 117.7(2), O3–C3–C4 120.4(3), O3–C3–C4–C5 –76.3(5).

In summary, the results obtained demonstrate an enhanced reactivity of sterically demanding cationic iron (alkynyl)aminocarbene complexes derived from aromatic amines (aniline, toluidine) compared to group-6 metal analogues.

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Experimental

Experimental procedures were performed as already described[10]. The yields refer to analytically pure compounds and are not optimized. – IR: FT-IR, Perkin-Elmer 1760 X. – ^1H and ^{13}C NMR: Bruker AM 400, Bruker AM 200. If not specially mentioned, chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual solvent signals. – MS: Varian MAT CH 7a, Finnigan MAT 95. – Melting points are uncorrected. – Column Chromatography: Fa. J. T. Baker (Type 0.063–0.200 mm). – $TiCl_4$ was purchased from Aldrich as 1 M solution in CH_2Cl_2.

Complex **2a**: To a solution of **1a** (360 mg, 0.69 mmol) in CH_2Cl_2 (8 ml) neat cyclopentadiene (0.92 ml, 20 equiv.) was added. The solution was stirred at ambient temp. in the dark. After 30 min, crystallization of the product from the reaction mixture was observed. The suspension was stirred for 3 h. The solvent was removed by means of a cannula, and the precipitate was washed with ether, dried under argon and oil-pump vacuum to yield 368 mg (91%) of **2a** as a yellow solid, m.p. 205–207 °C (dec.). – ^1H NMR (200 MHz, $[D_6]$DMSO): δ = 13.56 (s, 1H, NH), 7.64–7.23 (m, 6H, C_6H_5, =CH), 6.64 (m, J = 4.4 Hz, 1H, =CH), 5.63 (s, 5H, C_5H_5), 3.82 (s, 1H, CH), 3.69 (s, 1H, CH), 1.57 (d, J = 6.3 Hz, 1H, CH), 1.38 (d, J = 6.3 Hz, 1H, CH), –0.23 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (50.3 MHz, $[D_6]$DMSO): δ = 253.8 (Fe–Carbene), 212.2, 210.6 (CO), 168.7 (C-2), 140.7, 142.3, 141.4 (C-3,5,6), 135.5 ($C_{quat.}$ C_6H_5), 128.9, 124.8, 87.3 (C_5H_5), 64.8 (C-7), 56.9, 54.8 (C-1,4), –2.6 ($Si(CH_3)_3$). – IR (KBr): $\tilde{\nu}$ = 3312 (NH), 2050, 2006 (CO), 1518 (C=N), 845 (PF_6^-). – $C_{24}H_{26}F_6FeNO_2PSi$ (589.4): calcd. C 48.91, H 4.45, N 2.38; found C 48.87, H 4.36, N 2.27.

Complex **2b**: To a solution of 607 mg (1.13 mmol) of **1b** in CH_2Cl_2 (13 ml) neat cyclopentadiene (1.5 ml, 20 equiv.) was added, and the solution was stirred in the dark at ambient temp. for 1 h until complete consumption of the starting material (IR monitoring). The reaction mixture was diluted with petroleum ether (40 ml) to precipitate **2b**. The solvent was removed by means of a cannula, and the residue was washed with petroleum ether and dried to yield 641 mg (94%) of **2b** as a yellow solid, m.p. 193 °C (dec.). – ^1H NMR (200 MHz, $[D_6]$DMSO): δ = 13.47 (s, 1H, NH), 7.31–7.10 (m, 5H, C_6H_4, =CH), 6.63 (q, J = 4.8, J = 3.2 Hz, 1H, =CH), 5.62 (s, 5H, C_5H_5), 3.80 (s, 1H, CH), 3.69 (s, 1H, CH), 2.31 (s, 3H, CH_3), 1.57 (d, J = 6.5 Hz, 1H, CH), 1.39 (d, J = 6.5 Hz, 1H, CH), –0.23 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (50.3 MHz, $[D_6]$DMSO): δ = 252.0 (Fe–Carbene), 211.4, 209.9 (CO), 168.8, 139.9, 139.8, 137.7, 137.2, 134.5, 128.4, 123.8, 86.5 (C_5H_5), 64.1, 56.9, 54.8, 19.7 (CH_3), –3.4 [$Si(CH_3)_3$]. – IR (KBr): $\tilde{\nu}$ = 3301 (NH), 2046, 1998 (CO), 1511 (C=N), 845 (PF_6^-). – $C_{25}H_{28}F_6FeNO_2PSi$ (603.4): calcd. C 49.76, H 4.68, N 2.32; found C 49.66, H 4.75, N 2.35.

