

Reductive coupling reaction induced by remote-site oxidation in titanocene bis(metalloacenylacetylide), where metalloacenyl = ferrocenyl or ruthenocenyl: a novel route to C_n ($n = 4, 6, \text{ and } 8$) wire with the metalloacenyl groups at both terminals

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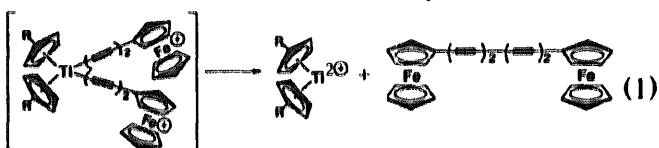
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Abstract

The titanocene bis(acetylide) complexes $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti}[(\text{C}\equiv\text{C})_m\text{-Mc}][(\text{C}\equiv\text{C})_n\text{-Mc}']$ ($\text{R} = \text{H}, \text{SiMe}_3$; $m, n = 1 \text{ or } 2$; $\text{Mc}, \text{Mc}' = \text{ferrocenyl or ruthenocenyl}$) have been prepared and found to be easily oxidized with 2 equiv. amount of AgPF_6 liberating a neutral product, $\text{Mc}-(\text{C}\equiv\text{C})_m(\text{C}\equiv\text{C})_n\text{-Mc}'$. Electrochemical studies indicate that the reaction is induced by initial oxidation of Mc and Mc' followed by unprecedented reductive coupling of the two alkynyl carbons bound to titanocene. © 1997 Elsevier Science S.A.

1. Introduction

A number of bis(alkynyl)titanocenes $(\eta^5\text{-C}_5\text{H}_4\text{R}')_2\text{Ti}(\text{C}\equiv\text{C-R})_2$ ($\text{R} = \text{Ph}, \text{CF}_3, \text{C}_6\text{H}_{11}, \text{CH}_2\text{C}(\text{H})\text{Ph}_2, \text{CH}_2\text{C}(\text{CN})\text{Ph}_2, \text{t-Bu}, \text{SiMe}_3, \text{(TMS)}$) have been described in the literature and are known to be stable [1]; interestingly, some of them exhibit non-linear optical (NLO) properties [2]. In relation to our project of binding heterometallic species with CC triple bonds and examining their physical properties, we became interested in whether ferrocenyl or ruthenocenyl substituted complexes of the form $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti}(\text{C}\equiv\text{C-Mc})_2$ ($\text{Mc} = \text{ferrocenyl or ruthenocenyl}$) or their diyne analogs $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti}(\text{C}\equiv\text{C-C}\equiv\text{C-Mc})_2$ could be prepared. In a previous communication we have reported the isolation of the diyne bridged titanocene-ferrocenyl complexes and their oxidation reaction with 2 equiv. amount of AgPF_6 , which yielded cleanly the coupling product of the two diyne units. The cyclic voltammetry experiment was consistent with the reaction outlined in Eq. (1) [3].



This is a reductive coupling reaction but is quite unique in that the valency of the central metal (Ti) does not change: the reduced species is the ferrocenium cation at the other end of the coupling carbon atoms.

