Nitrogen Chains

DOI: 10.1002/anie.200805631

Assembly of an $R_3N_5^{2-}$ Chain by Cycloaddition of a Hydrazinediide and an Azide at Zirconium and its Thermal Fragmentation**

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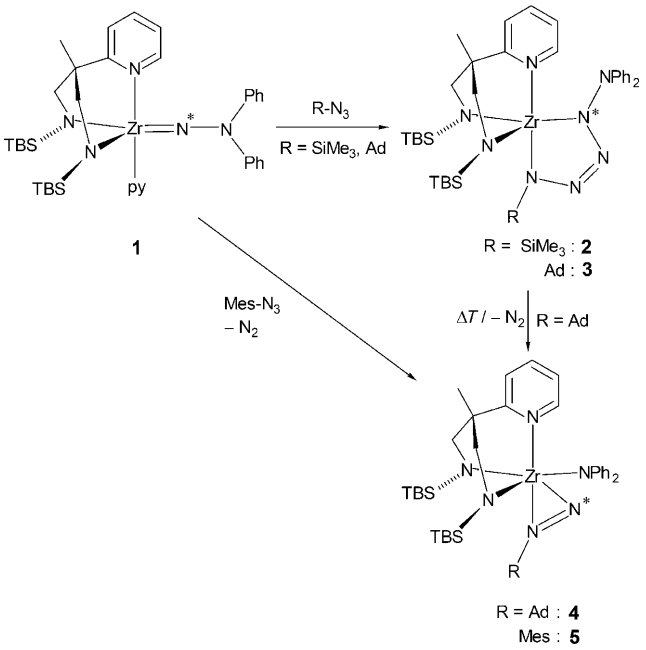
The assembly and fragmentation of nitrogen chains in ionic species and organic compounds, as well as those coordinated to metal centers,[1] have been investigated in the context of new high-energy molecular compounds.[2] As potentially reactive fragments, they have been stabilized by coordination to transition metals. A variety of singly and multiply bonded nitrogen-based molecular fragments have thus acted as ligands in transition-metal compounds. Metal–nitrogen multiple bonds in transition-metal imido complexes undergo [2+3] cycloaddition reactions with azides, giving tetrazenido units,[3,4] Bergman's study of the reaction of in situ-generated zirconium imides having been seminal in this context.[5] Based on earlier work by the same group,[6] we recently begun to explore the chemistry of the heavier Group 4 metal hydrazides, which has revealed exciting new patterns of reactivity.[7,8] Cycloadditions with azides, in particular, offered the possibility to access the chemistry of formally dianionic substituted N_5 chains[9] ligated to the early-transition-metal center and to probe their conversion into other coordinated N_x fragments.

Reaction of the hydrazinediido complex $[Zr(N_2{}^{TBS}N_{py})(NNPh_2)(py)]$ (**1**)[7] with trimethylsilylazide and 1-adamantylazide gave the corresponding [2+3] cycloaddition products $[Zr(N_2{}^{TBS}N_{py})\{N(R)N_3NPh_2\}]$ (R = $SiMe_3$: **2**, 1-adamantyl: **3**). The structural assignment (Scheme 1) is consistent with the analytical and spectroscopic data of both compounds.

The ^{15}N NMR spectroscopic data were of particular interest in the characterization of the metal-bound N_5 unit formed in the coupling between azide and hydrazinediide. Whereas the signal of the noncoordinated Ph_2N group was detected indirectly by (^{15}N,^1H) HMBC (heteronuclear multiple-bond correlation) spectroscopy (**2**: 121.4 ppm, **3**: 122.2 ppm; external reference compound: NH_3) all four ^{15}N resonances of the N_4 unit in the metallacycle could be directly detected at natural abundance. Assignment of the signals in the ^{15}N NMR spectra of complexes **2** and **3** [**2**: δ = 291.3 (Zr–N), 293.8 (N–$SiMe_3$), 378.6 (*N*=N), 411.4 (N=*N*); **3** (Figure 1): 292.4 (Zr–N), 303.8 (N–$C_{10}H_{15}$), 374.7 (*N*=N), 380.8 ppm (N=*N*)] was additionally supported by a theoretical gauge-independent atomic orbital (GIAO) study based on density functional theory (DFT), which gave excellent agreement with the experimental data (see the Supporting Information).[10]



Scheme 1. Synthesis of the 2-pentazene-1,4-diyl complexes **2** and **3** and thermal generation of the diazenido complexes **4** and **5**. N* = ^{15}N label; TBS = $SiMe_2tBu$; Ad = 1-adamantyl; Mes = mesityl.

