

CHEMISTRY

Silylamido supported dinitrogen heterobimetallic complexes: syntheses and their catalytic ability

Dan-dan Zhai¹, Si-jun Xie¹, Yi Xia¹, Hua-yi Fang^{1,*} and Zhang-jie Shi^{1,2,*}**ABSTRACT**

Molybdenum dinitrogen complexes supported by monodentate arylsilylamido ligand, $[\text{Ar}(\text{Me}_3\text{Si})\text{N}]_3\text{MoN}_2\text{Mg}(\text{THF})_2[\text{N}(\text{SiMe}_3)\text{Ar}]$ (**5**) and $[\text{Ar}(\text{Me}_3\text{Si})\text{N}]_3\text{MoN}_2\text{SiMe}_3$ (**6**) ($\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$) were synthesized and structurally characterized, and proved to be effective catalysts for the disproportionation of cyclohexadienes and isomerization of terminal alkenes. The ^1H NMR spectrum suggested that the bridging nitrogen ligand remains intact during the catalytic reaction, indicating possible catalytic ability of the Mo-N=N motif.

Keywords: dinitrogen fixation, dinitrogen-metal complex, catalytic ability, disproportionation, isomerization

INTRODUCTION

Exploring the reactivity of N_2 units of transition metal-nitrogen complexes is of great significance, but challenging in nitrogen transformation chemistry [1,2]. Since the first Ru- N_2 complex was prepared in 1965 [3], numerous well-defined transition metal-dinitrogen complexes have been prepared with different bonding modes, showing the potential to activate the inert dinitrogen molecule through coordination chemistry and allowing direct transformation of N_2 units [4–12]. In many cases, terminal end-on M- N_2 complexes as the most prevalent bonding mode were proved effective to catalyze reductive reactions of N_2 to afford ammonia or silylamines [13–16]; moreover, because of the nucleophilicity of the dinitrogen moiety, activated dinitrogen ligands in M- N_2 ($\text{M} = \text{Mo}$ [17–28], W [17–19,21,24–26], Fe [29,30], Co [29]) complexes were transformed into N-containing organic compounds with carbon-based electrophiles. On the other hand, late-transition metal- N_2 complexes ($\text{M} = \text{Co}$ [31–36], Ru [37–42], Ir [43], Fe [44–48]) have also been reported as precatalysts for organometallic transformations, including cycloaddition and hydrofunctionalization of olefins [31–35,44–48], semihydrogenation of alkynes [36], transfer hydrogenation of ketones [38,39] and acceptorless dehydrogenation of alcohols [40–42].

In these systems, dinitrogen (N_2) as a weakly π -accepting ligand to stabilize highly reactive and low valence-electron species, was proved not to be involved in the catalytic processes. Actually, there are only a few examples of M- N_2 units as active sites in catalytic organic transformations. In 2004, Hidai reported that Ti-W heterobimetallic dinitrogen complexes were excellent precursors for copolymerization of ethylene and 1-hexene, in which the W- N_2 fragment acted as a unique spectator ligand to the catalytically active titanium center [49]. The intriguing results hint at potential reactivity of the coordinated N_2 units in organometallic catalysis. Herein, we synthesized and structurally characterized molybdenum-nitrogen complexes supported by monodentate arylsilylamido ligand ($\text{L} = [\text{N}(\text{SiMe}_3)\text{Ar}]$). Meanwhile, we observed catalytic reactivity of the Mo- N_2 unit as a key motif in disproportionation of cyclohexadienes and isomerization of terminal alkenes where the - N_2 ligands unusually remain intact. In this catalytic reaction, the Mo-N=N motif was considered as a possible catalytic site to advance the hydrogen transfer (Scheme 1).

