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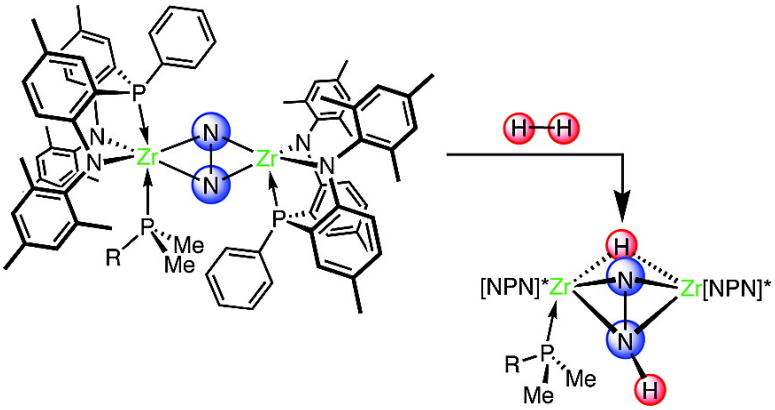

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New Side-On Bound Dinitrogen Complexes of Zirconium Supported by an Arene-Bridged Diamidophosphine Ligand and Their Reactivity with Dihydrogen

Erin A. MacLachlan, Fiona M. Hess, Brian O. Patrick, and Michael D. Fryzuk*

Contribution from the Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada, V6T 1Z1

Received May 24, 2007; E-mail: fryzuk@chem.ubc.ca

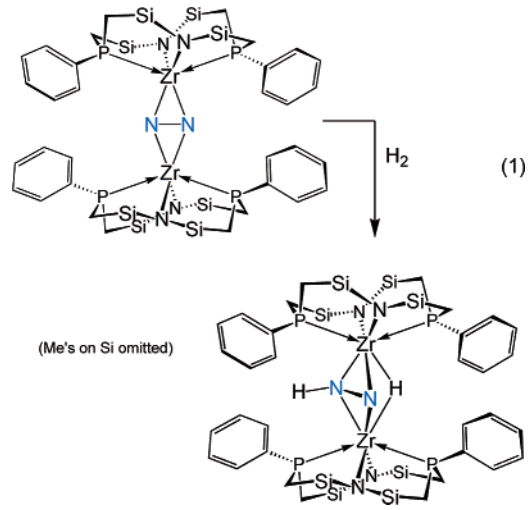
Abstract: A new dinitrogen complex, deep blue-green {[NPN]*Zr(THF)}$_2$(μ-η^2:η^2-N$_2$) ([NPN]* = {[*N*-(2,4,6-Me$_3$C$_6$H$_2$)(2-N-5-MeC$_6$H$_3$)]$_2$PPh}), was prepared in high yield by the reduction of [NPN]*ZrCl$_2$ with 2.2 equiv of KC$_8$ in THF under N$_2$. The solid-state molecular structure shows that N$_2$ is strongly activated (N−N bond length: 1.503(6) Å) and bound side-on to two Zr atoms. Coordinated THF can be readily replaced by adding pyridine (py) or PMe$_2$R (R = Me, Ph) to the complex to obtain {[NPN]*Zr(py)}$_2$(μ-η^2:η^2-N$_2$) or {[NPN]-*Zr(PMe$_2$R)}(μ-η^2:η^2-N$_2$){Zr[NPN]*} in high yield. X-ray diffraction experiments show that the N$_2$ moiety is strongly activated and remains side-on bound to Zr for the py and PMe$_2$Ph adducts; interestingly, only one PMe$_2$Ph coordinates to the Zr$_2$N$_2$ unit. {[NPN]*Zr(PMe$_2$R)}(μ-η^2:η^2-N$_2$){Zr[NPN]*} reacts slowly with H$_2$ to provide {[NPN]*Zr(PMe$_2$R)}(μ-H)(μ-η^2:η^2-N$_2$H){Zr[NPN]*}, as determined by isotopic labeling, and multinuclear NMR spectroscopy. The THF adduct does not react with H$_2$ even after an extended period, whereas the pyridine adduct does undergo a reaction with H$_2$, but to a mixture of products.

Introduction

The reaction of the molecular forms of nitrogen and hydrogen over activated iron or ruthenium heterogeneous catalysts to form ammonia is arguably one of the most important industrial processes practiced worldwide.[1] Nowadays known as the Haber−Bosch process, millions of tons of NH$_3$ are generated annually by this thermodynamically favorable, but kinetically sluggish, reaction and used further to generate fertilizers, explosives, and other commodity materials. The details of the interaction of N$_2$, H$_2$, and NH$_3$ over these heterogeneous catalysts are complicated by surface restructuring, formation of subnitrides, promoter effects, and the importance of defects.[2] Nevertheless, progress in the discovery of new catalyst systems, particularly metal alloys, does show promise.[3]

It is remarkable that no one has discovered a homogeneous catalyst that can produce ammonia from N$_2$ and H$_2$ in analogy to the Haber−Bosch process. Part of the explanation for this observation no doubt lies in the extreme inertness of molecular nitrogen. In fact, until recently, the outcome of the reaction of soluble metal−dinitrogen complexes with H$_2$ was typically loss of coordinated N$_2$ and the formation of a dihydrogen metal species or a hydride derivative.[4] In addition, unlike other small molecules, fundamental transformations of coordinated N$_2$ have not been well established.[5]

In 1997, we reported[6] the first ever formation of N−H bonds by the addition of H$_2$ to a dinitrogen complex. The reaction of ([P$_2$N$_2$]Zr)$_2$(μ-η^2:η^2-N$_2$) (where [P$_2$N$_2$] is [PhP(CH$_2$SiMe$_2$-NSiMe$_2$CH$_2$)$_2$PPh]) with dihydrogen produces ([P$_2$N$_2$]Zr)$_2$(μ-η^2:η^2-N$_2$H)(μ-H) as shown in eq 1.



Although initial theoretical calculations suggested[7] that an additional equivalent of H$_2$ could be activated by this system to generate the corresponding diazenido-dihydride, ([P$_2$N$_2$]Zr)$_2$-

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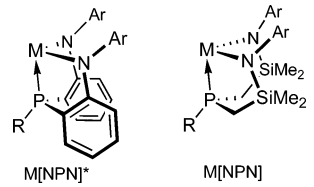
(μ-η^2:η^2-N_2H_2)(μ-H)$_2$, we were never able to detect this process in the laboratory.[8] However, it has been recently reported[9] that a bis(tetramethylcyclopentadienyl) zirconium dinitrogen complex [(η^5-$C_5Me_4H)_2Zr]_2$(μ-η^2:η^2-N_2) does react with 2 equiv of H_2 to generate the diazenido-dihydride species [(η^5-$C_5Me_4H)_2$-$ZrH]_2$(μ-η^2:η^2-N_2H_2). In these two aforementioned examples alone, one can see how important the ancillary ligands are to changing the outcome of the reaction, in that the macrocyclic diamidodiphosphine donor set allows activation of just one H_2 molecule, whereas the tetramethylcyclopentadienyl ligands promote reaction with 2 equiv of H_2. Even more remarkable are the subtle differences in substitution of the cyclopentadienyl ligand and their outcomes.[10] For example, use of the pentamethylcyclopentadienyl ligand coordinated to zirconium results in a different binding mode for N_2, that is, [(η^5-$C_5Me_5)_2ZrN_2]_2$-(μ-N_2), and displacement of dinitrogen upon reaction with H_2 to form (η^5-$C_5Me_5)_2ZrH_2$.[11] Other substitution patterns on the cyclopentadienyl unit also can lead to hydrogen activation. Clearly, trying to anticipate what systems might be amenable to both N_2 and H_2 activation is challenging with the rather small set of known dinitrogen complexes that react with dihydrogen to form N−H bonds.

Our goal in the area of dinitrogen activation has been to expand the known reactivity patterns of complexes that contain coordinated N_2. By focusing on those reactions that result in new nitrogen−hydrogen,[6,7] nitrogen−carbon,[12] and nitrogen−heteroatom bonds,[13] we hope to develop individual transformations that potentially can be combined into catalytic processes that result in the conversion of N_2 to higher-value nitrogen-containing materials. In this paper we disclose the synthesis of a series of new, dinuclear dinitrogen complexes of zirconium that contain side-on bound N_2. In addition, we also report the results of the reaction of these complexes with dihydrogen.

