Dinitrogen Functionalization

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Dinitrogen Activation by Group 4 Metal Complexes**

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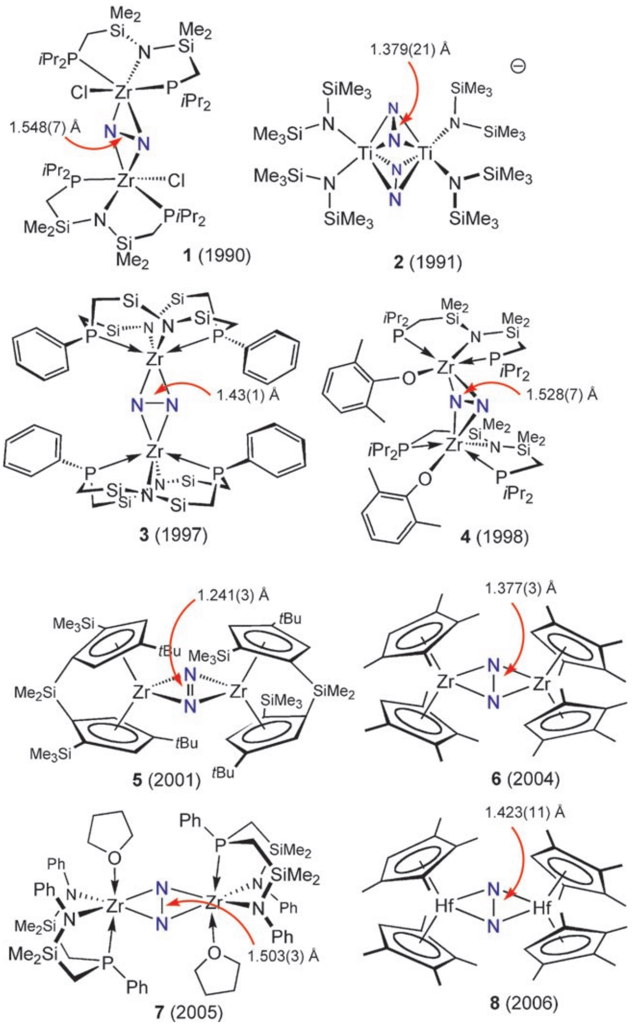
Activating molecular nitrogen by soluble metal complexes is a longstanding challenge in inorganic chemistry.[1] This simple, readily available small molecule is notoriously unreactive and generally resists coordination unless certain conditions are met. Since the first report of a dinitrogen complex in 1965,[2] much has been learned about bonding modes, methods of preparation, and reactivity patterns.[3–5] Yet what remains elusive is the discovery of a homogeneous catalytic process[6] that transforms molecular nitrogen into higher-value nitrogen-containing compounds. To be able to directly convert N_2 to N-heterocycles or amines would circumvent the energy-intensive Haber–Bosch process and represent a major breakthrough in energy saving and atom economy.[4]

Trying to design a catalytic cycle involving dinitrogen from first principles is fraught with difficulty.[6] As already mentioned, N_2 is not a good ligand and so binding is a problem, especially in the presence of other reagents that may be better donors. Even more troubling is the fact that there are not a lot of known reactivity patterns for a dinitrogen molecule coordinated to a metal complex.[5] But things are changing rapidly, and Group 4 metal complexes have figured prominently.

When suitably enticed, dinitrogen can bind to metal complexes in a variety of ways that range from end-on to one metal center ($[L_nM{-}N{\equiv}N]$), to a combination of side-on/end-on with two or more metal centers. For the Group 4 metals, a particularly prevalent mode of binding is side-on bridging,[5] represented as $[(L_nM)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$. The first example in Group 4 of this motif was the zirconium complex $[\{(PNP)ZrCl\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ (**1**; PNP = $N(SiMe_2CH_2P\mathit{i}Pr_2)_2$) reported in 1990.[7] Other examples of this coordination mode followed and are shown in Scheme 1, along with the years they



Scheme 1. Group 4 metal complexes with side-on bridging dinitrogen ligands. The Me groups on the macrocycle Si atoms in **3** have been omitted.