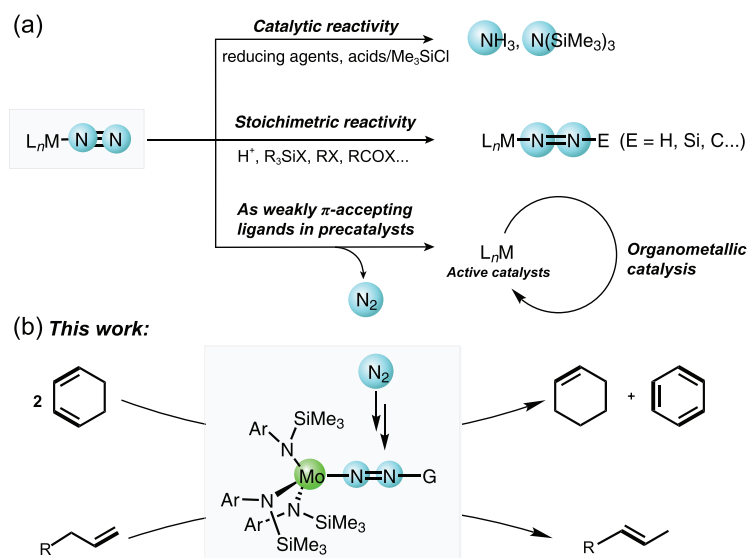
Inspired by gradually understanding the structure and mechanism of nitrogenase FeMo-cofactor in the reduction of atmospheric N_2 [50–54], the chemistry of Mo- N_2 complexes has been studied for decades, with Mo showing its uniqueness in terms

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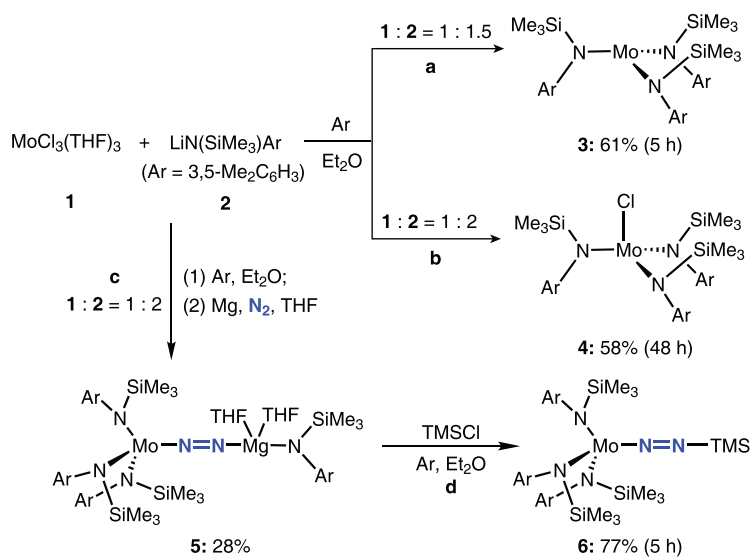
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Scheme 1. (a) Typical reactivity modes of $-N_2$ units in transition metal-dinitrogen complexes. (b) This work: catalytic reactivity of Mo- N_2 units in the disproportionation of cyclohexadienes and isomerization of terminal alkenes.



Scheme 2. Synthesis of molybdenum complexes **3–6**.

of variable oxidation states and readily forming complexes with N_2 [55–61]. To investigate the catalytic reactivity of molybdenum complexes with different structure characteristics in N_2 fixation, various supporting ligands were designed and developed, such as phosphine [17–22,24–26,62,63], triamidoamine [64–68] and pincer [69–72] ligands. Seminal studies by Cummins and co-workers demonstrated the ability of alkylarylamido ligands to stabilize low valent Mo(III) complexes and cleave N_2 [73,74]. As surrogates of this ligand set, monodentate *N*-aryl-*N*-silylamido ligands have not yet been investigated in a similar system, although $-N(SiMe_3)_2$ [75–78] or silylated multidentate amido ligands

$-(R_3SiNCH_2CH_2)_3N]^{3-}$ ($R_3Si = Me_3Si$ or tBuMe_2Si) [79–82], $-[N(SiMe_2CH_2P^iPr_2)_2]^-$ [83], $-[PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]^{2-}$ [84] and $-[PhP(CH_2SiMe_2NPh)_2]^{2-}$ [85] have been used to support transition-metal dinitrogen complexes since 1990. We envisaged that the ready introduction of the bulky silyl group would intrinsically tune the steric and electronic coordination sphere of amido donors, inducing new reactivity patterns of coordinated dinitrogen ligands in the Mo- N_2 complexes.

