Silylamido Supported Dinitrogen Heterobimetallic Complexes: Syntheses and Their Catalytic Ability

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ABSTRACT
Molybdenum dinitrogen complexes supported by monodentate arylsilylamido ligand, [Ar(Me$_3$Si)N]$_3$MoN$_2$Mg(THF)$_2$[N(SiMe$_3$)Ar] (5) and [Ar(Me$_3$Si)N]$_3$MoN$_2$SiMe$_3$ (6) (Ar = 3,5-Me$_2$C$_6$H$_3$) were synthesized and structurally characterized, which were proved to be effective catalysts for the disproportionation of cyclohexadienes and isomerization of terminal alkenes. $^1$H NMR spectrum suggested that the bridging nitrogen ligand remains intact during the catalytic reaction, indicating the possible catalytic ability of 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 and 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 the 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 to be effective to catalyze reductive reactions of N$_2$ to afford ammonia or silylamines [13-16]; moreover, due to the nucleophilicity of dinitrogen moiety, the activated dinitrogen ligands in M-N$_2$ (M = 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-N₂ complexes (M = 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 (N₂) as 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 of examples of M-N₂ units as active sites in catalytic organic transformations. In 2004, Hidai reported Ti-W heterobimetallic dinitrogen complexes were excellent precursors for copolymerization of ethylene and 1-hexene, in which the W-N₂ fragment acted as a unique spectator ligand to the catalytically active titanium center [49]. The intriguing results hint at potential activity of the coordinated N₂ units in organometallic catalysis. Herein, we synthesized and structurally characterized molybdenum-nitrogen complexes supported by monodentate arylsilylamido ligand (L = [N(SiMe₃)Ar]). Meanwhile, we observed catalytic reactivity of Mo-N₂ unit as a key motif in the disproportionation of cyclohexadienes and isomerization of terminal alkenes where the -N₂ ligands remained intact unusually. In this catalytic reaction, Mo-N=N motif was considered as a possible catalytic site to proceed the hydrogen transfer (Scheme 1).

Inspired by gradually understanding the structure and mechanism of nitrogenase FeMo–cofactor in the reduction of atmospheric N₂ [50-54], the chemistry of Mo-N₂ complexes has been well studied for decades, in which Mo showed its uniqueness owing to the variable oxidation states and readily forming complexes of N₂ [55-61]. To investigate catalytic reactivity of molybdenum complexes with different structure characteristics in N₂ 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 utility of alkylarylamido ligands were able to stabilize low valent Mo(III) complexes and cleave N₂ [73-74]. As surrogates of this ligand sets, monodentate N-aryl-N-silylamido ligands have not yet been investigated in the similar system, although -N(SiMe₃)₂ [75-78] or silylated multidentate amido ligands -[(R₃SiNCH₂CH₂)₃N]⁺ (R₃Si = Me₃Si or 'BuMe₂Si) [79-82], -[N(SiMe₂CH₂PPr₂)₂] [83],
-[PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh]²⁻ [84] and -[PhP(CH₂SiMe₂NPh)₂]²⁻ [85] have been utilized to support transition-metal dinitrogen complexes since 1990. We envisaged that the readily introduction of bulky silyl group should intrinsically tune steric and electronic coordination sphere of amido donors, inducing new reactivity patterns of coordinated dinitrogen ligands in the Mo-N₂ complexes.

RESULTS AND DISCUSSION
The reaction of MoCl₃(THF)₃ (1) with 1.5 equivalents of lithium N-(trimethylsilyl)anilide (2) in Et₂O for 5 h afforded the corresponding tris-anilide complex of Mo[N(SiMe₃)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 MoN₃ core (Figure 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 angels (126º) might arise from the slightly different steric hindrance and electronic pattern of silylamido ligand around the Mo center. Then we carried out reaction 3 with N₂ in the condition for conversion of Mo[N(tBu)Ar]₃ to N≡Mo[N(tBu)Ar]₃ (1 atm of N₂, d₈-toluene, -35 °C). Owing to less electron negativity and poor electron donating ability of silicon (Si), 3 was proved unreactive with N₂ molecules even under -35 °C for 5 days. Lengthening reaction time of MoCl₃(THF)₃ and lithium amide, the ¹H NMR spectrum of crude product mixture showed Mo³⁺ 3 was disappeared. The Mo⁴⁺-Cl complex 4 was observed as the only product along with a little amount of free ligand HN(SiMe₃)Ar (Scheme 2, b). Similar result was also reported by Fürstner group to isolate complex ClMo[N(tBu)Ar]₃ (Ar = 3,5-dimethoxyphenyl) [86].

Reduction of Mo⁴⁺-Cl reaction mixture with magnesium powder under N₂ atmosphere (1 atm) produced the Mo-N₂ complex (Scheme 2, c). Diamagnetic signals in proton NMR spectrum indicated a high oxidation state of the Mo center. X-ray study gave the unambiguous structure of [Ar(Me₃Si)N]₃MoN₂Mg(THF)₂[N(SiMe₃)Ar] (5), in which Mo and Mg were both supported by silylamido ligand, and bridged by dinitrogen ligand to form the heterobimetallic dinitrogen complex (Figure 2, a). The bond length of N-N is 1.194 Å, indicating the possible feature of N≡N double bond, similar to those found in the diazenido species {[N₃N]Mo-N≡N}₂Mg(THF)₂ (1.195(13) Å and 1.164(13) Å) [80]. Additionally, 5 could be silylated by trimethylsilyl chloride (Me₃SiCl) at the β (terminal) nitrogen atom to afford [Ar(Me₃Si)N]₃MoN₂SiMe₃ (6).
An X-ray analysis of this complex showed a long N-N bond (1.214 Å) (Figure 2, b). Analogous Mo-N=N-Mg complex supported by other silylamido ligand −N(SiMe₂Bu)Ar, was prepared using similar procedures and characterized by X-ray chromatography (please refer to SI, Figure S6). Unfortunately, attempts to obtain analytically pure material failed.

