

Supporting Information

for

**First Isolation of Fully Delocalized Mixed-valent Imido-bridged $[Ti_2]^{7+}$ Complexes by
One-electron Reduction of $[(C_5R_5)TiCl]_2(\mu\text{-}NAr)_2$**

Hayato Tsurugi, Haruki Nagae, and Kazushi Mashima*

*Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka,
Osaka 560-8531, Japan*

General procedure: All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard schlenk technique or argon-filled glovebox. $CpTiCl_3$ (**1a**) and Cp^*TiCl_3 (**1b**) were prepared according to the literatures.¹ Lithium amide **2** was prepared by lithiation of $HN(SiMe_3)(Ar)$ ($Ar = 3,5\text{-(CF}_3\text{)}_2C_6H_3$) using $^7\text{BuLi}$ in hexane.² Cp_2Co was purchased and used as received. Anhydrous hexane, toluene, THF, and dichloromethane were purchased from Kanto Chemical, and further purified by passage through activated alumina under positive argon pressure as described by Grubbs *et al.*³ Chloroform-*d*, methylene chloride-*d*₂, and benzene-*d*₆ were distilled over CaH_2 and thoroughly degassed by trap-to-trap distillation before use. ¹H NMR (300 MHz, 400 MHz) and ¹³C NMR (75 MHz, 100 MHz) spectra were measured on VARIAN UNITY INOVA-300 and BRUKER AVANCEIII-400 spectrometers. Assignments for ¹H and ¹³C NMR peaks for all complexes were aided by 2D ¹H-¹H COSY and 2D ¹H-¹³C HETCOR spectra, respectively. EPR spectrum was recorded at 298 K on BRUKER EMX-10/12 spectrometer. GC-MS analyses were performed with Shimadzu GCMS-QP505A spectrometer with Shimadzu GC-17A GC equipped with J&W Scientific DB-1

column. UV-vis spectra were recorded on Agilent 8453 and Hitachi U-3500 spectrometer. Cyclic voltammograms were measured by BAS ALS610D spectrometer using a standard three-electrode configuration with working electrode (glassy carbon), counter electrode (platinum), and reference electrode (silver). $[n\text{Bu}_4\text{N}][\text{PF}_6]$ was used as the electrolyte, and Cp_2Fe was used as the standard. Elemental analyses were recorded by using Perkin Elmer 2400 at the Faculty of Engineering Science, Osaka University.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2[\text{N}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5})]$ (3a): A solution of **2** (100 mg, 0.326 mmol) in toluene (5 mL) was added dropwise to a solution of **1a** (71.4 mg, 0.326 mmol) in toluene (5 mL) at room temperature, and the reaction mixture was stirred overnight. After removing the insoluble precipitate by centrifugation, all the solvent was evaporated to afford yellow-brown powder. The powder was extracted with hexane (10 mL) to give **3a** (134 mg, 0.299 mmol, 91% yield) as yellow solid (mp: 101–105 °C). ^1H NMR (400 MHz, C_6D_6 , 35 °C) δ 7.50 (s, 1H, *p*-Ar), 7.13 (s, 2H, *o*-Ar), 5.75 (s, 5H, C_5H_5), 0.22 (s, 9H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, C_6D_6 , 35 °C) δ 159.7 (s, *ipso*-Ar), 132.3 (q, $^2J_{\text{C-F}} = 33$ Hz, *m*-Ar), 124.4 (br q, $^3J_{\text{C-F}} = 3$ Hz, *o*-Ar), 123.6 (q, $^1J_{\text{C-F}} = 273$ Hz, CF_3), 120.9 (s, C_5H_5), 117.7 (sept, $^3J_{\text{C-F}} = 4$ Hz, *p*-Ar), 1.72 (s, $\text{Si}(\text{CH}_3)_3$). $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, C_6D_6 , 35 °C) δ -63.6 (s, 6F, CF_3). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{Cl}_2\text{F}_6\text{NSiTi}$: C, 39.69; H, 3.54; N, 2.89. Found: C, 39.54; H, 3.59; N, 2.70.

