

Dinitrogen Conversion

# Catalytic Dinitrogen Reduction at the Molybdenum Center Promoted by a Bulky Tetradentate Phosphine Ligand\*\*

Qian Liao, Nathalie Saffon-Merceron, and Nicolas Mézailles\*

In memory of Pascal Le Floch

**Abstract:** Stoichiometric reduction of  $N_2$  at a Mo center stabilized by a bulky tetradentate phosphine ligand ( $PP_3^{Cy}$ ) allowed isolation of Mo-imidoamine and Mo-imido complexes. Both complexes as well as the  $Mo^{II}$  precursor are equally suitable catalysts for the synthesis of  $NTMS_3$  ( $TMS$  = trimethylsilyl) from  $N_2$ ,  $TMSCl$ , and electron sources. Mechanistic studies prove the involvement of a TMS radical at least in one of the catalytic steps.

In the challenging domain of  $N_2$  functionalization using transition metal complexes,<sup>[1]</sup> catalyzed processes under ambient conditions are very rare. A common feature with nitrogenases is that, apart from the first example by Shiina,<sup>[2]</sup> they rely on either Mo or Fe complexes. Indeed, in 1989, Hidai reported the catalyzed transformation of  $N_2$  into silylamines ( $N(SiMe_3)_3$ ) using a  $Mo^0$  complex bearing monodentate phosphines as precursor.<sup>[3]</sup> This groundbreaking strategy was not followed for more than twenty years until 2011 when Nishibayashi, Yoshizawa, and co-workers reported that a carefully designed diphosphine/ $Mo^0$  catalytic system could promote the same transformation with greatly increased efficiency (TON of ca. 200).<sup>[4,5]</sup> The same authors reported recently the same reaction with several Fe complexes, yet with lower efficiency (TON up to 34).<sup>[6]</sup> In 2003, Schrock designed a trisamidoamine/ $Mo^{III}$  precursor that is able to catalytically transform  $N_2$  into  $NH_3$ .<sup>[7]</sup> Nishibayashi and co-workers reported in 2010 that a pincer PNP/ $Mo^0$  precursor could also effect this process<sup>[8–11]</sup> followed most recently by Peters and co-workers with the use of a tetradentate ligand/ $Fe^0$  precursor.<sup>[12,13]</sup> Although leading to related compounds,  $NH_3$  and  $N(SiMe_3)_3$ , using a similar approach (addition of sources of electrons and electrophiles) the catalyzed processes are proposed to follow different mechanisms. Indeed, Schrock has isolated a great number of

intermediates that may take part in the catalytic cycle ( $N_2$  to  $NH_3$ ) through sequences of protonation/one-electron reduction of  $N_2$  at the metal center,<sup>[14–20]</sup> whereas Hidai and co-workers proposed the intermediacy of  $SiMe_3$  radical.<sup>[3,21]</sup>

Nishibayashi, Yoshizawa, and co-workers have performed a DFT study<sup>[4]</sup> which corroborates that the mechanism could follow a radical pathway (in terms of energy requirements), but none of the postulated intermediates could be isolated (or observed), most likely because of the efficiency of the catalyst. In the overall process, they propose that the final N–N bond is cleaved once the  $(SiMe_3)_2N-N(SiMe_3)$  anion is decoordinated from the metal center and a low energy path involving necessary P–Mo decoordination/coordination (hemilabile character of the diphosphine). It is therefore of utmost importance to obtain mechanistic information on the nature of intermediates in this process in order to further develop catalysts for  $N_2$  functionalization.

Of interest to us is the “( $PP_3^{Cy}$ )Mo” fragment, which features a neutral tetradentate phosphine,  $PP_3^{Cy}$ , that should accommodate a mononuclear low-valent Mo center. Here we report the syntheses of two aminoimide complexes [ $(PP_3^{Cy})Mo=NNR_2$ ] and an imido complex [ $(PP_3^{Cy})Mo=NTMS$ ] by stepwise reduction of  $N_2$ . We also show that these two  $Mo^{II}$  complexes are equally suitable catalysts for the transformation of  $N_2$  into  $N(SiMe_3)_3$ , and prove that the overall catalytic transformation requires at least one step involving a silicon-based radical.

