Supporting Information

Coming Back to the Starting Position of Carbons Travelling in Organic Molecules on Titanium: Merry-Go-Round Reaction

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General Information.

All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. $^1$H NMR (at 400 or 600 MHz) and $^{13}$C NMR (at 101 or 151 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane or given relative to the respective residual solvent peaks ($^1$H: CHCl$_3$ at 7.26, C$_6$H$_6$ at 7.16, C$_7$H$_8$ (toluene) at 2.09, $^{13}$C: CHCl$_3$ at 77.0, C$_6$H$_6$ at 128.0, C$_7$H$_8$ (toluene) at 20.4). NMR yields were determined using dichloromethane, mesitylene, ethylbenzene or dioxane as internal standards. Benzene, hexane and tetrahydrofuran were distilled from benzophenone-ketyl under nitrogen prior to use. Toluene and p-xylene were distilled from Na under nitrogen prior to use. $^{13}$C-enriched titanocene dichloride was prepared according to literature procedures reported by our group (19). All chemicals were obtained from commercial sources unless noted. All yields were calculated according to the alkynes used in the formation of titanacyclopentadiene.

The following instruments were used for physical characterization of the compounds.

- **NMR**: JEOL JNM-ECX400 ($^1$H: 400 MHz, $^{13}$C: 101 MHz)  
  JEOL JNM-ECX600 ($^1$H: 600 MHz, $^{13}$C: 151 MHz)
- **GC**: SHIMADZU GC-14B gas chromatograph  
  SHIMADZU CBP1-M25-025 fused capillary column  
  SHIMADZU CR-6A-Chromatopac integrator
- **GPC**: Japan Analytical Industry LC-9201  
  JAIGEL column 2H, JAIGEL column H-P

For the column chromatography, silica gel 60N (spherical, neutral, 100-210μm) was used and the fraction was monitored by TLC (Merck TLC Silica gel 60 F$_{254}$). For the column chromatography, alumina activated 200 (abt. 200mesh) was used and the fraction was monitored by TLC (Merck TLC Aluminium oxide 60 F$_{254}$, neutral).
Synthesis of Diyne 14a.

A solution of 1,6-heptadiyne (3.43 ml, 30 mmol) in THF (60 mL) was cooled to –78 °C, and nBuLi (1.56 M in hexane, 42 mL, 66 mmol) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for 1 h and 30 min. After TMSCl (8.34 mL, 66 mmol) was added, the mixture was stirred for 12 h at the same temperature. The mixture was quenched with aqueous saturated NH₄Cl and extracted with Et₂O. The organic layer was washed with water and brine and dried over Na₂SO₄. After removal of the solvent, the crude product was purified by column chromatography on silica gel (eluent: hexane: ethyl acetate = 10:1) to give 14a as a colorless oil.

1,7-bis(trimethylsilyl)-1,6-heptadiyne (14a)

Isolated yield: 71%. CAS Registry Number [41268-43-3].

1H NMR (396 MHz, CDCl₃): δ 0.14 (s, 18H), 1.73 (quin, J = 7.1 Hz, 2H), 2.32 (t, J = 7.1 Hz, 4H). 13C{1H} NMR(100 MHz, CDCl₃): δ 19.0, 27.7, 85.0, 106.3.

Synthesis of Diyne 14b.

To a solution of trimethylsilylacetylene (22.1 mL, 160 mmol) in 100 mL THF was added ethylmagnesium bromide (1.0 M THF solution, 160 mL, 160 mmol) dropwise at 0 °C. The mixture was warmed up to room temperature and stirred for 1 h. To the resulting solution were added CuCl (1.98 g, 20 mmol) and 1,2-bis(bromomethyl)benzene (10.56 g, 40 mmol), and the mixture was heated to reflux for 5 h. After cooling to room temperature, the reaction mixture was quenched with aqueous saturated NH₄Cl and extracted with hexane. The combined organic phase was washed with water and brine and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluent: hexane: ethyl acetate = 50:1). After removal of the solvent, the title compound 14b was obtained as a colorless oil.

1,2-Bis(3-trimethylsilyl-2-propynyl)benzene (14b)

Isolated yield: 73%. CAS Registry Number [886050-81-3].