RESULTS AND DISCUSSION

The reaction of $MoCl_3(THF)_3$ (**1**) with 1.5 equivalents of lithium *N*-(trimethylsilyl)anilide (**2**) in Et_2O for 5 h afforded the corresponding tris-anilide complex of $Mo[N(SiMe_3)Ar]_3$ (**3**) in moderate yield (Scheme 2, a). X-ray diffraction on single crystals revealed that three-coordinate **3** was mononuclear with silylamino substituents arrangement above the trigonal plane of MoN_3 core (Fig. 1, a). Compared with complex $Mo[N(^tBu)Ar]_3$ [73,74], a long Mo-N1 distance (1.985 Å) and small Mo-N-Si bond angles (126°) might arise from the slightly different steric hindrance and electronic pattern of silylamido ligand around the Mo center. We then carried out reaction **3** with N_2 in the condition for conversion of $Mo[N(^tBu)Ar]_3$ to $N\equiv Mo[N(^tBu)Ar]_3$ (1 atm of N_2 , d_8 -toluene, $-35^\circ C$). With less electron negativity and the poor electron donating ability of silicon (Si), **3** was proved unreactive with N_2 molecules even at $-35^\circ C$ for 5 days. Lengthening the reaction time of $MoCl_3(THF)_3$ and lithium amide, the 1H NMR spectrum of the crude product mixture showed that Mo^{III} **3** had disappeared. The Mo^{IV} -Cl complex **4** was observed as the only product, along with a small amount of free ligand $HN(SiMe_3)Ar$ (Scheme 2, b). A similar result was reported by the Fürstner group to isolate complex $ClMo[N(^tBu)Ar]_3$ ($Ar = 3,5$ -dimethoxyphenyl) [86].

Reduction of the Mo^{IV} -Cl reaction mixture with magnesium powder under N_2 atmosphere (1 atm) produced the Mo- N_2 complex (Scheme 2, c). Diamagnetic signals in the proton NMR spectrum indicated a high oxidation state of the Mo center. X-ray study gave the unambiguous structure of $[Ar(Me_3Si)N]_3MoN_2Mg(THF)_2[N(SiMe_3)Ar]$ (**5**), in which Mo and Mg were both supported by silylamido ligand, and bridged by dinitrogen ligand to form the heterobimetallic dinitrogen complex (Fig. 2, a). The bond length of N–N is 1.194 Å, indicating the possible feature of

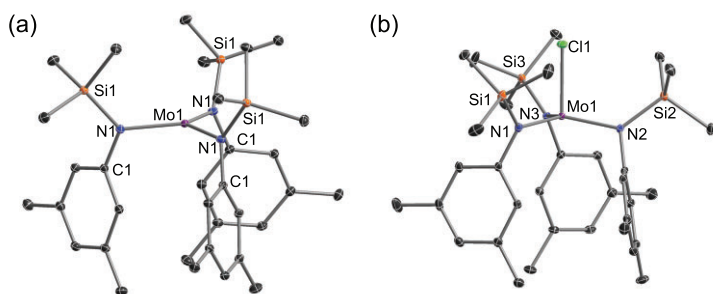


Figure 1. Molecular structures of **3–4** with thermal ellipsoids set at 10% probability. (a) $\text{Mo}[\text{N}(\text{SiMe}_3)\text{Ar}]_3$, **3**; (b) $\text{ClMo}[\text{N}(\text{SiMe}_3)\text{Ar}]_3$, **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): **3** Mo1–N1, 1.9854(16); N1–Si1, 1.7507(15); N1–Mo1–N1, 119.755(6); Mo1–N1–Si1, 126.306(112). **4** Mo1–N1, 1.9576(40); Mo1–N2, 1.9635(36); Mo1–N3, 1.9618(38); Mo1–Cl1, 2.3221(16); N1–Mo1–N2, 119.055(160); Cl1–Mo1–N1, 95.977(127).

N=N double bond, similar to those found in the diazenido species $\{[\text{N}_3\text{N}]\text{Mo}-\text{N}=\text{N}\}_2\text{Mg}(\text{THF})_2$ (1.195(13) Å and 1.164(13) Å) [80]. Additionally, **5** could be silylated by trimethylsilyl chloride (Me_3SiCl) at the β (terminal) nitrogen atom to afford $[\text{Ar}(\text{Me}_3\text{Si})\text{N}]_3\text{MoN}_2\text{SiMe}_3$ (**6**) (Scheme 2, d). An X-ray analysis of this complex showed a long N–N bond (1.214 Å) (Fig. 2, b). An analogous Mo–N=N–Mg complex supported by other silylamido ligand $-\text{N}(\text{SiMe}_2^t\text{Bu})\text{Ar}$ was prepared using similar procedures and characterized by X-ray chromatography (Fig. S6). Unfortunately, attempts to obtain analytically pure material failed.

