Facile Functionalizations of Permethyltitanocene Dichloride to Chiral Persubstituted Titanocene Complexes

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Summary: *The new class of compounds arising from unconventinal additions of 1,4-disubstituted 1,3-butadiynes to activated permethylmetallocene species of Ti and Zr can be used in facile functionalizations. For example, the chiral product* ***5****, obtained from the addition of tBuC≡CC≡CtBu to activated permethyltitanocene, has been derivatized by simple means, e.g., hydrogen chloride, bromine, or dihydrogen, affording practically useful functionalized titanocene compounds containing a chiral auxiliary ligand with an intramolecularly coordinated (compound* ***7****) or a free double bond (compounds* ***8a****,****b****). The new complexes have been characterized spectroscopically. Additionally, X-ray crystal structure analyses were performed for* ***7*** *and* ***8a****,****b****.*

Introduction

Functionalized chiral metallocenes can successfully be employed in various stoichiometric and catalytic reactions, including stereospecific polymerizations of prochiral olefins. For that reason there is a considerable demand for facile syntheses of compounds already known and also for developing new reaction pathways that afford novel metallocene derivatives.[1]

We have recently found out that the reduction of permethylmetallocene dichlorides [$Cp^*_2MCl_2$] (M = Ti (**1**), Zr) with magnesium in THF in the presence of commercially available disubstituted 1,3-butadiynes RC≡CC≡CR leads to a metallacyclopropene (M = Ti, R = $SiMe_3$), to some five-membered metallacyclocumulenes (M = Zr; R = Ph, Me, $SiMe_3$), or, via C−H activations and C−C coupling reactions, to coupling products such as **3**−**5** (Scheme 1).[2]

Another coupling product (**6**) has been obtained by thermally induced replacement of the coordinated alkyne in the permethyltitanocene source [$Cp^*_2Ti(\eta^2$-Me_3SiC_2-$SiMe_3)$] (**2**)[3] by the butadiyne *t*BuC≡CC≡C*t*Bu.[2c] In this reaction **5**[2b] has to be regarded as an intermediate, since a direct conversion of **5** into **6** is also possible (Scheme 2).[2c]

Here we report on further functionalizations of compounds **5** and **6** with simple reagents, e.g. hydrogen chloride, bromine, and dihydrogen, affording the novel, easily applicable chiral derivatives **7** and **8a**,**b** (Scheme 2).

Results and Discussion

All the chemistry depicted in Scheme 2 ensues from the reduction of the commercially available permethyltitanocene dichloride $Cp^*_2TiCl_2$ (**1**) by magnesium. This system in the presence of *t*BuC≡CC≡C*t*Bu affords the coupled alkyne compound **5** (reaction pathway **I**);[2b] the same system in the presence of $Me_3SiC{\equiv}CSiMe_3$ complex **2**,[3] on subsequent thermolysis with *t*BuC≡CC≡C*t*Bu, gives the coupled complex **6**.[2c] Both complexes **5** and **6** react smoothly with 2 equiv of HCl to yield the olefinic dichloride **8a** (reaction pathways **IV** and **V**, respectively). The two protons are added either to the triple bond of **5** or the two methylene groups of **6**. Importantly, complex **5** reacts quantitatively with molecular hydrogen to give the novel intramolecularly coordinated titanocene−olefin complex **7** (**III**). This compound is also obtained from **8a** by the removal of chlorine by magnesium (**VI**).

The reaction of **7** with HCl produces the paraffinic dichloride **9** (**VII**) only in a low yield. Instead, complex