$(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2[\text{N}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5})]$ (**3b**) was prepared similar manner to **3a**: 89% yield as red solid (mp: 111–115 °C). ^1H NMR (400 MHz, C_6D_6 , 35 °C) δ 7.57 (s, 2H, *o*-Ar), 7.55 (s, 1H, *p*-Ar), 1.68 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 0.16 (s, 9H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, C_6D_6 , 35 °C) δ 154.8 (s, *ipso*-Ar), 132.7 (s, $\text{C}_5(\text{CH}_3)_5$), 132.1 (q, $^2J_{\text{C-F}} = 33$ Hz, *m*-Ar), 127.2 (br q, $^3J_{\text{C-F}} = 3$ Hz, *o*-Ar), 124.0 (q, $^1J_{\text{C-F}} = 271$ Hz, CF_3), 117.3 (sept, $^3J_{\text{C-F}} = 4$ Hz, *p*-Ar), 13.1 (s, $\text{C}_5(\text{CH}_3)_5$), 2.87 (s,

Si(CH₃)₃). ¹⁹F{¹H} NMR (376 MHz, C₆D₆, 35 °C) δ -63.7 (s, 6F, CF₃). Anal. Calcd for C₂₁H₂₇Cl₂F₆NSiTi: C, 45.50; H, 4.91; N, 2.53. Found: C, 45.15; H, 4.74; N, 2.34.

Preparation of [(\eta⁵-C₅H₅)TiCl]₂[μ-N(C₆H₃(CF₃)₂-3,5)]₂ (4a): A complex **3a** (1.61 g, 3.60 mmol) was dissolved in THF (20 mL) at room temperature. After stirring the solution for 15 h, the solvent was removed under vacuum and washed with toluene (5 mL × 3) to give **4a** (1.25 g, 1.67 mmol, 92% yield) as green powder (mp: 288–291 °C). ¹H NMR (400 MHz, CDCl₃, 35 °C) δ 7.54 (s, 2H, *p*-Ar), 7.06 (s, 4H, *o*-Ar), 6.45 (s, 10H, C₅H₅). ¹H NMR (400 MHz, tol-d₈, 35 °C) δ 7.49 (s, 2H, *p*-Ar), 7.19 (s, 4H, *o*-Ar), 5.87 (s, 10H, C₅H₅). ¹H NMR (400 MHz, CD₂Cl₂, 35 °C) δ 7.57 (s, 2H, *p*-Ar), 7.10 (s, 4H, *o*-Ar), 6.47 (s, 10H, C₅H₅). ¹³C{¹H} NMR (100 MHz, CDCl₃, 35 °C) δ 156.4 (s, *ipso*-Ar), 133.0 (q, ²J_{C-F} = 33 Hz, *m*-Ar), 123.3 (q, ¹J_{C-F} = 272 Hz, CF₃), 120.5 (m, ³J_{C-F} = 3 Hz, *o*-Ar), 120.1 (s, C₅H₅), 118.7 (sept, ³J_{C-F} = 4 Hz, *p*-Ar). ¹⁹F{¹H} NMR (376 MHz, CDCl₃, 35 °C) δ -63.7 (s, 6F, CF₃). UV-vis (toluene), λ_{max} [nm] (ε): 450 (sh, 3.7 × 10³). Anal. Calcd for C₂₆H₁₆Cl₂F₆N₂Ti₂: C, 41.58; H, 2.15; N, 3.73. Found: C, 41.42; H, 1.82; N, 3.58.

[(\eta⁵-C₅Me₅)TiCl]₂[μ-N(C₆H₃(CF₃)₂-3,5)]₂ (**4b**) was prepared similar manner to **4a**: (0.58 g, 0.61 mmol, 45% yield) as deep red powder (mp: >300 °C). ¹H NMR (400 MHz, CDCl₃, 35 °C) δ 7.48 (s, 2H, *p*-Ar), 7.02 (s, 4H, *o*-Ar), 1.75 (s, 30H, C₅(CH₃)₅). ¹³C{¹H} NMR (100 MHz, CDCl₃, 35 °C) δ 155.7 (s, *ipso*-Ar), 132.1 (q, ²J_{C-F} = 33 Hz, *m*-Ar), 129.7 (s, C₅(CH₃)₅), 123.4 (q, ¹J_{C-F} = 271 Hz, CF₃), 122.7 (br q, ³J_{C-F} = 3 Hz, *o*-Ar), 116.6 (sept, ³J_{C-F} = 4 Hz, *p*-Ar), 11.8 (s, C₅(CH₃)₅). ¹⁹F{¹H} NMR (376 MHz, CDCl₃, 35 °C) δ -63.9 (s, 6F, CF₃). UV-vis (CH₂Cl₂), λ_{max} [nm] (ε): 302 (2.5 × 10⁴), 500 (9.5 × 10³). Anal. Calcd for C₃₆H₃₆Cl₂F₁₂N₂Ti₂: C, 48.51; H, 4.07; N, 3.14. Found: C, 48.84; H, 3.91; N, 3.12.