1H NMR (396 MHz, CDCl₃): δ 0.18 (s, 18H), 3.63 (s, 4H), 7.23-7.27 (m, 2H), 7.43-7.47 (m, 2H). 13C{1H} NMR(100 MHz, CDCl₃): δ 127.2, 128.6, 134.1.
Synthesis of Titanacyclopentadiene 10a and 10b.

A typical procedure is given for the synthesis of 10a. A mixture of Cp₂TiCl₂ (5.23 g, 21.0 mmol) and 1,7-bis(trimethylsilyl)-1,6-heptadiyne 14a (5.06 g, 21.0 mmol) in THF (105 mL) was added to Mg (612 mg, 25.2 mmol) activated by 1,2-dibromoethane (0.84 mmol, 72 µL) at room temperature. After stirring for 24 h at the same temperature, bis(cyclopentadienyl)-titanacyclopentadiene 10a was formed in a dark red solution. After removal of the solvent, the crude product was purified by column chromatography on alumina (eluent: benzene). After removing the solvent, the residue was washed with hexane or crystallized from toluene at –30 °C to give pure compound 10a.

3,3-Bis(cyclopentadienyl)-2,4-bis(trimethylsilyl)-3-titanabicyclo[3,3,0]-1,4-octadiene (10a)
Isolated yield: 54%. CAS Registry Number [124302-88-1].

1H NMR (400 MHz, CDCl₃): δ 0.10 (s, 18H), 1.39 (quin, J = 7.2 Hz, 2H), 2.05 (t, J = 7.2 Hz, 4H), 5.94 (s, 10H). 13C{1H} NMR (101 MHz, CDCl₃): δ 1.6, 22.9, 36.3, 111.3, 131.8, 204.2.

Titanium, bis(cyclopentadienyl)[1,4-dihydro-2,3-naphthalenediylidene]bis[(trimethylsilyl)methylidyne]– (10b)
Isolated yield: 53%.

1H NMR (600 MHz, C₇D₈): δ 0.14 (s, 18H), 3.12 (s, 4H), 5.80 (s, 10H), 7.00-7.04 (m, 4H). 13C{1H} NMR (151 MHz, C₇D₈): δ 3.07, 41.4, 112.9, 126.0, 126.3, 134.3, 138.4, 211.5.
Synthesis of Titanacyclopentadiene 10c

A solution of Cp₂TiCl₂ (8.96 g, 36.0 mmol) in THF (150 mL) was cooled to –78 °C, and nBuLi (1.60 M in hexane, 45 mL, 72 mmol) was added dropwise. After stirring at –78 °C for 1 h, 1-trimethylsilyl-1-propyne (9.0 mL, 60 mmol) was added. The reaction mixture was warmed up to 40 °C and stirred for 24 h. Bis(cyclopentadienyl)titanacyclopentadiene 10c was formed in a dark red solution. The solvent was removed under reduced pressure. Column chromatography on alumina (eluent: benzene) and crystallization from toluene at –30 °C afforded 10c as a single product.

1,1-Bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-titanacyclopentadiene (10c)

Isolated yield: 23%. CAS Registry Number [148540-24-3].

1H NMR (400 MHz, C₇D₈): δ 0.05 (s, 18H), 1.51 (s, 6H), 5.95 (s, 10H). 13C{1H} NMR (101 MHz, C₇D₈): δ 3.0, 23.7, 113.2, 138.9, 216.5.
Preparation for Dihydroindenyltitanium Complex 5a.

A toluene solution of bis(cyclopentadienyl)titanacyclopentadiene 10a (124 mg, 0.30 mmol) and trimethylphosphine (1.0 M in toluene, 4.8 mL, 4.8 mmol) was heated to 80 °C and stirred for 24 h in a sealed Schlenk tube. After removal of the solvent and the ligand under reduced pressure, dihydroindenyltitanium complex 5a was obtained as a dark green solid. Crystallization of 5a from toluene at −30 °C afforded single crystals suitable for X-ray crystallographic analysis. Mesitylene (42 µL, 0.30 mmol) was used as an internal standard.

(5a)  
NMR yield: 94%.

1H NMR (400 MHz, C6D6): δ 0.34 (s, 18H), 1.50-1.62 (m, 1H), 1.73 (s, 2H), 1.84-1.95 (m, 1H), 2.19-2.26 (m, 2H), 3.01-3.02 (m, 2H), 3.18-3.26 (m, 2H), 4.80 (s, 5H), 4.96 (t, J = 3.3 Hz, 1H). 13C{1H} NMR (101 MHz, C6D6): δ 3.19, 21.1, 26.6, 36.2, 52.4, 55.5, 99.4, 103.9, 106.0. HRMS (ESI) Calcd for C23H34Si2Ti: 414.16813. Found: 414.16901.

