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Preparation and reactivity of molybdenum–dinitrogen complexes bearing an arsenic-containing ANA-type pincer ligand†

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Novel mono- and dimolybdenum–dinitrogen complexes bearing an arsenic-containing ANA-type pincer ligand are prepared and characterized by X-ray analyses. These complexes afford a stoichiometric amount of ammonia by treatment with sulfuric acid at room temperature.

The preparation and reactivity of transition metal–dinitrogen complexes have been intensively explored in order to develop a new nitrogen fixation system under ambient conditions.[1] The choice and design of the ligands to compromise the coordination sphere are shown to be some of the most important points for the efficient coordination and activation of molecular dinitrogen. In fact, we have recently succeeded in constructing another catalytic system[2] to convert molecular dinitrogen directly into ammonia using a dinitrogen-bridged dimolybdenum complex *trans,trans*-[{Mo(N$_2$)$_2$(^{t}BuPNP)}$_2$(μ-N$_2$)] (**1a**), where up to 23 equiv. of ammonia have been produced based on the catalyst (12 equiv. of ammonia based on the molybdenum atom).[3]

As an extension of our study, we have now focused on the use of an arsenic-containing ANA-type pincer ligand (Chart 1), where phosphines in the PNP-type pincer ligand are substituted for arsines.[4] Arsines are known to have similar coordination modes to phosphines, but are also recognized to be more reluctant to oxidation, sterically bulkier, and poorer σ-donors and π-acceptors compared to phosphines. As a result, the use of arsines in the pincer ligand leads to contrasting steric and electronic effects on coordination spheres different from that of phosphines.[5] There have been some examples of transition metal–dinitrogen complexes with arsines as auxiliary ligands, however, their reactivities are not well investigated except for [Mo(N$_2$)(triphos)(diars)] (triphos = PhP(CH$_2$CH$_2$PPh$_2$)$_2$, diars = 1,2-bis(dimethylarsino)benzene) which contains both triphosphine and diarsine ligands.[6] Herein, we describe the preparation of molybdenum–dinitrogen complexes bearing an arsenic-containing ANA-type pincer ligand ^{t}BuANA (**2b**, 2,6-bis[(di-*tert*-butylarsino)methyl]pyridine) and their reactivity

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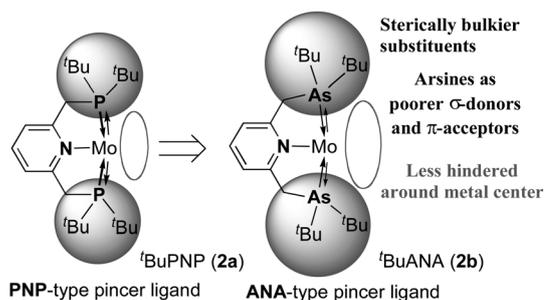
Chart 1 ANA-type pincer ligand: introduction of arsine moieties into the pincer ligand.

toward protonolysis to produce ammonia from the coordinated molecular dinitrogen.

The arsenic-containing tridentate pincer ligand ^{t}BuANA (**2b**) can be newly prepared in a similar way to the preparation of ^{t}BuPNP (**2a**).[7] Treatment of 2,6-lutidine with 2.5 equiv. of ^{n}BuLi in diethyl ether at reflux for 15 h gave a solution of dilithiated 2,6-lutidine, where 2.5 equiv. of ^{t}Bu$_2$AsCl in diethyl ether were slowly added at −78 °C. The reaction mixture was then gradually warmed up to room temperature to afford **2b** in 91% yield (Scheme 1). To the best of our knowledge, **2b** has been the first ANA-type pincer ligand reported so far.[8]

Next, we examined the preparation of molybdenum–dinitrogen complexes ligated by the ANA-type pincer ligand. Chelation of **2b** onto the molybdenum atom was successful when **2b** was treated with [MoCl$_3$(thf)$_3$] in THF at 55 °C for 20 h to afford the paramagnetic molybdenum(III) ANA-type pincer complex [MoCl$_3$(^{t}BuANA)] (**3b**) in 76% yield (Scheme 1). The molecular structure of **3b** was unambiguously determined by the X-ray analysis (Scheme 1 and Fig. S1, ESI†), which demonstrated that **3b** has a distorted octahedral geometry around the molybdenum center, as has been observed for the analogous PNP-type pincer complex [MoCl$_3$(^{t}BuPNP)] (**3a**).[3] In addition, **3b** appears to be slightly bulkier than **3a**, with the interatomic distances between molybdenum and arsenic atoms (2.65 Å, mean) and between arsenic and carbon atoms (2.00 Å, mean) in **3b** slightly longer than those between molybdenum and phosphorus atoms (2.61 Å, mean) and between phosphorus and carbon atoms
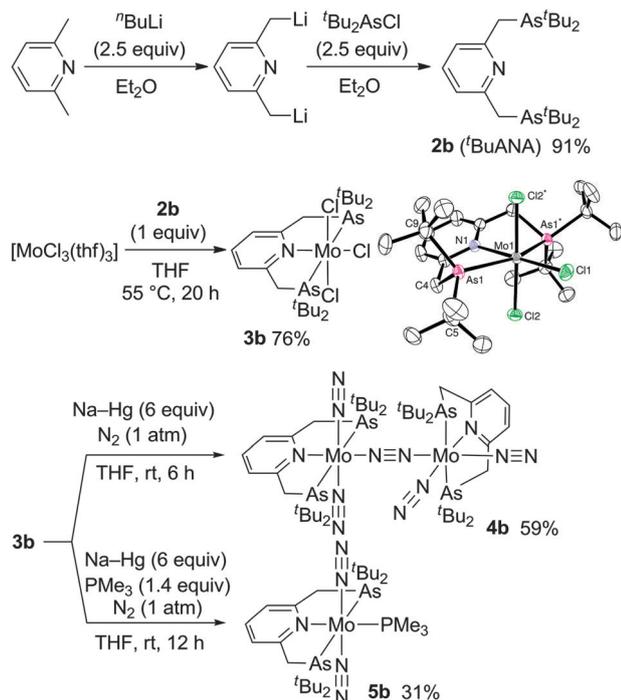
Scheme 1 Preparation of molybdenum–dinitrogen complexes bearing ANA-type pincer ligands.

