Reviews

Synthesis and Reactivity of Side-On-Bound Dinitrogen Metal Complexes

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Received December 9, 2005

An up-to-date account of the synthesis of side-on-bound dinitrogen complexes of the lanthanides, the actinides, and the transition elements over the past 40 years is given. In addition, the reactivity of these derivatives is summarized. There have been many complicated multinuclear cluster complexes with the N_2 imbedded in a fashion that corresponds to side-on N_2. There have been some suggestions, as early as 1960, that side-on dinitrogen complexes should exist. However, a key date in this area is 1988, which is when the disamarium complex $(Cp^*{}_2Sm)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ was reported. It is this date that is used in this account as the real starting point for the area of side-on dinitrogen coordination chemistry. After 1988, side-on dinitrogen complexes are reviewed from the point of view of synthesis, structure (N−N bond lengths, where applicable), and reactivity. What becomes apparent is that while there have been many new side-on dinitrogen complexes discovered recently, investigations into their reactivity patterns are still at a primitive stage.

Introduction

Transition-metal complexes that incorporate dinitrogen as a ligand have enjoyed a special status in inorganic coordination chemistry. The N_2 molecule is known to be very stable and a rather poor ligand,[1] quite in contrast to its isoelectronic analogue, carbon monoxide, which is both reactive and binds strongly to many transition-metal ions. While the coordination chemistry of dinitrogen is vastly outmatched by CO coordination chemistry,[2] in the time since the discovery of the first N_2 complex, $[Ru(NH_3)_5N_2]^{2+}$, in 1965,[3] much has been learned about how N_2 binds to one or more metals in a complex and what one can expect of it in terms of its reactivity patterns. For the most part, investigations of the reactivity of coordinated N_2 have focused on protonation protocols,[4] in an effort to mimic and perhaps unravel some of the processes that the nitrogenase enzymes undergo in the conversion of N_2 to ammonia.[5] Related to and extending these protonation studies have been investigations into the reactivity of dinitrogen complexes with electrophiles such as alkyl and acyl halides and metal and nonmetal halides, all focused on the nucleophilicity of coordinated N_2. Another well-known but nonproductive reaction of coordinated dinitrogen is its displacement by better donor ligands. The aforementioned reactivity with electrophiles and N_2 substitution sum up about the first three decades of research on dinitrogen coordination chemistry.[6]

In the past decade or so, the chemistry of coordinated dinitrogen has been reinvigorated by the discovery of new kinds of reactivity patterns that include N−N bond cleavage and functionalization of coordinated N_2.[1,7] What also has emerged as significant is the importance of the binding mode of the N_2 unit to one or more metals and the extent of activation of the coordinated dinitrogen moiety (Table 1). While the end-on-bound N_2 unit is certainly the most common binding motif, in 1988, the first planar side-on-bound N_2 complex $(Cp^*{}_2Sm)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ was communicated.[8] As it turned out, this pentamethylcyclopentadienyl derivative of samarium showed little or no activation of the dinitrogen unit, and its reactivity was rather simple, since the N_2 moiety dissociated easily from the complex both in solution and in the solid state. However, since that time many other side-on-bound dinitrogen complexes have been discovered and their reactivity patterns are starting to be investigated. What is apparent so far is that the side-on mode shows enhanced reactivity as compared to the end-on mode. In this review we will concentrate on examining just the side-on-bound N_2 unit in metal complexes by highlighting our own work as well as the history of this mode of binding and relevant research from other groups to put our results in context. We will also include, for the sake of completeness, the side-on−end-on bonding mode of N_2 (**E** in Table 1).

Side-On Coordination of N_2: Prior to 1988

Orgel first proposed the side-on bonding mode of N_2 in 1960 from a purely theoretical point of view, many years before any

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[1] (a) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. (b) Gambarotta, S.; Scott, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5298.

[2] Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 3rd ed.; Pearson Prentice Hall: Englewood Cliffs, NJ, 2004; p 467.

[3] (a) Allen, A. D.; Senoff, C. V. *Chem. Commun.* **1965**, 621. (b) Leigh, G. J. *Can. J. Chem.* **2005**, *83*, 277.

[4] Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

[5] (a) Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696. (b) Lee, S. C.; Holm, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3595.

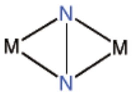
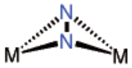
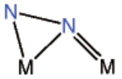
[6] (a) Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177. (b) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.

[7] (a) Shaver, M. P.; Fryzuk, M. D. *Adv. Synth. Catal.* **2003**, *345*, 1061. (b) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200−202*, 379.

[8] Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.

10.1021/om051055i CCC: $33.50

Table 1. General Bonding Modes of N_2 in Mononuclear and Dinuclear Metal Complexes[a]

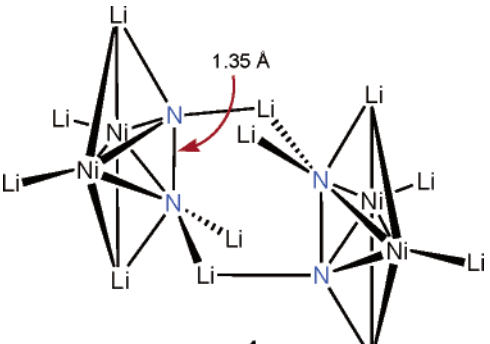
Weak Activation	Strong Activation	
$M-N\equiv N$		End-on Mononuclear
$M-N\equiv N-M$	$M=N-N=M$	End-on Dinuclear
 **A**	 **B**  **C**  **D**	Side-on Dinuclear
	 **E**	Side-on End-on Dinuclear

[a] Only the connectivity is indicated, along with extremes in N−N bond activation from weak activation (N−N triple bond) to strong activation (N−N double and single bonds).

bona fide examples existed.[9] One of the earliest mentions of the side-on mode in a real complex was in 1970, when the isotopically labeled Ru(II) derivatives $[(H_3N)_5Ru(^{14}N^{15}N)]Br_2$ and $[(H_3N)_5Ru(^{15}N^{14}N)]Br_2$ were observed by IR spectroscopy to interconvert over a few hours at room temperature.[10] Since the isomerization process was more rapid than the dissociation of N_2 from $(NH_3)_5Ru^{2+}$, it was concluded that the isomerization reaction must be intramolecular, proceeding via a mononuclear side-on transition state. In 1973, matrix isolation studies at 10 K of the reaction of Co atoms with N_2 produced the triatomic species $Co(\eta^2\text{-}N_2)$, as evidenced by IR spectroscopy.[11] In particular, the use of the mixed isotopomer $^{14}N^{15}N$ resulted in the observation of a single peak in the IR spectrum, indicating the presence of a symmetric, or side-on, CoN_2 species.

In 1978, a mononuclear side-on N_2 derivative was reported on the basis of EPR spectroscopy.[12] The complex $Cp_2ZrR(N_2)$ ($R = CH(SiMe_3)_2$) was prepared under $^{14}N_2$ or $^{15}N_2$ gas by reduction of $Cp_2ZrR(Cl)$ with Na/Hg amalgam in THF. The Zr(III) species converted to the diamagnetic purple compound $(Cp_2ZrR)_2(\mu\text{-}N_2)$, in which N_2 was proposed to be end-on bridging. The EPR spectrum of $Cp_2ZrR(^{14}N_2)$ showed a quintet at $g = 2.0037$ due to coupling to two equivalent ^{14}N nuclei ($I = 1$), while the spectrum of $Cp_2ZrR(^{15}N_2)$ was a triplet due to coupling to two equivalent ^{15}N nuclei ($I = {}^1/_2$). In both cases, satellites from ^{91}Zr hyperfine coupling were also observed ($I = {}^5/_2$, 11.2% natural abundance). Unfortunately, there was no confirmation by solid-state X-ray analysis, and thus this result has not been widely acknowledged.

The first crystallographically characterized side-on N_2 complex was reported in 1973 and involved the interaction of the N_2 unit with two nickel and four lithium ions.[13] $[\{(C_6H_5\text{-}Li)_3Ni\}_2N_2(OEt_2)_2]_2$ (**1**) was synthesized from *all-trans*-1,5,9-cyclododecatrienenickel, [(CDT)Ni], and PhLi in Et_2O under N_2. The complicated structure features N_2 elongated to 1.35 Å and bound side-on to two Ni atoms joined by a Ni−Ni bond (2.687 Å), as well as end-on to one or three lithium atoms. Shortly after the discovery of **1**, the authors reported using a mixture of PhLi and PhNa in the reaction with [(CDT)Ni] to obtain $\{(C_6H_5)[Na(OEt_2)]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OEt)_4(OEt_2)_2\}_2$ (**2**).[14] The N−N bond length is 1.359(18) Å, similar to that observed in **1**, and N_2 is bound side-on perpendicular to the Ni−Ni bond (2.749(7) Å) and side-on to two Na atoms, with the nitrogen lone pairs being directed between two Li atoms. Both of these complexes display N_2 coordination modes that best match **D** in Table 1.



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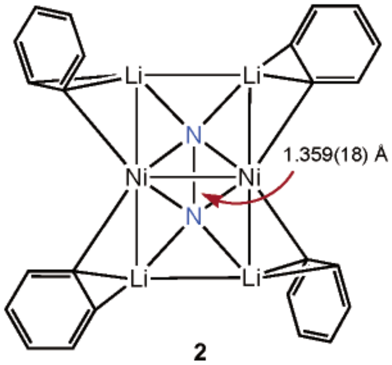

2

(only selected core atoms are indicated for clarity)

A rather curious mononuclear side-on N_2 complex, $RhCl(\eta^2\text{-}N_2)(P^iPr_3)_2$,was postulated in 1977 on the basis of a single-

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[9] Orgel, L. E. *An Introduction to Transition Metal Chemistry*; Methuen: London, 1960; p 137.

[10] Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1970**, *92*, 2560.

[11] Ozin, G. A.; Vander Voet, A. *Can. J. Chem.* **1973**, *51*, 637.

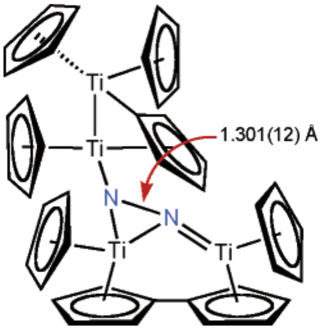
[12] (a) Gynane, M. J. S.; Jeffery, J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 34. (b) Jeffery, J.; Lappert, M. F.; Riley, P. I. *J. Organomet. Chem.* **1979**, *181*, 25.

[13] (a) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 997. (b) Kruger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 998.