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were reported and N–N bond lengths as determined by single-crystal X-ray diffraction.[8–14] As can be seen from the complexes in this scheme, most have quite long N–N bond lengths, approaching or exceeding that normally associated with an N–N single bond (1.47 Å), which formally corresponds to the presence of an $\{N_2\}^{4-}$ unit.

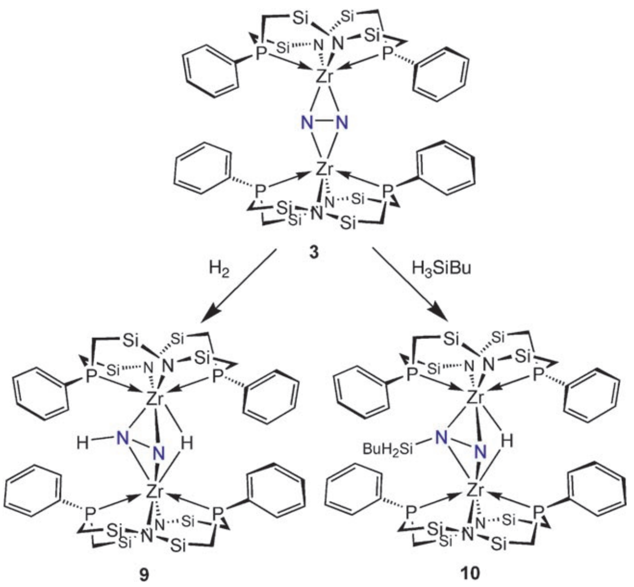
Since 1990, many of the recent breakthroughs in expanding the reactivity patterns of coordinated dinitrogen have been made with Group 4 metal complexes in which the dinitrogen ligand is side-on bound. The first example of the addition of dihydrogen to a dinitrogen complex was reported in 1997;[9] complex **3** undergoes a slow reaction with one equivalent of H_2 to generate **9** (Scheme 2) by heterolytic cleavage of dihydrogen. As also shown in Scheme 2, this same N_2 complex has also been shown to react with primary silanes as indicated by the formation of **10**.

An even more intriguing breakthrough was communicated in 2004 with the double 1,2-addition of H_2 to **6** to generate the diazenido dihydride **11**, as shown in Scheme 3.[12] Further thermolysis of **11** resulted in N–N bond cleavage to generate **12** and was accompanied by H_2 loss. The dinuclear hafnium dinitrogen complex **8** also reacts with H_2, which results in the formation of the corresponding diazenido dihydride **13**;[14] detailed kinetic studies have indicated that the hafnium complex reacts about four times faster with H_2 than the Zr analogue. Interestingly, thermolysis of the hafnium diazenido species **13** does not result in N–N bond cleavage, rather C–H bond activation occurs to generate **14**.

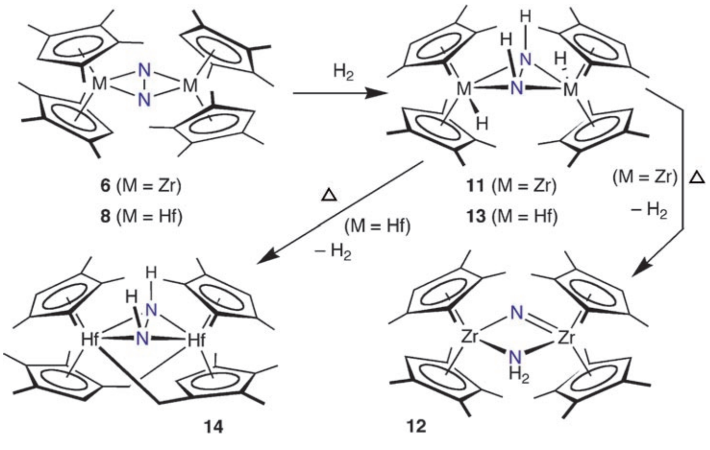
It is remarkable that the only dinitrogen complexes to date that result in N–H bond formation by reaction with H_2 are systems based on Group 4 metals, and furthermore, there is a strong influence of the ancillary ligands on the outcome of the reaction: use of amido–phosphine-based ligands (Scheme 2) results in just one equivalent of H_2 being added to the complex,[9] whereas substituted cyclopentadienyl systems (Scheme 3) result in the addition of two equivalents of H_2.[12,14] None of the other complexes in Scheme 1 has been reported to react with H_2 in any productive manner.

