Synthesis, Spectroscopic Characterization, and Crystal Structure Determination of Cationic [(Cyclopentadienyl)dicarbonyliron](alkynyl)-aminocarbene Complexes

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(Alkynoyl)iron complexes **1**, $Cp(CO)_2Fe(O{=}CC{\equiv}CR)$ (R = CH_3, Ph, $SiMe_3$), were synthesized by applying a mixed anhydride procedure and transformed into the cationic methoxycarbene complexes **2**, $[Cp(CO)_2Fe(C(OMe)C{\equiv}CR)^+][PF_6^-]$. Primary amines H_2NR' react with the methoxycarbene complexes to furnish exclusively cationic aminocarbene complexes **3**, $[Cp(CO)_2Fe(C(NHR')C{\equiv}CR)^+][PF_6^-]$, or (2-methoxyvinyl)aminocarbene complexes **5**. The spectroscopic properties of the new complexes are discussed. The (alkynyl)-aminocarbene complexes **3e** and **3f** were characterized by X-ray crystal structure analysis.

Alkoxycarbene complexes of group-6 metals[1,2] and tetracarbonyliron(0)[3] have become useful reagents in organic synthesis within the last twenty years, whereas the synthesis and application of aminocarbene complexes have been studied less extensively until recently[4,5]. This also holds true for cationic $[(C_5H_5)(CO)_2Fe]$aminocarbene complexes[6]. Over the past two decades studies of the synthesis of $[(C_5H_5)(CO)_2Fe]$aminocarbene complexes with one nitrogen atom at the carbene carbon atom were carried out by Brunner[7], Fehlhammer[8], and Angelici[9]. The methods described are based on the reaction of $[(C_5H_5)(CO)_2FeNa]$ with benzimidoyl chlorides[7], the protonation of ferraazetidine-type complexes[8], and the aminolysis of the (methylthio)carbene complex $[(C_5H_5)(CO)_2Fe(C(SMe)H)][CF_3SO_3]$[9]. However, several related phosphane-substituted complexes were synthesized by aminolysis of the parent methoxycarbene complexes applying an excess of amine[10].

Previously we have reported on a convenient access to new alkynyl-substituted acyliron complexes **1**[11]. The corresponding electrophilic alkynyl-substituted methoxycarbene complexes **2** were synthesized (Scheme 1), and the aminolysis with primary amines was studied. Thus, substitution at C-1 was observed exclusively at ambient temperature. A series of aminocarbene complexes **3** were obtained (Table 1), and (2-methoxyvinyl)aminocarbene complexes **5a**, **b** (Scheme 2) were isolated from aniline and **2a**, **c**, owing to the addition of the released methoxy group to the alkynyl residue. Even though a few electrophilic iron aminocarbene complexes have been prepared in the past, only very few structural data are available about this class of carbene complexes, e.g. *syn*/*anti* isomer formation and ratio[6–9]. For structure determination a selected set of previously unknown simple alkyl- and aryl-substituted aminocarbene complexes **4**, prepared from primary amines, was synthesized for comparison. In addition, the structures of two (alkynyl)aminocarbene complexes were assigned by X-ray crystallography. In this paper we give a detailed description of the syntheses of these complexes, published before in a preliminary communication[11], and their characterization.

Results and Discussion

The preparation of acyliron complexes **1** from carboxylic acid chlorides and the ferrates $(C_5H_5)(CO)_2FeM$ (M = Na, K) is well documented[12]. However, any attempts to obtain side chain-functionalized complexes in higher yield or propargylic acid derivatives failed. Therefore, we developed an alternative strategy using isobutyl chloroformate-derived mixed anhydrides of the carboxylic acids. This one-pot procedure provides access to the acyl complexes **1** in high yield after chromatographic purification. Results are given in Scheme 1 (see also Experimental). The spectroscopic properties of the alkynyl-substituted derivatives **1** are similar to those of other compounds[6], except the ^{13}C-NMR acyliron signal $[Cp(CO)_2Fe{-}\mathit{C}{=}\mathit{O}]$ being shifted upfield to about $\delta = 239$. In the IR spectra the iron acyl ν(CO) absorptions are shifted to 1587–1583 cm^{-1} and are about 40–50 cm^{-1} lower than for alkyl-, aryl-, or alkenyl-substituted acyl complexes $[Cp(CO)_2Fe(O{=}CR)]$[6].

The acyl complexes **1** were further converted into cationic methoxycarbene complexes **2** (Scheme 1). Thus, $[(MeO)_2CH^+][PF_6^-]$ was generated in CH_2Cl_2 at room temperature from trimethyl orthoformate and $[Ph_3CH^+][PF_6^-]$[11]. Solid acyl complexes were added neat to the methylating reagent, whereas oils were dissolved in CH_2Cl_2 prior to addition to the reaction mixture by means of a cannula. The

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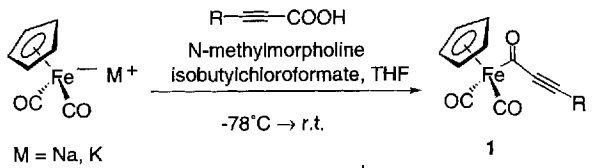
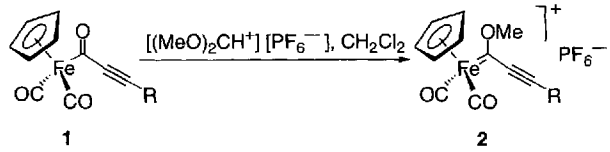
Scheme 1



1	R	yield (%)
a	$SiMe_3$	76
b	Ph	48
c	CH_3	67

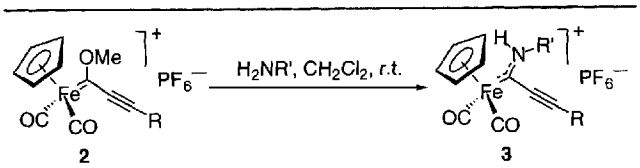


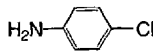
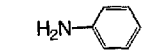
2	R	yield (%)
a	$SiMe_3$	86
b	Ph	80
c	CH_3	90

progress of the reaction was monitored by IR spectroscopy observing the characteristic ν(CO) absorptions of the products at about 2075 and 2035 cm^{-1} and of the starting compounds around 2030 and 1975 cm^{-1}, respectively. All methoxycarbene complexes were precipitated from the reaction mixture by dilution with Et_2O or petroleum ether (40–60°C). The compounds were isolated by removal of the solvent, washed and dried to furnish moisture-sensitive yellow solids or brown oils in 70–90% yield. Reactions performed with analogously prepared $[(MeO)_2CH^+][BF_4^-]$ and **2a** (R = $SiMe_3$) provided less stable and impure products. NMR studies of these substances were carried out in different solvents [(D]TFA, [D_6]DMSO, CD_3NO_2). Due to their solubility CD_3NO_2 proved to be the most suitable solvent. The ^{13}C-NMR spectra of the alkynyl complexes **2a** (R = $SiMe_3$) and **2c** (R = CH_3) display resonances at about δ = 290 for the carbene carbons shifted upfield more than 40 ppm compared to those of complex **2d** {[$Cp(CO)_2Fe(C(OMe)Me)$][PF_6]; $\delta(Fe-C_{carbene})$ = 335, see Experimental}. In contrast to the parent acyl complexes, the signals of the C≡C carbon atoms in **2** are more than 40 ppm apart [**2a**, R = $SiMe_3$, δ(C≡C) = 149.0 and 105.4] as a result of the higher electrophilicity at the carbene carbon atom, thus causing an increased polarization of the alkynyl substituent.