[14] Jonas, K.; Brauer, D. J.; Kruger, C.; Roberts, P. J.; Tsay, Y.-H. *J. Am. Chem. Soc.* **1976**, *98*, 74.

crystal X-ray structure;[15] however, further studies showed that this was in error and that, in fact, the N_2 unit is end-on bound.[16]

An intriguing example of dinitrogen bound to multiple metals, a component of which has the N_2 bound side-on end-on (**E** in Table 1), was reported in 1982. Upon exposure of solutions of $(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3Ti_2$ to N_2 a tetranuclear compound, $(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}N_2)[(\eta^5{:}\eta^5\text{-}C_{10}H_8)(\eta^5\text{-}C_5H_5)_2Ti_2][(\eta^1{:}\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3\text{-}Ti_2]$ (**3**), formed.[17] X-ray crystallography showed N_2 coordinated side-on to one Ti and end-on to two Ti atoms, with an N−N bond length of 1.301(12) Å.[18]



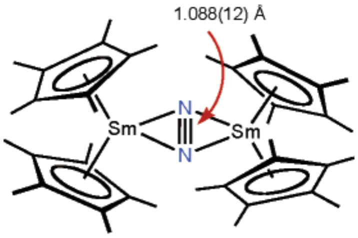
3

An early theoretical investigation into the bonding of CO and N_2 to metallocenes foreshadowed the uncanny ability of early transition metals, specifically those of group 4, to bind N_2 in a side-on fashion.[19] From the interaction diagram of $N_2 + Cp_2M$, it was argued that, if M has a d^2 configuration, only two electrons are available for π back-bonding and side-on bonding would be at least as stable as end-on bonding. If more than two d electrons were available, the formation of additional π back-bonding interactions would preempt the formation of the relatively weaker δ bond that stabilizes side-on N_2 complexes, and end-on bonding is predicted. The authors challenged synthetic chemists to focus their attention on early transition metals in the quest for side-on complexes of N_2.

While the above complexes certainly do contain side-on-bound N_2 units, it is clear that this is just a component of the description for these derivatives, because they also have other interactions that involve end-on N_2 types of activation. In 1988, a simple unequivocal example of a side-on bound N_2 complex was reported. For this reason, we arbitrarily pick this date as a milestone in dinitrogen coordination chemistry.

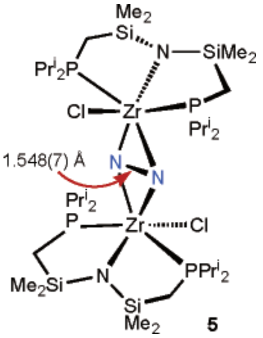
Side-On Coordination of N_2: Since 1988

In 1988, the first planar side-on dinitrogen complex was isolated and crystallographically characterized.[8] Crystals of the dinuclear complex $(Cp^*_2Sm)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**4**) formed when toluene solutions of Cp^*_2Sm were exposed to N_2; when **4** was dissolved in toluene, N_2 gas was lost under vacuum. Complex **4** was also the first compound in which N_2 was bound symmetrically bridging and side-on to two metal centers in a coplanar array. The crystal structure of **4** showed that the N−N bond length is 1.088(12) Å, not elongated over free N_2 (1.0975 Å), and thus the best description of the bridging side-on N_2 unit is **A** in Table 1. The two metallocene ends are perpendicular to each other, and the N_2 unit is canted: the Sm_2N_2 plane is at an angle of 62.9° to the Sm1−Cp*(centroid)$_2$ plane. Although the N_2 unit in **4** would appear to be uncharged on the basis of the lack of any significant bond elongation, the Sm−C(Cp*) bond lengths are typical for a Sm^{3+} species, as are the chemical shifts observed by ^{13}C NMR spectroscopy. To maintain charge neutrality, N_2^{2-} would have to be present in the complex, and an elongated N−N bond length would be predicted. The discrepancy between the expected and observed N−N bond lengths has not been fully rationalized.



4

In 1990, the second planar, dinuclear, side-on-bound dinitrogen complex was isolated and characterized crystallographically.[20] Dark blue $([PNP]ZrCl)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**5**; [PNP] = $(^iPr_2PCH_2SiMe_2)_2N$) was prepared in 44% yield by reduction of $[PNP]ZrCl_3$ with excess Na/Hg amalgam in toluene under 4 atm of N_2. The crystal structure showed N_2 bound side-on to two Zr atoms in a symmetric, planar Zr_2N_2 unit. The N−N bond length is 1.548(7) Å, longer than the single N−N bond in hydrazine and the longest measured for a transition-metal−N_2 complex; this mode most closely matches **C** in Table 1. This complex also represented the first side-on N_2 complex of zirconium.



5

Since the reports of the above two dinitrogen complexes **4** and **5**, numerous other lanthanide, actinide, and transition-metal complexes that contain side-on bound N_2 have been discovered. In the following sections, the syntheses and structures of these derivatives are presented. The final section in this review discusses the reactivity of the coordinated dinitrogen, with particular attention being paid to its bonding mode.

Side-On N_2 Complexes of the Lanthanides

Since the report of **4** in 1988, many other lanthanide dinitrogen compounds have been discovered. In the presence of N_2, the reaction of TmI_2 with 2 equiv of KCp* in Et_2O gave $(Cp^*_2Tm)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**6**) in 55% yield.[21] The low-resolution crystal structure of **6** shows that N_2 is bound side-on to the two Tm centers and has a planar Ln_2N_2 core, like that of **4**. Better structural data were obtained when Cp* was replaced with $[C_5H_3(SiMe_3)_2]$ and $[C_5H_4(SiMe_3)]$. The side-on N_2 complexes $\{[C_5H_3(SiMe_3)_2]_2Tm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**7**) and $\{[C_5H_4(SiMe_3)]_2\text{-}$

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(16) Thorn, D. L.; Tulip, T. H.; Ibers, J. A. *J. Chem. Soc., Dalton Trans.* **1979**, 2022.

(17) (a) Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072. (b) Pez, G. P.; Kwan, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 8079.

(18) Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482.

(19) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

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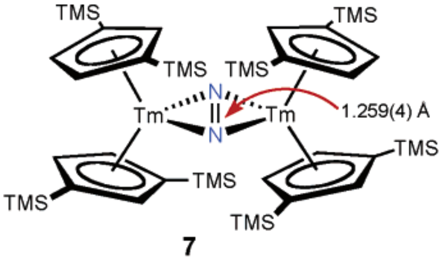
$Tm(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**8**) have N−N bond lengths of 1.259(4) and 1.236(8) Å, respectively. In **7** and **8**, N_2 has been reduced to N_2^{2-}, or diazenido, which may be due to the greater reduction potential of Tm(II) (−2.3 V compared to −1.5 V for Sm(II)). The corresponding dysprosium derivative, $\{[C_5H_3(SiMe_3)_2]_2Dy\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**9**), was prepared in 75% yield by the same route used to prepare **6**−**8**, from DyI_2 and $K[C_5H_3(SiMe_3)_2]$.[22] The low-resolution crystal structure of **9** showed N_2 bound side-on in a planar Dy_2N_2 core similar to that found in **7**.



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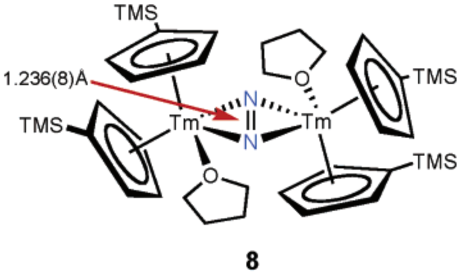

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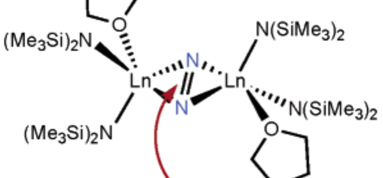
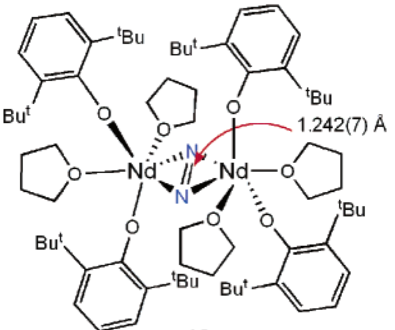
($TMS = SiMe_3$)

Attempts to form a neodymium N_2 complex using cyclopentadienyl-type ligands proved difficult. However, when harder ancillary ligands such as $[(Me_3Si)_2N]^-$ and $(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)^-$ were employed, dinitrogen derivatives of Nd as well as of Tm and Dy could be obtained. For example, the reaction of 2 equiv of $NaN(SiMe_3)_2$ with $TmI_2(THF)_3$ or DyI_2 in THF under N_2 gave $\{[(Me_3Si)_2N]_2Ln(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (Ln = Tm (**10**), Dy (**11**)). The Tm and Dy complexes are structurally analogous by X-ray crystallography, with N−N bond lengths of 1.264(7) and 1.305(6) Å, respectively. The first neodymium−N_2 complex, blue-green $[(ArO)_2Nd(THF)_2]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**12**; Ar = 2,6-^{t}-$Bu_2C_6H_3$), was prepared from NdI_2 and 2 equiv of KOAr in THF under N_2. Two THF molecules are coordinated to each Nd, and the N−N bond length is 1.242(7) Å.[23] The use of Tm^{2+}, Dy^{2+}, and Nd^{2+} was significant, since these species are extremely reducing and their molecular chemistry was very limited.[24]



10 Ln = Tm 1.264(7) Å
11 Ln = Dy 1.305(6) Å



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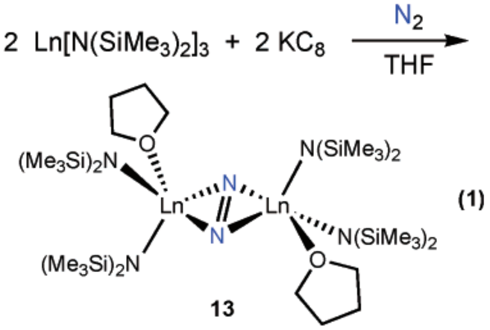
A very versatile route to lanthanide dinitrogen complexes has been recently reported, as shown in eq 1. In this sequence, the



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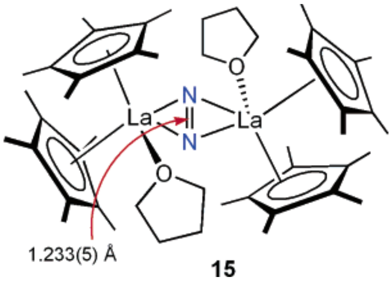
Ln = Tm, Dy, Nd, Gd, Ho, Tb, Y, Er, Lu

readily available Ln(III) precursors, $Ln[N(SiMe_3)_2]_3$, can be reduced with 1 equiv of KC_8 in THF under N_2 to yield $\{[(Me_3Si)_2N]_2Ln(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13**; Ln = Tm, Dy, Nd, Gd, Ho, Tb, Y, Er, Lu, La).[25] The crystal structures obtained have N−N bond lengths ranging from 1.258(3) Å for Ln = Nd to 1.305(6) Å for Ln = Dy.

