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C_2-Bridged Titanocene−Ferrocenyl Complexes: Synthesis, Reaction Chemistry, and Electrochemical Behavior

Stephan Back,[†] Hans Pritzkow,[‡] and Heinrich Lang[*,†]

Institut für Chemie, Lehrstuhl Anorganische Chemie, Technische Universität Chemnitz, Strasse der Nationen 62, D-09111 Chemnitz, Germany, and Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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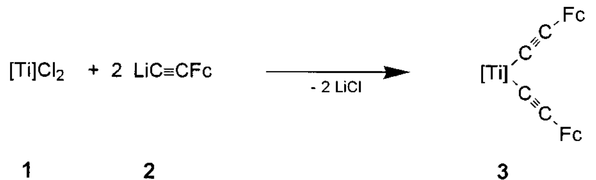
LiC≡CFc (**2**; Fc = $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe$) reacts with $[Ti]Cl_2$ (**1a**) ([Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$) in a 2:1 molar ratio to produce the C_2-bridged titanocene−ferrocenyl complex $[Ti](C{\equiv}CFc)_2$ (**3**). While treatment of heterotrinuclear **3** with $Ni(CO)_4$ (**4**) affords the heterotetranuclear tweezer complex $\{[Ti](C{\equiv}CFc)_2\}Ni(CO)$ (**5**), reaction of **3** with $NiCl_2$ (**6**) yields Fc−C≡CC≡C−Fc (**7**) along with $[Ti]Cl_2$ (**1a**) and Ni^0 in a redox reaction. **7** can also be synthesized in the chemical oxidation of **3** with 2 equiv of $AgPF_6$. The electrochemical behavior of compounds **3** and **5** is discussed. The X-ray structure analysis of complex **3** is reported.

Introduction

With respect to new material properties, a new class of compounds has attracted growing interest, in which linear carbon chains C_n (n = 1, 2, 3, ...) span different organometallic building blocks.[1−3] We discuss here the synthesis and chemical behavior of a heterometallic complex in which the early-transition-metal fragment [Ti] ([Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$) and the late-transition-metal entity Fc (Fc = $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe$) are linked by an acetylide bridge.

Results and Discussion

The titanocene dichloride $[Ti]Cl_2$ (**1a**; [Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$)[4] reacted at 0 °C in diethyl ether with 2 mol equiv of LiC≡CFc (**2**;[5] Fc = $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe$) to yield deep violet $[Ti](C{\equiv}CFc)_2$ (**3**) in 61% yield (eq 1).



1 2 3 (1)

The C_2-bridged titanocene−ferrocenyl complex **3** forms (after appropriate purification) dark violet crystals,

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[*] To whom correspondence should be addressed. E-mail: heinrich.lang@chemie.tu-chemnitz.de.

[†] Technische Universität Chemnitz.

[‡] Ruprecht-Karls-Universität Heidelberg.

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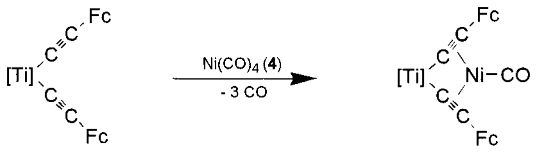
which are stable in the solid state for a long period of time. Solid heterometallic **3** can be handled in air for short periods, while it starts to decompose in solution on exposure to air.

Addition of $Ni(CO)_4$ (**4**) to complex **3** in an equimolar ratio in toluene at 25 °C results in the formation of the heterotetranuclear tweezer compound $\{[Ti](C{\equiv}CFc)_2\}Ni(CO)$ (**5**) in 75% yield (eq 2). This reaction can easily be monitored by an eye-catching color change from violet to brown.

