

Synthesis and Reductive N–N Bond Cleavage of Neutral and Cationic Titanium (1-Pyridinio)imido Complexes

Mikael Retbøll, Youichi Ishii, and Masanobu Hidai*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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Novel (1-pyridinio)imidotitanium(IV) complexes $[\text{Cp}'\text{TiCl}_2(\text{NNC}_5\text{H}_3\text{R}_2\text{-2,6})]$ (**3a**, $\text{Cp}' = \text{Cp}$, $\text{R} = \text{H}$; **3b**, $\text{Cp}' = \text{Cp}$, $\text{R} = \text{Me}$; **3c**, $\text{Cp}' = \text{Cp}^*$, $\text{R} = \text{Me}$) were synthesized in high yield from $[\text{Cp}'\text{TiCl}_3]$ and $[\text{NH}_2\text{NC}_5\text{H}_3\text{R}_2\text{-2,6}][\text{PF}_6]$ in the presence of base. Complex **3b** could also be prepared from $[\text{Cp}_2\text{TiCl}_2]$ and $[\text{NH}_2\text{NC}_5\text{H}_3\text{Me}_2\text{-2,6}][\text{PF}_6]$ in the presence of 1 equiv of BuLi. Cationic complexes $[\text{Cp}^*\text{Ti}(\text{OTf})(\text{NNC}_5\text{H}_3\text{Me}_2\text{-2,6})(\text{bpy})][\text{OTf}]$ (**4**) and $[\text{Cp}^*\text{Ti}(\text{NNC}_5\text{H}_3\text{Me}_2\text{-2,6})(\text{terpy})][\text{OTf}]_2$ (**5**) ($\text{bpy} = 2,2'$ -bipyridine) (**4**) and $[\text{Cp}^*\text{Ti}(\text{NNC}_5\text{H}_3\text{Me}_2\text{-2,6})(\text{terpy})][\text{OTf}]_2$ ($\text{terpy} = 2,2':6',2''$ -terpyridine) (**5**) were derived from **3c** through reaction with AgOTf in the presence of bpy and terpy, respectively. The structures of complexes **3a**, **3b**, **3c**, and **5** were determined by X-ray crystallography. The N–N bond of **3a–c** could be cleaved by reduction with sodium amalgam, liberating the corresponding pyridines in high yield, while the N–N bond in **4** and **5** could be reductively cleaved by cobaltocene in moderate yield. The N–N bond in **3a–c** could also be cleaved by cobaltocene in the presence of a proton analogue like Me_3SiCl .

Introduction

In the course of our ongoing investigation into reactivities of dinitrogen complexes of molybdenum and tungsten,¹ we have recently found that the tungsten dinitrogen complex *cis*- $[\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$ can be converted into (1-pyridinio)imido complexes such as $[\text{WCl}_2(\text{NNC}_5\text{H}_2\text{Me}_3\text{-2,4,6})(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{BF}_4]$.² Interestingly, the N–N bond of this complex was cleaved to give 2,4,6-collidine under relatively mild conditions. This reaction was the first example of the N–N bond cleavage in characterized hydrazidium type complexes ($\text{M} \equiv \text{N}-\text{NR}_3^+$). Although unsubstituted hydrazidium complexes are assumed to be involved in the N–N bond cleavage of coordinated dinitrogen at transition metal centers,^{1a,3} detailed studies on the reactivity have suffered from complication by intramolecular as well as intermolecular hydrogen migration between the nitrogen atoms.^{1a,4} In this context, (1-pyridinio)imido complexes have a locked structure which rules out the hydrogen migration between the nitrogen atoms and provides an interesting system for investigation of accelerating/limiting factors for the N–N bond cleavage. Intrigued by the high reactivity of the above-mentioned (1-pyridinio)imido complexes of tungsten, we embarked on establishing an effective synthetic route to (1-pyridinio)imido complexes of various metals. A general preparation method for imido complexes is the reaction of transition metal halides and amines or amides in the

presence of base.⁵ Thus, using easily preparable 1-aminopyridinium salts $[\text{NH}_2\text{NC}_5\text{H}_3\text{R}_2\text{-2,6}][\text{PF}_6]$ ($\text{R} = \text{H}, \text{Me}$) as the starting material, we have now synthesized several neutral and cationic (1-pyridinio)imidotitanium(IV) complexes. Here we describe their synthesis, structures, and reactivities toward the N–N bond cleavage.

