Supplementary Material
for
“Unprecedented Double C-C Bond Cleavage of a
Cyclopentadienyl Ligand”

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Experimental

General.

Manipulations were carried out under an atmosphere of Ar or N₂ using standard Schlenk line techniques. Tetrahydrofuran (THF) was dried over sodium and benzophenone under a nitrogen atmosphere. Titanocene dichloride and 3-hexyne were purchased from Aldrich Chemical Co., Inc. *n*-BuLi (1.59 M, hexane solution) and benzonitrile were purchased from KANTO Chemicals Co. Ltd. Other nitriles and 3,9-dodecadiyne were purchased from TCI Co., Ltd.

GC analysis was performed on a gas chromatograph (SHIMADZU GC-14A) equipped with a flame ionization detector using a fused silica capillary column (CBP1-M25-025) and SHIMADZU CR6A-Chromatopac integrator. GC yields were determined using suitable hydrocarbons as internal standards. ¹H NMR and ¹³C NMR spectra were recorded for CDCl₃ (containing 1% TMS) solution on Bruker ARX-400 and JEOL JNM-AL300.

Typical experimental procedure.

A solution of Cp₂TiCl₂ (299 mg, 1.2 mmol) in THF (5ml) was cooled to –78 °C.

n-BuLi (1.59 M solution in hexane, 1.51 ml, 2.4 mmol) was dropwise added to this solution. After stirring for 1 h at $-78\text{ }^{\circ}\text{C}$, alkyne (2.0 mmol) was added and mixture was stirred. After stirring for 3 h at $-10\text{ }^{\circ}\text{C}$, the color of the reaction mixture turned to dark green. And then to this mixture was added a nitrile (2.0 mmol). This mixture was refluxed for 1 h or stirred at 50°C for 12h – 20h. The reaction mixture was quenched with saturated NaHCO_3 aq, and then extracted with ethyl acetate. The extract was washed with water and brine and dried over MgSO_4 . The solvent was evaporated in vacuo. Column chromatography on silica gel afforded the benzene derivatives **2a-f** and pyridine derivatives **3a-d**.

1,2,3,4-Tetraethylbenzene (2a). Colorless liquid, 86 mg (GC yield 62%, Isolated yield 45%) ^1H NMR (CDCl_3 , Me_4Si) δ 1.16 ($J = 7.5\text{Hz}$, 6H), 1.23 (t, $J = 7.5\text{Hz}$, 6H), 2.60-2.72 (m, 8H), 7.00 (s, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 15.56, 15.62, 21.73, 25.66, 126.15, 139.57, 139.63. HRMS calcd for $\text{C}_{14}\text{H}_{22}$, 190.1721 found. 190.1690.

1,2,3,4-Tetrahydro-5,8-diethylnaphthalene (2b). Colorless liquid, 90 mg (GC yield 50%, Isolated yield 47%) ^1H NMR (CDCl_3 , Me_4Si) δ 1.20 (t, $J = 7.6\text{Hz}$, 6H), 1.77-1.81 (m, 4H), 2.57 (q, $J = 7.54$, 4H), 2.69-2.72 (m, 4H), 6.98 (s, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.29, 23.03, 25.49, 26.62, 124.99, 134.87, 139.64. Anal. Calcd for $\text{C}_{14}\text{H}_{20}$: C, 89.29; H, 10.71. Found C, 89.13; H, 10.77.

5,8-Di-*n*-propyl-1,2,3,4-tetrahydronaphthalene (2c). Colorless liquid, (GC yield 72%) ^1H NMR (CDCl_3 , Me_4Si) δ 0.99 (t, $J = 7.3\text{ Hz}$, 6H), 1.53-1.65 (m, 4H), 1.72-1.84 (m, 4H), 2.50 (t, $J = 7.9\text{ Hz}$, 4H), 2.63-2.79 (m, 4H), 6.94 (s, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.41, 23.01, 23.27, 26.71, 34.93, 125.79, 134.99, 138.26. HRMS calcd for $\text{C}_{16}\text{H}_{24}$, 216.1878, found 216.1894.