Preparation for Dihydroindenyltitanium Complex 9b and 9c.

A typical procedure is given for the synthesis of dihydroindenyltitanium complex 9b. A solution of bis(cyclopentadienyl)titanacyclopentadiene 10b (143 mg, 0.30 mmol) in toluene (3.6 mL) was heated to 80 °C and stirred for 24 h in a sealed Schlenk tube. After removal of the solvent under reduced pressure, titanium complex 9b was obtained as a dark green solid. Crystallization of 9b from toluene at −30 °C afforded crystals suitable for X-ray crystallographic analysis. Ethylbenzene (37 µL, 0.30 mmol) was used as an internal standard.

(9b)  
NMR yield: 94%.

1H NMR (396 MHz, C7D8): δ 0.39 (s, 18H), 1.58 (brs, 2H), 2.38 (brs, 2H), 2.84 (brs, 2H), 4.65 (s, 5H), 5.00(brs, 1H), 5.06 (brs, 2H), 6.77-6.80(m, 2H), 6.93-6.95 (m, 2H). 13C{1H} NMR (100 MHz, C7D8): δ 2.79, 40.1, 42.7, 57.6, 65.0, 89.5, 96.8, 101.7, 126.3, 127.5, 136.8. HRMS (ESI) Calcd for C28H36Si2Ti: 476.18384. Found: 476.18456.
NMR yield: 58%.

{9c}

$^{1}$H NMR (400 MHz, C$_7$D$_8$): $\delta$ 0.30 (s, 18H), 0.38 (s, 6H), 2.95 (d, $J = 3.2$ Hz, 2H), 4.71 (s, 5H), 5.03 (s, 2H), 5.23 (t, $J = 3.2$ Hz, 1H). $^{13}$C {$^{1}$H} NMR (101 MHz, C$_7$D$_8$): $\delta$ 2.70, 26.0, 35.7, 58.6, 66.3, 89.1, 96.7, 97.5. HRMS(ESI) Calcd for C$_{22}$H$_{34}$Si$_2$Ti: 402.16812. Found: 402.16851.
Reaction of Dihydroindenyltitanium Complex 5a with Azobenzene.

Complex 5a was prepared in the same way as described above. To a solution of 5a in toluene (1.5 mL) was added Azobenzene (109.3 mg, 0.6 mmol) at −10 °C. The mixture was warmed up to 50 °C and stirred for 24 h. The resulting mixture was quenched with 3 M aqueous HCl solution and extracted with hexane. The organic layer was dried over Na2SO4 and the solvent was removed under reduced pressure to give indene derivative 11a.

1,2,3,5-Tetrahydro-4,8-bis(trimethylsilyl)-s-indacene (11a)

NMR yield: 93%.

| Compound | 1H NMR (396 MHz, CDCl3) | 13C{1H} NMR (100 MHz, CDCl3) | HRMS (EI) Calcd for C18H28Si2 |
|----------|-------------------------|------------------------------|-----------------------------|
| 11a      | δ 0.40 (s, 9H), 0.41 (s, 9H), 2.05 (quin, J = 7.3 Hz, 2H), 2.97-3.01 (m, 4H), 3.38-3.41 (brs, 2H), 6.57 (dt, J = 5.7, 2.0 Hz, 1H), 7.15 (dt, J = 5.7, 1.8 Hz, 1H). | δ 1.61, 2.01, 26.0, 34.2, 34.3, 40.3, 126.6, 131.1, 132.9, 133.3, 145.7, 147.2, 147.4, 147.7 | Calcd for C18H28Si2: 300.17295. Found: 300.17205. |

Reactions of Titanacyclopentadiene 10b with Azobenzene.

A mixture of bis(cyclopentadienyl)titanacyclopentadiene 10b (201.3 mg, 0.50 mmol) and azobenzene (182.2 mg, 1.0 mmol) in toluene (2.5 mL) was heated to 80 °C and stirred for 24 h. The mixture was cooled to room temperature and quenched with 3 M aqueous HCl solution. After extraction with hexane, the organic layer was washed with brine and dried over Na2SO4. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane: ethyl acetate = 20:1) to give 11b as a colorless solid.

