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Synthesis and reactivity of titanium– and zirconium–dinitrogen complexes bearing anionic pyrrole-based PNP-type pincer ligands

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Dinitrogen-bridged dititanium and dizirconium complexes bearing anionic pyrrole-based PNP-type pincer ligands are prepared and characterized by X-ray analysis. Their catalytic activity is investigated toward reduction of nitrogen gas into ammonia and hydrazine under mild reaction conditions.

Ammonia is one of the most important compounds for human beings to survive because ammonia is mainly used as nitrogen fertilizer for agricultural crops. The Haber-Bosch process is well known for industrial ammonia production.¹ In the process, drastic reaction conditions such as high temperature and high pressure are required to produce ammonia effectively. In stark contrast to drastic reaction conditions, transition metal-catalysed nitrogen fixation has recently realized ammonia production under mild reaction conditions. In this system, the use of hydrogen gas produced from fossil fuels can be avoided for ammonia production.^{2,3}

In 2003, Schrock and co-worker found the first successful example of molybdenum-catalysed reduction of nitrogen gas into ammonia under ambient reaction conditions, where only less than 8 equiv of ammonia were produced based on the Mo atom.⁴ Since the Schrock's example, reduction of nitrogen gas has been reported by using some transition metal–dinitrogen complexes as catalysts for ammonia and hydrazine production from reactions of nitrogen gas with reducing reagents and proton sources under mild reaction conditions.⁵ Recently, based on our previous molybdenum-catalysed findings,⁶ we have found a novel reaction system, where some molybdenum–iodide complexes bearing a pyridine-based PNP-

pincer ligand have so-far the most effective catalytic activity toward ammonia production from nitrogen gas under ambient reaction conditions, up to 830 equiv of ammonia being produced based on the catalyst.⁷

As catalytic reaction systems other than molybdenum complexes, iron–^{8–10}, cobalt–^{11,12}, ruthenium–¹³, osmium–¹³, and vanadium–¹⁴ catalysed reduction of nitrogen gas into ammonia and hydrazine has recently been achieved at a low reaction temperature such as -78 °C to avoid the direct formation of hydrogen gas from reactions of K₂C₈ with conjugate acids as proton sources. These results indicate that not only the late-transition metal– but also early-transition metal–dinitrogen complexes worked as effective catalysts toward dinitrogen reduction under mild reaction conditions.

Quite recently, Liddle and co-workers have reported the titanium-catalysed reduction of nitrogen gas into ammonia mainly at -78 °C using dinitrogen-bridged dititanium complex bearing triamidomonoamine ligands as a catalyst.¹⁵ In this reaction system by Liddle and co-workers, only up to 9 equiv of ammonia were produced based on the titanium atom of the catalyst, however, this is the first successful example of the titanium-catalysed dinitrogen reduction into ammonia under mild reaction conditions.^{†,16}

As an extensive study of our work, we have now envisaged the preparation of titanium– and zirconium–dinitrogen complexes bearing an anionic pyrrole-based PNP-type pincer ligand. Based on our envision, we have now prepared dinitrogen-bridged dititanium and dizirconium complexes bearing anionic pyrrole-based PNP-type pincer ligands and characterized them by X-ray analysis. We have also investigated their catalytic activity toward dinitrogen reduction under mild reactions. Herein, we have reported preliminary results.

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According to the previous procedure,^{9,12,14} we prepared titanium–dichloride and zirconium–trichloride dimer complexes bearing an anionic pyrrole-based PNP-type pincer ligand. Treatment of $[\text{TiCl}_3(\text{thf})_3]$ (thf = tetrahydrofuran) with lithium 2,5-bis(di-*tert*-butylphosphinomethyl)pyrrole (PNP-Li), isolated from the corresponding pyrrole with *n*-BuLi in THF at room temperature, in toluene at -78°C for 1 h and at room temperature for 19 h gave the corresponding titanium–dichloride complex bearing a pyrrole-based PNP-type pincer ligand $[\text{TiCl}_2(\text{PNP})]$ (**1a**) in 91% yield (Scheme 1). Complex **1a** has a solution magnetic moment of $1.6 \pm 0.1 \mu_B$ at 296 K. The measured magnetic moment is consistent with the spin-only value for an $S = 1/2$ spin state ($1.73 \mu_B$). On the other hand, the reaction of $[\text{ZrCl}_4]$ with PNP-Li in toluene at room temperature for 8 days gave the corresponding chloride-bridged dizirconium–dichloride complex bearing pyrrole-based PNP-type pincer ligands $[\text{ZrCl}_2(\text{PNP})(\mu\text{-Cl})_2]$ (**2a**) in 69% yield (Scheme 1). Complex **2a** was characterized by ^1H and ^{31}P NMR in a THF- d_8 solution.