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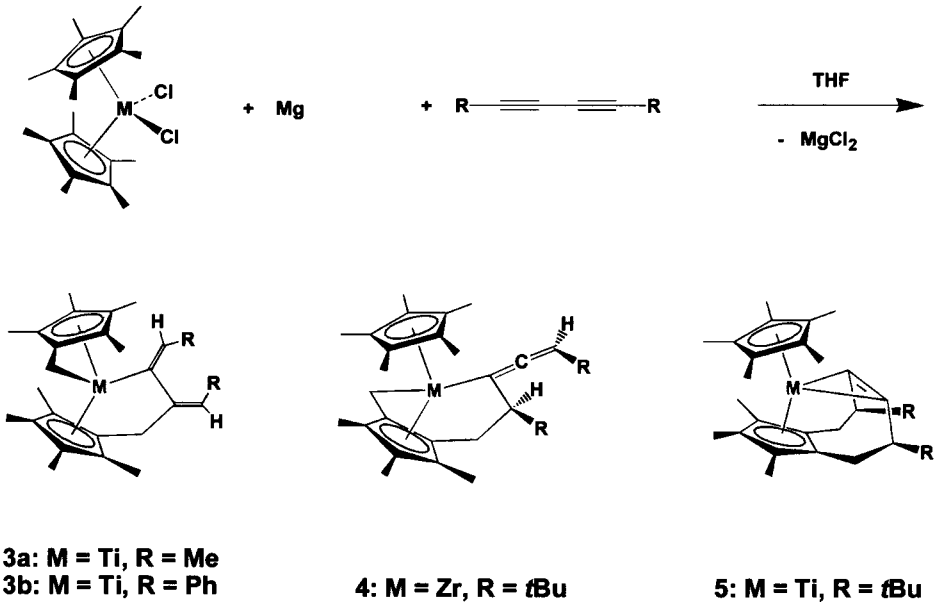
Scheme 1



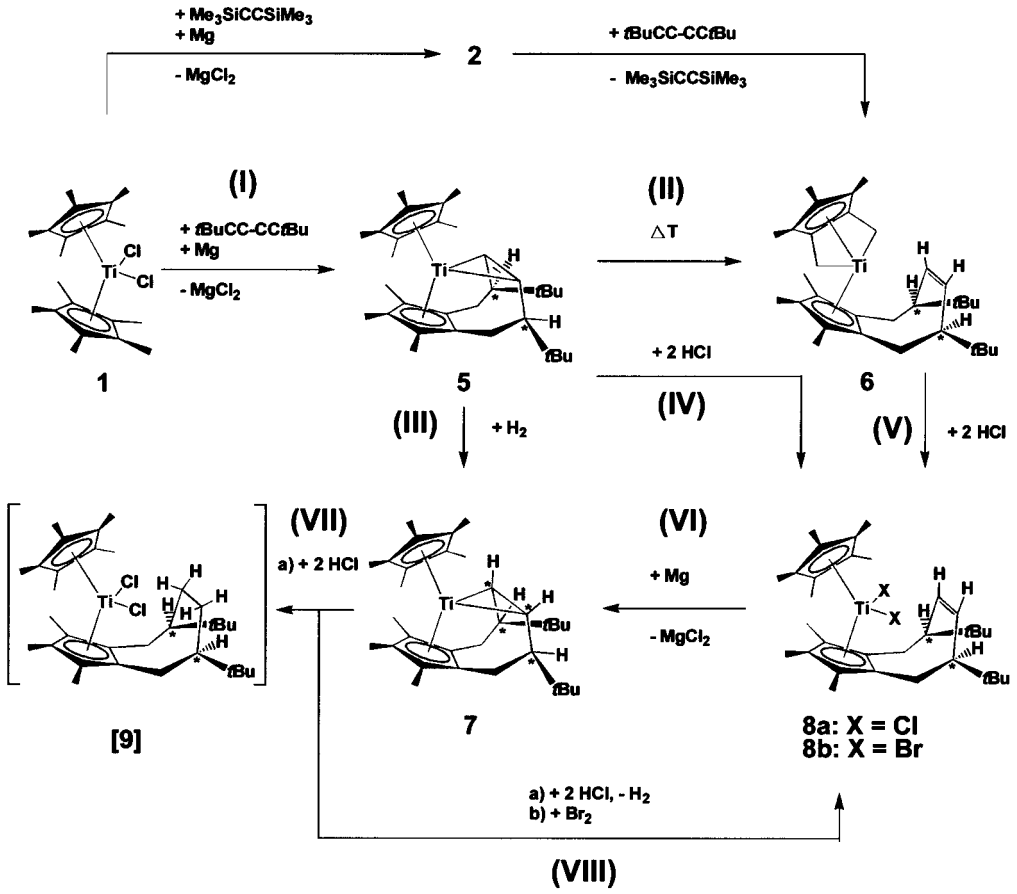
3a: M = Ti, R = Me
3b: M = Ti, R = Ph **4: M = Zr, R = *t*Bu** **5: M = Ti, R = *t*Bu**

8a is formed accompanied by hydrogen liberation (**VIII**). This implies that the hydrogen addition to the double bond is less feasible than the hydrogen elimination. Addition of a stoichiometric amount of elemental bromine to **7** affords the olefinic dibromide **8b** (**VIII**).

