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1,1′-Ferrocenyldicarboxylic Acid as Starting Material for the Formation of Trimetallic Ti(IV)−Fe(II)−Cu(I) and Pentametallic Ti_2(IV)−Fe(II)−Cu_2(I) Complexes[†]

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Summary: Reaction of $\{[Ti](C\equiv C^tBu)_2\}CuCH_3$ (***1***) $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti\}$ *with 1,1′-*$(\eta^5\text{-}C_5H_4CO_2H)_2Fe$ (***2***) *results in the formation of either the heterotrinuclear complex* $\{[Ti](C\equiv C^tBu)_2\}CuO_2C(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4CO_2H)$ (***3***) *or the pentametallic complex* $[\{[Ti](C\equiv C^tBu)_2\}CuO_2C(\eta^5\text{-}C_5H_4)]_2Fe$ (***4***)*, depending on the stoichiometric ratio of the reactants. Compound **4** can also be obtained by reacting **3** with 1 equiv of **1**. When **3** is reacted with a stoichiometric quantity of* $\{[Ti](C\equiv CSiMe_3)_2\}CuCH_3$ (***5***)*, the asymmetric complex* $\{[Ti](C\equiv C^tBu)_2\}CuO_2C(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)CO_2Cu\{(Me_3SiC\equiv C)_2[Ti]\}$ (***6***) *is produced. While in **4** two identical* $\{[Ti](C\equiv C^tBu)_2\}Cu$ *moieties are bridged by an* $[O_2C(\eta^5\text{-}C_5H_4)]_2Fe$ *entity, in **6** two different organometallic building blocks, such as* $\{[Ti](C\equiv C^tBu)_2\}Cu$ *and* $\{[Ti](C\equiv CSiMe_3)_2\}Cu$ *are linked by the same unit. The electrochemical behavior of complexes **3**, **4**, and **6** is discussed.*

Introduction

Due to their potential use as new materials, transition metal (TM) complexes in which the corresponding metal centers are connected by π-conjugated organic systems, e.g., σ-bonded linear all-carbon chains C_n ($n = 1, 2, 3, ...$), are of current interest since they may possess novel interesting electronic properties.[1−3] The appropriate π-conjugated organic systems may allow, for example, electronic communication between the different metal centers in bi- or oligometallic compounds.[4] Recently, we have reported the synthesis of several heterobimetallic complexes in which π-conjugated organic systems are used to connect early TM complex fragments to late TM metal centers.[5,6] The electronic properties of these compounds, with respect to their potential use as molecular dipoles and/or model compounds for nanoconducting materials, have been reported.

Since it is known that the ferrocenyl moiety can act as a transmitter unit for electronic information,[7] we here discuss the synthesis and electrochemical behavior of heterometallic complexes in which titanium−copper moieties are linked by an $[O_2C(\eta^5\text{-}C_5H_4)]_2Fe$ entity.

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[†] Dedicated to Prof. Dr. Dirk Walter on the occasion of his 60th birthday.

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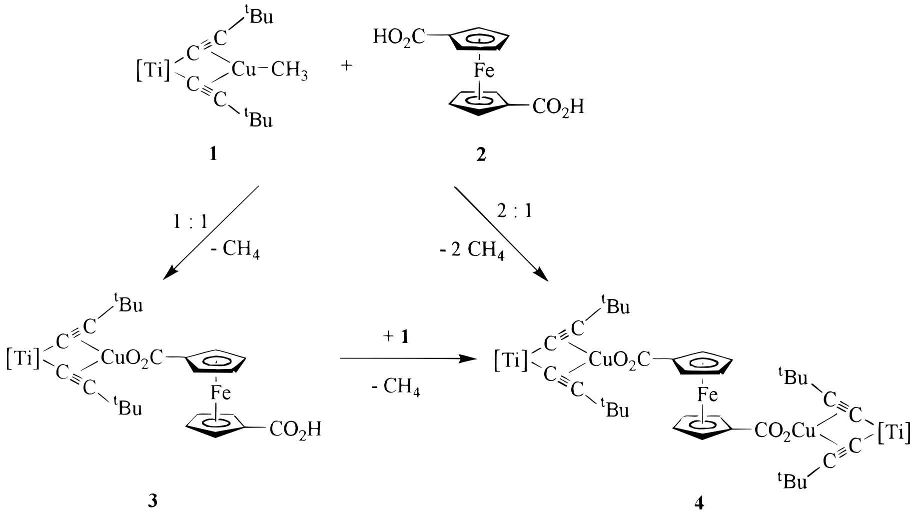
Scheme 1. Synthesis of 3 and 4 by the Reaction of 1 with 2

