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Metal–Nitrogen Multiple Bonds

Early Transition-Metal Hydrazido Complexes: Masked Metallanitrenes from N−N Bond Scission

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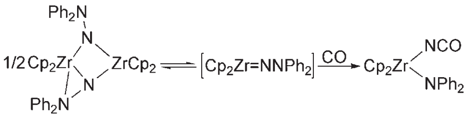
hydrazidos · metallanitrenes · nitrides · transition metals

Terminal metallanitrenes, alternatively known as radicaloid metal nitrides, are reactive functional groups in which the nitrogen atom in question reacts in an electrophilic fashion. This feature is especially true for electron-rich metal centers having d electron counts greater than two, as the empty d orbitals often invoked for constructive $M\equiv N$ bond formation are no longer available.[1] Consequently, the terminal nitride functionality can also resonate between radical structures ($M{=}N^{\bullet}\leftrightarrow M{-}N{:}$), or other canonical forms, because of poor or forbidden overlap between the metal and nitrogen orbitals. The terminal nitrogen group can therefore undergo a variety of transformations, such as oligomerization,[2] reductive coupling,[2,3] and N-addition reactions.[4] The latter type of transformation is especially important given the ability of a nitride to promote N−X bond formation (X = C or a heteroatom) under mild conditions and at the expense of transition-metal reduction (which is often a two-electron process).

The first example of an electrophilic nitride was reported by Griffith, by which rhenium or osmium nitrides reacted with phosphines to generate phosphinimides ($[R_3P{=}N]^-$) by an incomplete nitrogen-atom transfer from the metal to phosphorus.[4a–c] Analogous work was then further explored by Taube in 1991, and such a system involved the osmium(VI) complex $[Os(N)Cl_3(py)_2]$, which underwent reductive coupling by an overall $6\,e^-$ redox process in pyridine to extrude N_2 and form $[Os(py)_3Cl_3]$.[3a] In contrast, the microscopic reverse reaction, which entails the exothermic cleavage of N_2 (84 kcal mol^{-1}) by a highly π-reducing molybdenum complex $[Mo\{N(tBu)Ar\}_3]$ ($Ar = 3,5\text{-}Me_2C_6H_3$) to form $[N{\equiv}Mo\{N(tBu)Ar\}_3]$,[5] relies on the assembly of a very strong $Mo\equiv N$ linkage (155 kcal mol^{-1}).[6] Not surprisingly, harnessing the intrinsic reactivity at the electrophilic nitride or metallanitrene moiety can be difficult, and this type of group has been largely constrained to mid to late transition metals in exceedingly high oxidation states.

Until now, the ability of early transition metals to emulate the above reactions had not been realized, as the high oxidation state is the typical environment for these elements. This situation is especially true for the reduction of the high-valent metal, which is no longer a driving force because of a strong $M\equiv N$ bond dissociation enthalpy. Intuitively, however, formation of a metallanitrene can be rationalized in terms of having a good leaving group at the α-nitrogen atom while at the same time disfavoring $M{=}N$ or $M\equiv N$ bond formation. In the context of electron transfer, the outcome would of course be different, as the metal center in question would not undergo a redox change in such a process. Instead, the leaving group must migrate to the metal in order to mitigate "M−N" radical formation, and subsequently oxidizing the incoming substrate. Applying the latter set of principles, the groups of Gade[7] and Mountford[8] have devised a strategy to trap metallanitrenes of zirconium(IV) and titanium(IV), respectively. Expounding on Walsh, Carney, and Bergman's seminal work on the reactivity of the transient zirconium(IV) hydrazido complex "$[Cp_2Zr{=}NNPh_2]$" with CO to yield $[Cp_2Zr(NCO)(NPh_2)]$ (Scheme 1),[9] Gade has devised a similar approach to trapping metallanitrenes with CNtBu, episulfides, and $Ph_3P{=}Se$. As a result, the electrophilic zirconitrene motif, {Zr−N}, can form unusual functionalities, such as metallacarbodiimides by the coupling of the nitrene with CNtBu, as well as the assembly of dinitridosulfate(IV) and dinitridoselenate(IV) ligands onto zirconium(IV) by treating the hydrazido group with sulfide and selenide sources, respectively (Scheme 2).[7]

Mountford et al. independently reported the insertion of alkynes into the N−N bond of a titanium hydrazido ligand to generate an amido-substituted vinyl imide (Scheme 3).[8] Although Mountford's reaction does not ultimately result in migration of the $-NPh_2$ moiety to the metal, his system offers the advantage of being catalytic, as the titanium hydrazido reagent can not only promote the addition of NH_2 and NPh_2 across an alkyne, but can also be regenerated by transhydrazination with H_2NNPh_2 to form a 1,2-diamino-substituted olefin (Scheme 3).[8]



Scheme 1. Migration of an amino group from the nitrogen to the zirconium center with concomitant take-up of CO to give an isocyanate ligand.