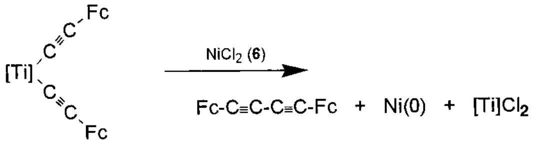


3 **5**

(2)

Compound **5** is soluble in most of the common organic solvents and can be precipitated as a brown solid by cooling a toluene/*n*-pentane solution to −40 °C. Compound **5** features a low-valent Ni(CO) entity with a nickel atom in a trigonal-planar environment.[6,7] Compounds of the type $\{[Ti](C{\equiv}CR)_2\}NiL$ (R = singly bonded organic ligand; L = two-electron-donor ligand) represent well-studied and -characterized molecules.[6,7]

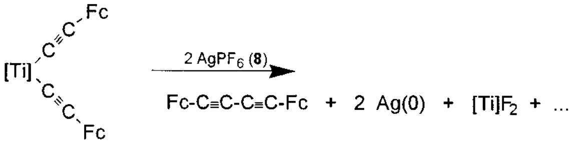
The change from the d^{10} nickel atom in compound **5** to the d^8 configured Ni^{2+} ion in $NiCl_2$ results in a redox-type reaction with the formation of $[Ti]Cl_2$ (**1a**), $Fc{-}C{\equiv}CC{\equiv}C{-}Fc$ (**7**), and Ni^0 (eq 3).



(3)

3 **7** **1a**

The latter reaction is strongly solvent dependent: no reaction takes place in diethyl ether or tetrahydrofuran as solvent, whereas in acetone compounds **1a** and **7** are formed along with Ni(0). The preparation of the C_4-bridged compound **7** also can be effected in 85% yield by the chemical oxidation of the titanocene−ferrocenyl complex **3** with 2 equiv of $AgPF_6$ in methylene dichloride or tetrahydrofuran as solvents at 25 °C (eq 4).



(4)

3

7 **1b**

Independently, compound **7** could be synthesized in an oxidative Glaser coupling reaction. The C_4-bridged ferrocenyl compound **7** can be considered as a coupling product of two $Fc{-}C{\equiv}C$ units. The all-carbon butadiynyl bridge of 1,4-diferrocenylbutadiyne (**7**) could be synthesized independently by starting out from other $Fc{-}C{\equiv}C$-containing molecules.[8]

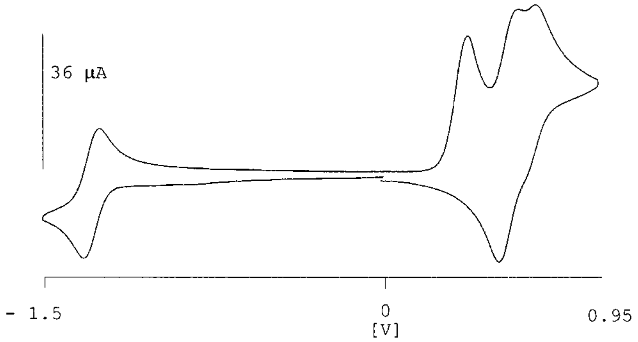


Figure 1. Cyclic voltammogram of the heteronuclear compound **3**: $c = 1 \times 10^{-3}$ mol dm^{-3} in acetonitrile in the presence of $(NBu_4)(PF_6)$ ($c = 0.1$ mol dm^{-3}) at 25 °C under Ar; scan rate 200 mV s^{-1}; potentials referenced to FcH/FcH$^+$ ($E_{1/2}$ = +390 mV).

Characteristic for d^0 titanium centers in bis(alkynyl)titanocenes, *e.g.* in $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ ($E_{1/2} = -1.17$ V (ΔE = 107 mV)), is the observation of only one reversible reduction wave in the cyclic voltammogram, assigned to the Ti(IV)/Ti(III) redox potential.[9] Similar observations have been made for the titanocene−ferrocenyl complex **3**: $E_{1/2} = -1.28$ V (ΔE = 73 mV) (Figure 1).

In addition to the reversible reduction wave, a total of three new oxidation waves has been observed at +0.37, +0.59, and +0.67 V for compound **3**, respectively, the last two of those being reversible (Figure 1). By comparison with authentic $Fc{-}C{\equiv}CC{\equiv}C{-}Fc$ (**7**),[10] the waves at +0.59 and +0.67 V can be assigned to the reversible Fe(II)/Fe(III) oxidation process of the coupling product **7** formed under the conditions of the measurement. The irreversible peak at +0.37 V corresponds to a two-electron-oxidation process, indicating the electrochemical independence of the two ferrocenyl units present in compound **3**. This assignment is in conformity with the total current: the Fe(II)/Fe(III) waves were about 4 times as large as for the one-electron reduction Ti(IV)/Ti(III). The disappearence of the oxidation peak at +0.37 V (**3**) and the appearance of the two redox waves with $E_{1/2}$ = +0.59 and +0.67 V suggests that the oxidative coupling product **7** is formed instantaneously after oxidation of the two ferrocenyl entities in compound **3** has taken place.