Results and Discussion

Synthesis and Structures of Titanium (1-Pyridinio)imido Complexes. Treatment of a suspension containing equimolar amounts of $[\text{CpTiCl}_3]$ (**1a**; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and $[\text{NH}_2\text{NC}_5\text{H}_5][\text{PF}_6]$ (**2a**) in CH_2Cl_2 with 2 equiv of $\text{NEtPr}^{1/2}$ resulted in the formation of $[\text{CpTiCl}_2(\text{NNC}_5\text{H}_5)]$ (**3a**). The amine salts concurrently formed were removed by treatment with NaH in THF. After filtration of the sodium salts, the solvent and the amine were removed in vacuo, and recrystallization of the residual solid from $\text{CH}_2\text{Cl}_2/\text{hexanes}$ afforded yellow crystals of **3a** in high yield. Since we have very recently observed that the reactivity of rhodium pyridine–imine complexes derived from 1-aminopyridinium salts are profoundly influenced by alkyl substituents on the pyridine ring,⁶ synthesis of titanium complexes having the sterically demanding 2,6-dimethyl-substituted (1-pyridinio)imido ligand was also examined. Thus, complexes $[\text{CpTiCl}_2(\text{NNC}_5\text{H}_3\text{Me}_2\text{-2,6})]$ (**3b**) and $[\text{Cp}^*\text{TiCl}_2(\text{NNC}_5\text{H}_3\text{Me}_2\text{-2,6})]$ (**3c**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) were prepared analogously by the reaction of $[\text{NH}_2\text{NC}_5\text{H}_3\text{Me}_2\text{-2,6}][\text{PF}_6]$ (**2b**) with **1a** and $[\text{Cp}^*\text{TiCl}_3]$ (**1b**), respectively. Complexes **3a** and **3b** are highly moisture sensitive, whereas **3c** is less moisture sensitive.

The structures of **3a**, **3b**, and **3c** were determined by X-ray crystallography. Their ORTEP drawings are given

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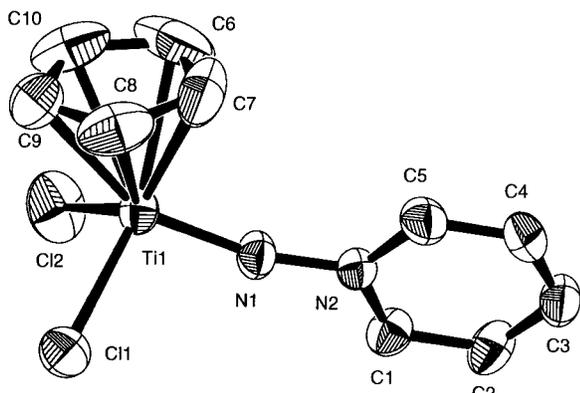


Figure 1. ORTEP drawing for $[\text{CpTiCl}_2(\text{NNC}_5\text{H}_5)]$ (**3a**). Hydrogen atoms are omitted for clarity.

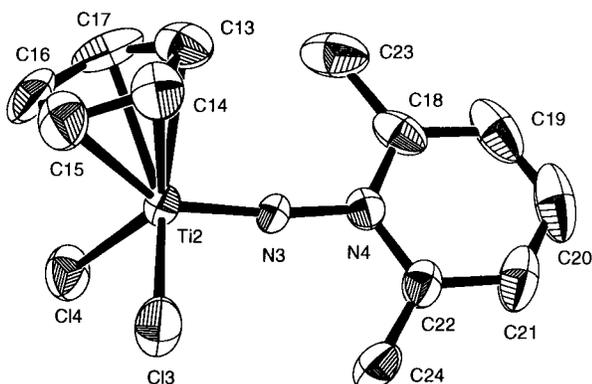
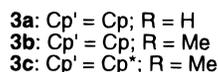
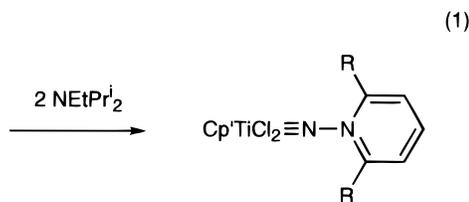
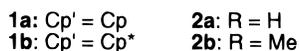
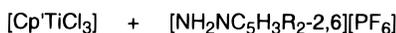


Figure 2. ORTEP drawing for $[\text{CpTiCl}_2(\text{NNC}_5\text{H}_3\text{Me}_2,2,6)]$ (**3b**). One of the two independent molecules in the unit cell is shown. Hydrogen atoms are omitted for clarity.



in Figures 1–3, and selected bond distances and angles are summarized in Tables 1–3. The unit cell of complex **3b** includes two independent molecules with similar metric features around the metal centers.