Complex **4a**: To a solution of **3a** (560 mg, 1.86 mmol) and cyclopentadiene (2.5 ml, 20 equiv.) in 20 ml of degassed benzene 0.2 equiv. of $TiCl_4$ (0.4 ml, 1 M solution in CH_2Cl_2) was added. The reaction mixture was stirred at ambient temp. for 4 h 20 min until complete consumption of the starting material (TLC monitoring). After dilution with CH_2Cl_2 (50 ml), the organic layer was washed with a satd. aqueous NH_4Cl solution (130 ml) and brine (100 ml, twice) and dried ($MgSO_4$). The solvent was concentrated in vacuo, and the residue was purified by column chromatography on silica gel with petroleum ether/ether (8:1) as eluent to yield 276 mg (40%) of **4a** as a yellow solid. Crystallization from petroleum ether/ether (50 ml, 4:1) afforded **4a** as yellow needles (157 mg, 23%), m.p. 125 °C. – ^1H NMR (200 MHz, $CDCl_3$): δ = 6.87 (dd, *J* = 3.0, 5.0 Hz, 1H, =CH), 6.67 (dd, *J* = 3.0, 5.0 Hz, 1H, =CH), 4.86 (s, 5H, C_5H_5), 3.78 (s, 1H, CH), 3.74 (s, 1H, CH), 1.93 (d, *J* = 6.2 Hz, 1H, CH_2), 1.84–1.80 (m, *J* = 6.2 Hz, 1H, CH_2), 0.03 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 254.3 (Fe–C=O), 214.2, 213.8 (CO), 176.6 (C-2), 142.7 (C–3), 142.3, 141.4 (C-5,6), 86.3 (C_5H_5), 71.2 (C-7), 54.7, 54.3 (C-1,4), –1.2 ($Si(CH_3)_3$). – IR (CH_2Cl_2): ṽ = 2020, 1963 (CO), 1601 (Fe–C=O). – $C_{18}H_{20}FeO_3Si$ (368.3): calcd. C 58.70, H 5.47; found C 58.69, H 5.35.

Complex **4b**: To a solution of **3b** (306 mg, 1 mmol) and cyclopentadiene (1.34 ml, 20 equiv.) in degassed CH_2Cl_2 (11 ml) 0.2 equiv. of $TiCl_4$ (0.2 ml, 1 M solution in CH_2Cl_2) was added. The solution was stirred for 3 h (TLC monitoring). Dilution with acetone afforded a white precipitate, which was removed by filtration through Celite. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel with petroleum ether/ether (2:1) as eluent. The solvent was removed by rotary evaporation. The residue was stored at –18 °C to afford yellow crystalline **4b**, collected by removal of the mother liquor by means of a cannula and dried under oil-pump vacuum: 268 mg (77%), m.p. 119–120 °C. – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.34–7.18 (m, 5H, C_6H_5), 7.03–6.95 (m, 2H, HC=CH), 4.63 (s, 5H, C_5H_5), 3.82 (s, 1H, CH), 3.68 (s, 1H, CH), 2.15 (d, *J* = 6.3 Hz, 1H, CH), 1.93 (d, *J* = 6.3 Hz, 1H, CH). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 259.5 (Fe–C=O), 214.0, 213.2, 160.9, 141.6, 141.0, 138.9, 135.9, 128.0, 127.3, 126.4, 86.4, 69.3, 54.2, 54.0. – IR (CH_2Cl_2): ṽ = 2021, 1965 (CO), 1602 (Fe–C=O). – $C_{21}H_{16}FeO_3$ (327.2): calcd. C 67.77, H 4.33; found C 67.77, H 4.35.

