# Formation of Cationic [(2-Aminoethenyl)carbene]iron Complexes by Treatment of (2-Methoxyethenyl)carbene Complexes with Primary Amines: Synthesis and Characterisation

**Jörg Kühn, Dieter Schollmeyer, and Karola Rück-Braun***

Institut für Organische Chemie der Universität Mainz,
Becherweg 18-20, D-55099 Mainz, Germany
Fax: (internat.) +49(0)6131/394786

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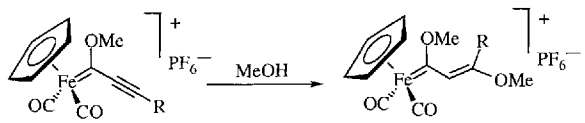
Cationic (2-methoxyethenyl)methoxycarbene iron complexes **2**, $[Cp(CO)_2Fe(C(OMe)CH{=}CR(OMe))^+][PF_6^-]$, are obtained by the addition of methanol to the corresponding (alkynyl)-methoxycarbene complexes **1**, $[Cp(CO)_2Fe(C(OMe)C{\equiv}CR)^+][PF_6^-]$. Primary amines, $H_2NR'$, react with these 1,3-dimethoxy-substituted (alkenyl)carbene complexes, **2**, through an addition/elimination process to yield cationic (2-aminoethenyl)methoxycarbene iron complexes, **3**, $[Cp(CO)_2Fe(C(OMe)CH{=}CR(NHR'))^+][PF_6^-]$ in an isolated yield of 71–90%. The complexes **3a–c** were characterized by X-ray structural analyses. Thus, previously isolated products, from the reaction, of the (alkynyl)methoxycarbene complexes **1a** and **1c**, with aniline at room temperature, are assigned to the structures **3c** and **3e**. The spectroscopic and structural data obtained are discussed.

In the last decade iron carbene complexes,[1] and in particular cationic cyclopentadienyl(dicarbonyl)iron-substituted compounds,[2] have not attracted as much interest as group VI metal carbene complexes[3] in their role as building blocks for organic synthesis. This holds especially true for the cationic alkynyl- and alkenyl-substituted cyclopentadienyl(dicarbonyl)methoxy- and aminocarbene iron complexes.[2e][4] Among the various chromium compounds studied so far, alkynyl-substituted compounds and 1-metalla-1,3-dienes, e.g. (2-aminoethenyl)methoxycarbene chromium complexes, have proved to be promising and versatile $C_3$ synthons.[3b][5][6] As we are interested in the reactivity of $Cp(CO)_2Fe$-substituted cationic carbene complexes in comparison with the neutral chromium analogues, we recently examined, and reported on, the synthesis of the cationic (alkynyl)methoxy carbene iron complexes $[Cp(CO)_2Fe(C(OMe)C{\equiv}CR)^+][PF_6^-]$ and their reactivity towards primary amines as nucleophiles.[4a][4b] Aminolysis reactions with a variety of primary amines were carried out, furnishing, through preferential substitution reactions at C-carbene,[7] a series of (alkynyl)amino carbene complexes at room temp. From the cationic (alkynyl)methoxy carbene iron complexes $[Cp(CO)_2Fe(C(OMe)C{\equiv}CR)^+][PF_6^-]$, R = Me (**1a**), Ph (**1c**) and aniline alkenyl-substituted complexes have been isolated.[4a][4b] However, due to the spectroscopic properties[8] of the products obtained, the structural assignment as cationic (2-methoxyethenyl)aminocarbene iron complexes, rather than (2-aminoethenyl)methoxycarbene iron complexes, seemed appropriate.[8][9][10]

To the best of our knowledge neither the (2-methoxyethenyl)aminocarbene iron complexes $[Cp(CO)_2Fe(C(NHR')CH{=}CR(OMe))^+][PF_6^-]$ nor the structurally isomeric (2-aminoethenyl)methoxycarbene iron complexes $[Cp(CO)_2Fe(C(OMe)CH{=}CR(NHR'))^+][PF_6^-]$ have been previously reported in the literature.[11] Thus, to elucidate the structure and the configuration of the alkenyl-substituted complexes unambigously, the synthesis of additional complexes seemed to be necessary. Surprisingly, for the complex obtained from $[Cp(CO)_2Fe(C(OMe)C{\equiv}CtBu)^+][PF_6^-]$ (**1b**) and aniline, the $^1$H-NMR spectra displays the methoxy signal [OMe] at $\delta$ = 3.5,[10] shifted upfield about 1 ppm compared to the equivalent signal for the compounds previously synthesized.[4b] Due to the concern over the structural assignment, and due to the fact that suitable single crystals for X-ray analysis could not be obtained, the synthesis of (2-methoxyethenyl)methoxycarbene iron complexes **2**, $[Cp(CO)_2Fe(C(OMe)CH{=}CR(OMe))^+][PF_6^-]$, and their aminolysis reactions were addressed for the synthesis of reference compounds. Therefore, the reactivity of the alkynyl moiety in (alkynyl)methoxycarbene iron complexes, **1**, towards the nucleophilic addition of methanol was examined via the synthesis of **2** (Scheme 1).

Scheme 1




| | R |
|---|---|
| **1a** | Me |
| **1b** | *t*Bu |

| | R |
|---|---|
| **2a** | Me |
| **2b** | *t*Bu |

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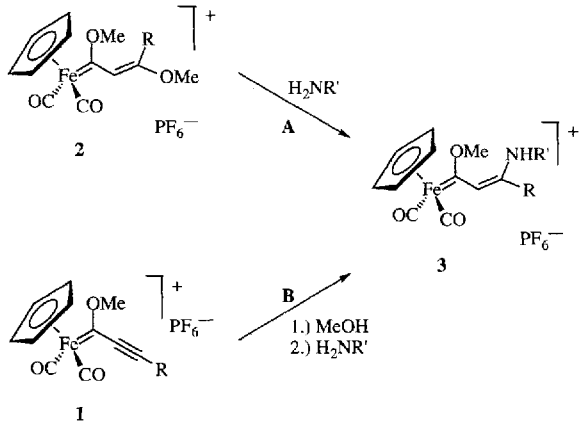
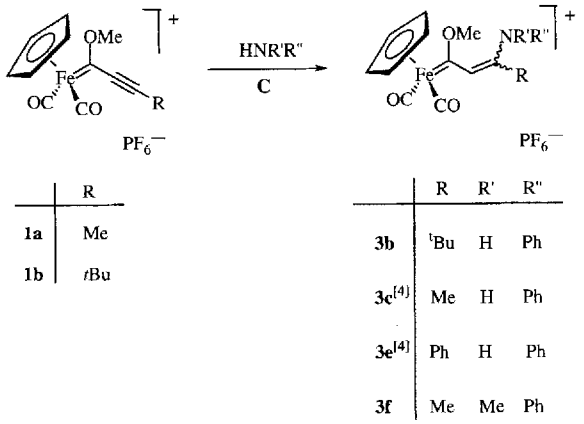
We describe here the aminolysis of these 1,3-dimethoxy-substituted cationic iron carbene complexes with primary amines to furnish (2-aminoethenyl)methoxycarbene iron complexes $[Cp(CO)_2Fe(C(OMe)CH=CR(NHR'))^+][PF_6^-]$, **3**, exclusively (Scheme 2). In addition a one-pot procedure for the synthesis of **3** starting from the (alkynyl)methoxy carbene complexes **1** will be described. The structures of three complexes were assigned by X-ray crystallography. NOE measurements, in $CD_3NO_2$ or in $CDCl_3$, are in agreement with the X-ray data obtained. The spectroscopic data of the (2-aminoethenyl)methoxy carbene complexes **3b** and **3c**, furnished by aminolysis of **2a** and **2b** with aniline (Scheme 2, Table 1), proved to be identical in all respects to that of the compounds previously reported, obtained from the reaction of (alkynyl)methoxycarbene complexes **1a–c** and aniline at room temp.(Scheme 3).[4a][4b]