4,7-Di-*n*-propyl-2,3-dihydroindene (2d). Colorless liquid, 222 mg (GC yield 70%, Isolated yield 52%) ^1H NMR (CDCl_3 , Me_4Si) δ 1.00 (t, $J = 7.3$ Hz, 6H), 1.64 (q, $J = 7.6$ Hz, 4H), 2.04-2.13 (m, 2H), 2.55 (t, $J = 7.8$ Hz, 4H), 2.90 (t, $J = 7.4$ Hz, 4H), 6.95 (s, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.18, 23.37, 24.56, 31.37, 35.51, 126.20, 135.68, 142.31; HRMS calcd for $\text{C}_{15}\text{H}_{22}$, 202.1722, found 202.1720.

2,6-Diphenylpyridine (3a). White solid, 103 mg (GC yield 46%, Isolated yield 45%). ^1H NMR, ^{13}C NMR data were consistent with the published data.¹

2,6-Di(4-fluorophenyl)pyridine (3b). Brown solid, 115 mg (Isolated yield 43%, GC yield 47%). ^1H NMR (CDCl_3 , Me_4Si) δ 7.13-7.23 (m, 4H), 7.60 (d, $J = 7.82$ Hz), 7.74-7.78 (m, 1H), 8.08-8.12 (m, 4H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 115.49, 115.70, 118.19, 128.69, 128.78, 135.45, 135.48, 137.66, 155.80, 162.35, 164.82. HRMS calcd for $\text{C}_{17}\text{H}_{11}\text{F}_2\text{N}$ 267.0860, found 267.0836.

2,6-Di(4-methylphenyl)pyridine (3c). White solid, 116 mg (GC yield 55%, Isolated yield 45%). ^1H NMR and ^{13}C NMR data were consistent with the published data.¹

2,6-Di-*n*-propylpyridine (3d). Colorless liquid, 44 mg (GC yield 54%, Isolated yield 27%). ^1H NMR (CDCl_3 , Me_4Si) δ 0.96 (t, $J = 7.3$ Hz, 6H), 1.68-1.78 (m, 4H), 2.73 (t, $J = 7.6$ Hz, 4H), 6.94 (d, $J = 7.7$ Hz, 2H), 7.48 (t, $J = 7.7$ Hz, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.9, 23.4, 40.5, 119.8, 136.4, 161.7. HRMS calcd for $\text{C}_{11}\text{H}_{17}\text{N}$, 163.1361 found 163.1362.

Bis(pentadeuteriocyclopentadienyl)titanium dichloride.

Hexadeuteriocyclopentadiene was prepared by the known method.² A solution of hexadeuteriocyclopentadiene (2.8ml, 35.0 mmol) in ether (10ml) was cooled to 0 °C. *n*-BuLi (2.46 M solution in hexane, 14.2 ml, 35.0 mmol) was dropwise added to this

solution. The C_5D_5Li solution was added slowly to a solution of $TiCl_4$ (1.86 ml, 17 mmol) in benzene (10 ml) at 0 °C. The reaction mixture was stirred at 50 °C for 3 h. After extraction with $CHCl_3$, the title complex was recrystallized in $CHCl_3$ and crystals were obtained (3.08 g, Isolated yield 68%, D-incorporation >97%). HRMS calcd for $C_{10}D_{10}Cl_2Ti$, 258.0257 Found 258.0262.

Reaction of bis(pentadeuteriocyclopentadienyl)tetraethyltitanacyclopentadiene (1a- d_{10}) with a benzonitrile. A solution of d_{10} - Cp_2TiCl_2 (311 mg, 1.2 mmol) in THF (5ml) was cooled to -78 °C. *n*-BuLi (1.59 M solution in hexane, 1.51 ml, 2.4 mmol) was dropwise added to this solution. After stirring for 1 h at -78 °C, 3-hexyne (227 μ l, 2.0 mmol) was added and then the mixture was stirred for 3 h at -10 °C. When the color of the reaction mixture turned to dark green, benzonitrile (2.0 mmol, 204 μ l) was added. The mixture was refluxed for 1 h. The reaction mixture was quenched with saturated $NaHCO_3$ aq, and then extracted with ethyl acetate. The extract was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo. After separation and purification by chromatography, 1,2-dideuterio-3,4,5,6-tetraethylbenzene (**2a- d_2**) and 3,4,5-trideuterio-2,6-diphenylpyridine (**3a- d_3**) were obtained.