Preparation of $[\text{Cp}_2\text{Co}][[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}]_2[\mu\text{-N}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5})]_2]$ (5a): A solution of Cp_2Co (25.2 mg, 0.133 mmol) in CH_2Cl_2 (2 mL) was added to a solution of **4a** (100.0 mg, 0.133 mmol) in CH_2Cl_2 (5 mL) at room temperature, and the reaction mixture was stirred for 30 minutes. The solvent was removed under vacuum, and the resulting solid was washed with toluene (5 mL \times 3) to give **5a** (103.9 mg, 0.083 mmol, 82% yield) as blue-green powder (mp: 265–268 °C (dec.)). EPR (THF): $g = 1.988$ ($A_{\text{iso}} = 3.1$ G). UV-Vis-NIR (CH_2Cl_2): 626 (1178 $\text{cm}^{-1}\text{M}^{-1}$), 1505 (98 $\text{cm}^{-1}\text{M}^{-1}$). Anal. Calcd for $\text{C}_{36}\text{H}_{26}\text{Cl}_2\text{CoF}_{12}\text{N}_2\text{Ti}_2(\text{C}_6\text{H}_5\text{CH}_3)_{0.5}$: C, 48.10; H, 3.07; N, 2.84. Found: C, 47.95; H, 2.88; N, 2.64.

$[\text{Cp}_2\text{Co}][[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}]_2[\mu\text{-N}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5})]_2]$ (**5b**) was prepared similar manner to **5a**: 72% yield as yellow-green powder (mp: 287–290 °C (dec.)). EPR (CH_2Cl_2): $g = 1.986$ ($A_{\text{iso}} = 3.2$ G). Anal. Calcd for $\text{C}_{46}\text{H}_{46}\text{Cl}_2\text{CoF}_{12}\text{N}_2\text{Ti}_2$: C, 51.14; H, 4.29; N, 2.59. Found: C, 51.49; H, 4.31; N, 2.50.

X-ray Diffraction Study: All crystals were handled similarly. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K α (0.71075 Å) radiation. Crystal data and structure refinement parameters were listed below (Table S1). The structures were solved by SHELXS-97,⁴ SIR-92⁵ or SIR-2008⁶ and refined on F^2 by full-matrix least-squares method, using SHELXL-97.⁴ Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ with $\sigma^2(F_o^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\sum |F_o| - |F_c|) / \sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$, respectively. Due to the positional disorder of CF₃ groups, the $R1$ value for **3b** and **4a** is relatively high. Refinement of the CF₃ groups by dividing the disordered atoms was unsuccessful. The ORTEP-3 program was used to draw the molecule.⁷ CCDC 811933 (**3a**), 811934 (**3b**), 811935 (**4a**), 811936 (**4b**), and 811937 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

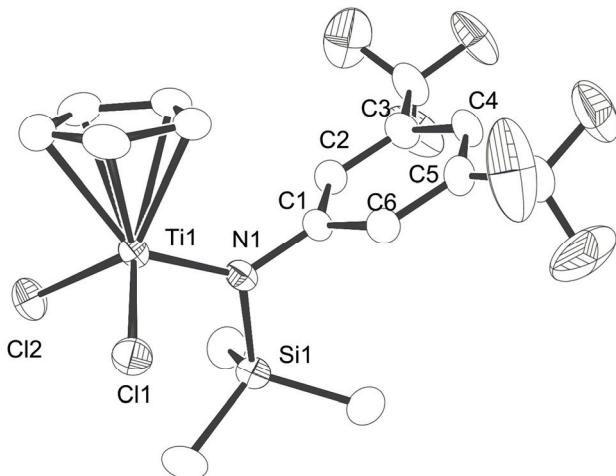


Figure S1. Molecular structure of complex **3a** with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances (\AA) and angles (deg.): Ti – N1 1.909(3), Ti – Cl1 2.2695(15), Ti – Cl2 2.2711(15), N – Si 1.809(3), N – C1 1.432(4), N – Ti – Cl1 102.84(10), N – Ti – Cl2 106.16(9), Cl1 – Ti – Cl2 104.29(6), Ti – N – Si 120.35(15), Ti – N – C1 129.0(2), Si – N – C1 110.7(2).