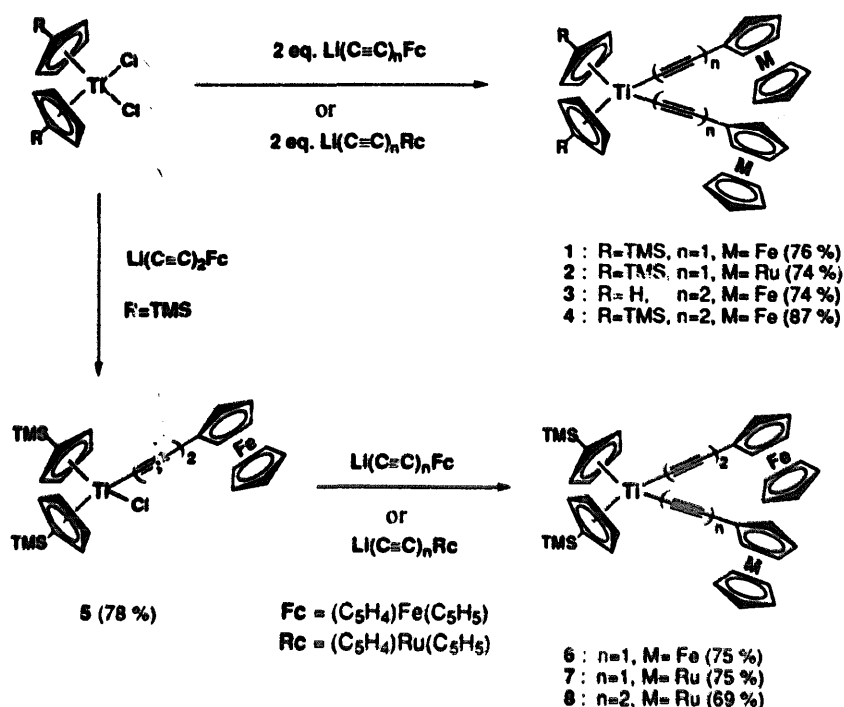
In this paper, we report that the coupling reaction induced by 2 equiv. of Ag^+ cation can successfully be applied to newly synthesized titanocene analogs with bis(monoyne) and (monoyne)(diyne) complexes having ferrocenyl and ruthenocenyl end groups, thus providing a convenient route to $C_4, C_6,$ and C_8 atom 'rigid-rod molecular wire' capped both terminals with ferrocenyl and ruthenocenyl groups.

2. Results and discussion

2.1. Synthesis of the bis(acetylide) complexes of titanocene

The titanocene bis(metalloacenylacetylide) complexes $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti}[(\text{C}\equiv\text{C})_n\text{-Mc}]_2$ ($n = 1 \text{ or } 2, \text{Mc} = \text{Fc or Rc}$ where $\text{Fc} = \text{ferrocenyl}, \text{Rc} = \text{ruthenocenyl}$) (1–4) were successfully isolated in good yields after the low temperature metathesis reaction between the corresponding $(\text{C}_5\text{H}_4\text{R})_2\text{TiCl}_2$ and 2 equiv. of $[\text{Li}(\text{C}\equiv\text{C})_n\text{Mc}]$ (Scheme 1). The unsymmetrical complexes 6–8 were obtained by the action of 1 equiv. of $\text{Li}(\text{C}\equiv\text{C})_2\text{Fc}$ fol-

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Scheme 1.

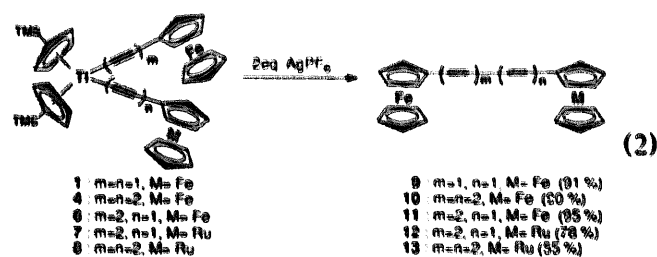
lowed by the addition of $\text{LiC}\equiv\text{CFc}$ or $\text{Li}(\text{C}\equiv\text{C})_n\text{Rc}$ via the isolated complex $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{Cl})[(\text{C}\equiv\text{C})_2\text{-Fc}]$ (**5**). The iron complexes have characteristic dark-blue (**1**) or moss-green (**3,4,6**) color, while the ruthenium complex **2** is red and the iron–ruthenium mixed complexes (**7,8**) are dark purple–red. The ruthenium complex **2** is sensitive to light and has to be treated in the dark. At room temperature, these complexes are thermally stable in solution under an inert atmosphere but tend to decompose readily in a small amount of air. The presence of TMS substituent on the titanocene cyclopentadienyl group is essential for increased solubility of the complexes, which promotes smooth reaction of the alkynyltitanocene complexes with the silver salt (*vide infra*). The X-ray structure of **4** was reported in a previous communication [3].

As expected [4], complexes **3**, **4** and **5** in solution exhibit two $\nu(\text{C}\equiv\text{C})$ IR bands (e.g. **3**: 2172, 2021 cm^{-1}) while **6** and **7** show three (e.g. **6**: 2173, 2054, 2024 cm^{-1}), of these the central band is assigned to that of the monoyne part since **1** and **2** show the corresponding band at 2056 and 2059 cm^{-1} respectively. For the unsymmetrical complex **8**, only two $\nu(\text{C}\equiv\text{C})$ bands are observed at 2173 and 2021 cm^{-1} , due to very small differences of Fc and Rc in the effect on $\text{C}\equiv\text{C}$ stretching vibrations.

