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A Zirconium (1-Pyridinio)imido Complex: Facile N−N Bond Cleavage and N−C Bond Formation

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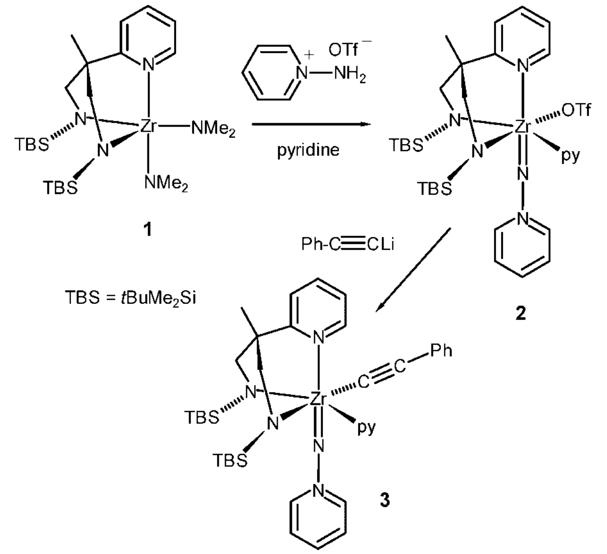
Summary: Reaction of a (1-pyridinio)imidozirconium complex with isocyanides or CO leads to instantaneous N−N bond cleavage and the concomitant formation of the carbodiimido complexes $[Zr(N_2{}^{TBS}N_{py})(N{=}C{=}NR)(OTf)(py)]$ *or the isocyanato complex* $[Zr(N_2{}^{TBS}N_{py})(NCO)(OTf)(py)]$*, respectively.*

Group 4 metal complexes have recently figured prominently in the discovery of new reactive patterns in the activation of dinitrogen,[1] a field otherwise dominated by the heavier group 6 elements.[2] The reduction and coordination of N_2 to Ti, Zr, and Hf in the form of (formally) highly charged hydrazido units has been shown to activate it toward hydrosilylation and hydrogenation, along with N−N bond cleavage.[3] Very recently, the reactivity of $[(Cp^*)_2Hf_2N_2]$ with unsaturated molecules has opened up a new way to functionalized N−N activation products.[4]

Rather than targeting the hydrogenation of dinitrogen to generate ammonia, research efforts pioneered in Leigh's and Hidai's groups have been aimed at the direct incorporation of nitrogen activation intermediates (principally hydrazides) into more complex organic substrates.[5] A key step in this work has been the conversion of a metal-bonded hydrazide to an N-heterocycle and the subsequent (reductive) scission of the N−N bond, liberating the organic product and (frequently unidentified) reduction products of the metal complex. This latter aspect has been studied in some detail for (1-pyridinio)imido complexes of tungsten as well as titanium.[6] Given the difficulty in the isolation of both fragments in such a reductive N−N cleavage which would allow a systematic investigation of the reaction itself, we have chosen a different approach in which N−N bond cleavage is coupled with C−N bond formation with an appropriate cosubstrate.

Scheme 1. Synthesis of the (1-Pyridinio)imidozirconium Complex 2 and the Substitution of the Triflato Ligand by Phenyl Acetylide



The model system employed in this study contains the tridentate diamidopyridyl ligand $[N_2{}^RN_{py}]^{2-}$ as a supporting ligand, which has proved suitable for the stabilization of complexes containing reactive M═N bonds and their derivatives.[7] Treatment of the diamidozirconium complex $[Zr(N_2{}^{TBS}N_{py})(NMe_2)_2]$ (**1**) with 1 molar equiv of 1-aminopyridinium triflate in the presence of 1 equiv of pyridine gave the (1-pyridinio)imidozirconium complex $[Zr(N_2{}^{TBS}N_{py})({=}NNC_5H_5)(OTf)(py)]$ (**2**) in good yield (Scheme 1). The triflate ligand in **2** is readily substituted by other anionic ligands, as was shown in its reaction with PhC≡CLi, giving the alkynyl complex $[Zr(N_2{}^{TBS}N_{py})({=}NNC_5H_5)(C_2Ph)(py)]$ (**3**). The molecular struc-