Scheme 2




Scheme 3




| | R |
|---|---|
| 1a | Me |
| 1b | *t*Bu |

| | R | R' | R" |
|---|---|---|---|
| 3b | $^t$Bu | H | Ph |
| 3c[4] | Me | H | Ph |
| 3e[4] | Ph | H | Ph |
| 3f | Me | Me | Ph |

## Results and Discussion

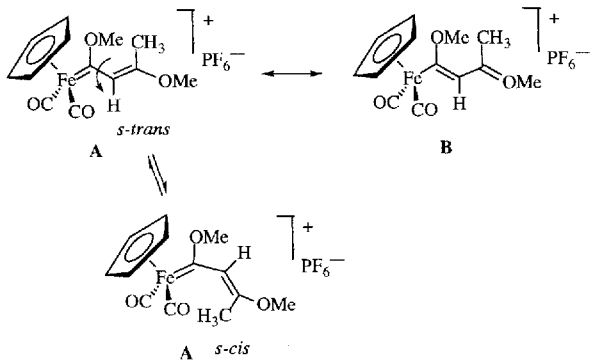
To synthesize the (2-methoxyethenyl)methoxycarbene iron complexes **2a** and **2b**, methanol (1–2 equiv.) was allowed to react with the corresponding (alkynyl)methoxycarbene complexes **1a** and **1b** at room temp. with $CH_2Cl_2$ as the solvent (Scheme 1). The addition products, which were formed smoothly within 1–2 hours (IR monitoring), were isolated in a yield of ≈ 90% as amorphous solids by the addition of petroleum ether (40–60 °C) to the reaction mixtures. Thus, due to the higher reactivity of the alkynyl side chain in these cationic methoxycarbene iron complexes,[4a][4b] and even in the case of the sterically demanding *t*-butyl group, base-catalysis can be avoided to enhance the reaction rate.[12]

Table 1. Synthesis of cationic (2-aminoethenyl)methoxycarbene iron complexes **3** according to Scheme 2

| 3 | R | R' | Reaction-conditions | Yield [%] |
|---|---|---|---|---|
| 3a | Me | (*L*)-CH(CH$_3$)CO$_2$*t*Bu | A | 90 |
| 3a | Me | (*L*)-CH(CH$_3$)CO$_2$*t*Bu | B | 88 |
| 3b | *t*Bu | Ph | A | 71 |
| 3c | Me | Ph | A | 83 |
| 3c | Me | Ph | B | 89 |
| 3d | Me | (*S*)-CH(CH$_3$)Ph | A | 85 |
| 3d | Me | (*S*)-CH(CH$_3$)Ph | B | 85 |

$^1$H-NMR spectra measured in $CD_3CN$ and $CD_3NO_2$ at ambient temp. indicated a mixture of isomers to be present in solution for **2a** (R = Me, 77:23) and **2b** (R = *t*Bu, 86:14, see Experimental Section). The presence of these isomers can be traced back to the considerable double bond character of the C1–C2 bond, attributed to the resonance contribution of the enol ether/oxonium ion structure **B** (Scheme 4).[13] These *s-cis*/*s-trans* isomers slowly interconvert in solution. The chemical exchange process was evident from the spin saturation transfer observed during NOE difference spectroscopy. On the basis of the NOE experiments performed in $CD_3NO_2$, the *s-trans* conformation and the 2-(*E*) configuration were assigned to the major isomer of **2a**, due to the positive interactions observed between 3-$CH_3$ and 1-OMe, 2-H and 3-OMe as well as 2-H and the $C_5H_5$ ligand.

Scheme 4



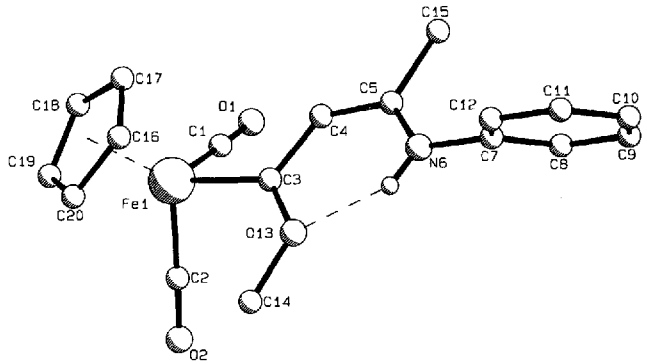

$^1$H-NMR spectroscopy and mass spectrometry of the crude product, isolated from the complex **1b** upon treatment with ethanol (1.1 equiv.) for 3 h, revealed that at least three products were formed {$[Cp(CO)_2Fe(C(OMe)CH=C(OMe)tBu)^+][PF_6^-]$ (MW = 333.2), $[Cp(CO)_2Fe(C(OMe)CH=C(OEt)tBu)^+][PF_6^-]$ or $[Cp(CO)_2Fe(C(OEt)CH=C(OMe)tBu)^+][PF_6^-]$ (MW = 347.1), and $[Cp(CO)_2Fe(C(OEt)CH=C(OEt)tBu)^+][PF_6^-]$ (MW = 361.1)}. Since the 1,3-diethoxy-substituted complex $[Cp(CO)_2Fe(C(OEt)CH=C(OEt)tBu)^+][PF_6^-]$ (MW = 361.1) was ob-

served, it can be concluded that attack of ethanol at the triple bond, and substitution of methanol by ethanol owing to attack at the carbene center, takes place.

Three primary amines (1–2 equiv.) were allowed to react with **2a** and **2b** in $CH_2Cl_2$ at room temp. The aminolysis reactions proceed rapidly according to IR monitoring of the reaction mixtures. The products formed were precipitated by the addition of petroleum ether (40–60 °C). The attack of the amines, either at C-carbene or at the β-carbon atom of the conjugated double bond (Structure **A**, Scheme 4) could not be assigned on the basis of the spectroscopic properties of the reaction products.[8][10] Interestingly, the compound obtained from **2b** and aniline proved to be identical, in all spectroscopic respects, to the (alkenyl)carbene complex obtained from the reaction of the (alkynyl)methoxycarbene complex **1b** and aniline at room temp.[4b]

Fortunately, suitable crystals for X-ray analysis were obtained for the complexes **3a–c** (Figures 1–3; experimental details of the X-ray structure analysis are given in Table 2). As shown by the structures in Figures 1,2 and 3, aminolysis reactions of **2** with primary amines lead to (2-aminoethenyl)methoxy carbene complexes, **3** (Scheme 2, Table 1). Apparently, attack of the primary amines at the conjugated double bond in **2** occurs and by an addition/elimination process the compounds **3** are formed. Additionally, a Michael-type addition has to be concluded for **1a–c** and aniline at room temp., contrary to previous assumptions (Scheme 3).[4a][4b]

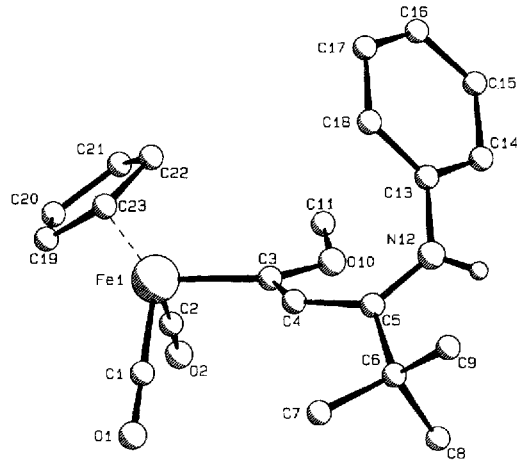
Figure 1. Crystal structure of **3a**[a]




[a] Selected bond lengths [Å] and angles [°]: Fe–C3 1.961(7), C3–O14 1.361(10), C3–C4 1.357(12), C4–C5 1.423(10), C5–N6 1.324(11), N6–H6 1.057(10), N6–C7 1.476(10), O14–H6 1.837(9), O9–H6 2.332(9), C7–C8 1.493(14), C8–O18 1.195(11), C8–O9 1.316(13); Fe–C3–O14 124.8(5), Fe–C3–C4 121.9(5), C4–C3–O14 113.2(6), C4–C5–C16 119.1(7), C4–C5–N6 121.4(6), C16–C5–N6 119.5(7), C5–N6–C7 125.3(6), Fe–C3–C4–C5 176.6(8), C3–C4–C5–N6 –2.2(9).