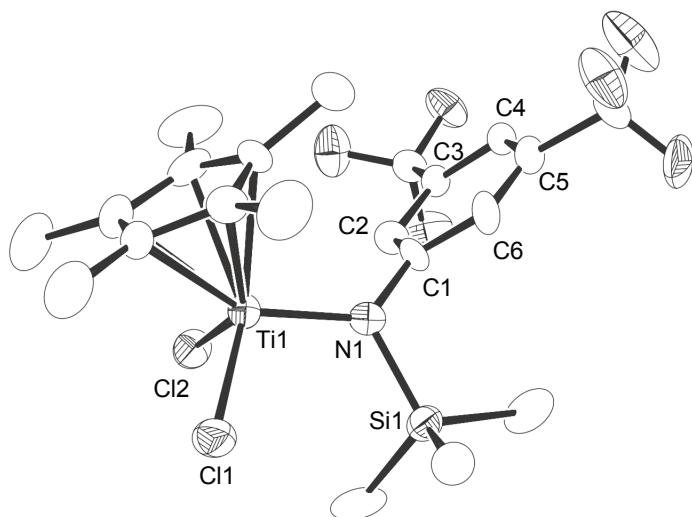


Figure S2. Molecular structure of complex **3b** with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances (\AA) and angles (deg.): Ti1 – N1 1.938(7), Ti1 – Cl1 2.258(3), Ti1 – Cl2 2.280(3), N1 – Si1 1.800(7), N1 – C1 1.445(11), N1 – Ti1 – Cl1 101.2(2), N – Ti – Cl2 103.6(2), Cl1 – Ti1 – Cl2 101.14(11), Ti1 – N1 – Si1 118.9(4), Ti1 – N1 – C1 132.2(6), Si1 – N1 – C1 108.9(6).

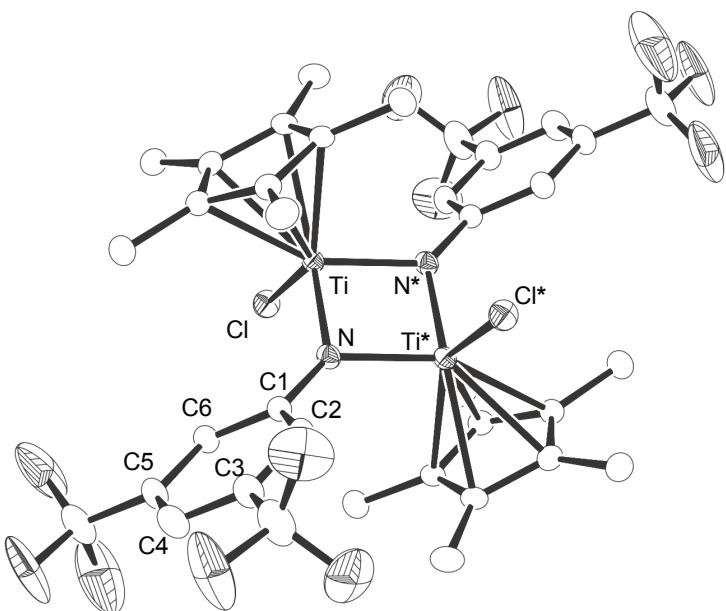


Figure S3. Molecular structure of complex **4b** with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances (\AA) and angles (deg.): Ti – N 1.919(2), Ti – N* 1.954(2), Ti – Cl 2.2958(8), N – C1 1.396(3), Ti – Ti* 2.8389(7), Ti – N – Ti 94.25(9), N – Ti – Cl 105.27(6), N* – Ti – Cl 103.25(6), Ti – N – C1 136.1(3), Ti* – N – C1 129.5(2).

Table S1. Crystal Data and Data Collection Parameters.