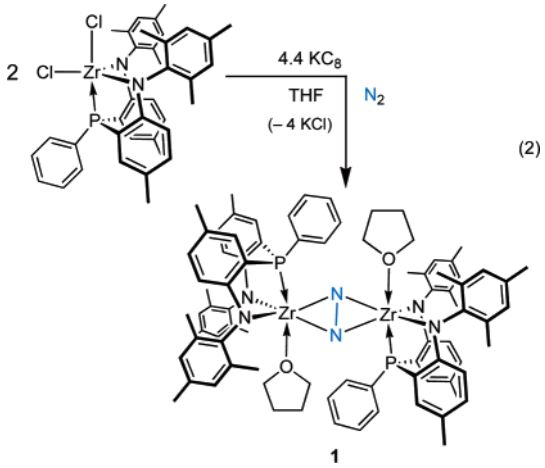
Results and Discussion

Synthesis of {[NPN]*Zr(THF)}$_2$(μ-η^2:η^2-N_2) (1). We have previously reported the synthesis of the diamidophosphine ligand [NPN]* (where [NPN]* is {[*N*-(2,4,6-$Me_3C_6H_2$)(2-N-5-MeC_6H_3)]$_2$PPh}), which incorporates substituted *o*-phenylene linkages between the phosphine and amido donors and the resulting coordination complex [NPN]*$ZrCl_2$.[14] These *o*-phenylene linkers were installed in this particular ligand design to overcome the lability of the N−Si bond and minimize the flexibility of the backbone in the earlier reported diamidophosphine donor set [NPN] (where [NPN] is [PhP(CH_2SiMe_2-NPh)$_2$]);[13,15] the comparison of generic metal coordination environments is shown in Chart 1.

Chart 1



The reduction of [NPN]*$ZrCl_2$ by 2.2 equiv of KC_8 in THF under 4 atm of N_2 provides deep blue-green {[NPN]*Zr(THF)}$_2$-(μ-η^2:η^2-N_2) (**1**) in 79% yield, as shown in eq 2.



Dinitrogen complex **1** decomposes to unknown products when powdered or crystalline samples are stored under vacuum overnight, or under N_2 at room temperature for several days; crystalline samples are dried under vacuum only briefly (15 min) prior to analysis. In solution under N_2, **1** is stable for extended periods although it is very sensitive to air and moisture.

An ORTEP representation of the solid-state molecular structure of **1** as determined by single-crystal X-ray diffraction is shown in Figure 1, along with selected bond lengths and angles. The dinuclear complex features two coordinated THF molecules, along with facially coordinated [NPN]* ligands. The dinitrogen moiety bridges the two Zr atoms side-on, and there is a slight butterfly distortion to the Zr_2N_2 fragment: the angle between the two ZrN_2 planes is 166°. The N−N bond length is 1.503(6) Å, which corresponds to reduction to N_2^{4-}, or hydrazido(4−). The Zr−N bond lengths to N_2 are slightly different: Zr1−N3 is 2.023(3) Å, and Zr1−N3′ is 2.089(3) Å. The zirconium amido bond distances, Zr−N1 and Zr−N2, are 2.184(3) and 2.224(3) Å, respectively, and are similar to those found in the starting dichloride [NPN]*$ZrCl_2$. The N−N bond length in **1** is identical to that of {[NPN]Zr(THF)}$_2$(μ-η^2:η^2-N_2) (1.503(3) Å)[15] but shorter than the N−N bond in {[PNP]-ZrCl}$_2$(μ-η^2:η^2-N_2) (1.548(7) Å), the longest intact N−N bond observed for a metal complex.[16] (Cp″$_2$Zr)$_2$(μ-η^2:η^2-N_2) (Cp″ = 1,3-$(SiMe_3)_2$-η^5-C_5H_3) has a similar N−N bond length to **1**,

(8) Yates, B. F.; Basch, H.; Musaev, D. G.; Morokuma, K. *J. Chem. Theory Comput.* **2006**, *2*, 1298.
(9) (a) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527. (b) An analogous hafnium complex shows similar reactivity, see: Bernskoetter, W. H.; Olmos, A. V.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 1021.
(10) Bernskoetter, W. H.; Lobovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 14051.
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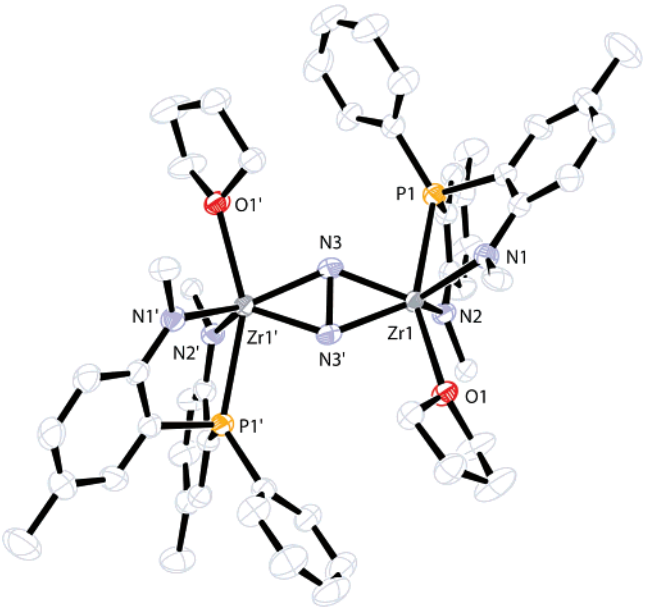

Figure 1. Solid-state molecular structure of **1** (ellipsoids at 50% probability). Carbon atoms of mesityl substituents (except C_{ipso}) and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Zr1−P1 2.6777(10), Zr1−N1 2.184(3), Zr1−N2 2.224(3), Zr1−O1 2.371(2), Zr1−N3 2.023(3), Zr1−N3′ 2.089(3), N3−N3′ 1.503(6), P1−Zr1−N1 71.84(8), P1−Zr1−N2 73.42(8), N3−Zr1−N3′ 42.85(15), Zr1−N3′−Zr1′ 135.02(15), O1−Zr1−P1 154.14(7), P1−Zr−N3 82.00(8).

within error, at 1.47(3) Å.[17] Other side-on bound Zr−N_2 complexes contain somewhat shorter N−N bonds: ({[P_2N_2]Zr}$_2$-(μ-η^2:η^2-N_2) (1.43(1) Å),[6] [(η^5-C_5Me_4H)$_2$Zr]$_2$(μ-η^2:η^2-N_2) (1.377(3) Å),[9a] and (*rac*-BpZr)$_2$(μ-η^2:η^2-N_2) (1.241(3) Å).[18] In comparison to the closely related derivative,{[NPN]Zr(THF)}$_2$-(μ-η^2:η^2-N_2), the Zr−P bond lengths for **1** are quite similar (2.6685(5) and 2.6777(10) Å, respectively); however, the THF molecules are much more tightly bound in {[NPN]Zr(THF)}$_2$-(μ-η^2:η^2-N_2) as compared to **1** as evidenced by the longer Zr−O bond distance of 2.371(2) Å in **1** as compared to 2.305(1) Å found in the former derivative. It is likely that the neutral THF donor in **1** experiences a larger steric repulsion from the bulkier N-mesityl groups as compared to the N-phenyl groups found in {[NPN]Zr(THF)}$_2$(μ-η^2:η^2-N_2).

There is a singlet at δ 5.0 in the $^{31}P\{^1H\}$ NMR spectrum of **1** in THF-d_8 indicating that both phosphines across the Zr_2(μ-η^2:η^2-N_2) unit are equivalent. The ^1H NMR spectrum shows four singlets between δ 2.2 and 1.7 due to the four distinct $ArCH_3$ groups of the linkers and the N-mesityl groups (as is observed in ^1H NMR spectra of [NPN]*$ZrCl_2$, rotation about the C_{ipso}–N_{Mes} bond is restricted at room temperature on the NMR time scale).[14] Resonances attributable to aromatic protons and to coordinated THF are also evident. Complex **1** is C_2 symmetric in the solid state, but C_{2h} symmetric in solution, with the mirror plane in the solution structure containing the Zr_2N_2 core that is butterfly distorted in the solid state. A fluxional process that flips N_2 from one side of the Zr−Zr axis to the other may be responsible for the higher symmetry of **1** in THF-d_8 solution on the NMR time scale, or more simply the structure in solution may have a rigid planar Zr_2N_2 core.