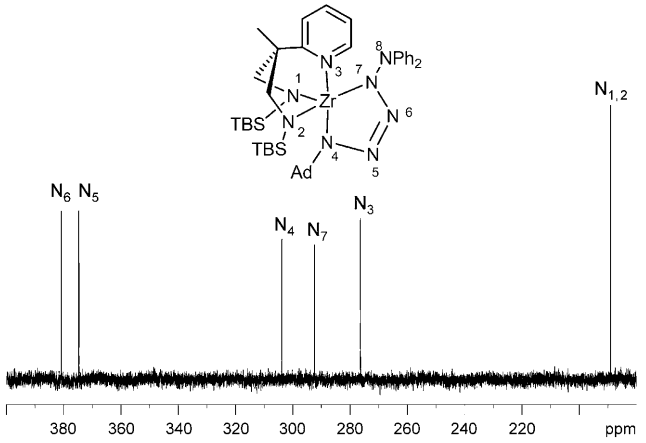


Figure 1. Natural abundance ^{15}N NMR spectrum of complex **3** along with the assignment of the resonances.

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[**] We thank the Deutsche Forschungsgemeinschaft for financial support and Dr. M. Enders for help with ^{15}N NMR spectroscopy as well as Solveig Scholl for contributing to the preparative work. J.L. thanks the EU for the award of a Marie Curie EIF postdoctoral fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200805631.

Single-crystal X-ray structure analyses of both **2** and **3** established the details of the unprecedented N_5 ligands in these complexes.[11] Since both molecular structures are closely related, only that of complex **2** is depicted in Figure 2 (the structure of **3** is depicted in the Supporting Information). Whereas the ancillary diamidopyridyl ligand $N_2^{TBS}N_{py}$ coordinates facially to the zirconium atom and protects a major part of the coordination sphere, the N_5 ligand occupies the two remaining coordination sites and is bonded to Zr through N4 and N7 (Zr–N4 2.139(2), Zr–N7 2.159(2) Å). Both bond lengths are within the expected range for amido-N–Zr bonds,[12] which is consistent with both being formally monoanionic donors.

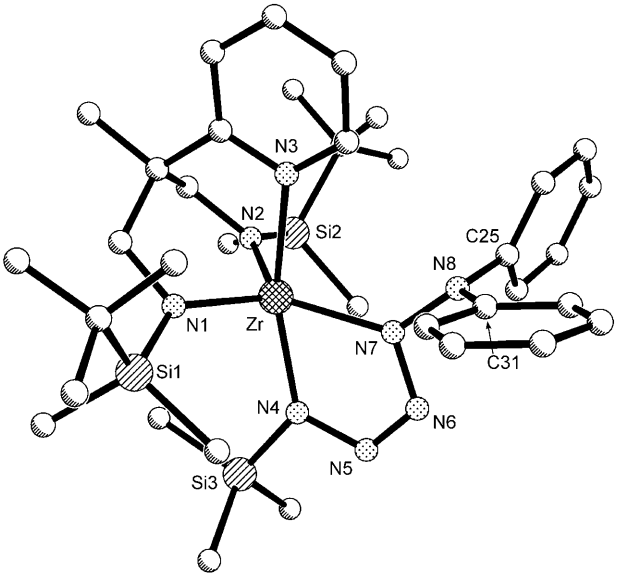


Figure 2. Molecular structure of complex **2**. Selected bond lengths [Å] and angles [°]: Zr–N1 2.042(2), Zr–N2 2.034(2), Zr–N3 2.326(2), Zr–N4 2.139(2), Zr–N7 2.159(2), N4–N5 1.397(3), N5–N6 1.260(3), N6–N7 1.395(3), N7–N8 1.415(3); Si3-N4-N5 108.4(1), N4-N5-N6 114.4(2), N5-N6-N7 114.1(2), N6-N7-N8 108.7(2), C25-N8-C31 122.0(2), N7-N8-C25 117.0(2), N7-N8-C31 116.6(2).