	3a	3b
empirical formula	C ₁₆ H ₁₇ Cl ₂ F ₆ NSiTi	C ₂₁ H ₂₇ Cl ₂ F ₆ NSiTi
formula weight	484.20	554.33
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	8.519(8)	8.9074(9)
<i>b</i> , Å	23.699(15)	14.6224(16)
<i>c</i> , Å	10.892(7)	38.661(5)
α, deg.	-	-
β, deg.	99.651(7)	91.014(7)
γ, deg.	-	-
<i>V</i> , Å ³	2066(2)	5034.7(10)
<i>Z</i>	4	8
<i>D</i> calcd, g/cm ⁻³	1.556	1.463
μ [Mo- <i>K</i> α], mm ⁻¹	0.784	0.654
<i>T</i> , K	113(2)	113(2)
crystal size, mm	0.40 x 0.24 x 0.22	0.25 x 0.20 x 0.07
θ range for data collection (deg.)	3.1 to 27.5	3.08 to 27.46
no. of reflections measured	19168	45285
unique data (<i>R</i> _{int})	4645 (0.048)	11349 (0.1669)
data / restraints / parameters	4645 / 0 / 245	11349 / 0 / 593
<i>R</i> 1 (<i>I</i> > 2.0σ(<i>I</i>))	0.0608	0.1166
<i>wR</i> 2 (<i>I</i> > 2.0σ(<i>I</i>))	0.1735	0.2918
<i>R</i> 1 (all data)	0.0798	0.2123
<i>wR</i> 2 (all data)	0.2014	0.3618
GOF on <i>F</i> ²	1.119	1.091
Δρ, e Å ⁻³	1.04, -0.90	0.74, -1.17

a) $R1 = (\sum ||Fo| - |Fc||)/(\sum |Fo|)$ b) $wR2 = [\{\sum w(Fo^2 - Fc^2)^2\}/\{\sum w(Fo^4)\}]^{1/2}$

	4a	4b
empirical formula	C ₂₆ H ₁₆ Cl ₂ F ₁₂ N ₂ Ti ₂ , C ₆ H ₆	C ₃₆ H ₃₆ Cl ₂ F ₁₂ N ₂ Ti ₂
formula weight	829.22	891.38
crystal system	monoclinic	monoclinic
space group	<i>C2/c</i> (No. 15)	<i>P2₁/n</i> (No. 14)
<i>a</i> , Å	15.882(6)	8.8477(16)
<i>b</i> , Å	8.044(3)	22.113(3)
<i>c</i> , Å	26.068(8)	10.0609(14)
α , deg.	-	-
β , deg.	98.757(16)	109.928(5)
γ , deg.	-	-
<i>V</i> , Å ³	3291.8(19)	1850.5(5)
<i>Z</i>	4	2
<i>D</i> calcd, g/cm ⁻³	1.673	1.60
μ [Mo- <i>K</i> α], mm ⁻¹	0.743	0.667
<i>T</i> , K	113(2)	113(2)
crystal size, mm	0.30 x 0.20 x 0.10	0.50 x 0.30 x 0.10
θ range for data collection (deg.)	3.01 to 227.32	3.2 to 27.5
no. of reflections measured	12742	16827
unique data (<i>R</i> _{int})	3583 (0.1325)	4181 (0.044)
data / restraints / parameters	3583 / 0 / 227	4181 / 0 / 245
<i>R</i> 1 (<i>I</i> > 2.0 σ (<i>I</i>))	0.1118	0.0527
<i>wR</i> 2 (<i>I</i> > 2.0 σ (<i>I</i>))	0.2845	0.1409
<i>R</i> 1 (all data)	0.2064	0.0625
<i>wR</i> 2 (all data)	0.3652	0.1494
GOF on <i>F</i> ²	0.995	1.077
$\Delta\rho$, e Å ⁻³	1.07, -1.35	1.25, -0.98

a) $R1 = (\sum ||Fo| - |Fc||)/(\sum |Fo|)$ b) $wR2 = [\{\sum w(Fo^2 - Fc^2)^2\}/\{\sum w(Fo^4)\}]^{1/2}$