2.2. Ag salt-induced coupling reaction

As reported previously, electrochemical oxidation of complexes **3** and **4** readily releases a formal reductive

elimination product $\text{Fc}-(\text{C}\equiv\text{C})_n-\text{Fc}$ (**10**) via the initial oxidation of the Fc units (Eq. (1)): chemical oxidation with AgPF_6 yielded the same coupling product together with $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti}^{2+}$ [**3**]. In the case of bis(monoyne) complex **1**, the oxidatively induced coupling reaction with the silver salt also proceeded smoothly in THF at room temperature giving **9** in high yield (Eq. (2)).



In contrast, the ruthenocenyl analog **2** did not yield the corresponding coupling product but resulted in sluggish decomposition. Importantly, the unsymmetrical complexes **6–8** reacted similarly to give novel bis(ferrocenyl) and (ferrocenyl)(ruthenocenyl) complexes **11–13** bridged by triyne or tetrayne units. When the ruthenocene moiety is present in the complex, the reaction takes longer (2 h for **1**, **4**, and **6** vs. 1 day for **7** and **8**). These orange colored coupling products are fairly stable in solution under argon and can be purified by column chromatography.

The reaction of $\text{Me}-(\text{C}\equiv\text{C})_2-\text{Fc}$ with 1 equiv. of AgPF_6 under a condition similar to that employed for the reaction (2) leads to immediate formation of $[\text{Me}-$

$(C\equiv C)_2-Fc^+ [PF_6^-]$, demonstrating that Ag^+ has enough potential to oxidize an alkynyl-bound ferrocenyl unit. When only an equimolar amount of $AgPF_6$ was used in reaction (2), the coupling product was still formed slowly but in much lower yields. Although free ruthenocene is known to undergo two-electron oxidation, the permethylated complex forms a cation $(\eta^5-C_5Me_5)_2Ru^+$ [5]. We believe reactions $7 \rightarrow 12$ and $8 \rightarrow 13$ proceed via the dication species $(Fc^+)(Rc^+)$ in analogy with the $(Fc^+)(Fc^+)$ intermediate illustrated in Eq. (1). For comparison, addition of 2 equiv. of $AgPF_6$ to a THF solution of $(\eta^5-C_5H_4TMS)_2Ti[(C\equiv C)_2-TMS]_2$ gave immediately a brown colored intractable precipitate (IR (KBr): $\nu(C\equiv C)$ 2165, 1982 cm^{-1}), which appeared to be a polymeric silver complex of the bis(alkynyl)titanocene, while no coupling product of the two alkynyl groups was detected in the solution even after several days. [The first bis(diynyl) complex of titanocene was reported by Lang and Weber [4], we independently prepared this complex and confirmed the structure by X-ray crystal analysis; for an example of monomeric silver complex formation with bis(alkynyl)titanocene by addition of an equimolar amount of silver salts, see Ref. [6].] The presence of bis(ferrocenyl) or (ferrocenyl)(ruthenocenyl) as the terminal substituents of bis(alkynyl)titanocene is thus essential for the facile coupling reaction. A somewhat related reaction has been reported by Sato et al. [7], where facile reductive elimination from a *cis*-($Fc^+-C\equiv C(Ph)Pt(II)$) complex gave neutral $Fc-C\equiv C-Ph$. The NLO properties of the 'molecular rods' synthesized here are currently under investigation.

2.3. Cyclic voltammogram of complex 8

The previously reported cyclic voltammogram (CV) of complex 4, which strongly supports the reaction

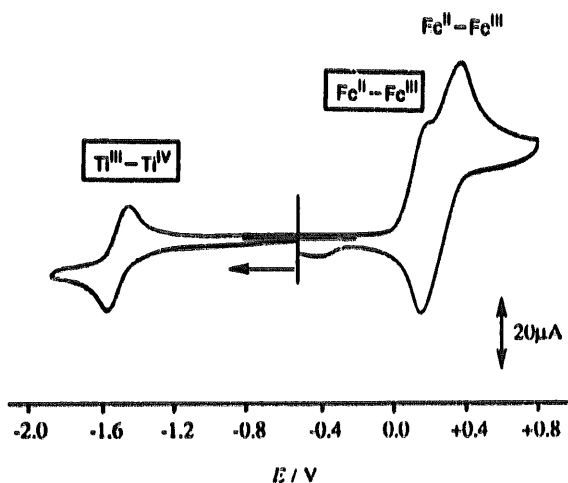


Fig. 1. Cyclic voltammogram of complex 4 (1 mM) [3]. The potentials are referenced to $FcH-FcH^+$. The assignments framed with a rectangle are for the complex whilst those outside the rectangle are for the coupling product.

