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Synthesis, reaction chemistry and electrochemical behaviour of $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}CFc)_2$

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Abstract

$[Hf]Cl_2$ (**1**) $\{[Hf] = (\eta^5\text{-}C_5H_4SiMe_3)_2Hf\}$ reacts with 2.0 mol equiv of LiC≡CFc (**2**) $[Fc = (\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe]$ to produce $[Hf](C{\equiv}CFc)_2$ (**3**). Treatment of **3** with $Ni(CO)_4$; (**4**) affords $\{[Hf](C{\equiv}CFc)_2\}Ni(CO)$ (**5**). The electrochemical behaviour of **3** is discussed. The X-ray structure analysis of **3** is reported; **3** crystallizes in the orthorhombic space group Pnna with cell constants $a = 11.431(2)$, $b = 16.521(2)$, $c = 19.130(2)$ Å, $V = 3612.7(9)$ Å^3; and $Z = 4$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hafnocene; Ferrocene; Alkyne; Nickelcarbonyl

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1. Introduction

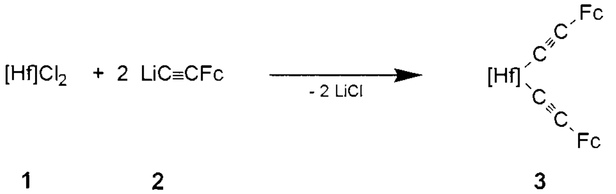
Transition metal complexes with linear π-conjugated organic systems, spanning different organometallic entities, e.g. $M\text{–}(C{\equiv}C)_n\text{–}M^1$ ($n = 1, 2, ...$; $M = M'$, $M \neq M'$) have been the subject of interest due to their potential as new materials with novel and interesting properties [1–3]. The interaction between two metal centres along a π-conjugated system has been demonstrated previously e.g. with Fc–C≡C–C≡C–Fc $[Fc = (\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe]$ ([4]d,e). The interaction between the two ferrocenyl entities is also noted when a late transition metal (e.g. Ru) is placed between the π-conjugated components, as it is found in Fc–C≡C–[Ru]–C≡C–Fc $\{[Ru] = Ru(dppm)_2$, dppm = bis(diphenylphosphino)-methane}. [3]p and q However, when the two FcC≡C entities are separated by an early transition metal moiety [Ti] $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti\}$ as in Fc–C≡C–[Ti]–C≡C–Fc, the interaction between the two ferrocenyl groups is minimized and therefore they become electrochemically independent [5].

In this study, we describe the synthesis, chemical behaviour, structure and bonding of the C_2-bridged hafnocene–ferrocenyl complex Fc–C≡C–[Hf]–C≡C–Fc $\{[Hf] = (\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}Hf\}$ in which two different metal complex fragments are attached to a C_2 building block.

2. Results and discussion

2.1. Synthesis of [Hf](C≡CFc)$_2$

$[Hf]Cl_2$ (**1**) $\{[Hf] = (\eta^5\text{-}C_5H_4SiMe_3)_2Hf\}$ [6] reacts with 2.0 mol equiv of LiC≡CFc (**2**) $[Fc = (\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe]$ [7] in diethyl ether at −78°C to produce $[Hf](C{\equiv}CFc)_2$ (**3**) in 72% isolated yield (Eq. 1)



1 **2** **3**

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Orange crystals of the mixed-valence hafnocene–ferrocenyl complex **3** were obtained by crystallization from diethyl ether solutions at −40°C. The crystals are stable for several weeks in the solid-state at low temperature. However, decomposition takes place readily at 25°C or on exposure to air. In solution, **3** begins to decompose within a few hours at 25°C.

2.1.1. Spectroscopy

In the IR spectrum, a distinct vibration is observed at 2066 cm^{-1}. This absorption is in a region typical for alkynyl-substituted titanocene, zirconocene and hafnocene compounds [8–14], and can be assigned to the $\nu_{C\equiv C}$, stretching vibration. This result corroborates with the formulation of **3** as a C_2-bridged transition metal complex.