Although many new lanthanide−N_2 complexes were prepared, single crystals of $\{[(Me_3Si)_2N]_2La(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, an attractive diamagnetic target, could not be obtained. However, crystalline lanthanum dinitrogen complexes were obtained in high yield with the judicious choice of substituted-Cp ligands for the trivalent starting material.[26] When $La(C_5Me_4H)_3$ was reduced with KC_8, $\{(C_5Me_4H)_2La(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**14**) was obtained. With the La(III) precursor $[Cp^*{}_2La][(\mu\text{-}Ph)_2BPh_2]$, reduction with KC_8 provided $\{Cp^*{}_2La(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**15**) in 93% yield. The N−N bond length was found to be 1.233(5) Å, corresponding to reduction to N_2^{2-}, and a singlet at δ 569 ppm was observed by ${}^{15}N$ NMR spectroscopy. The story of the



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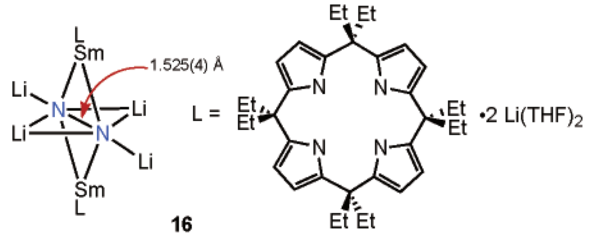
discovery of these dinuclear side-on lanthanide N_2 complexes has been recounted.[27] A very recent report details the preparation of the elusive lutetium(III) analogue $Lu(C_5Me_4H)_3$ and its conversion to $\{(C_5Me_4H)_2Lu(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ via reaction with KC_8 under N_2.[28] The bonding of N_2 to lanthanide metallocenes has also been recently investigated using DFT calculations.[29] The authors found that electron transfer from two Ln(II) ions to N_2 occurs to give the Ln^{3+}/N_2^{2-} complex. Although coplanar side-on binding of N_2 appears to be ubiquitous for this diverse group of compounds, further investigations may be necessary to understand their bonding, as well as the source of the anomalously short N−N bond in the original disamarium derivative **4**.

An interesting new type of side-on N_2 complex was reported in 1994 with the publication of the second lanthanide−N_2 compound. In a one-pot synthesis, a samarium tetrapyrrolide complex was prepared from $\{[Et_2C(\alpha\text{-}C_4H_2N)]_4\}Li_4(THF)_4$ and $SmCl_3(THF)_3$ and reduced with Li metal under N_2. From the reaction mixture, $[(THF)_2Li\{[Et_2C(\alpha\text{-}C_4H_2N)]_4\}Sm]_2(N_2Li_4)$ (**16**) was isolated. The crystal structure of **16** showed N_2 encapsulated in an Sm_2Li_4 octahedron; N_2 was bound side-on to two Sm and two Li ions and end-on to two Li ions. The N−N bond length of 1.525(4) Å is extremely long and corresponds to reduction to N_2^{4-}, or hydrazido.[30] When the ligand was changed to the closely related tetrapyrrolide ligand $[(CH_2)_5C(\alpha\text{-}C_4H_2N)]_4$, small quantities of the red labile side-on Sm_2N_2 complex $[\{[(CH_2)_5C(\alpha\text{-}C_4H_2N)]_4\}Sm[Li(THF)]_3(\mu_3\text{-}Cl)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)(THF)_2$ (**17**) formed from the deep green Sm(II) reduction product $[\{[(CH_2)_5C(\alpha\text{-}C_4H_2N)]_4\}Sm(THF)][Li(THF)]_2[Li(THF)_2](\mu_3\text{-}Cl)$ (**18**).[31] Dissolution of **17** regenerated **18** and 1 equiv of free N_2. The weak activation of N_2 in **17** was supported by the crystal structure, which showed N_2 side-on bound with an N−N bond length of 1.08(3) Å, nearly the same as the value for free N_2 within experimental error.



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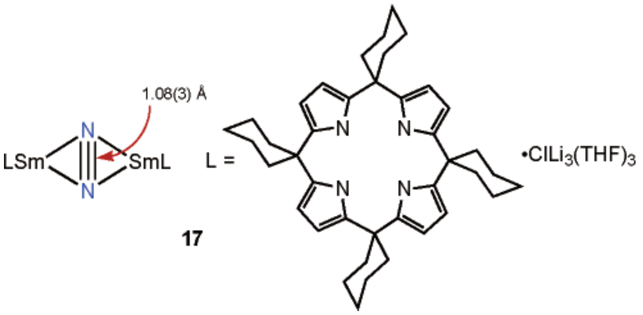

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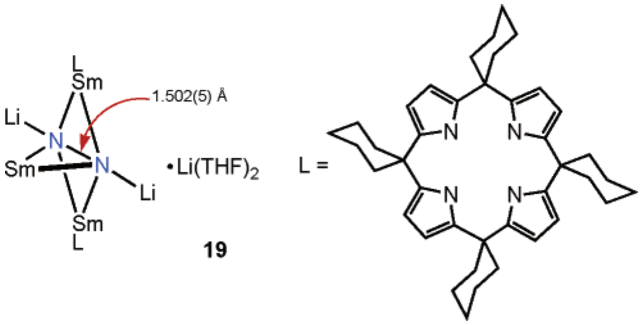
When solutions of **18** were concentrated under N_2, a strongly activated Sm_3N_2 complex could be obtained. The crystal structure of $[\{[(CH_2)_5C(\alpha\text{-}C_4H_2N)]_4\}_2Sm_3Li_2](\mu\text{-}N_2)[Li(THF)_2](THF)$ (**19**) featured N_2 bound side-on to three Sm atoms and end-on to two Li centers with an N−N bond length of 1.502(5) Å. Some effort has been made to unravel these complex reactions.[32]



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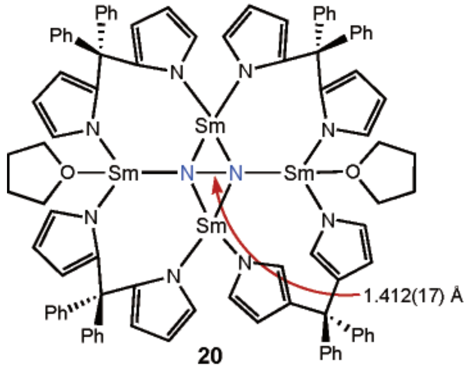
When dipyrrolide ligands were used instead of tetrapyrrolides, Sm(II) was once again observed to transform N_2 to N_2^{4-}. The reaction of $K_2[\mu\text{-}Ph_2C(\alpha\text{-}C_4H_3N)_2]$ with $SmI_2(THF)_2$ under N_2 gave the dinitrogen complex $\{[\mu\text{-}Ph_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)(THF)_2$ (**20**) in high yield. The N_2 unit is bound to four samarium atoms, side-on to two and end-on to two others as shown, to generate a Sm_4N_2 coplanar array. The N−N bond length is 1.412(17) Å.[33] A similar complex with coordinated Na ions was synthesized shortly thereafter by two different routes. Deprotonation of 1,1-dipyrrolylcyclohexane with KH, followed by reaction with $SmCl_3(THF)_3$, gave a yellow solution. Reduction with excess Na and catalytic naphthalene produced



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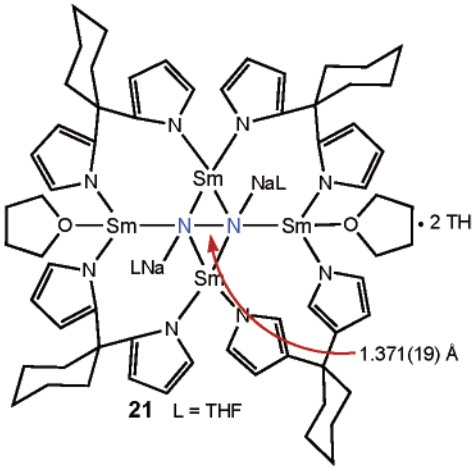

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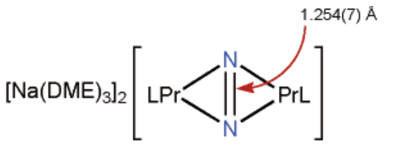
$\{[(CH_2)_5C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)[Na(THF)]_2(THF)_2$ (**21**). The crystal structure of **21** featured N_2 side-on bound to two Sm atoms, end-on bound to two other Sm centers, and interacting with two THF-solvated Na cations. The N−N bond length was 1.371(19) Å. A dinitrogen complex was also produced in high yield from the Sm(II) starting material, $[(Me_3Si)_2N]_2Sm(THF)_2$, and 1,1-dipyrrolylcyclohexane in THF. $\{[(CH_2)_5C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_{2.5}(\mu\text{-}N_2)$ (**22**) contains N_2 coordinated side-on to two samariums and end-on to two other Sm centers, similar to the case for **20**. The N−N bond length is 1.392(16) Å, as found by crystallography. A second route to **21** was found when THF solutions of **22** were stirred with 2 equiv of Na sand.[34] In fact, further transformations of **22** were possible; addition of excess Na to THF solutions of **22** gave a linear polymer of dipyrrolide Sm(II) units in low yield.[35]

$[(Me_3N)_2Si]_2Sm(THF)_2$ proved to be a versatile Sm(II) starting material for the preparation of Sm−N_2 complexes. When $[Et_2C(\alpha\text{-}C_4H_3NH)_2]$ was added to a THF solution of $[(Me_3N)_2Si]_2Sm(THF)_2$ under N_2, $[\{[Et_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_2](\mu\text{-}N_2)(THF)_2$ (**23**) was obtained; its crystal structure showed N_2 bound side-on to two Sm atoms and end-on to two Sm atoms similar to the case for compound **20**, with an N−N bond length of 1.415(3) Å. The same route was used to prepare a Sm_4N_2 complex, **24**, having $[PhMeC(\alpha\text{-}C_4H_3N)_2]$ as ancillary ligands and having a similar structure.[36] The reduction of N_2 on multimetallic frameworks was reviewed recently.[1b]

In 1998, lanthanide tetrapyrrolide complexes of Pr and Nd were also shown to activate dinitrogen. The reaction of $[\{[Et_2C(\alpha\text{-}C_4H_2N)]_4\}M(THF)][Na(THF)_2]$ (M = Pr, Nd) with sodium and substoichiometric naphthalene under N_2 provided the side-on-bound N_2 complexes upon crystallization. The crystal structure of complex **25** (M = Pr) features the pyrrole units bound η^1 and η^5 to Pr, with a coplanar Pr_2N_2 motif and an N−N bond length of 1.254(7) Å. Complex **26** (M = Nd) also contain η^1:η^5-bound pyrrole, with N_2 side-on bound to Nd. Two Na ions are also bound to N_2 and pyrrole, and the N−N bond length is 1.234(8) Å.[37] Thus, N_2 is reduced to N_2^{2-} in these complexes.