All complexes **3a–c** adopt a three-legged piano stool structure. The Ti–N–N bond angles range from 161.2(2)° to 178.3(4)°. We ascribe the bending to fitting into the unit cell during crystallization and regard the Ti–N–N entity as potentially linear. The Ti–N bond lengths are 1.734(2) Å (**3a**), 1.732(3) and 1.736(3) Å (**3b**), and 1.739(4) Å (**3c**) and are slightly longer than the Ti≡N triple-bond distances in $[\text{Cp}^*\text{TiCl}(\text{NBu}^t)(\text{NC}_5\text{H}_5)]$ (1.696(4) and 1.698(4) Å); two independent molecules in the asymmetric unit⁷ and in the tris(pyrazolyl)boratitanium complex $[\text{Tp}^{\text{Pri}}\text{TiCl}(\text{NBu}^t)(\text{NC}_5\text{H}_4\text{Bu}^t-4)]$

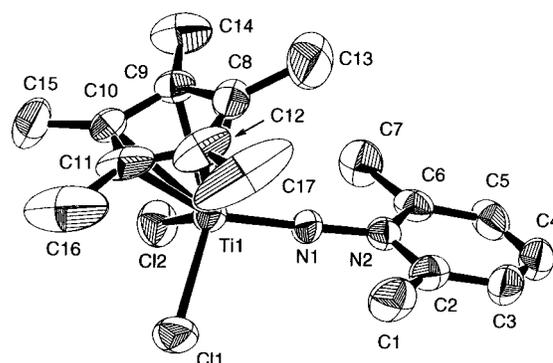


Figure 3. ORTEP drawing for $[\text{Cp}^*\text{TiCl}_2(\text{NNC}_5\text{H}_3\text{Me}_2,2,6)]$ (**3c**). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **3a**

Distances			
Ti(1)–Cl(1)	2.339(1)	Ti(1)–Cl(2)	2.3261(9)
Ti(1)–N(1)	1.734(2)	N(1)–N(2)	1.363(3)
Ti(1)–C(6)	2.322(4)	Ti(1)–C(7)	2.332(4)
Ti(1)–C(8)	2.360(3)	Ti(1)–C(9)	2.391(3)
Ti(1)–C(10)	2.370(4)	Ti(1)–Cp(cent)	2.049
Angles			
Cl(1)–Ti(1)–Cl(2)	101.59(4)	Cl(1)–Ti(1)–N(1)	102.17(8)
Cl(2)–Ti(1)–N(1)	102.64(7)	Ti(1)–N(1)–N(2)	165.1(2)

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3b**

Distances			
Ti(1)–Cl(1)	2.329(1)	Ti(1)–Cl(2)	2.332(1)
Ti(1)–N(1)	1.732(3)	N(1)–N(2)	1.364(3)
Ti(1)–C(1)	2.357(4)	Ti(1)–C(2)	2.330(5)
Ti(1)–C(3)	2.317(5)	Ti(1)–C(4)	2.381(4)
Ti(1)–C(5)	2.397(4)	Ti(1)–Cp(cent)	2.054
Ti(2)–Cl(3)	2.333(1)	Ti(2)–Cl(4)	2.322(1)
Ti(2)–N(3)	1.736(3)	N(3)–N(4)	1.361(3)
Ti(2)–C(13)	2.334(4)	Ti(2)–C(14)	2.346(4)
Ti(2)–C(15)	2.424(4)	Ti(2)–C(16)	2.419(4)
Ti(2)–C(17)	2.336(4)	Ti(2)–Cp(cent)	2.056
Angles			
Cl(1)–Ti(1)–Cl(2)	101.78(5)	Cl(1)–Ti(1)–N(1)	102.96(10)
Cl(2)–Ti(1)–N(1)	103.25(9)	Ti(1)–N(1)–N(2)	161.2(2)
Cl(3)–Ti(2)–Cl(4)	100.25(5)	Cl(3)–Ti(2)–N(3)	103.56(9)
Cl(4)–Ti(2)–N(3)	102.38(10)	Ti(2)–N(3)–N(4)	170.0(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3c**

Distances			
Ti(1)–Cl(1)	2.331(2)	Ti(1)–Cl(2)	2.334(2)
Ti(1)–N(1)	1.739(4)	N(1)–N(2)	1.367(5)
Ti(1)–C(8)	2.330(6)	Ti(1)–C(9)	2.354(5)
Ti(1)–C(10)	2.437(5)	Ti(1)–C(11)	2.425(6)
Ti(1)–C(12)	2.347(5)	Ti(1)–Cp*(cent)	2.063
Angles			
Cl(1)–Ti(1)–Cl(2)	100.87(7)	Cl(1)–Ti(1)–N(1)	101.9(1)
Cl(2)–Ti(1)–N(1)	102.2(1)	Ti(1)–N(1)–N(2)	178.3(4)

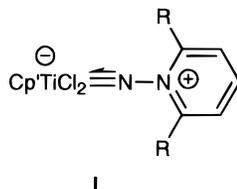
(1.708(6) Å; Tp^{Pri} = tris(3-isopropylpyrazolyl)hydroborate),⁸ but are definitely shorter than Ti=N double bonds as found in titanium amido complexes such as $[\text{TiCl}_2\{\eta^5-\eta^1-\text{C}_5\text{H}_4(\text{CH}_2)_3\text{NPr}^i\}]$ (1.8668(15) Å).⁹ The corresponding phosphinimato complex $[\text{CpTiCl}_2(\text{NPPH}_3)]$ has a longer Ti=N bond of 1.78(1) Å and has been