The ^{1}H- and $^{13}C\{^1H\}$-NMR spectra of **3** consist of well-resolved resonance signals for each of the organic groups present. The most informative feature in the ^{1}H-NMR spectrum is the appearance of a AA′XX′ resonance pattern in a 1:1:1:1 ratio in the region of 4.1–6.6 ppm assigned to the cyclopentadienyl protons of the $C_5H_4SiMe_3$ and $C{\equiv}CC_5H_4$ groups. The C_5H_4 building block of the ferrocenyl moieties appears at higher field with a coupling constant of $J_{HH} = 1.7$ Hz, when compared with the appropriate titanocene fragments ($J_{HH} = 2.3$ Hz). The C_5H_5 entity of the Fc moieties is visible as a singlet at 4.20 ppm.

The $^{13}C\{^1H\}$-NMR resonance signals of the C_2-units could be clearly assigned to two singlets at 127.0 (HfC≡*C*) and 151.1 ppm (Hf*C*≡C). The chemical shifts are in accordance with alkynyl functionalized hafnocene species [8,13–16].

The EI mass spectrum of **3** confirms a C_2-bridged transition metal complex with the M^+ ion observed at $m/z = 872$ as its base peak. Other fragments that are observed include: $(\eta\text{-}C_5H_4SiMe_3)_2Hf^+$ ($m/z = 454$, rel. int. 70%), $C_4Fc_2^+$ ($m/z = 418$, ref. int. 30%) and C_2Fc^+ ($m/z = 210$, rel. int. 65%).

2.1.2. Electrochemical behaviour

Cyclovoltammetric analysis of **3** from 0 to −2.2 V is characterized by a reversible one-electron reduction wave at $E_{1/2} = -1.99$ V ($\Delta E = 87$ mV), which can be assigned to the Hf(IV)/Hf(III) redox potential (Fig. 1) [14,17].

From 0 to +0.85 V the cyclic voltammogram is dominated by a total of three oxidation waves at +0.42, +0.59 and +0.68 V, of which the two latter ones are reversible [$E_{1/2} = +0.55$ V ($\Delta E = 85$ mV) and $E_{1/2} = +0.66$ V ($\Delta E = 40$ mV)]. A similar electrochemical behaviour has been observed for the structural titanocene–ferrocenyl complex $[Ti](C{\equiv}CFc)_2\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti\}$ [5] in which, as well as in **3**, the two latter waves can be assigned to the reversible Fe(II)/Fe(III) oxidation process of Fc–C≡C–C≡C–Fc [4]d. This molecule is formed by the coupling of two FcC≡C units under the conditions of the measurement. The irreversible peak at +0.42 V corresponds to a 2-electron oxidation. This indicates the electrochemical independence of the two Fc groups in **3**. The disappearance of the oxidation wave at +0.42 V and the appearance of the two redox waves with $E_{1/2} = +0.55$ V and $E_{1/2} = +0.66$ V suggest that the oxidative coupling of FcC≡C to produce Fc–C≡C–C≡C–Fc occurs instantaneously after the oxidation of the two electrochemically independent ferrocenyl units in **3** occurred. This assignment is also supported by the measurement of the total current, which for the Fe(II)/Fe(III) redox potential is about four times larger than that of the one-electron reduction of Hf(IV) to Hf(III).

A comparison of the redox potentials of a series of related titanocene and hafnocene compounds shows that by changing from $[Ti]Cl_2$ to $[Ti](C{\equiv}CSiMe_3)_2$ and $[Ti](C{\equiv}CFc)_2$, the redox potential is shifted from $E_{1/2} = -0.75$ V in $[Ti]Cl_2$ to −1.17 V or even −1.28 V in the appropriate bis(alkynyl) titanocenes [5,16,17]. This strongly indicates that the electron density of the Ti(IV) center is significantly increased by replacing the chloride by the acetylide entities. Nevertheless, the redox potentials of the seemly hafnocene compounds are virtually unchanged ($[Hf]Cl_2$: $E_{1/2} = -1.89$ V, $[Hf](C{\equiv}CC_6H_5)2$: $E_{1/2} = -1.85$ V, $[Hf](C{\equiv}CFc)_2$: $E_{1/2} = -1.99$ V). But as in the related titanium complex, a shift of the Hf(IV)/Hf(III) redox potential to a more negative value can be observed when changing from $[Hf](C{\equiv}CC_6H_5)_2$ to $[Hf](C{\equiv}CFc)_2$. In conclusion, the ferrocenyl entities in both the titanocene and the hafnocene complexes can be considered as weak electron donating ligands through the C_2-entities.