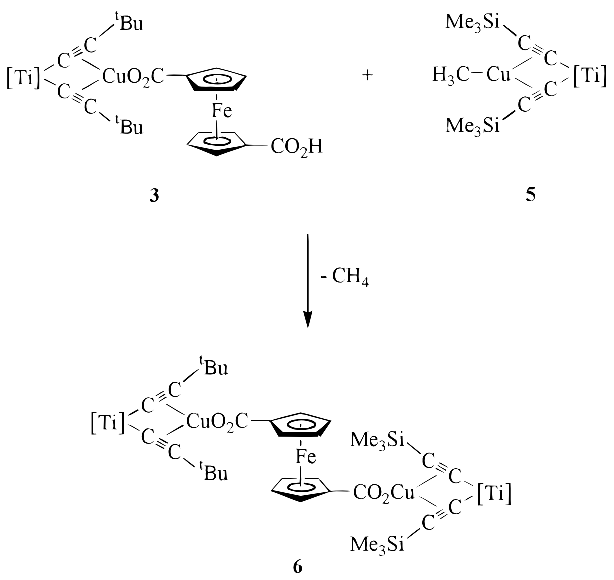


Results and Discussion

The monomeric bis(η^2-alkyne)-stabilized copper(I)-methyl complex $\{[Ti](C{\equiv}C^tBu)_2\}CuMe$ (**1**)[8] $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti\}$ reacts at −70 °C with 1 equiv of $(\eta^5\text{-}C_5H_4CO_2H)_2Fe$ (**2**) with loss of methane, producing orange-colored $\{[Ti](C{\equiv}C^tBu)_2\}CuO_2C(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4CO_2H)$ (**3**) in quantitative yield (Scheme 1). However, when 2 equiv of **1** are reacted with **2** at −20 °C the pentametallic ferrocenyl-bridged complex $[\{[Ti](C{\equiv}C^tBu)_2\}CuO_2C(\eta^5\text{-}C_5H_4)]_2Fe$ (**4**) is formed (Scheme 1). The latter molecule can also be obtained when **3** is reacted with **1** in a 1:1 ratio under similar reaction conditions (Scheme 1).

In compound **4**, the ferrocenyldicarboxylate ligand bridges two identical titanium−copper moieties. It is also possible for this ligand to bridge two different titanium−copper complex fragments. This is shown by the reaction of **3** with $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCH_3$ (**5**) at low temperature, which results in the formation of the asymmetric pentametallic complex $\{[Ti](C{\equiv}C^tBu)_2\}CuO_2C(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)CO_2Cu\{(Me_3SiC{\equiv}C)_2[Ti]\}$ (**6**) in high yield (Scheme 2). The yield is lowered somewhat at higher temperatures (81% at 0−25 °C, compared to 93% at −20 °C), due to concurrent decomposition of **5** to form the tetrametallic titanium−copper acetylide $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)\}_2$ (**7**), which has been previously characterized.[9,10]

Scheme 2. Synthesis of 6 by the Reaction of 3 with 5



Complexes **3**, **4**, and **6** can be isolated as orange-colored solids. In contrast to complexes **1** and **5**, which slowly decompose even at low temperature,[8] the ferrocenyldicarboxylate species are stable at low temperature for extended periods in solution and in the solid state. As solids, they can be handled briefly in air, but decompose slowly in solution upon exposure to air. While **1** and **5** are readily soluble in most common organic solvents, complexes **3**, **4**, and **6** only dissolve in polar organic ones, such as tetrahydrofuran, dichloromethane, or dimethyl sulfoxide. Complexes **3**, **4**, and **6** can be precipitated as orange solids by cooling their tetrahydrofuran/*n*-pentane solutions to −30 °C.