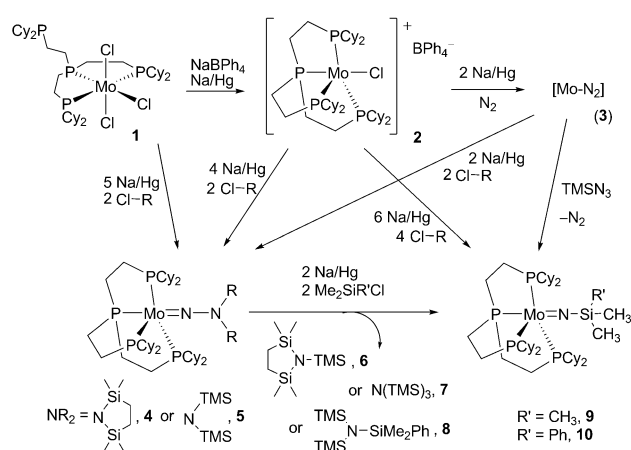
When stoichiometric amounts of  $PP_3^{Cy}$  and  $[MoCl_3(THF)_3]$  were mixed in THF, a novel paramagnetic complex was formed, as shown by the complete disappearance of the signals of the free ligand in the  $^{31}P$  spectrum. This complex is the expected [ $(PP_3^{Cy})MoCl_3$ ], **1** (Scheme 1), as shown by elemental analysis and X-ray diffraction (see the Supporting Information, SI). Interestingly, one of the phosphine arms is not coordinated to the  $Mo^{III}$  center which possesses a pseudo-octahedral geometry. Reduction of complex **1** by one equivalent of Na/Hg in the presence of  $NaBPh_4$  resulted in the formation of a blue diamagnetic complex, **2**. This complex is characterized in the  $^{31}P\{^1H\}$  spectrum by a quartet/doublet at 159 and 137 ppm, respectively, pointing to a symmetrical structure in which all three phosphine arms are bound to the  $Mo^{II}$  center. The diamagnetism of the complex strongly suggested an ML5 geometry and thus a cationic complex. An X-ray structure confirmed the trigonal bipyramid (TBP) geometry (Figure 1). Further reduction of complex **2** under  $N_2$  by two equivalents of Na/Hg resulted again in the loss of signals in the  $^{31}P\{^1H\}$  spectrum. An IR spectrum of the crude mixture showed two different  $\nu_{NN}$  stretches at 2016 and

[\*] Dr. Q. Liao, Dr. N. Mézailles  
Laboratoire Hétérochimie Fondamentale et Appliquée  
Université Paul Sabatier, CNRS  
118 Route de Narbonne, 31062 Toulouse (France)  
E-mail: mezaillies@chimie.ups-tlse.fr

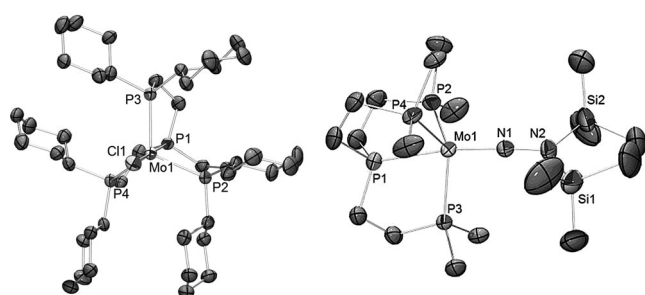
Dr. N. Saffon-Merceron  
Institut de Chimie de Toulouse ICT-FR2599  
Université Paul Sabatier, 31062 Toulouse Cedex (France)

[\*\*] The “Région Midi Pyrénées” is gratefully acknowledged for supporting this work. CNRS and the “Région Midi-Pyrénées” are gratefully acknowledged for a postdoctoral fellowship (Q. L.). N.M. thanks the “Région Midi-Pyrénées” for funding.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201408664>.