1,2-Dideuterio-3,4,5,6-tetraethylbenzene (2a- d_2). Colorless liquid, 111 mg (GC yield 59%, Isolated yield 58%, D-incorporation >97%). 1H NMR ($CDCl_3$, Me_4Si) δ 1.16 (t, J = 7.6 Hz, 6H), 1.23 (t, J = 7.5 Hz, 6H), 2.61-2.71 (m, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.56, 15.59, 21.70, 25.59, 125.68 (t), 139.46, 139.61. HRMS calcd for $C_{14}H_{20}D_2$ 192.1845, found 192.1849.

3,4,5-Trideuterio-2,6-diphenylpyridine (3a- d_3). White solid, 112 mg (GC yield 49%, Isolated yield 48%, D-incorporation >97%). 1H NMR ($CDCl_3$, Me_4Si) δ 7.40-7.50(m, 3H), 8.13-8.16 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 118.16 (t), 126.93, 128.65, 128.93,

136.92 (t), 139.41, 156.70. HRMS calcd for $C_{17}H_{10}D_3N$ 234.1233, found 234.1229.

Crossover reaction of 2 different titanacyclopentadienes with a nitrile

Two different titanacyclopentadienes prepared from $(C_5D_5)_2TiCl_2$ (310 mg, 1.2 mmol) with 4-octyne (293 μ l, 2.0 mmol) and $(C_5H_5)_2TiCl_2$ (299 mg, 1.2 mmol) with 2-butyne (157 μ l, 2.0 mmol) were mixed. To the mixture was added butyronitrile (4.0 mmol, 350 μ l). The mixture was stirred at 50 °C for 1 h. The reaction mixture was quenched with HCl, and then extracted with hexane. The extraction was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo, and separation and purification was done by column chromatography using hexane. After chromatography, two benzene derivatives were separated by distillation (90 °C, 6 mmHg).

1,2-Bisdeuterio-3,4,5,6-tetrapropylbenzene (2c-d₂). Colorless liquid, 106 mg (GC yield 59%, Isolated yield 43%, D-incorporation >97%). 1H NMR ($CDCl_3$, Me_4Si) δ 0.97-1.06 (m, 6H), 1.48-1.63 (m, 4H), 2.51-2.58 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.53, 15.03, 24.68, 24.74, 31.51, 35.21, 126.20 (t, $J=23.3$ Hz), 138.15, 138.64. HRMS calcd for $C_{18}H_{28}D_2$ 248.2471, found 248.2471.

3,4,5,6-Tetramethylbenzene (2f). Colorless liquid, 71 mg (GC yield 54%, Isolated yield 53%). 1H NMR ($CDCl_3$, Me_4Si) δ 2.18 (s, 6H), 2.25 (s, 6H), 6.90 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 118.16 (t), 126.93, 128.65, 128.93, 136.92 (t), 139.41, 156.70. HRMS calcd for $C_{10}H_{14}$ 134.1096, found 134.1078.

Monitoring the reaction of 1a with 2 eq of PhCN by checking the yield of 2a and 3a

The reaction was carried out as described above at 40°C. The yields of **2a** and **3a** were determined by GC. The yields are shown in the table.

Table. Yields of **2a** and **3a**

Time/h	PhCN	2a	3a
0	100	0	0
0.5	95	2	0
1	92	4	0
3	83	15	3
6	68	28	8
12	54	44	13
24	42	55	24
48	37	57	26
96	37	57	24

Procedure to prepare Ph¹³CN

To benzoic acid Ph¹³CN (2.0g, 16.2 mmol) solution in THF, thionyl chloride (1.18 ml, 16.2 mmol) was added. Reaction mixture was stirred for 48 h at room temperature. After quench of this reaction mixture with 20 – 30% NH₃ aq at 0 °C, white solid was extracted with ethyl acetate. Finally, Ph¹³CN was obtained by distillation over P₂O₅ (1.8 g, 5.3 mmol, 33%).

Reaction of Ph¹³CN and titanacyclopentadiene 1a.