Complexes **3**, **4**, and **6** were characterized by elemental analysis as well as IR, ^1H NMR, and $^{13}C\{^1H\}$ NMR spectroscopy.

The progress of all reported reactions can easily be monitored by IR and NMR studies. The IR spectra of **3** and **4** exhibit only one C≡C stretching vibration at 1989 and 1990 cm^{-1}, respectively. Since two different titanocene−copper tweezer moieties are present in **6**, two distinct $\nu_{C\equiv C}$ absorptions at 1989 and 1918 cm^{-1} are observed, of which the first one can be assigned to the corresponding $[Ti](C{\equiv}C^tBu)_2$ building block and the

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Table 1. Cyclic Voltammetric Data[a] of Compounds 2−4 and 6

		reduction $E_{1/2}$ [V] (ΔE [mV])		oxidation $E_{1/2}$ [V] (ΔE [mV])	
compound	Ti-containing unit	Ti^{IV}/Ti^{III}	Cu^{I}/Cu^{0}	Cu^{I}/Cu^{II}	Fe^{II}/Fe^{III}
2					0.46 (75)
3	[Ti](C≡C^{t}Bu)$_2$	−2.01 (100)	−1.79 (irr.)	0.11 (70)	0.40 (70)
4	[Ti](C≡C^{t}Bu)$_2$	−2.00 (120)	−1.84 (irr.)	0.09 (80)	0.39 (90)
6	[Ti](C≡C^{t}Bu)$_2$ [Ti](C≡CSiMe$_3$)$_2$	−1.99 (110) −2.17 (120)	−1.81 (irr.)	0.11 (60)	0.41 (60)

[a] The cyclic voltammograms have been recorded in tetrahydrofuran solutions in the presence of [^{n}Bu$_4$N][PF$_6$] ($c = 0.1$ mol dm^{-3}) at 25 °C under N$_2$; scan-rate 100 mV s^{-1}; potentials are referenced to the FcH/FcH$^+$ couple ($E_{1/2} = 0.00$ V).

second one to the [Ti](C≡CSiMe$_3$)$_2$ entity. A characteristic feature in the IR spectra of **3**, **4**, and **6** is the shift of the corresponding $\nu_{C\equiv C}$ vibrations to higher frequencies upon replacement of a methyl ligand with a carboxylate [cf. $\nu_{C\equiv C}$: 1909 cm^{-1} (**1**), 1867 cm^{-1} (**5**)].[8] This observation is consistent with the IR stretching frequencies previously reported for copper−carboxylate complexes of this sort.[11] This strongly suggests that a change from the η^1-bonded methyl ligand in **1** or **5** to a carboxylic unit in **3**, **4**, or **6** leads to a stronger carbon−carbon triple bond. Furthermore, this result demonstrates that the carboxylic entity is a weaker σ-donor ligand than the respective methyl group. In addition, IR spectra clearly show that the carboxylate ligands are only η^1-bonded to the copper(I) center through one oxygen atom: The difference of the symmetric (ca. 1700 cm^{-1}) and antisymmetric ν_{CO}-stretching vibration (at around 1560 cm^{-1}) is around 140 cm^{-1}, which is typical for this type of bonding.[11b] This result is consistent with, for example, monomeric alkyne-stabilized copper(I)−acetate or −benzoate species, which were additionally characterized by X-ray diffraction analysis.[10,11]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3**, **4**, and **6** consist of well-resolved resonance signals for each of the organic building blocks present. The resonance signals of the titanium-bound cyclopentadienyl protons appear as broad signals at 6.07 ppm in **3**, 6.01 and 6.04 ppm in **4**, and 6.03 ppm in **6**. These signals are significantly downfield of the signals for the starting materials **1** and **5** (5.13 and 5.67 ppm for **1**; 5.38 and 5.68 ppm for **5)** and are similar to values found for previously reported carboxylate compounds of this sort.[8,10] Additionally, the cyclopentadienyl protons of the ferrocenyl units appear as broadened signals at approximately 4.4 and 4.8 ppm. While in **4** and **6** the sum of the integrals for the protons of the titanocene and the ferrocenyl unit is 2:1, for complex **3** the expected 1:1 ratio is observed.