Fig. 1 ORTEP drawing of **4b** (upper) and **5b** (lower). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

(1.88 Å, mean) in **3a**,[3] due to the difference in covalent radii of arsenic and phosphorus atoms.[9] On the other hand, a cyclic voltammetric study of **3b** revealed the oxidation potential of the couples Mo(III)/Mo(IV) to be +0.15 V vs. Fc/Fc⁺ comparable to the value for **3a** (+0.14 V vs. Fc/Fc⁺), suggesting that the change in the electronic effect on the molybdenum center by the substitution of arsenic for phosphorus is rather small compared to the steric effect.

The reduction of **3b** with an excess amount of Na–Hg (6 equiv.) in THF at room temperature for 6 h under an atmospheric pressure of dinitrogen gave the dinitrogen-bridged dimolybdenum complex trans,cis-[{Mo(N₂)₂(ᵗBuPNP)}₂(μ-N₂)] (**4b**) in 59% yield (Scheme 1). A strong Raman band attributable to the bridging N≡N stretch is observed at 1904 cm⁻¹ for **4b**, which is not observed in the IR spectrum and is comparable to the value (1890 cm⁻¹) observed for **1a**.[5] On the other hand, the IR spectrum of **4b** exhibits two strong broadened absorptions at 1955 and 1870 cm⁻¹ attributable to N≡N stretching frequencies in contrast to the single absorption at 1936 cm⁻¹ observed for **1a**.[5] The ¹H NMR resonances due to protons in the ᵗBuANA ligand also appear to be unsymmetrical, with the methylene proton signals at δ 3.48, 3.43, and 3.39–3.28 in an intensity ratio of 2:2:4 and the tert-butyl proton signals at δ 1.32–1.23 and 1.17 in an intensity ratio of 54:18. These spectroscopic features indicate that the molecular structure of **4b** is different from that of **1a**.

The detailed structure of **4b** has been determined by an X-ray analysis of **4b**·C₆H₁₄, which clearly demonstrates that **4b** has an unsymmetrical structure where a trans-[Mo(N₂)₂(ᵗBuANA)] unit and a cis-[Mo(N₂)₂(ᵗBuANA)] unit are bridged by one dinitrogen ligand in an end-on fashion (Fig. 1). The difference in the coordination geometry around each molybdenum center is in good accord with the spectroscopic data, suggesting that the dimolybdenum structure bridged by a dinitrogen ligand with both cis- and trans-bis(dinitrogen)
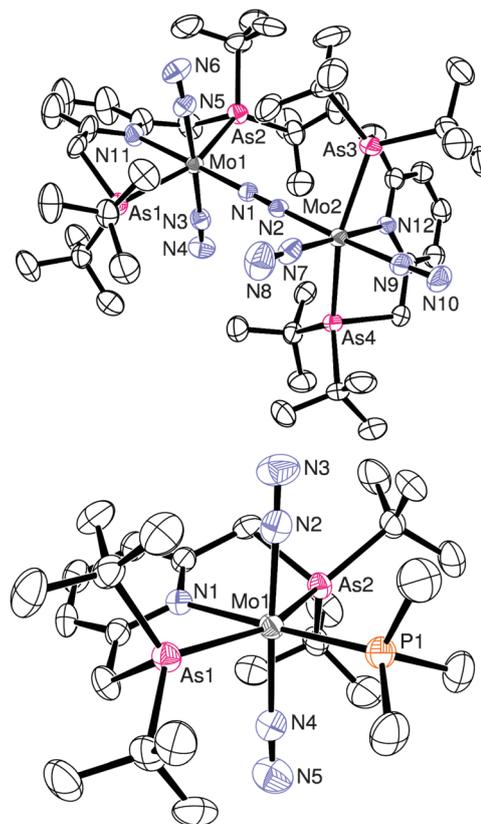
molybdenum units is maintained even in solution. It must be noted that we have recently isolated similar dinitrogen-bridged dimolybdenum complexes with unsymmetric PNP-type pincer ligands 2-R₂PCH₂-6-ᵗBu₂PCH₂-pyridine (ᵗBuRPNP; R = Ad, Ph, ᵢPr, Cy), where trans,trans-[{Mo(N₂)₂(ᵗBuRPNP)}₂(μ-N₂)] (**1c**: R = Ad, **1d**: R = Ph) and trans,cis-[{Mo(N₂)₂(ᵗBuRPNP)}₂(μ-N₂)] (**4e**: R = ᵢPr, **4f**: R = Cy) were obtained selectively depending on the varieties of PNP-type pincer ligands (Chart 2).[10] The reason why trans,cis isomer **4b** instead of the trans,trans isomer was obtained may be due to the less hindered environment around molybdenum atoms compared to the complex **1a** (Chart 1).