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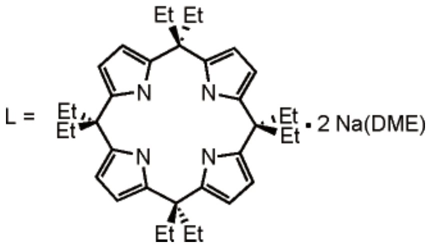
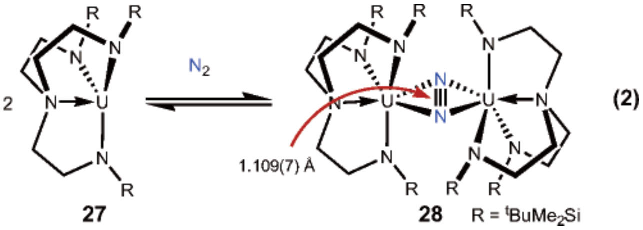


Since the original publication of the disamarium N_2 derivative **4** in 1988, side-on binding of N_2 has been found to be ubiquitous for lanthanide complexes. The coordinated N_2 unit varies from unactivated to highly activated, and there will likely be many more reports of N_2 coordination using Ln_2N_2 frameworks. Research into other aspects of lanthanide dinitrogen chemistry also continues. For example, side-on coordination of N_2 to lanthanides has also been observed by IR spectroscopy using matrix isolation techniques.[38]

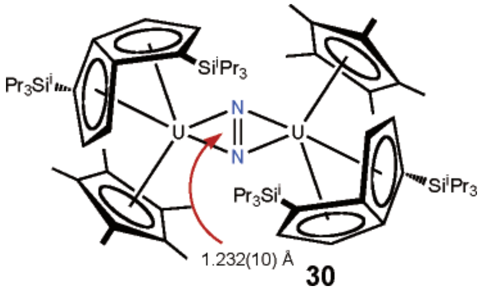
Side-On N_2 Complexes of the Actinides

The first actinide dinitrogen complex was reported in 1998.[39] Reduction of $[N_3N]UCl$ ($[N_3N] = N(CH_2CH_2NSi^tBuMe_2)_3$) with potassium in pentane produced a U(III) complex, $[N_3N]U$ (**27**) upon sublimation. Under 1 atm of N_2, $\{[N_3N]U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**28**) formed (eq 2). N_2 binding was reversible; under vacuum **27** was regenerated. At 1.109(7) Å, the N−N bond length is essentially unchanged from that of free dinitrogen. UV/visible spectroscopy and magnetic susceptibility measurements suggest that U(III) centers are present in **28** and that N_2 coordination does not increase the oxidation state of uranium.



Although these results would imply that the π bond of N_2 is a σ donor to U, a follow-up report showed that π back-bonding from U to N_2 was the only important U−N bonding interaction.[40] The model compound $[(NH_2)_3(NH_3)U]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**29**) was investigated by density functional theory (DFT), which showed that the π bonding MO of N_2 was too low in energy to overlap significantly with U; σ bonding was negligible in **29**. Even a DFT investigation into the triatomic compound UN_2 indicated that U(5f)→$N_2(\pi_g)$ back-bonding was the most important interaction if the N_2 unit was constrained to be side-on to U.[41] In fact, the N−N bond length in **28** may be so short because of steric factors. Although π back-bonding in **28** is expected to increase the N−N bond length and decrease the U−N bond length, the bulky $[N_3N]$ ligand may hinder the overlap of U f and N_2 π* orbitals. As expected, in the absence of ancillary ligand effects, **29** has longer N−N and shorter U−N bond lengths than **28**.[42]

An example of a side-on actinide N_2 complex that typifies **B** in Table 1 was reported in 2002.[43] In $\{Cp^*U(C_8H_4(Si^iPr_3)_2)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**30**) the N−N bond length is 1.232(10) Å. Despite the moderate activation of N_2 in **30**, its formation is reversible



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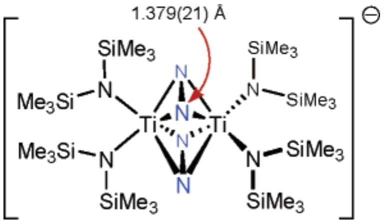
and the starting complex $Cp^*U(C_8H_4(Si^iPr_3)_2$ is regenerated under vacuum. DFT calculations on the model complex $[U_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)(\eta^5\text{-}Cp)(\eta^8\text{-}C_8H_6)_2]$ again indicated that U(5f)→$N_2(\pi_g)$ π back-bonding is substantial.[44] In fact, not only is the bonding in **30** reminiscent of that in **28** but also the U−N bond lengths are the same as well (**30**, 2.401(8)−2.423(8) Å; **28**, 2.394(5)−2.446(5) Å). Further physical and theoretical investigations may be required to get to the root of the different degrees of N_2 activation observed for these two compounds.

In contast to the lanthanide dinitrogen complexes, for which side-on dinuclear bonding appears for now to be ubiquitous, actinide dinitrogen chemistry is diverse. Since the first report of nitrogen fixation by a poorly characterized organometallic uranium complex reduced with lithium naphthalenide,[45] a heterodinuclear U−N_2 compound,[46] a mononuclear end-on U−N_2 compound,[47] and N_2 cleavage by a U compound[48] and by a Th compound[49] have all been reported.

Side-On N_2 Complexes of the Transition Metals

Since the discovery[20] of $([PNP]ZrCl)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**5**), numerous transition-metal complexes with side-on-bound N_2 have been reported. What follows is an attempt to document the examples of side-on dinitrogen complexes for the d-block elements. In the early 1990s and continuing on to the present, speculation on the binding mode of N_2 in nitrogenase has been an active area of inquiry. While still a matter of conjecture, there have been proposals that suggest side-on-bound N_2 to the Fe centers in the Fe/Mo cofactor of nitrogenase is possible.[50]

In 1991, an intriguing set of dinitrogen complexes was discovered and showed how capricious the bonding mode of N_2 could be.[51] The dinuclear end-on N_2 complex $\{[(Me_3Si)_2N]TiCl(TMEDA)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (**31**; TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) can be isolated from the reaction of *trans*-$(TMEDA)_2TiCl_2$ and 1 equiv of $(Me_3Si)_2NLi$ in toluene under N_2. The N−N bond length is 1.289(9) Å. When the same starting material, *trans*-$(TMEDA)_2TiCl_2$, is mixed with 2.5 equiv of $(Me_3Si)_2NLi$ and an excess of TMEDA in toluene under N_2, dark purple crystals of $[Li(TMEDA)_2]\{[\{(Me_3Si)_2N\}_2Ti]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)_2\}$ (**32**) form; the anion is shown. To date, complex **32** is unique in that it features two molecules of N_2 bound side-on to two Ti centers. The N−N bond lengths in **32** are 1.379(21) Å.



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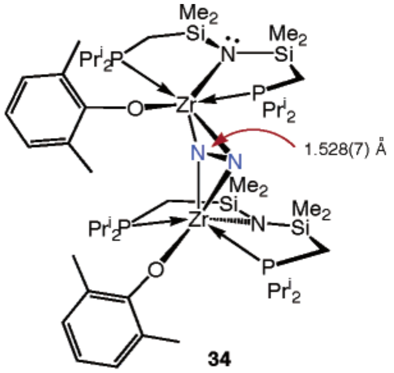
After the discovery of $([PNP]ZrCl)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**5**) in 1990, other zirconium−[PNP] dinitrogen complexes were prepared to determine the effect of ligand substitution on the structure and properties.[52] When $ZrCl_2(\eta^5\text{-}C_5H_5)[PNP]$ is reduced with Na/Hg amalgam under N_2, $([PNP]ZrCp)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**33**) is formed, wherein the dinitrogen is coordinated end-on to the two zirconium centers and the N−N bond length is 1.301(3) Å.[53] The N_2 moiety may be end-on in **33** rather than side-on because the replacement of the chloride for the π donor ligand Cp has made the d orbitals required for δ bonding unavailable; in addition, steric effects may also be important. In contrast, the reduction of $Zr(O\text{-}2,6\text{-}Me_2\text{-}C_6H_3)Cl_2[PNP]$ with Na/Hg amalgam under N_2 gives $\{[PNP]Zr(O\text{-}2,6\text{-}Me_2\text{-}C_6H_3)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**34**) in 40% yield. The solid-state structure of **34** reveals that N_2 is bound side-on to Zr with an N−N bond length of 1.528(7) Å. In contrast to **5**, the Zr_2N_2 core in **34** is not planar but has a butterfly or hinge distortion similar to **D** in Table 1; the angle between the two ZrN_2 planes is 156°. A peak at 751 cm^{-1} in the resonance Raman spectrum of **34** was assigned as the symmetric ν(N−N) vibration mode and is consistent with a long N−N bond.



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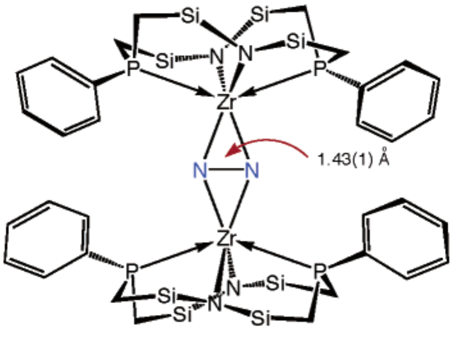

35 (Me's on Si omitted)

A second hard amido donor was incorporated into the ligand framework by synthesizing the macrocyclic bis(amidophosphine) ligand $[P_2N_2]$ ($[P_2N_2]$ = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$).

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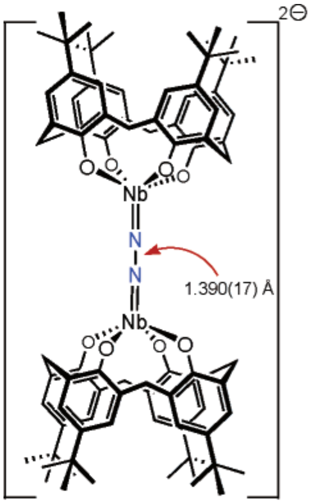
When $[P_2N_2]ZrCl_2$ is reduced with 2 equiv of KC_8 under N_2, dark blue $([P_2N_2]Zr)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**35**) forms. The N_2 unit is bound side-on in the planar Zr_2N_2 core with an N−N bond length of 1.43(1) Å;[54] detailed Raman and IR studies have been reported for **35**.[55] The reactivity of **35** will be discussed in the following section.

Side-on N_2 complexes have also been implicated as intermediates in the cleavage of N_2 by a niobium calixarene. In 1998, a communication[56] detailed how the end-on N_2 diniobium complex $[\{[p\text{-}^t\text{Bu-calix[4]-(O)}_4]\text{Nb}\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)][\text{Na(diglyme)}_2]_2$ (**36**) was converted to the bis(μ-nitrido) complex $\{[p\text{-}^t\text{Bu-calix[4]-(O)}_4]\text{Nb}\}_2(\mu\text{-N})_2[\text{Na(DME)}]_4$ upon reaction with sodium metal in THF. In a later full paper,[57] the side-on N_2 complex $[\{[p\text{-}^t\text{Bu-calix[4]-(O)}_4]\text{Nb}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)][\text{Na(DME)}]_4(\text{DME})$ (**37**), a possible intermediate in the N−N cleavage reaction, was prepared from **36** and Na in DME and was characterized by X-ray diffraction. The structure of **37** features N_2 bound side-on and perpendicular to a Nb−Nb bond and associated with three Na ions. The N−N bond length is 1.403(8) Å. Since the N−N bond length did not increase from the end-on complex **36** to the side-on complex **37**, it is apparent that the role of Na is to reduce Nb(V) to Nb(IV). The formation of the metal−metal bond forces N_2 out of the Nb_2 axis to become side-on bound. Upon heating, complex **37** yields a bis(μ-nitrido) product.



