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Facile Reductive Coupling Reaction of Bis(ruthenocenylethynyl)-titanocene Complexes via Visible Light-Activation of the Ruthenocenyl Terminal

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The irradiation of $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti(C}\equiv\text{CRc)}_2$ (R = Me, SiMe_3 (= TMS); Rc = ruthenocenyl) at the band assignable to CT from Rc to Ti in the presence of equimolar amounts of $\text{RcC}\equiv\text{CH}$ and $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ smoothly gave titanacyclic complexes $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti}\{\text{–C(Rc)=C(C}\equiv\text{CRc)–CH=C(Rc)–}\}$ and $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}\{\text{–C(C}\equiv\text{CRc)=C(Rc)–C(OMe)(C}\equiv\text{CCO}_2\text{Me)–O–}\}$, respectively, two of which were structurally characterized. The formation of these complexes has been explained by the extremely easy reductive coupling in $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti(C}\equiv\text{CRc)}_2$, brought about by photo-excitation at the Rc group, followed by metallacycle formation that involves the resulting diyne unit and the externally added alkynes.

A number of bis(alkynyl)titanocenes $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti(C}\equiv\text{CR}')_2$ (R′ = Ph, ^{t}Bu, TMS, C_6H_{11}, etc.) have been described in the literature and are known to be stable.[1–5] Interestingly, some of them exhibit non-linear optical (NLO) properties, and their photophysical characteristics have attracted great interest.[6] In our project of binding heterometallic species with CC triple bonds and examining their interaction through an sp-hybrid spacer, we have already reported on the synthesis of a series of bis(metallocenylalkynyl)titanocene 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 or 2; Mc = Fc (ferrocenyl) or Rc (ruthenocenyl)) and their oxidation reactions effected by AgPF_6 or electrochemical treatment.[7–9] Complexes with Fc terminals were easily oxidized at the Fc units to cleanly yield the neutral coupling product of the two metallocenyl acetylide units, $\text{Fc–(C}\equiv\text{C)}_{2n}\text{–Fc}$, and a $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti}^{2+}$ fragment.[7,8] In contrast, complexes with Rc terminals, $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti(C}\equiv\text{CRc)}_2$ (**1**: R = Me, **2**: R = TMS) did not give any appreciable product upon chemical or electrochemical oxidation. We have, however, noticed that they are extremely sensitive to light, and immediately begin to decompose upon exposure to normal room-illumination, whereas the ferrocenyl analog, $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Ti(C}\equiv\text{CFc)}_2$ (**3**: R = TMS), is quite stable toward roomlight. We now report on our study aimed at an elucidation of the net-reaction that occurs upon the photolysis of **1** and **2**.

Results and Discussion

The absorption spectra of **1**–**3** measured in benzene (= C_6H_6) are shown in Fig. 1. The spectrum of **3** has two distinct absorptions at 415 (ε 7400) and 585 nm (ε 5100), while the corresponding peaks of **1** and **2** are located closer, and overlap. An absorption peak at 665 nm found in Cp_2TiFc_2 (Cp = $\eta^5\text{-C}_5\text{H}_5$) has been assigned to the charge-transfer (CT) band from Fc to the LUMO of the directly bound Cp_2Ti fragment.[10] Since the HOMO of Fc in **3** is stabilized to some extent by the Cp-bound CC triple bond,[7,8] the CT from the Fc to $(\eta^5\text{-C}_5\text{H}_4\text{TMS})_2\text{Ti}$ would be shifted to a higher energy region. On the other hand, in the case of the bis(alkynyl)titanocenes $(\text{RCp})_2\text{Ti(C}\equiv\text{CR}')_2$ (RCp = $\eta^5\text{-C}_5\text{H}_4\text{R}$), the LMCT band from the σ-alkynyl unit to the Ti center is observed at around 380–420 nm,[5] e.g., 420 nm (ε 6400) when R = TMS and R′ = Ph, in C_6H_6. Based on these known UV data, the well-separated peaks at 585 and 415 nm of **3** may be attributed to the CT from the Fc to $(\text{TMSCp})_2\text{Ti}$, and the LMCT from the alkynyl unit to $(\text{TMSCp})_2\text{Ti}$, respectively. Analogously, the low-energy peaks of **1** at 490 nm (ε 6600) and **2** at 510 nm (ε 8300) are assumed to be the CT bands from Rc to $(\text{RCp})_2\text{Ti}$. The shift of this band to a higher energy region upon going from Fc to Rc is consistent with the lower HOMO energy-level of Rc compared with that of Fc.[11]