Treatment of the carbene complex **2a** (R = $SiMe_3$) with one equivalent of primary amine in dichloromethane at room temperature furnished smoothly the corresponding (alkynyl)aminocarbene complexes **3a–c** in yields of 65–92%, after simple crystallization from the reaction mixture (Table 1).

Table 1. Aminolysis of (alkynyl)methoxycarbene complexes **2a** and **2b** with primary amines

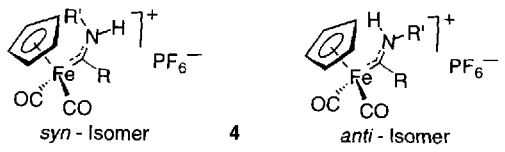


amine	R	3	Yield [%]	ν̃(CN) [KBr, cm^{-1}]
$H_2NCH_2CO_2tBu$	Si(CH3)3	**3a**	65	1544
(*L*)-$H_2NCH(CH_3)CO_2tBu$	Si(CH3)3	**3b**	72	1537
(*S*)-$H_2NCH(CH_3)Ph$	Si(CH3)3	**3c**	92	1537
(*L*)-$H_2NCH(CH_3)CO_2tBu$	Ph	**3d**	90	1543
	Si(CH3)3	**3e**	61	1515
	Si(CH3)3	**3f**	76	1519

Complete turnover was generally detected within 5 minutes. According to IR monitoring, the ν(CO) absorptions were shifted by about 10–15 cm^{-1} to 2060 and 2017 cm^{-1}, respectively. Compound **3d** was prepared analogously from the phenyl-substituted complex **2b** and L-alanine *tert*-butyl ester in 90% yield (Table 1). In addition, the aminocarbene complexes **3e** and **3f** were obtained from **2a** and the less basic amines aniline and toluidine (Table 1) at room temperature. The complexes were isolated as yellow or brown crystalline solids, which can be handled for prolonged periods without inert gas. It is well documented that aminocarbene complexes of group-6 metals and iron can be obtained as mixtures of rotamers, due to the restricted rotation around the C=N bond[1,4–9,13–15]. So far, none of the alkynyl-substituted aminocarbene complexes **3** showed any sign of being a mixture of isomers in solution according to NMR spectroscopy. In contrast, the aminocarbene complexes **4** were obtained as *syn/anti*-isomeric mixtures as indicated in Table 2[14]. Similar observations and trends were observed for analogously substituted chromium aminocarbene complexes[13]. For compounds **4** the ratio of rotamers, measured in [D_6]DMSO, ranges between 67:33 and 73:24 according to ^1H-NMR resonances of both isomers (Table 2)[15]. The deuterated solvent has been observed to effect the ratio of rotamers in solution. Only one isomer is observed for **4d** (R′ = Ph, R = CH_3, Table 2) in the ^1H-NMR spectra when measured in [D_1]TFA, most probably due to protonation of the nitrogen thus causing free rotation around the C–N bond[16]. Upon measuring of complex **4a** (R′ = C_6H_{11}, R = Ph, entry 1) in CD_3CN a 84:16 ratio was determined, probably due to traces of acid being present (see Experimental).

In the IR spectra (KBr) aminocarbene complexes (Tables 1 and 2) show a characteristic ν(C=N) absorption in the

Table 2. Synthesis of cationic aminocarbene iron complexes **4**



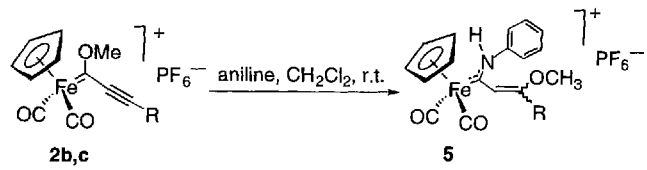
amine[a]	R	4	yield [%]	ν̃(CN) [KBr, cm^{-1}]	ratio of rotamers
$H_2NC_6H_{11}$		**4a**	53	1557	73 : 24
$H_2NCH_2CO_2tBu$		**4b**	68	1567	67 : 33
		**4c**	87	1530	65 : 35
	CH_3	**4d**	91	1533	67 : 33
		**4e**	77	1527	71 : 29

range from 1570 to 1515 cm^{-1}. In the case of less basic aromatic amines, the ν(C=N) stretching frequencies are generally observed somewhat lower at about 1530 to 1515 cm^{-1}. The ^{13}C-chemical shifts of C(carbene) range from δ = 258 to 254 for the complexes listed in Table 2, whereas for alkynyl-substituted compounds (Table 1) δ(Fe−$C_{carbene}$) shifts are observed between δ = 226 and 221. The exact configuration of the C=N bond for the observed rotamers of **4** (Table 2) cannot yet be elucidated. On the basis of NMR and IR measurements an assignment of signal sets to *syn* and *anti* isomers is not possible. However, formation of the *anti* isomer should be favored for steric reasons. Fortunately, from the alkynyl-substituted complexes **3e** and **3f** suitable crystals for X-ray structural determination were obtained revealing the proposed *anti* configuration in the solid state.

With the cationic $Cp(CO)_2Fe$ fragment compared to the $(CO)_5Cr$ group a sterically less demanding moiety is introduced, which additionally increases the electrophilicity of the carbene carbon, thereby favoring substitution at C-1. So far in none of the cases studied (Table 1) Michael-type addition of the amine instead of substitution at C-1, leading to (2-aminovinyl)methoxycarbene complexes or the formation of allenylidene-type complexes, was observed at room temperature, as known for chromium carbene complexes[5e,17]. To our surprise, treatment of the methoxycarbene complexes **2b** and **2c** with aniline (1 equiv.) at ambient temperature afforded exclusively the (2-methoxyvinyl)-aminocarbene complexes **5a** and **5b** (Scheme 2). The complexes precipitated after dilution of the reaction mixtures with diethyl ether.

The structural assignment is based on the spectroscopic properties of **5a, b**. The data are in agreement with those of

Scheme 2



5	R	yield (%)
a	Ph	74
b	CH_3	88

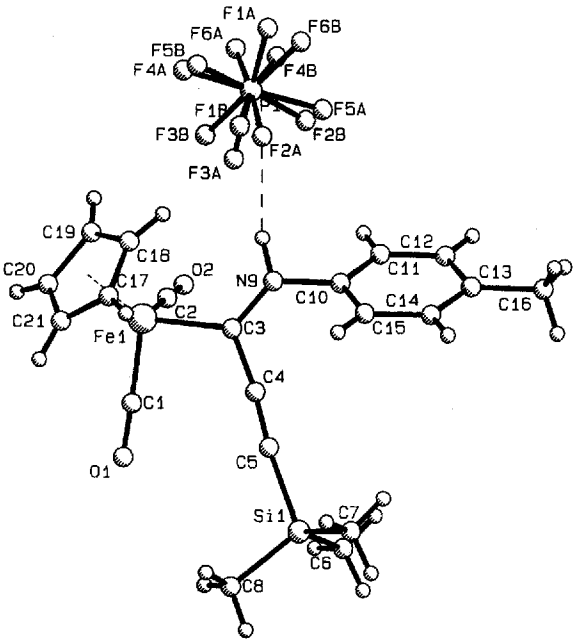
(alkenyl)aminocarbene complexes derived from aniline with δ(Fe−$C_{Carbene}$) at about δ = 255 and ν(CO) absorptions at about 2040 and 1990 cm^{-1}, respectively. In the light of these results the aminolysis of **2a** (R = $SiMe_3$) with aniline (1 equiv.) was examined at −78 °C and in refluxing dichloromethane, but no addition of the released methoxy group to the alkynyl moiety was observed (isolation of **3f**: −78 °C: 77%; +42 °C: 75%). Obviously, the sterically demanding $SiMe_3$ group at the terminus of the alkynyl moiety prevents from attack of the released methoxy group. Presently, the stereochemistry of the newly formed double bond remains unclear. ^{1}H- and ^{13}C-NMR spectra of **5a** in $CDCl_3$ and CD_3NO_2 showed a single isomer to be present in solution[18]. However, ^{1}H-NMR spectra of **5b** measured in CD_3NO_2 at ambient temperature indicated a single isomer, whereas in [D_6]DMSO a 1:1 mixture of isomers was observed. Due to the possibility of rotamers (*syn/anti* isomers) being present instead of stereoisomers (C=C bond) further investigations are necessary to elucidate the configuration of the products unambiguously[18].