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Table 1. UV−Vis Absorption Maxima of Some Group 4 N_2 Complexes in Toluene

N_2 complex	λ_{max} (nm)	ϵ ($\times 10^3$ L mol^{-1} cm^{-1})
1	652, 358	6.1, 10
2	736, 401, 366	6.1, 6.6, 10
4	699, 363	9.7, 11
([P_2N_2]Zr)$_2$(μ-η^2:η^2-N_2)[a]	670, 455, 390	*c*
[(*rac*-Bp)Zr]$_2$(μ-η^2:η^2-N_2)[b]	612, 392	*c*
[(η^5-C_5Me_4H)$_2$Zr]$_2$(μ-η^2:η^2-N_2)[d]	648, 351	*c*, 3.7
[(η^5-C_5Me_4H)$_2$Hf]$_2$(μ-η^2:η^2-N_2)[e]	886, 553	6.5, 0.38

[a] Ref 19. [b] (*rac*-Bp = Me_2Si(-2-Me_3Si-4-^{t}Bu-C_5H_2)$_2$]$^{2-}$) ref 18. [c] Not reported. [d] Ref 10. [e] Ref 9b.

The UV−vis absorption spectrum of **1** in toluene consists of two absorptions at 652 nm ($\epsilon = 6.1 \times 10^3$ L mol^{-1} cm^{-1}) and 358 nm ($\epsilon = 1.0 \times 10^4$ L mol^{-1} cm^{-1}). It should be noted that ϵ values are approximate because dilute solutions of **1** become less intensely colored over several hours under N_2 in a Teflon-sealed cuvette, likely due to reaction with trace O_2 and H_2O. By analogy with the UV−vis absorption spectrum of ([P_2N_2]-Zr)$_2$(μ-η^2:η^2-N_2),[19] the two maxima are tentatively assigned to charge-transfer (CT) transitions from the electron-rich N_2^{4-} unit to empty d orbitals on Zr(IV). The UV−vis absorption spectrum of **1** is similar to other group 4 dinitrogen complexes (Table 1).

When [NPN]*$ZrCl_2$ is reduced with KC_8 in the absence of N_2, blue-green **1** does not form, and instead, the reaction mixture turns brown. Several species are present in the mixture: singlets at δ −14.6 and −15.4 are observed by $^{31}P\{^1H\}$ NMR spectroscopy due to the major diamagnetic P-containing products, and singlets due to minor components are also apparent. The major products could not be separated from each other, and characterization of the mixture by ^1H NMR spectroscopy and mass spectrometry did not aid in identifying these compounds. Reduction of early transition-metal halide complexes in the absence of N_2 activation can lead to a variety of side reactions including C−H activation of toluene to yield an η^n-benzyl complex,[20] ancillary ligand activation,[21] or formation of a reduced complex that does not contain N_2 (e.g., mixtures of $ZrCl_4$ and PEt_3 react with sodium amalgam to give [$ZrCl_3$-(PEt_3)]$_2$).[22]

When [NPN]*$ZrCl_2$ is reduced under $^{15}N_2$, the nitrogen-15-labeled isotopologue **1-$^{15}N_2$** is obtained. In the $^{31}P\{^1H\}$ NMR spectrum of the labeled complex, one observes an apparent doublet ($^2J_{PN}$ = 6.7 Hz) at δ 5.0; a doublet is also present in the $^{15}N\{^1H\}$ NMR spectrum of **1-$^{15}N_2$** at δ 116.6 (relative to $MeNO_2$ at δ 0). This can be rationalized if one assumes that the ^{15}N and ^{31}P nuclei in **1-$^{15}N_2$** comprise an AA′XX′ spin system, with one coupling constant, $^2J_{PN}$, dominating the pattern. Thus, it appears that only one ^{15}N nucleus couples to one ^{31}P nucleus. Addition of $^{15}N_2$ to the unlabeled dinitrogen complex **1** does not result in the incorporation of labeled N_2.

Synthesis of the Pyridine Adduct {[NPN]*Zr(py)}$_2$(μ-η^2:η^2-N_2), 2. The addition of pyridine (py) to a blue-green C_6H_6 solution of **1** results in an immediate color change to dark forest

(19) Studt, F.; Morello, L.; Lehnert, N.; Fryzuk, M. D.; Tuczek, F. *Chem. Eur. J.* **2003**, *9*, 520.
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(21) Fryzuk, M. D.; Kozak, C. M.; Mehrkhodavandi, P.; Morello, L.; Patrick, B. O.; Rettig, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 516.
(22) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844.

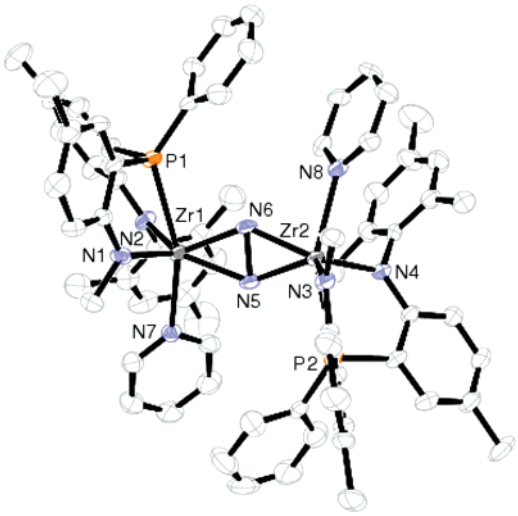
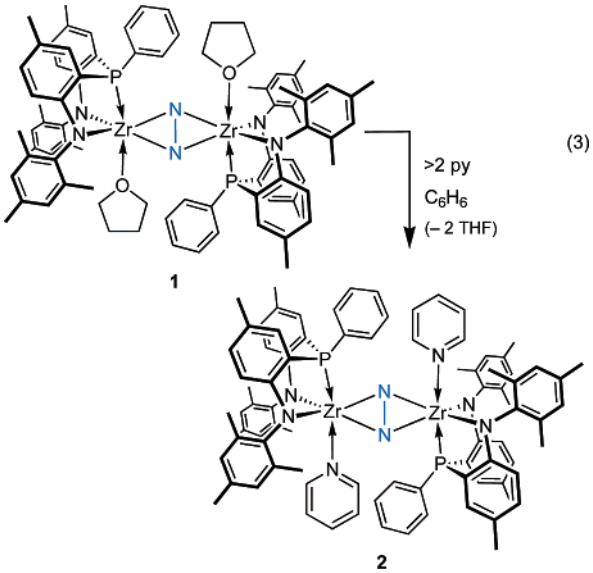


Figure 2. Solid-state molecular structure of **2** (ellipsoids at 50% probability). Carbon atoms of the mesityl substituents (except C_{ipso}) and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−P1 2.6699(12), Zr1−N1 2.203(4), Zr1−N2 2.166(4), Zr1−N5 2.002(4), Zr1−N6 2.092(4), Zr1−N7 2.448(4), Zr2−P2 2.6725(12), Zr2−N3 2.172(4), Zr2−N4 2.218(4), Zr2−N5 2.097(4), Zr2−N6 2.011(4), Zr2−N8 2.441(4), N5−N6 1.481(5), N5−Zr1−N6 42.33(14), N6−Zr2−N5 42.19(14), P1−Zr1−N7 156.80(9), N1−Zr1−N2 109.51(14), N7−Zr1−N5 119.68(13).