Table 1. Crystal and refinement data for iron acyl complexes **4a** and **4b**

	4a	**4b**
Emp. formula	$C_{18}H_{20}FeO_3Si$	$C_{21}H_{16}FeO_3$
Mol. mass	368.29 $gmol^{-1}$	372.19 $gmol^{-1}$
Cryst. size [mm^3]	0.10 × 0.13 × 1.02	0.10 × 0.16 × 0.64
Linear absorption coefficient	$\mu = 7.45\ mm^{-1}$ (DIFABS[12]) (Cu-K_α; $\lambda = 1.5418$ Å)	$\mu = 7.15\ mm^{-1}$ (DIFABS[12]) (Cu-K_α; $\lambda = 1.5418$ Å)
Range of transmission	$T_{min} = 0.244$, $T_{max} = 1.0$	$T_{min} = 0.17$, $T_{max} = 1.0$
Space group	$P2_1/c$ (monoclinic)	$P2_1/c$ (monoclinic)
Cell constants[13]	$a =$ 13.2159(9) Å $b =$ 11.4413(4) Å $c =$ 12.8825(8) Å $\beta = 112.517(4)°$ calculated from 25 reflections $65° < \Theta < 74°$	$a =$ 12.277(1) Å $b =$ 7.094(2) Å $c =$ 19.822(1) Å $\beta = 92.44(1)°$ calculated from 46 reflections $60° < \Theta < 74°$
Cell volume	$V = 1799.4(2)$ Å^3; $Z = 4$ $F(000) = 768$	$V = 1724.9(5)$ Å^3; $Z = 4$ $F(000) = 768$
Density	$d_{calcd.} = 1.359\ gcm^{-3}$	$d_{calcd.} = 1.427\ gcm^{-3}$
Scan type	$\omega/2\Theta$	ω/Θ
Range for data collection	$1.5° \le \Theta \le 75.0°$ $-16 \le h \le 15$ $0 \le k \le 14$ $0 \le l \le 16$	$1.5° \le \Theta \le 75.0°$ $0 \le h \le 15$ $-8 \le k \le 0$ $-24 \le l \le 24$
Reflns. collcd.	3407	3845
Unique reflns.	3407 ($R_{sigma} = 0.0324$)	3543 ($R_{sigma} = 0.0344$)
Obsd. rflns.	2540 ($\lvert F\rvert/\sigma(F) > 4.0$)	2554 ($\lvert F\rvert/\sigma(F) > 4.0$)
Structure solution	SIR92	SIR92
Structure refinement	SHELXL-93	SHELXL-93
Parameters varied	224	241
Weights	$w = 1/[\sigma^2(F_o^2) + (0.0736{*}P)^2 + 1.23{*}P]$ $P = (Max(F_o^2,0)+2{*}F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0713{*}P)^2 + 0.36{*}P]$ $P = (Max(F_o^2,0)+2{*}F_c^2)/3$
R values (refinement on F^2)	$wR2 = 0.1443$ ($R1 = 0.0494$ for obsd. reflns.)	$wR2 = 0.1337$ ($R1 = 0.0439$ for obsd. reflns.)
Goodness-of-fit	$S = 1.032$	$S = 1.048$
max, min peak in diff. Fourier map;	0.48, –0.36 eÅ^{-3}	0.35, –0.21 eÅ^{-3}
max shift of parameters	0.001*e.s.d	0.000*e.s.d

X-Ray Structure Determination: Examinations and data collections were carried out with Cu-K_α radiation (graphite-monochromated) with an Enfraf-Nonius CAD4 diffractometer. For structure refinement the full-matrix procedure was applied by using SHELXL 93. All non-hydrogen atoms were refined anisotropically. For both structures a riding model starting from calculated positions for the hydrogen atoms was employed [with the exception of H6 (C6) compound **4b**][14].