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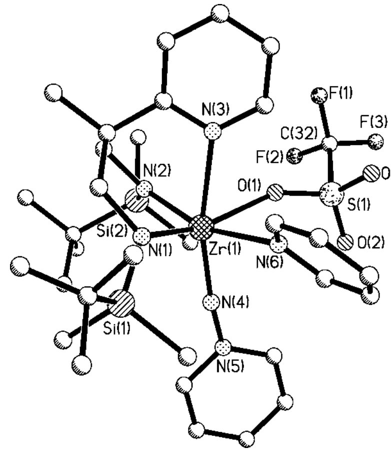
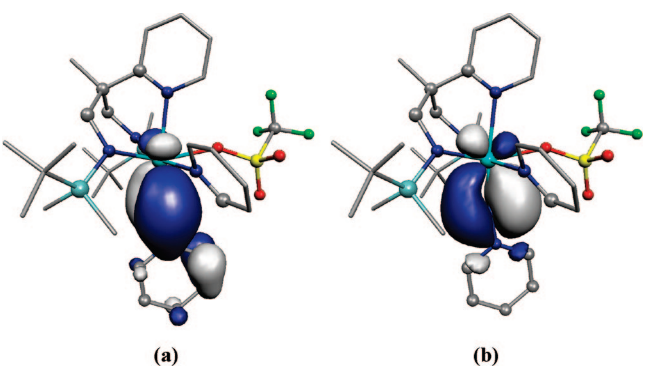


Figure 1. Molecular structure of complex **2**. Selected bond lengths (Å) and angles (deg): Zr(1)−N(1) = 2.102(3), Zr(1)−N(2) = 2.088(3), Zr(1)−N(3) = 2.405(3), Zr(1)−N(4) = 1.945(3), Zr(1)−N(6) = 2.456(3), N(4)−N(5) = 1.321(4), Zr(1)−O(1) = 2.286(2); N(1)−Zr(1)−N(2) = 93.85(10), N(1)−Zr(1)−N(3) = 82.28(10), N(1)−Zr(1)−N(4) = 106.37(12), N(2)−Zr(1)−N(3) = 83.27(10), N(3)−Zr(1)−N(4) = 166.64(11), Zr(1)−N(4)−N(5) = 171.4(3).

ture of the (1-pyridinio)imido compound **2** was established by X-ray diffraction (Figure 1).[8]

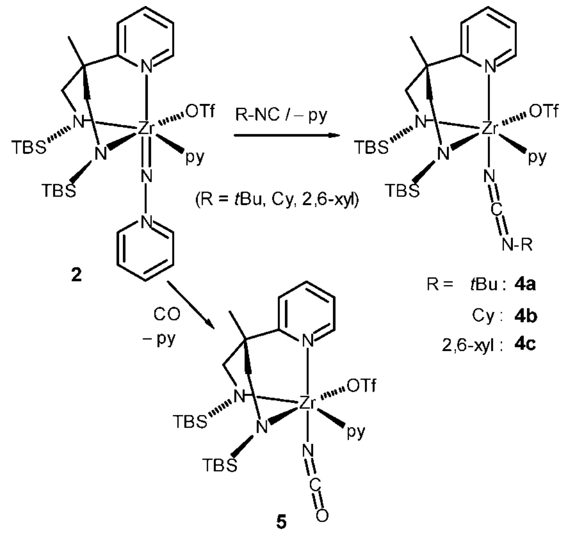
The overall structural arrangement in **2** is best described as distorted octahedral, with the (1-pyridinio)imido ligand disposed trans to the pyridyl unit of the facially coordinating polydentate ligand (Zr(1)−N(3) = 2.405(3) Å). The two amido functions, the pyridine, and the triflato ligand lie in the plane orthogonal to the (1-pyridinio)imido ligand. The latter bends away from the bulky *t*BuMe$_2$Si substituents of the amides (N(3)−Zr(1)−N(4) = 166.64(11)°) and the Zr−N−N chain in the "hydrazido" Zr=NNC$_5$H$_5$ fragment[9,10] also deviates slightly from linearity (Zr(1)−N(4)−N(5) = 171.4(3)°). Its Zr=N bond is longer (Zr(1)−N(4) = 1.945(3) Å) while the adjacent N−N bond is significantly shorter (N(4)−N(5) = 1.321(4) Å) than in Bergman's hydrazido complex [Cp$_2$Zr(N$_2$Ph$_2$)(dmap)] (1.873(7) and 1.364(10) Å, respectively);[9] however, the latter is similar to the N−N distances previously reported by Hidai and co-workers for titanium compounds with the (pyridinio)imido ligands (1.361–1.369 Å)[6c] and indicates the conjugation of the Zr=N and pyridine π-systems.



(a) (b)

Figure 2. The two π-bonding orbitals of the Zr=NNC$_5$H$_5{}^+$ unit: (a) the HOMO-3 Kohn–Sham frontier orbital (E = −0.225), illustrating the conjugation of the Zr=N bond with the pyridinium unit; (b) the HOMO (E = −0.195 au) representing the second, orthogonal π-bond.