5a

empirical formula	C ₂₆ H ₁₆ Cl ₂ F ₁₂ N ₂ Ti ₂ , C ₁₀ H ₁₀ Co, 2(CH ₂ Cl ₂)
formula weight	1110.07
crystal system	monoclinic
space group	P2 ₁ /c (No. 14)
<i>a</i> , Å	18.139(12)
<i>b</i> , Å	11.696(7)
<i>c</i> , Å	21.035(14)
α , deg.	-
β , deg.	93.064(7)
γ , deg.	-
<i>V</i> , Å ³	4456(5)
<i>Z</i>	4
<i>D</i> calcd, g/cm ⁻³	1.655
μ [Mo- <i>K</i> α], mm ⁻¹	1.159
<i>T</i> , K	113(2)
crystal size, mm	0.59 x 0.48 x 0.25
θ range for data collection (deg.)	3.48 to 27.52
no. of reflections measured	41425
unique data (<i>R</i> _{int})	10099 (0.0867)
data / restraints / parameters	10099 / 0 / 550
<i>R</i> 1 (<i>I</i> > 2.0 σ (<i>I</i>))	0.0964
<i>wR</i> 2 (<i>I</i> > 2.0 σ (<i>I</i>))	0.2514
<i>R</i> 1 (all data)	0.1462
<i>wR</i> 2 (all data)	0.2932
GOF on <i>F</i> ²	1.068
$\Delta\rho$, e Å ⁻³	1.59, -0.78

a) $R1 = (\sum ||Fo| - |Fc||)/(\sum |Fo|)$ b) $wR2 = [\{\sum w(Fo^2 - Fc^2)^2\}/\{\sum w(Fo^4)\}]^{1/2}$

Characterization of Complex 5b: Five-line splitting resonance ($g = 1.986$, $A_{\text{iso}}(\text{N}) = 3.2 \text{ G}$)

was observed with small satellite signals. The five-lined patterned signal was simulated as an unpaired electron on two equivalents nitrogen atoms ($I = 1$), while the satellite resonance is attributed to the non-zero nuclear spin isotope ^{47}Ti ($I = 5/2$, natural abundance 7.28%), ^{49}Ti ($I = 7/2$, natural abundance 5.51%), and two equivalents nitrogen atoms.

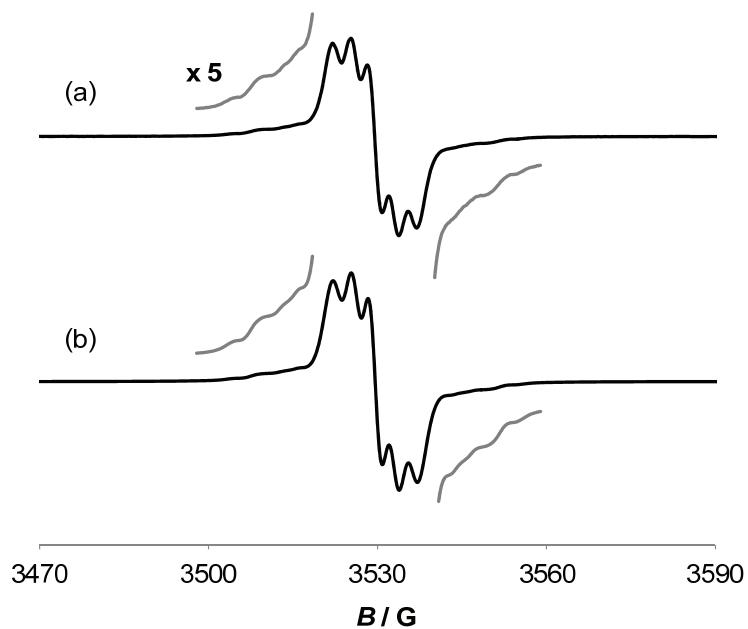
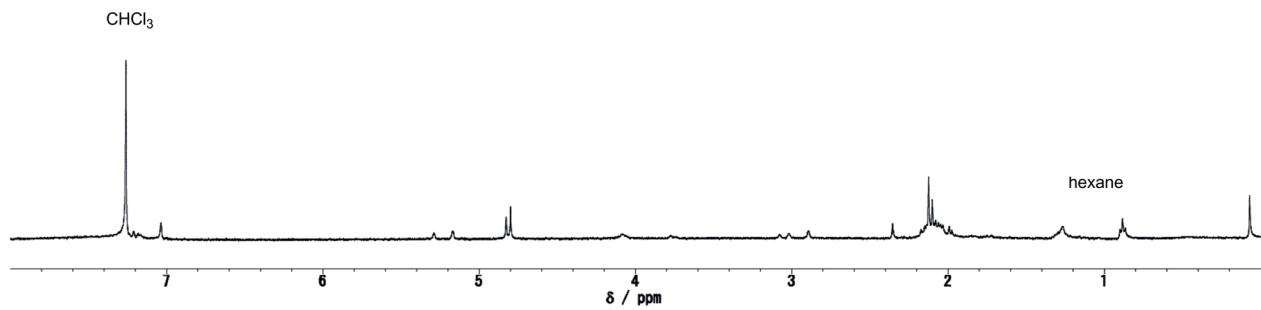