However, the oxidatively induced coupling of the two $Fc{-}C{\equiv}C$ moieties to yield $Fc{-}C{\equiv}CC{\equiv}C{-}Fc$ (**7**) is not even averted when both alkynyl ligands are η^2-coordinated to *e.g.* a low-valent Ni(CO) building block as given in compound **5**. Here, it is found that next to the redox

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Table 1. Crystal and Intensity Collection Data for Compound 3

empirical formula	$C_{40}H_{44}Fe_2Si_2Ti{\cdot}{}^1/_2C_7H_8{\cdot}{}^1/_2C_4H_8O$
fw	822.65
cryst syst	monoclinic
space group	*C*2/*c*
a, Å	15.675(10)
b, Å	33.00(3)
c, Å	16.71(2)
β, deg	108.10(6)
V, Å^3	8217(11)
Z	8
D_{calcd}, g cm^{-3}	1.330
temp, K	203
linear abs coeff, cm^{-1}	9.77
transmissn factor	0.673–1.000
cryst dimens, mm	0.5 × 0.45 × 0.2
index ranges	$-17 \le h \le 16$
	$0 \le k \le 36$
	$0 \le l \le 18$
total no. of rflns measd	5733
no. of unique rflns	5733
no. of obsd rflns ($I \ge 2\sigma(I)$)	3163
least-squares params	472
R1 ($I \ge 2\sigma(I)$)	0.0967
wR2 (all data)	0.2465
goodness of fit	1.106
max peak in final Fourier map, e Å^{-3}	0.836
min peak in final Fourier map, e Å^{-3}	−0.745

wave at $E_{1/2} = -1.83$ V ($\Delta E = 84$ mV) for comparison, $E_{1/2} = -1.28$ V for (η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CFc)$_2$ (**3**)) during the oxidative scan three oxidative waves at $E = +0.22$, $+0.59$, and $+0.67$ V are observed. While the first oxidation wave is irreversible, the last two are reversible and can be assigned to the oxidatively induced coupling of two Fc–C≡C units to afford compound **7**.

Furthermore, it should be noted that the reductive potential of Ti(IV)/Ti(III) is significantly shifted to a more negative value (for comparison: (η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$, $E_{1/2} = -1.17$ V; **3**, $E_{1/2} = -1.28$ V; **5**, $E_{1/2} = -1.83$ V).[9]

In order to establish the solid-state structure of compound **3**, an X-ray diffraction study has been carried out (see Table 1 for details) on a single crystal (Figure 2), which was obtained by cooling a toluene/tetrahydrofuran (3:1) solution of **3** to −40 °C.

Compound **3** crystallizes in the monoclinic space group *C*2/*c* together with one molecule of toluene and tetrahydrofuran per two molecules of **3**. The solvent molecules are disordered. The main characteristics of molecule **3** are similar to those of the well-known bis(alkynyl)titanocenes (η^5-$C_5H_4R^1$)$_2$Ti(C≡CR^2)$_2$ (R^1, R^2 = singly bonded organic ligand).[11] As in the latter compounds, the C_2-bridged titanocene–ferrocenyl complex **3** exhibits linear Ti–C≡C–Fc units (Figure 2). The interatomic carbon–carbon distances of the C_2 building blocks in compound **3** (C(1)–C(2) = 1.227(13) Å, C(3)–C(4) = 1.21(2) Å) correspond to typical C≡C separations found in organic as well as organometallic alkynes.[6a,12,13] The Ti(1)–C(1) and Ti(1)–C(3) distances at 2.104(10) and 2.088(13) Å in **3** are similar to those found in (η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CR)$_2$ (R = C_6H_5, 2.096(5) Å;[14] R = SiMe$_3$, 2.124(5), 2.103(5) Å[11a]). In comparison to titanium–carbon bonds, involving sp^3- or sp^2-hybridized carbon atoms, these bond lengths are remarkably shorter, indicating some π-conjugation between the d^0 early-transition-metal moiety [Ti] and the π-system of the alkynyl ligands Fc–C≡C.[15] As a consequence of the latter, the bite angle of the C(1)–Ti(1)–C(3) entity (98.4(4)°) is significantly larger than that found in metallocene complexes, which contain Ti–C(sp^3) σ-bonds.[15] The ferrocenyl ligands Fc are oriented in a fashion similar to that found in (η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CC≡CFc)$_2$.[16]