Molecular structures of **1a** and **2a** were confirmed by X-ray analysis. ORTEP drawings of **1a** and **2a** are shown in Figure 1(a) and 1(b), respectively. The crystal structure of **1a** displays a square pyramidal geometry around the titanium atom (the geometry index $\tau_5 = 0.14$, where $\tau_5 = 0.00$ for a perfect square pyramidal and $\tau_5 = 1.00$ for a trigonal bipyramidal geometry).¹⁷ Crystal structures of **2a** reveals that **2a** adopts a binuclear structure, where the two Zr atoms are bridged by two chloride atoms, respectively. The coordination sphere of seven-coordinate Zr(IV) center is described as a distorted pentagonal bipyramidal geometry.

At first, we tried to prepare the corresponding dinitrogen complexes from reactions of **1a** and **2a** with reducing reagents such as Na and KC_8 in various solvents at room temperature

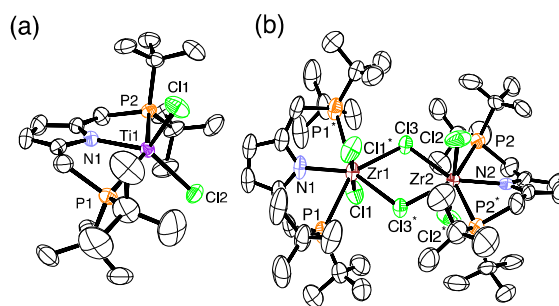


Fig. 1 ORTEP drawings of **1a** (a) and **2a** (b). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.

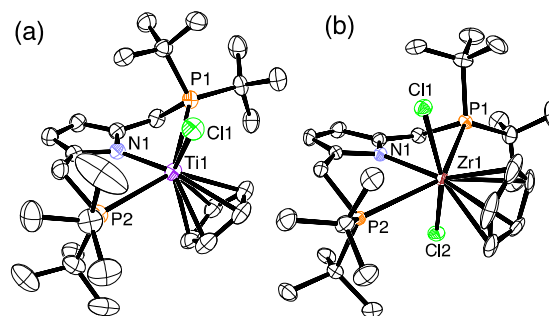
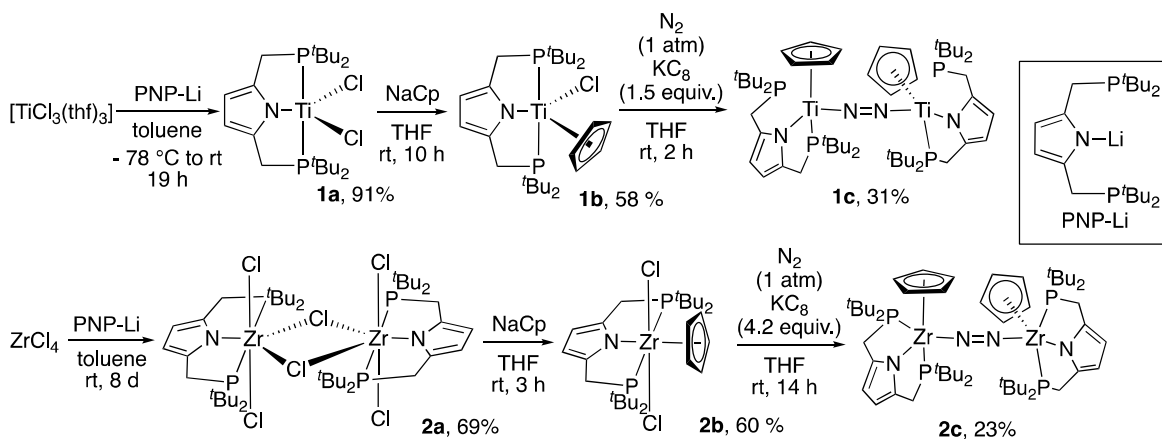


Fig. 2 ORTEP drawings of **1b** (a) and **2b** (b). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.