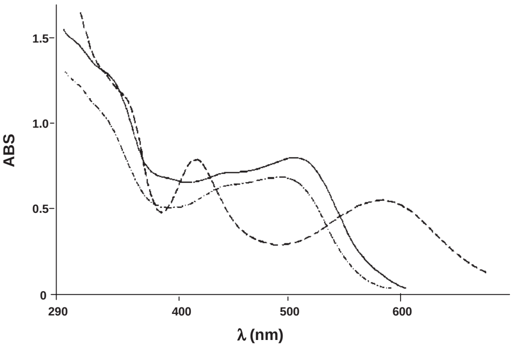

Fig. 1. UV–vis spectra of $(\text{RCp})_2\text{Ti(C}\equiv\text{CMc)}_2$ in C_6H_6: **1**, dashed line; **2**, solid line; **3**, dotted line.

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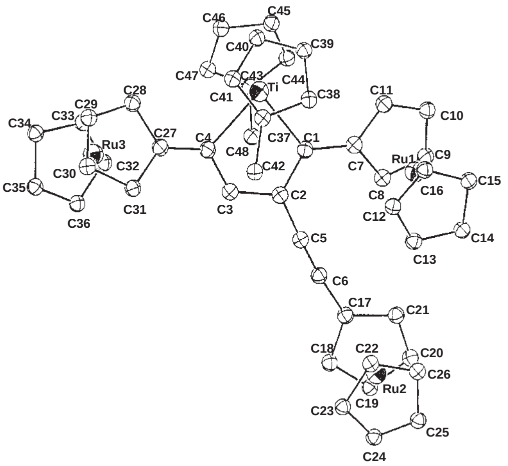


Fig. 2. Molecular structure of $(MeCp)_2Ti\{–C(Rc)=C(C\equiv CRc)–CH=C(Rc)–\}$ (**4**). Selected bond distances (Å) and angles (°): Ti–C1 = 2.14(1), Ti–C4 = 2.16(1), C1–C2 = 1.42(1), C3–C4 = 1.36(1), C2–C3 = 1.46(1), C5–C6 = 1.20(2), C1–Ti–C4 = 82.7(4), Ti–C1–C2 = 109.5(6), C1–C2–C3 = 116.9(9), C2–C3–C4 = 122.6(9), C3–C4–Ti = 108.3(7), C2–C5–C6 = 178(1), C5–C6–C17 = 171(1).