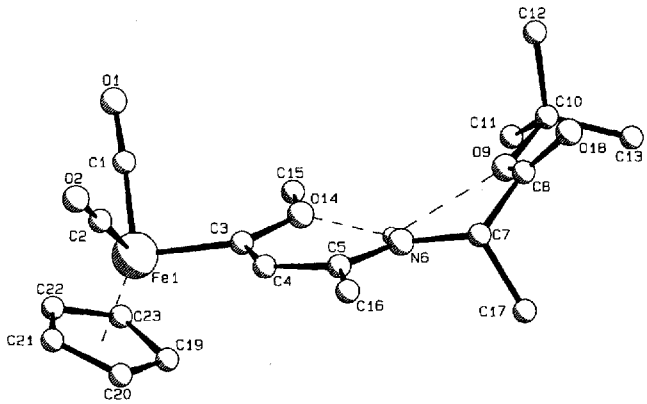
The high-field $^{13}C$ resonance observed for C-carbene (see Experimental Section), together with the bond lengths determined by X-ray crystallography for **3a–c**, indicate a thorough delocalisation of the lone pair at the nitrogen atom into the neighbouring C=C bond. Thus, it is concluded that there is a considerable contribution of the enol ether/iminium structure **B**, with reduced electron deficiency at "C-carbene", to the resonance hybrid this case (Scheme 5). For the complexes **3a** and **3c** the angle between the

Figure 2. Crystal structure of **3b**[a]




[a] Selected bond lengths [Å] and angles [°]: Fe–C3 1.968(6), C3–O10 1.336(7), C3–C4 1.384(7), C4–C5 1.421(8), C5–N12 1.314(7), N12–H12 0.860(7), H12–F1 2.217(7); Fe–C3–O10 126.5(3), Fe–C3–C4 120.2(4), C4–C3–O10 113.2(4), C4–C5–C6 119.2(4), C4–C5–N12 124.7(4), C6–C5–N12 116.1(4), C5–N12–C13 128.4(4), Fe–C3–C4–C5 179.7(5), C3–C4–C5–N12 34.3(7).

Figure 3. Crystal structure of **3c**[a]

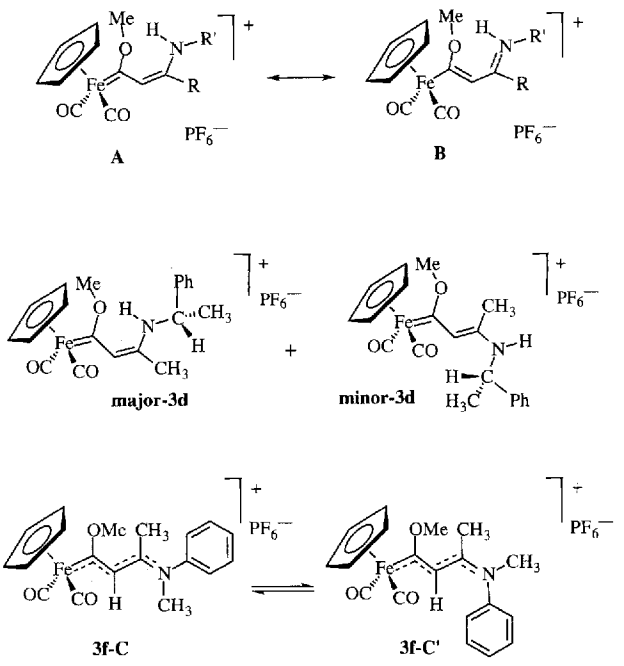



[a] Selected bond lengths [Å] and angles [°]: Fe–C3 1.960(4), C3–O13 1.323(5), C3–C4 1.396(6), C4–C5 1.392(6), C5–N6 1.306(6), O13–H6 2.053(5), O13–N6 2.667(5), N6–H6 0.872(6); Fe–C3–O13 126.5(3), Fe–C3–C4 119.9(3), C4–C3–O13 113.6(3), C4–C5–N6 124.1(4), C4–C5–C15 117.6(4), C15–C5–N6 118.3(4), C5–N6–C7 126.6(4), Fe–C3–C4–C5 177.5(5), C3–C4–C5–N6 –6.0(6).

O–C3–C4 and N–C4–C5 planes approaches 0° [**3a**: 5.9° (O13–C3–C4/C4–C5–N6), **3c**: 2.1° (O14–C3–C4/C4–C5–N6)]. For complex **3b**, an angle of 36.9° (O10–C3–C4/C4–C5–N12) is found (see also Figures 1–3 for further information).[16]

All the complexes **3a–c** are 2-(*Z*)-configured and adopt a *s-trans* conformation in the solid state. For the complexes **3a** and **3c** a weak hydrogen bridge between the N–H proton and the 1-OMe group is observed. NOE measurements of **3c** in $CD_3NO_2$ indicate positive interactions between 2-H and $C_5H_5$, 3-$CH_3$ and 2-H as well as for 1-OMe with N–H and $C_5H_5$, thus confirming that the same preferred conformation is present in solution. However, upon measuring $^1H$-NMR spectra of **3a** and **3c** in [$D_6$]DMSO or

Scheme 5




$CD_3CN$, mixtures of conformational isomers, presumably *s-cis*/*s-trans* isomers, were observed. For complex **3b** (Figure 2), with the *N*-phenyl substituent *trans* to the bulky *tert*-butyl group at the β-carbon, the solid state structure is in agreement with the results of the NOE experiments in solution ($CD_3NO_2$), displaying positive interactions between the *ortho* protons of the *N*-phenyl group and the $C_5H_5$ ligand, 1-OMe and $C_5H_5$, 1-OMe and the *N*-phenyl group, 2-H and $C_5H_5$ and for 3-*t*Bu with 2-H. Accordingly the unusual shift of the [OMe] group can be traced back to the anisotropic influence of the *N*-phenyl group, which is in close proximity.

To gain further insight in the structure and bonding of (2-aminoethenyl)methoxycarbene iron complexes, **3**, additional complexes were synthesized according to Scheme 2, pathway A. Fortunately, the complexes **3** can also be synthesized at room temp. by addition of methanol (1−2 equiv.) to the (alkynyl)carbene complexes **1** dissolved in $CH_2Cl_2$ (IR monitoring), and subsequent treatment with 1−2 equivalents of the primary amine. Thereby the (2-amino-ethenyl)methoxycarbene complexes **3** are obtained in a one-pot procedure (Scheme 2, pathway B) in a yield of ≈ 85%. So far, further attack of the amines at the carbene center has not been observed. The results are summarized in Table 1.

In addition, the complex **3d** was prepared from **2a** and (*S*)-phenylethylamine (Scheme 2, Table 1), whereas the complex **3f** was isolated from the reaction of **1a** with *N*-methylaniline according to Scheme 3. Both complexes were structurally analyzed using NOE measurements. For the major isomer of **3d** (ratio of isomers 86:14) a positive interaction between the $C_5H_5$ ligand and 2-H as well as 1-OMe, 3-$CH_3$ and 2-H, and an interaction of 3-$CH_3$ with the α-CH of the (*S*)-phenylethylamine moiety, is observed in $CDCl_3$, and therefore this isomer is assigned to the *s-trans* conformation and (2*Z*) configuration (Scheme 5). In these experiments spin saturation transfer upon irradiation of the resonance signals of the major component was not observed. For the minor component positive NOE effects were found for 2-H with the α-CH of the (*S*)-phenylethylamine residue, and for 1-OMe with the $C_5H_5$ ligand as well as with 3-$CH_3$. Consequently, the (2*E*)-configuration and *s-trans* conformation are attributed to the minor isomer of **3d**.