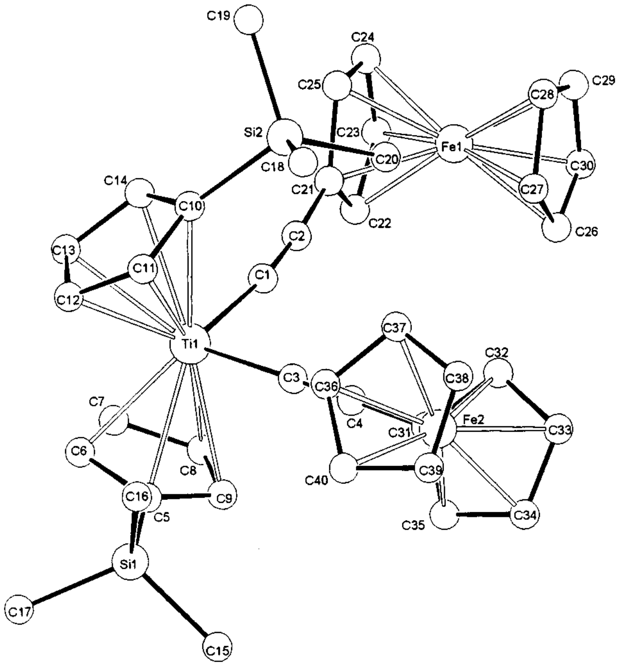

Figure 2. Molecular geometry and atom numbering scheme for the heteronuclear complex **3**. Important selected interatomic distances (Å) and angles (deg) are as follows: Ti(1)–C(1), 2.104(10); Ti(1)–C(3), 2.088(13); C(1)–C(2), 1.227(13); C(3)–C(4), 1.21(2); D(1)–Ti(1), 2.062; D(2)–Ti(1), 2.050; D(3)–Fe(1), 1.638; D(4)–Fe(1), 1.641; D(5)–Fe(2), 1.641; D(6)–Fe(2), 1.648; Ti(1)–C(1)–C(2), 172.8(9); Ti(1)–C(3)–C(4), 178.7(9); C(1)–Ti(1)–C(3), 98.8(4); C(1)–C(2)–C(21), 174.8(9); C(3)–C(4)–C(31), 177.4(9); D(1)–Ti(1)–D(2), 131(1). D(1)–D(6) = centroids of the cyclopentadienyl ligands.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of compounds **3** and **5** consist of sharp and well-resolved signals for each of the organic groupings present. Most significant, with respect to the chemical shift of the resonance signals for the sp-hybridized C_α and C_β carbon atoms, is the low-field shift of the C_α carbon atoms, whereas the resonance

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signals of the C_β carbon atoms are shifted to higher field in compound **5** as compared with **3** (**3**, $\delta(C_\alpha)$ 153.7, $\delta(C_\beta)$ 129.8; **5**, $\delta(C_\alpha)$ 184.9, $\delta(C_\beta)$ 119.7). Similar observations were generally made on changing from bis(alkynyl)titanocenes to organometallic π-tweezer compounds of the type $\{[Ti](C{\equiv}CR)_2\}MX$ ($[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; R = singly bonded organic ligand; MX = low-valent transition-metal fragment).[17] The η^2-coordination of both $Fc{-}C{\equiv}C$ ligands to the Ni(CO) building block in compound **5** is clearly evidenced by the IR spectra: the $C{\equiv}C$ stretching vibration at 2055 cm^{-1} in **3** is shifted to 1876 cm^{-1} in **5**, thus indicating a bond weakening of the $C{\equiv}C$ triple bonds, which is typical for changes from noncoordinated to η^2-coordinated alkynyl ligands.[17] The $\nu(CO)$ band in **5** is observed at 2008 cm^{-1} (for comparison: $\nu(CO)$ in $Ni(CO)_4$ is 2052 cm^{-1}).[6a]