Crystal Structure Determination of 3e, f

As shown by the structures in Figures 1 and 2 the compounds **3e** and **3f** exist as *anti* isomers in the solid state. The Fe−C(carbene) bond lengths are comparable to those of mono(alkylthio)carbene complexes, e.g. [$Cp(CO)_2Fe$(S-Me)Me^+][PF_6^-] as revealed by X-ray diffraction[19]. The C=N bond lengths observed for **3e** [1.303(6) Å] and for **3f** [1.305(6) Å] reflect the π bonding between the amino substituent and the carbene carbon atom (Figures 1 and 2). A hydrogen bond between one fluorine atom of the counter ion [PF_6^-] and the hydrogen atom of the amino substituent is observed for **3f** [H7−F2 2.155(5), N7−F2 3.023(5)] and **3e**[20].

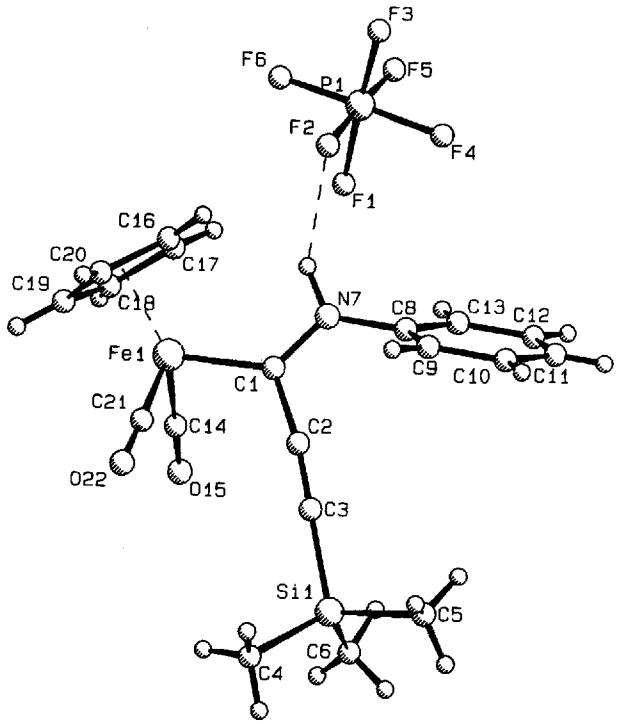
According to the angle of 12.8° between the Cp_{center}−Fe−$C_{carbene}$ and N−$C_{carbene}$−Fe planes, approaching 0°, complex **3f** exists in an "upright" conformation in the solid state (Figure 1). A "crosswise" or "orthogonal" conformation is formed if the corresponding dihedral angle is close to 90°. For complex **3e**, an angle of 69.7° is found. Even though the two complexes are very similar in constitution they show significant conformational differences in the solid state. Similar observations and additional conformations were found for sulfur-containing [$Cp(CO)_2Fe$]car-

Figure 1. Structure of Complex **3e**[a]



[a] Selected bond lengths [Å] and angles [°]: Fe–C3 1.940(5), Fe–C1 1.773(8), C1–O1 1.132(11), C3–C4 1.430(8), C3–N9 1.303(6), N9–C10 1.443(6), N9–H9 0.937(6), C4–C5 1.186(8), C5–Si 1.858(6), H9–F2a 2.091(18), N9–F2a 2.96(2); N9–H9–F2a 153.0(7), Fe–C3–C4 119.3(3), Fe–C3–N9 124.0(3), C4–C3–N9 116.6(4), C3–N9–C10 129.0(4).

Figure 2. Structure of Complex **3f**[a]



[a] Selected bond lengths [Å] and angles [°]: Fe–C1 1.928(4), Fe–C21 1.760(5), C21–O22 1.143(6), C1–C2 1.430(6), C1–N7 1.305(6), N7–C8 1.447(6), N7–H7 0.971(5), C2–C3 1.199(7), C3–Si 1.854(5), H7–F2 2.155(5), N7–F2 3.023(5); N7–H7–F2 148.2(3), Fe–C1–C2 117.1(3), Fe–C1–N7 127.9(3), C2–C1–N7 115.0(4), C1–N7–C8 125.6(3).

bene complexes in the solid state[19]. To our knowledge these are the first examples of cationic iron aminocarbene complexes characterized by X-ray crystallography.

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Experimental

All manipulations were carried out under argon. Solvents were dried by refluxing over potassium/benzophenone ketyl, $LiAlH_4$ (LAH) or CaH_2 and were freshly distilled and degassed (ultrasound) 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). – 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 (*: labeling of minor component in the case of mixtures of rotamers). – MS: Varian MAT CH 7a, Finnigan MAT 95. – Melting points are uncorrected.

Dicarbonyl(cyclopentadienyl)[3-(trimethylsilyl)propynoyl]iron (**1a**): A solution of 3-(trimethylsilyl)propynoic acid (1.01 g, 7.13 mmol) in 75 ml of degassed THF was cooled to 0 °C. *N*-Methylmorpholine (0.82 ml, 1.04 equiv.) and isobutyl chloroformate (0.96 ml, 1.04 equiv.) were added. The mixture was stirred at 0 °C for 15 min and cooled to −78 °C. After sedimentation of the hydrochloride (20 min) the solution was filtered in vacuo at −78 °C. The filtrate was added by means of a cannula to a suspension of [Cp(CO)$_2$FeK], prepared from [Cp(CO)$_2$Fe]$_2$ (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.[12b,c]. The solution was stirred at −78 °C for 25 min and allowed to warm to room temp. (50 min). To the reaction mixture a satd. aqueous NH_4Cl solution (0.14 ml) was added, and the solvent was subsequently removed in vacuo. The residue was purified by column chromatography on silica gel with petroleum ether/ether (4:1) to afford 1.65 g (76%) of yellow-brown crystalline **1a**, m.p. 33 °C, $R_f = 0.44$ (petroleum ether/ether, 2:1). – ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 5.16 (s, 5H, C_5H_5), 0.21 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 239.0 (Fe–C=O), 213.8 (CO), 105.9 (C≡C), 98.5 (C≡C), 88.0 (C_5H_5), −0.7 [$Si(CH_3)_3$]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2033, 1980 (CO), 1587 (Fe–C=O). – $C_{13}H_{14}FeO_3Si$ (302.2): calcd. C 51.67, H 4.67; found C 51.58, H 4.63.