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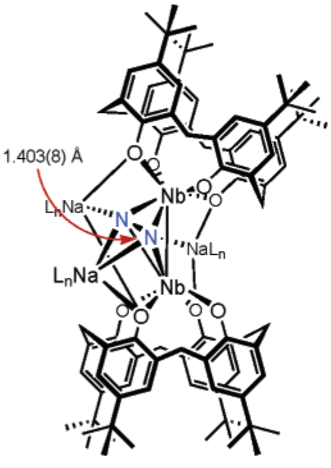

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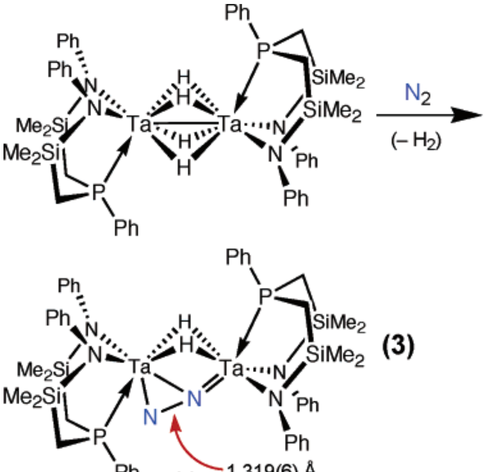
The side-on−end-on bonding mode of N_2 in a dinuclear complex has been reported for [NPN] (where $[\text{NPN}] = \text{PhP}(\text{CH}_2\text{SiMe}_2\text{NPh})_2$) complexes of tantalum.[58] When solutions of $[\text{NPN}]\text{TaMe}_3$ are exposed to hydrogen gas, the dinuclear tetrahydride $([\text{NPN}]\text{Ta})_2(\mu\text{-H})_4$ is produced. Surprisingly, this tetrahydride derivative was found to react with N_2 to give $([\text{NPN}]\text{Ta})_2(\mu\text{-H})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}N_2)$ (**38**) with loss of H_2 (eq 3). In **38**, the N_2 is bound side-on to one Ta and end-on to the other and shows a moderately activated dinitrogen unit with an N−N bond length of 1.319(6) Å. This reaction is remarkable for two reasons. First, hydrogen gas is the relatively mild reducing agent responsible for generating the highly reducing tetrahydride dimer, thus avoiding the use of strong alkali-metal reductants (e.g., KC_8, Na) or highly reducing metal starting materials (e.g., Sm(II)) for N_2 activation. Second, this is a rare example[59] of an early-transition-metal hydride complex that coordinates N_2 via displacement of H_2, although this reactivity is known for late transition metals.[60]

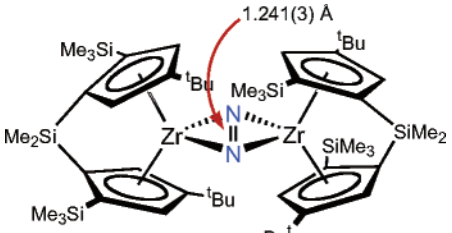


(3)

38

The IR and resonance Raman spectra of **38** were analyzed using quantum-chemistry-based normal-coordinate analysis, which confirmed that the side-on−end-on N_2 is considerably activated in this complex.[61] The N−N stretching frequency is 1165 cm^{-1}. From the force constants found, the coordinated N_2 is considerably weakened (2.430 mdyn $Å^{-1}$) compared to N_2 gas (22.42 mdyn $Å^{-1}$) and even hydrazine (4.3 mdyn $Å^{-1}$). The end-on Ta2−N2 bond was found to be stronger (2.517 mdyn $Å^{-1}$) than the side-on Ta−N_2 interaction (Ta−N1, 1.291 mdyn $Å^{-1}$; Ta1−N2, 0.917 mdyn $Å^{-1}$).

In 2001, another example of an early-transition-metal hydride coordinating and activating N_2 was reported.[62] The side-on Zr_2N_2 complex $[\{rac\text{-Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_2\text{-2-SiMe}_3\text{-4-}^t\text{Bu})_2\}\text{Zr}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, $(rac\text{-BpZr})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**39**), was synthesized from *rac*-BpZrH_2 and N_2 gas; *rac*-BpZrH_2 was prepared from *rac*-BpZrMe_2 and H_2 gas. The crystal structure of **39** shows that N_2 is bound side-on in a planar Zr_2N_2 core with an N−N bond length of 1.241(3) Å. In other words, N_2 is reduced to N_2^{2-}. The asymmetry in the Zr−N bond lengths and the presence of N_2^{2-} led the authors to conclude that Zr(III) centers are present.



39

An intermediate in the formation of a zirconocene−N_2 complex was discovered in 2003.[63] The addition of 2 equiv of ^{t}BuLi to $\text{Cp}''\text{ZrCl}_2$ ($\text{Cp}'' = 1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3$) generates the side-

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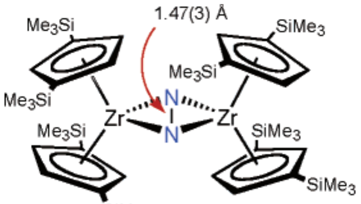
on Zr_2N_2 complex $[Cp''_2Zr]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**40**). It has an N−N bond length of 1.47(3) Å, the longest that has been observed for any metallocene−N_2 complex. Complex **40** is paramagnetic with two Zr(III) centers. The formation of **40** was followed by NMR spectroscopy. At low temperature, $Cp''_2Zr(H)Cl$, excess ^tBuLi and free isobutylene were observed. When the sample was warmed to −10 °C, $Cp''_2Zr(H)(CH_2CHMe_2)$ formed quantitatively. The zirconocene alkyl hydride then eliminates isobutene to give the cyclometalated zirconocene hydride $\{(Cp'')[\eta^5\text{-}(Me_3Si)C_5H_3\text{-}3\text{-}\mu\text{-}SiMe_2CH_2]ZrH\}$ (**41**), which reacts with N_2 to produce the side-on dinitrogen complex **40**. Although attempts to isolate **41** as a solid failed, preparation of **40** via this masked low-valent zirconocene represents a new pathway to side-on N_2 complexes. The authors also described related cyclometalated zirconocene hydrides, such as $\{(Cp^*)[\eta^5\text{-}(Me_3Si)C_5H_3\text{-}3\text{-}\mu\text{-}SiMe_2CH_2]ZrH\}$, that are inert to exposure to N_2. Thus, the synthesis and reactivity of zirconocene dinitrogen complexes seem to be sensitively dependent on the Cp ring substituents.



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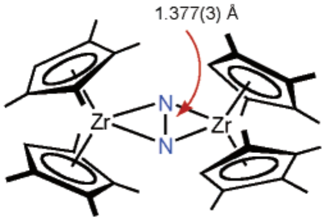
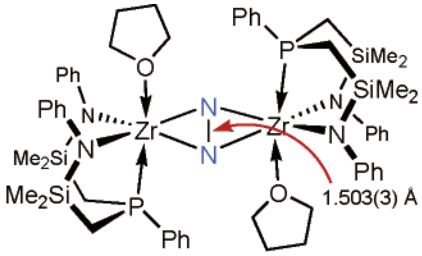


42

In 1974, the reduction of $Cp^*_2ZrCl_2$ to form $[Cp^*_2Zr(\eta^1\text{-}N_2)]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$, in which N_2 was bound in the end-on terminal and bridging modes, was reported.[64] With a slight modification to the ancillary ligand, from pentamethyl to tetramethyl, N_2 was observed to coordinate in the side-on dinuclear mode. Thus, the reduction of $(\eta^5\text{-}C_5Me_4H)_2ZrCl_2$ with Na/Hg amalgam under N_2 gave $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**42**).[65] The crystal structure of **42** showed N_2 bound side-on to Zr in a planar Zr_2N_2 unit with an N−N bond length of 1.377(3) Å. The two zirconocene ends in **42** are also canted with respect to each other; the dihedral angle between the $(C_5Me_4H)_2Zr$ ends is 65.3°. The presence of just one additional methyl group per zirconocene causes the end-on N_2 product to form; reduction of $Cp^*(C_5Me_4H)ZrI_2$ with KC_8 yielded $[Cp^*(C_5Me_4H)Zr(\eta^1\text{-}N_2)]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ (**43**).[66] Thus, the bulkier Cp* ligand prevents the formation of a side-on N_2 complex. Very recently, the hafnium analogue of **42**, namely $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, has been prepared and structurally characterized;[67] the N−N bond length in the hafnium complex is 1.423(11) Å, slightly elongated when compared to the distance of 1.377(3) Å reported for the zirconium congener **42**.

While most of the discussion on side-on N_2 has been with multinuclear metal complexes, there is evidence for a metastable mononuclear side-on N_2 complex of Os(II). When single crystals of $[(H_3N)_5Os(\eta^1\text{-}N_2)][PF_6]_2$ are photolyzed, isomerization to generate some of the side-on derivative $[(H_3N)_5Os(\eta^2\text{-}N_2)][PF_6]_2$ is observed.[68] Analysis of X-ray crystallography and IR spectroscopy confirmed the presence of the side-on isomer. Although any change in the N−N bond length was within the error limits for the structure, the Os−N(N_2) bond lengths increased by 0.263(17) Å for the side-on complex compared to the Os−N_α(N_2) first observed. The N−N stretching frequency is 187 cm^{-1} lower for the η^2-N_2 species relative to the η^1-N_2 starting material, implying a decrease in the N_2 bond order. Detection of this species provides further support for investigations into the end-to-end rotation mechanism of N_2 isomerization in η^1-N_2 complexes. For example, ^{15}N NMR spectroscopy was used to show that intramolecular nondissociative isomerization occurs in $Cp'Re(CO)(L)(^{15}N^{14}N)$ (for Cp′ = Cp, L = CO; for Cp′ = Cp*, L = CO, PMe_3, $P(OMe)_3$) via the side-on η^2-N_2 intermediate.[69] This also confirms the findings originally reported for the Ru(II) ion $[Ru(NH_3)_5N_2]^{2+}$ mentioned previously.[10]

Very recently,[70] the [NPN] discussed in eq 3 has been applied to Zr(IV) to generate side-on-bound N_2 complexes. Reduction of $[NPN]ZrCl_2$ with 2 equiv of KC_8 in THF under N_2 gives the purple complex $\{[NPN]Zr(THF)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**44**) in 87% yield. The crystal structure shows that N_2 is bound side-on with an N−N bond length of 1.503(3) Å. The reactivity of **44** is currently being investigated.



44

Reactivity of Side-On Dinitrogen Complexes

Prior to 1997, there were very few reports on the reactivity of side-on N_2 complexes, and what was in the literature was limited to protonation studies where variable amounts of hydrazine were detected. In fact, as will be seen below, only those side-on N_2 complexes from the d-block elements have shown any reactivity of the coordinated N_2 unit; it is notable that none of the numerous lanthanide side-on dinitrogen complexes mentioned above have shown any reactivity patterns to date that involve the N_2 moiety.