5,10-Dihydro-4,11-bis(trimethylsilyl)-1H-cyclopenta[b]anthracene (11b)

NMR yield: 95%, Isolated yield 82%.

| Compound | 1H NMR (400 MHz, CDCl3) | 13C{1H} NMR (101 MHz, CDCl3) | HRMS (EI) Calcd for C23H30Si2 |
|----------|-------------------------|------------------------------|-----------------------------|
| 11b      | δ 0.51 (s, 9H), 0.52 (s, 9H), 3.38 (brs, 2H), 4.03 (s, 2H), 4.04 (s, 2H), 6.53 (dt, J = 5.8, 2.0 Hz, 1H), 7.14-7.19 (m (three peaks were overlapped), 3H), 7.27-7.29 (m (two peaks were overlapped), 2H). | δ 2.91, 3.26, 38.3, 40.9, 126.0, 126.0, 126.1, 130.7, 132.9, 133.5, 138.6, 138.7, 140.1, 142.0, 147.1, 147.5 | Calcd for C23H30Si2: 362.18860. Found: 362.18849. |
**1H NMR Monitoring Reaction of Dihydroindenyltitanium Complex 9b with Azobenzene.**

A solution of dihydroindenyltitanium complex 9b (23.8 mg, 0.05 mmol) and azobenzene (18.2 mg, 0.10 mmol) in \( p \)-xylene-\( d_{10} \) (0.6 mL) was heated to 115 °C for 72 h in a sealed NMR tube. \(^1\)H NMR monitoring of the reaction revealed that complex 9b was converted into indene derivative 11b in 88% yield (Fig. S24-26). Formation of 11b was confirmed by co-injection with isolated 11b into the reaction mixture.

The reaction of acyclic-substituent analogue 9c also gave indene derivative 11c.

**5,6-Dimethyl-4,7-bis(trimethylsilyl)-1H-indene (11c)**

NMR yield: 56%, Isolated yield 37%.

\(^1\)H NMR (400 MHz, CDCl3): \( \delta \) 0.43 (s, 9H), 0.44 (s, 9H), 2.40 (s, 6H), 3.38-3.40 (bs, 2H), 6.50 (dt, \( J = 5.7, 2.0 \) Hz, 1H), 7.17 (dt, \( J = 5.7, 1.8 \) Hz, 1H). \(^13\)C\(^{\text{1H}}\) NMR (101 MHz, CDCl3): \( \delta \) 2.94, 3.29, 21.6, 21.7, 41.0, 132.5, 132.9, 133.0, 134.6, 138.4, 140.3, 147.0, 147.4. HRMS(EI) Calcd for C\(_{17}\)H\(_{28}\)Si\(_2\): 288.17295. Found: 288.17242.
Isotope-labelled Experiment. ~ Synthesis of Titanacyclopentadiene 10b-\(^{13}\text{C}\) ~

Titanacyclopentadiene 10b-\(^{13}\text{C}\) was prepared in the same way as described above. Comparison of \(^{13}\text{C}\) NMR spectra between 10b and 10b-\(^{13}\text{C}\) revealed \(^{13}\text{C}\) enriched carbon atoms. Underlined peaks were characterized as \(^{13}\text{C}\)-enriched carbon atoms.

\((10b-^{13}\text{C})\)

Isolated yield: 53%.

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR(151 MHz, C}_7\text{D}_8\): } \delta \text{ 3.07, 41.4, 112.9, 126.0, 126.3, 134.3, 138.4, 211.5.}

Isotope-labelled Experiment. ~ Preparation for Dihydroindenyltitanium Complex 9b-\(^{13}\text{C}\) ~

A solution of bis(cyclopentadienyl)titanacyclopentadiene 10b-\(^{13}\text{C}\) (23.8 mg, 0.05 mmol) in toluene-\(d_8\) (0.6 mL) was heated to 90 °C for 18 h in a sealed NMR tube. Comparison of \(^{13}\text{C}\) NMR spectra between 9b and 9b-\(^{13}\text{C}\) revealed positions of \(^{13}\text{C}\) enriched carbon atoms. Underlined peaks were characterized as \(^{13}\text{C}\)-enriched carbon atoms.

\((9b-^{13}\text{C})\)

NMR yield: 92%.

