

Azide Addition To Give a Tetra-azazirconacycle Complex

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Addition of the dilithium salt, *ortho*-(Me₃SiNLi)₂C₆H₄, to ZrCl₄ affords a base-free, D_{2d}-symmetric complex Zr^{IV}[*ortho*-(Me₃SiN)₂C₆H₄]₂ (**2**), with rigorously planar *ortho*-phenylenediamine ligands. Lewis acidic **2** readily coordinates donor ligands such as NHEt₂ to give the five-coordinate complex, Zr^{IV}(NHEt₂)[*ortho*-(Me₃SiN)₂C₆H₄]₂ (**3**), which is also accessible by the reaction of Zr(NEt₂)₄ with 2 equiv of *ortho*-(Me₃SiNH)₂C₆H₄. Aryl azides react with **2** and **3** to give an unusual tetra-azametallacycle complex, **4**, via 1,2-addition of a ligand N–Si bond to the organic azide. An X-ray crystal structure of **4** reveals a planar, five-membered metallacycle comprising the zirconium atom, one nitrogen atom of the *ortho*-(Me₃SiN)₂C₆H₄ ligand, and all three nitrogen atoms of the aryl azide.

Organic azide reactions with transition metal complexes have attracted considerable attention in recent years. Detailed mechanistic studies of azide activation have been carried out with Cp₂TaMe(PMe₃).^{1,2} In this system, an initial, η¹-terminal coordination mode for the azide substrate was supplanted via rearrangement by a four-centered metallacycle intermediate. Extrusion of N₂ from this intermediate gave a terminal metal imido complex, a common final product for reactions of organic azides and transition metal complexes.^{3–8} Organic azides also show a rich insertion chemistry with transition metal complexes. Azides react with metal carbonyls via N₂ extrusion and nitrene insertion into the M–CO bond to give isocyanates,^{5,9} whereas metal-stabilized phosphazido species (RN=N–N=PR'₃) can be obtained upon insertion of an azide into a metal phosphine bond.¹⁰ Insertion of an azide into a metal hydride bond gives an initial triazenido

ligand, which releases N₂ and forms a coordinated amide after a 1,3-proton shift.¹¹ Metal mediated coupling of two organic azides forms a tetra-azabutadiene fragment (RN=N–N=NR), which is stabilized when coordinated to the metal center.^{9,12–14} The two-electron reduced congener tetrazenes (RN–N=N–NR²⁻) have been prepared by 1,3-NH-addition of an arylamide to an aryl azide followed by deprotonation.¹⁵ Alternatively, coordinated tetrazene fragments have been obtained by the [3 + 2] reaction of an organic azide with a zirconium imide complex.^{16,17} In the course of studies on the coordination chemistry of the *ortho*-phenylenediamine derived ligand [*ortho*-(Me₃SiN)₂C₆H₄]₂²⁻ with group 4 metals, we discovered an unusual azide reaction leading to the formation of a tetra-azametallacycle complex, Zr^{IV}[ArNN(SiMe₃)NNC₆H₄NSiMe₃][*ortho*-(Me₃SiN)₂-C₆H₄] (**4**, Ar = *para*-CH₃C₆H₄). Formally, the product-forming reaction corresponds to a 1,2-NSi-addition to the incoming azide. An X-ray crystal structure reveals short N–N bond lengths within the tetra-azametallacycle fragment, consistent with a delocalized electronic structure that is intermediate between a formally dianionic tetrazene fragment and a formally neutral tetra-azabutadiene fragment.

Metalation of diamine **1**^{18,19} was readily achieved upon deprotonation with *n*BuLi and subsequent addition of half of an equivalent of ZrCl₄ according to Scheme 1. Solvent removal gave the crude product, Zr^{IV}[*ortho*-(Me₃SiN)₂C₆H₄]₂ (**2**), in nearly quantitative yield as a bright orange powder. Recrystallization of crude **2** from CH₂Cl₂ at –35 °C gave large orange blocks of the product in 47% overall yield; the results of an X-ray diffraction experiment are shown in

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- (1) Proulx, G.; Bergman, R. G. *Organometallics* **1996**, *15*, 684–692.
- (2) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 6382–6383.
- (3) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239–482.
- (4) Lwowski, W. *Nitrenes*; Interscience Publishers: New York, 1970.
- (5) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322–323.
- (6) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 11238–11239.
- (7) Guillemot, G.; Solari, E.; Floriani, C.; Rizzoli, C. *Organometallics* **2001**, *20*, 607–615.
- (8) Fickes, M. G.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 6384–6385.
- (9) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279–293.
- (10) Hillhouse, G. L.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1982**, *21*, 2064–2071.