Complex **8a**, however, is unstable toward an excess of hydrogen chloride. NMR analysis showed its slow conversion to a mixture of [Cp*$TiCl_3$] and [{η^5-C_5Me_3-($-CH_2CH(t\text{Bu})CH{=}CHCH(t\text{Bu})CH_2-$}$TiCl_3$], implying acidolysis of Cp* or the modified Cp* ligand. The bromine analogues of these two complexes are side products of the formation of complex **8b** (**VIII**).

The yellow complex **7** and the brownish red complexes **8a,b** were prepared according to the described procedure. They are readily soluble in THF, toluene, and *n*-hexane. Their spectral data verify the constitutional formulas shown in Scheme 2. The presence of noncoordinated double bonds in **8a**,**b** is confirmed by signals in both the ^{1}H (δ 5.29−5.38) and ^{13}C NMR spectra (δ 130.4, 131.6), while the complexation of the double bond in **7**

Scheme 2



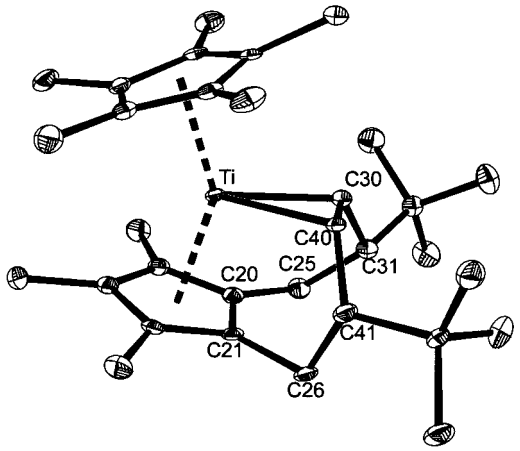


Figure 1. Molecular structure of **7** in the crystal. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Ti−C30 2.205(2), Ti−C40 2.171(2), C30−C40 1.462(4), C30−C31 1.541(3), C31−C25 1.534(4), C25−C20 1.500(4), C40−C41 1.530(3), C41−C26 1.530(4), C26−C21 1.502(3); C30−Ti−C40 39.03(9), C30−C40−C41 131.3(2), C40−C41−C26 109.2(2), C41−C26−C21 108.3(2), C40−C30−C31 125.3(2), C30−C31−C25 110.0(2), C31−C25−C20 111.3(2).

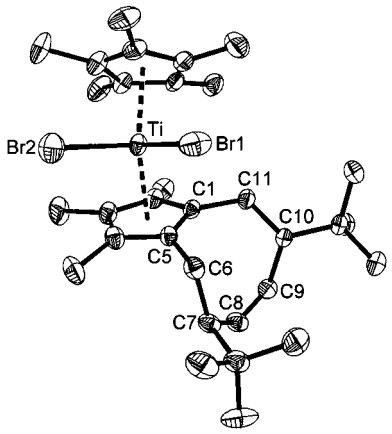


Figure 2. Molecular structure of **8b** in the crystal. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Ti−Br1 2.516(1), Ti−Br2 2.522(1), C5−C6 1.501(8), C6−C7 1.539(9), C7−C8 1.503-(9), C8−C9 1.318 (8), C9−C10 1.522(8), C11−C1 1.508(8); Br1−Ti−Br2 91.11(5), C5−C6−C7 112.3(5), C6−C7−C8 114.8(5), C7−C8−C9 131.3(6), C8−C9−C10 128.0 (6), C9−C10−C11 109.0(5), C10−C11−C1 116.7(5).