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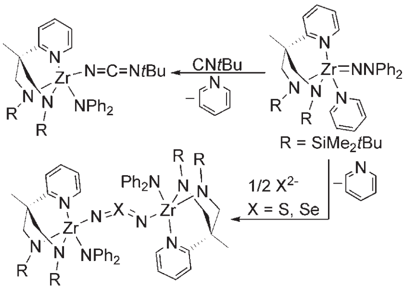
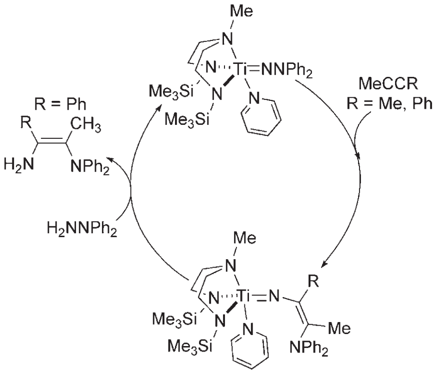
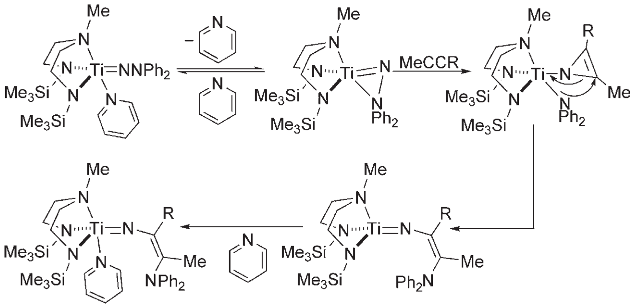


Scheme 2. Examples of the trapping of metallanitrenes formed by diphenylamide migration.



Scheme 3. Catalytic cycle involving formal insertion of an alkyne into the N–N bond, and reaction with *N*,*N*-diphenylhydrazine to form 1,2-diaminoalkenes and regenerate the hydrazido complex.

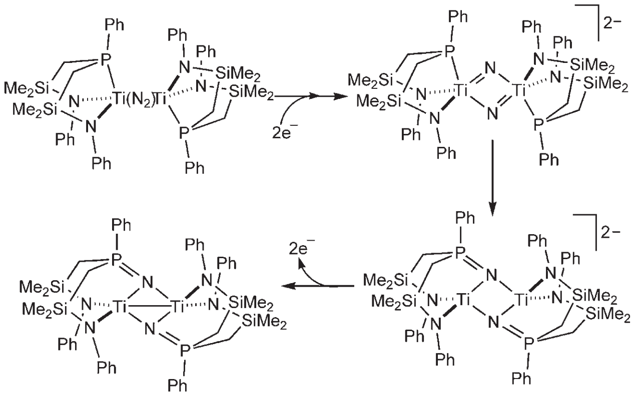
Although a mechanism for cumulene formation in the zirconium(IV) system or the alkyne insertion into the N–N bond of the hydrazido ligand in the titanium(IV) complex has not been proposed, it is very likely that these reactions involve a chelating hydrazido intermediate, which then places the strained α-nitrogen in position for the incoming substrate. In both cases, the possibility of N–N bond cleavage and reaction as equivalent for a metallanitrene is not unreasonable to propose. Preliminary calculations by Gade et al. suggest the η^1 and η^2 hydrazido isomers to be essentially isothermal. Although N–N cleavage to give a terminal metallanitrene is not thermodynamically accessible, binding of the substrate must be responsible for making the large energy gap between the two species (ca. 60 kcal mol^{-1}) more within thermodynamic reach.[7] Mountford and co-workers have reported DFT calculations suggesting that the -$N_\beta R_2$ group on the α-nitrogen destabilizes the Ti=N_α linkage by an N_α-N_β π^* antibonding contribution from the N–N bond of the hydrazido to the HOMO.[10] If a change in hapticity at the hydrazido motif from η^1 to η^2 promotes metallanitrene formation, then the addition of Lewis bases should slow down the rate for these transformations. It is unlikely that a naked or terminal metallanitrene is generated in this set of reactions as the substrate must first interact with the α-nitrogen before irreversible N–N bond rupture ensues. In Mountford's case,[8] is it possible that the alkyne undergoes [2+1] cycloaddition to the α-nitrogen in an η^2-hydrazido intermediate to produce an arizenide via N–N bond scission and migration of $^-NPh_2$ to the metal center? Such an arizenide intermediate would then be amenable to ring-opening by $^-NPh_2$ to yield the diphenyl-substituted vinyl imide (Scheme 4). We anticipate that mechanistic studies will assess which intermediates are formed during the nitrogen-atom transfer process.



