Ionic liquid promotes N\textsubscript{2} coordination to titanocene(III) monochloride
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Electronic Supplementary Information

Experimental S1
Chemicals S1
Purification of ionic liquid S2
Instrumentation S2
Measurement of EPR spectra under \textsuperscript{14}N\textsubscript{2} atmosphere S3
Measurement of EPR spectra under \textsuperscript{15}N\textsubscript{2} atmosphere S3
Fig. S1 The picture of a gas purification column for \textsuperscript{15}N\textsubscript{2} S3
Fig. S2 EPR spectrum of 0.5 mM [(Cp\textsubscript{2}TiCl\textsubscript{2})\textsubscript{2}] in toluene S4
Fig. S3 EPR spectrum of 1 mM [(Cp\textsubscript{2}TiCl\textsubscript{2})\textsubscript{2}] in 0.2 M Pyr\textsubscript{4}FAP/THF S5
Fig. S5 UV-vis/NIR spectrum of 5 mM [(Cp\textsubscript{2}TiCl\textsubscript{2})\textsubscript{2}] in Pyr\textsubscript{4}FAP S6
Fig. S6 UV-vis/NIR spectrum of 5 mM [(Cp\textsubscript{2}TiCl\textsubscript{2})\textsubscript{2}] in 0.2 M Pyr\textsubscript{4}FAP/THF S6
Fig. S7 UV-vis/NIR spectrum of 5 mM [(Cp\textsubscript{2}TiCl\textsubscript{2})\textsubscript{2}] in toluene S7
Fig. S8 UV-vis/NIR spectrum of 5 mM [Cp\textsuperscript{*2}TiCl] in toluene S7
Fig. S9 UV-vis/NIR spectrum of 5 mM [Cp\textsubscript{2}VCl\textsubscript{2}] in toluene S8
Table S1. Summary of UV-vis/NIR spectra S8
Fig. S10 UV-vis/NIR spectra of 2, 4, 8, and 12 mM [(Cp\textsubscript{2}TiCl\textsubscript{2})\textsubscript{2}] in Pyr\textsubscript{4}FAP S9
Fig. S11 UV-vis/NIR spectra of 2, 4, 8 and 12 mM [(Cp\textsubscript{2}TiCl\textsubscript{2})\textsubscript{2}] in toluene S9
Fig. S12 UV-vis/NIR spectra of 2, 4, 8 and 12 mM [(Cp\textsubscript{2}TiCl\textsubscript{2})\textsubscript{2}] in THF S10
References S11
Experimental

All manipulations were performed using standard Schlenk-line techniques or in an MBraun dry box under Ar or N₂ atmosphere (< 1 ppm O₂/H₂O).

Chemicals

Bis(cyclopentadienyl)titanium(IV) dichloride, [Cp₂TiCl₂], was purchased from Tokyo Chemical Industry Co., Ltd. Bis(pentamethylcyclopentadienyl)titanium(IV) dichloride, [Cp*₂TiCl₂], was purchased from Wako Pure Chemical Industries Ltd. Bis(cyclopentadienyl)vanadium(IV) dichloride, [Cp₂VCl₂], was purchased from Sigma-Aldrich. These reagents were used after recrystallization from hexane. 1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, Pyr₄FAP, was purchased from Merck Ltd. and purified referring to previous literature (see purification of ionic liquid section). KC₈ was prepared according to the literature. Solvents were purified by the method of Grubbs, where the solvents were passed over columns of activated alumina and supported copper catalyst supplied by ultimate purification system (Glass Contour System, NIKKO HANSEN & CO., LTD), transferred to the glovebox without exposure to air, and stored over molecular sieves 4Å. Bis[(dicyclopentadienyl)titanium(III) chloride], [(Cp₂TiCl)₂], and bis[(dipentamethylcyclopentadienyl)titanium(III) chloride], [Cp*₂TiCl], were synthesized according to the literature.

Purification of ionic liquid

Pyr₄FAP (50 g) was dissolved in distilled EtOH (100 mL), and to the solution was added an activated charcoal (5g, Sigma-Aldrich). And then, the activated charcoal was remove by filtrate and the solvent was removed by evaporator. If the color was not colorless, the purification was repeated using the activated charcoal. After the purification was finished, Pyr₄FAP was vacuumed at 80°C for 3 days and dried over molecular sieves (4 Å) for 1 week.

Instrumentation

Electrochemistry was studied using a potentiostat (BAS, ALS/600). UV–vis/NIR absorption spectra were measured with a Jasco V–770 spectrophotometer using a 1 mm light-pass–length quartz cell. X-band EPR spectra of frozen solution were recorded at 77 K using JEOL RE-1X ESR spectrometer.
**Measurement of EPR spectra under $^{14}$N$_2$ atmosphere**

The sample preparation was carried out in the glove box under $^{14}$N$_2$ atmosphere. Pyr$_4$FAP, which was stirred for 1 week under $^{14}$N$_2$, was used for EPR measurement. The concentration of [(Cp$_2$TiCl)$_2$] was adjusted to 1 mM for each solvent. EPR tube (φ 4 mm) with a ground glass joint (15/25) was employed as the glass stopper (15/25) for measurement under $^{14}$N$_2$.