**Scheme 1.** Molybdenum complexes and the amine syntheses.

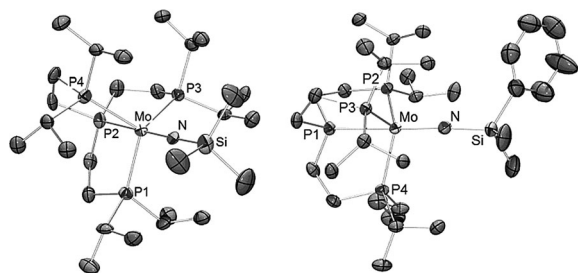


**Figure 1.** POV-Ray plots of complexes **2** (cationic part only) and **4** (50% thermal ellipsoids are shown). Hydrogen atoms have been omitted and only C atoms of the Cy groups have been kept for clarity in complex **4**. Selected bond lengths [Å] and angles [°]: **2**: Mo1–Cl1 2.3468(13), Mo1–P1 2.4201(13), Mo1–P2 2.4439(14), Mo1–P3 2.4420(14), Mo1–P4 2.4398(14); Cl1–Mo1–P1 179.47(5), P1–Mo1–P2 75.39(5), P1–Mo1–P3 75.76(5), P1–Mo1–P4 75.42(5), P2–Mo1–P3 113.66(5), P2–Mo1–P4 114.28(5), P3–Mo1–P4 113.98(5). **4**: Mo1–N1 1.828(3), N1–N2 1.387(4), N2–Si1 1.756(4), N2–Si2 1.752(4), Mo1–P1 2.4548(11), N2–N1–Mo1 177.1(3); N1–N2–Si1 123.5(3), N1–N2–Si2 124.5(3), Si2–N2–Si1 111.99(19), N1–Mo1–P1 170.48(12).

1945  $\text{cm}^{-1}$ . The synthesis of the plausible octahedral complex  $[(\text{PPCy})\text{Mo}(\text{N}_2)_2]$  can be ruled out as it would be diamagnetic. It thus appears that the  $\text{PPCy}$  ligand strongly stabilizes ML5 geometries at the metal center as initially envisioned to form  $[(\text{PPCy})\text{Mo}(\text{N}_2)]$  complexes (mixture of TBP and square-based pyramid, both paramagnetic  $d^4$  complexes). Unexpectedly, it further appeared that the dinitrogen is only weakly bound to the  $\text{Mo}^0$  center, as the mixture evolved when submitted to vacuum (loss of  $\nu_{\text{NN}}$  stretch by IR). Nevertheless, this complex is sufficiently stable in solution and reaction with a slight excess of Na/Hg in the presence of 1,2-bis(chlorodimethylsilyl)ethane or two equivalents of  $\text{SiMe}_3\text{Cl}$  under 1 atm  $\text{N}_2$  lead to the formation of the dark pink aminoimide complexes **4** and **5**, respectively. Both complexes are diamagnetic, as shown by the quartet/doublet pattern in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, at 158 and 118 ppm for complex **4** and at 157 and 116 ppm for complex **5**, again suggesting ML5 geometry at the  $\text{Mo}^{\text{II}}$  centers. Interestingly, in these ML5

complexes, the chemical shift of the  $\text{PCy}_2$  moieties (equatorial positions) is strongly affected by a change in the ligand in *cis* position (upfield shift of ca. 20 ppm between **2** and **4** or **5**), whereas the chemical shift of the P (axial position) is almost unchanged by the ligand in *trans* position. In complex **4**, the  $^{29}\text{Si}$  spectrum shows a single resonance at 2.6 ppm, consistent with the formation of the expected five-membered ring “ $\text{NSiCH}_2\text{CH}_2\text{Si}$ ” featuring two Si–N bonds. The corresponding spectrum for complex **5** showed a singlet at  $-0.3$  ppm. Crystals of complex **4** could be grown, and its structure analysis corroborated the NMR data (Figure 1). Such a silylaminoimide fragment obtained by direct reduction of  $\text{N}_2$  at the Mo center is unknown, and has rarely been isolated, except at Fe centers.<sup>[22–24]</sup> Notable is the linear arrangement at the proximal N atom in this structure (Mo1–N1–N2 angle of  $177.1(3)^\circ$ ). The Mo–N bond of 1.828(3) Å lies on the high side of the reported Mo=N (between 1.64 and 1.83 Å) and Mo≡N (between 1.64 and 1.79 Å) bonds in the CCDC database. A related ML5 complex is calculated to be a high-energy intermediate (square pyramid) in the system modeled by Nishibayashi, Yoshizawa, and co-workers, leading to phosphine dissociation.<sup>[4]</sup> In the present case, the  $\text{PPCy}$  ligand strongly stabilizes the TBP geometry.