The most diagnostic signals in the ^{13}C{^{1}H} NMR spectra are those of the bridging alkynyl ligands. The C$_\alpha$ carbon atoms of the alkynyl groups give rise to signals that are shifted to higher field with respect to the starting materials; the signals for the ^{t}Bu−acetylide C$_\alpha$ nuclei of **3**, **4**, and **6** appear at 147.7 and 147.8 ppm (compared to 169.1 ppm in **1**), while that of the trimethylsilyl acetylide ligand appears at 180.4 ppm (compared to 203.6 in **5**). In contrast, the resonance signals of the C$_\beta$ atoms are shifted to lower field in compounds **3**, **4**, and **6** [**3**, 134.7 ppm; **4**, 135.2 ppm; **6**, 135.2 (TiC≡*C*^{t}Bu), 143.1 ppm (TiC≡*C*SiMe$_3$)], when compared with **1** (123.4 ppm) or **5** (138.6 ppm).[8,10] The resonance signals of the carbon atoms of the corresponding carboxylic units are found at 175.4 (**3**), 175.8 (**4**), and 175.6 ppm (**6**). Unfortunately, the carbon resonance signal for the noncoordinated CO$_2$H moiety in **3** could not be unequivocally detected. The resonance signals of the titanocene cyclopentadienyl carbon atoms are found in the normal range of 115−125 ppm, and the corresponding signals of the ferrocenyl carbon atoms are found at higher field between 65 and 80 ppm, which is typical for ferrocenyl complexes.[5]

Also significant in the ^{13}C{^{1}H} NMR spectra of **3**, **4**, and **6** is the disappearance of the resonace signal of the copper σ-bonded methyl group, found at −7.4 ppm in **1** or −9.2 ppm in **5,** respectively.[8,10]

In molecules **3**, **4**, and **6**, a ferrocenyl unit is connected to the copper(I) center of a heterobimetallic titanium−copper moiety via a carboxylic unit. Because of this, the electrochemical behavior of these complexes is of interest, since three different metal centers, Ti(IV), Fe(II), and Cu(I), are connected via π-conjugated organic units. Therefore, these complexes have been subjected to cyclovoltammetric measurements. The electrochemical data obtained for **2**, **3**, **4**, and **6** are listed in Table 1.

For 1,1′-(η^5-C$_5$H$_4$CO$_2$H)$_2$Fe (**2**), a reversible one-electron oxidation has been observed at $E_{1/2} = 0.46$ V with $\Delta E = 75$ mV (Table 1). In comparison to the reference couple FcH/FcH$^+$ this indicates that the oxidative process has been made more difficult by the two electron-withdrawing carboxylate substituents. Similar influences of electron-withdrawing[12a] or electron-donating[12b] substituents on the Fe^{II}/Fe^{III} redox process in ferrocenyl species have been reported. In comparison to **2**, the respective redox responses of the Cu(I)-bound ferrocenyl carboxylates are shifted slightly to a more positive potential. This indicates that the electron-withdrawing properties of the carboxylate functionalities have been somewhat decreased by replacement of the carboxylic acid hydrogen atom with a copper center (Table 1). At around 0.1 V a redox process is found, which can be interpreted as the one-electron reversible Cu^I/Cu^{II} oxidation (Table 1). This interpretation is corroborated by findings reported recently for similar copper(I)-containing titanium tweezer molecules.[13] While the Cu^I/Cu^{II} redox couple is reversible under the conditions applied (vide supra), the Cu^I/Cu^0 reduction shows a differing behavior: For complexes **3**, **4**, and **6** irreversible reductions are found at −1.79, −1.84, and −1.81