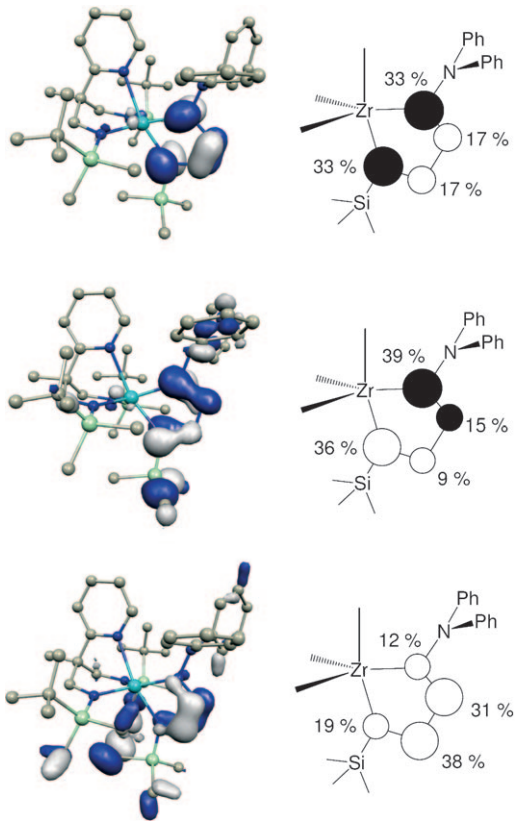


Figure 3. Kohn–Sham molecular orbitals representing the π bonding within the N_4 fragment of the metallacycle in **2** and **3**. C gray, N blue, Si green, Zr turquoise.

The N–N bond-length pattern in the metallacycle (N4–N5 1.397(3), N5–N6 1.260(3), N6–N7 1.395(3) Å) indicates a double bond between N5 and N6, whereas the other two N–N distances are close to those of N–N single bonds, albeit with some multiple-bond character owing to conjugation. The N–N bond to the exocyclic NPh_2 unit is the longest within the N_5 chain (N7–N8 1.415(3) Å). As expected, the exocyclic N8 atom is nonplanar ($\Sigma\sphericalangle_{N8} = 355.6°$). The $R_3N_5^{2-}$ fragment coordinated to the metal may therefore be interpreted as a 2-pentazene-1,4-diyl ligand, the first to be characterized.

To gain further insight into the bonding in the $\{R_3N_5Zr\}$ unit of complex **2**, DFT calculations (B3PW91) were carried out (see the Supporting Information).[10] The interpretation of the N_4 fragment within the metallacycle as a formal six-π-electron unit is reflected in the analysis of the relevant molecular Kohn–Sham orbitals (Figure 3). Apart from the in-phase π orbital (HOMO-54), there are two occupied single-node π orbitals at higher energy, which make this fragment equivalent to a butadiene dianion, in agreement with the experimentally determined double bond between N5 and N6. The formally dianionic nature of the 2-pentazene-1,4-diyl unit is also supported by natural population analysis (NPA), which indicates negative charges at N4 (−1.16 e) and N7 (−0.57 e), the greater negative charge on N4 being due to the stabilizing effect of the neighboring TMS group.