Scheme 1 Preparation of dinitrogen–bridged dititanium and dizirconium complexes bearing pyrrole-based anionic PNP-type pincer ligands.

under 1 atm of N_2 , however, only unidentified compounds were obtained even after many trials, in both cases. Next, we designed new titanium and zirconium complexes by the introduction of one bulky ligand such as Cp ($\eta^5\text{-C}_5\text{H}_5$) group to the titanium and zirconium centres because the presence of a bulky ligand on the titanium and zirconium atoms may change

the configuration around the titanium and zirconium centres to lead the formation of the corresponding titanium– and zirconium–dinitrogen complexes. In fact, Fryzuk and co-workers previously found that exchange of chloride by Cp ligand stabilizes the end-on coordination in the dinitrogen-bridged dizirconium complexes.¹⁸

Reactions of **1a** and **2a** with 1 equiv of sodium cyclopentadienide (CpNa) in THF at room temperature gave the corresponding mononuclear complexes $[\text{MCl}_n(\text{PNP})\text{Cp}]$ (**1b** $\text{M} = \text{Ti}$ and $n = 1$; **2b** and $\text{M} = \text{Zr}$ and $n = 2$) in 58% and 60% yields, respectively (Scheme 1). Complex **1b** has a solution magnetic moment of $1.6 \pm 0.1 \mu_B$ at 296 K. The measured magnetic moment is consistent with the spin-only value for an $S = 1/2$ spin state ($1.73 \mu_B$). No characteristic peaks were observed in ^1H NMR of **1b**, however, complex **2b** was characterized by ^1H and ^{31}P NMR in a benzene- d_6 solution. Molecular structures of **1b** and **2b** were confirmed by X-ray analysis. ORTEP drawings of **1b** and **2b** are shown in Figures 2(a) and 2(b), respectively. Crystal structures of **1b** and **2b** have four-legged piano-stool and distorted octahedral geometries around the titanium and zirconium atoms, respectively.

Reduction of **1b** and **2b** with 1.5 and 4.2 equiv of KC_8 in THF at room temperature under 1 atm of N_2 for 2 h and 14 h gave dinitrogen-bridged dititanium-complex $[\text{Ti}(\text{PNP})\text{Cp}]_2(\mu\text{-N}_2)$ (**1c**) and dinitrogen-bridged dizirconium-complex $[\text{Zr}(\text{PNP})\text{Cp}]_2(\mu\text{-N}_2)$ (**2c**) in 31% and 23% yields, respectively (Scheme 1). No characteristic peaks were observed in ^1H NMR of complex **1c**, however, complex **2c** was characterized by ^1H and ^{31}P NMR in a benzene- d_6 solution. Unfortunately, no Raman band attributable to the bridging dinitrogen ligand or no IR band attributable to the terminal dinitrogen ligand was observed for both complexes. Detailed molecular structures of **1c** and **2c** were determined by X-ray analysis and the formation of dinuclear complexes bridged by a dinitrogen ligand in an end-on fashion was confirmed. ORTEP drawings of **1c** and **2c** are shown in Figures 3(a) and 3(b), respectively. Crystal structures of **1c** and **2c** have three- and four-legged piano-stool geometries around each titanium and zirconium atoms, respectively. The coordination mode of the PNP-type pincer ligand to the titanium atom in **1c** is quite different from that in **2c**. The distances between one of the phosphorus and the titanium in **1c** are too long (3.1507(8) Å and 3.2206(8) Å) to be a dative bond.