- (11) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025–1029.
- (12) Barloy, L.; Gauvin, R. M.; Osborn, J. A.; Sizun, C.; Graff, R.; Kyritsakas, N. *Eur. J. Inorg. Chem.* **2001**, 1699–1707.
- (13) Johnson, C. E.; Trogler, W. C. *Inorg. Chem.* **1982**, *21*, 427–429.
- (14) Gross, M. E.; Trogler, W. C. *J. Organomet. Chem.* **1981**, *209*, 407–414.
- (15) Lee, S. W.; Miller, G. A.; Campana, C. F.; Maciejewski, M. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5050–5051.
- (16) Michelman, R. I.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1993**, *12*, 2741–2751.
- (17) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974–985.
- (18) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378–3380.
- (19) Boncella, J. M.; Wang, S.-Y. S.; VanderLende, D. D.; Leigh, H. R.; Abboud, K. A.; Vaughn, W. M. *J. Organomet. Chem.* **1997**, *530*, 59–70.

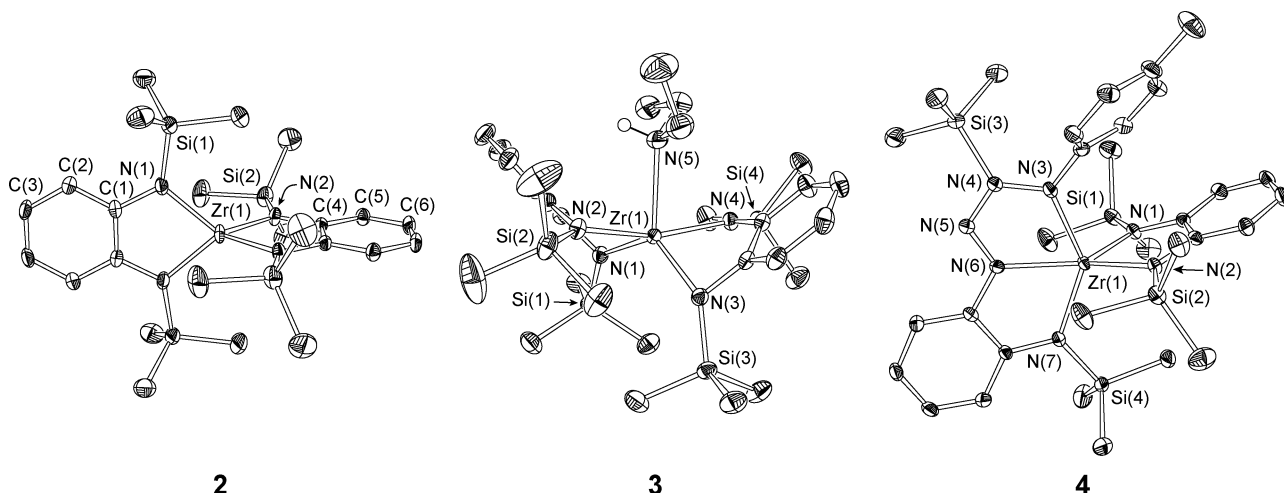
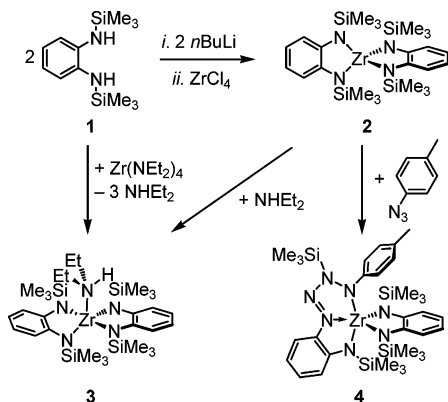


Figure 1. ORTEP representations of $\text{Zr}^{\text{IV}}[\text{ortho}-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]_2$ (**2**), $\text{Zr}^{\text{IV}}(\text{NHET}_2)[\text{ortho}-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]_2$ (**3**), and $\text{Zr}^{\text{IV}}[\text{ArNN}(\text{SiMe}_3)\text{NNC}_6\text{H}_4\text{NSiMe}_3][\text{ortho}-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]$ (**4**, Ar = *para*- $\text{CH}_3\text{C}_6\text{H}_4$). Ellipsoids are drawn at 50% probability, and hydrogen atoms have been removed for clarity.

Figure 1 as an ORTEP diagram.²⁰ The zirconium coordination environment in **2** is D_{2d} -symmetric with planar sp^2 -hybridized amide nitrogen atoms. The *ortho*-phenylenediamine ligands are planar and offset from each other by a $91(1)^\circ$ dihedral angle. This stands in stark contrast to other complexes of zirconium with *ortho*-phenylenediamine ligands.^{21,22} In these structures, the chelating ligands were puckered, suggesting a possible η^4 -type interaction between the electrophilic metal center and *ortho*-phenylenediamine ring electrons. Despite the difference in ligand conformation, the average Zr–N distance in **2** (2.08 Å) is comparable to the Zr–N distances in these previously reported zirconium complexes (2.06–2.10 Å).