Alternatively, direct syntheses of these complexes can be realized from either the  $\text{Mo}^{\text{III}}$  complex **1** or the  $\text{Mo}^{\text{II}}$  complex **2** with the appropriate amount of reducing agent Na/Hg under  $\text{N}_2$  in the presence of the chlorosilane derivatives (Scheme 1). One of the key questions in the formation of amine (either  $\text{NH}_3$  or  $\text{NTMS}_3$ ) from  $\text{N}_2$  is the sequence of addition of the H or Si atoms. In the Chatt mechanism, H atoms (proton + electron) are sequentially added to the distal N, resulting in the formation of one equivalent of  $\text{NH}_3$  and an  $\text{M}\equiv\text{N}$  intermediate which is then further reduced. On the other hand, following Hidai's proposal, Nishibayashi, Yoshizawa, and co-workers calculated that a  $\text{SiMe}_3$  radical could add onto the proximal N atom of the  $\text{Mo}(\text{NN}(\text{SiMe}_3)_2)$  intermediate, leading to the corresponding  $\text{Mo}-\text{N}(\text{SiMe}_3)-\text{N}(\text{SiMe}_3)_2$  complex. This latter intermediate would then liberate the anionic tris(trimethylsilyl) hydrazide upon one-electron reduction. Nevertheless, they were not successful in isolating or at least observing any intermediate in this reaction. We therefore studied the reaction of complexes **4** and **5** with two equivalents of Na/Hg and  $\text{TMSCl}$ . A transformation of both complexes into the same, diamagnetic purple complex **9** was observed. This complex is characterized also by a quartet and a doublet at 159 and 135 ppm, respectively. Here again, the signal for the P atom *trans* to the N atom is only marginally affected upon the transformation, whereas the signal for the three equivalent phosphines of the equatorial plane are shifted downfield by ca. 20 ppm. The concomitant formation of the silylamines **6** and **7** was proven by  $^{29}\text{Si}$  NMR spectroscopy as well as GC-MS. Together this data suggested complex **9** to be a Mo-imido complex. Alternatively, complex **9** was also obtained cleanly from the stoichiometric reaction between the non-isolated  $\text{Mo}^0-\text{N}_2$  intermediate presented above and  $\text{TMSN}_3$ . An X-ray structure analysis confirmed the postulated structure (Figure 2), which has a linear arrangement at the N atom (Mo–N–Si angle of  $178.3(3)^\circ$ ) and possesses a C3 axis that runs through the Si–Mo axis.



**Figure 2.** POV-Ray plots of complexes **9** and **10** (50% thermal ellipsoids are shown). Hydrogen atoms have been omitted and only *iPr* fragments of the Cy have been kept for clarity. Selected bond lengths [Å] and angles [°]: **9**: Mo–N 1.798(5), N–Si 1.740(5), Mo–P1 2.4319(18), Mo–P2 2.4822(17), Mo–P3 2.4170(18), Mo–P4 2.4271(18); N–Mo–P2 179.59(18), Mo–N–Si 178.3(3), P1–Mo–P2 75.45(6), P1–Mo–P3 113.03(7), P1–Mo–P4 114.85(6), P2–Mo–P3 75.62(6), P2–Mo–P4 74.76(6), P3–Mo–P4 113.43(6). **10**: Mo–N 1.839(2), N–Si 1.718(2), Mo–P1 2.4911(7), Mo–P2 2.4281(6), Mo–P3 2.4342(6), Mo–P4 2.4221(7); N–Mo–P1 178.06(7), Mo–N–Si 177.01(15), P1–Mo–P2 74.33(2), P1–Mo–P3 75.02(2), P1–Mo–P4 75.71(2), P2–Mo–P3 114.82(2), P2–Mo–P4 113.41(2), P3–Mo–P4 112.44(2).