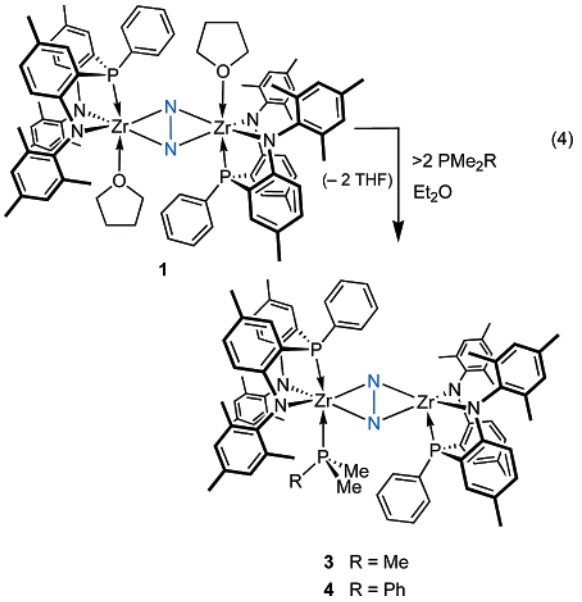
green (eq 3) to generate {[NPN]*Zr(py)}$_2$(μ-η^2:η^2-N_2), **2**, which is isolated in high yield as a dark-green powder upon workup. Unlike the THF adduct **1**, complex **2** is stable to vacuum in the solid state and can be stored under N_2 for weeks.



An ORTEP representation of the solid-state molecular structure of **2** is shown in Figure 2, along with selected bond lengths and angles. The dinuclear structure is similar to that observed for **1**. The N−N bond length is 1.481(5) Å, about the same as that observed for **1**, within error. Also similar to **1**, the N−N bond is not exactly perpendicular to the Zr−Zr axis: the Zr1−N5 and Zr2−N6 bonds average to 2.00 Å, and the Zr1−N6 and Zr2−N5 bonds average to 2.09 Å. One pyridine is coordinated to each Zr, and the Zr1−N7 and Zr2−N8 bond lengths are the same within error at about 2.44 Å and lie within the expected range. There is also a butterfly distortion in the Zr_2N_2 core: the two ZrN_2 planes meet at a 168° angle.

Similar to **1**, there is a singlet in the $^{31}P\{^1H\}$ NMR spectrum of **2** in C_6D_6 at δ 6.0. The ^1H NMR spectrum is consistent with the C_{2h} symmetric structure proposed, although two of the expected four $ArCH_3$ singlets appear to overlap (the singlet at δ 2.03 integrates to 24H). {[NPN]*Zr(py-d_5)}$_2$(μ-η^2:η^2-N_2), **2-*d*$_{10}$**, can be prepared from **1** and py-d_5 by the same method used to prepare **2** and has been characterized by NMR spectroscopy and electron impact mass spectrometry (EI-MS). ^{15}N-labeled {[NPN]*Zr(py)}$_2$(μ-η^2:η^2-$^{15}N_2$), **2-$^{15}N_2$**, can be prepared from **1-$^{15}N_2$** and py in C_6H_6 solution. There is a 1:2:1 triplet at δ 6.0 in the $^{31}P\{^1H\}$ NMR spectrum of **2-$^{15}N_2$** that corresponds to an apparent AX_2 pattern (each ^{31}P nucleus couples to two magnetically equivalent ^{15}N nuclei). A multiplet appears at δ 118.2 in the $^{15}N\{^1H\}$ NMR spectrum that corresponds to an AA′XX′ spin system with $^2J_{NP}$ = 7 Hz, $^2J_{NP'}$ = 3 Hz, and $^1J_{NN'}$ = 2 Hz. Similar to **1**, the UV−vis absorption spectrum of **2** in toluene has two maxima at 736 nm (ϵ = 6.1 × 10^3 L mol^{-1} cm^{-1}) and 366 nm (ϵ = 1.0 × 10^4 L mol^{-1} cm^{-1}), with a shoulder at 401 nm (ϵ = 6.6 × 10^3 L mol^{-1} cm^{-1}).

Synthesis of Phosphine Adducts {[NPN]*Zr(PMe$_2$R}(μ-η^2:η^2-N$_2$){Zr[NPN]*}, 3 (R = Me), and 4 (R = Ph). The addition of an excess of PMe_3 to a solution of **1** in Et_2O causes an immediate blue-green to bright green color change. {[NPN]-*Zr(PMe_3)}(μ-η^2:η^2-N_2){Zr[NPN]*}, **3**, is isolated as a hexanes-soluble bright green powder in quantitative yield upon workup (eq 4). Complex **3** has been observed to decompose in the solid state at room temperature or at −35 °C or upon prolonged exposure to vacuum. Samples of **3** are synthesized immediately before use or are stored for a few days in hexanes solutions with a small amount of added PMe_3 at −35 °C. Although small crystals of **3** can be obtained from toluene/HMDSO in the presence of PMe_3 at −35 °C, they were found to be unsuitable for X-ray analysis. A hexamethyldisiloxane of crystallization was observed by microanalysis and by ^1H NMR spectroscopy.



The $^{31}P\{^1H\}$ NMR spectrum of **3** at room temperature in C_6D_6 indicates that there are three distinct phosphine environments in this complex: two doublets at δ 5.1 and −33.1 ($^2J_{PP}$ = 44 Hz), and a singlet at δ 2.5, each integrating to 1P. These are assigned to the phosphine donor in [NPN]* and the PMe_3

coordinated to one Zr atom (44 Hz coupling is consistent with two-bond P−P coupling between trans-disposed phosphines in an early transition-metal complex[23,24]), and the singlet is due to [NPN]* coordinated to the other Zr atom, respectively. The ^{1}H NMR spectrum is also consistent with the C_s symmetric structure proposed above: there are eight $ArCH_3$ singlets, a doublet at δ 0.27 ($^2J_{PH}$ = 6 Hz, 9H) attributable to one molecule of coordinated PMe_3, and the expected ArH resonances. The absence of resonances for free or coordinated THF in the ^{1}H and ^{13}C{^{1}H} NMR spectra also supports the proposed structure.

Since attempts to grow single crystals of **3** were hindered by its high solubility and its thermal lability, PMe_2Ph instead of PMe_3 was used to synthesize an analogous phosphine adduct of the Zr−N_2 complex. The addition of excess PMe_2Ph to a toluene solution of **1** causes an immediate blue-green to bright green color change. Benzene-soluble {[NPN]*Zr(PMe_2Ph)}(μ-η^2:η^2-N_2){Zr[NPN]*}, **4**, is isolated as an emerald green powder in 82% yield upon workup (eq 4). In contrast to **3**, **4** is thermally stable and can be placed under vacuum for several hours without decomposition. Small crystals of **4** can be grown from C_6H_6/HMDSO at room temperature; the presence of cocrystallized solvent was confirmed by microanalysis and ^{1}H NMR spectra of **4** acquired in toluene-d_8. Single crystals of **4** suitable for X-ray analysis were grown by slow evaporation of a hexanes solution.

The ^{31}P{^{1}H} NMR spectrum of **4** in C_6D_6 is similar to that of **3** at room temperature; there are two doublets at δ 7.3 and −22.5 ($^2J_{PP}$ = 46 Hz) and a singlet at δ 1.9 assigned to [NPN]* and PMe_2Ph coordinated to one Zr, and [NPN]* coordinated to the second Zr atom, respectively. In the ^{1}H NMR spectrum there are eight $ArCH_3$ singlets, a doublet at δ 0.80 ($^2J_{HP}$ = 6 Hz) corresponding to the coordinated $P(CH_3)_2Ph$, and peaks in the ArH region consistent with the C_s symmetric structure proposed for **4**. There are two peaks in the UV−vis absorption spectrum of **4** in toluene solution at 699 nm (ϵ = 9.7 × 10^3 L mol^{-1} cm^{-1}) and 363 nm (ϵ = 1.1 × 10^4 L mol^{-1} cm^{-1}) tentatively assigned to N_2 → Zr CT transitions.