To a solution of bis(cyclopentadienyl)tetraethyltitanacyclopentadiene **1a** was added ¹³C-enriched PhCN (206 µl, 2.0 mmol). The mixture was refluxed for 1 h. The reaction mixture was quenched with saturated NaHCO₃ aq, and then extracted with ethyl acetate. The extract was washed with water and brine and dried over MgSO₄. The solvent was evaporated in vacuo. Column chromatography on silica gel afforded 1,2,3,4-tetraethylbenzene (**2a**)(GC yield 59%) and ¹³C-enriched 2,6-diphenylpyridine-2,6-¹³C₂ (**3a- Ph¹³CN**) (GC yield 52%).

¹³C-enriched 2,6-Diphenylpyridine-2,6-¹³C₂ (3a- Ph¹³CN) GC yield 52%. ¹H NMR

spectrum showed the same peaks as that of **3a**. ^{13}C NMR (CDCl_3 , Me_4Si) δ 118.60 (dd), 126.97, 128.67 (m), 128.96, 137.47, 139.43 (dd), 156.77 (m). ^{13}C NMR-Inversegate showed that ^{13}C atoms are in C2 and C6 in compound **2a**. HRMS calcd for $^{13}\text{C}_2\text{C}_{15}\text{H}_{13}\text{N}$ 233.1115, found 233.1109.

Procedure for the preparation of ^{13}C -enriched Cp_2TiCl_2

Procedure of the preparation of 1,1-dibromo-2-vinylcyclopropane-1- ^{13}C .

1,1-Dibromo-2-vinylcyclopropane-1- ^{13}C was prepared by the known method³. To a pentane solution of 1,3-butadiene was added $^{13}\text{CHBr}_3$ (708 mg, 2.79 mmol) - CHCl_3 (2820 mg, 11.16 mmol) mixture dropwise at -78°C . After stirring for 1 h at room temperature, the reaction mixture was quenched by 3N HCl, and extracted with pentane. Kugel distillation (40 mmHg, 100°C) afforded 1,1-dibromo-2-vinylcyclopropane-1- ^{13}C (1.8 g, 8.1 mmol, Isolated yield 58%).

Procedure of the preparation of ^{13}C -cyclopentadiene.

To a solution of 1,1-dibromo-2-vinylcyclopropane-1- ^{13}C (1.8 g, 8.1 mmol) in ether, MeLi (1.04 M solution in ether, 7.8 ml, 8.1 mmol) was dropwise added at -78°C . After stirring at 0°C for 1 h, ^{13}C -cyclopentadiene (as an ether solution) was transferred *in vacuo* to a tube to remove the LiBr salts. The yield was determined by NMR using mesitylene as an internal standard (4.5 mmol, 56%)

Procedure of the preparation of (¹³C-enriched Cp)₂TiCl₂ (**1a**-¹³C)

To an ether solution of ¹³C-cyclopentadiene, *n*-BuLi (1.59 M solution in hexane, 2.8 ml, 4.5 mmol) was dropwise added at −78 °C. After stirring for 1 h at 0 °C, white suspension was formed. TiCl₄ (2.25 mmol, 0.25ml) was slowly added to this suspension and the color of the mixture changed into red. After stirring it for 3 h at room temperature, the reaction mixture was quenched by 3N HCl and extracted with CHCl₃. The crude product was sublimed (6mmHg, 230 °C) to crystalline complex (¹³C-enriched Cp)₂TiCl₂ (¹³C-enrichment: 4.7 times, Isolated yield 61%). ¹H-NMR spectra showed satellites around the Cp-signal due to the enriched ¹³C. From the ¹³C-NMR-Inversegate spectrum, ¹³C enrichment was calculated using mesitylene as an internal standard. (HRMS calcd for ¹³C₂¹²C₈H₁₀³⁷Cl₂ 253.9647, found 253.9642.