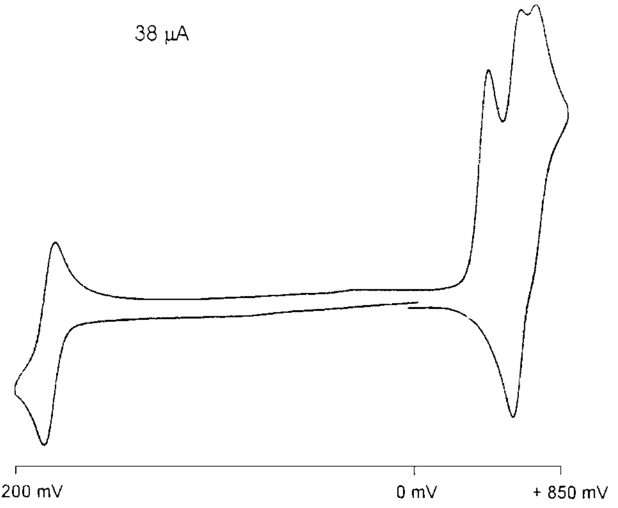


Fig. 1. Cyclic voltammogram of **3**; $c = 1 \cdot 10^{-3}$ mol dm^{-3} in acetonitrile in the presence of $(NBu_4)(PF_6)$ ($c = 0.1$ mol dm^{-3}) at 25°C under Ar; scan-rate 200 mV s^{-1}; potentials are referenced to FcH/FcH^+ ($E_{1/2} = +0.39$ V).

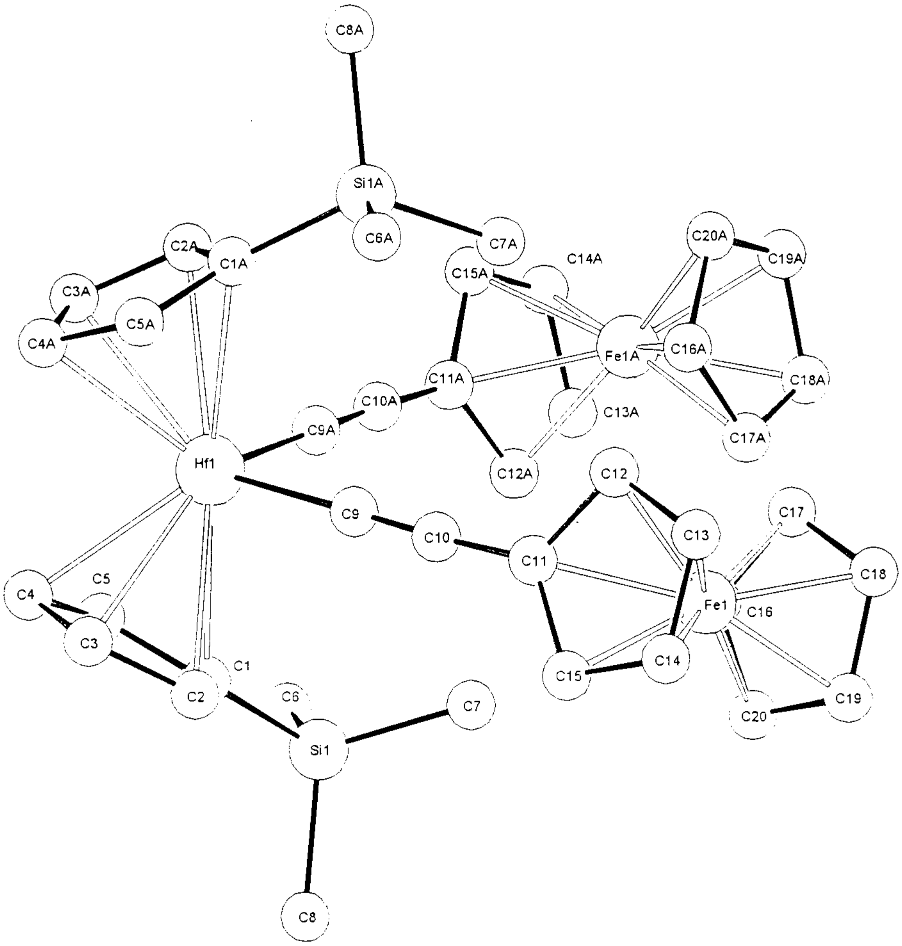


Fig. 2. Molecular geometry and atom numbering scheme of **3**.