However, for **3f** (ratio of isomers 70:30) spin saturation transfer was noticed during the NOE experiments, indicating configurationally unstable isomers to be present in solution, as has already been observed for **2a**. NOE interactions were found for the complex **3f** in $CDCl_3$ between 1-OMe and 3-Me, the *ortho* protons of the *N*-phenyl group and 3-Me, as well as for the *N*-methyl group with 2-H, indicating the *s-trans* conformation and (2*E*) configuration given for **3f** in Scheme 5. In addition positive NOE effects were observed between the 3-Me and the *N*-methyl group. Thus, as a consequence of the hindered rotation around the C=N$^+$ bond in compound **3f**, the conformational isomers **3f-C** and **3f-C'** in Scheme 5 have to be considered. The spectroscopic data indicate additional evidence for a mesomeric interaction between the carbene fragment and the enamine side chain (structure **A**, Scheme 5) in the complexes **3**, and accordingly for considerable contributions of the enol ether/iminium salt resonance structure **B** to the resonance hybrid.

(2-Aminoethenyl)methoxycarbene chromium complexes are most conveniently synthesized by a Michael-type addition of primary amines to the (alkynyl)methoxycarbene chromium complexes at room temp.[5][6][7] Using this approach, the cationic (2-anilinoethenyl)methoxycarbene iron complexes (Scheme 3) were also obtained. The methods described above have been developed for the synthesis of cationic (2-aminoethenyl)methoxycarbene iron complexes, e.g. **3a**, which can not be prepared by this route.[4a][4b] Thus, by treatment of the corresponding 1,3-dimethoxy-substituted (alkenyl)carbene complexes **2** (Scheme 2) with primary amines, the cationic (2-aminoethenyl)-substituted carbene complexes are easily accessible and generated stereoselectively, even in a one-pot procedure, starting from the (alkynyl)methoxycarbene precursors.

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## Experimental Section

*General:* All operations were carried out under argon. Solvents were dried by refluxing over potassium/benzophenone ketyl, $LiAlH_4$ (LAH) or $CaH_2$ and were freshly distilled prior to use. Petroleum ether (40−60 °C) was dried by distillation from $P_2O_5$. − Column chromatography: Baker silica gel (Type 0.063−0.200 mm). − The 4,4-Dimethyl-1-pentyne acid[14] was prepared according to literature procedures. − IR: FT-IR Perkin-Elmer 1760 X. − $^1H$ and $^{13}C$ NMR: Bruker AM 400, Bruker AM 200. If not specifically mentioned, chemical shifts refer to $\delta_{TMS} = 0.00$ according to the

chemical shifts of residual solvent signals ($^+$: labeling of minor component in the case of mixtures of conformational isomers). – MS: Varian MAT CH 7a, Finnigan MAT 95. – Melting points are uncorrected.

*Dicarbonyl(cyclopentadienyl)[(methoxy)-3,3-dimethyl-1-butynyl-carbene]iron Hexafluorophosphate* (**1b**): For the preparation of **1b**, dicarbonyl(cyclopentadienyl)(3,3-dimethyl-1-butynoyl)iron was synthesized as described previously.[4b] Thus, a solution of 4,4-dimethyl-1-pentyne acid[14] (899 mg, 7.13 mmol) in 50 ml of degassed THF was cooled to 0 °C. *N*-Methylmorpholine (0.82 ml, 7.41 mmol, 1.04 equiv.) and isobutyl chloroformate (0.96 ml, 7.41 mmol, 1.04 equiv.) were added. The reaction mixture was stirred at 0 °C for 15 min. After having been cooled to −78 °C for 20 min the solution was filtered in vacuo at −78 °C to separate the precipitated *N*-methylmorpholine hydrochloride. The filtrate was added by means of a cannula to a suspension of $[Cp(CO)_2FeK]$, prepared from $[Cp(CO)_2Fe]_2$ (1.33 g, 3.75 mmol) and 9.4 ml of K-Selectride (2.5 equiv., 1 M solution in THF), in 17 ml of THF at room temp.. The reaction mixture was stirred at −78°C for 30 min and then allowed to warm to room temp. (60 min). To the reaction mixture a satd. aqueous $NH_4Cl$ solution (0.15 ml) was added, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with petroleum ether/ether (8:1) to yield 1.5 g (74%) of the iron acyl complex as a yellow-brown crystalline solid, m.p. 41°C, $R_f$ = 0.28 (petroleum ether/ether, 8:1). – $^1$H NMR (200 MHz, $CDCl_3$): δ = 4.89 (s, 5 H, $C_5H_5$), 1.26 [s, 9 H, $C(CH_3)_3$]. – $^{13}$C NMR (50.3 MHz, $CD_3NO_2$): δ = 238.9 (C=O), 213.2 (C=O, ligand), 106.0 (C≡C), 86.9 ($C_5H_5$), 85.0 (C≡C), 32.7, 30.1. – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 2188 cm$^{-1}$ (C≡C), 2028, 2075 (C=O, ligand), 1594 (CO). – $C_{14}H_{14}Fe0_3$ (286.1): calcd. C 58.77, H 4.93; found C 58.54, H 4.91. A solution of the iron acyl complex (1.19 g, 4.16 mmol) in $CH_2Cl_2$ (8 ml) was added to $[(MeO)_2CH][PF_6]$ prepared from 1.53 g of $[Ph_3C][PF_6]$ (3.95 mmol, 0.95 equiv.) and 0.57 ml of $(MeO)_3CH$ (5.20 mmol, 1.25 equiv.) in $CH_2Cl_2$ (32 ml) as already described.[4a][4b] The reaction mixture was stirred for 1 h and then diluted with petroleum ether (200 ml) to precipitate a red oil. The general work-up[4b] procedure yielded 1.6 g (91%) of **1b** as a yellow-brown solid, m.p. 94°C. – $^1$H NMR (200 MHz, $CD_3NO_2$): δ = 5.49 (s, 5 H, $C_5H_5$), 4.62 (s, 3 H, $OCH_3$), 1.44 [s, 9 H, $C(CH_3)_3$]. – $^1$H NMR (200 MHz, $CD_3CN$): δ = 5.37 (s, 5 H, $C_5H_5$), 4.49 (s, 3 H, $OCH_3$), 1.39 [s, 9 H, $C(CH_3)_3$]. – $^{13}$C NMR (50.3 MHz, $CD_3NO_2$): δ = 290.1 (Fe=C), 209.6 (CO), 151.8 (C≡C), 91.3 ($C_5H_5$), 87.5 (C≡C), 70.9 ($OCH_3$), 31.3, 29.2. – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 2176 cm$^{-1}$ (C≡C), 2074, 2034 (CO), 847 ($PF_6^-$). – $C_{15}H_{17}F_6FeO_3P$ (446.1): calcd. C 40.39, H 3.84; found C 40.28, H 3.62.

*Dicarbonyl(cyclopentadienyl)[methoxy(2-methoxy-1-propenyl)-carbene]iron Hexafluorophosphate* (**2a**): To a solution of **1a**[4b] (1.45 g, 3.59 mmol) in $CH_2Cl_2$ (30 ml) methanol (2 equiv., 0.29 ml, 7.18 mmol) was added. The reaction mixture was stirred for 100 min (IR monitoring) and then diluted with petroleum ether (150 ml) to precipitate **2a** as a red-brown solid. The product was isolated by filtration on air, washed with petroleum ether and dried under oil pump vacuum to yield 1.39 g (89%) of **2a** as a red-brown powder, m.p. 160 °C. – $^1$H NMR (200 MHz, $CD_3NO_2$, 77:23 mixture of isomers; $^+$: minor component): δ = 6.93, 6.46$^+$ (s, 1 H, =CH), 5.38, 5.21$^+$ (s, 5 H, $C_5H_5$), 4.67, 4.30$^+$ (s, 3 H, $OCH_3$), 4.28$^+$, 3.99 (s, 3 H, $OCH_3$), 2.47$^+$, 2.35 (s, 3 H, $CH_3$). – $^1$H NMR (200 MHz, $CD_3CN$, 76:24 mixture of isomers; $^+$: minor component): δ = 6.76, 6.33$^+$ (s, 1 H, 2-CH), 5.27, 5.10$^+$ (s, 5 H, $C_5H_5$), 4.53, 4.14$^+$ (s, 3 H, $OCH_3$), 4.18$^+$, 3.89 (s, 3 H, $OCH_3$), 2.35$^+$, 2.26 (s, 3 H, 3-$CH_3$). – $^{13}$C NMR (50.3 MHz, $CD_3NO_2$, 77:23 mixture of isomers; $^+$: minor component): δ = 289.2, 280.9$^+$ (Fe=C), 212.7$^+$, 211.8 (CO), 188.7$^+$, 175.2 (=C), 121.4, 118.2$^+$ (=CH), 88.6, 88.4$^+$ ($C_5H_5$), 68.4, 64.6$^+$ ($OCH_3$), 59.2$^+$, 58.8 ($OCH_3$), 23.9, 21.9$^+$ ($CH_3$). – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 2051 cm$^{-1}$, 2005 (CO), 1529 (C=$COCH_3$), 847 ($PF_6^-$). – IR (KBr): $\tilde{\nu}$ = 2049 cm$^{-1}$, 1998 (CO), 1532 (C=$COCH_3$), 845 ($PF_6^-$). – $C_{13}H_{15}F_6FeP$ (436.07): calcd. C 35.81, H 3.47; found C 35.71, H 3.59.

