Reductive elimination by remote electron transfer activation in C_4-bridged titanocene-ferrocenyl complexes

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Of the new titanocene derivatives $[Ti(C{\equiv}CC{\equiv}CR)_2(\eta^5\text{-}C_5H_4R')_2]$ [R = ferrocenyl (Fc); R′ = H 1, $SiMe_3$ 2; R = R′ = $SiMe_3$ 3], 3 is inert towards electrochemical or chemical oxidation while both 1 and 2 readily release a formal reductive elimination product $Fc(C{\equiv}C)_4Fc$ *via* initial oxidation of the Fc units, suggesting that the process is induced by electron transfer from the Ti–C fragment to Fc^+ through the conjugated diacetylide bridges.

There is a rapidly growing interest in the chemical and physical properties of compounds in which conjugated carbon chains span two transition-metal moieties.[1] Besides the viewpoint of applications as potentially useful materials, they have attracted fundamental attention as probes for examining intramolecular long-distance electron transfer.[2] While such complexes reported so far cover wide range of homometallic and heterometallic pairs of late transition metals,[1] including ferrocenyl and related compounds,[3] the combinations of early and late transition metals remain very rare.[4] Herein, we describe the synthesis and unique redox activities of diacetylide bridged titanocene–ferrocenyl complexes.

The smooth reaction of titanocene dichloride $[TiCl_2(\eta^5\text{-}C_5H_4R')_2]$ with 2 equiv. of $FcC{\equiv}CC{\equiv}CLi$ in thf gave the expected $[Ti(C{\equiv}CC{\equiv}CFc)_2(\eta^5\text{-}C_5H_4R')_2]$ (R′ = H **1**, $SiMe_3$ **2**) as deep green solids in 74% (**1**) and 87% (**2**) yield, respectively. For comparison, a nonferrocenyl analogue $[Ti(C{\equiv}CC{\equiv}CSiMe_3)_2(\eta^5\text{-}C_5H_4SiMe_3)_2]$ **3** was prepared in a similar fashion.† The molecular structure of **2** was resolved by X-ray crystallography (Fig. 1).‡ These complexes are thermally stable but prolonged heating under argon caused slow decomposition to intractable materials.

The cyclic voltammogram (CV) of complex **3** in CH_2Cl_2 exhibits a reversible reduction wave for Ti^{III}–Ti^{IV} at $E_{1/2}$ = −1.43 V (*vs.* ferrocene–ferrocenium). No oxidation wave was observed up to +1.0 V, the positive limit of the solvent redox window. The CV of complex **2** in CH_2Cl_2 is shown in Fig. 2. In addition to the reversible Ti wave at −1.53 V, two new redox waves were observed at +0.16 and +0.23 V during the oxidative scan. By comparison with an authentic sample of $Fc(C{\equiv}C)_4Fc$ **4**[5] the wave at +0.23 V was assigned to the reversible couple Fc^{II}–Fc^{III} of the new product **4**, while the irreversible peak at $E_{1/2}$ = +0.16 V corresponds to the same change of the two Fc units in complex **2**, the couple for authentic $H(C{\equiv}C)_2Fc$ being +0.20 V. In accord with this assignment, the total current for these Fc^{II}–Fc^{III} waves in Fig. 2 was approximately four times as large as that for the one-electron process Ti^{III}–Ti^{IV}. The appearance of the redox wave of the product suggests that **4** is liberated as soon as the two Fc moieties in **2** are oxidized to Fc^{III}. Complex **1** behaves similarly but shows slightly shifted potentials ($E_{1/2}$ = −1.48 V, E_{pa} = +0.21 V). Controlled oxidations of complexes **1** and **2** at +0.1 V with a Pt gauze electrode, followed by chromatography on SiO_2 gave the expected coupling product **4** in good yields of *ca.* 75%. The rest (*ca.* 25% yield) was confirmed to be the hydrolysed product $H(C{\equiv}C)_2Fc$.