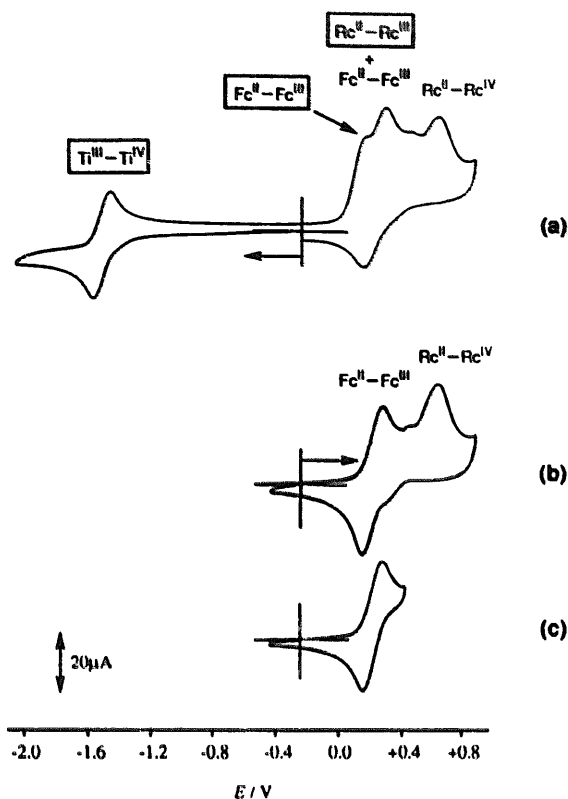


Fig. 2. Cyclic voltammograms of (a) complex 8 (1 mM) and (b, c) the coupling product 13. The potentials are referenced to $FcH-FcH^+$. The assignments framed with a rectangle are for the complex whilst those outside the rectangle are for the coupling product. Scan range: (a) -2.0 – $+0.9$ V, (b) -0.4 – $+0.9$ V, (c) -0.4 – $+0.4$ V.

process of Eq. (1), is shown again in Fig. 1. The oxidation peak marked $Fc^{II}-Fc^{III}$ in the rectangle corresponds to the oxidation wave for the two ferrocenyl units in the titanocene complex 4, and that outside the rectangle is for the oxidation of the liberated coupling product 10 [3]. The CV of complex 8 is illustrated in Fig. 2(a), while those for the coupling product derived from it (13) are shown in Fig. 2(b) Fig. 2(c).

The CV of the coupling product (Fig. 2(b)) consists of a reversible couple of $Fc^{II}-Fc^{III}$ at $+0.30$ V and an irreversible two-electron oxidation of the ruthenocenyl unit ($Rc^{II}-Rc^{IV}$) at $+0.65$ V (for the two-electron oxidation of ruthenocenes, see Ref. [8]). In addition to the reversible $Ti^{III}-Ti^{IV}$ couple, the parent complex exhibits (Fig. 2(a)) three peaks at $+0.19$, $+0.31$, and $+0.65$ V during the oxidation scan. Comparing these CV peaks with those of the bis(ferrocenyl) analog 4 (Fig. 1) and the coupling product 13 (Fig. 2(b) Fig. 2(c)), we assign these waves to $Fc^{II}-Fc^{III}$ (0.19 V) in the complex, $Fc^{II}-Fc^{III}$ ($+0.31$ V, reversible) in the coupling product, and $Rc^{II}-Rc^{III}$ ($+0.65$ V, irreversible) in the coupling product respectively. We believe that the one-electron oxidation process of the ruthenocenyl unit in complex 8, i.e. $Rc^{II}-Ru^{III}$, overlaps with the $Fc^{II}-Fc^{III}$ wave at $+0.31$ V and this is in accord with the total

current for this peak which is almost equal to that for the two-electron oxidation process $\text{Rc}^{\text{II}}-\text{Rc}^{\text{IV}}$ at +0.65 V.