Heating complexes **2** and **3** at 70 °C led to the evolution of N_2. Monitoring this conversion by NMR spectroscopy, non-selective degradation was detected for **2**, whereas the 1-adamantyl-substituted complex **3** was selectively converted into a new compound **4**, which was isolated and for which the analytical data were found to be consistent with the loss of N_2. A complex with analogous composition was directly obtained upon treatment of **1** with mesityl azide, which led to the evolution of N_2 and yielded complex **5** (Scheme 1). Complexes **4** and **5** gave very similar NMR spectra. Next to the ^{15}N NMR signals of the tripodal ancillary ligand [**4**/**5**: $\delta =$ 164.3/166.4 ppm ($NSiMe_2tBu$), $\delta = 286.9/284.1$ ppm (py)], there are three resonances assigned to the fragmented nitrogen chain, of which the signals at $\delta = 804.2$ and 810.9 ppm for **4** and **5**, respectively, are particularly diagnostic and belong to the most downfield-shifted ^{15}N resonances detected to date. We note, however, that even greater deshielding of ^{15}N nuclei has been detected for nitrido ligands.[13]

A single crystal X-ray structure analysis of compound **5** established the molecular structure of the N_2 extrusion products (Figure 4). The N_5 chain in the primary [2+3] cycloaddition products has fragmented, and the Ph_2N unit of

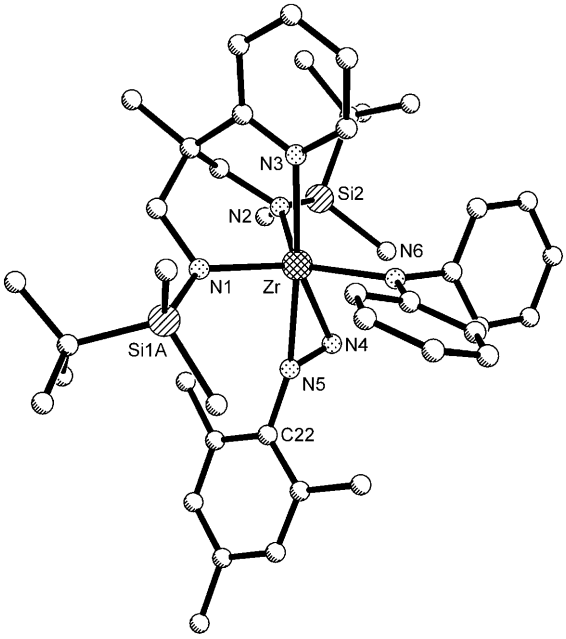


Figure 4. Molecular structure of complex **5**. Selected bond lengths [Å] and angles [°]: Zr–N1 2.101(3), Zr–N2 2.065(3), Zr–N3 2.377(3), Zr–N4 2.231(4), Zr–N5 2.223(3), Zr–N6 2.170(3), N4–N5 1.182(5); Zr-N4-N5 74.2(3), Zr-N5-N4 75.0(3), N4-N5-C22 119.8(4).

the original hydrazinediide is bonded as a diphenylamido ligand in the equatorial position (Zr–N6 2.170(3) Å). The axial coordination site *trans* to the pyridyl group of the tripod ligand is occupied by an η^2-coordinated mesityl–N_2 group (Zr–N4 2.231(4), Zr–N5 2.223(3) Å; Zr-N4-N5 74.2(3), Zr-N5-N4 75.0(3), C22-N5-N4 119.8(4)°) in which the N4–N5 bond length of 1.182(5) Å is consistent with a (short) double bond. The mesityl–N_2 unit is a rare example of a nonbridging side-on-coordinated alkyl- or aryldiazenido ligand.[14] A similar η^2-RN_2 coordination was reported for the titanium complex $[Ti(C_5H_5)Cl_2(\eta^2\text{-}N_2Ph)]$ (N–N 1.215(8) Å)[15] as well as the nickel complex $[(dtbpe)Ni(\eta^2\text{-}N_2C_6H_4OMe)]$ (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane; N–N 1.224(3) Å).[16]

The bonding in complex **5** was modeled in a DFT (B3PW91) study.[10] The selected frontier molecular orbitals (MO, Figure 5) clearly represent a double bond between the nitrogen atoms in the $\{Mes\text{-}N{=}N\}^{-1}$ fragment. Furthermore, the interaction of the $\{RN_2\}^{-1}$ unit and the metal is reflected in the populated Kohn–Sham MO composed of an orthogonal out-of-phase combination of the nitrogen atomic p orbitals and a d orbital of the zirconium atom. A full analysis of the ^{15}N NMR spectra of **4** and **5** was again achieved by a DFT-based GIAO analysis, which allowed the assignment of the unusually downfield-shifted resonances to the substituent-free N atoms (N4 in Figure 4) of the η^2-RN_2 units.