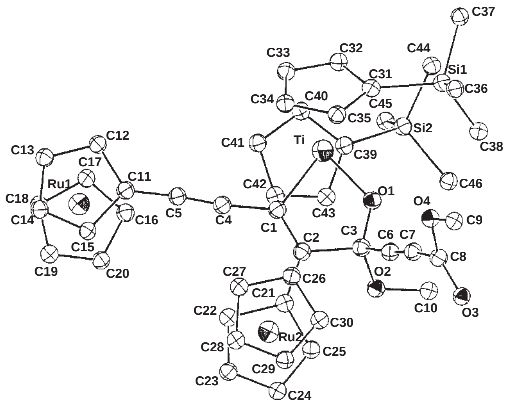


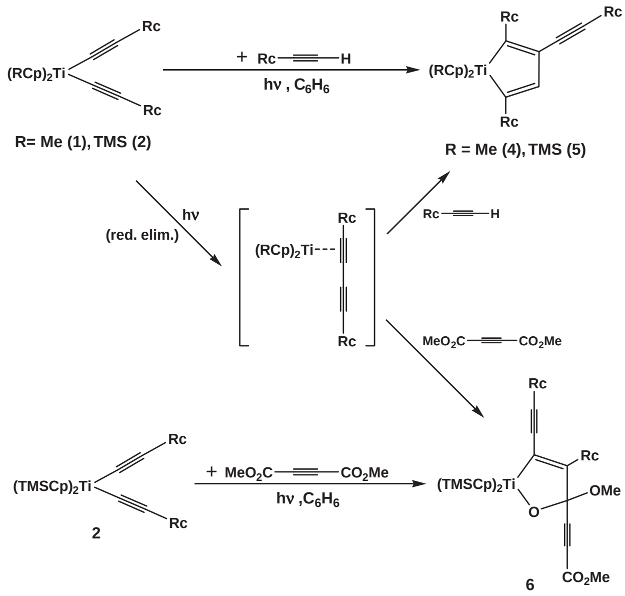
Fig. 3. Molecular structure of $(TMSCp)_2Ti\{–C(C\equiv CRc)=C(Rc)–C(OMe)(C\equiv CCO_2Me)–O–\}$ (**6**). Selected bond distances (Å) and angles (°): Ti–C1 = 2.19(1), Ti–O1 = 1.883(8), C1–C2 = 1.36(2), C2–C3 = 1.53(2), O1–C3 = 1.40(1), C4–C5 = 1.20(2), C6–C7 = 1.21(2), C8–O3 = 1.20(2), C1–Ti–O1 = 77.8(4), Ti–C1–C2 = 112.5(9), C1–C2–C3 = 115(1), C2–C3–O1 = 109.4(9), C3–O1–Ti = 124.9(7), C1–C4–C5 = 172(1), C3–C6–C7 = 177(1).

A photolysis experiment was performed with 545 nm light generated by a 100 W high-pressure Hg lamp equipped with a UV cut-off filter, so that mainly the Rc-to-Ti CT band was excited. Immediate decomposition was noted upon the irradiation of **1** and **2** within ca. 30 min, leading to an intractable mixture of species. We could, however, isolate a trace amount of a stable crystalline complex (**4**) after recrystallization of the reaction mixture from C_6H_6, whose ^1H NMR spectrum indicated the presence of three different Rc units with peaks at δ 4.82 (t), 4.66 (s), 4.61 (s), 4.59 (t), 4.54 (s), 4.49 (t), 4.41 (t), 4.28 (t), and 4.03 (t) in CD_2Cl_2. Complex **4** was obtained in 72% yield when the photolysis reaction of **1** was carried out in the presence of 1 equiv of $RcC\equiv CH$. A similar complex (**5**) was isolated in 56% yield when the photoreaction of **2** was conducted in the presence of 1 equiv of $RcC\equiv CH$.

Yellow-green crystals of **4** suitable for single-crystal X-ray diffraction were obtained by recrystallization from C_6H_6 at room temperature. The molecular structure illustrated in Fig. 2 has revealed that this is a titanacyclopentadiene derivative substituted with two Rc units and one $RcC\equiv C–$ group. The two Rc-groups at the α-positions are placed on the opposite side with respect to the titanacycle plane. One of the C=C bonds of the titanacyclopentadiene framework with adjacent Rc- and $RcC\equiv C–$ substituents has a bond length of 1.42(1) Å, slightly longer than the other one (1.36(1) Å), the latter being close to a C=C bond length expected for typical titanacyclopentadiene complexes.[12] The C≡C bond length (1.20(2) Å) in the $RcC\equiv C–$ group is normal.