3. Experimental

^1H and ^{13}C NMR spectra were measured on a JEOL JNM-EX270 spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra (FAB⁺) were obtained on a JEOL JMS-HX110 mass spectrometer. Cyclic voltammograms were measured in CH_2Cl_2 solution containing 0.1 M $n\text{Bu}_4\text{NClO}_4$ under Ar at room temperature with a scan rate of 100 mV s^{-1} . Ferrocenylacetylene [9] and ferrocenylbutadiyne [10] were prepared by literature methods, and their ruthenoceny analogs were prepared by the same route. All manipulations were performed under argon. In addition, all reactions of AgPF_6 were carried out in a flask covered with aluminum foil to shield it from the light. Solvents were purified and distilled prior to use.

3.1. Synthesis of $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti}(\text{C}\equiv\text{C})_n\text{Fc}$ ($R = \text{H}$ or TMS, $n = 1$ or 2)

$(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{C}\equiv\text{CC}\equiv\text{CFc})_2$ (**4**): a THF (90 ml) solution of $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{TiCl}_2$ (472 mg, 1.2 mmol) was added dropwise to a solution of THF (12 ml) containing $\text{Li}(\text{C}\equiv\text{C})_2\text{Fc}$ (2.4 mmol) at -78°C . After the mixture was stirred for 1 h at 0°C , the resulting solution was evaporated in vacuo. The residue was extracted with benzene and the extract was filtered. After evaporation of benzene to dryness, recrystallization from toluene/hexane at -30°C gave **4** as deep green crystals (yield 820 mg, 87%). Anal. Found: C, 67.04; H, 5.70. $\text{C}_{44}\text{H}_{44}\text{Fe}_2\text{Si}_2\text{Ti}$ Calc.: C, 67.02; H, 5.62%. ^1H NMR (C_6D_6): δ 6.46 (t, $J = 2.3$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Ti}$), 5.93 (t, $J = 2.3$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Ti}$), 4.36 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.02 (s, 10H, $\text{C}_5\text{H}_5\text{-Fe}$), 3.87 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Fe}$), 0.39 (s, 18H, TMS). ^{13}C NMR (C_6D_6): δ 149.4 ($\equiv\text{C-Ti}$), 126.2, 121.7 ($\text{C}_5\text{H}_4\text{-Ti}$), 119.7 ($\text{C}\equiv\text{C-Ti}$), 114.6 ($\text{C}_5\text{H}_4\text{-Ti}$), 89.5 ($\text{C}\equiv\text{C-Fc}$), 72.5, 72.3, 70.4, 69.5 ($-\text{Fc}$), 66.0 ($\equiv\text{C-Fc}$), 0.3 (TMS). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2171, 2021 cm^{-1} . MS (FAB⁺) m/z : 789 [M]⁺.

Complexes **1** and **3** were prepared similarly. The crude product of **3** was purified by column chromatography on SiO_2 with CH_2Cl_2 as eluent.

$(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{C}\equiv\text{CFc})_2$ (**1**): deep blue needles. Anal. Found: C, 64.78; H, 5.86. $\text{C}_{30}\text{H}_{34}\text{Fe}_2\text{Si}_2\text{Ti}$ Calc.: C, 64.88; H, 5.99%. ^1H NMR (C_6D_6): δ 6.61 (t, $J = 2.3$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Ti}$), 5.91 (t, $J = 2.3$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Ti}$), 4.40 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.19 (s, 10H, $\text{C}_5\text{H}_5\text{-Fe}$), 4.00 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Fe}$),

0.51 (s, 18H, TMS). ^{13}C NMR (C_6D_6): δ 155.0 ($\equiv\text{C-Ti}$), 130.3 ($\equiv\text{C-Fc}$), 123.7, 122.1, 113.0 ($\text{C}_5\text{H}_4\text{-Ti}$), 71.1, 70.1, 69.0, 68.8 ($-\text{Fc}$), 0.8 (TMS). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2056 cm^{-1} . MS (FAB⁺) m/z : 740 [M]⁺.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}\equiv\text{CC}\equiv\text{CFc})_2$ (**3**): moss-green powder. Anal. Found: C, 68.36; H, 4.25. $\text{C}_{38}\text{H}_{28}\text{Fe}_2\text{Ti} \cdot 1/3\text{CH}_2\text{Cl}_2$ Calc.: C, 68.46; H, 4.30%. ^1H NMR (CD_2Cl_2): δ 6.42 (s, 10H, $\text{C}_5\text{H}_5\text{-Ti}$), 4.45 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.27 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.24 (s, 10H, $\text{C}_5\text{H}_5\text{-Fe}$). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2172, 2021 cm^{-1} . MS (FAB⁺) m/z : 644 [M]⁺.