According to those structure 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 good precursors to transfer two nitrogen atoms to organic molecules through [4+2] cycloaddition [87-88]. However, treatment of 5 with stoichiometric amount of 1,3-cyclohexadiene (7) in C₆D₆ at 100 °C for 24 h, it was found that featured signals of the complex remained in the ¹H NMR spectrum of reaction mixture, implying the remarkable stability of 5 under the reaction condition.

To our interest, the substrate 7 completely consumed and two new sets of ¹H NMR signals appeared, which were perfectly fit for the disproportionation products benzene (8) and cyclohexene (9) (Figure S7). Despite such a disproportionation has been studied with different transition-metal catalysts [89-96], the catalytic ability of complexes with metal-dinitrogen moiety particularly from N₂ gas, has not yet been observed. This study might stimulate new avenues to develop efficient catalysts directly from N₂. On the other hand, identification the active centers (Mo or Mg) of the bimetallic complex and their exact behaviors also attracted us to unveil the catalytic disproportionation.

To prove the catalytic reactivity of 5, two experiment protocols have been underwent. Firstly, having confirmed the stoichiometric conversion of 1,3-cyclohexadiene, we further added additional amount of the substrate up to 60 equivalents in portions. Indeed, 90% of 7 converted to 8 and 9 after 18 days (Figure S8, catalyst/substrate = 0.016/1), showing the catalyst still living. We also conducted the reaction by adding 60 equivalent of 7 into the C₆D₆ solution of 5 in one portion. After 180 h, the conversion of 7 was 99% monitored by in-situ NMR (Figure S9). A small amount of cyclohexane (10) was detected during the process, suggesting the potential in hydrogen-transfer reduction of non-conjugate alkene with this catalyst. Meanwhile the isomerized 1,4-cyclohexadiene (11) was also observed, which could also further transform into 8 and 9 by catalytic disproportionation (Figure S13). The reaction pathway was different from the previously reported case 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 activities towards the disproportionation under the 100 °C for 24 h on a 0.30 mmol scale (entry 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 (Figure S10 and S14), suggesting that the activated -N₂ units were retained during catalysis. These observations were different from the previous reported catalytic transformations in which the electrically neutral and weakly activated N₂ units were as substitutable ligands for substrate binding [31-48]. When performed in 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 of its low catalytic competence (entry 5). Related [N]₃MoIV-Cl complex failed for promoting such a disproportionation efficiently (entry 6). Magnesium and lithium N-(trimethylsilyl)-3,5-dimethylanilides were also tested while failed (entry 7 and 8). Therefore, these results indicated that Mo-N=N moiety was a key structure and the active site was located on Mo center. Kinetic studies showed that the initial rate of disproportionation depend on the concentration of catalyst 5 was the first order (please refer to SI, Figure S25), further providing the evidence of 5 not as 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 Nα atom through ligand-to-ligand hydrogen transfer (LLHT) [98-101], to form 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 coordination with another molecule of 1,3-cyclohexadiene and subsequent insertion (or hydromolybdenation) to generate cyclohexenyl-Mo species (E), further undergoing the 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 in high efficiency to afford thermodynamic trans-adduct 13 as a major 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 the C-H cleavage was not involved in the rate-determining step (Scheme 4, eq 4-6), which was consistent with the feature of hydrogen transfer between ligands [99].

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

DATA AVAILABILITY
The X-ray crystallographic coordinates for the structures of 3, 4, 5, 6 and Mg(THF)$_2[N(\text{SiMe}_3)\text{Ar}]_2$ 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 online.

FUNDING
This work was supported by the National Basic Research Program of China (2015CB856600), the National Natural Science Foundation of China (21431008, 21761132027, 91645111 and 21801044), the Shanghai City (18YF1401800 and 18JC1411300), the Fudan-SIMM Joint Research Fund and the China Postdoctoral Science Foundation (2019M661335).

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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Scheme 1. (a) Typical Reactivity Modes of $\text{-N}_2$ Units in Transition Metal-Dinitrogen Complexes; (b) This Work: Catalytic Reactivity of Mo-$\text{N}_2$ Units in the Disproportionation of Cyclohexadienes and Isomerization of Terminal Alkenes.
Scheme 2. Synthesis of Molybdenum Complexes 3-6.
Scheme 3. Proposed Mechanism for the Disproportionation of 1,3-Cyclohexadiene.
Scheme 4. Catalytic Isomerization of Terminal Alkenes and Kinetic Isotope Effect Experiment.
Figure 1. Molecular structures of 3-4 with thermal ellipsoids set at 10% probability. (a) Mo[N(SiMe₃)Ar], 3; (b) ClMo[N(SiMe₃)Ar], 4. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): 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).
Figure 2. Molecular structures of 5-6 with thermal ellipsoids set at 10% probability. (a) [Ar(Me$_3$Si)N$_3$MoN$_2$Mg(THF)$_2$N(SiMe$_3$)Ar], 5; (b) [Ar(Me$_3$Si)N$_3$MoN$_2$SiMe$_3$], 6. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): 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 $^a$.

![Chemical reaction diagram](https://example.com/chemical-diagram.png)

| 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            |

$^a$Conditions: 1,3-Cyclohexadiene (0.30 mmol), Catalyst (10 mol%), 100 °C, C$_6$D$_6$ (0.5 mL), N$_2$ atmosphere (1 atm);

$^b$Determined by $^1$H NMR spectroscopy; $^c$In an Ar atmosphere; $^d$The reaction was carried out in an autoclave pressurized with 10 atm of N$_2$. 