The first example of a side-on N_2 complex that showed functionalization of coordinated dinitrogen was $([P_2N_2]Zr)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**35**) in 1997. When **35** is stirred under H_2 for an extended period, $([P_2N_2]Zr)_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H)$ (**45**) is formed. The single-crystal X-ray data were originally interpreted in error as having side-on-bound μ-H_2 and μ-N_2 units.[54] However, the solid-state structure determined by neutron diffraction provided

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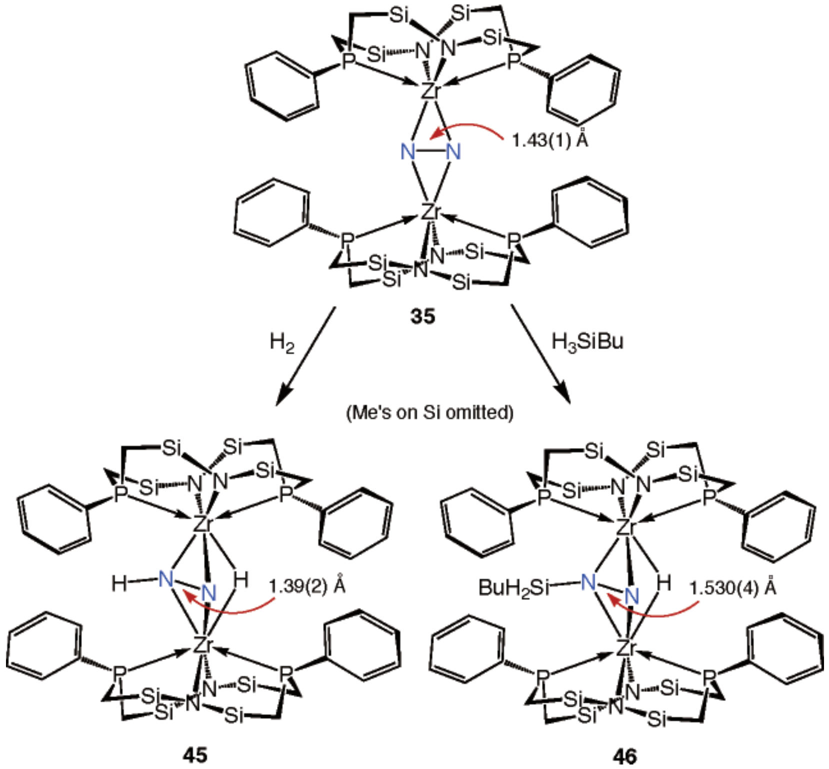
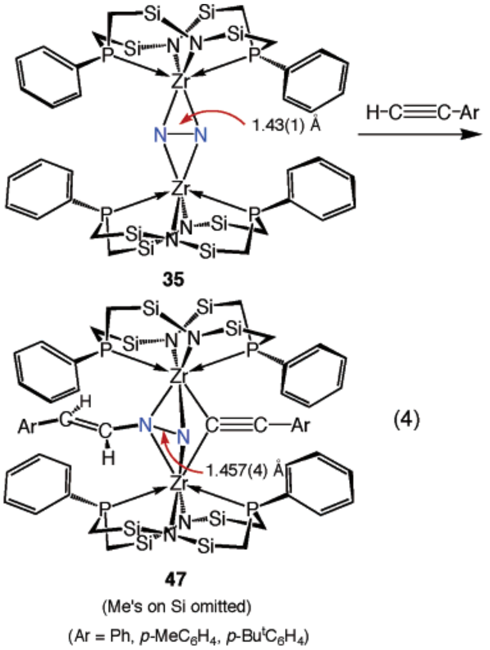
Scheme 1



the correct assignment, wherein bridging hydride, Zr(μ-H)Zr, and bridging diazenido units, Zr(μ-η^2:η^2-N_2H)Zr, are present.[71] The NNH moiety is oriented side-on to both Zr atoms with an N−N bond length of 1.39(2) Å and an N−H bond length of 0.93(6) Å. The neutron structure is consistent with the solution structure observed by NMR spectroscopy. In a similar fashion, a new N−Si bond is observed upon addition of ^{n}BuSiH$_3$ to **35**. Yellow crystals of ([P_2N_2]Zr)$_2$(μ-H)(μ-η^2:η^2-$N_2Si(H)_2{}^nBu$) (**46**) were found to have a side-on-bound NNSi(H)$_2{}^n$Bu moiety with an N−N bond length of 1.530(4) Å, slightly longer than in **35**.[54] This is summarized in Scheme 1.

The hydrogenation and hydrosilylation of **35** to generate **45** and **46**, respectively, represent new kinds of transformations for coordinated dinitrogen that transcend the typical reaction with electrophiles found with end-on dinitrogen complexes. The formation of a new N−H bond in **45** was the first-ever observation of this kind of reaction; typically, the addition of H_2 to an N_2 complex leads to N_2 displacement. These new transformations of coordinated N_2 were investigated computationally by DFT calculations[72] on the model complex ([p_2n_2]$_2$-Zr)$_2$(μ-η^2:η^2-N_2) ([p_2n_2] = $(PH_3)_2(NH_2)_2$). The reaction of the model side-on N_2 complex with both H_2 and SiH_4 was found to be thermodynamically favorable and to proceed via a σ bond metathesis type transition state. In addition, for the hydrogenation studies, the computational results suggested that a second equivalent of H_2 should be able to add to generate ([p_2n_2]Zr)$_2$-(μ-η^2:η^2-N_2H_2)(μ-H)$_2$.[73] Although this latter result has not been confirmed experimentally with **35**, such a transformation has been observed for other dinuclear zirconium dinitrogen complexes (see below).

Another unprecedented transformation for coordinated dinitrogen was the reaction of **35** with terminal alkynes to generate new N−C bonds.[74] The addition of 2 equiv of ArCCH (Ar = Ph, *p*-MeC$_6$H$_4$, *p*-^{t}BuC$_6$H$_4$) to **35** results in the formation of ([P_2N_2]Zr)$_2$(μ-CCR)(μ-η^2:η^2-$N_2C(H){=}C(H)Ar$) (**47**). For Ar = *p*-MeC$_6$H$_4$, the single-crystal structure indicates the presence of a bridging acetylide and a side-on-bound *p*-methylstyryl−hydrazido unit with an N−N bond distance of 1.457(4) Å. The proposed mechanism invokes an initial 2 + 2 cycloaddition of the terminal alkyne across the Zr−N bond of the Zr(μ-η^2:η^2-N_2)Zr core of **35** to generate a zirconaazacyclobutene intermediate, followed by Zr−C bond cleavage via a proposed protonation (from the second ArCCH). This two-step process is expected to yield the alkene unit with the observed *E* stereochemistry and a bridging alkyne.



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(71) Basch, H.; Musaev, D. G.; Morokuma, K.; Fryzuk, M. D.; Love, J. B.; Seidel, W. W.; Albinati, A.; Koetzle, T. F.; Klooster, W. T.; Mason, S. A.; Eckert, J. *J. Am. Chem. Soc.* **1999**, *121*, 523.

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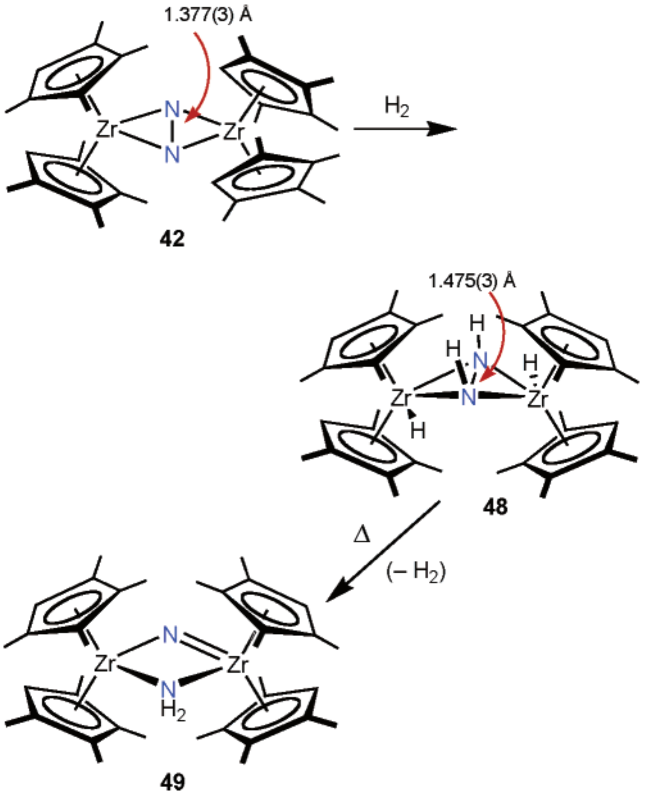
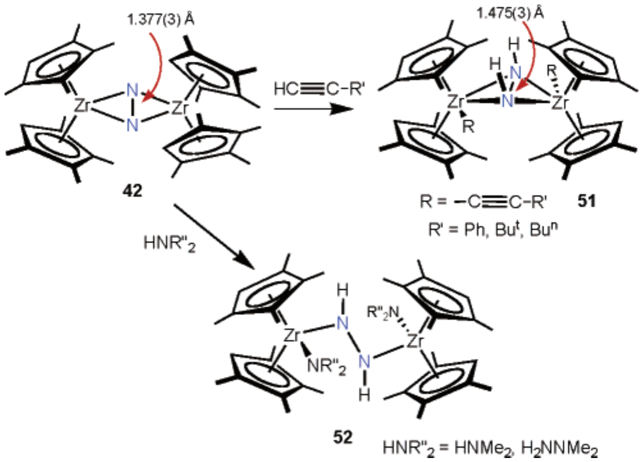
Scheme 2



Scheme 3



Recently, the formation of new N−H bonds was also observed for the zirconocene dinitrogen complexes with side-on-bound N_2.[65] When $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**42**) is exposed to H_2, the dinuclear product $[(\eta^5\text{-}C_5Me_4H)_2Zr(H)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H_2)$ (**48**) is produced, which features a side-on-bound diazenido unit with an N−N bond length of 1.475(3) Å, as well as two new Zr−H bonds (Scheme 2). This reaction is the first example of the hydrogenation of a well-defined transition-metal−N_2 complex to produce a transition-metal-bound diazenido species, $N_2H_2^{2-}$. Heating complex **48** in the presence of hydrogen produces a small amount of ammonia, while heating **48** in the absence of H_2 generates $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu\text{-}N)(\mu\text{-}NH_2)$ (**49**), in which the N−N bond is cleaved. This discovery illustrates how a small change to an ancillary ligand (i.e., one fewer methyl substituent as compared to Cp*) can impact not only the extent of activation of coordinated N_2 but also the reactivity of the N_2 complex. The use of $\eta^5\text{-}C_5Me_4H$ ligands has enabled the formation of new N−H bonds, a rare transformation, rather than the extrusion of N_2 observed upon reaction of $[Cp^*_2Zr(\eta^1\text{-}N_2)]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ with H_2.[61] Predictably, $[Cp^*(C_5Me_4H)Zr(\eta^1\text{-}N_2)]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ (**43**), with end-on dinuclear N_2, gives a zirconocene dihydride upon addition of H_2. The continuing story of the Cp substituent effects on zirconocene−N_2 complex reactivity was recounted recently.[75]

The mechanism of hydrogenation of side-on zirconocene−N_2 complexes has been investigated with the related N_2 complex $[(\eta^5\text{-}Cp^*)(\eta^5\text{-}C_5Me_3H_2)Zr]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**50**).[76] The reaction was found to be first order in H_2 and **50** with a large negative entropy of activation. The primary isotope effect indicates that H−H bond breaking is the rate-determining step. Together these observations are consistent with 1,2-addition of H_2 via an ordered transition state with simultaneous Zr−H and N−H bond formation. A similar kinetic analysis using the hafnium analogue of **42** showed a rate enhancement by a factor of 4.3 for the reaction of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ with H_2 to produce $[(\eta^5\text{-}C_5Me_4H)_2HfH]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H_2)$; the reason for the faster rate for Hf as compared to that for Zr is unclear and unexpected. DFT calculations were recently performed to probe the hydrogenation of the methyl-less model complex $[(\eta^5\text{-}C_5H_5)_2Zr]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.[77]