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[1] For reviews, see: [1a] K. H. Dötz, *New J. Chem.* **1990**, *14*, 433–445. – [1b] W. D. Wulff in *Comprehensive Organic Synthesis*, vol. 5 (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, p. 1065.

[2] For applications in cycloaddition reactions, see: [2a] W. D. Wulff, W. E. Bauta, R. W. Kaesler, P. J. Lankford, R. A. Miller, C. K. Murray, D. C. Yang, *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659. – [2b] W. D. Wulff, D. C. Yang, C. K. Murray, *J. Am. Chem. Soc.* **1988**, *110*, 2653–2655. – [2c] S. L. B. Wang, W. D. Wulff, *J. Am. Chem. Soc.* **1990**, *112*, 4550–4552. – [2d] W. D. Wulff, D. C. Yang, *J. Am. Chem. Soc.* **1984**, *106*, 7565.

[3] See, for example: [3a] K. S. Chan, W. D. Wulff, *J. Am. Chem. Soc.* **1986**, *108*, 5229–5236. – [3b] K. S. Chan, M. L. Yeung, W.-K. Chan, R.-J. Wang, T. C. W. Mak, *J. Org. Chem.* **1985**, *60*, 1741–1747. – [3c] J. Barluenga, F. Aznar, S. Barluenga, *J. Chem. Soc., Chem. Commun.* **1995**, 1973.

[4] For [4 + 2] cycloaddition reactions between [(alkynyl)ethoxymethylene]Fe(CO)$_4$ complexes and cyclopentadiene, see: J. Park, S. Kang, C. Won, D. Whang, K. Kim, *Organometallics* **1993**, *12*, 4704, and references cited.

[5] For reviews, see: [5a] D. B. Grotjahn, K. H. Dötz, *Synlett* **1991**, 381. – [5b] M. A. Schwindt, J. R. Müller, L. S. Hegedus, *J. Organomet. Chem.* **1991**, *413*, 143–153. – [5c] A. Hafner, L. S. Hegedus, G. de Weck, B. Hawkins, K. H. Dötz, *J. Am. Chem. Soc.* **1988**, *110*, 8413–8421.

[6] For examples of recent applications, see: [6a] B. C. Söderberg, L. S. Hegedus, *J. Org. Chem.* **1991**, *56*, 2209–2212. – [6b] W. D. Wulff, A. M. Gilbert, R. P. Hsung, A. Rahm, *J. Org. Chem.* **1991**, *60*, 4566–4575, and references cited.

[7] K. H. Dötz, W. Kuhn, *J. Organomet. Chem.* **1985**, *286*, C23.

[8] A. Rahm, W. D. Wulff, A. L. Rheingold, *Organometallics* **1993**, *12*, 597.

[9] K. Rück-Braun, J. Kühn, *Synlett* **1995**, 1194.

[10] K. Rück-Braun, J. Kühn, D. Schollmeyer, *Chem. Ber.* **1996**, *129*, 937–944.

[11] For [4 + 2] cycloaddition reactions of analogous α,β-unsaturated acyl-iron complexes with dienes, see: [11a] J. W. Herndon, *J. Org. Chem.* **1986**, *51*, 2853–2855. – [11b] S. G. Davies, J. C. Walker, *J. Chem. Soc., Chem. Commun.* **1986**, 609.

[12] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, **1983**, *39*, 158–166.

[13] C. Svenson, *Celsius, Program for Refinement of Lattice Parameters*, Lund, Schweden, **1974**.

[14] Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen. Any request for this material should quote the full literature citation and the reference numbers CSD-405155 for compound **4a** and CSD-405154 for compound **4b**.

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