To identify the Rc group brought into the complex by the added ruthenocenylacetylene, a similar photoreaction of **2** was examined in the presence of $MeO_2CC\equiv CCO_2Me$ instead of $RcC\equiv CH$. The obtained complex (**6**) was not thermally stable, but its good crystallinity allowed us to isolate it in 61% yield as well as allowing a structural characterization. Brown-red crystals suitable for X-ray analysis were grown in C_6H_6/hexane at 5 °C. During data collection using Mo $K\alpha$ radiation, constant decay of the reflection intensity was inevitable because of its thermal instability. The ORTEP drawing in Fig. 3 shows that complex **6** has an oxatitanacyclopentene framework as the result of carbonyl group incorporation, rather than the CC triple bond. The Ti–O(1) distance, 1.883(8) Å, is longer than those found in the oxatitanacyclopentene complex of $Cp_2Ti\{–C(Ph)=C(Ph)–C(Me)_2–O–\}$[13] and the $Cp_2Ti–O–TiCp_2$ complexes,[14,15] but shorter than that in the titanacarboxylate complex, $Cp_2Ti(O_2CC_6H_4)$.[16] All of the other functional groups in **6** have typical bond lengths and angles. Interestingly, the positions of the Rc and $RcC\equiv C–$ groups, which are now known to arise from the starting complex **2**, are reversed from those in complex **4**. The regioselection in the titanacycle is most likely controlled by steric factors within the preceding Ti(II) π-complex intermediates (vide infra).

Apparently, the precursors for the titanacycle complexes **4**–**6** are the π-complexes of Cp_2Ti, i.e., $(RCp)_2Ti(\eta^2–RcC\equiv C–C\equiv CRc)(\eta^2–RcC\equiv CH)$ and $(RCp)_2Ti(\eta^2–RcC\equiv C–C\equiv CRc)\{\eta^2\text{-(C,O)-}MeO_2CC\equiv CCO_2Me\}$. The formation of the titanacyclopentadienes from an in situ generated titanocene fragment, $[Cp_2Ti]$, with 2 molecules of acetylenic species has been well-documented.[17] Oxatitanacyclopentenes are known to form by the combination of $[Cp_2Ti]$, an alkyne, and a carbonyl compound such as ketones[13,18] and CO_2.[16,19,20] Therefore, it is reasonable to assume that the primary product formed from **1** and **2** upon activation with 545 nm light has the composition of $(RCp)_2Ti(\eta^2–RcC\equiv C–C\equiv CRc)$, which in turn suggests that reductive coupling of the two alkynyl units has taken place (Scheme 1). The diyne unit in this intermediate must be strongly linked to Ti, because liberation of the Rc-substituted diyne has not been observed upon spontaneous decomposition of this intermediate, and its fate could not be traced. However, any transient species as-



Scheme 1. Photolysis of (RCp)$_2$Ti(C≡CRc)$_2$ (**1** and **2**) with 1 equiv of RcC≡CH or MeO$_2$CC≡CCO$_2$Me.

signable to such an intermediate as (RCp)$_2$Ti(η^2–RcC≡C–C≡CRc) could also not be confirmed through our reactions.

On the other hand, Rosenthal et al. reported a related reductive coupling reaction observed upon the photolysis of Cp$_2$Ti(C≡C^{t}Bu)$_2$ (**A**) at the LMCT from the alkynyl to Ti, whose primary product incorporating the net coupling product of ^{t}BuC≡C-C≡C^{t}Bu is identified as a five-membered titanacyclocumulene complex, Cp$_2$Ti{–C(^{t}Bu)=C=C=C(^{t}Bu)–} (**B**).[21] The photolysis of **A** under our conditions with RcC≡CH or other alkynes gave only an intractable reaction mixture comprised of several non-isolable products, while the formation of **B** was confirmed in the beginning of the reaction, as expected. These observations reasonably support that the primary product in our system is considered to be (RCp)$_2$Ti(η^2–RcC≡C–C≡CRc) rather than the corresponding titanacyclocumulene species, because the former can allow added alkynes to insert more smoothly than the latter.

