

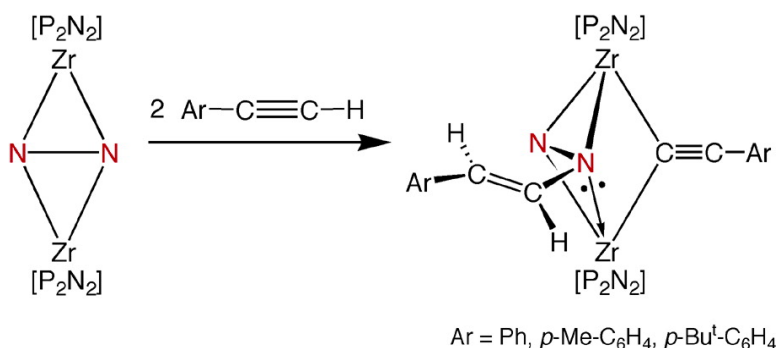
Communication

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Lara Morello, Jason B. Love, Brian O. Patrick, and Michael D. Fryzuk

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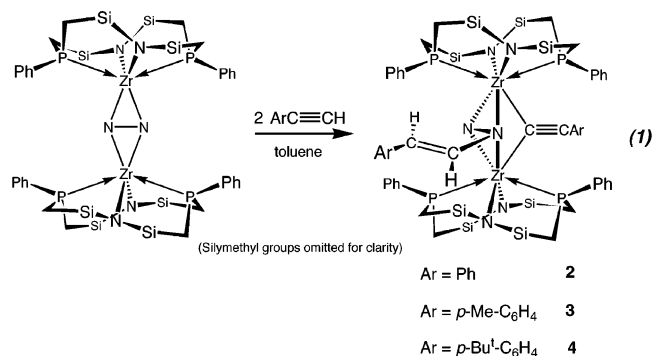
Lara Morello, Jason B. Love, Brian O. Patrick, and Michael D. Fryzuk*

Department of Chemistry, University of British Columbia, 2036 Main Mall,
Vancouver, British Columbia V6T 1Z1, Canada

Received January 28, 2004; E-mail: fryzuk@chem.ubc.ca

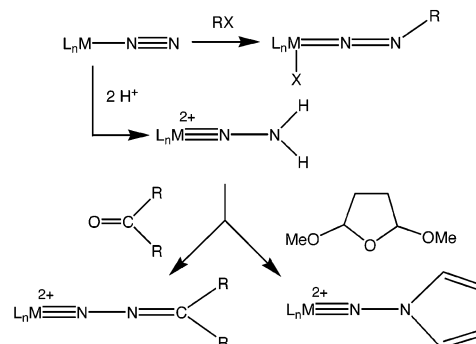
Functionalization of coordinated dinitrogen to generate carbon–nitrogen bonds is an essential step in the formation of organo-nitrogen materials from molecular nitrogen.¹ Demonstration of this process has been largely limited to the reaction of isolable group 6 metal dinitrogen complexes with *electrophilic* reagents such as alkyl and acyl halides or by an initial protonation process followed by condensation with aldehydes or ketones (Scheme 1).² In both cases, the use of electrophiles is essential but unfortunately not applicable to a catalytic process since these conditions are incompatible³ with the reductive process required to regenerate the starting N₂ complexes (typically L_nM = Mo(N₂)(dppe)₂). To avoid the incompatibility issue, dinitrogen can be prereduced by lithium in the presence of Ti(IV) and Me₃SiCl to generate an ill-defined material that has been deployed in natural product synthesis.⁴ In this report, we detail a new reaction for coordinated dinitrogen that uses a well-defined bimetallic zirconium complex and results in the formation of a carbon–nitrogen bond but does not involve electrophilic reagents.

We have previously reported⁵ the formation of N–H and N–Si bonds by the reaction of dihydrogen and silanes, respectively, with the dinuclear side-on dinitrogen complex ([P₂N₂]Zr)₂(μ-η²:η²-N₂), **1**, (where [P₂N₂] = PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh). The reaction of **1** with a slight excess of phenylacetylene (PhC≡CH) results in the slow discharge of the deep blue-green color of the starting dinitrogen complex and the formation of a bright orange solution from which orange crystals of **2** can be obtained.⁷ Other terminal alkynes also can be utilized in this process; addition of *p*-tolylacetylene results in the formation of **3**, while the use of *p*-Bu^t-C₆H₄C≡CH generates **4** (eq 1). At room temperature, the ¹H NMR spectrum of these species



is broad and not very informative; at lower temperatures, a very complicated set of sharp peaks is observed, indicative of a very unsymmetrical structure. To determine the identity of this species, a single-crystal X-ray analysis⁸ was undertaken (Figure 1). As is evident from the solid-state structure, two equivalents of *p*-tolylacetylene have been incorporated between the Zr centers; one acetylide acts as a bridging unit, whereas the other unit has been