*Dicarbonyl(cyclopentadienyl)[methoxy(2-methoxy-3,3-dimethyl-1-butenyl)carbene]iron Hexafluorophosphate* (**2b**): To a solution of **1b** (1.29 g, 2.88 mmol) in 24 ml of $CH_2Cl_2$ methanol (2 equiv., 0.23 ml, 5.76 mmol) was added. The reaction mixture was stirred for 80 min (IR monitoring) and then diluted with petroleum ether (200 ml) to precipitate **2b** as an oil. After having been stirred for 50 min a yellow-brown solid was obtained. The petroleum ether was removed by means of a cannula. The precipitate was dried under oil pump vacuum to yield 1.25 g (91%) of **2b** as a yellow-brown powder, m.p. 83–84 °C. – $^1$H NMR (200 MHz, $CD_3NO_2$, 86:14 mixture of isomers; $^+$: minor component): δ = 6.96$^+$, 6.74 (s, 1 H, 2-CH), 5.46$^+$, 5.41 (s, 5 H, $C_5H_5$), 4.71$^+$, 4.63 (s, 3 H, $OCH_3$), 3.95 (s, 3 H, $OCH_3$), 1.26$^+$, 1.23 [s, 9 H, 3-$C(CH_3)_3$]. – $^1$H NMR (200 MHz, $CD_3CN$): δ = 6.59 (s, 1 H, 2-CH), 5.30 (s, 5 H, $C_5H_5$), 4.50 (s, 3 H, $OCH_3$), 3.83 (s, 3 H, $OCH_3$), 1.18 [s, 9 H, $C(CH_3)_3$]. – $^{13}$C NMR (50.3 MHz, $CD_3NO_2$, 88:12 mixture of isomers; $^+$: minor component): δ = 287.4 (Fe=C), 211.4 (CO), 183.3$^+$, 182.9 (=C), 119.9$^+$, 119.7 (=CH), 89.1, 88.7$^+$ ($C_5H_5$), 68.8 ($OCH_3$), 64.8 (br. $OCH_3$), 40.6 [$C(CH_3)_3$], 28.0, 27.7$^+$ [$C(CH_3)_3$]. – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 2053 cm$^{-1}$, 2008 (CO), 1520 (C=$COCH_3$), 845 ($PF_6^-$). – $C_{16}H_{21}F_6FeO_4P$ (478.15): FD, *m/z* (%): 333.0 (100) [$M^+$ – $PF_6^-$].

*{1-[2-(Alanin-N-yl tert-butyl ester)-1-propenyl](methoxy)-carbene}dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate* (**3a**). – *Method A*: Alanine *tert*-butyl ester (364 mg, 2.51 mmol) dissolved in $CH_2Cl_2$ (10 ml) was added to a solution of **2a** (1.09 g, 2.51 mmol) in 40 ml of $CH_2Cl_2$. The reaction mixture was stirred at room temp. in the dark for 25 min (IR monitoring). The solution was treated with petroleum ether (200 ml) to precipitate **3a**. The mother liquor was removed by means of a cannula and the residue was dried under oil pump vacuum to yield 1.23 g (90%) of **3a** as a yellow powder.

*Method B*: Methanol (1.6 equiv., 0.15 ml) was added to a solution of **1a** (926 mg, 2.29 mmol) in 40 ml of $CH_2Cl_2$. The progress of the reaction was monitored by IR spectroscopy. After having been stirred for 130 min a solution of alanine *tert*-butyl ester (333 mg, 2.29 mmol) in 10 ml of $CH_2Cl_2$ was added. The reaction mixture was stirred for 90 min (IR monitoring) and then diluted with petroleum ether (200 ml) to precipitate **3a**. The mother liquor was removed by means of a cannula. The residue was washed with petroleum ether (50 ml), dried in a stream of argon and under oil pump vacuum to yield 1.11 g (88%) of **3a** as a yellow powder, m.p. 150 °C (dec.). – $^1$H NMR (200 MHz, $CDCl_3$, 91:9 mixture of isomers; $^+$: minor component): δ = 10.06–10.03 (d, *J* = 6.3 Hz, 1 H, NH), 5.98 (s, 1 H, 2-CH), 5.28$^+$, 5.16 (s, 5 H, $C_5H_5$), 4.27–4.20 (m, *J* = 7.3 Hz, 4 H, $OCH_3$ and $CHCH_3$), 2.14$^+$, 2.09 (s, 3 H, $CH_3$), 1.54–1.50 (d, *J* = 7.3 Hz, 3 H, $CHCH_3$), 1.48 [s, 9 H, $C(CH_3)_3$]. – $^1$H NMR (200 MHz, $CD_3NO_3$, 92:8 mixture of isomers; $^+$: minor component): δ = 10.06–10.02 (d, *J* = 6.5 Hz, 1 H, NH), 6.21$^+$, 6.16 (s, 1 H, 2-CH), 5.29 (s, 5 H, $C_5H_5$), 4.51–4.43 (m, *J* = 7.3 Hz, 1 H, $CHCH_3$), 4.36 (s, 3 H, $OCH_3$), 2.17 (s, 3 H, $CH_3$), 1.56–1.53 (d, *J* = 7.3 Hz, 3 H, $CHCH_3$), 1.51 [s, 9 H, $C(CH_3)_3$]. – $^1$H NMR (200 MHz, $CD_3CN$, 88:12 mixture of isomers, $^+$: minor component): δ = 9.86 (s, 1 H, NH), 6.03 (s, 1 H, 2-CH), 5.19, 5.17$^+$ (s, 5 H, $C_5H_5$), 4.41–4.33 (m, *J* = 7.5 Hz, 1 H, $CHCH_3$), 4.23, 4.17$^+$ (s, 3 H, $OCH_3$), 2.33$^+$ and 2.07 (s, 3 H, $CH_3$), 1.47 and 1.43 [s, 12 H, $CHCH_3$ and $C(CH_3)_3$]. – $^{13}$C NMR (50.3 MHz, $CDCl_3$): δ = 243.9 (Fe=C), 212.0, 211.9 (CO), 169.8 (C=

O), 161.1 (=C), 119.8 (=CH), 87.1 ($C_5H_5$), 84.0 [$C(CH_3)_3$], 64.4 ($OCH_3$), 53.5 ($CHCH_3$), 27.9 [$C(CH_3)_3$], 19.7, 18.9 ($CHCH_3$, $CH_3$). – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3275 $cm^{-1}$ (NH), 2043, 1995 (CO), 1733, 1597, 1516, 847 ($PF_6^-$). – IR (KBr): $\tilde{\nu}$ = 3369 cm-1, 3324 (NH), 2039, 1989 (CO), 1734, 1521, 845 ($PF_6^-$). – $C_{19}H_{26}F_6FeNO_5P$ (549.23): FD, *m/z* (%): 404.7 (100) [$M^+ - PF_6^-$].