The Mo–N bond of 1.798(5) Å is shorter than in complex **4** but still lies on the high side of the reported Mo=N and Mo≡N bonds. A related complex **10** was synthesized in a one-pot procedure from complex **2** by subsequent reductions in the presence of TMSCl (to form **5** in situ) and then PhSiMe<sub>2</sub>Cl. The corresponding amine **8** was observed by GC-MS analysis. Complex **10**, characterized also by a quartet and a doublet at 158 and 133 ppm, respectively, in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, was crystallized (Figure 2). The structure presents very similar features to that of **9**, such as the linear arrangement of Mo–N–Si and the TBP geometry, yet with a slightly elongated Mo=N bond (1.839(2) Å in **10** versus 1.798(5) Å in **9**). These complexes are the first examples, in which the Mo–imido bond is generated through N<sub>2</sub> functionalization. It also proves that the chosen ligand, despite its bulkiness, favors amine elimination through in-sphere N–N splitting rather than hydrazine derivative elimination.

With a series of Mo complexes in hand that are able to transform N<sub>2</sub> into N(SiMe<sub>3</sub>)<sub>3</sub> or N(SiMe<sub>3</sub>)(SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>) by the stoichiometric reduction/functionalization of N<sub>2</sub>, their performance in the catalytic formation of N(SiMe<sub>3</sub>)<sub>3</sub> from N<sub>2</sub>, TMSX (X = Cl, Br, and I), and various sources of reducing agents was studied. Most importantly, their relative efficiency in the catalytic process will provide information on their involvement in the catalytic cycle versus being dead-end species. In a first series of experiments, “blank” reactions (without Mo complex) were carried out. These were crucial to prove the involvement of Si-centered radicals during the process. Indeed, when TMSCl was reacted with K or Na/K in THF at room temperature, TMS–TMS was formed as expected from the efficient and fast generation of SiMe<sub>3</sub> radical. When the reaction was carried out with Na, Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>4</sub>OSiMe<sub>3</sub> was formed as a result of the reaction of the radical with THF, in addition to TMS–TMS as previously observed by Nishibayashi, Yoshizawa, and co-workers.<sup>[4]</sup>

On the other hand, although the redox potential of Na/Hg is low enough to allow the effective reduction of TMSCl, the

kinetics of this reduction appeared very slow. Indeed, even upon heating at 60 °C for 48 h, only TMSCl was observed in the reaction mixture. This experiment clearly proved that under these conditions the TMS radical is not formed. In a second stage, the Mo-catalyzed transformation of N<sub>2</sub> into N(TMS)<sub>3</sub> was studied (Table 1). The formation of N(TMS)<sub>3</sub> as the sole amine was verified by <sup>29</sup>Si NMR spectroscopy, and