Scheme 2. Reaction of 2 with Isonitriles and CO: Cleavage of the N−N Bond and Coupling with the Metallanitrene Fragment To Give the Carbodiimido Complexes 4a–c and the Isocyanato Complex 5



The bonding in **2** was analyzed using the B3PW91 computational tool (6-31g(d) basis set for C, N, S, O, and F, 6-31g basis set for H, and lanl2dz basis set for Zr) combined with an ONIOM modeling of the ligand substituents in N$_2{}^{TBS}$N$_{py}$.[11] The two relevant π-bonding (NLMO) frontier orbitals are depicted in parts a and b of Figure 2, the former representing the conjugation of the imido unit with the attached pyridine ring. The Zr=N bond length determined in this model study (calcd 1.970 Å) is consistent with the observed value and the N−N bond contraction due to the conjugation is nicely reproduced (1.311 Å). The importance of the latter is apparent from the N−N distance in the modeled analogous Zr=NNMe$_3{}^+$ complex, which was found to be ca. 0.1 Å greater (1.410 Å).

Upon reaction of **2** with 1 molar equiv of RNC (Scheme 2), N−N bond cleavage in the (1-pyridinio)imido unit took place to yield the respective carbodiimido complexes [Zr(N$_2{}^{TBS}$N$_{py}$](N=C=NR)(OTf)(py)] (R = *t*Bu (**4a**), Cy (**4b**), 2,6-xyl (**4c**)). The details of the molecular structure of complex **4a** have been established by X-ray diffraction and are depicted in Figure 3 along with the principal bond lengths and angles.

The arrangement of the ligands in **4a** is similar to that in the starting material, the (1-pyridinio)imido group having been

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[8] Crystal data for **2**: C$_{32}$H$_{51}$F$_3$N$_6$O$_3$SSi$_2$Zr•C$_7$H$_8$, triclinic, $P\bar{1}$, a = 10.8684(11) Å, b = 13.9752(15) Å, c = 15.6286(17) Å, α = 82.742(2)°, β = 81.840(2)°, γ = 75.184(2)°; 43 129 total reflections, 9610 independent reflections; R1 = 0.0524, wR2 = 0.1373 ($I > 2\sigma(I)$, 7017 reflections). Crystal data for **4a**: C$_{32}$H$_{55}$F$_3$N$_6$O$_3$SSi$_2$Zr, monoclinic, $P2_1/n$, a = 10.4937(5) Å, b = 19.0633(9) Å, c = 20.8233(10) Å, β = 102.123(1)°; 98 728 total reflections, 12 423 independent reflections; R1 = 0.0417, wR2 = 0.0966 [($I > 2\sigma(I)$, 8972 reflections. Crystal data for **5**: C$_{28}$H$_{46}$F$_3$N$_5$O$_4$SSi$_2$Zr • 1.5C$_7$H$_8$, triclinic, $P\bar{1}$, a = 9.9979(6) Å, b = 13.3201(9) Å, c = 18.5380(11) Å, α = 92.160(1)°, β = 103.483(1)°, γ = 110.444(1)°; 52 847 total reflections, 13 011 independent reflections; R1 = 0.0393, wR2 = 0.0975 ($I > 2\sigma(I)$, 10 278 reflections). For all studies, a Bruker AXS Smart 1000 CCD diffractometer was used (Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å, 150 K (**2**) or 100 K).

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[11] For details concerning the computational study, see the Supporting Information.

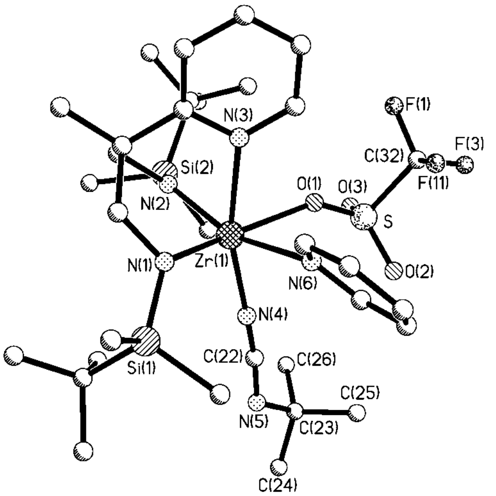

Figure 3. Molecular structure of complex **4a**. Selected bond lengths (Å) and angles (deg): Zr(1)−N(1) = 2.048(2), Zr(1)−N(2) = 2.060(2), Zr(1)−N(3) = 2.353(2), Zr(1)−N(4) = 2.081(2), Zr(1)−N(6) = 2.457(2), C(22)−N(4) = 1.201(3), C(22)−N(5) = 1.227(3), Zr(1)−O(1) = 2.261(1); N(1)−Zr(1)−N(2) = 92.85(7), N(3)−Zr(1)−N(4) = 165.17(6), Zr(1)−N(4)−C(22) = 174.6(2), N(4)−C(22)−N(5) = 172.7(2), C(22)−N(5)−C(23) = 126.2(2).