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V, respectively (Table 1). However, the $\mathrm{Ti^{IV}/Ti^{III}}$ reduction is found to be reversible (Table 1). Thus, for the $[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2$ fragments, a reversible wave at around −2.0 V is observed, while the Ti(IV) center of the $[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2$ unit is reduced reversibly at a more negative potential ($E_{1/2} = -2.17$ V, $\Delta E = 120$ mV). This directly indicates that the reduction of the titanium(IV) center in the latter building block becomes more difficult, due to an increased electron density on the titanium core.[5] The fact that only one pair of redox processes is observed for the copper(I) centers of the dicopper complexes **4** and **6** indicates that electronic communication between the corresponding metal centers is not favored. Moreover, it seems that in this case the carboxylate units of the ferrocenyl connectivity act as an impedance rather than as a transmitter.

Experimental Section

General Methods. All reactions were carried out in an atmosphere of nitrogen using standard Schlenk techniques. Solvents were purified by distillation over appropriate drying agents: *n*-pentane and dichloromethane, calcium hydride; diethyl ether and tetrahydrofuran, sodium/benzophenone ketyl; toluene, sodium. FT-IR spectra were obtained on a Perkin-Elmer FT-IR 1000 spectrometer (KBr pellets, as film between NaCl plates, or as solutions between $\mathrm{CaF_2}$ plates). NMR spectra were recorded on a Bruker Avance 250 spectrometer, operating in the Fourier transform mode. ^{1}H NMR spectra were recorded at 250.130 MHz (internal standard relative to $\mathrm{CDCl_3}$, $\delta = 7.27$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra were recorded at 67.890 MHz (standard intern, relative to $\mathrm{CDCl_3}$, $\delta = 77.0$). Chemical shifts are reported in δ units (ppm) downfield from $\mathrm{SiMe_4}$ with the solvent as reference signal. Melting points were determined using analytically pure samples, sealed off in nitrogen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Organic Department at the Technical University of Chemnitz.

Electrochemical measurements were performed by cyclic voltammetry in a solution of $[\mathrm{N(^nBu)_4}]\mathrm{PF_6}$ (0.1 mol/dm^3) in tetrahydrofuran at 25 °C, using a standard three-electrode cell (Pt, Pt, SCE) on a Radiometer DEA 101 digital electrochemical analyzer. All potentials were referred to the ferrocene−ferrocenium couple [$\mathrm{FcH/FcH^+}$: $E = 0.00$ mV] as internal standard; $\Delta E = E_{\mathrm{pa}} - E_{\mathrm{pc}}$.

General Remarks. Compounds **1** and **5** were prepared by published procedures.[8] All other chemicals were purchased by commercial suppliers and were used as received.

Synthesis of $\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4CO_2H})$ (3). $(\eta^5\text{-}\mathrm{C_5H_4CO_2H})_2\mathrm{Fe}$ (**2**) (90 mg, 0.320 mmol) was added in one portion to a solution of $\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuCH_3}$ (**1**) (180 mg, 0.320 mmol) in 50 mL of tetrahydrofuran at −70 °C. After stirring for 30 min at this temperature, the reaction mixture was slowly warmed to 25 °C and stirred additionally for 1 h. All volatile materials were removed in vacuo. The orange residue was washed with cold *n*-pentane (3 × 10 mL). $\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4CO_2H})$ (**3**) was obtained in quantitative yields.