In addition to the hydrogenation of **42**, its reactivity with terminal alkynes, amines, alcohols, and water has been explored.[78] When 2 equiv of a terminal acetylene, R′CCH (R′ = Ph, ^{t}Bu, ^{n}Bu), is added to **42** at room temperature, C−H activation by the N_2 complex is observed. The zirconocene complex $[(\eta^5\text{-}C_5Me_4H)_2Zr(CCR')]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H_2)$ (**51**) features one η^1-acetylide per Zr and a bridging diazenido unit. The formation of N−H bonds from the reaction of an alkyne with a dinitrogen complex was previously unknown; its outcome stands in contrast to the alkyne cycloaddition observed for **35** to generate N−C bonds when amidophosphine ancillary ligands are used.[74] This difference may be linked to the greater bulk of the substituted cyclopentadienyl ligand that may hinder cycloaddition. The single-crystal structure was determined for the ^{t}BuCCH addition product. A side-on-bound diazenido ligand (**51**) is observed with an N−N bond length of 1.454(2) Å. Unfortunately, these terminal acetylide complexes are thermally robust to 115 °C; heating to 160 °C caused loss of alkyne and formation of unidentified Zr-containing products. Also, no exchange between coordinated acetylide and free acetylene could be observed by heating **51** with excess RCCH. From the mechanism postulated for the hydrogenation of **42**, 1,2-elimination of H_2 occurs before α-migration. Thus, the energy barrier to 1,2-elimination of alkynes may be too high for this mechanism to operate.

The reaction of **42** with water yields hydrazine and $(\eta^5\text{-}C_5Me_4H)_2Zr(OH)_2$.[78] In contrast, the addition of H_2O to $[Cp^*_2Zr(\eta^1\text{-}N_2)]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ produces free N_2 and $[Cp^*_2ZrH]_2(\mu\text{-}O)$.[79] The addition of excess EtOH to **42** gives hydrazine and

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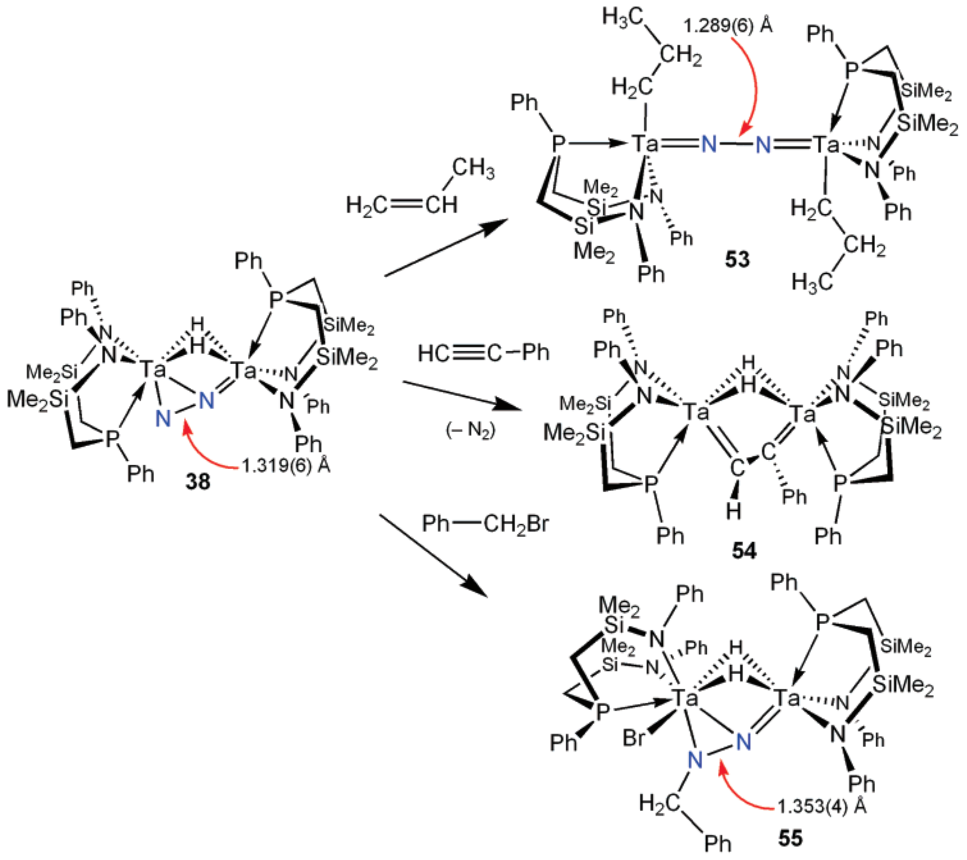
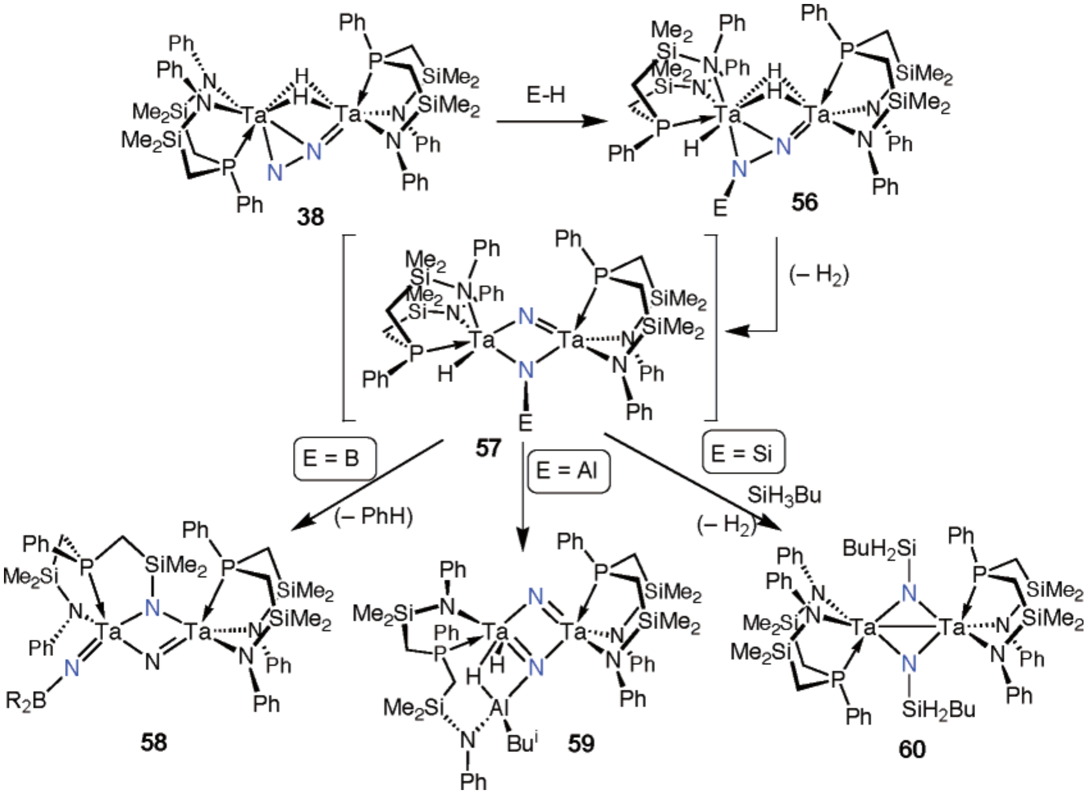
Scheme 4



Scheme 5



$(\eta^5\text{-}C_5Me_4H)_2Zr(OEt)_2$. When dimethylamine or 1,1-dimethylhydrazine is added to **42**, the end-on-coordinated diazenido complex $\{(\eta^5\text{-}C_5Me_4H)_2Zr(NR_2)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2H_2)$ (**52**; $NR_2 = NMe_2$, $NHNMe_2$) is formed (Scheme 3), which also yields hydrazine upon treatment with EtOH. In these latter reactions, the dinitrogen unit in **42** is acting as a strong base and deprotonating dimethylamine and 1,1-dimethylhydrazine, resulting in its transformation into a bridging diazenido unit.[78]

Table 2. Selection of Side-On N_2 Complexes and Related Species for Which N−N Bond Lengths Are Known, along with ^{15}N NMR Chemical Shifts and IR and Raman Data If Available