Dicarbonyl(cyclopentadienyl)(3-phenylpropynoyl)iron (**1b**): The active ester was synthesized according to the procedure described for **1a** starting from 3-phenylpropynoic acid (392 mg, 2.68 mmol) dissolved in 30 ml of THF. After filtration of the precipitated *N*-methylmorpholine hydrochloride, a solution of [Cp(CO)$_2$FeNa], prepared from [Cp(CO)$_2$Fe]$_2$ (500 mg, 1.41 mmol) and 4.87 g of Na/Hg (2% sodium), in 14 ml of THF was added by means of a cannula at −78 °C to the filtrate. The solution was stirred for 30 min at −78 °C and then warmed to room temp. (50 min). It was then treated with a satd. aqueous NH_4Cl solution (0.05 ml) and concentrated in vacuo. Column chromatography (petroleum ether/ether, 4:1) of the residue on silica gel afforded 399 mg (48%) of yellow-brown **1b**, m.p. 53–54 °C, $R_f = 0.16$ (petroleum ether/ether, 2:1). – ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 7.56–7.45 (m, 5H, C_6H_5), 5.23 (s, 5H, C_5H_5). – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.50–7.24 (m, 5H, C_6H_5), 4.90 (s, 5H, C_5H_5). – ^{13}C NMR (100.6

MHz, [D_6]DMSO): δ = 237.0 (Fe–C=O), 213.7 (CO), 131.7, 130.0, 128.7, 120.4 (C-*ipso*, C_6H_5), 93.2 (C≡C), 92.2 (C≡C), 87.7. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 238.7 (Fe–C=O), 212.8 (CO), 131.9, 129.6, 128.3, 121.0 (C-*ipso*, C_6H_5), 94.4 (C≡C), 92.7 (C≡C), 85.1. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2168 (C≡C), 2031, 1978 (CO), 1587 (Fe–C=O). – $C_{16}H_{10}FeO_3$ (306.1): calcd. C 62.79, H 3.29; found C 62.66, H 3.25.

2-Butynoyldicarbonyl(cyclopentadienyl)iron (**1c**): According to the general procedure described for **1a** tetrolic acid[21] (599 mg, 7.13 mmol) was converted to the active ester and treated with [$Cp(CO)_2$-FeK]. Column chromatography (petroleum ether/ether, 4:1) gave 1.16 g (67%) of yellow-brown crystalline **1c**, m.p. 68 °C, R_f = 0.2 (petroleum ether/ether, 2:1). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.86 (s, 5H, C_5H_5), 1.98 (s, 3H, CH_3). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 239.1 (Fe–C=O), 212.9 (CO), 92.6 (C≡C), 87.1 (C≡C), 86.8 (C_5H_5), 4.0 (CH_3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2171 (C≡C), 2030, 1976 (CO), 1583 (Fe–C=O). – $C_{11}H_8FeO_3$ (244.0): calcd. C 54.14, H 3.30; found C 53.92, H 3.16.

Dicarbonyl(cyclopentadienyl)(methacryloyl)iron (**1d**)[22]: According to the procedure described for **1a**, compound **1d** was prepared from methacrylic acid (0.61 ml, 7.13 mmol) and [$Cp(CO)_2$-FeK] to furnish 1.12 g (64%) of yellow-brown crystalline **1d** after column chromatography (toluene/ethanol, 100:1), m.p. 27 °C, R_f = 0.5 (petroleum ether/ether, 2:1). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.36 (s, 1H, C=CH_2), 5.27 (s, 1H, C=CH_2), 4.84 (s, 5H, C_5H_5), 1.73 (s, 3H, CH_3). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 256.0 (Fe–C=O), 214.2 (CO), 157.9, 118.6, 86.2, 18.6. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2021, 1962 (CO), 1629 (Fe–C=O), 1602 (C=C). – $C_{11}H_{10}FeO_3$ (246.0): calcd. C 53.70, H 4.10; found C 53.67, H 4.13.

Dicarbonyl(cyclopentadienyl){methoxy[(trimethylsilyl)ethynyl]carbene}iron Hexafluorophosphate (**2a**): A solution of **1a** (1.52 g, 5.02 mmol) in CH_2Cl_2 (25 ml) was added to [$(MeO)_2CH$][PF_6][23] prepared in situ in 50 ml of CH_2Cl_2 as described for **2c**. The reaction mixture was stirred for 2 h and then added by means of a cannula to petroleum ether (200 ml) to provide precipitated **2a** according to the general work-up procedure: 1.7 g (86%) as a red-brown oil. – ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 5.15 (s, 5H, C_5H_5), 3.15 (s, 3H, OCH_3), 0.20 [s, 9H, $Si(CH_3)_3$]. – ^{1}H NMR (200 MHz, CD_3NO_2): δ = 5.52 (s, 5H, C_5H_5), 4.67 (s, 3H, OCH_3), 0.38 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (50.3 MHz, CD_3NO_2): δ = 290.8 (Fe=C), 209.1 (CO), 149.0 (C≡C), 105.4 (C≡C), 91.8 (C_5H_5), 71.6 (OCH_3), –1.7 [$Si(CH_3)_3$]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2117 (C≡C), 2077, 2038 (CO). – $C_{14}H_{17}F_6FeO_3PSi$ (462.1): FD, *m/z* (%): 317.5 (29) [$M^+ - PF_6^-$].

Dicarbonyl(cyclopentadienyl)[methoxy(phenylethynyl)carbene]iron Hexafluorophosphate (**2b**): To a solution of [$(MeO)_2CH$][PF_6][23] in 23 ml of CH_2Cl_2, prepared in situ according to the procedure described for **2c**, a solution of **1b** (615 mg, 2 mmol) in 6 ml of CH_2Cl_2 was added. The reaction mixture was stirred for 1 h (IR monitoring) and then diluted with ether (150 ml) to precipitate **2b** which was isolated as a yellow solid: 640 mg (80%), m.p. 121–123 °C (dec.). – ^{1}H NMR (200 MHz, CD_3NO_2): δ = 7.82–7.63 (m, 5H, C_6H_5), 5.58 (s, 5H, C_5H_5), 4.75 (s, 3H, OCH_3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2161 (C≡C), 2074, 2033 (CO), 847 (PF_6^-). – $C_{17}H_{13}F_6FeO_3P$ (466.0): calcd. C 43.80, H 2.81; found C 43.72, H 2.86.

Dicarbonyl(cyclopentadienyl[methoxy(1-propynyl)carbene]iron Hexafluorophosphate (**2c**) was prepared according to the procedure published by Cutler et al.[23] for the in situ preparation of [$(MeO)_2CH$][PF_6] from [Ph_3C][PF_6] (1.43 g, 3.7 mmol) and $(MeO)_3CH$ (0.53 ml, 4.86 mmol) in CH_2Cl_2 (33 ml). After the mixture had been stirred for 15 min in the dark, a solution of **1c** (948 mg, 3.89 mmol) in 8 ml of CH_2Cl_2 was added by means of cannula, and the solution was stirred at ambient temp. The progress of the reaction was monitored by IR spectroscopy. After complete consumption of the starting material (2 h), the reaction mixture was diluted with petroleum ether (100 ml) to precipitate **2c**. The mother liquor was removed by means of a cannula. The residue was washed with ether, dried in a stream of argon and under oil-pump vacuum to afford 1.34 g (90%) of **2c** as a yellow solid, m.p. 73 °C. – ^{1}H NMR (200 MHz, CD_3NO_2): δ = 5.50 (s, 5H, C_5H_5), 4.62 (s, 3H, OCH_3), 2.59 (s, 3H, CH_3). – ^{13}C NMR (50.3 MHz, CD_3NO_2): δ = 290.8 (Fe=C), 209.5 (CO), 143.7 (C≡C), 91.3 (C_5H_5), 87.8 (C≡C), 71.0 (OCH_3), 6.6 (CH_3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2192 (C≡C), 2074, 2034 (CO), 847 (PF_6^-). – $C_{12}H_{11}F_6FeO_3P$ (404.0): calcd. C 35.67, H 2.74; found C 35.53, H 2.63.