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identified as having a three-electron-donor nitrogen atom and multiple N=P bond character.¹⁰ In contrast, the N–N bond lengths in complexes **3a–c** are 1.363(3) Å, 1.364(3) and 1.361(3) Å, and 1.367(5) Å, respectively, and can be regarded as in the range of N–N single bonds. These values are similar to that found in the (1-pyridinio)imido complex $[\text{WCl}_2(\text{NNC}_5\text{H}_2\text{Me}_3\text{-2,4,6})\text{(CO)(PMe}_2\text{Ph)}_2][\text{OTf}]$ (1.366(10) Å; OTf = OSO_2CF_3),² and slightly shorter than those in the related hydrazidium complexes $[\text{WCl}(\text{NNH}_3)(\text{PMe}_3)_4]\text{Cl}_2$ (1.396(20) Å),¹¹ $[\text{Cp}^*\text{MoMe}_3(\text{NNMe}_3)][\text{OTf}]$ (1.426(5) Å),^{4b} and $[\text{Cp}^*\text{TaS}(\text{SBu}^t)(\text{NNMe}_2\text{Bu}^t)]$ (1.46(1) Å).¹² Complexes **3a–c** contain a titanium center coordinated by one Cp (or Cp*), two chlorine atoms, and one imido nitrogen atom, making the complexes monomeric. In contrast, monocyclopentadienyl titanium imido complexes with just one halogen atom have a dimeric structure $[(\text{Cp}^*\text{TiX})_2(\mu\text{-NR})_2]$ (X = F, Cl; R = alkyl, aryl) in the absence of added ligand.¹³ Complexes **3a–c** rather resemble imido complexes of the type $\text{Cp}'\text{MCl}_2(\text{N-R})$ (Cp' = Cp, Cp*; R = alkyl, aryl) having four-electron-donor imido ligands (taking the imido ligand as a neutral ligand for electron-counting) and group 5, 6, and 7 metal centers: Nb and Ta,¹⁴ Mo and W,¹⁵ and Re.¹⁶ The (1-pyridinio)imido ligand is formally a five-electron donor and therefore uniquely different from the imido ligand. Complexes **3a–c** are zwitterionic and formally have an anionic titanium center (structure I). Furthermore, the cyclic voltammograms of Ti(IV) complexes **3a–c** show an irreversible oxidation wave at ca. +1.3–1.4 V (usually absent in Ti(IV) complexes). The zwitterionic nature of these compounds may account for the low solubility of **3a–c** in aromatic hydrocarbon solvents.



Treatment of $[\text{NH}_2\text{NC}_5\text{H}_3\text{Me}_2\text{-2,6}][\text{PF}_6]$ (**3b**) with 1 equiv of BuLi in THF followed by addition of $[\text{Cp}_2\text{TiCl}_2]$ also resulted in the formation of **3b** in good yield. The formation of **3b** involves displacement of one of the Cp ligands by the (1-pyridinio)imido ligand. However, this procedure could not be applied to the preparation of **3a**.

To obtain information about the nature of the metal center which limits/accelerates the N–N bond cleavage,

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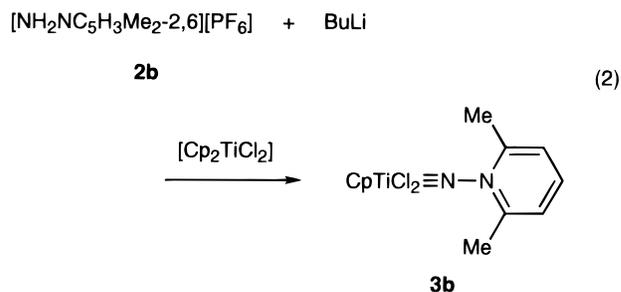
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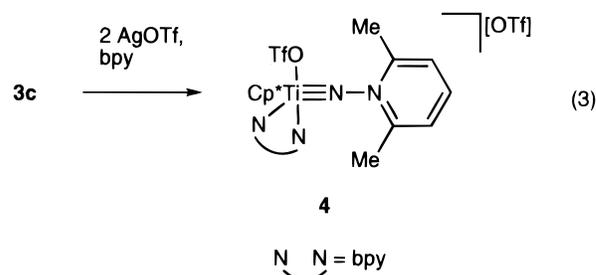
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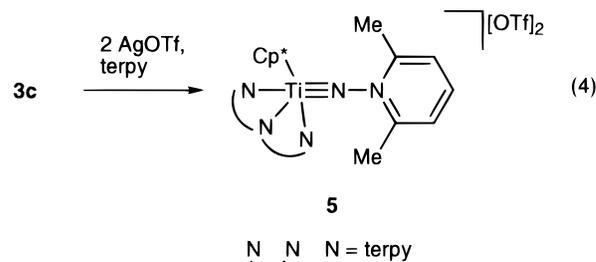
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we also prepared cationic titanium complexes having the (1-pyridinio)imido ligand, which may be more easily reducible. Treatment of **3c** with 2 equiv of AgOTf in the presence of 2,2'-bipyridine generated the monocationic complex $[\text{Cp}^*\text{Ti}(\text{OTf})(\text{NNC}_5\text{H}_3\text{Me}_2\text{-2,6})(\text{bpy})][\text{OTf}]$ (**4**; bpy = 2,2'-bipyridine) (eq 3). The structure of **4** is based on preliminary X-ray crystallography structure determination.¹⁷