can be deduced from the corresponding ^{1}H (δ 1.32, 2.77) and ^{13}C (δ 119.4, 122.5) NMR signals, which are found in the region typical for titanacyclopropanes, e.g. [Cp*$_2$-Ti(η^2-$H_2C_2H_2$)] (δ 2.02; δ 105.1).[5]

The crystal structure analyses of **7** and **8a**,**b**[4] (the molecular structures of **7** and **8b** are presented in Figures 1 and 2) show a bent-sandwich arrangement with one pentamethylcyclopentadienyl ligand and one 3,4,5-trimethylcyclopentadienyl ligand annellated in 1,2-positions with 3,6-di-*tert*-butylcyclooct-4-ene.

In the chlorine-free complex **7**, the double bond coordinates to the metal center,[6] forming a titanacyclopropane entity (Ti−C30 2.205(2) Å, Ti−C40 2.171(2) Å, C30−C40 1.462(4) Å). The C−C distance in **7** is similar to that in the analogous ethylene complex [Cp*$_2$Ti(η^2-$H_2C_2H_2$)] (1.438(5) Å).[5] Altogether the molecular structure of **7** can be compared to that of the titanacyclopropene **5**, where an interaction of the titanium with a triple bond[6] elongated the C−C bond (1.297(4) Å) close to the value found in **2** (1.309(4) Å).[3a,b] In contrast, the halogen-bearing complexes **8a**,**b** feature noncomplexed double bonds (**8a**, C18−C19 = 1.313(6) Å; **8b**, C8−C9 = 1.318(8) Å), whose posture and distance are in good accordance with that in complex **6** (1.330(9) Å).[2c]

The bite angles between the functionalized and nonfunctionalized pentamethylcyclopentadienyl ligands in the halogen-free complexes (**5**, 147°; **7**, 146°) are larger as in the halogen-bearing examples (**8a**, 138°; **8b**, 136°); the latter are similar to those found for **2** (139°) and similar compounds.[7]

Complexes **7** and **8a**,**b** are chiral, each of them forming one pair of enantiomers, as did compounds **5** and **6**.[2b,c] The key step determining the configuration of the two *t*Bu-substituted stereogenic centers (*R*,*R* in one enantiomer and *S*,*S* in the other) is the formation of complex **5** (step **I** in Scheme 2). Obtaining only one of the possible diastereomeric pairs in high yield seems to be controlled by steric requirements during the hydrogen transfer and CC bond formation between the pentamethylcyclopentadienyl ligand and 1,4-di-*tert*-butylbuta-1,3-diyne. Once defined, this chirality is preserved in all subsequent reactions of **5** and its successors. For all compounds, a resolution of the two enantiomers has not been attempted yet.

The reactions of Scheme 2 represent the first simple case of derivatization of a new class of compounds arising from additions of 1,4-disubstituted 1,3-butadiynes to activated permethylmetallocene species of titanium and zirconium. Further derivatizations of compounds involved in Scheme 2 by, for example, thermolysis, insertion reactions with carbon dioxide and other highly polar compounds, and acidolyses are under way, promising a broad spectrum of interesting chiral metallocene compounds.

(4) Crystal data for **7**: triclinic, $P\bar{1}$, a = 9.371(1) Å, b = 11.874(2) Å, c = 13.434(2) Å, α = 88.06(1)°, β = 82.11(1)°, γ = 70.50(1)°, V = 1395.5-(3) Å^3, Z = 2, ρ = 1.149 g cm^{-3}, 4901 measured reflections, 4900 symmetry-independent reflections, 4900 of which were considered as observed ($I > 2\sigma(I)$), 498 refined parameters, R1 = 0.062, wR2 = 0.171 (all data), residual electron density 0.998 e Å^{-3}. Crystal data for **8a**: monoclinic, $P2_1/c$, a = 10.558(2) Å, b = 17.869(4) Å, c = 16.501(3) Å, β = 93.56(3)°, V = 3107.1(11) Å^3, Z = 4, ρ = 1.183 g cm^{-3}, 6171 measured reflections, 3200 symmetry-independent reflections, 1854 of which were considered as observed ($I > 2\sigma(I)$), 324 refined parameters, R1 = 0.042, wR2 = 0.091 (all data), residual electron density 0.308 e Å^{-3}. Crystal data for **8b**: monoclinic, $P2_1/n$, a = 8.622(2) Å, b = 24.544(5) Å, c = 15.026(3) Å, β = 100.22(3)°, V = 3129.3(12) Å^3, Z = 4, ρ = 1.364 g cm^{-3}, 6207 measured reflections, 3309 symmetry-independent reflections, 2452 of which were considered as observed ($I > 2\sigma(I)$), 316 refined parameters, R1 = 0.049, wR2 = 0.137 (all data), residual electron density 0.855 e Å^{-3}.