3.2. Synthesis of $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{C}\equiv\text{CRc})_2$ (**2**)

The reaction and successive work up were carried out in flasks shielded with aluminum foil. $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{TiCl}_2$ (197 mg, 0.5 mmol) in benzene (80 ml) was added dropwise to a benzene (5 ml) solution of $\text{Li}(\text{C}\equiv\text{C})_2\text{Rc}$ (1.0 mmol) at room temperature and stirred for 1 h. After the solution was concentrated to small volume, it was filtered. The filtrate was evaporated to dryness at 30°C in vacuo. The resulting residue was recrystallized from hexane at -30°C to give **2** as red crystals (yield 306 mg, 74%). Anal. Found: C, 57.95; H, 5.48. $\text{C}_{40}\text{H}_{44}\text{Ru}_2\text{Si}_2\text{Ti}$ Calc.: C, 57.81; H, 5.34%. ^1H NMR (C_6D_6): δ 6.57 (t, $J = 2.3$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Ti}$), 5.79 (t, $J = 2.3$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Ti}$), 4.85 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.60 (s, 10H, $\text{C}_5\text{H}_5\text{-Ru}$), 4.42 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Ru}$), 0.47 (s, 18H, TMS). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2059 cm^{-1} . MS (FAB⁺) m/z : 832 [M]⁺.

3.3. Synthesis of $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{C}\equiv\text{CC}\equiv\text{CFc})$ (**5**)

$(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{TiCl}_2$ (315 mg, 0.8 mmol) in THF (40 ml) was added to a THF (44 ml) solution of $\text{Li}(\text{C}\equiv\text{C})_2\text{Fc}$ (0.8 mmol) at -78°C . After the mixture was vigorously stirred for 1.5 h at the same temperature, the resulting solution was evaporated in vacuo. The residue was extracted with Et_2O and the extract was filtered. After the solution was evaporated to dryness, recrystallization from Et_2O /hexane at -30°C gave **5** as dark red needles (yield 370 mg, 78%). Anal. Found: C, 60.89; H, 5.99. $\text{C}_{40}\text{H}_{44}\text{ClFeSi}_2\text{Ti}$ Calc.: C, 60.97; H, 5.97%. ^1H NMR (C_6D_6): δ 6.62 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 6.25 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 6.03 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 5.69 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 4.39 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.04 (s, 5H, $\text{C}_5\text{H}_5\text{-Fe}$), 3.88 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 0.37 (s, 18H, TMS). ^{13}C NMR (C_6D_6): δ 143.4 ($\equiv\text{C-Ti}$), 128.9, 126.3, 124.7 ($\text{C}_5\text{H}_4\text{-Ti}$), 117.5 ($\text{C}\equiv\text{C-Ti}$), 114.1 ($\text{C}_5\text{H}_4\text{-Ti}$), 87.2 ($\text{C}\equiv\text{C-Fc}$), 72.6, 72.3, 70.4, 69.4 ($-\text{Fc}$), 66.0 ($\equiv\text{C-Fc}$), 0.2 (TMS). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2175, 2028 cm^{-1} . MS (FAB⁺) m/z : 590 [M]⁺.

3.4. Synthesis of $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{X}=\text{C}\equiv\text{CFc}, \text{C}\equiv\text{CRc} \text{ or } \text{C}\equiv\text{CC}\equiv\text{CRc})$