An ORTEP representation of the solid-state molecular structure of **4** is shown in Figure 3, along with selected bond lengths and angles. Zr1 is coordinated to one [NPN]* ligand and side-on bound N_2; Zr2 is coordinated to one [NPN]* ligand, PMe_2Ph, and side-on bound N_2. At 1.488(2) Å, the N−N bond length compares well to those in **1** and **2**, within error. The Zr−P bond lengths to [NPN]* (Zr1−P1 2.6967(6), Zr2−P2 2.6445(6) Å) are also similar to those of **1** and **2**, but the Zr2−P3 bond length to PMe_2Ph is much longer at 2.9139(6) Å. The Zr2−P3 bond length is comparable to other long Zr−P bonds to tertiary phosphines reported in the literature.[25] As with **1** and **2**, there is a butterfly distortion between the two ZrN_2 planes of 165° in the C_1 symmetric solid-state structure. P1 and P2 are staggered across the Zr−Zr axis (P1−Zr1−Zr2−P2 torsion angle is 179.9°), whereas P1 and P3 are nearly eclipsed (P1−Zr1−Zr2−P3 torsion angle is 7.8°). Since **4** is C_s symmetric in solution, the Zr_2N_2 core is either planar or there is a fluxional process that allows N_2 to sample both sides of the Zr−Zr axis on the NMR time scale.

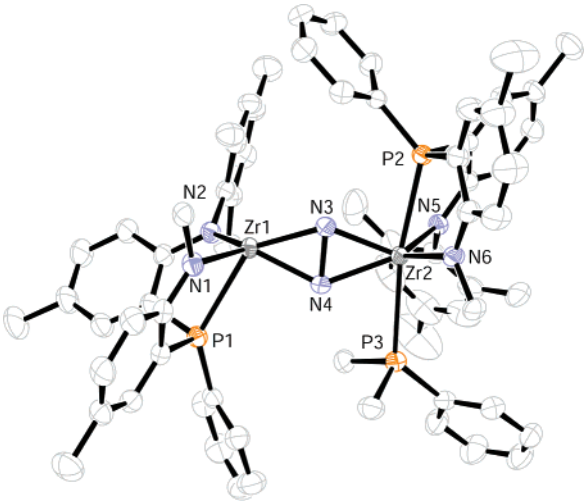


Figure 3. Solid-state molecular structure of **4** (ellipsoids at 50% probability). Carbon atoms of the front mesityl substituents (except C_{ipso}) and the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−P1 2.6967(6), Zr2−P2 2.6445(6), Zr1−N1 2.1370(18), Zr1−N2 2.1689(18), Zr2−N5 2.1818(18), Zr2−N6 2.1747(17), Zr1−N3 2.0450(17), Zr1−N4 2.0315(17), Zr2−N3 2.0371(18), Zr2−N4 2.1153(17), Zr2−P3 2.9139(6), N3−N4 1.488(2), N3−Zr1−N4 42.83(7), Zr1−N3−Zr2 137.18(9), P2−Zr2−P3 166.605(19), P1−Zr1−N4 94.18(5), P1−Zr1−N3 136.91(5), P1−Zr1−N1 71.28(5), P1−Zr1−N2 75.25(5), N1−Zr1−N3 118.84(7), N1−Zr1−N4 115.84(7).

The solid-state molecular structure of **4** provides some clue as to why only 1 equiv of PMe_2Ph coordinates to the dimer: the presence of PMe_2Ph on Zr2 causes [NPN]* on Zr1 to adopt a position that effectively blocks the coordination of PMe_2Ph to Zr1. Complex **4** is unique among zirconium−dinitrogen complexes because the coordination environments at each Zr atom are different.

Isotopically labeled **4-$^{15}N_2$** can be prepared from **1-$^{15}N_2$** and PMe_2Ph by the same method used to prepare **4**. The ^{31}P{^{1}H} NMR spectrum of **4-$^{15}N_2$** in C_6D_6 acquired at room temperature is similar to that of **4**, but additional P−N coupling appears when a sample of **4** in toluene-d_8 is analyzed at 253 K. There is a doublet of doublets of doublets at δ 7.3 ($^2J_{PP}$ = 46 Hz, $^2J_{PN}$ = 4 Hz, $^2J_{PN}$ = 7 Hz), a singlet at δ −1.9, and a doublet of doublets at δ −22.5 ($^2J_{PP}$ = 46 Hz, $^2J_{PN}$ = 7 Hz). It is unclear why the singlet at δ −1.9 is not split by ^{15}N. There are two AA′XX′ multiplets ($^2J_{NN}$ = 8 Hz, $^2J_{PN}$ = 4 Hz, $^2J_{PN}$ = 7 Hz) in the ^{15}N{^{1}H} NMR spectrum at 253 K at δ 119.0 and 118.0, each integrating to 1N.

Reactivity of the Dinitrogen Complexes with H_2. When a blue-green toluene solution of the THF complex **1** is stirred under 4 atm of H_2 gas for 6 weeks at room temperature, there is no color change, and no new peaks appear in the ^{31}P{^{1}H} or ^{1}H NMR spectra. In contrast, when a toluene solution of the pyridine derivative **2** is stirred under 4 atm of H_2 for 8 weeks, there is a gradual color change from green to yellow-brown. By ^{31}P{^{1}H} NMR spectroscopy, there is a mixture of products, including [NPN]*H_2. In the ^{1}H NMR spectrum, no peaks diagnostic of bridging hydride or NNH protons are observed. Unfortunately, the major products could not be separated from each other on the basis of solubility.

(23) Gozum, J. E.; Wilson, J. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1992**, *114*, 9483.
(24) (a) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1989**, *8*, 1723. (b) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1988**, *7*, 1224.
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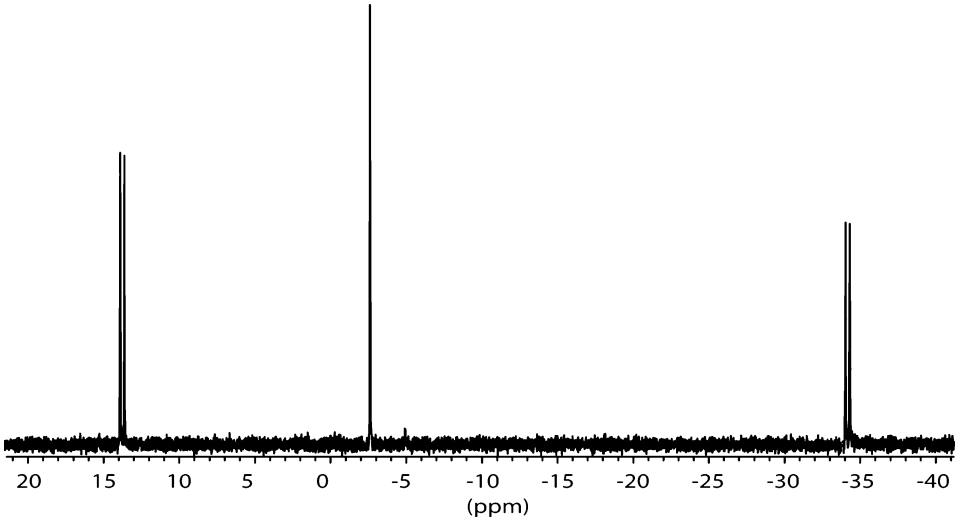
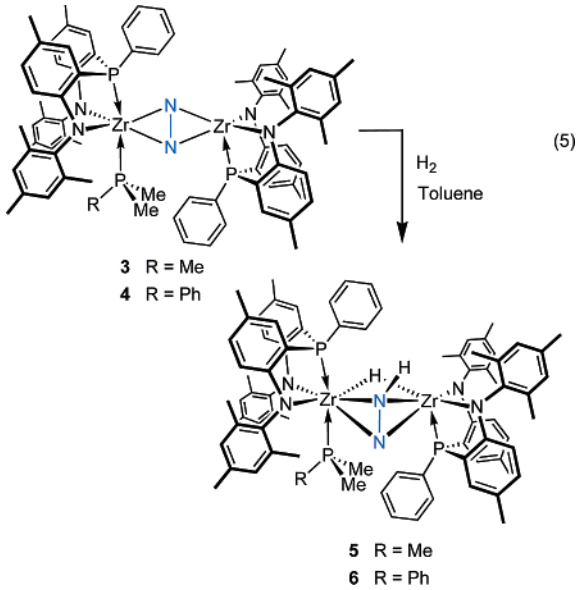


Figure 4. 202 MHz $^{31}P\{^1H\}$ NMR spectrum of **5** in toluene-d_8 at 273 K.