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Experimental Section

All research was carried out under the exclusion of oxygen and moisture. Compounds **5** and **6** were prepared according to methods given in ref 2c. NMR data were recorded on a Bruker ARX-400 spectrometer at $T = 297$ K in solutions of C_6D_6. X-ray crystal structure investigations were conducted according to ref 8.

Synthesis of 7. From 5. The argon atmosphere over a solution of **5** (0.88 g, 1.83 mmol) in 30 mL of *n*-hexane was carefully replaced by hydrogen, and the solution was stirred under hydrogen for 3 h at room temperature, while the color slightly darkened from yellow to brownish yellow. Filtration, concentration to about 5 mL, and crystallization at −78 °C for 1 day gave yellow crystals of **7** (0.79 g, 90%).

From 8a. A suspension of **8a** (0.30 g, 0.54 mmol), magnesium (0.1 g, 4.0 mmol), and bis(trimethylsilyl)acetylene (1.0 mL, 4.5 mmol) in 20 mL of THF was stirred at 60 °C for 4 h. Within 0.5 h the starting red suspension turned yellow. The resulting solution was filtered, all volatile material was removed under vacuum, and the residue was extracted with 30 mL of *n*-hexane. Concentration to about 3 mL and crystallization at −78 °C for 2 days afforded yellow crystals. Decanting, recrystallizing from *n*-hexane, and drying under vacuum yielded **7** (0.23 g, 88%). Mp: 163 °C. Anal. Calcd for $C_{32}H_{50}Ti$ (482.62): C, 79.64; H, 10.44. Found: C, 79.67; H, 10.45. MS (70 eV, 230 °C): *m*/*z* 483 ([M$^+$]), 426 ([M − *t*Bu]$^+$). IR (KBr, cm^{-1}): 3004 (m), 2940 (vs, b), 2894 (vs, b), 2856 (vs), 2813 (m), 1467 (s), 1460 (vs), 1440 (m), 1387 (s), 1373 (s), 1358 (vs), 1300 (s), 1285 (vw), 1260 (vw), 1227 (m), 1200 (m), 1127 (vw), 1075 (vw), 1060 (w), 1020 (s), 967 (vw), 853 (vw), 840 (vw), 826 (vw), 800 (w), 785 (m), 754 (m), 673 (vw), 640 (w), 620 (vw), 587 (m), 540 (w), 507 (w), 447 (sh), 430 (s). UV−near-IR (*n*-hexane, nm): 300 (sh) > 380 (sh) ≫ 1055. ^{1}H NMR: δ 0.13 (ddd, 1 H, $^3J_{HH}$ = 3.2, 8.7, 12.9 Hz, C*H B*), 0.42, 0.76 (2 × s, 9 H, (CH_3)$_3$C), 0.78, 0.83 (2 s, 3 H, CH_3), 1.32 (dd, 1 H, $^3J_{HH}$ = 2.7, 12.5 Hz, η^2-C*H*═CH *A*), 1.39 (s, 3 H, CH_3), 1.61 (s, 15 H, (CH_3)C$_5$), 2.64 (dd, 1 H, $^3J_{HH}$ = 9.8, $^2J_{HH}$ = 13.7 Hz, CH_2 *A*), 2.77 (dd, 1 H, $^3J_{HH}$ = 3.2, 12.5 Hz, η^2-C*H*═CH *B*), 3.50 (ddd, 1 H, $^3J_{HH}$ = 8.7, $^2J_{HH}$ = 12.9, J_{HH} = 1.1 Hz, CH_2 *B*), 4.15 (dd, 1 H, $^3J_{HH}$ = 7.4, $^2J_{HH}$ = 13.7 Hz, CH_2 *A*), 4.24 (ddd, 1 H, $^3J_{HH}$ = 2.7, 7.4, 9.8 Hz, C*H A*), 4.37 (dd, 1 H, $^3J_{HH} \approx {}^2J_{HH} \approx$ 12.9 Hz, CH_2 *B*). ^{13}C{^{1}H} NMR: δ 8.7 (δ_H 0.83), 9.3 (δ_H 0.78), 11.0 (δ_H 1.39) (3 × *C*H$_3$);, 11.3 ((*C*H$_3$)$_5$C$_5$), 27.1 ((*C*H$_3$)$_3$C, δ_H 0.42), 27.2 (*C*H$_2$ *B*), 28.7 ((CH$_3$)$_3$C, δ_H 0.76), 32.1 (*C*H$_2$ *A*), 34.4, 36.4 (2 × (CH$_3$)$_3$*C*), 62.7 (*C*H *A*), 65.6 (*C*H *B*), 115.9, 119.4, 119.4 (3 × *C*CH$_3$), 119.4 (η^2-*C*H═CH *A*), 119.7 ((CH$_3$)*C*$_5$), 122.5 (η^2-*C*H═CH *B*), 139.0, 140.9 (2 × *C*CH$_2$).