Scheme 1



The electrophilicity of **2** is evident from its rapid coordination of NHET_2 in solution to give $\text{Zr}^{\text{IV}}(\text{NHET}_2)[\text{ortho}-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]_2$ (**3**). Alternatively, **3** may be prepared directly by the reaction of **1** with $\text{Zr}(\text{NHET}_2)_4$. An X-ray diffraction experiment, performed on a yellow crystal of **3** obtained from

chilled pentane solution, showed pseudo-trigonal-bipyramidal coordination geometry about zirconium; the ORTEP diagram for **3** is shown in Figure 1.²³ Two axial and two equatorial sites are occupied by anilide nitrogen atoms of the *ortho*-phenylenediamine ligand. The axial Zr–N distances are long (Zr–N(2) 2.1642(16) Å and Zr–N(4) 2.1710(15) Å) relative to the equatorial Zr–N bond distances (Zr–N(1) 2.0640(15) Å and Zr–N(3) 2.0692(15) Å). Though all four anilide nitrogen atoms are planar, the chelating ligands adopt a puckered or bent conformation as previously observed.^{21,22} The Zr–N distance for the diethylamine ligand is 2.3953(18) Å, and the nitrogen atom is clearly sp^3 hybridized; the amine hydrogen was located in the Fourier map.

NMR spectroscopy identified a fluxional coordination environment for **3** in solution. At ambient temperature, the ^1H NMR spectrum of **3** shows broadened resonances for both the aryl ring and the coordinated NHET_2 ligand, suggesting that **3** is fluxional in solution. Variable-temperature ^1H NMR experiments were used to probe this isomerization process. The low-temperature ^1H NMR spectrum is consistent with the five-coordinate, pseudo-trigonal-bipyramidal geometry determined in the X-ray diffraction experiment. Distinct SiMe_3 resonances were observed at 0.35 and 0.41 ppm, consistent with one axial-oriented and one equatorial-oriented SiMe_3 group on each *ortho*-phenylenediamine ligand. Diastereotopic resonances were observed for the coordinated NHET_2 ligand at low temperature. Upon warming, exchange between the axial and equatorial sites in **3** becomes facile, and a single environment was observed for the SiMe_3 groups of the *ortho*-phenylenediamine ligands. Similarly, the diastereotopic resonances for the coordinated NHET_2 ligand collapse at elevated temperatures. The resonances for the SiMe_3 groups were used to determine isomerization rates between -35 and $+5$ °C; activation parameters were extracted from an Eyring plot: $\Delta H^\ddagger = 13.1 \pm 0.9$ kcal mol $^{-1}$ and $\Delta S^\ddagger = 0 \pm 4$ eu.

(20) Crystallographic data for **2** follow. $\text{C}_{24}\text{H}_{44}\text{N}_4\text{Si}_4\text{Zr}$, fw 592.21, monoclinic, $C2/c$, $a = 15.362(4)$ Å, $b = 14.093(4)$ Å, $c = 14.677(4)$ Å, $\beta = 90.082(4)^\circ$, $V = 3177.6(13)$ Å 3 , $Z = 4$, $\lambda = 0.71073$ Å, $\rho_{\text{calc}} = 1.238$ Mg/m 3 , $\mu = 0.515$ mm $^{-1}$, $R1 = 0.0192$, $wR2 = 0.0528$, $\text{GOF} = 1.094$.

(21) Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923–927.

(22) Pindado, G. J.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1998**, 393–400.

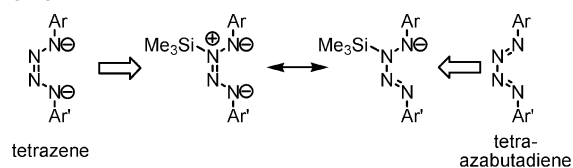
(23) Crystallographic data for **3** follow. $\text{C}_{28}\text{H}_{55}\text{N}_5\text{Si}_4\text{Zr}$, fw 665.35, monoclinic, $P2_1/n$, $a = 11.8325(9)$ Å, $b = 22.8851(18)$ Å, $c = 13.4664(11)$ Å, $\beta = 95.8120(10)^\circ$, $V = 3627.8(5)$ Å 3 , $Z = 4$, $\lambda = 0.71073$ Å, $\rho_{\text{calc}} = 1.218$ Mg/m 3 , $\mu = 0.459$ mm $^{-1}$, $R1 = 0.0283$, $wR2 = 0.0689$, $\text{GOF} = 1.096$.