According to those structural features, we envisioned that the hydrazine-like Mo–N=N–Mg backbone (**5**) with synergetic effects of both alkaline-earth metal and transition metal might be a good precursor to transfer two nitrogen atoms to organic

molecules through $[4 + 2]$ cycloaddition [87,88]. However, after treatment of **5** with a stoichiometric amount of 1,3-cyclohexadiene (**7**) in C_6D_6 at 100°C for 24 h, it was found that featured signals of the complex remained in the ^1H NMR spectrum of the reaction mixture, implying the remarkable stability of **5** under the reaction conditions. The substrate **7** was completely consumed and two new sets of ^1H NMR signals appeared, which were a perfect fit for the disproportionation products benzene (**8**) and cyclohexene (**9**) (Fig. S7). Such disproportionation has been studied with different transition-metal catalysts [89–96], but the catalytic ability of complexes with metal-dinitrogen moiety, particularly from N_2 gas, has not yet been observed. This study could stimulate new avenues to develop efficient catalysts directly from N_2 . On the other hand, identification of the active centers (Mo or Mg) of the bimetallic complex and their exact behaviors also attracted us to unveiling of the catalytic disproportionation.

To prove the catalytic reactivity of **5**, two experimental protocols were followed. Firstly, having confirmed the stoichiometric conversion of 1,3-cyclohexadiene, we added an additional amount of the substrate up to 60 equivalents in portions. Indeed, 90% of **7** converted to **8** and **9** after 18 days (Fig. S8, catalyst/substrate = 0.016/1), showing that the catalyst remained active. We also conducted the reaction by adding 60 equivalents of **7** into the C_6D_6 solution of **5** in one portion. After 180 h, the conversion of **7** was 99%, monitored by *in situ* NMR (Fig. S9). A small amount of cyclohexane (**10**) was detected during the process, suggesting potential hydrogen-transfer reduction of non-conjugate alkene with this catalyst. Isomerized

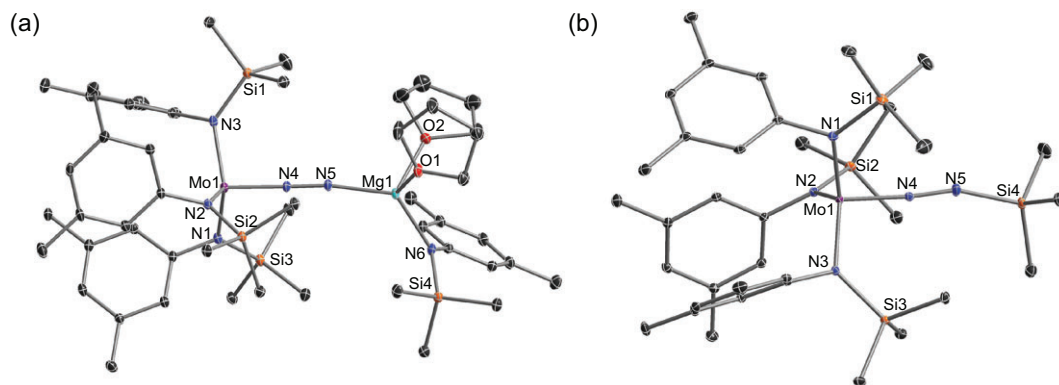
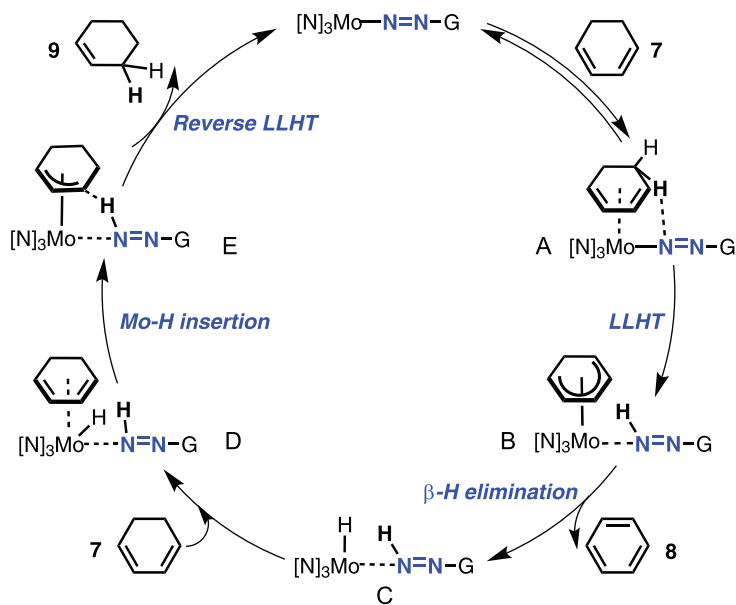