Synthesis of 8a. From 6. Gaseous HCl (about 3 mmol) was condensed into a cooled solution (−30 °C) of **6** (0.5 g, 1.04 mmol) in 30 mL of *n*-hexane. When the solution was warmed to room temperature, the color changed from blue to red. After concentration to about 3 mL and crystallization at −5 °C for 2 days, complex **8a** formed fine brownish red needles, which were filtered and dried under vacuum. Yield: 0.51 g (92%).

From 5. Complex **5** (0.36 g, 0.74 mmol) was dissolved in 25 mL of *n*-hexane under argon. After filtration of the yellow solution it was treated with a solution of HCl in 1,4-dioxane (0.8 mL, 0.32 mmol). The color of the mixture rapidly changed from yellow to red-brown. After 10 min the solvent was evaporated under vacuum to yield 0.39 g (95%) of pure **8a** (by NMR). Recrystallization of **8a** from *n*-hexane afforded red-brown crystals. Mp: 210−211 °C. Anal. Calcd for $C_{32}H_{50}TiCl_2$ (553.52): C, 69.44; H, 9.10. Found: C, 69.48; H, 9.16. MS (70 eV): *m*/*z* 552 ([M]$^+$), 517 ([M − Cl]$^+$), 417 ([M − Cp*]$^+$), 290 ([M − Cp*TiCl$_2$]$^+$); IR (KBr, cm^{-1}): 3004 (m), 2952 (vs, b), 2900 (vs), 2863 (s), 1470 (s, b), 1433 (m), 1391 (m), 1375 (s), 1363 (s), 1278 (vw), 1260 (vw), 1226 (m), 1107 (w), 1063 (w), 1014 (m), 940 (vw), 920 (w), 866 (w), 824 (w), 794 (m), 709 (m), 680 (vw), 604 (vw), 467 (vw). ^{1}H NMR: δ 0.97, 1.00 (2 × s, 9 H, (CH_3)$_3$C), 1.74 (s, 3 H, CH_3), 1.91 (s, 15 H, (CH_3)C$_5$), 2.00 (2 × s, 3 H, CH_3), 2.02−2.10 (m, 1 H, C*H B*), 2.33 (dd, 1 H, $^3J_{HH}$ = 12.6, $^2J_{HH}$ = 15.9 Hz, CH_2 *A*), 2.88 (dd, 1 H, $^3J_{HH}$ = 5.2, $^2J_{HH}$ = 14.0 Hz, CH_2 *B*), 2.91 (dd, 1 H, $^3J_{HH}$ = 5.2, $^2J_{HH}$ = 15.9 Hz, CH_2 *A*), 3.27−3.35 (m, 1 H, C*H A*), 3.46 (dd, 1 H, $^3J_{HH} \approx {}^2J_{HH} \approx$ 14.0 Hz, CH_2 *B*), 5.29−5.38 (m, 2 H, C*H*═C*H A,B*). ^{13}C{^{1}H} NMR: δ 12.4 (δ_H 1.74), 12.9 (δ_H 2.00) (2 × *C*H$_3$), 13.2 ((*C*H$_3$)$_5$C$_5$), 13.8 (CH$_3$, δ_H 2.00), 27.6 (δ_H 0.97), 28.2 (δ_H 1.00) (2 × (*C*H$_3$)$_3$C), 29.1 (*C*H$_2$ *B*), 30.0 (*C*H$_2$ *A*), 33.3, 35.3 (2 × (CH$_3$)$_3$*C*), 45.4 (*C*H *A*), 52.3 (*C*H *B*), 124.9 (*C*CH$_3$), 128.1 ((CH$_3$)$_5$*C*$_5$), 128.3, 129.5 (2 × *C*CH$_3$), 130.4, 131.6 (*C*H═*C*H *A,B*); 131.3, 133.8 (2 × *C*CH$_3$).