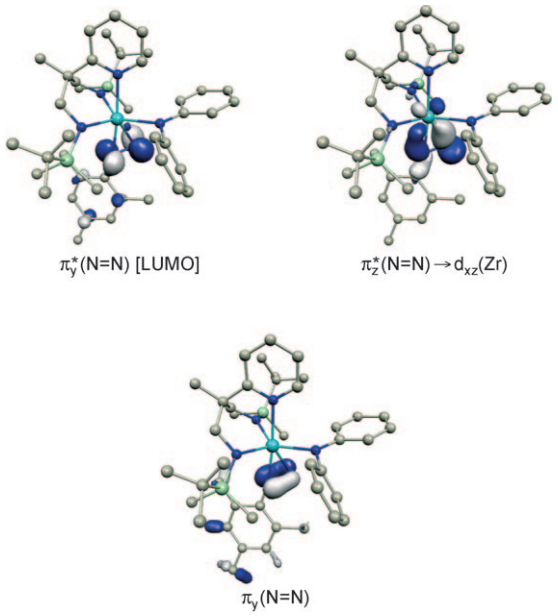


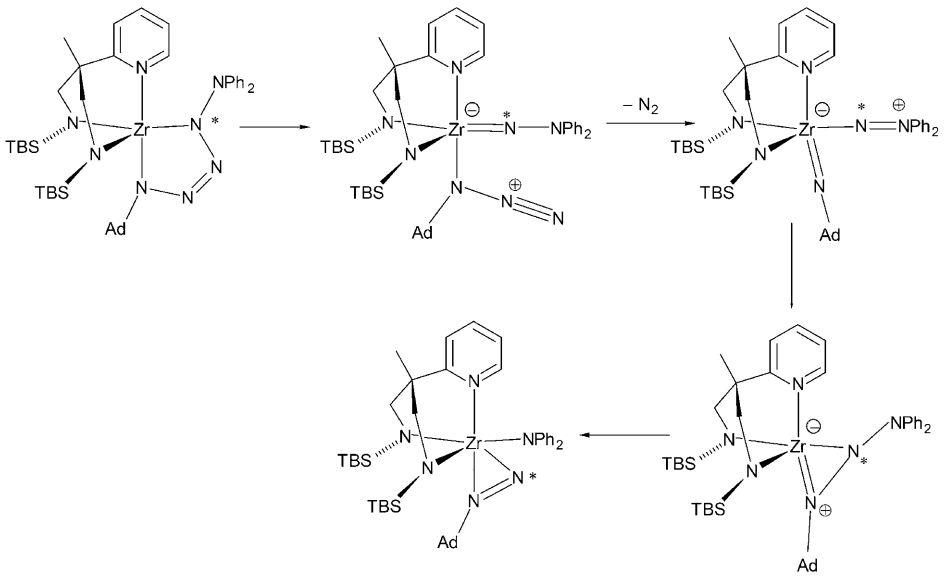
Figure 5. Selected frontier molecular Kohn–Sham orbitals of the $\{Mes\text{-}N{=}N\}^{-1}$ fragment, representing the double bond between the nitrogen atoms in the fragment. C gray, N blue, Si green, Zr turquoise.

To gain some insight into the reaction pathway leading to complexes **4** and **5**, the hydrazinediido compound **1** was ^{15}N-labeled in the N(α)-position (indicated by an asterisk in Scheme 1). Reaction with AdN_3 and $MesN_3$ and subsequent N_2 elimination gave complexes **4** and **5**, in which the substituent-free N4 position carried the label, implying the fragmentation of the hydrazido N–N bond and the transfer of the labeled nitrogen atom to the N atom (in the original azide) which is adjacent to the 1-adamantyl or mesityl substituent. The conversion into **4** and **5** following N_2 elimination must therefore occur via an $\{R\text{-}N\text{-}N\text{-}NPh_2\}$ state. A preliminary DFT (B3PW91)/ONIOM study of the fragmentation and N_2 extrusion process indicates such a species as an intermediate in the transformation of **3** into **4** (Scheme 2 and the Supporting Information).[17] The thermal fragmentation differs from the cycloreversion reported for the corresponding tetraazenides which regenerate the imide and the free azide.[5,18]

We have reported the first example of a [2+3] cycloaddition[19] involving a hydrazinediido ligand, which gave rise to a new N_5 unit. In this case, as in our previous study, the hydrazinediido ligand fragmented subsequently to the interaction with a substrate and transferred a nitrogen atom to an electronically unsaturated ligand fragment. As a general reactive principle it is expected to give access to further new structural units.