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR(151 MHz, C}_7\text{D}_8\): } \delta \text{ 2.94, 40.6, 42.9, 58.1, 65.8, 90.0, 97.1, 101.5, 126.4, 127.6, 137.0.}
Isotope-labelled Experiment. ~ Preparation for Indene Derivative 11b-\textsuperscript{13}C ~

A solution of dihydroindenyltitanium complex 9b-\textsuperscript{13}C (23.8 mg, 0.05 mmol) and azobenzene (18.2 mg, 0.10 mmol) in \textit{p}-xylene-\textit{d}_{10} (0.6 mL) was heated to 115 °C for 72 h in a sealed NMR tube. Comparison of \textsuperscript{13}C NMR spectra between 11b and 11b-\textsuperscript{13}C revealed \textsuperscript{13}C enriched carbon atoms. Underlined peaks were characterized as \textsuperscript{13}C-enriched carbon atoms.

(11b-\textsuperscript{13}C) NMR yield: 85%, Isolated yield 74%.

\textsuperscript{13}C\{\textsuperscript{1}H\} NMR(101 MHz, CDCl\textsubscript{3}): \delta 2.90, 3.24, 38.3, \underline{40.9}, 126.0, 126.0, 126.1, 130.7, \underline{132.9}, \underline{133.5}, 138.6, 138.7, 140.1, 142.0, \underline{147.1}, \underline{147.5}.
**X-ray Crystallographic Studies**

All measurements were made on a Rigaku R-RAXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods SHELXS97 and refined on $F^2$ using SHELXL97. All calculations were performed using the CrystalStructure crystallographic software package. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms attached to carbon atoms were refined isotropically. X-ray crystallographic data and refinement details for compound 5a and 9b are summarized in Table S1 and S2, respectively.
Fig. S1. X-ray Structure of Complex 5a. Hydrogen atoms of a Cp ligand and two TMS groups are omitted for clarity.
### Table S1. X-ray Crystallographic Data and Refinement Details for Dihydroindenyltitanium Complex 5a.

|                          | 5a                                      |
|--------------------------|-----------------------------------------|
| **Formula**              | C$_{23}$H$_{34}$Si$_2$Ti                |
| **$FW$**                 | 414.58                                  |
| **$T$ / K**              | 298                                     |
| **Colour, shape**        | Green, prism                            |
| **Crystal size / mm**    | 0.35 x 0.20 x 0.15                      |
| **Crystal system**       | orthorhombic                            |
| **Space group, $Z$**     | Pbca, 8                                 |
| **$a$ / Å**              | 14.191(3)                               |
| **$b$ / Å**              | 13.761(3)                               |
| **$c$ / Å**              | 23.254(4)                               |
| **$V$ / Å$^3$**          | 4541.3(15)                              |
| **$D_x$ / Mg m$^{-3}$**  | 1.213                                   |
| **$F(000)$**             | 1776                                    |
| **$\mu$(Mo K$_\alpha$) / mm$^{-1}$** | 0.487  |
| **$T_{\text{min}}, T_{\text{max}}$** | 0.8480, 0.9305 |
| **$R_{\text{int}}$**    | 0.1955                                  |
| **Refln./param. ratio**  | 5175/279                                |
| **$R1[F_o^2 > 2\sigma(F_o^2)]$** | 0.0559 |
| **$wR2$ (all refln)**   | 0.1411                                  |
| **GoF**                  | 0.885                                   |
Fig. S2. X-ray Structure of 9b. All hydrogen atoms are omitted for clarity.
**Table S2.** X-ray Crystallographic Data and Refinement Details for Dihydroindenyltitanium Complex 9b.