The dicationic complex $[\text{Cp}^*\text{Ti}(\text{NNC}_5\text{H}_3\text{Me}_2\text{-2,6})(\text{terpy})][\text{OTf}]_2$ (**5**; terpy = 2,2':6':2''-terpyridine) was prepared analogously to complex **4** in the presence of excess 2,2':6':2''-terpyridine (eq 4). The structure of **5** was fully determined by X-ray crystallography. The ORTEP drawing and important bond distances and angles are given in Figure 4 and Table 4, respectively. The titanium atom takes a square pyramidal geometry with the Cp* ligand at the apex. The metrical features in the Ti–N–N moiety are essentially unchanged by the ligand exchange. On the other hand, the Ti–Cp*(cent) distance at 2.107 Å is slightly longer as compared with that in **3c** (2.063 Å). NMR spectra of **4** and **5** could not be obtained due to the low solubility of their crystals in THF-*d*₈ and CDCl₃ as well as their decomposition in CD₃CN.



(17) Due to significant disordering of both triflate anions as well as considerable decay (46.3%) of the crystal during the reflection data collection, we could not refine the structure satisfactorily. Anisotropic refinement of all non-hydrogen atoms with 2583 observations ($I > 3\sigma(I)$) led to R_w and GOF values of 0.053, 0.063, and 1.60, respectively (reflection/parameter ratio 5.10). Crystallographic data for **4**: $P1$, $a = 8.809(3)$ Å, $b = 12.399(2)$ Å, $c = 15.673(2)$ Å, $\alpha = 86.67(1)^\circ$, $\beta = 79.49(2)^\circ$, $\gamma = 82.67(2)^\circ$, $V = 1668.3(6)$ Å³, $Z = 2$, $\mu(\text{Mo K}\alpha) = 4.63$ cm⁻¹.

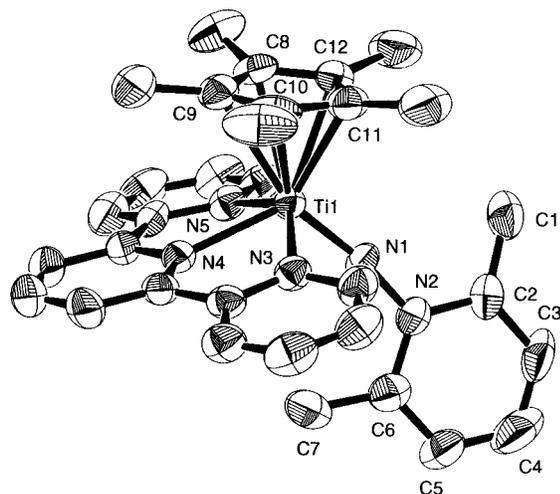
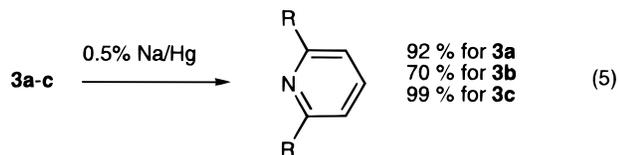


Figure 4. ORTEP drawing for the cationic part of $[\text{Cp}^*\text{Ti}(\text{NNC}_5\text{H}_3\text{Me}_2\text{-}2,6)(\text{terpy})][\text{OTf}]_2$ (**5**). Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **5**

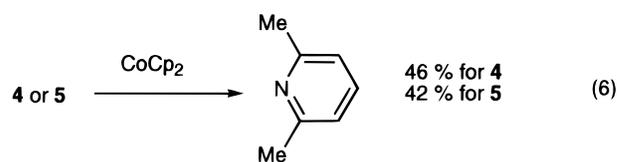
Distances			
Ti(1)–N(1)	1.755(4)	Ti(1)–N(3)	2.216(4)
Ti(1)–N(4)	2.171(4)	Ti(1)–N(5)	2.197(4)
N(1)–N(2)	1.369(5)	Ti(1)–C(8)	2.465(6)
Ti(1)–C(9)	2.481(6)	Ti(1)–C(10)	2.442(6)
Ti(1)–C(11)	2.350(6)	Ti(1)–C(12)	2.369(5)
Ti(1)–Cp*(cent)	2.107		
Angles			
N(1)–Ti(1)–N(3)	89.0(2)	N(1)–Ti(1)–N(4)	117.1(2)
N(1)–Ti(1)–N(5)	91.7(2)	Ti(1)–N(1)–N(2)	167.9(4)

Reductive Cleavage of the N–N Bond. The cyclic voltammograms of complexes **3a–c** showed an irreversible reduction wave between -1.3 and -1.4 V. These values are very high, and accordingly **3a–c** showed no reaction with the moderate electron donor cobaltocene. The N–N bond could, though, be cleaved by use of excess 0.5% sodium amalgam, liberating the corresponding pyridines in high yields (eq 5). The titanium species generated could not be characterized.