Received: November 18, 2008
Published online: February 9, 2009

Keywords: azides · cycloaddition · density functional calculations · nitrogen · zirconium



Scheme 2. Proposed reaction pathway for the conversion of **3** into **4**, based on an ONIOM (B3PW91:UFF) study. All species depicted correspond to local energy minima (confirmed by frequency analyses) and are therefore intermediates.

[1] Selected examples for all three cases: a) K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004; b) D. Mackay, D. D. McIntyre, N. J. Taylor, *J. Org. Chem.* **1982**, *47*, 532; c) C. M. Fitchett, C. Richardson, P. J. Steel, *Org. Biomol. Chem.* **2005**, *3*, 498; d) R. E. Cowley, J. Elhaïk, N. A. Eckert, W. W. Brennessel, E. Bill, P. L. Holland, *J. Am. Chem. Soc.* **2008**, *130*, 6074. See also e.g.: e) R. Engelke, *J. Phys. Chem.* **1992**, *96*, 10789; f) M. T. Nguyen, T.-K. Ha, *Chem. Ber.* **1996**, *129*, 1157.

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[4] Tetrazenido ligands were also obtained by reductive coupling of diazonium ions at low-valent transition-metal centers as well as thermal or photochemical degradation of aryl azides. Selected examples: a) A. B. Gilchrist, F. W. B. Einstein, G. W. Rayner-Canham, D. Sutton, *J. Am. Chem. Soc.* **1971**, *93*, 1826; b) P. Overbosch, G. van Koten, O. Overbeek, *J. Am. Chem. Soc.* **1980**, *102*, 2091; c) C. E. Johnson, W. C. Trogler, *J. Am. Chem. Soc.* **1981**, *103*, 6352; d) M. J. Maroney, W. C. Trogler, *J. Am. Chem. Soc.* **1984**, *106*, 4144; e) S. W. Leen, G. A. Miller, C. F. Campana, W. C. Trogler, *Inorg. Chem.* **1988**, *27*, 1215. Tetrazenides have also been generated in the coordination sphere of main-group metals. Examples: f) U. Fooken, W. Saak, M. Weidenbruch, *J. Organomet. Chem.* **1999**, *579*, 280; g) C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **2000**, *112*, 4705; *Angew. Chem. Int. Ed.* **2000**, *39*, 4531; h) N. J. Hardman, P. P. Power, *Chem. Commun.* **2001**, 1184.

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[10] All the calculations, including orbital analysis (NBO 3.0), were carried out using the Gaussian 03 program package.[10a] A detailed description of the methods is provided in the supporting info; a) Gaussian 03, Revision B.03, M. J. Frisch, et al., see the Supporting Information.