$(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{C}\equiv\text{CFc})(\text{C}\equiv\text{CC}\equiv\text{CFc})$ (**6**): complex **5** (177 mg, 0.30 mmol) in THF (18 ml) was added to a solution of THF (25 ml) containing $\text{LiC}\equiv\text{CFc}$ (0.30 mmol) at -78°C . After the mixture was vigorously stirred for 1 h at 0°C , the resulting solution was evaporated in vacuo. The residue was extracted with benzene and the extract was filtered. After evaporation to dryness, the residue was recrystallized from Et_2O /hexane at -30°C to give **6** as deep green needles (yield 173 mg, 75%). Anal. Found: C, 65.83; H, 5.84. $\text{C}_{42}\text{H}_{44}\text{Fe}_2\text{Si}_2\text{Ti}$ Calc.: C, 65.98; H, 5.80%. ^1H NMR (C_6D_6): δ 6.59 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 6.45 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 6.00 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 5.85 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 4.41 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.34 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.21 (s, 5H, $\text{C}_5\text{H}_5\text{-Fe}$), 4.04 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.01 (s, 5H, $\text{C}_5\text{H}_5\text{-Fe}$), 3.83 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 0.45 (s, 18H, TMS). ^{13}C NMR (C_6D_6): δ 159.4 ($\equiv\text{C-Ti}$), 147.2 ($\equiv\text{C-Ti}$), 133.2 ($\equiv\text{C-Fe}$), 125.0, 121.9, 121.4 ($\text{C}_5\text{H}_4\text{-Ti}$), 116.5 ($\text{C}\equiv\text{C-Ti}$), 114.5, 113.2 ($\text{C}_5\text{H}_4\text{-Ti}$), 86.7 ($\text{C}\equiv\text{C-Fe}$), 72.7, 72.3, 71.6, 70.4, 70.3, 69.4, 69.3, 67.9 (-Fe), 66.2 ($\equiv\text{C-Fe}$), 0.5 (TMS). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2173, 2054, 2024 cm^{-1} . MS (FAB $^+$) m/z : 764 [M] $^+$.

Complex **7** was prepared similarly from **5** and an equivalent amount of $\text{LiC}\equiv\text{CRc}$. $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{C}\equiv\text{CRc})$ (**7**): yield 75%; purple-red needles. Anal. Found: C, 62.30; H, 5.68. $\text{C}_{42}\text{H}_{44}\text{FeRuSi}_2\text{Ti}$ Calc.: C, 62.29; H, 5.48%. ^1H NMR (C_6D_6): δ 6.60 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 6.41 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 5.94 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 5.77 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 4.84 (t, $J = 1.7$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.60 (s, 5H, $\text{C}_5\text{H}_5\text{-Ru}$), 4.44 (t, $J = 1.7$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.37 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.04 (s, 5H, $\text{C}_5\text{H}_5\text{-Fe}$), 3.84 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 0.43 (s, 18H, TMS). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2173, 2058, 2023 cm^{-1} . MS (FAB $^+$) m/z : 810 [M] $^+$.

$(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{C}\equiv\text{CC}\equiv\text{CRc})$ (**8**): complex **5** (200 mg, 0.34 mmol) in THF (30 ml) was added to a solution of $\text{Li}(\text{C}\equiv\text{C})_2\text{Rc}$ (0.38 mmol) in hexane/THF (40 ml/10 ml) at 0°C . After the mixture was vigorously stirred for 1 h at the same temperature, the resulting solution was evaporated in vacuo. The residue was extracted with benzene and the extract was filtered. After evaporation to dryness, recrystallization of the residue from Et_2O /hexane at -30°C gave **8** as dark-purple crystals (yield 195 mg, 69%). Anal. Found: C, 62.82; H, 5.31. $\text{C}_{44}\text{H}_{44}\text{FeRuSi}_2\text{Ti}$ Calc.: C, 63.38; H, 5.32%. ^1H NMR (C_6D_6): δ 6.45 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 6.42 (m, 2H, $\text{C}_5\text{H}_4\text{-Ti}$), 5.91 (m, 4H, $\text{C}_5\text{H}_4\text{-Ti}$), 4.83 (bs, 2H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.44 (s, 5H, $\text{C}_5\text{H}_5\text{-Ru}$), 4.37 (bs, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.28 (bs, 2H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.03 (s, 5H, $\text{C}_5\text{H}_5\text{-Fe}$), 3.86 (bs, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 0.38 (s, 18H,

TMS). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2173, 2021 cm^{-1} . MS (FAB $^+$) m/z : 835 [$\text{M} + \text{H}$] $^+$.