The Fc-analogue **3** did not show any photo-reactivity even upon irradiation with a Hg lamp at its LMCT band and CT band from Fc to (RCp)$_2$Ti. This difference in reactivity between Ti–Fc and Ti–Rc complexes cannot be well explained at present, because the mechanism of the photo-induced reductive coupling reaction of **1**, **2**, or **A**, itself, remains unclear concerning whether one or two radicals of [$^\bullet$C≡CR′] are formed during the first step of the reaction.[22] If one radical, [$^\bullet$C≡CR′], is formed at first, and attacks another Ti–C bond to cause a reductive coupling process, the Ti–C bonds of the Ti–Fc complex **3** might be stronger than those of the Ti–Rc complexes, **1** and **2**, and not be cleaved.

In conclusion, the irradiation of the Rc-to-Ti CT band with visible light gives rise to efficient homolytic splitting of the Ti–alkynyl bond, resulting in reductive coupling of the two alkynyl groups. The formation of such an intermediate as (RCp)$_2$Ti(η^2–RcC≡C–C≡CRc) provides an easy route to titanacycle bearing ruthenocenyl substituents when the reaction is carried out in the presence of appropriate alkynes.

Experimental

The ^{1}H and ^{13}C NMR spectra were measured using a JEOL JNM-EX270 spectrometer. The IR spectra were recorded using a Perkin-Elmer 1600 FT-IR spectrometer. The mass spectra (FAB$^+$) were obtained using a JEOL JMS-HX110 mass spectrometer. (TMSCp)$_2$Ti(C≡CRc)$_2$ (**2**),[8] (TMSCp)$_2$Ti(C≡CFc)$_2$ (**3**),[7,8] Cp$_2$Ti(C≡C^{t}Bu)$_2$ (**A**),[5] and (TMSCp)$_2$Ti(C≡CPh)$_2$[5] were prepared as previously reported. (MeCp)$_2$Ti(C≡CRc)$_2$ (**1**) was prepared in a manner similar to complex **2**. Ruthenocenylacetylene was prepared by modifications of the methods for ferrocenylacetylene.[23,24] Dimethyl acetylenedicarboxylate, MeO$_2$CC≡CCO$_2$Me, was used without further purification. All solvents were purified or distilled prior to use. Especially, the preparations of (RCp)$_2$Ti(C≡CR′)$_2$ (**1**, **2**, and **A**) were carried out in a flask covered with aluminum foil to protect it from light, and all manipulations were performed under argon and in the dark, unless photolysis. All NMR tube-reactions were conducted under the stated condition with ca. 30 mM of each complex in C$_6$D$_6$.