*{[2-Anilino-3,3-dimethyl-1-butenyl]methoxycarbene}dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate* (**3b**). – *Method A:* Aniline (144 mg, 1.55 mmol) dissolved in 3 ml of $CH_2Cl_2$ was added to a solution of **2b** (370 mg, 0.77 mmol) in 9 ml of $CH_2Cl_2$. The reaction mixture was stirred for 1 h 35 min at room temp. in the dark and then diluted with petroleum ether (50 ml) to precipitate **3b** as a yellow-red oil. After having been stirred for 60 min a red-brown solid was obtained. After work-up 296 mg (71%) of **3b** as a red-brown solid, m.p. 148 °C (dec.) was obtained. – $^1H$ NMR (200 MHz, $CD_3NO_2$): δ = 8.93 (s, 1 H, NH), 7.52– .29 (m, 5 H, $C_6H_5$), 6.45 (s, 1 H, 2-CH), 5.20 (s, 5 H, $C_5H_5$), 3.56 (s, 3 H, $OCH_3$), 1.43 [s, 9 H, $C(CH_3)_3$]. – $^{13}C$ NMR (50.3 MHz, $CD_3NO_2$): δ = 248.1 (Fe=C), 213.4 (CO), 172.4, 141.8, 130.4, 128.8, 123.4, 115.8, 87.9 ($C_5H_5$), 64.4 ($OCH_3$), 40.3 [$C(CH_3)_3$], 28.5 [$C(CH_3)_3$]. – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3379 $cm^{-1}$ (NH), 2041, 1994 (CO), 1621, 1597, 1556, 1486, 847 ($PF_6^-$). – IR (KBr): $\tilde{\nu}$ = 3338 $cm^{-1}$ (NH), 2029, 1983 (CO), 1597, 1559, 1486, 845 ($PF_6^-$). – $C_{21}H_{24}F_6FeNO_3P$ (539.24): calcd. C 46.78, H 4.49, N 2.60; found C 46.68, H 4.49, N 2.63.

*Method C:* Aniline (0.18 ml, 1.94 mmol) was added neat to a solution of **1b** (867 mg, 1.94 mmol) in 25 ml of $CH_2Cl_2$. The reaction mixture was stirred for 30 min (IR monitoring) and diluted with 200 ml of petroleum ether to precipitate a brown oil which was washed with 10 ml of petroleum ether. The oil was dried under oil pump vacuum to yield 785 mg (75%) of **3b** as a yellow-brown solid.

*{[2-Anilino-1-propenyl]methoxycarbene}dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate* (**3c**). – *Method A:* Aniline (357 mg, 3.83 mmol) dissolved in 10 ml of $CH_2Cl_2$ was added to a solution of **2a** (1.12 g, 2.74 mmol) in $CH_2Cl_2$ (20 ml) and the reaction mixture was stirred for 7 h. Then petroleum ether (200 ml) was added to precipitate **3c**, which was isolated by filtration (air), washed with petroleum ether and dried under oil pump vacuum to yield 1.13 g (83%) of **3c** as a red-brown powder.

*Method B:* Methanol (1.6 equiv., 0.05 ml) was added at room temp. to a solution of **1a** (300 mg, 0.74 mmol) in $CH_2Cl_2$ (16 ml). After having been stirred for 1 h 50 min in the dark (IR monitoring) a solution of aniline (69 mg, 0.74 mmol) in 5 ml of $CH_2Cl_2$ was added and stirring was continued for 2 h. The reaction mixture was diluted with petroleum ether (70 ml) to precipitate an orange, fluffy solid (363 mg), which proved to be a mixture of **2a** and **3c** ($^1H$ NMR spectroscopy). Aniline (0.05 ml, 0.55 mmol) was added to a solution of the crude product (318 mg) in $CH_2Cl_2$ (10 ml). The reaction mixture was stirred for 2 h and then diluted with petroleum ether (70 ml) to precipitate **3c** as a yellow-brown fluffy solid. The mother liquor was removed by means of a cannula. The residue was dried in a stream of argon and under oil pump vacuum to afford 330 mg (89%) of **3c** as a red-brown powder, m.p. 170 °C (dec.). – $^1H$ NMR (200 MHz, $CD_3NO_2$): δ = 10.99 (s, 1 H, NH), 7.57–7.42 (m, 3 H, $C_6H_5$), 7.32–7.29 (m, 2 H, $C_6H_5$), 6.36 (s, 1 H, 2-CH), 5.34 (s, 5 H, $C_5H_5$), 4.41 (s, 3 H , $OCH_3$), 2.12 (s, 3 H, 3-$CH_3$). – $^1H$ NMR (200 MHz, [$D_6$]DMSO, 52:48 mixture of isomers; $^+$: minor component): δ = 11.30, 11.09$^+$ (s, 1 H, NH), 7.53–7.29 (m, 5 H, $C_6H_5$), 6.32$^+$, 6.21 (s, 1 H, 2-CH), 5.75 ($CH_2Cl_2$), 5.47$^+$, 5.34 (s, 5 H, $C_5H_5$), 4.23$^+$, 4.15 (s, 3 H, $OCH_3$), 2.47$^+$, 2.05 (s, 3 H, 3-$CH_3$). – $^{13}C$ NMR (50.3 MHz, $CD_3NO_2$): δ = 250.3 (Fe=C), 213.5 (CO), 162.2 (=C), 137.4 (C-ipso), 130.6, 129.6, 126.6 ($C_6H_5$), 120.6 (=CH), 88.3 ($C_5H_5$), 65.8 ($OCH_3$), 20.9 ($CH_3$). – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3305 $cm^{-1}$ (NH), 2043, 1995 (CO), 1594, 1568, 1520, 1497, 847 ($PF_6^-$). – IR (KBr): $\tilde{\nu}$ = 3350 $cm^{-1}$, 3306 (NH), 2038, 1988 (CO), 1594, 1567, 1520, 1497, 844 ($PF_6^-$). – $C_{18}H_{18}F_6FeNO_3P$ (497.16): FD, m/z (%): 352.0 (100) [$M^+ - PF_6^-$]. – $C_{18}H_{18}F_6FeNO_3P \cdot CH_2Cl_2$ (582.09): calcd. C 39.21, H 3.46, N 2.41; found C 39.39, H 3.46, N 2.46.

*Dicarbonyl(cyclopentadienyl){2-[(S)-1-phenylethylamino)-1-propenyl]methoxycarbene}iron Hexafluorophosphate* (**3d**). – *Method A:* (*S*)-1-phenylethylamine (0.19 ml, 1.49 mmol, 2 equiv.) was added to a solution of **2a** (324 mg, 0.74 mmol) in 12 ml of $CH_2Cl_2$. The reaction mixture was stirred for 1 h and then diluted with 50 ml of petroleum ether to precipitate an orange oil, which was dried under oil pump vacuum to afford **3d** as a yellow solid: 332 mg (85%).