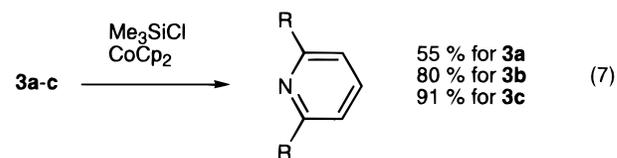


The stability of neutral complexes **3a–c** toward the reductive N–N bond cleavage in the presence of cobaltocene led us to investigate the reactivity of the cationic analogues **4** and **5** toward cobaltocene. In fact, complexes **4** and **5** could be reduced by cobaltocene to give lutidine in moderate yields (eq 6). These yields are lower than those of the sodium reduction of complexes **3a–c**, but the results indicate that the charge of the metal center has a large influence on receiving electrons before the N–N bond breaking. The reaction therefore presumably takes place via electron transfer to the LUMO, which is expected to be a titanium–nitrogen antibonding orbital, followed by the N–N bond cleavage, rather than direct reduction at the pyridine ring. The N–N bond cleavage seems independent of the electron count around the metal center (both **4** and **5** are 18-electron

complexes before reduction), although liberation of the OTf ligand from complex **4** or bending of the (1-pyridinio)imido ligand in either **4** or **5** may create a 16-electron intermediary species. Interestingly, reductive N–N bond cleavage was not observed for $[\text{Cp}^*\text{MoMe}_3(\text{NNMe}_3)][\text{OTf}]$ with zinc-amalgam or cobaltocene, and on the basis of this fact it was suggested that hydrazidium complexes ($\text{M}\equiv\text{N}-\text{NH}_3^+$) are not intermediates of the most facile N–N bond cleavage reaction path of hydrazine and hydrazido ligands.^{4b} On the other hand, the N–N bond in the cationic W(IV) complex $[\text{WCl}_2(\text{NNC}_5\text{H}_2\text{Me}_3\text{-}2,4,6)(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{OTf}]$ could be reductively cleaved by cobaltocene (vide supra).² Furthermore, it has been demonstrated by Holm and co-workers that N–N bond cleavage easily takes place in the reaction between TsNNC_5H_5 (Ts = tosyl) and the Mo(IV) complex $[\text{MoO}(\text{Et}_2\text{dtc})_2]$ (Et₂dtc = diethyldithiocarbamate).¹⁸



It should also be noted that addition of a sterically large proton analogue, Me_3SiCl , to the unreactive reaction mixtures of **3a–c** and cobaltocene also led to the N–N bond cleavage to form pyridines in moderate to high yields. We presume the in situ generation of a cationic pyridine–imine complex like $[\text{Cp}'\text{TiCl}_2\{\text{N}(\text{SiMe}_3)\text{NC}_5\text{H}_3\text{R}_2\text{-}2,6\}]\text{Cl}$ ($\text{Cp}' = \text{Cp}, \text{Cp}^*$; $\text{R} = \text{H}, \text{Me}$), which then shows a higher reactivity toward the reduction by cobaltocene and subsequent N–N bond cleavage.



Experimental Section

General Remarks. All reactions were carried out at room temperature unless otherwise noted under dinitrogen using standard Schlenk techniques. CH_2Cl_2 was dried over P_2O_5 , degassed, and stored under nitrogen. All other solvents were dried and distilled under nitrogen just prior to use. CDCl_3 was distilled over and stored over P_2O_5 and vacuum transferred into NMR tubes containing the samples. Complexes **1a** and **1b** were purchased from Strem Chemicals. 1-Aminopyridinium salts **2a** and **2b** were prepared according to the established procedures (using HPF_6 as the acid).¹⁹ ^1H NMR (270 MHz) spectra were recorded using a JEOL JNM-EX-270 spectrometer. IR spectra were recorded as KBr disks using a Shimadzu FTIR-8100M spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 II CHN analyzer.