Chemical oxidation of complexes **1** (in CH_2Cl_2) and **2** (in THF) with 2 equiv. of $AgPF_6$ was found to proceed more cleanly. The reaction mixture obtained from **1** was examined with ^1H NMR spectroscopy after removal of Ag metal and CH_2Cl_2; the rather simple spectrum showed a peak of $[TiF_2(\eta^5\text{-}C_5H_5)_2]$ (δ 6.41, CD_2Cl_2)[6] and peaks due to **4** in expected

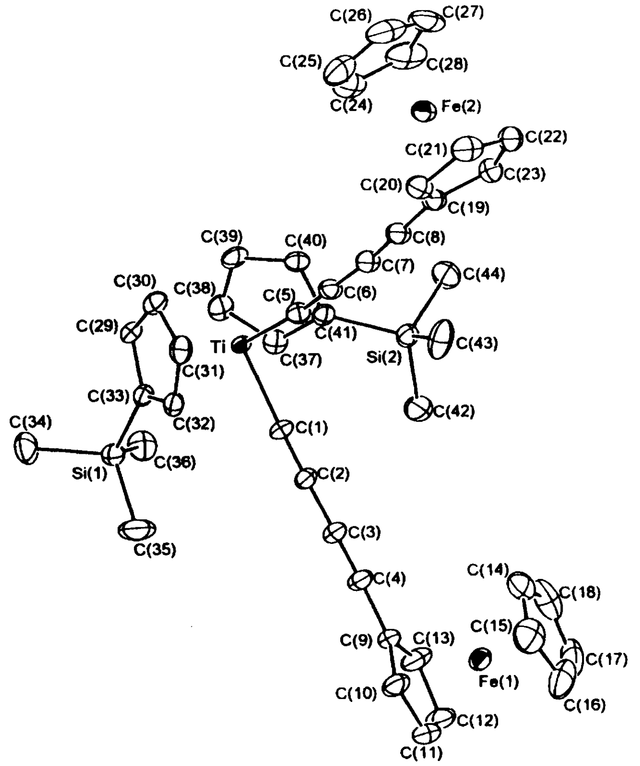


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Ti–C(1) 2.099(7), Ti–C(5) 2.090(7), C(1)–C(2) 1.224(10), C(2)–C(3) 1.377(10), C(3)–C(4) 1.195(11), C(5)–C(6) 1.224(10), C(6)–C(7) 1.377(10), C(7)–C(8) 1.210(11); C(1)–Ti–C(5) 97.2(3).

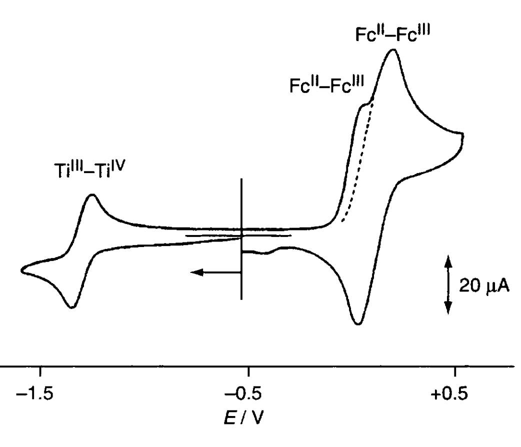
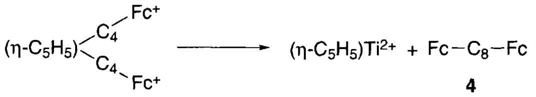


Fig. 2 Cyclic voltammogram of complex **2** (1.0×10^{-3} mol dm^{-3}) in CH_2Cl_2 in the presence of $NBu^n{}_4ClO_4$ (0.1 mol dm^{-3}) at room temperature under Ar; scan rate 100 mV s^{-1}; potentials are referenced to FcH–FcH^+



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Scheme 1

intensity ratios (Scheme 1). After chromatography, the coupling product **4** was isolated in yields of 98% (**1**) and 90% (**2**). Contrary to this, complex **3** is not oxidized by $AgPF_6$, as expected from the CV experiment. Mere coordination of Ag^+ to the CC triple bonds of $[Ti(C{\equiv}CSiMe_3)_2(\eta^5\text{-}C_5H_5)_2]$ has been known.[7]

In the case of late transition-metal complexes, the promotion of reductive elimination through an increase in the oxidation state of central metal has been achieved by the coordination of π acids,[8] oxidation of Pt^{II} bound alkynylferrocene,[9] or bimolecular electron transfer.[10] In d^0 metal complexes such as $[MR_2(\eta^5\text{-}C_5H_5)_2]$ (M = Ti, Zr; R = Ph, CH_2Ph) where the metal has no d electrons to be removed, added oxidants such as Ag^+ and FcH^+ remove an electron at the metal–carbon σ bond to generate M^+ and $R\cdot$.[11] In the present bis(alkynyl) derivative of titanocene, however, the large electronegativity of the sp-hybridized carbon prevents oxidation as observed in the case of **3**.