*Method B:* To a solution of **1a** (458 mg, 1.13 mmol) in 18 ml of $CH_2Cl_2$ methanol (0.1 ml, 2.2 equiv.) was added and the reaction mixture was stirred for 45 min. After complete consumption of the starting material (IR monitoring) 0.15 ml of neat (*S*)-1-phenylethylamine (1 equiv., 1.13 mmol) was added. The reaction mixture was stirred for 2 h 45 min (IR monitoring) and then diluted with petroleum ether (50 ml) to precipitate **3d** as a yellow-red oil. The mother liquor was removed by means of a cannula. The oil was dried under oil pump vacuum to furnish 506 mg (85%) of **3d** as a yellow solid, m.p. 60 °C (dec.). – $^1H$ NMR (200 MHz, $CDCl_3$, 86:14 mixture of isomers; $^+$: minor component): δ = 9.67 (s, 1 H, NH), 7.38–7.24 (m, 5 H, $C_6H_5$), 5.91, 5.86$^+$ (s, 1 H, 2-CH), 5.16, 4.78$^+$ (s, 5 H, $C_5H_5$), 4.81–4.74 (m, 1 H, *J* = 6.3 Hz, $CHCH_3$), 4.25, 4.10$^+$ (s, 3 H, $OCH_3$), 2.39$^+$, 1.99 (s, 3 H, 3-$CH_3$), 1.64, 1.60 (d, 3 H, *J* = 6.7 Hz, $CHCH_3$). – $^{13}C$ NMR (50.3 MHz, $CDCl_3$, 84:16 mixture of isomers; $^+$: minor component): δ = 244.8$^+$, 243.4 (Fe=C), 212.2$^+$, 212.0, 211.9, 211.6$^+$ (CO), 162.2, 161.6$^+$ (=C), 142.1, 140.9$^+$ (C-ipso), 129.3, 129.2$^+$, 128.2, 127.8$^+$, 125.7 ($C_6H_5$), 119.4, 117.6$^+$ (=CH), 87.0, 86.8$^+$ ($C_5H_5$), 64.5, 64.2$^+$ ($OCH_3$), 55.4 ($CHCH_3$), 23.2, 23.1$^+$ ($CHCH_3$), 20.0 ($CH_3$). – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3358 $cm^{-1}$, 3323 (NH), 2042, 1994 (CO), 1592, 1525, 1581, 847 ($PF_6^-$). – IR (KBr): $\tilde{\nu}$ = 3366 $cm^{-1}$, 3322 (NH), 2037, 1987 (CO), 1525, 844 ($PF_6^-$). – $C_{20}H_{22}F_6FeNO_3P$ (525.21): calcd. C 45.73, H 4.22, N 2.67; found C 45.58, H 4.25, N 2.54.

*Dicarbonyl(cyclopentadienyl){[2-(N)-(methyl)phenylamino)-1-propenyl]methoxycarbene}iron Hexafluorophosphate* (**3f**): *N*-methylaniline (79 mg, 0.74 mmol) dissolved in 2 ml of $CH_2Cl_2$ was added to a solution of **1a** (300 mg, 0.74 mmol) in $CH_2Cl_2$ (8 ml). After the reaction mixture had been stirred for 15 min, IR monitoring indicated complete consumption of the starting material. Then petroleum ether (80 ml) was added to precipitate **3f**. The mother liquor was removed by means of a cannula and the oil was washed with petroleum ether (20 ml) and dried under oil pump vacuum to yield 370 mg (97%) of **3f** as a yellow solid, m.p. 135 °C (dec.). – $^1H$ NMR (200 MHz, $CDCl_3$, 70:30 mixture of isomers; $^+$: minor component): δ = 7.50–7.14 (m, 5 H, $C_6H_5$), 6.40, 5.59$^+$ (s, 1 H, =CH), 5.19, 4.88$^+$ (s, 5 H, $C_5H_5$), 4.16, 4.07$^+$ (s, 3 H, $OCH_3$), 3.52 (s, 3 H, $NCH_3$), 2.58$^+$, 2.10 (s, 3 H, $CH_3$). – $^{13}C$ NMR (50.3 MHz, $CDCl_3$, 70:30 mixture of isomers; $^+$: minor component): δ = 249.0 (Fe=C), 212.4, 212.0 (CO), 163.1 (=C), 144.0 (C-ipso), 130.6$^+$, 130.4, 129.2, 125.7 ($C_6H_5$), 120.9$^+$, 118.6 (=CH), 87.3, 86.9$^+$ ($C_5H_5$), 64.3, 64.0$^+$ ($OCH_3$), 43.8, 42.4$^+$ ($NCH_3$), 22.5, 19.8 ($CH_3$). – IR ($CH_2Cl_2$): $\tilde{\nu}$ = 2040 $cm^{-1}$, 1991 (CO), 1524, 1499. – IR (KBr): $\tilde{\nu}$ = 2038 $cm^{-1}$, 1985 (CO), 1526, 1499, 1479, 845 ($PF_6^-$). – $C_{19}H_{20}F_6FeNO_3P$ (511.18): FD, *m/z* (%): 366.0 (100) [$M^+ - PF_6^-$].

*X-ray Structure Determination:* For the examination and data collections an Enraf-Nonius Turbo-CAD4 diffractometer was em-

Table 2. Crystallographic data for **3a–c**

| | **3a** | **3b** | **3c** |
|---|---|---|---|
| Empirical formula | $C_{19}H_{26}F_6FeNO_5P\cdot CH_2Cl_2$ | $C_{21}H_{24}F_6FeNO_3P$ | $C_{18}H_{18}F_6FeNO_3P\cdot CH_2Cl_2$ |
| Formula mass | 634.2 g mol$^{-1}$ | 539.2 g mol$^{-1}$ | 582.1 g mol$^{-1}$ |
| Cryst. size [mm$^3$] | 0.10 × 0.32 × 0.45 | 0.12 × 0.12 × 0.5 | 0.13 × 0.32 × 0.45 |
| Linear absorption coefficient | $\mu$ = 7.26 mm$^{-1}$; correction of absorption using $\phi$-Scans | $\mu$ = 6.25 mm$^{-1}$; correction of absorption using $\phi$-Scans | $\mu$ = 8.09 mm$^{-1}$; correction of absorption using $\phi$-Scans; |
| Range of transmission | $T_{min}$ = 0.42, $T_{max}$ = 1.0 | $T_{min}$ = 0.88, $T_{max}$ = 0.99 | $T_{min}$ = 0.30, $T_{max}$ = 1.0 |
| Space group | $P2_12_12_1$ (orthorhombic) | $P2_12_12_1$ (orthorhombic) | $P\bar{1}$ (triclinic) |
| Cell constants[15] | $a$ = 10.681(2) Å<br>$b$ = 10.658(1) Å<br>$c$ = 24.612(2) Å; calculated from 25 reflections (45°< Θ < 54°) | $a$ = 8.363(1) Å<br>$b$ = 11.4527(5) Å<br>$c$ = 25.306(3) Å; calculated from 48 reflections (60°< Θ < 71°) | $a$ = 10.674(2) Å; α = 69.782(8)<br>$b$ = 10.804(2) Å; β = 83.540(8)<br>$c$ = 11.5782(7) Å; γ = 83.188(12)<br>calculated from 25 reflections (35°< Θ < 44°) |
| Cell volume [Å$^3$] | $V$ = 2801.7(5) $Z$ = 4<br>$F$(000) = 1296 | $V$ = 2423.9(4) $Z$ = 4<br>$F$(000) = 1104 | $V$ = 1240.3(3) $Z$ = 2<br>$F$(000) = 588 |
| Density | $d_{calcd.}$ = 1.503 g cm$^{-3}$ | $d_{calcd.}$ = 1.478 g cm$^{-3}$ | $d_{calcd.}$ = 1.558 g cm$^{-3}$ |
| Range for data collection | 1.5° ≤ Θ ≤ 75.0° ; 0 ≤ $h$ ≤ 13<br>0 ≤ $k$ ≤ 13; 0 ≤ $l$ ≤ 30 | 1.5° ≤ Θ ≤ 75.0° , 0 ≤ $h$ ≤ 10<br>0 ≤ $k$ ≤ 14; 0 ≤ $l$ ≤ 31 | 1.5° ≤ Θ ≤ 75.0°; –13 ≤ $h$ ≤ 0<br>–13 ≤ $k$ ≤ 13; –14 ≤ $l$ ≤ 14 |
| Collcd. Reflexions | 6266 (with Friedel pairs) | 5656 (with Friedel pairs) | 5384 (with Friedel pairs) |
| Unique reflexions | 5502 ($R_{int}$ = 0.0584) | 4979 ($R_{int}$ = 0.0314) | 5097 ($R_{int}$ = 0.0193) |
| Obsd. reflexions | 3679 ($\|F\|/\sigma(F) > 4.0$) | 3665 ($\|F\|/\sigma(F) > 4.0$) | 3969 ($\|F\|/\sigma(F) > 4.0$) |
| Parameters refined | 344 | 313 | 345 |
| Weights | $w = 1/[\sigma^2(F_o^2)+(0.1564\cdot P)^2 + 2.14\cdot P]$, $P = [\max(F_o^2,0)+2\cdot F_c^2]/3$ | $w = 1/[\sigma^2(F_o^2)+(0.0481\cdot P)^2 + 1.20\cdot P]$, $P = [\max(F_o^2,0)+2\cdot F_c^2]/3$ | $w = 1/[\sigma^2(F_o^2)+(0.1610\cdot P)^2 + 0.48\cdot P]$, $P = [\max(F_o^2,0)+2\cdot F_c^2]/3$ |
| $R$ values (Refinement on $F^2$) | $wR2$ = 0.2636 ($R1$=0.0866 for obsd. rflns.) | $wR2$ = 0.1716 ($R1$=0.0685 for obsd. rflns.) | $wR2$ = 0.2371 ($R1$=0.0781 for obsd. rflns.) |
| Goodness of fit | $S$ = 1.026<br>Flack parameter: $x$ = –0.01(1)<br>Extinction: $g$ = 0.0006(2) | $S$ = 1.385 | $S$ = 1.050<br>Extinction: $g$ = 0.0036(9) |
| Max, min peak in Fourier map | 0.68, –0.62 eÅ$^{-3}$ | 0.39, –0.36 eÅ$^{-3}$ | 0.88, –0.72 eÅ$^{-3}$ |