Dicarbonyl(cyclopentadienyl)(methoxymethylcarbene)iron Hexafluorophosphate (**2d**) was prepared from [$(MeO)_2CH$][PF_6] in 30 ml of CH_2Cl_2 and [$Cp(CO)_2Fe(C=O)CH_3$][12a–c] (1.1 g, 5 mmol), then added neat to the reaction mixture. After the mixture had been stirred for 1 h, it was treated with ether (150 ml) to provide pure **2d** as a yellow powder: 1.18 g (62%), m.p. 140–141 °C (dec.). – ^{1}H NMR (200 MHz, [D]TFA): δ = 5.25 (s, 5H, C_5H_5), 4.51 (s, 3H, OCH_3), 3.05 (s, 3H, CH_3). – ^{1}H NMR (200 MHz, CD_3NO_2): δ = 5.45 (s, 5H, C_5H_5), 4.62 (s, 3H, OCH_3), 3.21 (s, 3H, CH_3). – ^{13}C NMR (50.3 MHz,CD_3NO_2): δ = 335.3 (Fe=C), 210.2 (CO), 89.8 (C_5H_5), 88.3 (OCH_3), 68.3 (CH_3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2067, 2022 (CO), 847 (PF_6^-). – $C_{10}H_{11}F_6FeO_3P$ (380.0): calcd. C 31.61, H 2.92; found C 31.49, H 3.01.

Dicarbonyl(cyclopentadienyl)[methoxy(1-methylethenyl)carbene]iron Hexafluorophosphate (**2e**): A solution of **1d**[22] (687 mg, 2.8 mmol) in 5 ml of CH_2Cl_2 was used. Precipitation by addition of ether (40 ml) afforded 746 mg (77%) of **2e** as a yellow powder, m.p. 110 °C (dec.). – ^{1}H NMR (200 MHz, [D]TFA): δ = 5.60 (m, 7H, C_5H_5, C=CH_2), 4.87 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2067, 2025 (CO), 847 (PF_6^-).

Dicarbonyl(cyclopentadienyl){(glycin-N-yl tert-butyl ester)[(trimethylsilyl)ethynyl]carbene}iron Hexafluorophosphate (**3a**); *General Work-up Procedure:* To a solution of methoxycarbene complex **2a** (1.22 g, 2.64 mmol) in 20 ml of CH_2Cl_2 a solution of glycine *tert*-butyl ester (346 mg, 2.64 mmol) in 5 ml of CH_2Cl_2 was added, and the reaction mixture was stirred for 35 min (IR monitoring). The solution was treated with petroleum ether/ether (120 ml, 5:1). After the solution had been stored at –18 °C overnight, the mother liquor was removed by means of a cannula. The formed precipitate was washed with ether, dried in a stream of argon and under oil-pump vacuum to yield 970 mg (65%) of yellow-brown **3a**, m.p. 117 °C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.44 (s, 1H, NH), 5.25 (s, 5H, C_5H_5), 4.48 (s, 2H, CH_2), 1.46 [s, 9H, $C(CH_3)_3$], 0.27 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 229.2 (Fe=C), 209.4 (CO), 164.6 (C=O), 139.9 (C≡C), 102.5 (C≡C), 87.1 (C_5H_5), 84.0 (CH_2), 54.8 [*C*(CH_3)$_3$], 27.9 [C(*C*H_3)$_3$], –1.0 [$Si(CH_3)_3$]. – IR (CH_2Cl_2): $\tilde{\nu}$ = 3329 (NH), 2127 (C≡C), 2059, 2017 (CO), 1742 (C=O), 850 (PF_6^-). – IR (KBr): $\tilde{\nu}$ = 3349 (NH), 2128 (C≡C), 2063, 2014 (CO), 1745 (CO_2tBu), 1544 (C=N), 845 (PF_6^-). – $C_{19}H_{26}F_6FeNO_4PSi$ (561.3): calcd. C 40.65, H 4.66, N 2.49; found C 40.29, H 4.54, N 2.93.

{(Alanin-N-yl tert-butyl ester)[(trimethylsilyl)ethynyl]carbene}dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate (**3b**): To a solution of 930 mg (2.01 mmol) of **2a** in 30 ml of CH_2Cl_2 a solution of 292 mg (2.01 mmol) of alanine *tert*-butyl ester in 10 ml of CH_2Cl_2 was added. After having been stirred for 10 min (IR monitoring) the reaction mixture was treated with petroleum ether (200 ml) to yield 830 mg (72%) of **3b** as a brown powder after the

general work-up procedure, m.p. 148–150°C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.33 (s, 1H, NH), 5.25 (s, 5H, C_5H_5), 4.81–4.77 (m, 1H, C*H*CH_3), 1.67 (d, *J* = 6.8 Hz, 3H, CHC*H*$_3$), 1.46 [s, 9H, C(CH_3)$_3$], 0.27 [s, 9H, Si(CH_3)$_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 228.0 (Fe=C), 209.7 (CO), 209.1 (CO), 167.5 (C=O), 141.2 (C≡C), 102.6 (C≡C), 87.2 (C_5H_5), 84.1 [*C*(CH_3)$_3$], 63.3 ($CHCH_3$), 27.8 [C(*C*H$_3$)$_3$], 16.2 ($CHCH_3$), –1.0 [Si(CH_3)$_3$]. – IR (CH_2Cl_2): ṽ = 3308 (NH), 2127 (C≡C), 2060, 2016 (CO), 1738 (CO_2tBu), 850 (PF_6^-). – IR (KBr): ṽ = 3326 (NH), 2129 (C≡C), 2066, 2012 (CO), 1743 (CO_2tBu), 1537 (C=N), 846 (PF_6^-). – $C_{20}H_{28}F_6FeNO_4PSi$ (575.3): FD, *m/z* (%): 430.1 (100) [M^+ – PF_6^-].

Dicarbonyl(cyclopentadienyl){[(S)-(1-phenylethyl)amino][(trimethylsilyl)ethynyl]carbene}iron Hexafluorophosphate (**3c**): To a solution of 603 mg (1.30 mmol) of **2a** in 23 ml of CH_2Cl_2 0.17 ml (1.30 mmol) of neat (*S*)-(1-phenylethyl)amine was added, and the reaction mixture was stirred for 25 min (IR monitoring). Dilution with petroleum ether (50 ml) followed by the general work-up procedure furnished 663 mg (92%) of **3e** as a yellow powder, m.p. 208°C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.73 (s, 1H, NH), 7.37–7.26 (m, 5H, C_6H_5), 5.41–5.27 (q, *J* = 6.9 Hz, 1H, C*H*CH_3), 5.12 (s, 5H, C_5H_5), 1.78 (d, *J* = 6.9 Hz, 3H, CHC*H*$_3$), 0.28 [s, 9H, Si(CH_3)$_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 223.6 (Fe=C), 209.5 (CO), 209.3 (CO), 142.0 (C≡C), 140.2 (C-*ipso*, C_6H_5), 129.2, 128.6, 126.8 (C_6H_5), 103.0 (C≡C), 87.0 (C_5H_5), 66.1 ($CHCH_3$), 20.8 ($CHCH_3$), –1.0 [Si(CH_3)$_3$]. – IR (CH_2Cl_2): ṽ = 3306 (NH), 2130 (C≡C), 2060, 2016 (CO). – IR (KBr): ṽ = 3317 (NH), 2141 (C≡C), 2052, 2006 (CO), 1537 (C=N), 842 (PF_6^-). – $C_{21}H_{24}F_6FeNO_2PSi$ (551.3): calcd. C 45.73, H 4.39, N 2.54; found C 45.47, H 4.78, N 2.62.