[11] Crystal data: **2**: $C_{50}H_{76}N_8Si_3Zr$; monoclinic; space group $P2_1/n$; $a = 12.089(1)$, $b = 24.999(2)$, $c = 16.865(1)$ Å; $\beta = 97.037(2)°$; $V = 5058.4(7)$ Å^3; $Z = 4$; $\mu = 0.330$ mm^{-1}; $F_{000} = 2056$. θ range 1.9 to 25.0°. Index ranges h, k, l (indep. set): −14–14, 0–29, 0–20. Reflections coll. 85154, indep. 8898 [$R_{int} = 0.0454$], obs. [$I > 2\sigma(I)$] 7469. Final R indices [$F_o > 4\sigma(F_o)$]: $R(F) = 0.0346$, $wR(F^2) = 0.0932$, $GooF = 1.075$. **5**: $C_{42}H_{62}N_6Si_2Zr$; monoclinic; space group $P2_1/c$; $a = 14.713(2)$, $b = 10.0813(15)$, $c = 28.870(4)$ Å; $\beta = 98.683(3)°$; $V = 4233(1)$ Å^3; $Z = 4$; $\mu = 0.352$ mm^{-1}; $F_{000} = 1696$. θ range 12.1 to 30.0°. Index ranges h, k, l (indep. set): −20–20, 0–14, 0–40. Reflections coll. 79980, indep. 12354 [$R_{int} = 0.0537$], obs. [$I > 2\sigma(I)$]: 8709. Final R indices [$F_o > 4\sigma(F_o)$]: $R(F) = 0.0665$, $wR(F^2) = 0.1923$, $GooF = 1.111$. Bruker AXS Smart 1000 CCD diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator, $\lambda = 0.71073$ Å, $T = 100(2)$ K. Structure solution: direct methods with dual-space recycling (SHELXD)[11a] (**2**) and heavy atom method combined with structure expansion by direct methods (DIRDIF)[11b] (**5**). Refinement: full-matrix least squares methods based on F^2;[11c] all non-hydrogen atoms anisotropic, hydrogen atoms at calculated positions (refined riding). Some electron density attributed to solvent of crystallization (disordered toluene) was removed from the structure (and the corresponding F_{obs}) of **2** (BYPASS/SQUEEZE).[11d] CCDC-708824 (**2**) and 708825 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; a) "Ab initio phasing": G. M. Sheldrick, H. A. Hauptman, C. M. Weeks, R. Miller, I. Usón in *International Tables for Crystallography, Vol. F* (Eds.: M. G. Rossmann, E. Arnold), IUCr and Kluwer Academic Publishers, Dordrecht, **2001**, pp. 333–351;

G. M. Sheldrick, *SHELXD*, University of Göttingen and Bruker Nonius, **2000–2004**; b) P. T. Beurskens in *Crystallographic Computing 3* (Eds.: G. M. Sheldrick, C. Krüger, R. Goddard), Clarendon, Oxford, UK, **1985**, p. 216; P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda, R. O. Gould, *DIRDIF-2008*, Radboud University Nijmegen, The Netherlands, **2008**; c) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**; G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112; d) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194; *PLATON*, Utrecht University, The Netherlands: A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7.

[12] Structures containing amido-N–Zr bonds: 1263 examples, from 1.877–2.529 Å in CSD, Cambridge, Version 5.29, Update 2 (August 2008).

[13] ^{15}N chemical shifts (ref $^{15}NH_3$) for selected nitrido ligands in transition-metal complexes a) [(N*t*BuAr)$_3$MoN] ($\delta = 840$ ppm): C. E. Laplaza, C. C. Cummins, *Science* **1995**, *268*, 861; b) [HIPTN$_3$N]MoN (898 ppm): D. V. Yandulov, R. R. Schrock, *J. Am. Chem. Soc.* **2002**, *124*, 6252; c) [(PhBP$^{i\mathrm{Pr}}_3$)FeN] ($\delta =$ 952 ppm): T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2004**, *126*, 6252; d) Na[(NNpAr)$_3$NbN] ($\delta = 754$ ppm): J. S. Figueroa, N. A. Piro, C. R. Clough, C. C. Cummins, *J. Am. Chem. Soc.* **2006**, *128*, 940; e) [(*t*BuO$_3$)WN] ($\delta = 732$ ppm) and [(*t*BuO$_3$)MoN] ($\delta = 829$ ppm): B. A. Burroughs, B. E. Bursten, S. Chen, M. H. Chisholm, A. R. Kidwell, *Inorg. Chem.* **2008**, *47*, 5377; f) [(TIMEN^{mes})FeN]BPh$_4$ ($\delta = 1121$ ppm): C. Vogel, F. W. Heinemann, J. Sutter, C. Anthon, K. Meyer, *Angew. Chem.* **2008**, *120*, 2721; *Angew. Chem. Int. Ed.* **2008**, *47*, 2681.