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Compound **2** reacts with *para*-tolyl azide at room temperature to afford a unique tetra-azametallacyclopentene product formed by 1,2-addition of a single N–Si bond to the organic azide. Addition of *para*-tolyl azide to a suspension of **2** in toluene gave a cherry-red solution. Pure product was obtained by adding heptane to induce precipitation. An X-ray crystal structure revealed the product to be $\text{Zr}^{\text{IV}}[\text{ArNN}(\text{SiMe}_3)\text{NNC}_6\text{H}_4\text{NSiMe}_3][\textit{ortho}-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]$ (**4**, Ar = *para*- $\text{CH}_3\text{C}_6\text{H}_4$), a tetra-azametallacyclopentene complex shown as an ORTEP structure in Figure 1.²⁴

Compound **4**, formed by 1,2-*NSi*-addition to the organic azide, is a tetra-azametallacycle, intermediate between the dianionic tetrazene and neutral tetra-azabutadiene congeners. Apparently, addition of the SiMe_3 group to the azide β nitrogen traps the one-electron reduced azide in the metal-cyclic structure. The X-ray crystal data for **4** shows short N–N bond lengths within the tetra-azametallacycle ring (N(3)–N(4) = 1.396(2) Å, N(4)–N(5) = 1.301(3) Å, N(5)–N(6) = 1.312(3) Å), comparable to the N–N bond lengths observed in both tetrazene¹⁷ and tetra-azabutadiene²⁵ complexes. The planar arrangement of the four nitrogen atoms is consistent with delocalization of electron density throughout the fragment by the two resonance structures shown in Scheme 2. The monoanionic, diazene–diazide form seems

Scheme 2



most plausible on the basis of charge minimization and would suggest that N(6) is coordinated to zirconium as a neutral two-electron donor atom. The observed elongation of the Zr–N(6) bond (2.2305(18) Å) relative to the other amide Zr–N distances in the X-ray structure of **4** is consistent with this

(24) Crystallographic data for **4** follow. $\text{C}_{31}\text{H}_{51}\text{N}_7\text{Si}_4\text{Zr}$, fw 725.37, triclinic, $P1$, $a = 10.0465(9)$ Å, $b = 12.0462(11)$ Å, $c = 16.4033(15)$ Å, $\alpha = 99.963(2)^\circ$, $\beta = 94.636(2)^\circ$, $\gamma = 99.203(2)^\circ$, $V = 1918.0(3)$ Å³, $Z = 2$, $\lambda = 0.71073$ Å, $\rho_{\text{calc}} = 1.256$ Mg/m³, $\mu = 0.442$ mm⁻¹, $R1 = 0.0329$, $wR2 = 0.0778$, $\text{GOF} = 1.080$.

(25) Lee, S. W.; Troglor, W. C. *Organometallics* **1990**, *9*, 1470–1478.

proposal. The aryl ring of the activated *ortho*-phenylenediamine ligand is coplanar with the tetra-azametallacycle as a consequence of chelation. Conversely, the *para*-tolyl ring of the azide is almost perfectly staggered with respect to the tetra-azametallacycle. This orientation of the tolyl ring is likely due to steric interactions with the proximal SiMe_3 group. One of the *ortho*-phenylenediamine ligands remains unperturbed in **4**, with the phenyl ring bent up by 13° with respect to the plane defined by N(1)–Zr(1)–N(2).

Preliminary experiments suggest that the reaction between **2** and *para*-tolyl azide requires the presence of the electrophilic zirconium metal center. First, 1:1 solutions of *para*-tolyl azide and **1** in C_6D_6 showed no evidence of reaction after several days at room temperature. Second, the reaction of *para*-tolyl azide with **3** proceeds to give **4**, albeit at a reduced rate. This qualitative result is consistent with dissociation of the NHET_2 ligand from **3**, to give **2**, prior to formation of a reactive zirconium–azide adduct. The nature of this zirconium–azide intermediate and the mechanistic details leading to formation of **4** are the subject of ongoing studies.

The coordination geometry of **4** is preserved in solution. The unperturbed *ortho*-phenylene diamine ligand is characterized by a single SiMe_3 peak and the normal AA'BB' aromatic resonance pattern in the ¹H NMR spectrum. The SiMe_3 of the azametallacycle fragment is observed as a sharp singlet at 0.06 ppm, and the CH_3 of the tolyl group is observed clearly as a singlet at 1.92 ppm. Heating solutions of **4** under argon results in decomposition of the metal complex. Decomposition reactions monitored by ¹H NMR spectroscopy showed clean first-order decay of the resonances associated with **4**, but no new NMR-observable species was observed. Current efforts are directed toward elucidating the decomposition and reactivity pathways of **4**.

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Supporting Information Available: X-ray crystallographic data (CIF format) and detailed experimental methods (PDF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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