**Measurement of EPR spectra under $^{15}$N$_2$ atmosphere**

The sample preparation was carried out in the glove box under Ar atmosphere. Pyr$_4$FAP used was vacuumed overnight, and then, stirred for 1 week under $^{15}$N$_2$ before use. The $^{15}$N$_2$ gas (99.9 Atom %), which was purchased from SI Science Co., Ltd., was purified by passing the column containing KC$_8$ (see Fig. S1), and used after replacement of the gas from Ar to $^{15}$N$_2$ by using vacuum line equipped in the glovebox. The replacement is carried out by connecting the gas outlet with vacuum line and the gas inlet with $^{15}$N$_2$ gas cylinder. The concentration of [(Cp$_2$TiCl)$_2$] was adjusted to 1 mM for each solvent. EPR tube (φ 4 mm) with a ground glass joint (15/25) was used with a three-way glass stopcock (15/25) for measurement under $^{15}$N$_2$ atmosphere. After adding the sample in EPR tube, the atmosphere in EPR tube was replaced from Ar to $^{15}$N$_2$.

![Fig. S1 The picture of a gas purification column for $^{15}$N$_2$](image-url)
Fig. S2 EPR spectrum of 0.5 mM [(Cp₂TiCl)₂] in toluene. Experimental conditions are as follows: temperature $T = 77$ K, frequency $\nu = 9.142$ GHz, power 1 mW, and modulation 0.63 mT. The observed spectrum (blue) and simulation (red) are as follows; $g$ values estimated from the spectrum are as follows; $g_x = 1.998$, $g_y = 1.980$, $g_z = 1.950$, and simulated $g$ values are $g_x = 1.998$, $g_y = 1.980$, $g_z = 1.950$. 
Fig. S3 EPR spectrum of 1 mM [(Cp₂TiCl)₂] in 0.2 M Pyr₄FAP/THF. Experimental conditions are as follows; temperature $T = 77$ K, frequency $\nu = 9.125$ GHz, power 1 mW, and modulation 0.63 mT. The observed spectrum (blue) and simulation (red) are as follows; $g$ values estimated from spectrum are $g_x = 1.997$, $g_y = 1.977$, $g_z = 1.946$, and simulated $g$ values are $g_x = 1.997$, $g_y = 1.979$, $g_z = 1.950$. 
Fig. S5 UV-vis/NIR spectrum of 5 mM [(Cp$_2$TiCl)$_2$] in Pyr$_4$FAP

Fig. S6 UV-vis/NIR spectrum of 5 mM [(Cp$_2$TiCl)$_2$] in 0.2 M Pyr$_4$FAP/THF
Fig. S7 UV-vis/NIR spectrum of 5 mM [(Cp₂TiCl)₂] in toluene

Fig. S8 UV-vis/NIR spectrum of 5 mM [Cp₂TiCl] in toluene
Fig. S9 UV-vis/NIR spectrum of 5 mM [Cp₂VCl₂] in toluene

Table S1. Summary of UV-vis/NIR spectra

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>(\lambda_{\text{max}})/nm ((\varepsilon/M\cdot\text{cm}^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cp₂TiCl)₂</td>
<td>Pyr₄FAP</td>
<td>449 (930), 697 (89), 817 (77), 1167 (28)</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>0.2 M Pyr₄FAP/THF</td>
<td>452 (120), 751 (88), 817 (86), 1138 (46)</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>456 nm(⁵)</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>456 (1300), 690 (98), 813 (82), 1164 (23)</td>
<td>this work</td>
</tr>
<tr>
<td>Cp*₂TiCl</td>
<td>Toluene</td>
<td>558 (110), 640 (77)</td>
<td>this work</td>
</tr>
<tr>
<td>Cp*₂TiCl</td>
<td>Toluene</td>
<td>560 (144)</td>
<td>6</td>
</tr>
<tr>
<td>Cp₂VCl₂</td>
<td>Toluene</td>
<td>755 (82), 905 (93)</td>
<td>this work</td>
</tr>
</tbody>
</table>

(⁵) \(\varepsilon\) values are noted in \(M^{-1}\cdot\text{cm}^{-1}\) in the parentheses.
Fig. S10 UV-vis/NIR spectra of 2, 4, 8, and 12 mM [(Cp₂TiCl)₂] in Pyr₄FAP

Fig. S11 UV-vis/NIR spectra of 2, 4, 8, and 12 mM [(Cp₂TiCl)₂] in toluene
Fig. S12 UV-vis/NIR spectra of 2, 4, 8, and 12 mM [(Cp₂TiCl)₂] in THF
References