Figure 2. Molecular structures of **5–6** with thermal ellipsoids set at 10% probability. (a) $[\text{Ar}(\text{Me}_3\text{Si})\text{N}]_3\text{MoN}_2\text{Mg}(\text{THF})_2[\text{N}(\text{SiMe}_3)\text{Ar}]$, **5**; (b) $[\text{Ar}(\text{Me}_3\text{Si})\text{N}]_3\text{MoN}_2\text{SiMe}_3$, **6**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): **5** Mo1–N1, 1.998(4); Mo1–N2, 2.0066(34); Mo1–N3, 2.0150(39); Mo1–N4, 1.8110(34); N4–N5, 1.1942(48); Mg1–N5, 1.9621(35); Mg1–N6, 1.9924(31); Mo1–N4–N5, 178.107(287); N4–N5–Mg1, 171.026(282). **6** Mo1–N1, 1.9815(14); Mo1–N2, 1.9911(12); Mo1–N3, 1.9785(12); Mo1–N4, 1.7707(12); N4–N5, 1.2139(18); Si4–N5, 1.7092(16); Mo1–N4–N5, 174.306(118); N4–N5–Si4, 160.513(136).

Table 1. Catalytic disproportionation reaction of 1,3-cyclohexadiene^a.

Entry	Catalysts	Conv. (%) ^{a,b}
1	5 (24 h)	99%
2	6 (12 h)	94%
3	5 (24 h), Ar	98% ^c
4	5 (24 h), N ₂ (10 atm)	99% ^d
5	3 (24 h)	15%
6	4 (24 h)	13%
7	Mg[N(SiMe ₃)Ar] ₂ (36 h)	NR
8	Li[N(SiMe ₃)Ar] (19 h)	NR

^aConditions: 1,3-cyclohexadiene (0.30 mmol), catalyst (10 mol%), 100 °C, C₆D₆ (0.5 mL), N₂ atmosphere (1 atm). ^bDetermined by ¹H NMR spectroscopy. ^cIn an Ar atmosphere. ^dThe reaction was carried out in an autoclave pressurized with 10 atm of N₂.

**Scheme 3.** Proposed mechanism for the disproportionation of 1,3-cyclohexadiene.

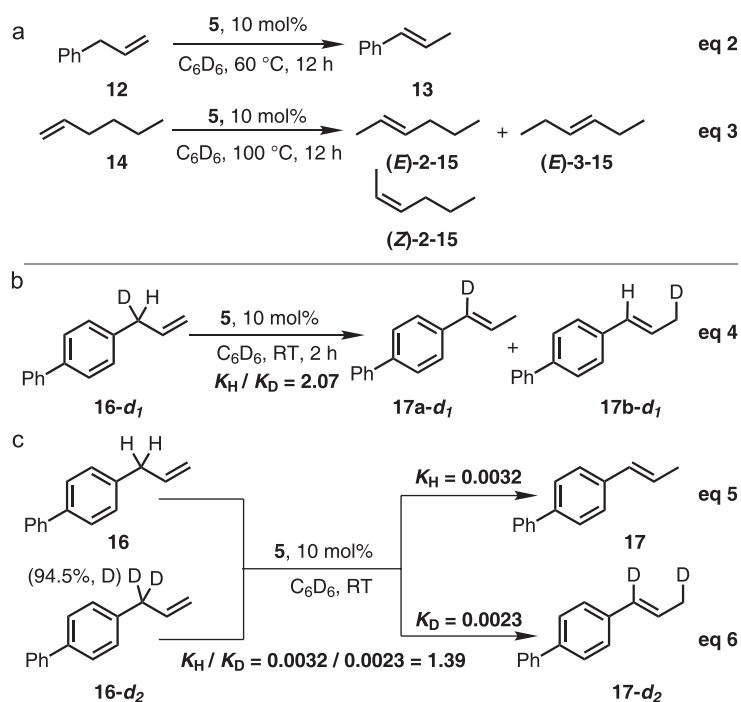
1,4-cyclohexadiene (**11**) was also observed, which could also further transform into **8** and **9** by catalytic disproportionation (Fig. S13). The reaction pathway was different from a previously reported case in which a cationic molybdenum nitride species transferred a hydrogen atom from **11** to afford molybdenum imide complex and **8** in a stoichiometric manner [97].