Reaction of ¹³C-enriched titanacyclopentadiene (**1a**-¹³C) with benzonitrile

A

solution of (¹³C-enriched Cp)₂TiCl₂ (149.64 mg, 0.6 mmol) in THF (3ml) was cooled to −78 °C. *n*-BuLi (1.59 M solution in hexane, 1.59 ml, 1.2 mmol) was dropwise added to this solution. After stirring for 1 h at −78 °C, 3-hexyne (114 μl, 1.0 mmol) was added and the mixture was stirred. After stirring for 3 h at −10 °C, the color of the reaction mixture turned to dark green. And then to this mixture was added benzonitrile (102 μl, 1.0 mmol). This mixture was refluxed for 1 h. The reaction mixture was quenched with saturated NaHCO₃ aq, and then extracted with ethyl acetate. The extract was washed with water and brine and dried over MgSO₄. The solvent was evaporated in vacuo. Column chromatography on silica gel afforded the 1,2,3,4-tetraethylbenzene-5,6-¹³C-enriched **2a**-¹³C and 2,6-diphenylpyridine-3,4,5-¹³C-enriched **3a**-¹³C.

Synthesis of (*d*₅-Cyclopentadienyl)(methylcyclopentadienyl)titanium dichloride

To a ether solution of *d*₅-cyclopentadienyltitanium trichloride (2.46 mmol, 552 mg) , (MeCp)Li was added and stirred for 1h at r.t. Reaction mixture was quenched by 3 N HCl aq, and The organic layer was extracted with chloroform. Crystallization in chloroform afforded 545 mg of (*d*₅-Cyclopentadienyl)(methylcyclopentadienyl)titanium dichloride as red crystals. Isolated yield 81%. ¹H NMR (CDCl₃, Me₄Si) δ 2.36 (s, 3 H), 6.32 (d, *J* = 2.4, 2.4 Hz, 2 H), 6.43 (dd, *J* = 2.4, 2.4 Hz, 2 H); ¹³C NMR (CDCl₃, Me₄Si) δ 16.41, 115.66, 119.12 (t, *J* = 26.3 Hz), 123.80, 134.66.

Reaction of (*d*₅-Cyclopentadienyl)(methylcyclopentadienyl)titanacyclopentadiene with benzonitrile

(*d*₅-Cyclopentadienyl)(methylcyclopentadienyl)titanium dichloride (0.6 mmol, 161 mg) prepared above was solved in THF, and to this was added *n*-BuLi (1.2 mmol, 1.58 M, 0.75 ml). The mixture was stirred at 0 °C. 3-Hexyne (1.0 mmol, 114 μl) was added to this reaction mixture and stirred for 1 h at -78 °C. After addition of benzonitrile (1.0 mmol, 102 μl), the reaction mixture was refluxed for 1h. And then the mixture was quenched with water. Organic layer was extracted with ethyl acetate. After washing with brine and water, it was dried with anhydrous MgSO₄. After filtration and evaporation, 1,2,3,4-tetraethylbenzene (**2a**: 25% yield), 1,2-bisdeuterio-3,4,5,6-tetrapropylbenzene (**2a-d**₂: 17% yield; D incorporation 95%), **3a-d**₃ (11% yield) and were obtained 4-methyl-2,5-diphenyl-pyridine (8% yield). The formation of **3a** and 3-methyl-2,5-diphenylpyridine were not detected.

Detect of nitrogen as ammonia formed in the reaction.

To a THF solution of tetraethyltitanacyclopentadiene **1a** was added 2 eq of Ph-CN and the mixture was stirred for 12h at 50 °C. This reaction mixture was quenched with 3 N HCl solution and stirred for 24h.

Water soluble compounds were extracted with water and the combined water layer was distilled into 3N HCl solution. Ammonia was detected by indophenol method. The result is shown in Table.

Table 1. The Amount of the Nitrogen after the Reaction of Titanacyclopentadiene with PhCN

	PhCN		NH ₄ ⁺	total N
Before	2.0 mmol	—	—	2.0 mmol
After	0.10 mmol	0.52 mmol	1.21 mmol	1.83 mmol

More than 90% of N was detected as pyridine 3a, ammonia and unreacted PhCN. Origin of ammonia can be titanium nitride or titanium imide complex. However, the clean formation of such titanium complexes was not observed.

Reference

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Suggested Mechanism for the formation of a benzene derivative and a pyridine derivative from a cyclopentadienyl ligand