2.1.3. X-ray diffraction study

The molecular structure of **3** has been established by a single crystal X-ray diffraction analysis. The structure of **3** is shown in Fig. 2. Selected geometrical details are listed in Table 1 and the crystallographic data are given in Table 2.

Table 1
Selected bond lengths (Å) and angles (°) for **3**

Bond Lengths	
Hf(1)–C(9)	2.217(6)
C(9)–C(10)	1.214(8)
C(10)–C(11)	1.429(8)
D(1)–Hf(1)[a]	2.191
D(2)–Fe(1)[a]	1.645
D(3)–Fe(1)[a]	1.652
Angles	
C(9A)–Hf(1)–C(9)	99.0(3)
Hf(1)–C(9)–C(10)	170.0(6)
C(9)–C(10)–C(11)	176.7(6)
D(1)–Hf(1)–D(1A)	125.5

[a] D(1)–D(3): centroids of the cyclopentadienyl ligands. Standard deviation in units of the last significant figure in parentheses.

Compound **3** crystallizes in the orthorhombic space group Pnna. The structure of **3** contains a crystallographic two-fold axis. The main characteristics of **3** in the solid-state are comparable with those of other known bis(alkynyl) metallocenes of general type (η^5-$C_5H_4R^1)_2M(C{\equiv}CR^2)_2$ M = Ti, Zr, Hf; R^1, R^2 = singly bonded organic ligand) [8]d, [3,10,18–21]. As in these compounds, the C_2-bridged hafnocene–ferrocenyl complex **3** exhibits almost linear Hf–C≡C–Fc units [Hf(1)–C(9)–C(10) 170.0(6)°, C(9)–C(10)–C(11) 176.7(6)°] (Table 1). The interatomic distances of the C_2-building blocks in **3** [C(9)–C(10) 1.214(8) Å] correspond to typical C≡C separations found in organic as well as organometallic alkynes [2,3,8–10,22]. The Hf(1)–C(9) distance at 2.217(6) Å resembles those found in $[Hf](C{\equiv}CC_6H_5)_2$, [8]c but are significantly shorter than those hafnium-to-carbon bonds which involve sp^3-hybridized carbon atoms as experimentally observed in e.g. $(\eta^5\text{-}C_5H_5)_2HfMe_2$ [2.491(12) Å] [23] or $(\eta^5\text{-}C_5H_5)_2Hf[CH(C_6H_5)_2]_2$ [2.46(5) Å] [24]. Similar observations were made in bis(alkynyl) titanocenes in which the obtained data indicate some π-interaction between the d^0-configurated titanium(IV) centre and the π-system of

Table 2
Crystal and intensity collection data for **3**

Empirical formula	$C_{20}H_{22}FeHf_{0.5}Si$
Molecular mass	871.12
Crystal system	Orthorhombic
Space group	*Pnna*
a (Å)	11.431(2)
b (Å)	16.521(2)
c (Å)	19.130(2)
V (Å^3)	3612.7(9) Å^3
ρ_{calc} (g cm^{-1})	1.602
Z	4
Crystal dimensions (mm)	0.25x0.20x0.25
Diffractometer Model	Siemens (Nicolet–Syntex) R3m/V
Absorption coefficient (cm^{-1})	37.52
Radiation (λ)	Mo–K$_\alpha$ (0.71069 Å)
Temperature (K)	200
Scan mode	ω-scan, $\Delta\omega = 0.45°$
Scan range (°)	$4.2 \leq 2\theta \leq 50.0$
Scan speed (° min^{-1})	$7.0 \leq \omega \leq 7.0$
Extinction coefficient	0.00033(10)
Index ranges	$0 \leq h \leq 15$ $0 \leq k \leq 21$ $0 \leq l \leq 25$
Unique reflections	3194
Observed reflections [$I > 2\sigma(I)$]	2382
Refined parameters	211
R_1^a [$I > 2\sigma(I)$]	0.0332
R_w^b (all data)	0.0941
Max. peak in final Fourier map (e Å^{-3})	1.218
Min. peak in final Fourier map (e Å^{-3})	-0.857