Experimental Section

General Methods. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were purified by distillation from sodium/benzophenone ketyl; *n*-pentane was purified by distillation from calcium hydride. Infrared spectra were obtained with a Perkin-Elmer 983G spectrometer. ^1H NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.132 MHz in the Fourier transform mode; ^{13}C NMR spectra were recorded at 50.323 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal. FD, EI, and FAB mass spectra were recorded on a Finnigan 8400 mass spectrometer operating in the positive-ion mode. Melting points were determined with use of analytically pure samples, which were sealed in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Organisch-Chemisches Institut der Universität Heidelberg. Electrochemical measurements were made with cyclic voltammetry in a solution of $[N(n\text{-}Bu)_4]PF_6$ (0.1 mol dm^{-3}) in acetonitrile at 25 °C, using a standard three-electrode cell on a Princeton Applied Research EG&G 273 analyzer. All potentials were referenced to the ferrocene–ferrocenium couple, which had a potential of +0.39 V vs Hg/Hg_2Cl_2 in this medium.

(A) Synthesis of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CFc)_2$ (3). To a suspension of 0.190 g (0.47 mmol) of **1a**[4] in 20 mL of diethyl ether at −78 °C was added 2 equiv (0.205 g, 0.95 mmol) of $LiC{\equiv}CFc$[5] (**2**). The solution was stirred for 2 h at 25 °C. In the course of the reaction the formerly red solution turns deep violet. After evaporation of all volatiles *in vacuo*, the residue was extracted first with 30 mL of ^{n}pentane and then with 30 mL of *n*-pentane/diethyl ether (1:1). After filtration through a pad of Celite, the *n*-pentane/diethyl ether fraction was concentrated to 10 mL and cooled to −40 °C. Compound **3** (215 mg, 0.29 mmol, 61% based on **1a**) crystallized as a deep violet powder. Mp: 134 °C. IR (KBr): 2055 cm^{-1} (m) ($\nu_{C\equiv CTi}$). ^1H NMR ($CDCl_3$): δ 0.43 (s, 18 H, Si*Me*$_3$), 4.17 (bs, 4 H, $C_5H_4C{\equiv}C$), 4.19 (s, 10 H, C_5H_5), 4.27 (bs, 4 H, $C_5H_4C{\equiv}C$), 6.19 (bs, 4 H, $C_5H_4SiMe_3$), 6.69 (bs, 4 H, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.3 (Si*Me*$_3$), 68.0 ($^iC/C_5H_4C{\equiv}C$), 68.3 ($C_5H_4C{\equiv}C$), 69.4 (C_5H_5), 70.4 ($C_5H_4C{\equiv}C$), 112.3 ($C_5H_4SiMe_3$), 121.8 ($C_5H_4SiMe_3$), 123.3 ($^iC/C_5H_4SiMe_3$), 129.8 ($TiC{\equiv}C$), 153.7 ($TiC{\equiv}C$). CV ($CH_3C{\equiv}N$; 0.1 M $N(n\text{-}Bu)_4PF_6$; 25 °C; scan rate 200 mV s^{-1}): $E_{1/2} = -1.28$ V ($\Delta E = 73$ mV), $E_{1/2} = +0.37$ V, $E_{1/2} = +0.59$ V, $E_{1/2} = 0.67$ V. MS (FAB, *m/z*, relative intensity): 741 (30) M^+, 531 (100) $M^+ - C_2Fc$, 418 (50) $C_4Fc_2^+$. Anal. Calcd for $C_{40}H_{44}Fe_2Si_2Ti$ (740.53): C, 64.88; H, 5.99. Found: C, 65.08; H, 6.47.

Structure Determination and Refinement of Compound 3. X-ray data were collected on a Siemens-Stoe AED2 diffractometer (Mo Kα radiation, ω scan, 203 K). Accurate unit-cell parameters and an orientation matrix were derived from the setting angles of 24 well-centered reflections in the range $29° \le 2\theta \le 31°$. Data were corrected for Lorentz–polarization and absorption effects (ψ scans). The structure was solved by direct methods and subsequent difference Fourier techniques (SHELXS 86[18]). Refinement on F^2 with all measured reflections was carried out by full-matrix least-squares techniques (SHELXL 93[19]). Hydrogen atoms were included in calculated positions (riding model). Non-hydrogen atoms were refined with anisotropic displacement parameters.