The bridging N–N bond distances in **1c** and **2c** are 1.247(3) Å and 1.287(5) Å, respectively. The bond distances of the bridging dinitrogen ligand are close to a typical double N–N bond length (1.22 Å) rather than those of triple bond length of

free nitrogen gas (1.10 Å) and a typical single bond N–N bond length (1.46 Å). Thus, bond lengths of the bridging dinitrogen ligand in **1c** and **2c** signal two-electron reduction with a typical N=N bond coordinated to the titanium and zirconium atoms. In fact, Fryzuk and co-workers previously reported a similar dinitrogen-bridged zirconium complex bearing anionic PNP-type pincer and Cp ligands, where the bridging N–N bond distance is 1.301(3) Å.¹⁹

We carried out DFT calculations at the B3LYP-D3 level of theory for the discussion on the structures of **1c** and **2c** in the solvent. The closed-shell singlet state is the energetically most stable for both **1c** and **2c**. As shown in Figure S7 in the SI, the optimized structures in THF reasonably reproduced the crystal structures of **1c** and **2c**. For example, one of two phosphorous atoms in each PNP ligand was optimized to be separated from the corresponding titanium atom ($\text{Ti} \cdots \text{P} = 3.713$ Å for both Ti units) in **1c**, while all phosphorous atoms form dative bonds with each zirconium atom ($\text{Zr} - \text{P} = 2.86\text{--}2.99$ Å) in **2c**. The $\text{Ti} \cdots \text{P}$ distances calculated for the separated phosphorous arms are much longer than the distances in the crystal structure, probably due to the optimization of a single molecule in the solvent. These results indicate that the bulky Cp ligand inhibits the coordination of one of two phosphorous arms to a Ti center having smaller atomic radius than a Zr center.

The bridging N–N bond distances in **1c** and **2c** are 1.261 Å and 1.281 Å, both of which are very close to the experimental values. The Mayer bond orders of the N–N bonds are 1.40 for **1c** and 1.21 for **2c**. The long N–N distances as well as the significantly small N–N bond orders compared with free N_2 suggest that the bridging dinitrogen ligand in **1c** and **2c** should be reduced at least by two electrons.

Next, we investigated the catalytic nitrogen fixation in a modified experimental procedure (See the Supporting Information for details) investigated by our group,^{9,12,14} originally reported by Peters and co-workers.⁸ The reaction of atmospheric pressure of nitrogen gas with 40 equiv of KC_8 as a reductant and 38 equiv of $[\text{H}(\text{OEt}_2)_2][\text{BAR}^F_4]$ as a proton source in the presence of a catalytic amount of **1c** in Et_2O at -78°C for 1 h gave 1.0 equiv of ammonia and 0 equiv of hydrazine based on the titanium atom of the catalyst together with 5.3 equiv of hydrogen gas (Table 1, Entry 1). For comparison, **1b** was found to work as a less effective catalyst than **1c**, where only 0.13 equiv of ammonia were produced together with 2.9 equiv of hydrogen gas (Table 1, Entry 2). The use of **2c** as a catalyst, in place of **1c**, gave 1.3 equiv of ammonia and 0.31 equiv of hydrazine based on the zirconium atom of the catalyst together with 7.6 equiv of hydrogen gas (Table 1, Entry 3). When larger amounts of KC_8 as a reductant (80 equiv) and

Table 1 Titanium- and zirconium-catalyzed reduction of dinitrogen to ammonia and hydrazine^a

		$\text{N}_2 + \text{KC}_8 + [\text{H}(\text{OEt}_2)_2][\text{BAR}^F_4]$		Catalyst		$\text{Et}_2\text{O}, -78^\circ\text{C}$		$\text{NH}_3 + \text{N}_2\text{H}_4$	
		1 atm				1 h			
Entry	Catalyst	KC_8 (equiv) ^b	$[\text{H}(\text{OEt}_2)_2][\text{BAR}^F_4]$ (equiv) ^b	NH_3 (equiv) ^b	N_2H_4 (equiv) ^b	Fixed N atom (equiv) ^b	H_2 (equiv) ^b		
1	1c	40	38	1.0	0	1.0	5.3		
2	1b	40	38	0.13	0	0.1	2.9		
3	2c	40	38	1.3	0.31	1.9	7.6		
4	2c	80	76	1.3	0	1.3	17		
5 ^c	2c	36	48	0.52	0.45	1.4	0.81		
6	2a	40	38	0.31					

^aTo a mixture of the catalysts, KC_8 , and $[\text{H}(\text{OEt}_2)_2][\text{BAR}^F_4]$ was added Et_2O at -78°C , and then the resultant mixture was stirred at -78°C for 1 h. ^bEquivalents based on the metal atom. ^c CoCp^*_2 and $[\text{Ph}_2\text{NH}_2]\text{OTf}$ were used as reductant and proton source, respectively.