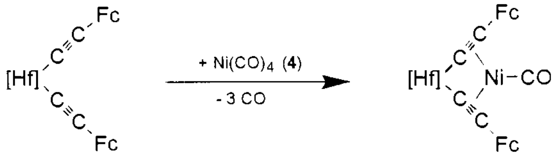
[a] $R_1 = \Sigma([|F_{obs}| - |F_{calc}|)/\Sigma\, |F_{calc}|$.
[b] $R_w = \{\Sigma[w(|F_{obs}| - |F_{calc}|)^2]/\Sigma[w(F_{obs}^2)_2]\}^{1/2}$

the C_2-building blocks [18,19,25]. As a consequence of the latter, the bite angle C(9)–Hf(1)–C(9A) with 99.0(3)° is markedly larger than those of complexes, which contain Hf–C(sp^3) σ-bonds [23,24]. The angle D(1)–Hf–D(1A) [125.5°; D(1), D(1A) = centroids of the cyclopentadienyl ligands] in **3** is smaller when compared with hafnocene dichloride [24,26] or other disubstituted compounds {c.f.: $(\eta^5\text{-}C_5H_5)_2HfMe_2$ 133.0° [23]; $(\eta^5\text{-}C_5H_5)_2Hf[CH(C_6H_5)_2]_2$ 128.2° [24]}.

A comparison of **3** with the C_2-bridged titanocene analogue $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CFc)_2$ [5] and $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CC{\equiv}CFc)_2$ [27] points out that the orientation of the ferrocenyl ligands is different. In **3** the ferrocenyl units are directed towards each other, while in the titanium–ferrocenyl species the ferrocenyl entities are pointing in the same direction [5,27].

2.2. Reaction chemistry

Complex **3** reacts with 1 equiv of $Ni(CO)_4$ (**4**) in toluene at 0°C by elimination of carbon monoxide to form the brown tetrametallic tweezer compound {[Hf](C≡CFc)$_2$}Ni(CO) (**5**) in 86% isolated yield (Eq. 2).



3 **5**

Appropriate purification of **5** yielded brown crystals, which are stable in the solid-state at low temperature. The crystals are soluble in most common organic solvents, such as n-pentane, toluene and diethyl ether. In the solid-state, **5** can be handled in air for short periods, while in solution it readily decomposes.

Compound **5** contains a low-valent nickel-monocarbonyl entity which is stabilized by the η^2-coordination of both alkynyl ligands FcC≡C. This results in a trigonal-planar environment around the nickel atom. Low-valent nickel moieties of type NiL [L = CO, PR_3, $P(OR)_3$; R = singly bonded organic ligand] have been stabilized in a similar way by the chelating effect of bis(alkynyl) titanocenes [8,9,28].

When **3** is reacted with equimolar amounts of different inorganic, [CuX] (X = halide or pseudohalide), or organic copper(I) complexes, [CuR], the formation of a multitude of reaction products is found. However, none of these could be separated into pure components. A similar result was obtained by the reaction of **3** with $FeCl_2$ or $NiCl_2$, respectively. These findings are in contrast with the well-known reaction chemistry of related titanocene compounds, which successfully can be used as organometallic tweezer complexes for the stabilization of a variety of different low-valent transition metal fragments [8,9,18,29].

2.2.1. Spectroscopy

Due to the η^2-coordination of the two FcC≡C building blocks to the nickel atom in **5**, the C≡C stretching vibration at 2066 cm in **3** is shifted to lower wave numbers in **5** [$\nu_{(C\equiv C)} = 1876$ cm^{-1}].

This indicates a weakening of the C≡C triple bonds. This shifting is similar to that generally noticed for the π-bonding of alkynes to transition metal fragments in which the alkyne is acting as a two-electron donor and is in agreement with the increased participation of the backbonding component in the alkyne-to-metal bond [9,10,18]. A second characteristic feature in the IR spectrum of **5** is the appearance of the CO-stretching vibration of the Ni(CO) moiety at 2002 cm^{-1}. For comparison, the ν_{CO}-frequency of $Ni(CO)_4$ is 2052 cm^{-1} [8]d, [30].

The ^{1}H-NMR spectrum of **5** consists of sharp well-resolved resonance signals for each of the groups that are present: i.e. one singlet for the C_5H_5 group and each two pseudo-triplets for the $C_5H_4C{\equiv}C$ as well as the $C_5H_4SiMe_3$ cyclopentadienyl protons.