**Table 1:** Catalytic investigations.

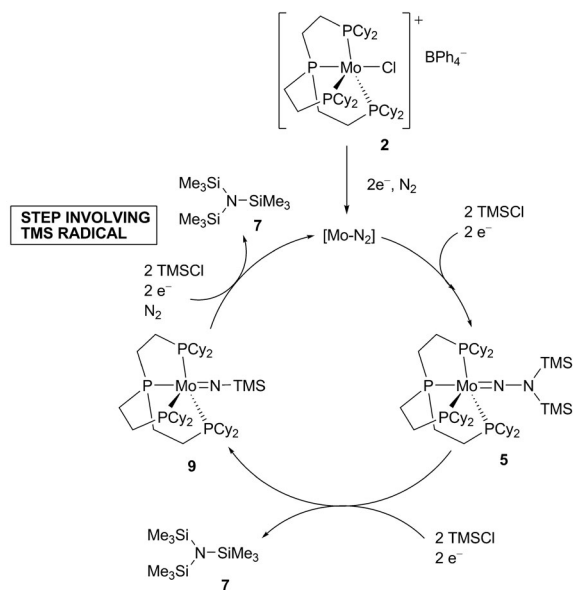
| Entry             | Reductant | Additive | Catalyst | T [°C] | NTMS <sub>3</sub> <sup>[a]</sup> [equiv] | Yield of NTMS <sub>3</sub> <sup>[b]</sup> |
|-------------------|-----------|----------|----------|--------|------------------------------------------|-------------------------------------------|
| 1                 | Na sand   | –        | <b>5</b> | 25     | 5.8                                      | 8.7                                       |
| 2                 | Na sand   | NaI      | <b>5</b> | 50     | 2.8                                      | 4.2                                       |
| 3                 | Na/Hg     | –        | <b>5</b> | 25     | 2.1                                      | 3.2                                       |
| 4                 | Na/Hg     | –        | <b>5</b> | 50     | 2.4                                      | 3.6                                       |
| 5                 | Na/Hg     | –        | <b>9</b> | 50     | 1.4                                      | 2.1                                       |
| 6                 | Na/K      | –        | <b>5</b> | 50     | 11.7                                     | 17.6                                      |
| 7                 | Na/K      | NaI      | <b>5</b> | 90     | 10.2                                     | 15.3                                      |
| 8                 | K         | –        | <b>5</b> | 25     | 10.5                                     | 15.8                                      |
| 9 <sup>[c]</sup>  | K         | –        | <b>5</b> | 25     | 11.4                                     | 17.1                                      |
| 10 <sup>[d]</sup> | K         | –        | <b>5</b> | 25     | 4.4                                      | 6.6                                       |
| 11                | K         | –        | <b>5</b> | 50     | 15.0                                     | 22.5                                      |
| 12                | K         | –        | <b>5</b> | 90     | 8.3                                      | 12.5                                      |
| 13                | K         | NaI      | <b>5</b> | 50     | 13.3                                     | 20.0                                      |
| 14                | K         | –        | <b>9</b> | 50     | 11.8                                     | 17.7                                      |
| 15                | K         | –        | <b>2</b> | 50     | 11.7                                     | 17.6                                      |

[a] Equivalents of NTMS<sub>3</sub> = equiv amine/cat. [b] Yield of NTMS<sub>3</sub> based on initial TMSCl. [c] The reaction time was 4 days. [d] TMSBr was used instead of TMSCl.

quantified by the indophenol method.<sup>[25,26]</sup> Complex **5** was used to optimize the experimental conditions. The nature of the reducing agent was probed at 25 °C (entries 1, 3, and 8), showing that Na/Hg did not allow a catalytic reaction to occur (2.1 equiv of NTMS<sub>3</sub>: the amount of NH<sub>3</sub> measured by the indophenol method results from the hydrolysis of complex **5**, which already contains two N atoms). This was corroborated by the reaction with complex **9**, which only provided 1.4 equiv of NTMS<sub>3</sub> (entry 5). Potassium provided the best results (10.5 equiv of NTMS<sub>3</sub>, entry 8) of the reducing agents. When the reaction was performed for a longer time (4 days, entry 9), the outcome was very similar (11.4 versus 10.5 equiv NTMS<sub>3</sub>), which indicated catalyst decomposition after 2 days. Most importantly, these experiments together with the above-mentioned catalyst-free reactions prove the involvement of a TMS radical in the catalytic process. As the reactions appeared quite slow, the effect of temperature (entries 8, 11, and 12) as well as the nature of the Si derivative were probed (entries 2, 7, 10, and 13). The best results were obtained at 50 °C [15.0 equiv of NTMS<sub>3</sub>, entry 11 versus 10.5 equiv (entry 8) and 8.3 equiv (entry 12) at 25 °C and 90 °C, respectively]. In contrast to Hidai’s observation, the addition of neither TMSBr nor TMSI (generated in situ by the reaction between TMSCl and NaI) improved the catalysis. The results with TMSI were at best similar to those with TMSCl (13.3 versus 15.0 equiv NTMS<sub>3</sub>, entry 13 versus 11, respectively). Finally, with the optimized conditions (50 °C, TMSCl, and K), the three complexes **2**, **5**, and **9** could be compared, and

appeared to be equally suitable for the catalytic transformation of  $N_2$  to  $N(TMS)_3$ .

Indeed, they provided very similar results (11.7, 15.0, and 11.8 equiv  $NTMS_3$ , entries 15, 11, and 14, respectively). Thus, not only is complex **2** a competent precatalyst, as expected from the stoichiometric reactions presented above, but also both complexes **5** and **9** are intermediates in the catalytic cycle. Overall, the stoichiometric and catalytic reactions between  $N_2$ ,  $TMSCl$ , reducing agents, and the three complexes **2**, **5**, and **9** support the catalytic cycle presented in Scheme 2, involving a TMS radical at least in the step between complex **9** and the “ $Mo(N_2)$ ” intermediate.