compd	^{15}N NMR (δ vs $MeNO_2$)[a]	bond length (Å)	ν(NN) (cm^{-1})[b]	ref
N_2	293.4[c,d]	1.0975(2)[e]	2331[f]	
trans-$PhN{=}NPh$	129.0[g]	1.255[h]	1441 (R)[i]	
H_2NNH_2	689.7[j]	1.47[k]	1111 (R)[l]	
$[\{(C_6H_5Li)_3Ni\}_2N_2(OEt)_2]_2$ (**1**)		1.35		13
$\{(C_6H_5)[Na(OEt_2)]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OEt)_4(OEt_2)_2\}_2$ (**2**)		1.359(18)		14
$(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}N_2)[\eta^5{:}\eta^5\text{-}C_{10}H_8)(\eta^5\text{-}C_5H_5)_2Ti_2][(\eta^1{:}\eta^1\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)_3Ti_2]$ (**3**)		1.301(12)	1282 ($^{15}N_2$: 1240) (IR)	17, 18
$[Cp^*{}_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**4**)		1.088(12)		8
$\{[PNP]ZrCl\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**5**)	619.9[m]	1.548(7)	731 (R)	20
$\{[C_5H_3(SiMe_3)_2]_2Tm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**7**)		1.259(4)		22
$\{[C_5H_4(SiMe_3)]_2Tm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**8**)		1.236(8)		22
$\{[(Me_3Si)_2N]_2Tm(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**10**)		1.264(7)		23
$\{[(Me_3Si)_2N]_2Dy(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**11**)		1.305(6)		23
$\{[O\text{-}2,6\text{-}{}^tBu_2C_6H_3]_2Nd(THF)_2]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**12**)		1.242(7)		23
$\{[(Me_3Si)_2N]_2Lu(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Lu**)	557.0			25
$\{[(Me_3Si)_2N]_2Y(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Y**)	513.3 ($J_{YN} = 7$ Hz)	1.268(3)		25
$\{[(Me_3Si)_2N]_2La(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-La**)	516			25
$\{[(Me_3Si)_2N]_2Nd(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Nd**)		1.258(3)		25
$\{[(Me_3Si)_2N]_2Gd(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Gd**)		1.278(4)		25
$\{[(Me_3Si)_2N]_2Tb(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Tb**)		1.271(4)		25
$\{[(Me_3Si)_2N]_2Dy(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Dy**)		1.305(6)		25
$\{[(Me_3Si)_2N]_2Ho(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Ho**)		1.264(4)		25
$\{[(Me_3Si)_2N]_2Er(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Er**)		1.276(5)		25
$\{[(Me_3Si)_2N]_2Tm(THF)]\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**13-Tm**)		1.261(4)		25
$[(C_5Me_4H)_2La(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**14**)	495.0	1.285(4)		26
$[(C_5Me_4H)_2Lu(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**14-Lu**)	521			28
$[Cp^*{}_2La(THF)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**15**)	569.1	1.233(5)		26
$[(THF)_2Li\{[Et_2C(\alpha\text{-}C_4H_2N)_4\}Sm]_2(N_2Li_4)$ (**16**)		1.525(4)		30
$[\{[(CH_2)_5C(\alpha\text{-}C_4H_2N)]_4Sm[Li(THF)]_3(\mu_3\text{-}Cl)]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)(THF)_2$ (**17**)		1.08(3)		31
$[\{[(CH_2)_5C(\alpha\text{-}C_4H_2N)]_4\}_2Sm_3Li_2](\mu\text{-}N_2)[Li(THF)_2]$ (THF) (**19**)		1.502(5)		31
$\{[\mu\text{-}Ph_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)(THF)_2$ (**20**)		1.412(17)		33
$\{[(CH_2)_5C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_2(\mu\text{-}N_2)[Na(THF)]_2(THF)_2$ (**21**)		1.371(19)		34
$\{[(CH_2)_5C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_{2.5}(\mu\text{-}N_2)$ (**22**)		1.392(16)		34
$[\{[Et_2C(\alpha\text{-}C_4H_3N)_2]Sm\}_4(THF)_2](\mu\text{-}N_2)(THF)_2$ (**23**)		1.415(3)		36
$\{(OEPG)Pr\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)[Na(DME)_3]_2$ (**25**)		1.254(7)		37
$\{(OEPG)Nd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)[Na(dioxane)]_2[Na(dioxane)_2]_2$ (**26**)		1.234(8)		37
$\{[N_3N]U\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**28**)		1.109(7)		39
$\{Cp^*U(C_8H_4(Si^iPr_3)_2)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**30**)		1.232(10)		43
$[Li(TMEDA)_2][\{[(Me_3Si)_2N]_2Ti\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)_2]$ (**32**)		1.379(21)		51
$([PNP]Zr(O\text{-}2,6\text{-}Me_2\text{-}C_6H_3)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**34**)	608.1	1.528(7)	751 ($^{15}N_2$: 725) (R)	52
$([P_2N_2]Zr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**35**)		1.43(1)	775 ($^{15}N_2$: 753) (R)	54, 55
$[\{[p\text{-}{}^tBu\text{-}calix[4]\text{-}(O)_4]Nb\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)][Na(DME)]_4(DME)$ (**37**)	−30.6	1.403(8)		57
$([NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)$ (**38**)	−20.4, 163.6 ($^1J_{NN} = 21.5$ Hz)	1.319(6)	1165 (R)	58, 61
(*rac*-$BpZr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**39**)		1.241(3)		62
$[Cp''{}_2Zr]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**40**)[n]		1.47(3)		63
$[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**42**)	621.1	1.377(3)		65
$[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$	590.5	1.423(11)		67
$\{[NPN]Zr(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**44**)		1.503(3)		70

[a] Liquid $MeNO_2$ is δ 361 relative to aqueous NH_4^+ (5 M NH_4NO_3/2 M HNO_3). For more information on nitrogen NMR, see: Mason, J. *Chem. Rev.* **1981**, *81*, 205. [b] R = Raman; IR = infrared. [c] Originally δ −67.6 as referenced to NO_3^- in a 5 M solution of NH_4NO_3 in 2 M HNO_3. [d] Bradley, C. H.; Hawkes, G. E.; Randall, E. W.; Roberts, J. D. *J. Am. Chem. Soc.* **1975**, *97*, 1958. [e] *Tables of Interatomic Distances and Configurations in Molecules and Ions*; Chem. Soc. Spec. Publ. 11; Sutton, L. E., Ed.; The Chemical Society: London, 1958. [f] Medina, F. D.; Daniels, W. B. *J. Chem. Phys.* **1973**, *59*, 6175. [g] Lyèka, A. *Collect. Czech. Chem. Commun.* **1982**, *47*, 1112. [h] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1. [i] Schroetter, H. W.; Pollett, R.; Weissmann, C. *Naturwissenschaften* **1967**, *54*, 513. [j] Originally referenced to NO_3^-: Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 4904. [k] Sutton, L. E.; *Tables of Interatomic Distances and Configurations in Molecules and Ions*; Chem. Soc. Spec. Publ. 11; Sutton, L. E., Ed.; The Chemical Society: London, 1958. [l] Durig, J. R.; Bush, S. F.; Mercer, E. E. *J. Chem. Phys.* **1966**, *44*, 4238. [m] Originally measured as δ 350.92 referenced to formamide at δ 0. [n] Cp'' = 1,3-$(Me_3Si)_2C_5H_3$.

The dinuclear tantalum complex **38**, with a side-on−end-on bound dinitrogen, is remarkable in its breadth of reactivity. Some reactivity patterns involve just the bridging hydrides alone; for example, the reaction with propene results in migratory insertion and the formation of the propyl derivative and isomerization of the dinitrogen unit to end-on bridging in **53**.[80] With terminal alkynes such as phenylacetylene, the N_2 is displaced and the bridging bis(μ-alkylidene) species **54** is generated.[81] The coordinated N_2 unit in **38** can also react as a nucleophile, as evidenced by the reaction with benzyl bromide, in which the *N*-benzyl derivative $\{[NPN]Ta(\mu\text{-}H)\}_2(Br)\{\mu\text{-}\eta^1{:}\eta^2\text{-}NN(CH_2C_6H_5)\}$ (**55**) results;[80] this last complex has an N−N bond length of 1.353(4) Å, slightly elongated compared to that in the starting material **38**. These reactions are summarized in Scheme 4.

The reaction of **38** with boranes,[82] silanes,[83] and alanes[84] provided even more dramatic transformations. The addition of

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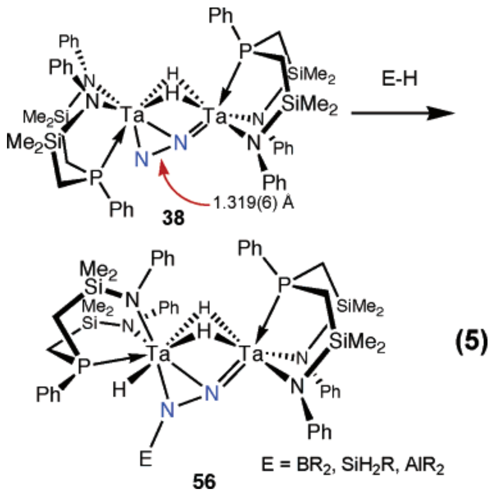
(79) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

(80) Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, *123*, 3960.

(81) Shaver, M. P.; Johnson, S. A.; Fryzuk, M. D. *Can. J. Chem.* **2005**, *83*, 652.

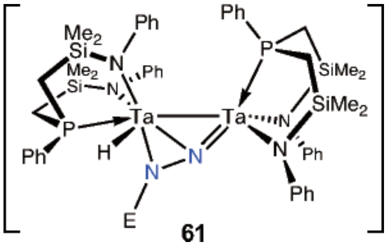
simple hydride reagents of the general formula E−H, where E−H = 9-BBN (HBR_2), DIBAL, H_3SiBu^n, all lead to the formation of the common intermediate ([NPN]TaH)(μ-H)$_2$(μ-η^1:η^2-N_2E)(Ta[NPN]) (**56**) as shown in eq 5. When E = BR_2, SiH_2Bu^n, this intermediate was characterized by X-ray crystallography and the structures confirm the solution spectroscopic data; for E = $AlBu^i{}_2$, the intermediate **56** could only be characterized at low temperature by NMR spectroscopy. This particular addition of E−H across the side-on−end-on N_2 unit of **38** is yet another new transformation of coordinated dinitrogen and also represents a starting point for further chemistry.



(5)

Depending on the nature of the simple organometallic hydride reagent E−H, solutions of the intermediate **56** have different outcomes. For the hydroborated products, the [NPN] ligand undergoes degradation and eventually results[82] in the formation of [(PhNSiMe$_2$CH$_2$P(Ph)CH$_2$SiMe$_2$-μ-N)Ta(=NBC$_8$H$_{14}$)](μ-N)-(Ta[NPN]) (**58**); this product is accompanied by elimination of benzene (from one of the N−Ph groups of the [NPN] and the B−H) and H_2 (from the bridging hydrides). A key aspect in the production of **58** is that the N−N bond has been cleaved and functionalized. Isolation of key intermediates along with specific labeling experiments allowed delineation of a probable mechanism for this process. The use of diisobutylaluminum hydride (DIBAL) results in N−N bond cleavage and functionalization as well, as evidenced by the isolation of ([NPN]TaH)-(μ-H)$_2$(μ-η^1:η^2-N_2Al(μ-H)^{i}Bu)(Ta[NPN]) (**59**);[84] interestingly, there is no ligand degradation in **59**; rather, one end of the [NPN] ancillary ligand migrates from Ta to Al. Also observed is elimination of 1 equiv of isobutene. The addition of butylsilane (H_3SiBu^n) results in the formation of the very symmetrical disilylimide species ([NPN]Ta)$_2$(μ-NSiH$_2$Bu^n)$_2$ (**60**).[83] Here again, N−N bond cleavage and functionalization have occurred, but in contrast to hydroboration and hydroalumination, no ancillary ligand degradation or rearrangement has occurred. These E−H addition reactions are summarized in Scheme 5.

Recently, additional mechanistic insight into these processes has been obtained via DFT calculations.[85] As shown in Scheme 5, the process that leads to N−N bond cleavage and the formation of intermediate **57** is triggered by H_2 elimination from the addition product **56**. Using the E = SiH_3 adduct, computational studies suggest that, prior to the formation of **57**, a species with a tantalum−tantalum bond such as **61** is a likely transition state. The electrons required for N−N cleavage to generate **57** are contained in the Ta−Ta bond.



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Conclusions and Future Prospects

This perspective has attempted to summarize a rather narrow area of dinitrogen coordination chemistry by discussing only those complexes in which the side-on-bonding mode of N_2 is present. What should be apparent is that this particular mode of ligation is no longer rare, as there are approximately 50 examples of complexes where side-on dinitrogen has been confirmed using X-ray crystallography (see Table 2). In terms of the extent of activation of the dinitrogen fragment, there are no obvious trends: complexes of the lanthanides show N−N bond lengths that range from unactivated to essentially N−N single bonds. Similarly, transition-metal complexes that display this side-on bonding mode also show wide variation in the extent of activation as measured by N−N bond distances, although in general, more complexes in this latter group approach the longer end of the activation scale.

What is very evident is that more investigations into the reactivity of the side-on dinitrogen moiety are warranted. In the cases described above, it is clear that new kinds of reactions have been discovered and these transformations of the N_2 unit seem to correlate with the bonding mode observed. Whether or not these reactivity patterns can be harnessed in some catalytic cycle to produce useful organonitrogen products remains to be seen. However, the future is bright for side-on N_2, at least from this perspective.

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[85] Studt, F.; MacKay, B. A.; Fryzuk, M. D.; Tuczek, F. *Dalton Trans.* **2006**, 1137.