ployed at $T$ = 298 K by using a graphite-monochromated Cu-$K_\alpha$ radiation (λ = 1.5418 Å; scan type: ω/2Θ). The structures were solved by direct methods (SIR 92) and were refined by means of the full-matrix least-squares procedures using SHELX 93: Lorentz and polarization corrections were applied to the data. All non-hydrogen atoms were refined anistropically. For **3a**, **3b** and **3c** a riding model starting from the calculated positions for the hydrogen atoms was employed, except for H6 (**3a**), H12 (**3b**) and H6 (**3c**), respectively. The $PF_6^-$ counterions were disordered.[16]


[1] For synthesis and application of tetracarbonyliron(0) carbene complexes, see: [1a] D. Dvorak, *Organometallics* **1995**, *14*, 570–573. – [1b] J. Park, S. Kang, C. Won, D. Whang, K. Kim, *Organometallics* **1993**, *12*, 4704–4707. – [1c] M. F. Semmelhack, J. Park, *Organometallics* **1986**, *5*, 2550–2552, and references cited.

[2] For reviews and leading citations, see: [2a] W. Petz in *Iron-Carbene Complexes* (Ed.: Gmelin-Institut), Springer-Verlag, Berlin, **1993**. – [2b] V. Guerchais, *Bull. Soc. Chim. Fr.* **1994**, *131*, 803–811. – [2c] P. Helquist in *Advances in Metal-Organic Chemistry* (Ed.: L. S. Liebeskind) JAI Press LTD, **1991**, vol. 2, p. 143–194. – [2d] M. Brookhart, W. B. Studabaker, *Chem. Rev.* **1987**, *87*, 411–432. – [2e] B. E. Landrum, J. O. Lay Jr., N. T. Allison, *Organometallics* **1988**, *7*, 787–788, and references cited.

[3] For recent reviews, see: [3a] L. S. Hegedus, *Tetrahedron*, **1997**, *53*, 4105–4128. – [3b] A. de Meijere, *Pure Appl. Chem.* **1996**, *68*, 61–72. – [3c] W. D. Wulff in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**, vol. 12., pp. 470 –547. – [3d] W. D. Wulff in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Flemming), Pergamon Press, Oxford, **1991**, vol. 5., p. 1065–1113. – [3e] K. H. Dötz, *Angew. Chem.* **1984**, *96*, 573–594; *Angew. Chem.* Int. Ed. Engl. **1984**, *23*, 587.

[4] [4a] K. Rück-Braun, J. Kühn, *Synlett* **1995**, 1194–1196. – [4b] K. Rück-Braun, J. Kühn, D. Schollmeyer, *Chem. Ber.* **1996**, *129*, 937–944. – [4c] K. Rück-Braun, J. Kühn, *Chem. Ber.* **1996**, *129*, 1057–1059.

[5] [5a] R. Aumann, B. Jasper, R. Fröhlich, *Organometallics* **1996**, *15*, 1942–1950. – [5b] R. Aumann, B. Jasper, R. Fröhlich, *Organometallics* **1995**, *14*, 3173–3177, and references therein.

[6] [6a] M. Duetsch, F. Stein, R. Lackmann, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Chem. Ber.* **1992**, *125*, 2051–2065. – [6b] F. Stein, M. Duetsch, E. Pohl, R. Herbst-Irmer, A. de Meijere, *Organometallics* **1993**, *12*, 2556–2564.

[7] For reactions of chromium carbene complexes [$(CO)_5Cr$(C(O-Et)C≡CR)], e.g. R = *c*Pr, $C(CH_3)_2OEt$, $OSiMe_3$ with primary amines ($H_2NR'$, R' = *i*Pr, *n*Pr, *c*Hex) furnishing either the corresponding (2-aminoethenyl)methoxy carbene complexes or allenylidene-type complexes as major products, see ref.[6b].

[8] The structural assignment was based on the spectroscopic properties, which were in agreement with data of other aminocarbene complexes derived from aniline, e.g. [$Cp(CO)_2$-Fe(C(NHPh)C($CH_3$)=$CH_2$)$^+$][$PF_6$], δ(Fe–$C_{Carbene}$) = 255; $\tilde{\nu}$ (CO) = 2040, 1990 cm$^{-1}$], see ref.[4b].

[9] For the synthesis and structural assignment of (2-(NH)anilinoethenyl)carbene chromium complexes derived from the corresponding (alkynyl)chromium carbene complexes and aniline, see R. Aumann, *Chem. Ber.* **1993**, *126*, 2325–2330, and references therein.

[10] In the group VI series the (2-methoxyethenyl)aminocarbene complexes and the structurally isomeric (2-aminoethenyl)methoxycarbene complexes have been distinguished by NMR spectroscopy according to Aumann et al.. For example, complex (*E*)-{$(CO)_5W$=C(OEt)CH=C($CH_3$)$NMe_2$} exhibits the resonance signal for the 1-$OCH_2$-group at δ = 4.53, whereas for (*E*)-{$(CO)_5W$=C($NMe_2$)CH=C($CH_3$)OEt} the 3-$OCH_2$-group is found at about δ = 3.47. For further details, see: R. Aumann, P. Hinterding, *Chem. Ber.* **1990**, *123*, 611–620, and references cited.

[11] For iron(0) alkynyl(ethoxy)carbene complexes the aminolysis of $(CO)_4$Fe[C(OEt)C≡C*t*Bu] with dimethylamine at 25 °C was re-

ported by Park et al. (ref.[1b]), leading to an ($\eta^3$-(β-acylvinyl)-carbene)$Fe(CO)_3$ complex as unexpected product, through the initial Michael-type addition of $HNMe_2$ and subsequent rearrangements.

[12] For the synthesis of (2-methoxyethenyl)methoxy carbene chromium complexes from the corresponding (alkynyl)methoxy carbene complexes in the presence of DBU, see:

[12a] F. Camps, A. Llebaria, J. M. Moretó, S. Ricart, J. M. Vinas, *J. Organomet. Chem.* **1991**, *401*, C17–C19. – [12b] A. Llebaria, J. M. Moretó, S. Ricart, J. Ros, J. M. Vinas, R. Yánez, *J. Organomet. Chem.* **1992**, *440*, 79–90. The application of alkoxides as catalysts has been reported by de Meijere et al., see ref.[6].

[13] For the observation of *s-cis/s-trans* conformers of (2-aminoethenyl)methoxycarbene chromium complexes in the solid state and in solution, see: [13a] L. Lattuada, E. Licandro, A. Papagni, S. Maiorana, A. C. Villa, C. Guastini, *J. Chem. Soc., Chem. Commun.* **1988**, 1092–1093; – [13b] R. Aumann, P. Hinterding, *Chem. Ber.* **1990**, *123*, 611–620, references cited therein and ref.[6].

[14] L. A. Carpino, J. Am. Chem. Soc. **1958**, *80*, 599–601.

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

[16] Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen. Any request for this material should quote the full literature citation and the reference numbers CSD-406892 for **3a**, -406891 for **3b** and -406893 for **3c**.

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