Scheme 1



converted into a *p*-Me-styryl–hydrazido unit via N–C bond formation to the side-on dinitrogen unit. The N–N bond length in **3** is 1.457(4) Å, virtually identical to that of the starting acetylide unit is 1.202(6) Å, while the styryl moiety attached to the dinitrogen unit has a C–C bond length of 1.330(6) Å, indicating a double bond.

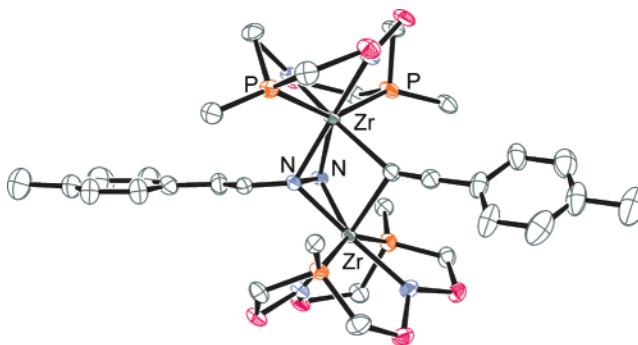
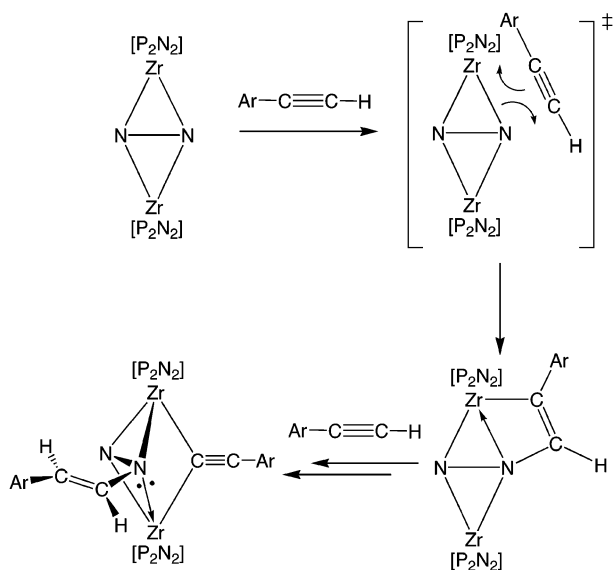


Figure 1. ORTEP representation of the molecular structure of the *p*-tolylacetylide complex **3**; the silylmethyl groups have been removed for clarity; only the ipso carbons of the P-phenyl groups are shown.

All of these reactions require approximately one week for completion and are easily monitored by the loss of the deep blue-green color of the starting dinitrogen complex **1** and the formation of orange solutions of the alkynyl products **2–4**. Monitoring the reaction by ³¹P NMR spectroscopy does not indicate the presence of intermediates; in fact, if only one equivalent of terminal alkyne is used, one observes the formation of product and unreacted starting material. The rates of the disappearance of the dinitrogen complex were studied in the presence of phenylacetylene and *d*₁-phenylacetylene and found to be identical within experimental error, indicating a *k*_H/*k*_D of 1.0(1). On the basis of the lack of a primary isotope effect, the mechanism shown in Scheme 2 is proposed. Cycloaddition⁹ of alkyne across a Zr–N bond results in the

Scheme 2



formation of a zircona-aza-cyclobutene intermediate that subsequently undergoes cleavage of the Zr–C bond by protonation with the second equivalent of terminal alkyne. This two step process results in the requisite *E* stereochemistry across the C=C bond and the formation the Zr–CCAr unit that rearranges to a bridging mode. Obviously other mechanisms can be considered, including initial deprotonation of the terminal alkyne by the dinitrogen complex to form transient $([P_2N_2]Zr)_2(\mu-\eta^2:\eta^2-NNH)(\mu-CCAr)$ followed by N–H addition across the second equivalent of $ArCCCH$;¹⁰ however, this latter process would be expected to show a primary isotope effect.