Synthesis of (η^5-C$_5$H$_4$R)$_2$Ti{–C(Rc)=C(C≡CRc)–CH=C(Rc)–} (R = Me (4) or TMS (5)). (η^5-C$_5$H$_4$Me)$_2$Ti{–C(Rc)=C(C≡CRc)–CH=C(Rc)–} (**4**): A solution of complex **1** (72 mg, 0.1 mmol) and ruthenocenylacetylene (26 mg, 0.1 mmol) in benzene (8 mL) was photoirradiated at room temperature for 1 h. After the solution was evaporated, the resulting solid was thoroughly washed with hexane, and then extracted by THF. After the extract was evaporated to dryness, the residue was recrystallized from THF/hexane at −30 °C to give **4** as yellow-green needles (yield 70 mg, 72%). Anal. Found: C, 59.90; H, 5.06%. C$_{48}$H$_{42}$Ru$_3$Ti•THF Calcd: C, 59.94; H, 4.84%. The presence of 1 equiv of THF was also confirmed by a ^{1}H NMR measurement. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.30 (m, 4H, C$_5$H$_4$–Ti), 6.10 (s, 1H, Ti–C=CH), 5.84 (m, 2H, C$_5$H$_4$–Ti), 5.77 (m, 2H, C$_5$H$_4$–Ti), 4.82 (t, J = 1.6 Hz, 2H, C$_5$H$_4$–Ru), 4.66 (s, 5H, C$_5$H$_5$–Ru), 4.61 (s, 5H, C$_5$H$_5$–Ru), 4.59 (t, J = 1.8 Hz, 2H, C$_5$H$_4$–Ru), 4.54 (s, 5H, C$_5$H$_5$–Ru), 4.49 (t, J = 1.8 Hz, 2H, C$_5$H$_4$–Ru), 4.41 (t, J = 1.6 Hz, 2H, C$_5$H$_4$–Ru), 4.28 (t, J = 1.6 Hz, 2H, C$_5$H$_4$–Ru), 4.03 (t, J = 1.6 Hz, 2H, C$_5$H$_4$–Ru), 2.12 (s, 6H, Me). ^{13}C NMR (CD$_2$Cl$_2$): δ 204.0 (Ti–$\underline{C}$=), 196.9 (Ti–$\underline{C}$=), 126.2 (–C=$\underline{C}$H–C=), 121.1 (Me$\underline{C}_5$H$_4$–Ti), 116.6 (Me$\underline{C}_5$H$_4$–Ti), 116.2 (Me$\underline{C}_5$H$_4$–Ti), 112.7 (Ti–C=$\underline{C}$(C≡CRc)–), 108.3 (Me$\underline{C}_5$H$_4$–Ti), 108.2 (Me$\underline{C}_5$H$_4$–Ti), 97.0 (–$\underline{C}$≡C–Rc), 93.8 (–C≡$\underline{C}$–Rc), 90.2 (–Rc), 85.7 (–Rc), 73.5 (–Rc), 71.9 (–Rc), 71.8 (–Rc), 71.6 (–Rc), 71.5 (–Rc), 70.6 (–Rc), 70.1 (–Rc), 69.7 (–Rc), 69.5 (–Rc), 16.4 (Me). MS (FAB$^+$) m/z: 971 [M]$^+$.

(η^5-C$_5$H$_4$TMS)$_2$Ti{–C(Rc)=C(C≡CRc)–CH=C(Rc)–} (5): A solution of complex **2** (166 mg, 0.20 mmol) and ruthenocenylacetylene (51 mg, 0.20 mmol) in benzene (8 mL) was photoirradiated at room temperature for 3 h. After the solution was evaporated, the resulting solid was washed using hexane. The residue was recrystallized from toluene/hexane at −30 °C to give **5** as red-green needles (yield 117 mg, 56%). Anal. Found: C, 57.70; H, 5.11%. C$_{52}$H$_{54}$Ru$_3$Si$_2$Ti Calcd: C, 57.50; H, 5.01%. ^{1}H NMR (C$_6$D$_6$): δ 6.58 (m, 4H, C$_5$H$_4$–Ti), 6.54 (m, 4H, C$_5$H$_4$–Ti), 6.39 (s, 1H, Ti–C=CH), 4.96 (bs, 2H, C$_5$H$_4$–Ru), 4.82 (s, 5H, C$_5$H$_5$–Ru), 4.71 (bs, 2H, C$_5$H$_4$–Ru), 4.64 (bs, 2H, C$_5$H$_4$–Ru), 4.62 (s, 5H, C$_5$H$_5$–Ru), 4.53 (s, 5H, C$_5$H$_5$–Ru), 4.42 (bs, 2H, C$_5$H$_4$–Ru), 4.38 (bs, 2H, C$_5$H$_4$–Ru), 4.14 (bs, 2H, C$_5$H$_4$–Ru), 0.26 (s, 18H, TMS). MS (FAB$^+$) m/z: 1086 [M]$^+$.