Mp: 107 °C (dec). IR (NaCl, ν, cm^{-1}): 1989 (C≡C), 1698 (CO, sym), 1558 (CO, as). ^{1}H NMR ($\mathrm{CDCl_3}$): 0.27 (s, 18H, $\mathrm{SiMe_3}$), 1.33 (s, 18H, ^{t}Bu), 4.35 (bs, 4H, $\mathrm{C_5H_4Fe}$), 4.70 (bs, 4H, $\mathrm{C_5H_4Fe}$), 6.07 (bs, 8H, $\mathrm{C_5H_4Ti}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): 0.1 ($\mathrm{SiMe_3}$), 31.1 (^{t}Bu), 31.8 (^{t}Bu, $\mathrm{C_q}$), 71.7 (m, $\mathrm{C_5H_4Fe}$), 77.2 ($\mathrm{C_5H_4Fe}$, $\mathrm{C_{ipso}}$; the other $\mathrm{C_{ipso}}$ signal is covered by the $\mathrm{CDCl_3}$ resonance), 114.0 ($\mathrm{C_5H_4Ti}$), 116.7 ($\mathrm{C_5H_4Ti}$), 119.8 ($\mathrm{C_5H_4Ti}$, $\mathrm{C_{ipso}}$), 134.7 (TiC≡*C*^{t}Bu), 147.7 (Ti*C*≡C^{t}Bu), 175.4 ($\mathrm{CO_2}$), the signal of the $\mathrm{CO_2H}$ group could not be unequivocally detected. Anal. Calcd for $\mathrm{C_{40}H_{53}CuFeO_4Si_2Ti}$ (821.30): C, 58.50; H, 6.50. Found: C, 58.12; H, 6.33.

Synthesis of $[\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})]_2\mathrm{Fe}$ (4). Method A: $[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuCH_3}$ (**1**) (90 mg, 0.164 mmol) in 20 mL of tetrahydrofuran was added dropwise to a tetrahydrofuran (30 mL) solution containing $\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4CO_2H})$ (**3**) (135 mg, 0.164 mmol) at −20 °C. After stirring for 30 min at this temperature, the reaction mixture was warmed to 25 °C and stirred for 1 h. All volatiles were removed in vacuo. The orange-colored residue was washed with cold *n*-pentane (2 × 5 mL) to afford $[\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})]_2\mathrm{Fe}$ (**4**) in quantitative yields.

Method B: $(\eta^5\text{-}\mathrm{C_5H_4CO_2H})_2\mathrm{Fe}$ (**2**) (40 mg, 0.15 mmol) was added in one portion to $\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuCH_3}$ (**1**) (170 mg, 0.30 mmol) in 30 mL of tetrahydrofuran at −20 °C. After stirring for 1 h at this temperature, the reaction mixture was warmed to 25 °C and stirred for another 30 min. Then, all volatile materials were removed in vacuo. The orange-colored residue was washed twice with cold *n*-pentane (5 mL). $[\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})]_2\mathrm{Fe}$ (**4**) was obtained quantitatively.

Mp: 151 °C (dec). IR (NaCl, ν, cm^{-1}): 1990 (C≡C), 1699 (CO, sym), 1558 (CO, as). ^{1}H NMR ($\mathrm{CDCl_3}$): 0.28 (s, 36H, $\mathrm{SiMe_3}$), 1.32 (s, 36H, ^{t}Bu), 4.37 (bs, 4H, $\mathrm{C_5H_4Fe}$), 4.76 (bs, 4H, $\mathrm{C_5H_4Fe}$), 6.01 (bs, 8H, $\mathrm{C_5H_4Ti}$), 6.04 (bs, 8H, $\mathrm{C_5H_4Ti}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): 0.1 ($\mathrm{SiMe_3}$), 31.1 (^{t}Bu), 31.4 (^{t}Bu, $\mathrm{C_q}$), 70.5 ($\mathrm{C_5H_4Fe}$), 70.8 ($\mathrm{C_5H_4Fe}$), 80.4 ($\mathrm{C_5H_4Fe}$, $\mathrm{C_{ipso}}$), 113.9 ($\mathrm{C_5H_4Ti}$), 116.6 ($\mathrm{C_5H_4Ti}$), 119.4 ($\mathrm{C_5H_4Ti}$, $\mathrm{C_{ipso}}$), 135.2 (TiC≡*C*^{t}Bu), 147.7 (Ti*C*≡C^{t}Bu), 175.8 ($\mathrm{CO_2}$). Anal. Calcd for $\mathrm{C_{68}H_{96}Cu_2FeO_4Si_4Ti_2}$ (1368.54): C, 59.68; H, 7.07. Found: C, 60.03; H, 7.13.