Preparation of $[\text{CpTiCl}_2(\text{NNC}_5\text{H}_5)]$ (3a**).** To a suspension of **1a** (2.00 g, 9.12 mmol) and **2a** (2.20 g, 9.16 mmol) in CH_2Cl_2 (100 mL) was added NETPr_3 (3.2 mL, 18.4 mmol), upon which the solution immediately turned deep red. After 2 h, the solvent was removed in vacuo, and THF (40 mL) was added. Then NaH (0.484 g, 20.2 mmol) was added to the THF solution, and the mixture was kept at 50°C for 2 h, during

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Table 5. X-ray Crystallographic Data for **3a**, **3b**, **3c**, and **5**

	3a	3b	3c	5
formula	C ₁₀ H ₁₀ Cl ₂ N ₂ Ti	C ₁₂ H ₁₄ Cl ₂ N ₂ Ti	C ₁₇ H ₂₄ Cl ₂ N ₂ Ti	C ₃₄ H ₃₅ F ₆ N ₅ O ₆ S ₂ Ti
fw	277.01	305.06	375.20	835.69
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
cryst color	yellow	orange	orange-red	orange
cryst dimens, mm	0.8 × 0.6 × 0.3	0.5 × 0.5 × 0.5	0.5 × 0.4 × 0.2	0.8 × 0.4 × 0.05
<i>a</i> , Å	10.012(2)	9.984(2)	14.941(4)	8.892(4)
<i>b</i> , Å	8.392(2)	19.623(1)	8.392(4)	32.571(4)
<i>c</i> , Å	15.033(2)	14.5148(9)	16.634(4)	12.942(3)
β, deg	109.08(1)	107.103(7)	116.37(2)	97.44(2)
<i>V</i> , Å ³	1193.7(4)	2718.1(5)	1868(1)	3716(1)
<i>Z</i>	4	8	4	4
<i>D</i> _c , g cm ⁻³	1.541	1.491	1.334	1.493
<i>F</i> (000), e	560	1248	784	1720
μ(Mo Kα), cm ⁻¹	11.31	10.01	7.42	4.24
no. of unique reflns	2924	6435	4594	8539
transmission factors	0.7781–1.0000	0.9239–0.9997	0.9667–1.0000	0.7595–0.9952
no. of data used (<i>I</i> > 3σ(<i>I</i>))	1901	3431	1810	3477
no. of variables	137	308	199	488
<i>R</i> ^a	0.037	0.041	0.052	0.057
<i>R</i> _w ^a	0.025	0.023	0.030	0.034
GOF ^b	2.68	1.92	2.39	2.03
max residual, e Å ⁻³	0.39	0.34	0.39	0.38

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. ^b GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parms}})]^{1/2}$.

which time evolution of H₂ was observed. After filtration and removal of the solvent in vacuo, the residual solid was recrystallized from CH₂Cl₂/hexanes to give yellow crystals of **3a** in 88% yield. ¹H NMR (CDCl₃): δ 8.28 (d, *J* = 7.6 Hz, 2H, ortho), 7.74 (t, *J* = 7.6 Hz, 1H, para), 7.58 (t, *J* = 7.6 Hz, 2H, meta), 6.63 (s, 5H, Cp). IR (KBr): 1622 (m), 1593 (m), 1515 (s), 1480 (s) cm⁻¹. Anal. Calcd for C₁₀H₁₀Cl₂N₂Ti: C, 43.36; H, 3.64; N, 10.11. Found: C, 43.07; H, 3.66; N, 10.01.

Preparation of [Cp*TiCl₂(NNC₅H₃Me₂-2,6)] (3b). To a suspension of **2b** (0.215 g, 0.802 mmol) in THF (10 mL) at -78 °C was added BuLi (1.61 M, 0.50 mL, 0.81 mmol) and then [Cp₂TiCl₂] (0.200 g, 0.803 mmol). After stirring at this temperature for 15 min, the mixture was warmed to room temperature over 30 min and stirred for a further 2 h. The resulting suspension was filtered, concentrated, and layered with hexanes to give orange crystals of **3b**. Yield: 57%. Complex **3b** could also be prepared analogously to **3a** from **1a** and **2b** in 67% yield. ¹H NMR (CDCl₃): δ 7.91 (t, *J* = 7.6 Hz, 1H, para), 7.55 (d, *J* = 7.6 Hz, 2H, meta), 6.59 (s, 5H, Cp), 3.00 (s, 6H, Me). IR (KBr): 1628 (s), 1561 (m), 1491 (s) cm⁻¹. Anal. Calcd for C₁₂H₁₄Cl₂N₂Ti: C, 47.25; H, 4.63; N, 9.18. Found: C, 47.27; H, 4.79; N, 9.15.

Preparation of [Cp*TiCl₂(NNC₅H₃Me₂-2,6)] (3c). This compound was prepared analogously to **3a** from **1b** and **2b** as orange-red crystals in 92% yield. ¹H NMR (CDCl₃): δ 7.33 (t, *J* = 7.6 Hz, 1H, para), 7.22 (d, *J* = 7.6 Hz, 2H, meta), 2.73 (s, 6H, Me), 2.07 (s, 15H, Cp*). IR (KBr): 1626 (s), 1561 (s) cm⁻¹. Anal. Calcd for C₁₇H₂₄Cl₂N₂Ti: C, 54.42; H, 6.45; N, 7.47. Found: C, 54.21; H, 6.58; N, 7.43.