Figure S4. EPR spectra of complex 5b: (a) Experimental spectrum of 5b in CH_2Cl_2 , (b) Simulated spectrum.

Reaction of 5b with chloroform:

(a)



(b)

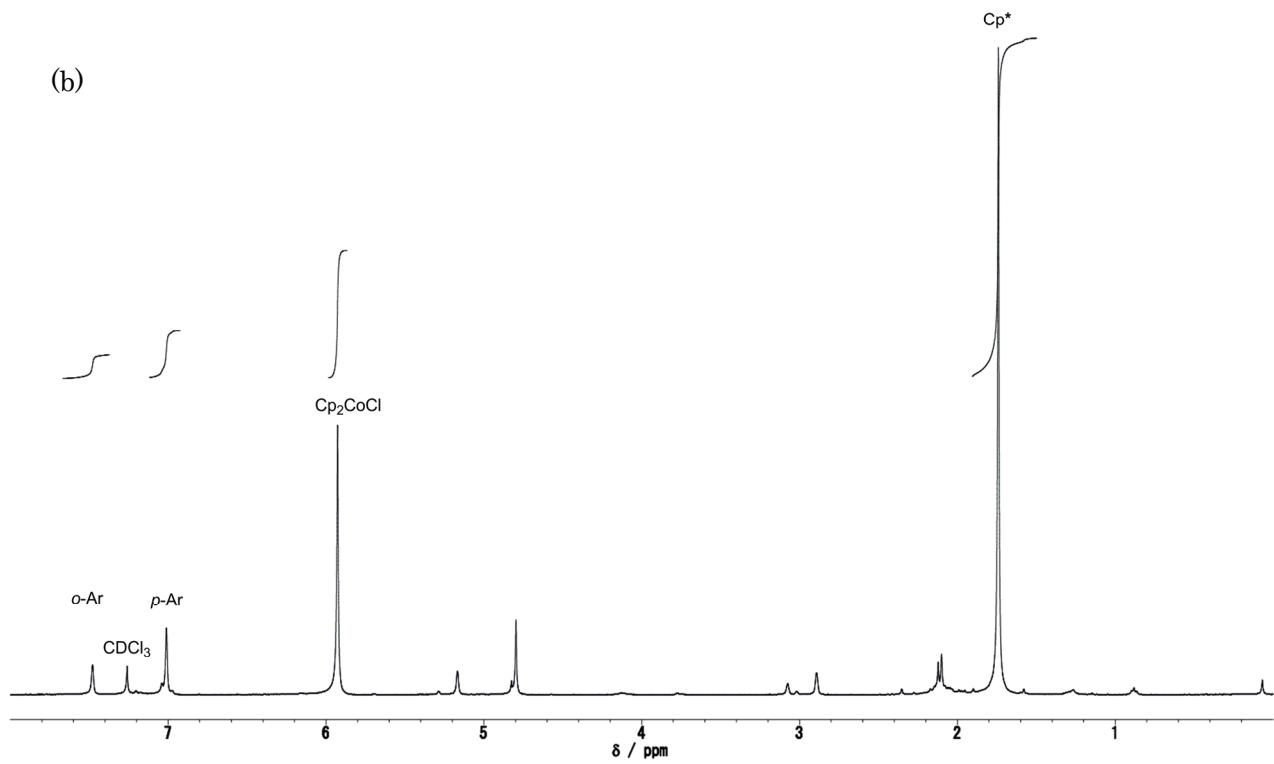


Figure S5. Conversion of complex **5b** to **4b** in the ¹H NMR spectra in CDCl₃: (a) ¹H NMR spectrum of complex **5b** in CDCl₃, (b) After heating at 60 °C for 3 h.