**Scheme 2.** Operative mechanism for the catalytic transformation of  $N_2$  to  $N(TMS)_3$  using the “ $(PP_3)Mo$ ” fragment.

In conclusion, we show here that a tetradentate phosphine ligand “ $PP_3$ ”, featuring strongly donating moieties favors the TBP geometry for the  $Mo^{II}$  center. This enforced geometry allowed us to isolate three intermediates in the stepwise reduction of  $N_2$ : two imidoamine complexes, **4** and **5**, and an imido complex, **9**. The latter imido complex **9** as well as complex **10** are the first examples of a  $M=NTMS$  fragment generated upon  $N_2$  reduction at a metal center. Finally, catalytic investigations with various sources of reducing agent prove the involvement of a Si-centered radical in the  $N_2$  to  $NTMS_3$  reduction process, at least in the  $Mo=NTMS$  to  $Mo(N_2)$  step.

## Experimental Section

Synthesis of  $[(PP_3^C)Mo(NN(SiMe_2CH_2)_2)]$  (**4**) as a representative example: To a suspension of  $[Mo(PP_3^C)Cl]BPh_4$  (0.05 mmol, prepared from  $[Mo(PP_3^C)Cl_3]$ ) in THF (2.5 mL) was added freshly prepared sodium amalgam (5.8 mg, 0.25 mmol Na; 600 mg Hg) and bis(chlorodimethylsilyl)ethane (12 mg, 0.055 mmol). The mixture was stirred vigorously for 12 h under  $N_2$ , forming a dark red-purple solution. A

$^{31}P\{H\}$  NMR spectrum of the crude reaction mixture was recorded. The NMR yield (70 %) was measured by integration versus an internal standard ( $PPh_3$ ) in a capillary. THF was then removed under vacuum, and the residue was extracted with pentane ( $\approx 1$  mL). The volume was reduced to 0.1 mL, and crystals were obtained by cooling the concentrated solution to  $-80^\circ C$  for 2 days. The mother liquor was filtered and the crystals were collected and dried. Yield of the isolated product: 27 mg, 55 %.  $^1H$  NMR (300 MHz,  $[D_8]toluene$ ):  $\delta = 2.19$ – $2.15$  (m, 6H,  $CH_2^{arm}$ ),  $1.95$ – $1.91$  (m, 6H,  $CH_2^{arm}$ ),  $1.83$ – $1.77$  (m, 12H,  $CyH$ ),  $1.68$ – $1.45$  (m, 24H,  $CyH$ ),  $1.34$ – $1.10$  (m, 30H,  $CyH$ ),  $0.81$  (s, 4H,  $SiCH_2CH_2Si$ ),  $0.37$  ppm (s, 12H,  $Si(CH_3)_2$ );  $^{31}P\{H\}$  NMR (121.5 MHz,  $[D_8]toluene$ ):  $\delta = 158$  (q,  $^2J = 28$  Hz, 1P), 118 ppm (d,  $^2J = 28$  Hz, 3P);  $^{29}Si\{H\}$  NMR (59.6 MHz, THF):  $\delta = 2.6$  ppm.