Upon η^2-coordination of the alkynyl ligands to the low-valent Ni(CO) entity in **5**, the ^{13}C-NMR resonance signals of the $\mathrm{C{\equiv}C}$ units in the $\mathrm{Hf{-}C{\equiv}C{-}C_5H_4}$ entity at 122.5 ($\mathrm{HfC{\equiv}}C$) and 171.7 ppm ($\mathrm{Hf}C\mathrm{{\equiv}C}$) are shifted downfield for the carbon atom σ-bonded to the hafnium center and upfield for $\mathrm{HfC{\equiv}}C$, when compared with the corresponding resonance signals in **3**. This phenomenon is typical for tweezer molecules of type $[(\eta^5\text{-}\mathrm{C_5H_4R^1})_2\mathrm{M(C{\equiv}CR^2)_2}]\mathrm{M'L}_n$ (M = Ti, Zr, Hf; $\mathrm{R^1}$, $\mathrm{R^2}$ = singly bonded organic ligand; $\mathrm{M'L}_n$ = low-valent transition metal fragment) [8,9,18,29].

The FD mass spectrum of **5** contains the expected molecule ion peak $\mathrm{M^+}$ at $m/z = 958$.

3. Experimental section

3.1. General methods

All reactions were carried out under an atmosphere of dry 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. ^{1}H-NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.132 MHz in the Fourier transform mode, and the $^{13}\mathrm{C}\{^1\mathrm{H}\}$-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 internal reference signal. EI and FD mass spectra were recorded on a Finnigan 8400 mass spectrometer operating in the positive-ion mode. Melting points were determined with the 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 performed by cyclic voltammetry in a solution of $[\mathrm{N}(n\text{-}\mathrm{Bu})_4]\ \mathrm{PF_6}$ (0.1 mol $\mathrm{dm^{-1}}$) in acetonitrile at 25°C, using a standard three-electrode cell on a Princeton applied Research EG&G 273 analyser. All potentials were referenced to the ferrocene/ferrocenium couple, which had a potential of $+0.39$ V vs $\mathrm{Hg/Hg_2Cl_2}$ in this medium.

*3.2. Synthesis of [Hf](C≡CFc)₂ (**3**)*

To a suspension of 240 mg (0.47 mmol) of $[\mathrm{Hf}]\mathrm{Cl_2}$ (**1**) $\{[\mathrm{Hf}] = (\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Hf}\}$ [6] in 40 ml of diethyl ether at -78°C were added 2 equiv (205 mg, 0.95 mmol) of $\mathrm{LiC{\equiv}CFc}$ (**2**) $[\mathrm{Fc} = (\eta^5\text{-}\mathrm{C_5H_4})(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe}]$ [7]. The reaction mixture was stirred for 1.5 h at 25°C. After evaporation of all volatile materials in vacuo, the resulting residue was extracted with 30 ml of *n*-pentane and then with 40 ml of diethyl ether. After filtration through a pad of Celite, the diethyl ether fraction was concentrated to 10 ml and cooled to -40°C. 300 mg (0.34 mmol, 72% based on **1**) of orange **3** could be obtained.