replaced by the *tert*-butylcarbodiimido unit. The latter has a typical diazacumulene structure (C(22)−N(4) = 1.201(3) Å, C(22)−N(5) = 1.227(3) Å, N(4)−C(22)−N(5) = 172.7(2)°), which has resulted from a formal nitrene−isocyanide coupling, similar to that observed in the thermal degradation of palladium azides.[12] Whereas there is no precedent for a carbodiimido−zirconium compound, several titanium complexes have been reported. However, all of these were synthesized by reaction of a Ti precursor with metalated preformed carbodiimide.[13]

There has been no report of a terminal group 4 metal nitrido complex in the literature to date,[14] and it is unlikely that such a species is formed in the transformation of **2** to **4a**–**c**. The N−N bond splitting does not appear to be induced by a simple nucleophilic attack at the α-N atom of the pyridinio−imide, as illustrated by its inertness in the conversion of **2** to the acetylide **3**. It appears to be the amphiphilic nature, i.e. the combined donor/acceptor properties, of an isocyanide which induced the bond cleavage/bond formation process. This notion is further supported by the reaction of **2** with CO, which occurs immediately at ambient pressure and yields the isocyanato complex $[Zr(N_2{}^{TBS}N_{py})](NCO)(OTf)(py)]$ (**5**). A similar behavior was reported for the hydrazido complex $[Cp_2Zr(N_2Ph_2)(dmap)]$, in which the formation of the isocyanate was accompanied by a rearrangement of the $\{Ph_2N\}$ of the hydrazide(2−) to the metal center as an amido ligand.[9]

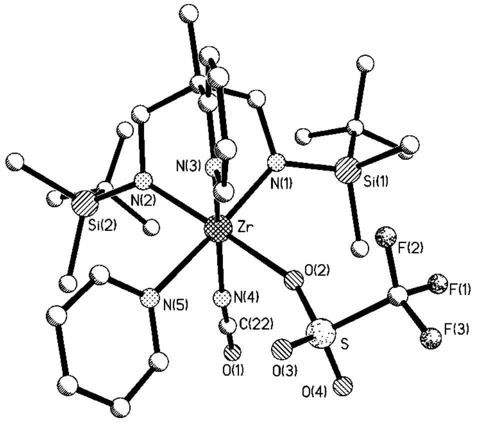

Figure 4. Molecular structure of complex **5**. Selected bond lengths (Å) and angles (deg): Zr−N(1) = 2.045(2), Zr−N(2) = 2.035(2), Zr−N(3) = 2.348(2), Zr−N(4) = 2.121(2), Zr−N(5) = 2.431(2), N(4)−C(22) = 1.177(3), C(22)−O(1) = 1.187(3); N(1)−Zr−N(3) = 83.00(6), N(1)−Zr−N(4) = 108.58(6), N(2)−Zr−N(3) = 85.17(6), N(2)−Zr−N(4) = 104.67(6), N(2)−Zr−N(5) = 88.43(6), N(2)−Zr−O(2) = 162.88(6), N(3)−Zr−N(4) = 163.89(6), Zr−N(4)−C(22) = 167.5(2), N(4)−C(22)−O(1) = 179.1(3).

The details of the molecular structure of complex **5** have been determined in an X-ray structure analysis (Figure 4). The arrangement of the ligands is similar to that in **4a**, with the position trans to the pyridyl unit of the tripod ligand being occupied by the isocyanate. The latter adopts a slightly bent coordination mode (Zr−N(4)−C(22) = 167.54(16)°) which is thought to be electronically induced, rather than sterically, in view of the close to linear arrangement observed for the bulkier carbodiimide (**4a**: Zr(1)−N(4)−C(22) = 174.57(18)].

This study has shed new light on the possibility to couple N−N cleavage in the coordination sphere of an early transition metal with C−N bond formation in the reaction of a hydrazido type ligand with an unsaturated substrate. Our current work is aimed at extending the concept and establishing the mechanism of this intriguing transformation.

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Supporting Information Available: Text, figures, and CIF files giving experimental procedures, characterization data, and crystallographic details for **2**, **3**, **4a**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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