With respect to nitrogen–carbon bond formation, here again breakthroughs have been reported with Group 4 metal dinitrogen complexes. Terminal alkynes were found[15] to react with **3** to generate alkenyl hydrazido species with bridging acetylide ligands incorporated into the framework, as shown in Scheme 4a. In contrast, **6** reacts with terminal alkynes[16] to form Zr–C and N–H bonds by a process that resembles deprotonation (Scheme 4b), again illustrating the importance of the ancillary ligands on reaction outcomes.

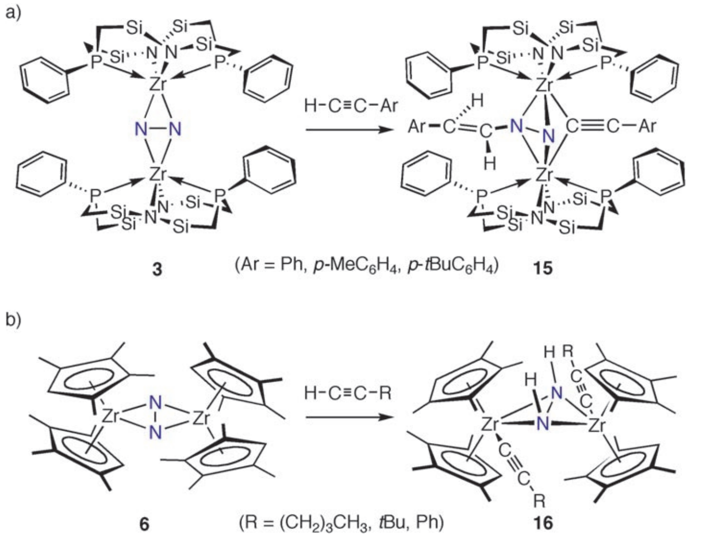
Hafnium is an infrequent participant in dinitrogen activation because it is the most difficult Group 4 metal to reduce.[14,17] This is reflected in the synthesis of **8** for which the best reported yield is 27%, even after optimizing the system with iodide leaving groups and testing different reducing agents. But what the hafnium dinitrogen complex **8** offers is a broader range of reactivity patterns as compared to its zirconium congener **6**. This has been attributed[13] to the observation of an equilibrium between the side-on and end-on dinuclear forms, which for the hafnium complex **8** lies more towards the side-on form. And it is the side-on form that is more reactive especially to polar reagents. For example, the addition of phenylisocyanate to **8** results in the formation of two new N–C bonds apparently by a tandem cycloaddition/insertion process involving the coordinated dinitrogen ligand (Scheme 5).[18] Con-



Scheme 2. Reactions of **3** with H_2 and H_3SiBu. The Me groups on the macrocycle Si atoms have been omitted.