[(Alanin-N-yl tert-butyl ester)(phenylethynyl)carbene]dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate (**3d**): To a solution of 542 mg (1.16 mmol) of **2b** in 10 ml of CH_2Cl_2 a solution of 168 mg (1.16 mmol) of alanine *tert*-butyl ester in CH_2Cl_2 (5 ml) was added. The reaction mixture was stirred for 15 min, then diluted with petroleum ether/ether (120 ml, 5:1) and stored at –18°C overnight. The general work-up procedure afforded 603 mg (90%) of yellow crystalline **3d**, m.p. 110°C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.15 (s, 1H, NH), 7.57–7.35 (m, 5H, C_6H_5), 5.29 (s, 5H, C_5H_5), 4.85 (q, *J* = 7.2 Hz, 1H, C*H*CH_3), 1.70 (d, *J* = 7.2 Hz, 3H, CHC*H*$_3$), 1.43 [s, 9H, C(CH_3)$_3$]. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 226.1 (Fe=C), 209.8 (CO), 209.4 (CO), 167.9 (CO_2tBu), 132.7, 132.5, 131.9, 129.1, 119.6 (C_6H_5, C≡C), 89.9 (C≡C), 87.2 (C_5H_5), 83.9 [C(CH_3)$_3$], 63.0 ($CHCH_3$), 27.8 [C(CH_3)$_3$], 16.3 ($CHCH_3$). – IR (CH_2Cl_2): ṽ = 3311 (NH), 2175 (C≡C), 2058, 2014 (CO), 1735 (CO_2tBu). – IR (KBr): ṽ = 3325 (NH), 2177 (C≡C), 2053, 2008 (CO), 1735 (CO_2tBu), 1543 (C=N), 845 (PF_6^-). – $C_{23}H_{24}F_6FeNO_4P$ (579.2): FD, *m/z* (%): 434.1 (100) [M^+ – PF_6^-].

Dicarbonyl(cyclopentadienyl){(4-methylanilino)[(trimethylsilyl)ethynyl]carbene}iron Hexafluorophosphate (**3e**): To a solution of 918 mg (1.98 mmol) of **2a** in 20 ml of CH_2Cl_2 a solution of 213 mg (1.98 mmol) of toluidine in 13 ml of CH_2Cl_2 was added. The reaction mixture was stirred for 40 min (IR monitoring), then diluted with petroleum ether/ether (40 ml, 1:1) and stored at –18°C overnight to yield **3e** according to the general work-up procedure: 649 mg (61%) of yellow crystalline **3e**, m.p. 188°C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.64 (s, 1H, NH), 7.53–7.15 (m, 5H, C_6H_5), 5.25 (s, 5H, C_5H_5), 2.34 (s, 3H, CH_3), 0.21 [s, 9H, Si(CH_3)$_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 221.2 (Fe=C), 209.7 (CO), 142.2 (C≡C), 139.9 (C-*ipso*, C_6H_5), 139.0, 129.4, 122.7, 104.8 (C≡C), 87.1 (C_5H_5), 21.2 (CH_3), –1.2 [Si(CH_3)$_3$]. – IR (CH_2Cl_2): ṽ = 3296 (NH), 2127 (C≡C), 2060, 2017 (CO). – IR (KBr): ṽ = 3311 (NH), 2137 (C≡C), 2053, 2006 (CO), 1515.0 (C=N). – $C_{20}H_{22}F_6FeNO_2PSi$ (537.3): calcd. C 44.71, H 4.13, N 2.61; found C 44.72, H 4.00, N 2.62.

{Anilino[(trimethylsilyl)ethynyl]carbene}dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate (**3f**): To a solution of **2a** (495 mg, 1.07 mmol) in CH_2Cl_2 (30 ml) a solution of aniline (99 mg, 1.0 equiv.) in 10 ml of CH_2Cl_2 was added. After the mixture had been stirred for 5 min, IR monitoring indicated complete consumption of the starting material. The solution was added dropwise to 200 ml of ether, and the mixture was stored at –18°C overnight to yield 427 mg (76%) of **3f** as brown needles after the general work-up procedure, m.p. 152–154°C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 11.59 (s, 1H, NH), 7.59–7.36 (m, 5H, C_6H_5), 5.25 (s, 5H, C_5H_5), 0.19 [s, 9H, Si(CH_3)$_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 226.9 (Fe=C), 209.5 (CO), 143.8 (C≡C), 140.9 (C-*ipso*, C_6H_5), 129.7, 129.0, 123.4, 104.5 (C≡C), 87.3 (C_5H_5), –1.3 [Si(CH_3)$_3$]. – IR (CH_2Cl_2): ṽ = 3294 (NH), 2128 (C≡C), 2061, 2018 (CO), 849 (PF_6^-). – IR (KBr): ṽ = 3349 (NH), 2128 (C≡C), 2054, 2001 (CO), 1519.0 (C=N), 850 (PF_6^-). – $C_{19}H_{20}F_6FeNO_2PSi$ (523.3): calcd. C 43.61, H 3.85, N 2.67; found C 43.64, H 3.81, N 2.56.

Dicarbonyl[(cyclohexylamino)phenylcarbene](cyclopentadienyl)iron Hexafluorophosphate (**4a**): To a solution of $[Cp(CO)_2Fe(C(OMe)Ph)^+][PF_6^-]$[23] (1.36 g, 3.1 mmol) in 75 ml of CH_2Cl_2 neat cyclohexylamine (0.35 ml, 1 equiv.) was added. The mixture was stirred for 1 h, then treated with ether (180 ml) to yield 830 mg (53%) of a yellow solid **4a**, m.p. 205°C (dec.). – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 11.83 (s, 1H, NH), 7.42 (br. s, 3H, C_6H_5), 7.15 (br. s, 2H, C_6H_5), 5.53, 5.44* (s, 5H, C_5H_5), 3.95 (s, 1H, CHN), 1.91–0.77 (m, 10H, CH_2). – ^{1}H NMR (200 MHz, CD_3CN, ratio of isomers 84:16): δ = 10.06 (s, 1H, NH), 7.43 (br. s, 3H, C_6H_5), 7.13, 6.97* (br. s, 2H, C_6H_5), 5.32, 5.22* (s, 5H, C_5H_5), 4.06, 3.39* (CHN), 1.92–1.06 (10H, CH_2). – IR (KBr): ṽ = 3303 (NH), 2049, 2004 (CO), 1557 (C=N). – $C_{20}H_{20}F_6FeNO_2P$ (509.15): calcd. C 47.18, H 4.36, N 2.75; found C 46.88, H 4.71, N 2.79.