Mp.: 126°C. IR (KBr): 2066 $\mathrm{cm^{-1}}$ (m) $[\nu_{\mathrm{C{\equiv}CHf}}]$. ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 0.45 (s, 18 H, $\mathrm{Si}Me_3$), 4.16 (pt, $J_{\mathrm{HH}} = 1.7$ Hz, 4 H, $\mathrm{C_5}H_4\mathrm{C{\equiv}C}$), 4.20 (s, 5 H, $\mathrm{C_5}H_5$), 4.34 (pt, $J_{\mathrm{HH}} = 1.7$ Hz, 4 H, $\mathrm{C_5}H_4\mathrm{C{\equiv}C}$), 6.19 $J_{\mathrm{HH}} = 2.5$ Hz, 4 H, $\mathrm{C_5}H_4\mathrm{SiMe_3}$), 6.60 (pt, $J_{\mathrm{HH}} = 2.5$ Hz, 4 H, $\mathrm{C_5}H_4\mathrm{SiMe_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 0.3 ($\mathrm{Si}Me_3$), 67.2 ($^i\mathrm{C}/C_5\mathrm{H_4C{\equiv}C}$), 68.2 ($C_5\mathrm{H_4C{\equiv}C}$), 69.5 ($C_5\mathrm{H_5}$), 70.8 ($C_5\mathrm{H_4C{\equiv}C}$), 109.5 ($C_5\mathrm{H_4SiMe_3}$), 118.9 ($C_5\mathrm{H_4SiMe_3}$), 119.9 ($^i\mathrm{C}/C_5\mathrm{H_4SiMe_3}$), 127.0 ($\mathrm{HfC{\equiv}}C$), 151.1 ($\mathrm{Hf}C\mathrm{{\equiv}C}$). MS (EI, m/z relative intensity): 872 (100) $\mathrm{M^+}$, 454 (70) $\mathrm{M^+\text{-}C_4Fc_2^+}$' 418 (70) $\mathrm{C_4Fc^+}$, 210 (65) $\mathrm{C_2Fc^+}$. Anal. Calcd for $\mathrm{C_{40}H_{44}Fe_2HfSi_2}$ (871.1): C, 55.15; H, 5.09. Found: C, 55.11; H, 5.31.

*3.2.1. X-ray structure determination of **3** [31]*

The structure of **3** was determined from single crystal X-ray diffraction, which were collected on a Siemens R3m/V (Nicolet–Syntex) diffractometer. Crystallographic data of **3** are given in Table 2. The structure was solved by direct methods (Sheldrick, G.M.; SHELXTL-Plus; University of Göttingen, Göttingen, Germany, 1988). An empirical absorption correction was applied. The structure was refined by the least squares method based on F^2 with all reflections (Sheldrick, G.M.; SHELXL93; University of Göttingen, Göttingen, Germany, 1993). All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in calculated positions. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3; anisotropic displacement parameters are listed in Table 4.

*3.3. Synthesis of {[Hf](C≡CFc)₂}Ni(CO) (**5**)*

To a solution of 300 mg (0.34 mmol) of **3** in 50 ml of toluene was added 330 mg (1.93 mmol) of Ni(CO) (**4**) at 0°C. After stirring for 1.5 h, all volatile materials were evaporated in vacuo. The resulting orange–brown residue was diluted in 10 ml of *n*-pentane and cooled to -40°C. 280 mg (0.28 mmol, 86% based on **3**) of **5** crystallized as brown solid.

M.p.: 117°C (dec.). IR (KBr): 1876 $\mathrm{cm^{-1}}$ (m) $[\nu_{\mathrm{C{\equiv}C}}]$, 2002 $\mathrm{cm^{-1}}$ (s) $[\nu\mathrm{C{\equiv}O}]$. ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 0.39 (s, 18 H, $\mathrm{Si}Me_3$), 4.25 (s, 5 H, $\mathrm{C_5}H_5$), 4.42 (pt, $J_{\mathrm{HH}} = 1.6$ Hz, 4 H, $\mathrm{C_5}H_4\mathrm{C{\equiv}C}$), 4.77 (pt, $J_{\mathrm{HH}} = 1.6$ Hz, 4 H, $\mathrm{C_5}H_4\mathrm{C{\equiv}C}$), 5.64 (pt, $J_{\mathrm{HH}} = 1.8$ Hz, 4 H, $\mathrm{C_5}H_4\mathrm{SiMe_3}$), 6.10 (pt, $J_{\mathrm{HH}} = 1.8$ Hz, 4 H, $\mathrm{C_5}H_4\mathrm{SiMe_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR ($\mathrm{CDCl_3}$): δ 0.5 ($\mathrm{Si}Me_3$), 68.5 ($C_5\mathrm{H_4C{\equiv}C}$), 69.6 ($C_5\mathrm{H_5}$), 71.2 ($C_5\mathrm{H_4C{\equiv}C}$), 74.2 ($^i\mathrm{C}/C_5\mathrm{H_4C{\equiv}C}$), 108.1 ($C_5\mathrm{H_4SiMe_3}$), 111.2 ($C_5\mathrm{H_4SiMe_3}$), 114.2 ($^i\mathrm{C}/C_5\mathrm{H_4SiMe_3}$), 122.5 ($\mathrm{HfC{\equiv}}C$), 171.7 ($\mathrm{Hf}C\mathrm{{\equiv}C}$), 201.5