UV-vis spectra of complexes **4a** and **5a**:

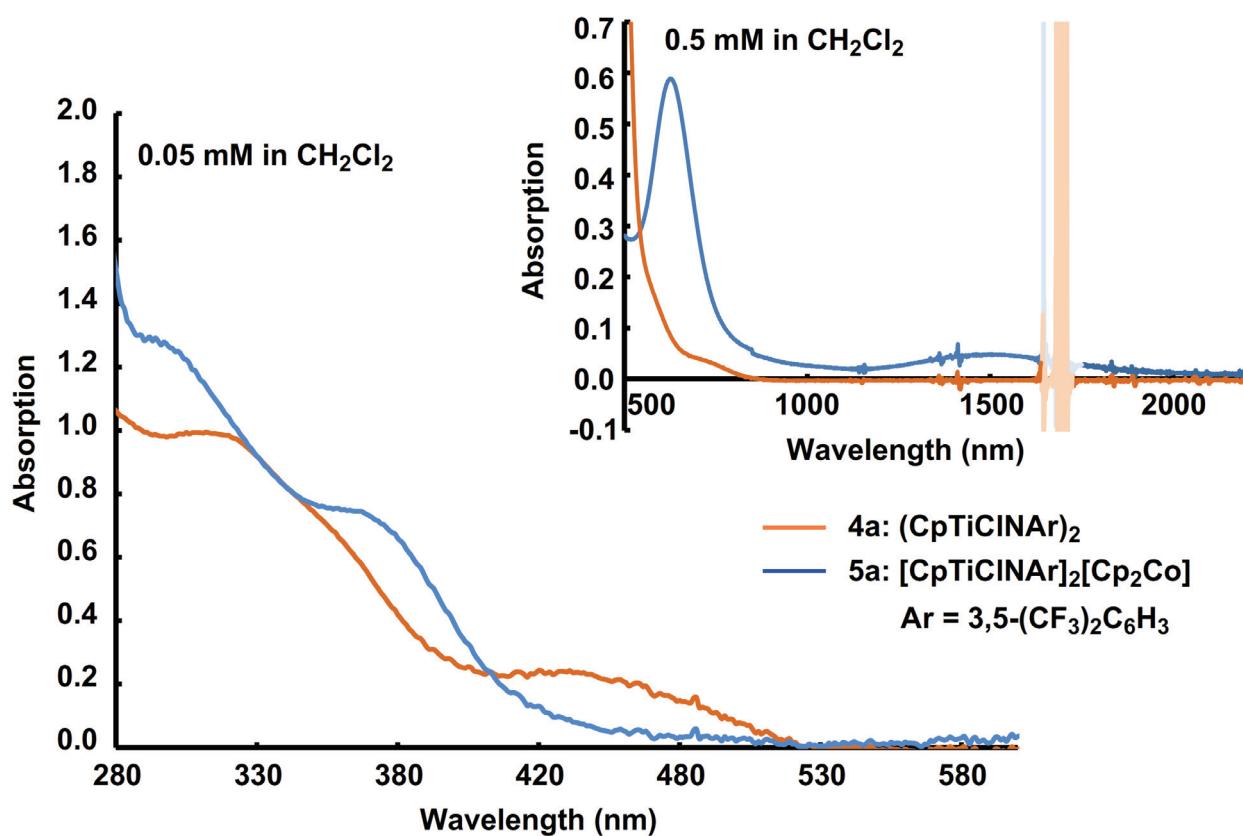


Figure S6. Absorption spectra of **4a** and **5a** in CH_2Cl_2 .

References and Note

- 1) Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 4744.
- 2) Jean, P. B.; Peter, B. H.; Michael, F. L. Philippe, G. M. *J. Chem. Soc., Dalton Trans.* **2001**, 816.
- 3) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- 4) Sheldrich, G. M. (2008) *Acta Cryst. A* **64**, 112-122.
- 5) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.
- 6) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Caro, L. D.; Giacovazzo, C.; Polidori, G.; Siliqi, D.; Spagna, R. *J. Appl. Cryst.* **2007**, *40*, 609-613.
- 7) Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837.