Crystal data and numerical details of structure determination and refinement are collected in Table 1.

(B) Synthesis of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CFc)_2]Ni(CO)$ (5). To a solution of 0.200 g (0.27 mmol) of **3** in 40 mL of toluene was added 0.330 g (1.93 mmol) of $Ni(CO)_4$ at 25 °C. After the mixture was stirred for 1 h, all volatiles were evaporated, and to the resulting brown residue was added 30 mL of *n*-pentane; this solution was then filtered through a pad of Celite. Concentration of the *n*-pentane solution and cooling to −40 °C yielded **5** (160 mg, 0.2 mmol, 73% based on **3**) as a brown solid. Mp: 100 °C dec. IR (KBr): 1876 cm^{-1} (m) ($\nu_{C\equiv CTi}$), 2008 cm^{-1} (s) (ν_{CO}). ^1H NMR ($CDCl_3$): δ 0.36 (s, 18 H, Si*Me*$_3$), 4.21 (s, 10 H, C_5H_5), 4.30 (pt, $J_{HH} = 1.5$ Hz, 4 H, $C_5H_4C{\equiv}C$), 4.66 (pt, $J_{HH} = 1.5$ Hz, 4 H, $C_5H_4C{\equiv}C$), 5.19 (pt, $J_{HH} = 1.8$ Hz, 4 H, $C_5H_4SiMe_3$), 5.77 (pt, 4 H, $J_{HH} = 1.8$ Hz, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.4 (Si*Me*$_3$), 68.3 ($C_5H_4C{\equiv}C$), 69.5 (C_5H_5), 70.6 ($C_5H_4C{\equiv}C$), 74.1 ($^iC/C_5H_4C{\equiv}C$), 107.7 ($C_5H_4SiMe_3$), 111.6 ($C_5H_4SiMe_3$), 113.0 ($^iC/C_5H_4SiMe_3$), 119.7 ($TiC{\equiv}C$), 184.9 ($TiC{\equiv}C$), 202.2 (*C*O). CV ($CH_3C{\equiv}N$; 0.1 M $N(n\text{-}Bu)_4PF_6$; 25 °C; scan rate 200 mV s^{-1}): $E_{1/2} = -1.83$ V ($\Delta E = 84$ mV), $E_{1/2} = +0.22$ V, $E_{1/2} = +0.59$ V, $E_{1/2} = 0.67$ V. MS (FD, *m/z*, relative intensity): 826 (30) M^+, 798 (100) $M^+ - CO$. Anal. Calcd for $C_{41}H_{44}Fe_2NiOTiSi_2$ (827.23): C, 59.53; H, 5.36. Found: C, 60.11; H, 5.51.

(C) Synthesis of $Fc{-}C{\equiv}CC{\equiv}C{-}Fc$ (7).[8] Method 1: Reaction of 3 with $NiCl_2$. To a suspension of 40 mg (0.28 mmol) of $NiCl_2$ in acetone was added 200 mg (0.27 mmol) of **3** in one portion at 25 °C. Within 1 h of stirring the reaction mixture turned red. Evaporation of all volatiles *in vacuo* gave a red residue, which was extracted with 40 mL of *n*-pentane and the extract filtered through a pad of Celite. Evaporation yielded **7** (40 mg, 0.19 mmol, 73% based on **3**).

Method 2: Reaction of 3 with $AgPF_6$. To a suspension of 0.145 g (0.56 mmol) of $AgPF_6$ in acetone was added 0.200 g (0.27 mmol) of **3** in one portion at 25 °C. After it was stirred for 1 h under the exclusion of light, the reaction mixture was worked up as described above. Yield: 170 mg (0.23 mmol, 85% based on **3**). The analytical and spectroscopic data of compound **7** are consistent with those for authentic **7** and are published in ref 8c–e.

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Supporting Information Available: Tables of crystal data collection and refinement details, positional and thermal parameters, and bond distances and angles and a figure giving an additional view of **3** (12 pages). Ordering information is given on any current masthead page.

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