Synthesis of $\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{CO_2Cu}\{_2(\mathrm{Me_3SiC{\equiv}C})[\mathrm{Ti}]\}$ (6). $[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{CuCH_3}$ (**5**) (100 mg, 0.165 mmol) was dissolved in 30 mL of tetrahydrofuran and added dropwise to $\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4CO_2H})$ (**3**) (135 mg, 0.165 mmol) in 50 mL of tetrahydrofuran at −20 °C. After stirring for 30 min at this temperature, the reaction mixture was allowed to warm to 25 °C. After 1 h, all volatiles were removed in vacuo. The orange-colored residue was washed twice with cold *n*-pentane (10 mL), and the remaining solid was crystallized from diethyl ether at −30 °C to produce $\{[\mathrm{Ti}](\mathrm{C{\equiv}C^tBu})_2\}\mathrm{CuO_2C}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{CO_2Cu}\{(\mathrm{Me_3SiC{\equiv}C})_2[\mathrm{Ti}]\}$ (**6**) (220 mg, 93% yield based on **3**).

Mp: 144 °C (dec). IR (NaCl, ν, cm^{-1}): 1989 (C≡C^{t}Bu), 1918 (C≡CSiMe$_3$), 1698 (CO, sym), 1585 (CO, as). ^{1}H NMR ($\mathrm{CDCl_3}$): 0.26 (m, 54H, $\mathrm{SiMe_3}$), 1.32 (s, 18H, ^{t}Bu), 4.33 (bs, 4H, $\mathrm{C_5H_4Fe}$), 4.74 (bs, 4H, $\mathrm{C_5H_4Fe}$), 6.03 (m, 16H, $\mathrm{C_5H_4Ti}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): 0.1 ($\mathrm{SiMe_3}$), 0.3 ($\mathrm{SiMe_3}$), 0.5 ($\mathrm{SiMe_3}$), 30.7 (^{t}Bu), 31.0 (^{t}Bu, $\mathrm{C_q}$), 70.4 (bs, $\mathrm{C_5H_4Fe}$), 70.7 (bs, $\mathrm{C_5H_4Fe}$), 80.1 (bs, $\mathrm{C_5H_4Fe}$, $\mathrm{C_{ipso}}$), 113.8 ($\mathrm{C_5H_4Ti}$), 114.2 ($\mathrm{C_5H_4Ti}$), 116.6 ($\mathrm{C_5H_4Ti}$), 117.8 ($\mathrm{C_5H_4Ti}$), 119.3 ($\mathrm{C_5H_4Ti}$, $\mathrm{C_{ipso}}$), 121.5 ($\mathrm{C_5H_4Ti}$, $\mathrm{C_{ipso}}$), 135.2 (TiC≡*C*^{t}Bu), 143.1 (TiC≡*C*SiMe$_3$), 147.8 (Ti*C*≡C^{t}Bu), 175.6 ($\mathrm{CO_2}$), 180.4 (Ti*C*≡CSiMe$_3$). Anal. Calcd for $\mathrm{C_{66}H_{96}Cu_2FeO_4Si_6Ti_2}$ (1400.69): C, 56.60; H, 6.91. Found: C, 56.24; H, 6.76.

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