Synthesis of 8b. From 7. A freshly prepared solution of Br_2 in *n*-hexane (0.39 M, 1.40 mL, 0.55 mmol) was added to a solution of **7** (0.26 g, 0.55 mmol) in 10 mL of *n*-hexane. The color of the mixture changed quickly from yellow to brown, and within 5−10 min dark crystals started to precipitate. After 3 h the crystalline material was separated from the mother liquor, washed with cold *n*-hexane, and dried in vacuo (154 mg). The mother liquor was cooled to −30 °C to afford a second fraction of 118 mg of **8b**. Total yield: 0.27 g (78%). Mp: 186−187 °C. Anal. Calcd for $C_{32}H_{50}TiBr_2$ (642.44): C, 59.83; H, 7.84. Found: C, 59.88; H, 7.97. MS (70 eV): *m*/*z* 642 ([M]$^+$), 563 ([M − Br]$^+$), 507 ([M − Cp*]$^+$), 299 ([M − Cp*TiBr$_2$]$^+$). ^{1}H NMR: δ 0.97, 1.02 (2 s, 9 H each, (CH_3)$_3$C), 1.76 (s, 3 H, CH_3), 1.99 (s, 15 H, (CH_3)C$_5$), 2.12 (2 s, 3 H each, CH_3), 2.11 (m, 1 H, C*H B*), 2.36 (dd, 1 H, $^3J_{HH}$ = 12.5, $^2J_{HH}$ = 15.8 Hz, *C*H$_2$ *A*), 2.84 (dd, 1 H, $^3J_{HH}$ = 5.4, $^2J_{HH}$ = 15.8 Hz, CH_2 *A*), 2.99 (dd, 1 H, $^3J_{HH}$ = 5.0, $^2J_{HH}$ = 14 Hz, CH_2 *B*), 3.33 (ddd, 1 H, $^3J_{HH}$ = 12.5/8.6/5.4 Hz, C*H A*), 3.64 (t, 1 H, $^3J_{HH} \approx {}^2J_{HH} \approx$ 14 Hz, CH_2 *B*), 5.34 (m, 1 H, ═C*H A*), 5.36 (m, 1 H, ═C*H B*). ^{13}C{^{1}H} NMR: δ 13.1 (δ_H 1.76), 14.1 (δ_H 2.12), 14.2 ((*C*H$_3$)$_5$C$_5$), 14.8 (δ_H 2.12), 27.6 (δ_H 0.97), 28.2 (δ_H 1.02), 30.4 (*C*H$_2$ *B* and *C*H$_2$ *A*), 33.4, 35.4 (2 × (CH$_3$)$_3$*C*), 45.4 (*C*H *A*), 52.4 (*C*H *B*), 128.8 ((CH$_3$)$_5$*C*$_5$), 125.5, 129.4, 129.5, 131.6, 135.1 (5 × *C*CH$_3$), 130.6 (═*C*H *B*), 131.4 (═*C*H *A*).

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **7** and **8a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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