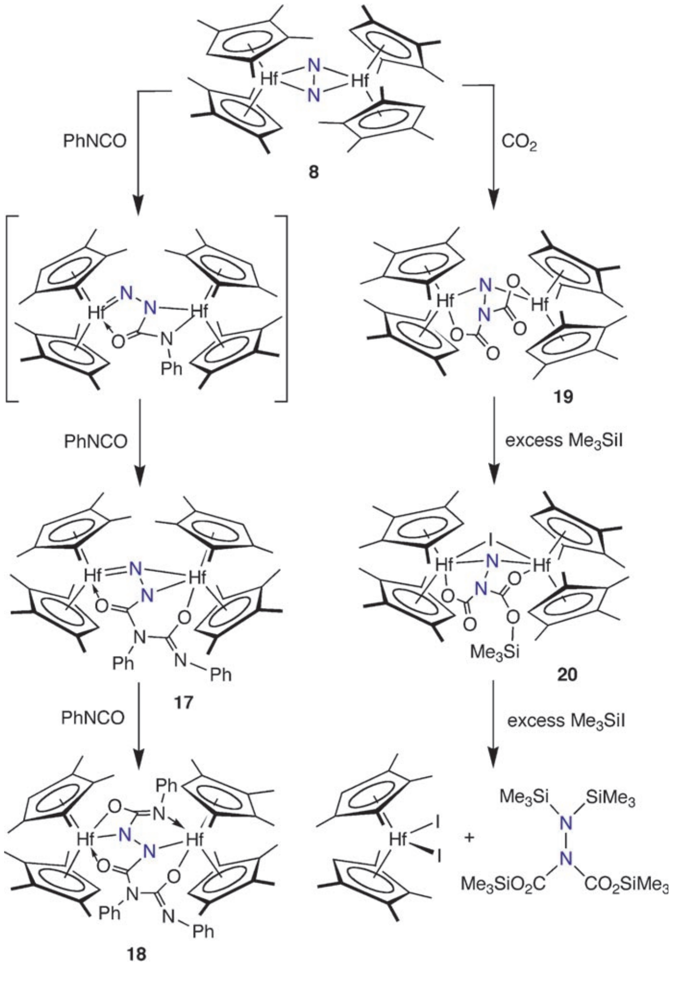


Scheme 3. Reactions of **6** and **8** with H_2.



Scheme 4. a) Reaction of **3** with HC≡CAr; the Me groups on the macrocycle Si atoms have been omitted. b) Reaction of **6** with HC≡CR.

trolled addition of two equivalents of phenylisocyanate to **8** resulted in the formation of the key intermediate **17**, which still contains a hafnium–imido-type functionality; further addition of an equivalent of phenylisocyanate results in the formation of the final product **18**.



Scheme 5. Reactions of **8** with PhNCO and CO_2.

An interesting extension of this work was recently reported in this journal[19] in which the reactivity of the hafnium dinitrogen complex with carbon dioxide was examined (Scheme 5). Addition of CO_2 to **8** results in a double insertion to generate **19**, which has been structurally characterized. Even more interesting is the further functionalization of this species to produce the silylated species **20**, from which the unsymmetrically functionalized hydrazine, $(Me_3Si)_2NN(CO_2SiMe_3)_2$, could be detected after further addition of excess Me_3SiI.

The reaction of the dinuclear hafnium dinitrogen complex **8** with aryl isocyanates and carbon dioxide has certainly expanded the kinds of transformations of coordinated dinitrogen. But have they brought us closer to the Holy Grail, the catalytic cycle? The answer is, of course, no. Both of these reagents are strong electrophiles, as is the Me_3SiI added to release the functionalized hydrazine. The dinitrogen unit in **8** is nucleophilic, as are most of the activated N_2 ligands coordinated to Group 4 metal centers. Quenching a nucleophile with an electrophile is not a new transformation for coordinated dinitrogen. In fact, the key stumbling block to turning this process over catalytically is to get the N_2 coordinated to the metal center; for the preparation of the hafnium dinitrogen complex **8** and most other Group 4 metal dinitrogen complexes, strong reducing agents are required and, as already mentioned for complex **8**, its yield is unfortunately quite low. Nevertheless, this is the first example of an N_2 complex reacting productively with CO_2 and for that reason optimism for further advances in dinitrogen functionalization remains.

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