Table 3
Functional atomic coordinates and equivalent isotropic displacement parameters *U* (eq) (Å × 10^3) for **3**[a]

Atom	*x*	*y*	*z*	*U* (eq)
Hf(1)	6150(1)	2500	2500	24(1)
Fe(1)	1588(1)	1531(1)	837(1)	26(1)
Si(1)	4816(2)	712(1)	3602(1)	31(1)
C(1)	6060(5)	1135(3)	3100(3)	29(1)
C(2)	6338(5)	993(3)	2390(3)	33(1)
C(3)	7434(6)	1331(4)	2227(3)	38(2)
C(4)	7886(6)	1681(4)	2843(4)	41(2)
C(5)	7049(5)	1569(4)	3373(3)	35(1)
C(6)	4920(6)	1062(4)	4527(3)	40(2)
C(7)	3382(5)	992(4)	3193(4)	40(2)
C(8)	4966(6)	−415(4)	3572(3)	43(2)
C(9)	4891(5)	2171(4)	1666(3)	23(1)
C(10)	4168(5)	1978(3)	1232(3)	26(1)
C(11)	3332(5)	1792(3)	700(3)	25(1)
C(12)	2604(5)	2354(3)	332(3)	30(1)
C(13)	1909(5)	1910(4)	−157(3)	31(1)
C(14)	2202(5)	1084(4)	—92(3)	31(1)
C(15)	3065(5)	1003(4)	442(3)	30(1)
C(16)	1232(5)	1606(4)	1879(3)	39(2)
C(17)	560(5)	2183(4)	1504(3)	38(1)
C(18)	−149(5)	1755(4)	1021(3)	39(2)
C(19)	100(5)	914(4)	1098(3)	40(2)
C(20)	938(5)	831(4)	1630(3)	41(2)

[a] *U* (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Anisotropic displacement parameters of **3** (Å^2 × 10^3)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hf(1)	24(1)	25(1)	25(1)	−2(1)	0	0
Fe(1)	27(1)	28(1)	24(1)	1(1)	−1(1)	−1(1)
Sl(1)	35(1)	26(1)	33(1)	3(1)	1(1)	3(1)
C(1)	29(3)	23(3)	35(3)	−2(3)	−2(2)	2(2)
C(2)	42(3)	23(3)	33(3)	−7(2)	4(3)	11(3)
C(3)	35(3)	34(4)	45(3)	2(3)	9(3)	8(3)
C(4)	32(3)	38(4)	52(4)	10(3)	−4(3)	−1(3)
C(5)	42(3)	32(3)	32(3)	0(3)	−8(3)	7(3)
C(6)	47(4)	39(4)	34(3)	3(3)	2(3)	8(3)
C(7)	40(3)	28(3)	53(4)	4(3)	2(3)	−2(3)
C(8)	51(4)	37(4)	42(4)	4(3)	1(3)	3(3)
C(9)	33(3)	24(3)	28(3)	−1(2)	−1(3)	9(3)
C(10)	26(3)	22(3)	29(3)	3(2)	6(2)	1(2)
C(11)	29(3)	22(3)	23(3)	0(2)	0(2)	−2(2)
C(12)	34(3)	26(3)	30(3)	5(2)	5(2)	−1(2)
C(13)	31(3)	35(3)	28(3)	6(3)	−2(2)	1(3)
C(14)	32(3)	35(3)	26(3)	−3(3)	3(2)	−7(3)
C(15)	32(3)	29(3)	30(3)	−4(2)	2(2)	−1(2)
C(16)	33(3)	59(4)	24(3)	2(3)	2(2)	6(3)
C(17)	36(3)	44(3)	33(3)	−1(3)	6(3)	4(3)
C(18)	29(3)	55(4)	33(3)	2(3)	−1(3)	2(3)
C(19)	37(3)	42(4)	41(4)	0(3)	9(3)	−10(3)
C(20)	43(4)	41(4)	38(4)	15(3)	13(3)	−4(3)

[a] Standard deviation in units of the last significant figure in parentheses.

(*C*O). MS (FD, *m*/*z*): 958 M^+. Anal. Calcd for $C_{41}H_{44}Fe_2HfNiOSi_2$ (957.84): C, 51.41; H, 4.63. Found: C, 51.69; H, 4.81.

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