3.5. Oxidative coupling reaction of complexes **1**, **4** and **6–8** with 2 equiv. of AgPF_6

To complex **4** (63 mg, 0.08 mmol) in THF (40 ml) was added THF (54 ml) solution of AgPF_6 (41 mg, 0.16 mmol) at room temperature and the mixture was stirred for 2 h. After the solvent was evaporated, the residue was purified by column chromatography on SiO_2 to give the known complex $\text{Fc}(\text{C}\equiv\text{C})_4\text{Fc}$ (**10**) [10] in 90% yield.

The reactions of complexes **1** and **6** were carried out similarly to give the coupling products $\text{Fc}(\text{C}\equiv\text{C})_2\text{Fc}$ (**9**) [9] and $\text{Fc}(\text{C}\equiv\text{C})_3\text{Fc}$ (**11**) in yield of 91% and 95% respectively. The reactions of complexes **7** and **8** were also carried out in a similar manner except that the reaction time was 1 day. The coupling products $\text{Fc}(\text{C}\equiv\text{C})_3\text{Rc}$ (**12**) and $\text{Fc}(\text{C}\equiv\text{C})_4\text{Rc}$ (**13**) were obtained in yields of 78% and 55% respectively.

$\text{Fc}(\text{C}\equiv\text{C})_3\text{Fc}$ (**11**): orange crystalline solid. Anal. Found: C, 70.34; H, 4.01; Fe, 25.33. $\text{C}_{26}\text{H}_{18}\text{Fe}_2$ Calc.: C, 70.63; H, 4.10; Fe, 25.26%. ^1H NMR (CDCl_3): δ 4.54 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.28 (t, $J = 1.8$ Hz, 4H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.26 (s, 10H, $\text{C}_5\text{H}_5\text{-Fe}$). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2196 cm^{-1} . MS (FAB $^+$) m/z : 442 [M] $^+$.

$\text{Fc}(\text{C}\equiv\text{C})_3\text{Rc}$ (**12**): orange crystalline solid. Anal. Found: C, 63.96; H, 3.65. $\text{C}_{26}\text{H}_{18}\text{FeRu}$ Calc.: C, 64.08; H, 3.72%. ^1H NMR (CDCl_3): δ 4.91 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.63 (s, 5H, $\text{C}_5\text{H}_5\text{-Ru}$), 4.59 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.52 (t, $J = 2.0$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.27 (t, $J = 2.0$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.25 (s, 5H, $\text{C}_5\text{H}_5\text{-Fe}$). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2197 cm^{-1} . MS (FAB $^+$) m/z : 488 [M] $^+$.

$\text{Fc}(\text{C}\equiv\text{C})_4\text{Rc}$ (**13**): orange crystalline solid. Anal. Found: C, 63.94; H, 3.57. $\text{C}_{28}\text{H}_{18}\text{FeRu} \cdot 1/4\text{CH}_2\text{Cl}_2$ Calc.: C, 63.71; H, 3.50%. The presence of CH_2Cl_2 in the analytical sample was confirmed by the NMR spectrum. ^1H NMR (CDCl_3): δ 4.91 (t, $J = 1.6$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.64 (s, 5H, $\text{C}_5\text{H}_5\text{-Ru}$), 4.61 (t, $J = 1.6$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Ru}$), 4.55 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.29 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{-Fe}$), 4.26 (s, 5H, $\text{C}_5\text{H}_5\text{-Fe}$). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})$: 2198 cm^{-1} . MS (FAB $^+$) m/z : 512 [M] $^+$.

3.6. Oxidation of $\text{MeC}\equiv\text{CC}\equiv\text{CFc}$ with AgPF_6

To a THF (50 ml) solution of $\text{MeC}\equiv\text{CC}\equiv\text{CFc}$ (50 mg, 0.20 mmol) was added AgPF_6 (0.20 mmol) in THF (118 ml). Monitoring of the reaction by IR $\nu(\text{C}\equiv\text{C})$ region indicated that the starting diyne (2239(m), 2155(vs) cm^{-1}) disappeared immediately while the species with $\nu(\text{C}\equiv\text{C})$ at 2241 cm^{-1} was formed predominantly. Concentration of the mixture and addition of hexane yielded a green crystalline solid of pure

[MeC≡CC≡CFc⁺][PF₆⁻] in 44% yield. Anal. Found: C, 40.13; H, 2.73. C₁₅H₁₂F₆FeP · CH₂Cl₂ Calc.: C, 40.20; H, 2.95%. MS (FAB⁺) *m/z*: 248 [M – (PF₆⁻)⁺].

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