Inertness of **3** towards oxidation was further demonstrated by an electrochemical reaction; $H(C{\equiv}C)_2Fc$ ($E_{1/2}$ = +0.20 V) was subjected to controlled oxidation at +0.3 V until all the $H(C{\equiv}C)_2Fc$ were converted to ferrocenium. Thereafter 0.5 equiv. of **3** was added, but no appreciable reaction was observed over 20 min; neither were organic products nor the neutral $H(C{\equiv}C)_2Fc$ detected.[§] Accordingly, bimolecular electron transfer from **3** to $H(C{\equiv}C)_2Fc^+$ was not observed under these conditions. However, when titanocene and ferrocenyl are covalently bonded through the C(sp) conjugated rod as is the case in complexes **1** and **2**, oxidatively induced reductive elimination occurs instantaneously at +0.16 and +0.21 V, respectively (*vide supra*). Apparently intramolecular electron transfer from the Ti–C bonds to each ferrocenium, generating Ti^{2+} and two $C\cdot$, appears to be effective according to the present observations, and this seems to be a consequence of the delocalization in the $Ti(C{\equiv}C)_2Fc$ system. Although this reaction is formally a reductive elimination, it is not the metal centre (Ti) that is reduced, where C–C bond formation occurs, but the remote ferrocenium units at the other end of the conjugated chain.

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Footnotes

[†] Satisfactory elemental and FAB MS analyses were obtained for the new complexes. **1**: ^1H NMR (270 MHz, CD_2Cl_2) δ 6.42 (s, 10 H, C_5H_5Ti), 4.45 (t, *J* 1.8 Hz, 4 H, C_5H_4), 4.27 (t, *J* 1.8 Hz, 4 H, C_5H_4), 4.24 (s, 10 H, C_5H_5Fe). IR (KBr) ν/cm^{-1} 2179, 2022. **2**: ^1H NMR (C_6D_6) δ 6.46 (t, *J* 2.3 Hz, 4 H, C_5H_4Ti), 5.93 (t, *J* 2.3 Hz, 4 H, C_5H_4Ti), 4.36 (t, *J* 1.8 Hz, 4 H, C_5H_4Fe), 4.02 (s, 10 H, C_5H_5Fe), 3.87 (t, *J* 1.8 Hz, 4 H, C_5H_4Fe), 0.39 (s. 18 H, $SiMe_3$). IR (KBr) ν/cm^{-1} 2164, 2015. **3**: ^1H NMR (C_6D_6) δ 6.37 (t, *J* 2.0 Hz, 4 H, C_5H_4) 5.84 (t, *J* 2.0 Hz, 4 H, C_5H_4), 0.30 (s, 18 H, $SiMe_3$), 0.13 (s, 18 H, $SiMe_3$). IR (KBr) ν/cm^{-1} 2004.

[‡] *Crystal data for* **2**: $C_{44}H_{44}Fe_2Si_2Ti$, M = 788.60, monoclinic, space group $P2_1$, a = 14.017(4), b = 12.219(5), c = 12.026(3) Å, β = 106.97(2)°, U = 1970 Å^3, Z = 2, D_c = 1.33 g cm^{-3}, $F(000)$ = 819, μ = 10.11 cm^{-1}, crystal size 0.18 × 0.35 × 0.85 mm, radiation Mo-Kα (λ = 0.7107 Å), no. of data ($I \geqslant 3\sigma$) 3847, no. of parameters 441, final R 0.0458, R_w 0.0508. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/130.

[§] The reaction was examined by the ν(C≡C) absorptions in IR spectroscopy (CH_2Cl_2): $H(C{\equiv}C)_2Fc$ 2210, $H(C{\equiv}C)_2Fc^+$ 2019, $Me_3Si(C{\equiv}C)_4SiMe_3$ 2179, 2046, $H(C{\equiv}C)_2SiMe_3$ 2035, 2190 [ν(CH) 3300] cm^{-1}. After 20 min a CV scan showed the presence of unchanged **3**, which was also confirmed by TLC analysis. After several hours, however, some decomposition of **3** was noted giving uncharacterizable materials.

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