The substituted styryl–hydrazido complexes **2–4** all display a fluxional process as evidenced by variable-temperature NMR spectroscopy. At low temperatures, the ³¹P NMR spectra of these products show the presence of four inequivalent phosphorus donors, each resonance appears as a doublet due to coupling to the other inequivalent P donor in the same macrocyclic ligand. Also at low temperatures, the ¹H NMR spectrum is extremely complicated, indicative of *C*₁ symmetry. As the temperature is raised, the signals in the ³¹P NMR spectrum coalesce to a broad resonance, and with slight heating, a broadened doublet is observed. Similar broadening in the ¹H NMR spectrum is also observed, but the spectra are too complicated to glean useful information from these data. Nevertheless, one can propose a process that accounts for the fluxional behavior and the change in symmetry as the temperature is varied. The two ends of the dinuclear zirconium complex are identical, but they are slightly staggered with respect to one another when examined along the Zr–Zr vector. Because of the lack of symmetry in the bridging $\eta^2:\eta^2-N-N-CH=CHAr$ moiety, each phosphorus nucleus resides in a unique environment in the low-temperature limit analogous to the solid-state molecular structure. As the temperature is raised, the two ends of the dinuclear complex rotate so that the phosphorus donors are eclipsed and eventually rotate past each other. Such a rocking motion would equilibrate the Zr[P₂N₂] ends of the molecule, resulting in overall *C*_s symmetry in the high-temperature limit.

While this new reaction for coordinated dinitrogen expands the repertoire of known carbon–nitrogen bond-forming processes, the above transformations are nevertheless still stoichiometric because highly reducing conditions are necessary for the production of the starting dinitrogen complex **1**. Indeed, the next breakthroughs in the activation of molecular nitrogen¹¹ will require new, milder methods¹² for coordination of dinitrogen in concert with milder, less electrophilic reactivity patterns and finally a method to release the functionalized nitrogen-containing moiety. Such efforts are being actively pursued in our laboratory.

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Supporting Information Available: Complete experimental details, information on X-ray data collection and processing for **2–4**. X-ray crystallographic data for **2–4** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) A typical experimental procedure is given for the formation of **3**: A slight excess of (*p*-tolyl)acetylene (0.06 M, 8 mL, 0.48 mmol) was added to a stirred solution of $([P_2N_2]Zr)_2(\mu-\eta^2:\eta^2-N_2)$ (250 mg, 0.20 mmol) in toluene (10 mL) at room temperature and allowed to sit without stirring for one week. Over this period, a color change from blue-green to orange was observed. Orange crystalline platelets of **3** were deposited in situ from the slow evaporation of toluene/hexanes. Yield: 133 mg, 45%. Anal. Calcd for C₆₆H₁₀₀N₆P₄Si₈Zr₂: C, 52.55; H, 6.68; N, 5.57. Found: C, 52.95; H, 6.87; N, 5.74. MS EI Low res. (*M*⁺) *m/z*: 1509. Isolated yields of **2** and **4** are similar.
- (8) Crystal data for **3**: empirical formula: Zr₂P₄Si₈N₆C₆₉H₁₀₇; molecular weight: 1551.66 g mol⁻¹; crystal system: triclinic; space group: *P*1 (no. 2); volume: 4026.6(4) Å³; *Z* = 2; μ (MoK α) = 4.98 cm⁻¹; unit cell dimensions: *a* = 12.5329(7) Å, *b* = 13.3989(5) Å, *c* = 25.997(2) Å, α = 91.876(2)°, β = 103.279(1)°, γ = 107.544(2)°; crystal size = 0.40 mm × 0.20 mm × 0.07 mm; total no. of reflections = 32629; total no. of unique reflections = 15659; correction factors: 0.7231–1.0000; no. of variables = 824; R1 (*F*², *I* > 2 σ (*I*)): 0.055; *R*_w(*F*², all data) = 0.136; *gof*: 1.12. Data were collected at –100 ± 1 °C on a Rigaku/ADSC CCD diffractometer. Data were collected and processed using d*TREK Area Detector Software, version 4.13, Molecular Structure Corporation (1996–1998). The structures of **3** and **4** were solved by direct methods (SIR92 or SIR97) and expanded using Fourier techniques (DIRDIF94). Hydrogen atoms were included but not refined. Non-hydrogen atoms were refined anisotropically.
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