When a toluene solution of the PMe_3 derivative **3** is stirred under H_2, the bright green solution becomes yellow over 2−3 weeks, and an orange precipitate forms after 5 weeks. The yellow-orange toluene-soluble product, {[NPN]*Zr(PMe_3)}(μ-H)(μ-NNH){Zr[NPN]*}, **5**, can be prepared in high yield from **3** and PMe_3 in toluene solution under H_2 (1 atm) (eq 5). Complex **5** can also be synthesized from **3** and H_2 without added PMe_3, but an unidentified brown byproduct forms in about 10% yield by this method. Samples of **5** are stable in solution and in the solid state for months under N_2 at −35 °C.



At 298 K, the $^{31}P\{^1H\}$ NMR spectrum of **5** shows three broad peaks at δ ∼13, −2.5, and −36, which sharpen at 273 K to two doublets at δ 13.8 and −34.5 ($^2J_{PP}$ = 56.7 Hz) and a singlet at δ −2.2 (Figure 4). Because the spectrum is reminiscent of the starting material **3**, a dinuclear structure for **5** is proposed in which one Zr atom is coordinated to [NPN]* (δ −2.2) and the other Zr atom is coordinated to [NPN]* (δ 13.8) and PMe_3 (δ −34.5). The 56.7 Hz P−P coupling constant is typical for a two-bond coupling between trans-disposed phosphines in an early transition-metal complex.[23,24]

The ^1H NMR spectrum acquired at 298 K shows a triplet (δ 4.83, $^2J_{HP}$ = 11 Hz) and a broad singlet (δ 4.78) that each integrate to 1H and are assigned to a bridging hydride (Zr-μ-*H*-Zr) and a hydrogen atom of bridging NN*H* (Figure 5). The other resonances are somewhat broad at this temperature. At 253 K, the peaks in the ^1H NMR spectrum are sharper, and thirteen singlets are observed at δ ∼2.0 that are assigned to $ArCH_3$ groups. Sixteen singlets are expected based on the C_1 symmetry of the product, but six of these singlets overlap and integrate to 6H each. A broad singlet at δ 0.09 is due to coordinated PMe_3, and the peaks due to Zr-μ-*H*-Zr and NN*H* groups appear as an overlapping triplet at δ 4.84 and broad singlet at δ 4.82.

In the $^1H\{^{31}P\}$ NMR spectrum at 253 K, the resonances assigned to the bridging hydride (Zr-μ-*H*-Zr) and NN*H* appear as two singlets at δ 4.84 and 4.82. Thus, the bridging hydride is a triplet in the ^1H NMR spectrum because it couples to only two inequivalent ^{31}P nuclei. It is likely that the Zr-μ-*H*-Zr moiety couples to the ^{31}P nuclei of two [NPN]* ligands and not to the loosely bound PMe_3 donor; further support of this is discussed below.

Attempts to generate crystals of the dihydrogen adduct were partially successful. An X-ray crystal structure was obtained of **5**; however, the data for this structure are of poor quality and only the connectivity of the non-hydrogen atoms could be established. What is evident is that there is a much larger butterfly distortion of the Zr_2N_2 unit in **5** consistent with the introduction of a hydrogen atom to one of the nitrogen centers of the bridging N_2 unit and a bridging hydride.

To confirm that the resonances at δ 4.84 and 4.82 originate from H_2 gas, toluene-d_8 solutions of **3** have been stored under H_2 or D_2 gas in sealed NMR tubes and monitored for several weeks. Whereas the reaction of **3** with H_2 is complete in 6

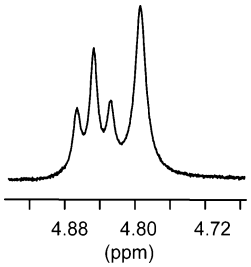


Figure 5. Zr-μ-*H*-Zr and NN*H* resonances in the 500 MHz ^1H NMR spectrum of **5** in toluene-d_8 at 298 K.

weeks, the reaction with D_2 takes about 3 months, and a mixture of {[NPN]*Zr(PMe_3)}(μ-D)(μ-NND){Zr[NPN]*}, **5-*d*$_2$**, and **5** is produced. In the ^{1}H NMR spectrum at 253 K, the triplet and singlet resonances at δ 4.84 and 4.82 integrate to about 0.02H each relative to one of the $ArCH_3$ resonances (set to 3H). Thus, the bridging hydride and NNH protons in **5** originate from H_2 gas. The resonances at δ 4.84 and 4.82 appear in spectra of **5-*d*$_2$** because there are trace HD impurities (0.4%) in the D_2; presumably **5-*d*$_1$** is also present in this mixture. Since **3** reacts with H_2 faster than it reacts with D_2, the formation of **5** in this reaction cannot be prevented. Complex **5-*d*$_2$** (along with the d_1 isotopologue) can also be prepared as an orange solid on a larger scale (300 mg) from **3**, PMe_3, and D_2 (4 atm). By integration of the resonances at δ 4.84 and 4.82 in the ^{1}H NMR spectrum in toluene-d_8 acquired at 253 K, **5-*d*$_1$** and **5** are present as 10% of the labeled product. A signal attributable to the parent ion, [**5-*d*$_2$**]$^+$, appears in the mass spectrum of the compound.

To determine if the hydrogenation of **3** can be extended to the PMe_2Ph congener **4**, a toluene solution of **4** and PMe_2Ph was stirred under 1 atm of H_2 gas. The green solution turns yellow after 3 weeks at room temperature, and a yellow precipitate forms after 6 weeks. Upon workup, {[NPN]*Zr(PMe_2Ph)}(μ-H)(μ-NNH){Zr[NPN]*}, **6**, is isolated as a yellow solid in good yield (eq 5).

Similar to **5**, the ^{31}P{^{1}H} NMR spectrum of **6** in toluene-d_8 at 298 K shows three broad singlets at δ 15, −2, and −25. At 253 K, the broad resonances sharpen and a doublet at δ 14.6 ($^2J_{PP}$ = 57.4 Hz), a broad doublet at δ −24.6, and a broad singlet at δ −2.3 are observed. These signals correspond to [NPN]* and PMe_2Ph coordinated to one Zr, and [NPN]* coordinated to the other Zr, respectively. In the presence of a small amount of PMe_2Ph, the spectra of **6** are more broad and require lower temperatures to decoalesce. In the ^{1}H NMR spectrum at 233 K, the expected signals due to ArH, $ArCH_3$, and PMe_2Ph groups in the C_1 symmetric dimer are apparent. In addition, a broad singlet at δ 4.94, and a poorly resolved triplet at δ 4.88, are attributable to NN*H* and Zr-μ-*H*-Zr protons, respectively; these chemical shifts are reversed from the PMe_3 adduct **5** (Figure 5). When the downfield ^{31}P NMR signals due to the [NPN]* units at δ 14.6 and −2.3 are each selectively decoupled, the triplet at δ 4.88 collapses in turn to a broad doublet; when the ^{31}P NMR peak at δ −24.6 due to the coordinated PMe_2Ph is irradiated, the triplet resonance due to the bridging hydride is unaffected. This clearly indicates that only the [NPN]* phosphine donors on each zirconium engage in coupling to the hydride, which in turns supports the bridging mode of bonding.

The formation of a new N−H bond upon hydrogenation of **4** has been confirmed by an isotopic labeling experiment. {[NPN]*Zr(PMe_2Ph)}(μ-H(μ-^{15}N^{15}NH){Zr[NPN]*}, **6-^{15}N$_2$**, can be prepared from **4-^{15}N$_2$**, PMe_2Ph and H_2 (1 atm) in toluene solution. At 273 K, the ^{31}P{^{1}H} NMR spectrum of **6-^{15}N$_2$** shows the same peaks as that of **6**, but the broad singlet at δ −24.6 is split into a broad doublet. In the ^{1}H NMR spectrum acquired at 233 K, the ArH, $ArCH_3$, and PMe_2Ph resonances are analogous to those of **6**, but the peak at δ 4.94 is a doublet ($^1J_{HN}$ = 72 Hz), and the peak at δ 4.88 is a broad triplet ($^2J_{HP}$ = 9.7 Hz). In the ^{1}H{^{31}P} NMR spectrum, the doublet at δ 4.94 is apparent, but the resonance at δ 4.88 is a singlet. The 72 Hz ^{15}N−^{1}H coupling constant is typical for one-bond coupling[26] and is similar to that observed for ([P_2N_2]Zr)$_2$(μ-H)(μ-^{15}N^{15}NH).[6] The ^{15}N{^{1}H} NMR spectrum at 273 K shows a singlet at δ 143.9 and a doublet at δ 29.8 ($^2J_{NP}$ = 10 Hz). In the mass spectrum, a peak due to [M − PMe_2Ph]$^+$ is apparent.