Preparation of [Cp*Ti(OTf)(NNC₅H₃Me₂-2,6)(bpy)][OTf] (4). THF (6 mL) was added to powders of **3c** (0.0806 g, 0.215 mmol), AgOTf (0.110 g, 0.428 mmol), and 2,2'-bipyridine (0.100 g, 0.640 mmol). After stirring for 4 h, the resulting suspension was filtered, concentrated, and layered with hexanes to give orange crystals of **4**. Yield: 83%. Anal. Calcd for C₂₉H₃₂F₆N₄O₆S₂Ti: C, 45.92; H, 4.25; N, 7.39. Found: C, 45.78; H, 4.35; N, 7.43.

Preparation of [Cp*Ti(NNC₅H₃Me₂-2,6)(terpy)][OTf]₂ (5). THF (10 mL) was added to powders of **3c** (0.0747 g, 0.199 mmol), AgOTf (0.1275 g, 0.496 mmol), and 2,2':6',2''-terpyridine (0.186 g, 0.797 mmol), and the mixture was stirred for 4 h. The resulting suspension was filtered, concentrated, and layered with hexanes to give orange needles of **5**. Yield: 82%. Anal. Calcd for C₃₄H₃₅F₆N₅O₆S₂Ti: C, 48.87; H, 4.22; N, 8.38. Found: C, 48.63; H, 4.04; N, 8.28.

Reductive N–N Bond Cleavage of 3a–c. Complex **3a** (0.0326 g, 0.118 mmol) was added to a 0.5% sodium amalgam suspension prepared from Na (0.020 g) and Hg (4.0 g) in THF (5 mL). The mixture quickly became dark violet, and after 3 h the volatiles were transferred to another Schlenk tube under vacuum. After addition of CH₃(CH₂)₉CH₃ as internal standard the yield of pyridine was determined by GC to be 92%. Reductive N–N bond cleavage of **3b** and **3c** was performed analogously, giving 2,6-lutidine in 70% and 99%, respectively.

Reductive N–N Bond Cleavage of 4 and 5. When cobaltocene (0.0623 g, 0.329 mmol) was added to a suspension of **4** (0.050 g, 0.066 mmol) in THF (5 mL), the color changed to dark brown. After 24 h the volatiles were transferred under vacuum to another Schlenk tube. The yield of 2,6-lutidine was determined to be 46% by GC analysis using CH₃(CH₂)₉CH₃ as internal standard. Reductive N–N bond cleavage of **5** performed analogously gave 2,6-lutidine in 42% yield.

Reductive N–N Bond Cleavage with Cobaltocene and Me₃SiCl. Me₃SiCl (0.0295 g, 0.272 mmol) in THF (2 mL) was added slowly over 2 h to a THF (5 mL) solution containing cobaltocene (0.077 g, 0.407 mmol) and **3a** (0.0362 g, 0.131 mmol). After 20 h the volatiles were transferred under vacuum to another Schlenk tube. The yield of pyridine was determined to be 55% by GC analysis using CH₃(CH₂)₉CH₃ as internal standard. Reductive N–N bond cleavage of **3b** and **3c** performed analogously gave 2,6-lutidine in 80% and 91% yield, respectively.

X-ray Diffraction Studies. Single crystals suitable for X-ray analysis were sealed in glass capillaries under nitrogen and mounted on a Rigaku AFC7R four-circle diffractometer equipped with a graphite-monochromatized Mo Kα source (λ = 0.7107 Å). Orientation matrixes and unit cell parameters were determined by least-squares refinement of 25 machine-centered reflections with 37.5° < 2θ < 39.8° for **3a**, 39.5° < 2θ < 40.0° for **3b**, 36.4° < 2θ < 40.0° for **3c**, and 36.7° < 2θ < 39.8° for **5**. The data collection was performed at room temperature using the ω–2θ scan technique for **3a**, **3b**, and **3c** and the ω scan technique for **5** at a rate of 32 deg min⁻¹ (5° < 2θ < 55°). Intensity data were corrected for Lorentz–polarization effects and for absorption (ψ scans). For crystals of **3a** and **5**, no significant decay was observed for respective three standard reflections monitored every 150 reflections during the data collection. For crystals of **3b** and **3c**, slight decay (**3b**, 1.73%; **3c**, 4.35%) was observed during the data collection, and a correction for decay was applied. Details of

crystal and data collection parameters are summarized in Table 5. Structure solution and refinements were carried out by using the teXsan program package.²⁰ The positions of the non-hydrogen atoms were determined by direct methods (SIR92)²¹ for **5** and Patterson methods (DIRDIF PATTY)²² for **3a**, **3b**, and **3c**, and subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. All hydrogen atoms were placed at calculated positions; these hydrogen atoms were included in the final stages of refinements with fixed parameters. The

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atomic scattering factors were taken from ref 23, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 24.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **3a**, **3b**, **3c**, and **5** (33 pages). Ordering information is given on any current masthead page.

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