Attempts were made to gain insight into the catalytic reaction (Table 1). Complex **5** exhibited comparable activity towards the disproportionation under 100 °C for 24 h on a 0.30 mmol scale (en-

try 1), while **6** displayed high catalytic reactivity with 94% conversion within 12 h (entry 2). It was noteworthy that those catalysts remained intact after complete conversion of **7** (Figs S10 and S14), suggesting that the activated -N₂ units were retained during catalysis. These observations were different from previously reported catalytic transformations in which the electrically neutral and weakly activated N₂ units were substitutable ligands for substrate binding [31–48]. When performed under an Ar atmosphere or 10 atm of N₂, reactions also smoothly occurred (entry 3 and 4). Unlike Mo-N₂ complexes, featured signals of **3** could not be detected after heating at 100 °C for a short time (< 5 h) despite its low catalytic competence (entry 5). Related [N]₃Mo^{IV}-Cl complex failed to promote such disproportionation efficiently (entry 6). Magnesium and lithium *N*-(trimethylsilyl)-3,5-dimethylanilides were also tested, but failed (entry 7 and 8). Therefore, these results indicate that Mo-N=N moiety was a key structure and the active site was located at the Mo center. Kinetic studies showed that the initial rate of disproportionation dependent on the concentration of catalyst **5** was first order (Fig. S25), further evidence that **5** was not a precatalyst in the transformation.

Based on these observations, we proposed a plausible catalytic pathway shown in Scheme 3. After coordination of diene **7** to the Mo center (A), the resulting activated allylic hydrogen was transferred from 1,3-cyclohexadiene to N_α atom through ligand-to-ligand hydrogen transfer (LLHT) [98–101], to form a cyclohexadienyl-Mo complex (B) with hydrazine as a ligand. β-hydride elimination of B released benzene and afforded the key intermediate Mo-H species (C), which coordinated with another molecule of 1,3-cyclohexadiene with subsequent insertion (or hydromolybdatation) to generate a cyclohexenyl-Mo species (E), further undergoing reverse LLHT to produce cyclohexene and regenerate the catalyst.

According to the above proposal, complex **5** should be suitable to catalyze alkene isomerization through LLHT-reverse LLHT process. We examined allylbenzene (**12**) as substrate and found that the isomerization indeed took place at high efficiency to afford thermodynamic *trans*-adduct **13** as the product (Scheme 4, eq 2). 1-Hexene (**14**) was also submitted to the reaction system and internal alkenes were produced, albeit with poor site- and regio-selectivity (Scheme 4, eq 3). Kinetic studies indicated that C-H cleavage was not involved in the rate-determining step (Scheme 4, eq 4–6), consistent with the feature of hydrogen transfer between ligands [99].



Scheme 4. Catalytic isomerization of terminal alkenes and kinetic isotope effect experiment.

CONCLUSIONS

In summary, we demonstrated that monodentate silylamido substituents could serve as excellent ligands for supporting low-valence complexes $[\text{N}]_3\text{Mo}$ and heterobimetallic dinitrogen complexes $[\text{N}]_3\text{Mo-N}_2\text{-Mg}[\text{N}]$, which showed great catalytic ability in the disproportionation of cyclohexadiene and isomerization of terminal alkenes with -N_2 ligands intact. Preliminary mechanistic studies indicated that the active catalytic center was the Mo-N_2 moiety through a ligand-to-ligand hydrogen transfer process. The detailed mechanism and new catalytic applications of these M-N_2 complexes in organic transformations are currently under consideration.

DATA AVAILABILITY

The X-ray crystallographic coordinates for the structures of 3, 4, 5, 6 and $\text{Mg}(\text{THF})_2[\text{N}(\text{SiMe}_3)\text{Ar}]_2$ reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 1963795, 1963701, 1963702, 1963703 and 1963706. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk/data_request/cif.

SUPPLEMENTARY DATA

Supplementary data are available at [NSR](https://doi.org/10.1093/nsr/nwab290) online.

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AUTHOR CONTRIBUTIONS

Z.-J.S. and H.-Y.F. proposed and supervised the project. D.-D.Z. carried out the synthesis, structural characterizations and analyzed the data. S.-J.X. and Y.X. assisted with the experiments and characterizations. Z.-J.S. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflict of interest statement. None declared.

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