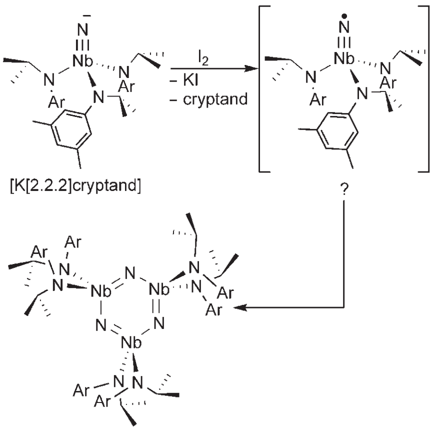
Scheme 4. Proposed mechanism for the formation of 1,2-diaminoalkenes from the hydrazido complex in Scheme 3. R = Me, Ph.

The systems discovered by the groups of Bergman,[9] Gade,[7] and Mountford[8] are not the only early transition-metal examples of metallanitrene equivalents generated by N–N bond rupture. Recently, Fryzuk and co-workers have proposed an electrophilic titanium nitride as an intermediate from N_2 activation, reduction, cleavage, and incomplete transfer to a pendant phosphine arm of a pincer ligand (Scheme 5).[11] Cummins et al. also reported the oxidation of a niobium nitride anion [K[2.2.2]cryptand)][N≡Nb{N(*i*Pr)Ar}$_3$] (Ar = 3,5-$Me_2C_6H_3$) with I_2 to give a niobazene cyclic trimer (Scheme 6).[12] The former nitride anion was derived from N_2 activation and reductive cleavage, and its oxidation may involve a transient nitride radical intermediate (Scheme 6).[12]

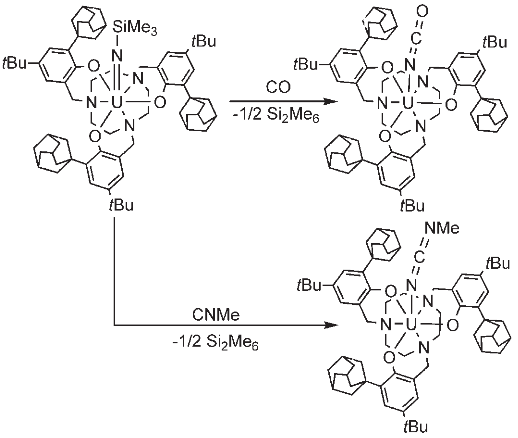
Notably, N–N bond cleavage is not the only avenue to formation of metallanitrenes. The Meyer group has also discovered a source of metallanitrene equivalent by N–Si bond rupture when a uranium trimethylsilylimide precursor is subjected to small π-acids.[13] Accordingly, [(Me_3Si)N=U{(*t*BuArO)$_3$tacn)}] ((*t*BuArOH)$_3$tacn = 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane) transforms cleanly into the isocyanate [(OCN)U{(*t*BuArO)$_3$tacn)}] and carbodiimide [(MeNCN)U{(*t*BuArO)$_3$tacn)}] complexes when treated with CO and



Scheme 5. Activation of N_2 followed by reduction, cleavage, and incomplete transfer of nitrogen to a pendant phosphine ligand.



Scheme 6. Oxidation of a nitride complex with iodine leading to trimerization after loss of one HN*i*PrAr ligand. Ar = 3,5-$Me_2C_6H_3$.



Scheme 7. Loss of the trimethylsilyl group of a uranium trimethylsilylimide complex and treatment with CO and MeNC to give isocyanate and carbodiimide complexes.

CNMe, respectively (Scheme 7).[13] Formation of Si_2Me_6 in the reaction mixture suggests that a radical pathway could also be operative. Therefore, such a possibility should not be overlooked for the N–N bond scission reactions reported by the groups of Gade,[7] Mountford,[8] and Bergman and Walsh.[9] It is possible, however, the sterically congested environment about the uranium center prevents migration of the trimethylsilyl group to the metal center.

The potential reactivity offered by early transition-metal complexes having an electrophilic nitride represents a research topic in its infancy. This is especially true given the insufficient number of access points to such a functional group. Early transition-metal hydrazides, systems often sought only for catalytic processes, such as hydrohydrazination[14] and iminohydrazination[14g,15] of alkynes, can now be considered masked metallanitrenes that are revealed by means of an N–N bond activation step. Mechanistic studies geared towards the understanding of complexes that behave as a masked metallanitrene should provide conspicuous clues on how to catalytically employ and perhaps even isolate this type of reactive functional group.

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