Dicarbonyl(cyclopentadienyl)[(glycin-N-yl tert-butyl ester)phenylcarbene]iron Hexafluorophosphate (**4b**): To a solution of $[Cp(CO)_2Fe(C(OMe)Ph)^+][PF_6^-]$[23] (780 mg, 1.76 mmol) in CH_2Cl_2 (15 ml) a solution of glycine *tert*-butyl ester (231 mg, 1 equiv.) in 5 ml of CH_2Cl_2 was added. After having been stirred for 15 min, the reaction mixture was diluted with petroleum ether/ether (120 ml, 5:1) and stored at –18°C overnight. Work-up as usual afforded 649 mg (68%) of yellow crystalline **4b**, m.p. 130–132°C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.60, 9.91* (s, 1H, NH), 7.43–7.29 (m, 3H, C_6H_5), 6.86–6.83 (d, *J* = 6.7 Hz, 2H, C_6H_5), 5.30, 5.03* (s, 5H, C_5H_5), 4.72*, 4.12 (s, 2H, CH_2), 1.51*, 1.39 [s, 9H, C(CH_3)$_3$]. – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 7.49–7.38 (m, 3H, C_6H_5), 7.38–7.25*, 6.99–6.96 (d, 2H, C_6H_5), 5.58*, 5.52 (s, 5H, C_5H_5), 4.70*, 4.12 (s, 2H, CH_2), 1.49*, 1.38 [s, 9H, C(CH_3)$_3$]. – ^{1}H NMR (200 MHz, CD_3NO_2, ratio of isomers 72:28): δ = 10.37 (s, 1H, CHN), 7.54–7.03 (m, 5H, C_6H_5), 5.50*, 5.42 (s, 5H, C_5H_5), 4.84*, 4.20 (s, 2H, CH_2), 1.53*, 1.44 [s, 9H, C(CH_3)$_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 257.4, 254.7* (Fe=C), 209.5*, 209.4 (CO), 166.18*, 165.4 (CO_2tBu), 151.6*, 147.4 (C-*ipso*, C_6H_5), 131.3*, 129.4, 124.0*, 120.4, 87.3*, 87.2 (C_5H_5), 84.9*, 84.1 (CH_2), 54.8*, 53.0 [C(CH_3)$_3$], 27.8 [C(CH_3)$_3$]. – IR (CH_2Cl_2): ṽ = 2057, 2012 (CO), 1739 (CO_2tBu). – IR (KBr): ṽ = 3351, 3284 (NH), 2055, 2011 (CO), 1756, 1738 (CO_2tBu), 1567 (C=N). – $C_{20}H_{22}F_6FeNO_4P$ (541.1): calcd. C 44.39, H 4.10, N 2.59; found C 44.35, H 4.15, N 2.60.

(Anilinophenylcarbene)dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate (**4c**): To a solution of $[Cp(CO)_2Fe(C(OMe)Ph)^+][PF_6^-]$[23] (442 mg, 1 mmol) in 30 ml of CH_2Cl_2 a solution of aniline (93 mg, 1 equiv.) in 10 ml of CH_2Cl_2 was added. After having been stirred for 10 min, the reaction mixture was diluted with ether (150 ml). Isolation of the precipitate yielded 435 mg (87%) of **4c** as a yellow solid, m.p. 198–200°C (dec.). – ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 13.74 (s, 1H, NH), 7.62–6.97 (m, 5H, C_6H_5), 5.63, 5.20* (s, 5H, C_5H_5). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3310 (NH), 2057, 2013 (CO). – IR (KBr): $\tilde{\nu}$ = 3310 (NH), 2059, 2017 (CO), 1530 (C=N). – $C_{20}H_{16}F_6FeNO_2P$ (503.2): calcd. C 47.74, H 3.21, N 2.78; found C 47.66, H 3.11, N 2.85.

(Anilinomethylcarbene)dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate (**4d**): To a solution of **2d** $[Cp(CO)_2Fe(C(OMe)Me)^+][PF_6^-]$[23] (290 mg, 0.8 mmol) in 6 ml of CH_2Cl_2 aniline (70 µl, 1 equiv.) was added. After having been stirred for 2 h (IR monitoring), the reaction mixture was added to ether (50 ml) by means of a cannula to precipitate **4d** as a yellow solid. This solid was isolated according to the general work-up procedure to afford 320 mg (91%), m.p. 167°C (dec.). – ^1H NMR (200 MHz, CD_3NO_2): δ = 11.59 (s, 1H, NH), 7.61–7.53 (m, 3H, C_6H_5), 7.35–7.30 (m, 2H, C_6H_5), 5.39 (s, 5H, C_6H_5), 2.82 (s, 3H, CH_3). – ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 13.30 (s, 1H, NH), 7.56–7.36 (m, 5H, C_6H_5), 5.48, 5.36* (s, 5H, C_5H_5), 2.93*, 2.69 (s, 3H, CH_3). – ^1H NMR (200 MHz, [D]TFA): δ = 7.61 (s br. 3H, C_6H_5), 7.24 (s br, 2H, C_6H_5), 5.36 (s, 5H, C_5H_5), 3.62 (s, 3H, CH_3). – ^{13}C NMR (50.3 MHz, CD_3NO_2): δ = 262.9 (Fe=C), 211.9 (CO), 139.6 (C-*ipso*, C_6H_5), 130.7, 130.6, 126.0 (C_6H_5), 88.2 (C_5H_5), 39.7 (CH_3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3296 (NH), 2055, 2007 (CO). – IR (KBr): $\tilde{\nu}$ = 3323 (NH), 2060, 2002 (CO), 1533 (C=N). – $C_{15}H_{14}F_6FeNO_2P$ (441.1): calcd. C 40.82, H 3.20, N 3.18; found C 41.04, H 3.19, N 3.24.

[Anilino(1-methylethenyl)carbene]dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate (**4e**): To a solution of **2e** (400 mg, 0.98 mmol) in 20 ml of CH_2Cl_2 neat aniline (89 µl, 1 equiv.) was added. The reaction mixture was stirred for 30 min (IR monitoring), then diluted with ether (50 ml) to precipitate **4e** as a yellow solid which was isolated according to the general work-up procedure: 355 mg (77%), m.p. 158–160°C (dec.). – ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 13.45 (s, 1H, NH), 7.45–7.13 (m, 5H, C_6H_5), 5.61, 5.23* (s, 5H, C_5H_5), 5.22*, 5.18*, 4.93, 4.73 (s, 2H, $=CH_2$), 2.08*, 1.74 (s, 3H, CH_3). – ^{13}C NMR (100.6 MHz, [D$_6$]DMSO), major isomer: δ = 255.1 (Fe=C), 211.3 (CO), 151.9 (=C), 139.9, 129.0, 128.8, 124.8, 110.6 ($=CH_2$), 87.6 (C_5H_5), 19.8 (CH_3). – IR (KBr): $\tilde{\nu}$ = 3312 (NH), 2061, 2007 (CO), 1527 (C=N). – $C_{17}H_{16}F_6FeNO_2P$ (467.1): FD, *m/z* (%): 322.1 (100) [$M^+ - PF_6^-$].