|                          | 9b          |
|--------------------------|-------------|
| **Formula**              | C\textsubscript{28}H\textsubscript{36}Si\textsubscript{2}Ti\textsubscript{1}/4C\textsubscript{7}H\textsubscript{8} |
| **FW**                   | 499.68      |
| **T / K**                | 223         |
| **Colour, shape**        | Green, prism|
| **Crystal size / mm**    | 0.70 x 0.10 x 0.10 |
| **Crystal system**       | monoclinic  |
| **Space group, Z**       | P2\textsubscript{1}/c, 8 |
| **a / Å**                | 10.774(2)   |
| **b / Å**                | 12.751(3)   |
| **c / Å**                | 40.033(10)  |
| **β / deg.**             | 95.412(9)   |
| **V / Å\textsuperscript{3}** | 5475(2)    |
| **D\textsubscript{x} / Mg m\textsuperscript{-3}** | 1.212       |
| **F(000)**               | 2132        |
| **μ(Mo K\textsubscript{α}) / mm\textsuperscript{-1}** | 0.416       |
| **T\textsubscript{min}, T\textsubscript{max}** | 0.7595, 0.9596 |
| **R\textsubscript{int}** | 0.1818      |
| **Refln./param. ratio**  | 12495/892   |
| **R1 [F\textsuperscript{o} \textsuperscript{2} > 2σ(F\textsuperscript{o} \textsuperscript{2})]** | 0.0709      |
| **wR2 (all refln)**     | 0.1655      |
| **GoF**                  | 0.952       |
**Fig. S3.** $^1$H NMR Spectrum of 3,3-Bis(cyclopentadienyl)-2,4-bis(trimethylsilyl)-3-titanabicyclo[3,3,0]-1,4-octadiene (10a).

**Fig. S4.** $^{13}$C NMR Spectrum of 3,3-Bis(cyclopentadienyl)-2,4-bis(trimethylsilyl)-3-titanabicyclo[3,3,0]-1,4-octadiene (10a).
Fig. S5. $^1$H NMR Spectrum of Titanium, bis(cyclopentadienyl)[(1,4-dihydro-2,3-naphthalenediylidene)bis[(trimethylsilyl)methylidyne]]- (10b).

Fig. S6. $^{13}$C NMR Spectrum of Titanium, bis(cyclopentadienyl)[(1,4-dihydro-2,3-naphthalenediylidene)bis[(trimethylsilyl)methylidyne]]- (10b).
Fig. S7. $^1$H NMR Spectrum of 1,1-Bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-titanacyclopentadiene (10c).

Fig. S8. $^{13}$C NMR Spectrum of 1,1-Bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-titanacyclopentadiene (10c).
Fig. S9. $^1$H NMR Spectrum of Dihydroindenyltitanium Complex (5a).

Fig. S10. $^{13}$C NMR Spectrum of Dihydroindenyltitanium Complex (5a).
Fig. S11. $^1$H NMR Spectrum of Dihydroindenyltitanium Complex (9b).

Fig. S12. $^{13}$C NMR Spectrum of Dihydroindenyltitanium Complex (9b).
**Fig. S13.** $^1$H NMR Spectrum of Dihydroindenyltitanium Complex (9c).

**Fig. S14.** $^{13}$C NMR Spectrum of Dihydroindenyltitanium Complex (9c).
Fig. S15. $^1$H NMR Spectrum of 1,2,3,5-Tetrahydro-4,8-bis(trimethylsilyl)-s-indacene (11a).

Fig. S16. $^{13}$C NMR Spectrum of 1,2,3,5-Tetrahydro-4,8-bis(trimethylsilyl)-s-indacene (11a).
Fig. S17. $^1$H NMR Spectrum of 5,10-Dihydro-4,11-bis(trimethylsilyl)-1H-cyclopenta[b]anthracene (11b).

Fig. S18. $^{13}$C NMR Spectrum of 5,10-Dihydro-4,11-bis(trimethylsilyl)-1H-cyclopenta[b]anthracene (11b).
Fig. S19. $^1$H NMR Spectrum of 5,6-Dimethyl-4,7-bis(trimethylsilyl)-1H-indene (11c).

Fig. S20. $^{13}$C NMR Spectrum of 5,6-Dimethyl-4,7-bis(trimethylsilyl)-1H-indene (11c).
Fig. S21. Comparison of $^{13}$C NMR Spectra between 10b and 10b-$^{13}$C.
Fig. S22. Comparison of $^{13}$C NMR Spectra between 9b and 9b-$^{13}$C.
Fig. S23. Comparison of $^{13}$C NMR Spectra between 11b and 11b-$^{13}$C.
Fig. S24. $^1$H NMR Monitoring Reaction of Dihydroindenyltitanium Complex 9b with Azobenzene.
Fig. S25. Comparison of 1H NMR Spectra between the Reaction Mixture (72 h) and Co-injection with Isolated 11b (2.3-4.1 ppm).
Fig. S26. Comparison of $^1$H NMR Spectra between the Reaction Mixture (72 h) and Co-injection with Isolated 11b (0.1-1.1 ppm).
We have previously proposed a reaction mechanism for the travelling of two carbons from complex 5 to 6 as shown below (ref. 23).