[14] There are many examples of structurally characterized complexes bearing diazenido ligands in end-on coordination mode. For an overview, see: a) S. Kahlal, J.-Y. Saillard, J.-R. Hamon, C. Manzur, D. Carrillo, *New J. Chem.* **2001**, *25*, 231. For recent examples see: b) A. R. Cowley, J. R. Dilworth, P. S. Donelly, S. J. Ross, *Dalton Trans.* **2007**, 73; c) W.-M. Cheung, Q.-F. Zhang, I. D. Williams, W.-H. Leung, *Inorg. Chem.* **2007**, *46*, 5754. Structurally characterized bridging diazenido ligands: Examples for (μ^2-η^2) ligation: d) L. K. Bell, W. A. Herrmann, M. L. Ziegler, H. Pfisterer, *Organometallics* **1982**, *1*, 1673; e) D. E. Samkoff, J. R. Shapley, M. R. Churchill, H. J. Wasserman, *Inorg. Chem.* **1984**, *23*, 397; f) F. W. B. Einstein, X. Yan, D. Sutton, *J. Chem. Soc. Chem. Commun.* **1990**, 1466; g) X. Yan, R. J. Batchelor, F. W. B. Einstein, D. Sutton, *Inorg. Chem.* **1996**, *35*, 7818. Examples for (μ^2-η^1) ligation: h) G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morell, S. Cenini, F. Bonati, *Chem. Commun.* **1967**, 739; i) M. R. Churchill, K.-K. G. Lin, *Inorg. Chem.* **1975**, *14*, 1133; j) M. R. Churchill, H. J. Wasserman, *Inorg. Chem.* **1981**, *20*, 1580; k) M. I. Bruce, M. L. Williams, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1986**, *309*, 157; l) F. Neve, M. Ghedini, G. De Munno, A. Crispini, *Inorg. Chem.* **1992**, *31*, 2979; m) P. Schollhammer, E. Guenin, F. Y. Petillon, J. Talarmin, K. W. Muir, D. S. Yufit, *Organometallics* **1998**, *17*, 1922; n) Y. Gao, M. C. Jennings, R. J. Puddephatt, H. A. Jenkins, *Organometallics* **2001**, *20*, 3500. Bridging diazenides have also been characterized in several studies on the activation of N_2 using Group 4 metal complexes. For a recent overview, see: o) Y. Ohki, M. D. Fryzuk, *Angew. Chem.* **2007**, *119*, 3242; *Angew. Chem. Int. Ed.* **2007**, *46*, 3180.

[15] J. R. Dilworth, I. A. Latham, G. J. Leigh, G. Huttner, I. Jibril, *J. Chem. Soc. Chem. Commun.* **1983**, 1368.

[16] V. M. Iluc, A. J. M. Miller, G. L. Hillhouse, *Chem. Commun.* **2005**, 5091.

[17] The elimination of dinitrogen from the Zr–N$_5$ compounds by a radical mechanism and subsequent recombination to give the N$_3$ intermediates has been considered in a preliminary computational study. In principle, an initial diradical intermediate, generated by N_2 elimination, could be in a triplet or singlet state. The DFT calculation (B3PW91) of the triplet state gives an intermediate which is geometrically similar to that found in the formally "heterolytic" cleavage but higher in energy by 15 kcal mol^{-1}. All attempts to calculate the diradical singlet state were unsuccessful. Instead of the diradical singlet, the electronic structure collapsed into the closed-shell state, reproducing the exact geometry and energies of the closed-shell calculations supporting the mechanism proposed in this work. These preliminary results suggest that the "heterolytic mechanism", as displayed in Scheme 2, is lower in energy for the case at hand.

[18] For a recent review covering the reactions of organic azides with transition-metal complexes, see: S. Cenini, E. Gallo, A. Caselli, F. Ragaini, S. Fantauzzi, C. Piangiolino, *Coord. Chem. Rev.* **2006**, *250*, 1234.

[19] This result is in contrast to several [2+2] cycloadditions reported recently by Mountford et al.: D. Selby, A. D. Schwarz, C. Schulten, E. Clot, C. Jones, P. Mountford, *Chem. Commun.* **2008**, 5101.