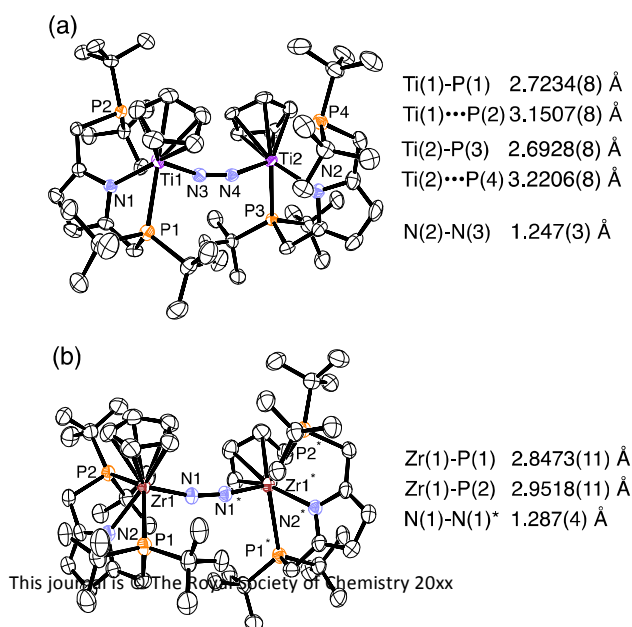


Fig. 3 ORTEP drawings of **1c** (a) and **2c** (b). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.

[H(OEt)₂][BAR^F₄] as a proton source (76 equiv) were used under the same reaction conditions, 1.3 equiv of ammonia were produced based on the zirconium atom and no hydrazine was produced in the reaction using **2c** as a catalyst (Table 1, Entry 4). On the other hand, a mixture of ammonia and hydrazine (0.52 equiv and 0.45 equiv based on the zirconium atom, respectively) was obtained in the reaction using **2c** as a catalyst when 36 equiv of CoCp*₂ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) as a reductant and 48 equiv of [Ph₂NH₂][OTf] (OTf = OSO₂CF₃) as a proton source (Table 1, Entry 5). For comparison, **2a** was found to work as a less effective catalyst than **2c**, where only 0.31 equiv of ammonia were produced together with 5.9 equiv of hydrogen gas (Table 1, Entry 6). The use of the dinitrogen-bridged dizirconium complex **2c** produced slightly larger amounts of ammonia and hydrazine than the dinitrogen-bridged dititanium complex **1c**. However, these results indicate that both dinitrogen-bridged dititanium and dizirconium complexes bearing anionic pyrrole-based PNP-type pincer and Cp ligands did not work as catalysts toward dinitrogen reduction under mild reaction conditions although stoichiometric amounts of ammonia and hydrazine were produced based on the complexes in both cases. At present, we consider that mononuclear titanium- and zirconium-dinitrogen complexes, which are generated in situ from the corresponding dinitrogen-bridged dinuclear complexes, work as active species toward the stoichiometric transformation. A similar catalytic transformation has quite recently been observed in the dinitrogen-bridged divanadium complexes by our research group.¹⁴

In summary, we have newly designed and prepared some titanium and zirconium complexes bearing a pyrrole-based PNP-type pincer ligand. Dinitrogen-bridged dititanium and dizirconium complexes bearing both pincer and Cp ligands have been prepared and characterized by X-ray analysis. The nature of the bridging dinitrogen ligand has been characterized by DFT calculations. Unfortunately, both dinitrogen-bridged dititanium and dizirconium complexes produced only stoichiometric amounts of ammonia and hydrazine under mild reaction conditions, however, we believe the present result described in this paper provides useful information to develop more effective titanium- and zirconium-dinitrogen complexes toward catalytic nitrogen fixation in near future. Further study is currently in progress.

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Notes and references

‡ Previously Vol'pin group and Shilov group tried to develop catalytic reduction of molecular dinitrogen using titanium complexes under ambient reaction conditions; however, only up to a stoichiometric amount of ammonia was produced based on the titanium atom of the catalyst.¹⁶

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