H_2 may add to **3** or **4** by a 1,2-addition mechanism across the Zr−N bond via a four-centered transition state: one N of dinitrogen acts as a nucleophile and Zr acts as an electrophile in this reaction, which is an example of heterolytic H−H activation. A similar mechanism has been invoked for the addition of H_2 to ([P_2N_2]Zr)$_2$(μ-η^2:η^2-N_2).[6] This latter reaction, reported in 1997, was the first example of a N_2 complex reacting with H_2 to yield a new N−H bond. Yellow ([P_2N_2]Zr)$_2$(μ-H)-(μ-NNH) forms under 1 or 4 atm of H_2, and a broad singlet at δ 5.53 and a multiplet at δ 2.07 appear in the ^{1}H NMR spectrum. These peaks are due to μ-NNH and μ-H groups, respectively, as determined by isotopic labeling; when the reaction is conducted under D_2 gas, these resonances disappear, and when H_2 reacts with ([P_2N_2]Zr)$_2$(μ-^{15}N$_2$), the peak at δ 5.53 is split into a doublet ($^1J_{HN}$ = 71.3 Hz). The resonances attributable to the bridging hydride Zr-μ-H-Zr for **5** and **6** are about 3 ppm downfield compared to the hydride observed for ([P_2N_2]Zr)$_2$-(μ-H)(μ-NNH) but are within the range of known chemical shifts for hydrides bridging two Zr atoms.[27]

Conclusions

In this article, the synthesis, structure, and reactivity of {[NPN]*Zr(THF)}$_2$(μ-η^2:η^2-N_2) (**1**) are reported. The coordinated N_2 has been formally reduced to N_2^{4-} in the complex and is bound in the bridging side-on mode to two Zr atoms. The substitution of THF for pyridine or PMe_2R (R = Me, Ph) is readily carried out by adding the donor molecule to a solution of **1**. Whereas {[NPN]*Zr(py)}$_2$(μ-η^2:η^2-N_2) (**2**) is structurally analogous to **1** except for the identity of the donor, in {[NPN]-*Zr(PMe_2R)}(μ-η^2:η^2-N_2){Zr[NPN]*} (**3**, R = Me; **4**, R = Ph), only one of the two Zr atoms is coordinated to PMe_2R, even in the presence of excess phosphine. The solid-state molecular structure of **4** shows that PMe_2Ph bound to one Zr atom leads to a rearrangement of [NPN]* on the second Zr atom, effectively blocking the coordination of a second PMe_2Ph. The synthesis of the pyridine and PMe_2R adducts from **1** represents a simple, high-yield method for tuning the coordination environment of the metal in a strongly activated N_2 complex.

Dinitrogen complexes **1**−**4** display different reactivity with H_2 in toluene solution. THF adduct **1** does not react with H_2 at 4 atm pressure over several weeks. While a toluene solution of pyridine adduct **2** changes color when stirred under H_2 for weeks at room temperature, multiple products form that could not be separated or identified. In contrast, a new N−H bond forms when PMe_2R adducts **3** and **4** are stirred under H_2 in toluene; {[NPN]*Zr(PMe_2R)}(μ-H)(μ-η^2:η^2-N_2H){Zr[NPN]*} (R = Me, **5**; R = Ph, **6**) forms in high yield and has been characterized by isotopic labeling, multinuclear NMR spectroscopy, and a solid-state structure of **5**. The lack of reactivity of the THF adduct **1** with H_2 parallels that of the related complex {[NPN]-

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Zr(THF)}$_2$(μ-η^2:η^2-N_2); it is likely that the strongly bound THF molecules impede the reaction with H_2 in both complexes, and not until an additional soft phosphine donor is present does the 1,2-addition take place. In addition, it could also be that the PR_3 adducts display enhanced reactivity due to the presence of one open site at the uncoordinated Zr center. The latter feature augers well for further reactivity studies, which are currently in progress.

Experimental Section

General Considerations. Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free N_2 or Ar by means of standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with an MO-40-2H purification system and a −35 °C freezer). Ar and N_2 were dried and deoxygenated by passing the gases through a column containing molecular sieves and MnO. Hexanes, toluene, tetrahydrofuran, pentane, benzene, and diethyl ether were purchased anhydrous from Aldrich, sparged with N_2, and passed through columns containing activated alumina and Ridox catalyst. Tetrahydrofuran was then stored over purple sodium benzophenone ketyl indicator and degassed by three freeze−pump−thaw cycles. Pyridine was dried over CaH_2 and distilled under N_2 prior to use. THF-d_8, C_7D_8, and C_6D_6 were dried over Na/K alloy under partial pressure, trap-to-trap distilled, and freeze−pump−thaw degassed three times. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AV-300, Bruker AV-400, or Bruker AMX-500 spectrometer, operating at 300.1, 400.0, and 500.1 MHz for ^{1}H spectra, respectively. ^{7}Li{^{1}H} NMR spectra were recorded on the AV-400 or AMX-500. Unless otherwise noted, all spectra were recorded at room temperature. ^{1}H NMR spectra were referenced to residual protons in the deuterated solvent: C_6D_6 (δ 7.16), $CDCl_3$ (δ 7.24), C_7D_8 (δ 2.09), or THF-d_8 (δ 3.58). ^{31}P{^{1}H} NMR spectra were referenced to external $P(OMe)_3$ (δ 141.0 with respect to 85% H_3PO_4 at δ 0.0). ^{13}C{^{1}H} NMR spectra are referenced as indicated: C_6D_6 (δ 128.0), $CDCl_3$ (δ 77.23), or THF-d_8 (δ 67.4). ^{15}N{^{1}H} NMR spectra were recorded on a Bruker AV-400 direct detect spectrometer operating at 400.1 MHz for ^{1}H NMR spectra and were referenced externally to $MeNO_2$ at δ 0. Chemical shifts (δ) listed are in ppm, and absolute values of the coupling constants are in Hz. NMR simulations were performed using the program MestReC. UV−vis spectra were recorded on a Varian/Cary 5000 UV−vis spectrometer using a 1 cm Teflon-sealed cuvette. Mass spectrometry (EI-MS) and microanalyses (C, H, N) were performed at the Department of Chemistry at the University of British Columbia. Flasks sealed under N_2 gas at liquid-nitrogen temperature reach a pressure of 4 atm at room temperature and should be thawed completely behind a blast shield and handled with care. ^{15}N-labeled complexes were isolated and handled under unlabeled N_2. [NPN]*$ZrCl_2$[12] and potassium graphite (KC_8) were prepared according to literature methods.[28] Trimethylphosphine and dimethylphenylphosphine were purchased from Strem Chemical Ltd. and used without further purification. $^{15}N_2$ gas (isotopic purity 98+%, 1 or 2 L) was purchased from Cambridge Isotopes Ltd. in a small carbon steel lecture bottle and used as received. Hydrogen was obtained from Praxair, and deuterium gas (HD 0.4%) was purchased from Cambridge Isotopes Ltd, and both were used as received.