Synthesis of (η^5-C$_5$H$_4$TMS)$_2$Ti{–C(C≡CRc)=C(Rc)–C-(OMe)(C≡CCO$_2$Me)–O–} (6). A solution of complex **2** (166 mg, 0.20 mmol) and MeO$_2$CC≡CCO$_2$Me (40 µL, 0.32 mmol) in benzene (7 mL) was photoirradiated at room temperature for 1 h. After the solution was evaporated, the resulting solid was washed with hexane (1–1.5 mL × 2). The residue was recrystallized from Et_2O/hexane at -30 °C to give **6** as brown-red needles (yield 119 mg, 61%). Anal. Found: C, 56.81; H, 5.36%. $C_{46}H_{50}O_4Ru_2Si_2Ti$ Calcd: C, 56.78; H, 5.18%. ^{1}H NMR (C_6D_6): δ 7.35 (m, 1H, C_5H_4–Ti), 7.06 (m, 1H, C_5H_4–Ti), 6.74 (m, 1H, C_5H_4–Ti), 6.60 (m, 1H, C_5H_4–Ti), 6.55 (m, 1H, C_5H_4–Ti), 6.53 (m, 1H, C_5H_4–Ti), 6.21 (m, 1H, C_5H_4–Ti), 5.93 (m, 1H, C_5H_4–Ti), 5.89 (bs, 1H, C_5H_4–Ru), 5.67 (bs, 1H, C_5H_4–Ru), 4.90 (bs, 7H, C_5H_4–Ru + C_5H_5–Ru), 4.66 (bs, 7H, C_5H_4–Ru + C_5H_5–Ru), 4.42 (bs, 2H, C_5H_4–Ru), 3.39 (s, 3H, OMe), 3.25 (s, 3H, OMe), 0.25 (s, 9H, TMS), 0.20 (s, 9H, TMS). IR (C_6H_6, cm^{-1}): 2224 (m, $\nu_{C\equiv C}$), 1717 (vs, ν_{CO}).

X-ray Crystallography. A small crystal of **4** (Orthorhombic, $P2_12_12_1$, $C_{48}H_{42}Ru_3Ti$, FW $= 969.93$, $0.15 \times 0.22 \times 0.09$ mm^3) was mounted on top of a glass fiber for data collection, which was performed using an Enraf-Nonius CAD4 diffractometer with Cu Kα radiation ($\lambda = 1.54184$ Å) at room temperature. Other crystallographic data of **4**: $a = 14.156(1)$, $b = 15.520(1)$, $c = 16.810(1)$ Å, $V = 3693.0(5)$ Å^3, $Z = 4$, ρ (calcd) $= 1.745$ g cm^{-3}, $\mu = 11.778$ mm^{-1}, $F(000) = 1936$, $\theta_{max} = 69.40°$, measured 3894, independent 3866 reflections, $R_{int} = 0.0191$, 469 parameters, $R = 0.0560$, $R_w = 0.1391$, $S = 1.071$. A brown-red needle of **6** (Triclinic, $P\bar{1}$, $C_{46}H_{50}O_4Ru_2Si_2Ti$, FW $= 973.08$, $0.30 \times 0.10 \times 0.10$ mm^3) was also mounted on top of a glass fiber for data collection, which was performed using a Mac Science MXC18 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Other crystallographic data of **6**: $a = 10.466(3)$, $b = 11.382(3)$, $c = 22.771(3)$ Å, $\alpha = 85.49(1)$, $\beta = 77.05(2)$, $\gamma = 63.96(2)°$, $V = 2374.6(9)$ Å^3, $Z = 2$, ρ (calcd) $= 1.361$ g cm^{-3}, $\mu = 0.880$ mm^{-1}, $F(000) = 992$, $\theta_{max} = 25.0°$, measured 9124, independent 8384 reflections, $R_{int} = 0.0763$, 496 parameters, $R = 0.0835$, $R_w = 0.2346$, $S = 1.119$. The structures were solved by a direct method using SIR92,[25] and refined anisotropically for all non-hydrogen atoms by a full-matrix least-squares method with the program SHELXL97.[26] The hydrogen atoms were not located.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-261313 for complex **4** and CCDC-261314 for complex **6**. Copies of the data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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