When the reduction of **3b** with an excess amount of Na–Hg (6 equiv.) in THF at room temperature for 12 h under an atmospheric pressure of dinitrogen was carried out in the presence of 1.4 equiv. of trimethylphosphine, the corresponding mononuclear molybdenum–dinitrogen complex bearing both the ANA-type pincer and phosphine ligands trans-[Mo(N₂)₂(PMe₃)(ᵗBuANA)] (**5b**) was obtained in 31% yield (Scheme 1). The IR spectrum exhibits a strong absorption assignable to the N≡N asymmetric stretching at 1915 cm⁻¹, which is almost the same as that in the corresponding PNP-type pincer complex trans-[Mo(N₂)₂(PMe₃)(ᵗBuPNP)] (**5a**) ($\nu_{N\equiv N}$ = 1915 cm⁻¹), which has been prepared recently by our group.[11] The molecular structure of **5b** was confirmed by X-ray crystallography, where the trimethylphosphine ligand occupies the position trans to the pyridine group of an ANA ligand as shown in Fig. 1. The N–N (1.07 Å, mean) bond distances in **5b** are slightly

trans-Mo(N₂)₂–(N₂)–*trans*-Mo(N₂)₂   *trans*-Mo(N₂)₂–(N₂)–*cis*-Mo(N₂)₂

Chart 2 Comparison of structures of dinitrogen-bridged dimolybdenum–dinitrogen complexes.

Scheme 2 Protonation of molybdenum–dinitrogen complexes.

shorter than those in **5a** (1.13 Å, mean), which may suggest that the dinitrogen ligands in **5b** may be less activated than **5a** owing to weaker σ-donation from arsines.

We next investigated the reactivity of these molybdenum–dinitrogen complexes bearing ANA-type pincer ligands toward protonolysis. When dimolybdenum complex **4b** was treated with an excess amount of sulfuric acid in THF at room temperature for 24 h, 0.6 equiv. of ammonia was obtained based on the molybdenum atom (Scheme 2), which is almost the same as those obtained from the protonolysis of **1a** (0.6 equiv. of ammonia and 0.06 equiv. of hydrazine).[11] On the other hand, the amount of ammonia obtained from the protonolysis of **5b** is rather small (0.3 equiv. of ammonia), compared to that obtained from the protonolysis of **5a** (0.9 equiv. of ammonia and 0.08 equiv. of hydrazine).[11] No formation of hydrazine was observed in the protonolysis of **4b** and **5b**.

The catalytic reduction of molecular dinitrogen to ammonia by using **4b** as a catalyst was investigated according to the previous procedure.[10] Unfortunately, we observed only 2 equiv. of ammonia based on the catalyst (1 equiv. of ammonia based on the Mo atom in **4b**) together with 16 equiv. of molecular dihydrogen based on the catalyst. This result indicates that only a stoichiometric amount of ammonia was formed, and most of the cobaltocene was consumed to form molecular dihydrogen from the proton source. This is in sharp contrast to the catalytic formation of ammonia using **1a** as a catalyst, where 12 equiv. of ammonia were produced based on the catalyst (6 equiv. of ammonia based on the Mo atom in **1a**).[3] We have not yet obtained the exact

reason why the dinitrogen-bridged dimolybdenum complex with ANA-type pincer ligands **4b** did not work as a catalyst toward the formation of ammonia under the same reaction conditions, but we previously confirmed that similar dinitrogen-bridged dimolybdenum complexes with PNP-type pincer ligands **4e** and **4f**, which have *trans,cis* structures, also did not work as catalysts.[10]

In summary, we have synthesized a series of molybdenum–dinitrogen complexes bearing an arsenic-containing ANA-type pincer ligand. Protonation of the dinitrogen-bridged dimolybdenum–dinitrogen complex with an excess amount of sulfuric acid in THF afforded ammonia in good yields. Further studies[12] on the preparation and reactivity of other transition metal complexes bearing ANA-type pincer ligands are currently underway.

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