Received: August 29, 2014

Published online: October 19, 2014

**Keywords:** amine formation · dinitrogen conversion · dinitrogen reduction · Mo complexes · silicon radicals

- [1] For reviews, see: a) Y. Tanabe, Y. Nishibayashi, *Coord. Chem. Rev.* **2013**, 257, 2551; b) K. C. MacLeod, P. L. Holland, *Nat. Chem.* **2013**, 5, 559; c) Y. Nishibayashi, *Dalton Trans.* **2012**, 41, 7447; d) N. Hazari, *Chem. Soc. Rev.* **2010**, 39, 4044; e) J. L. Crossland, D. R. Tyler, *Coord. Chem. Rev.* **2010**, 254, 1883; f) M. Mori, *Heterocycles* **2009**, 78, 281; g) M. Mori, *J. Organomet. Chem.* **2004**, 689, 4210; h) P. J. Chirik, *Dalton Trans.* **2007**, 16; i) M. Hidaï, Y. Mizobe, *Pure Appl. Chem.* **2001**, 73, 261; j) M. Hidaï, Y. Ishii, *J. Mol. Catal. A* **1996**, 107, 105; k) S. Gambarotta, *J. Organomet. Chem.* **1995**, 500, 117; l) T. A. Bazhenova, A. E. Shilov, *Coord. Chem. Rev.* **1995**, 144, 69.
- [2] K. Shiina, *J. Am. Chem. Soc.* **1972**, 94, 9266.
- [3] K. Komori, H. Oshita, Y. Mizobe, M. Hidaï, *J. Am. Chem. Soc.* **1989**, 111, 1939.
- [4] H. Tanaka, A. Sasada, T. Kouno, M. Yuki, Y. Miyake, H. Nakanishi, Y. Nishibayashi, K. Yoshizawa, *J. Am. Chem. Soc.* **2011**, 133, 3498.
- [5] Very low TON of silylamine from  $N_2$  was recently reported: T. Ogawa, Y. Kajita, Y. Wasada-Tsutsui, H. Wasada, H. Masuda, *Inorg. Chem.* **2013**, 52, 182.
- [6] M. Yuki, H. Tanaka, K. Sasaki, Y. Miyake, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2012**, 3, 2261.
- [7] D. V. Yandulov, R. R. Schrock, *Science* **2003**, 301, 76.
- [8] K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nat. Chem.* **2011**, 3, 120.
- [9] E. Kinoshita, K. Arashiba, S. Kuriyama, Y. Miyake, R. Shimazaki, H. Nakanishi, Y. Nishibayashi, *Organometallics* **2012**, 31, 8437.
- [10] S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, N. Kamaru, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* **2014**, 136, 9719.
- [11] H. Tanaka, K. Arashiba, S. Kuriyama, K. Nakajima, Y. Nishibayashi, A. Sasada, K. Yoshizawa, *Nat. Commun.* **2014**, 5, 3737.
- [12] J. S. Anderson, J. Rittle, J. C. Peters, *Nature* **2013**, 501, 84.
- [13] S. E. Creutz, J. C. Peters, *J. Am. Chem. Soc.* **2014**, 136, 1105.
- [14] D. V. Yandulov, R. R. Schrock, A. L. Rheingold, C. Ceccarelli, W. M. Davis, *Inorg. Chem.* **2003**, 42, 796.
- [15] R. R. Schrock, *Angew. Chem. Int. Ed.* **2008**, 47, 5512; *Angew. Chem.* **2008**, 120, 5594.
- [16] R. R. Schrock, *Acc. Chem. Res.* **2005**, 38, 955.
- [17] D. V. Yandulov, R. R. Schrock, *J. Am. Chem. Soc.* **2002**, 124, 6252.
- [18] D. V. Yandulov, R. R. Schrock, *Inorg. Chem.* **2005**, 44, 1103.
- [19] V. Ritleng, D. V. Yandulov, W. W. Weare, R. R. Schrock, A. S. Hock, W. M. Davis, *J. Am. Chem. Soc.* **2004**, 126, 6150.



- [20] M. R. Reithofer, R. R. Schrock, P. Müller, *J. Am. Chem. Soc.* **2010**, *132*, 8349.
- [21] M. Hidai, Y. Mizobe, *Chem. Rev.* **1995**, *95*, 1115.
- [22] D. L. M. Suess, J. C. Peters, *J. Am. Chem. Soc.* **2013**, *135*, 4938.
- [23] M. Marc-Etienne, J. C. Peters, *J. Am. Chem. Soc.* **2011**, *133*, 18118.
- [24] P. A. Rudd, N. Planas, E. Bill, L. Gagliardi, C. C. Lu, *Eur. J. Inorg. Chem.* **2013**, 3898.
- [25] A. L. Chaney, E. P. Marbach, *Clin. Chem.* **1962**, *8*, 130.
- [26] N. M. Tzollas, G. A. Zachariadis, A. N. Anthemidis, J. A. Stratis, *Int. J. Environ. Anal. Chem.* **2010**, *90*, 115.
-