[Anilino(2-methoxy-2-phenylethenyl)carbene]dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate (**5a**): To a solution of **2b** (452 mg, 0.97 mmol) in CH_2Cl_2 (30 ml) a solution of aniline (90 mg, 1 equiv.) in 10 ml of CH_2Cl_2 was added. After the mixture had been stirred for 5 min, IR monitoring indicated complete consumption of the starting material. The reaction mixture was then added dropwise to ether (200 ml) by means of a cannula, and the solution was stored at –18°C overnight to yield 402 mg (74%) of yellow crystalline **5a** after the general work-up procedure, m.p. 183–184°C (dec.). – ^1H NMR (200 MHz, CD_3NO_2): δ = 10.95 (s, 1H, NH), 7.42–7.05 (m, 10H, C_6H_5), 6.52 (s, 1H, =CH), 5.38 (s, 5H, C_5H_5), 4.53 (s, 3H, OCH_3). – ^1H NMR (200 MHz, $CDCl_3$): δ = 10.75 (s, 1H, NH), 7.38–7.03 (m, 10H, C_6H_5), 6.21 (s, 1H, $=CH_2$), 5.23 (s, 5H, C_5H_5), 4.46 (s, 3H, OCH_3). – ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 11.33 (s, 1H, NH), 7.48 (br. s, 10H, C_6H_5), 6.39 (s, 1H, =CH), 5.46 (br. s, 5H, C_5H_5), 4.30–4.00 and 3.95–3.60 (br. s, 3H, OCH_3). – ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 252 (br.) and 255 (br., Fe=C), 212.1 (CO), 156 (br.) and 158 (br., =CH), 137.5, 134.6 (br.), 130.6 (br.), 128.8, 128.3, 128.0, 126.9, 124.6 (br.), 118.9 (br.) (C_6H_5), 87.3 (C_5H_5), 64.5 (br.) and 63.5 (br., OCH_3). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 253.2 (Fe=C), 211.9 (CO), 157.1, 137.0, 133.5, 131.2, 129.3, 129.2, 128.9, 127.3, 124.8, 120.9, 87.3 (C_5H_5), 65.9 (OCH_3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3312 (NH), 2043, 1996 (CO). – IR (KBr): $\tilde{\nu}$ = 3320, 3124 (NH), 2044, 1992 (CO), 1551, 1518 (C=N), 846.0 (PF_6^-). – $C_{23}H_{20}F_6FeNO_3P$ (559.2): calcd. C 49.40, H 3.60, N 2.50; found C 49.61, H 3.72, N 2.65.

[Anilino(2-methoxy-1-propenyl)carbene]dicarbonyl(cyclopentadienyl)iron Hexafluorophosphate (**5b**): To a solution of **2c** (500 mg, 1.24 mmol) in CH_2Cl_2 (13 ml) a solution of aniline (116 mg, 1 equiv.) in 4 ml of CH_2Cl_2 was added. The reaction mixture was stirred for 90 min (IR monitoring) and then diluted with ether (20 ml) to precipitate **5b** as a yellow solid isolated according to the general work-up procedure: 542 mg (88%), m.p. 170°C (dec.). – ^1H NMR (200 MHz, [D$_6$]DMSO, 1:1 mixture of isomers; ^{i}: minor component): δ = 11.29, 11.08^+ (s, 1H, NH), 7.51–7.28 (m, 5H, C_6H_5), 6.31, 6.20^+ (s, 1H, =CH), 5.46, 5.33^+ (s, 5H, C_5H_5), 4.22, 4.14^+ (s, 3H, OCH_3), 2.46, 2.05^+ (s, 3H, CH_3). – ^1H NMR (200 MHz, CD_3NO_2): δ = 10.99 (s, 1H, NH), 7.56–7.28 (m, 5H, C_6H_5), 6.36 (s, 1H, =CH), 5.33 (s, 5H, C_5H_5), 4.40 (s, 3H, OCH_3), 2.11 (s, 1H, CH_3). – ^{13}C NMR (50.3 MHz, CD_3NO_2): δ = 250.3 (Fe=C), 213.5 (CO), 162.17, 137.4, 130.6, 129.6, 126.6, 121.5, 120.6, 88.3 (C_5H_5), 65.8 (OCH_3), 20.9 (CH_3). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2043, 1995 (CO), 1568, 1520 (C=N). – IR (KBr): $\tilde{\nu}$ = 3306, 3125

Table 3. Crystal and refinement data for aminocarbene complexes **3e** and **3f**

	3e	**3f**
Emp. formula	$C_{20}H_{22}F_6FeNO_2PSi$	$C_{19}H_{20}F_6FeNO_2PSi$
Mol. mass	537.29 gmol^{-1}	523.30 gmol^{-1}
Cryst. size [mm^3]	0.13 × 0.38 × 0.82	0.06 × 0.10 × 0.64
Linear absorption coefficient	µ = 6.47 mm^{-1}; correction of absorption using ϕ SCANS (Cu-K_α; λ = 1.5418 Å)	µ = 6.67 mm^{-1}; correction of absorption using DIFABS[24] (Cu-K_α; λ = 1.5418 Å)
Range of transmission	T_{min} = 0.21, T_{max} = 1.0	T_{min} = 0.35, T_{max} = 1.0
Space group	$P2_1/c$ (monoclinic)	$Pca2_1$ (orthorhombic)
cell constants[25]	a = 13.238(2) Å b = 16.086(1) Å c = 13.064(2) Å β = 115.965(10)°; calculated from 50 reflections (60° < Θ < 73°)	a = 24.415(2) Å b = 6.634(1) Å c = 14.9478(5) Å calculated from 32 reflections (60° < Θ < 73°)
Cell volume	V = 2504.7(5) Å^3, Z = 4 $F(000)$ = 1096	V = 2420.9(5) Å^3, Z = 4 $F(000)$ = 1064
Density	d_{calc} = 1.427 gcm^{-3}	d_{calc} = 1.436 gcm^{-3}
Scan type	ω/2Θ	ω/2Θ
Range for data collection	2.4° ≤ Θ ≤ 75.0° –16 ≤ h ≤ 16 –20 ≤ k ≤ 0; –16 ≤ l ≤ 16	1.5° ≤ Θ ≤ 75.0° 0 ≤ h ≤ 30 0 ≤ k ≤ 8; 0 ≤ l ≤ 18
Collcd. reflexions	11139	5643 (with Friedel pairs)
Unique reflexions	5139 (R_{int} = 0.0771)	4884 (R_{int} = 0.0315)
Obsd. reflexions	2769 ($\|F\|/\sigma(F) > 4.0$)	3781 ($\|F\|/\sigma(F) > 4.0$)
Structure solution	program: SIR92 (direct method)	program: SIR92 (direct method)
Structure refinement	SHELXL-93	SHELXL-93
Parameters refined	344	308
Weights	$w = 1/[\sigma^2(F_o^2)+(0.0995*P)^2+1.60*P]$, $P = (Max(F_o^2,0)+2*F_c^2)/3$	$w = 1/[\sigma^2(F_o^2)+(0.485*P)^2+1.05*P]$ $P = (Max(F_o^2,0)+2*F_c^2)/3$
R values (refinement on F^2)	$wR2$ = 0.2245 ($R1$=0.0616 for obsd. rflns.)	$wR2$ = 0.1149 ($R1$=0.0433 for obsd. rflns.)
Goodness offit	S = 1.046 extinction: g = 0.0006(2)	S = 1.047 Flack parameter: x = 0.005(5)
max, min peak in diff. Fourier map;	0.72, –0.52 eÅ^{-3}	0.27, –0.40 eÅ^{-3}
max shift of parameters	0.000* e.s.d	0.000* e.s.d

(NH), 2038, 1988 (CO), 1567, 1520 (C=N). – $C_{18}H_{18}F_6FeNO_3P$ (497.15): FD, *m/z* (%): 352.0 (100) [$M^+ - PF_6^-$].

X-ray Structure Determination: For the examinations and data collections an Enraf-Nonius CAD4 diffractometer was employed at $T = 296$ K by using a graphite-monochromated Cu-K_α radiation (scan type: $\omega/2\Theta$). The structures were solved by direct methods (SIR 92). The structure was refined by means of the full-matrix least-squares procedure using SHELXL 93. Lorentz and polarization corrections were applied to the data. All non-hydrogen atoms were refined anisotropically. For **3e** a riding model starting from calculated positions for the hydrogen atoms was employed, except for H9. The PF_6^- counterion is disordered. For **3f** all hydrogen (except H7) were refined by an analogous riding model. In **3f** the trimethylsilyl group is disordered[26].

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[26] 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-405157 for **3e** and -405156 for **3f**.

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