{[NPN]*Zr(THF)}$_2$(μ-η^2:η^2-N_2) (1). THF (10 mL) was vacuum-transferred onto an intimate mixture of [NPN]*$ZrCl_2$ (1.00 g, 1.40 mmol) and KC_8 (0.414 g, 3.07 mmol) in a 400 mL Teflon-sealed thick-walled bomb at 77 K. The flask was filled with N_2 gas at this temperature, sealed, and warmed slowly to room temperature in a liquid-N_2/EtOH slurry behind a blast shield. As soon as the mixture had melted, it was stirred vigorously. The flask was periodically inverted to coat the walls of the flask with the concentrated reaction mixture. The solution turned purple after 2 h, and bright blue-green after 5 h, and was stirred overnight. The pressure was vented, and the suspension was diluted with THF (10 mL) and filtered through Celite in the glovebox. The Celite was washed with additional THF (∼10−20 mL). The filtrate was concentrated to a volume of ∼10 mL, layered with pentane (30−50 mL), and chilled to −35 °C. Black crystals formed over several days that were collected on a frit, washed with pentane (5 mL), and dried under vacuum for 15 min (0.802 g, 0.548 mmol, 79%). Storing crystals of **1** under vacuum overnight gave a white powder that contained benzene-soluble and -insoluble fractions. Crystals of **1** suitable for X-ray analysis were grown in a large Teflon-sealed bomb by vapor diffusion of hexanes into a concentrated benzene/THF solution of the compound in an NMR tube over 3 weeks. Crystals of **1** grown from THF/hexanes at −35 °C contain 2 equiv of cocrystallized THF as determined by elemental analysis and confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR (THF-d_8, 500 MHz): δ = 7.42 (t, 4H, 7.5 Hz), 7.22 (m, 6H), 7.08 (d, 4H, 7.5 Hz), 6.82 (s, 4H), 6.73 (s, 4H), 6.64 (d, 4H, 8.5 Hz), and 5.43 (dd, 4H, J_{HH} = 8 Hz, J_{HP} = 6 Hz) (ArH), 3.54 (bs, THF), 2.18 (s, 12H), 2.07 (s, 12H), 1.94 (s, 12H), and 1.74 (s, 12H) ($ArCH_3$), 1.69 (bs, THF). ^{31}P{^{1}H} NMR (THF-d_8, 202 MHz): δ = 5.0 (s). ^{13}C{^{1}H} NMR (THF-d_8, 126 MHz): δ = 163.1 (d, 11 Hz), 144.7, 137.9, 136.7, 136.4, 134.9, 134.1, 133.8, 130.0, 129.9, 128.9, 128.8, 125.1, 118.2, 117.9, and 113.7 (d, 10 Hz) (ArC), 68.2, and 26.4 (THF), 20.9, 20.4, 20.3, and 19.2 ($ArCH_3$). EI-MS (*m*/*z*): 1432 (1, [M − N_2]$^+$), 1320 (2, [M − 2THF]$^+$), 541 (100, {[NPN]*H_2 − Me}$^+$). Anal. Calcd for **1**·2THF, $C_{92}H_{110}N_6O_4P_2Zr_2$: C, 68.71; H, 6.89; N, 5.23. Found: C, 68.34; H, 7.24; N, 4.90. UV−vis (toluene) λ_{max} (ϵ) = 358 (1.0×10^4), 652 (6.1×10^3) nm (L mol^{-1} cm^{-1}).

Reduction of [NPN]*$ZrCl_2$ in the absence of N_2. Using the procedure outlined above, THF (10 mL) was transferred to a mixture of [NPN]*$ZrCl_2$ (0.350 g, 0.488 mmol) and KC_8 (0.145 g, 1.07 mmol) at 77 K, and the flask was evacuated and sealed. The reaction mixture was a brown suspension while warming to room temperature. The mixture was stirred overnight, the pressure was vented, and an aliquot of the reaction mixture was analyzed by ^{31}P{^{1}H} NMR spectroscopy. The reaction mixture was filtered, and the filtrate was concentrated and layered with pentane, but no crystals were obtained. After 2 days, the brown solution was taken to dryness to obtain a brown powder. ^{31}P{^{1}H} NMR spectroscopy indicated the reaction mixture and solid obtained upon workup had the same composition. ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ = 20.3 (s, ∼5%), 17.9 (s, ∼5%), −14.6 (s, ∼30%), −15.4 (s, ∼40%), −31.4 (s, ∼20%).

{[NPN]*Zr(THF)}$_2$(μ-η^2:η^2-$^{15}N_2$) (1-$^{15}N_2$). Complex **1-$^{15}N_2$** (0.254 g, 0.173 mmol, 83%) was prepared from [NPN]*$ZrCl_2$ (0.321 g, 0.448 mmol) and KC_8 (0.133 g, 0.985 mmol) in a 200 mL Teflon-sealed bomb by the same general method used to prepare **1**. After vacuum-transferring THF (5 mL) to the flask at 77 K, the sealed, frozen flask was connected to a lecture bottle of $^{15}N_2$ gas (1 L, 1−2 atm pressure) via a small transfer bridge. The apparatus was evacuated and backfilled three times, the flask containing the frozen solution was opened, and the entire apparatus was evacuated and then closed to the Schlenk line. The lecture bottle was slowly opened in the closed system. The flask was warmed to room temperature in a liquid-N_2/EtOH slurry (4 atm N_2) behind a blast shield with vigorous stirring. The ^{1}H NMR spectrum was the same as for **1**. ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz): δ = 5.0 (d, $^2J_{PN}$ = 6.7 Hz). ^{15}N{^{1}H} NMR (THF-d_8, 40 MHz): δ = 116.6 (d, $^2J_{PN}$ = 6.7 Hz). EI-MS (*m*/*z*): 1432 (8, [M − N_2]$^+$), 1322 (6, [M − 2THF]$^+$), 541 (100, {[NPN]*H_2 − Me}$^+$).

{[NPN]*Zr(py)}$_2$(μ-η^2:η^2-N_2) (2). To a stirred blue-green suspension of **1** (0.815 g, 0.557 mmol) in C_6H_6 (15 mL) was added pyridine (0.98 g, 1.0 mL, 12 mmol) dropwise. The solution turned dark evergreen instantly. After 15 min the reaction mixture was taken to dryness to obtain a dark-green powder that was suspended in hexanes, collected on a frit, rinsed with hexanes (5 mL), and dried (0.723 g, 0.489 mmol, 88%). Large black crystals suitable for X-ray analysis were grown by slow evaporation of a benzene solution of the compound in an NMR tube. ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.55 (bm, 4H), 7.45 (d, 4H, 6

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Hz), 7.12 (m, 4H, py), 6.84 (d, 4H, 8 Hz), 6.77 (s, 4H), 6.65 (bs, 6H), 6.55 (t, 2H, 8 Hz, py), and 6.47 (s, 4H) (ArH), 6.00 (m, 8H, ArH and py), 2.23 (s, 12H), 2.11 (s, 12H), and 2.03 (s, 24H) ($ArCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz): $\delta = 6.0$ (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz): $\delta = 162.7$ (d, 33 Hz), 149.9, 143.9, 137.3, 136.8, 136.0, 134.6, 133.7, 133.2, 133.0, 129.6, 129.5, 128.3, 127.6 (d, 8 Hz), 127.5, 125.6, 125.1, 121.9, and 114.0 (d, 10 Hz) (ArC), 20.8, 20.4, 20.1, and 19.3 ($ArCH_3$). EI-MS (*m*/*z*): 1399 (30, $[M - py]^+$), 1320 (30, $[M - 2py]^+$), 541 (100, $\{[NPN]^*H_2 - Me\}^+$). Anal. Calcd for $C_{86}H_{88}N_8P_2Zr_2$: C, 69.88; H, 6.00; N, 7.58. Found: C, 70.20; H, 6.31; N, 7.20. UV−vis (toluene) λ_{max} (ϵ) = 366 (1.0×10^4), 401 (6.6×10^3), 736 (6.1×10^3) nm (L mol^{-1} cm^{-1}).

$\{[NPN]^*Zr(py\text{-}d_5)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (2-d_{10}). Using the procedure outlined above, pyridine-d_5 (0.53 g, 0.50 mL, 6.3 mmol) was added to **1** (0.290 g, 0.198 mmol) in C_6H_6 (5 mL). A dark-green powder (0.270 g, 0.181 mmol, 91%) was isolated upon workup. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra are the same as those of **2**. ^1H NMR (C_6D_6, 500 MHz): $\delta = 7.55$ (m, 4H), 7.45 (d, 4H, 7 Hz), 6.84 (d, 4H, 8 Hz), 6.77 (s, 4H), 6.65 (bs, 6H), 6.46 (s, 4H), and 6.01 (dd, 4H, $J_{HP} = 6$ Hz, $J_{HH} = 8$ Hz) (ArH), 2.23 (s, 12H), 2.11 (s, 12H), and 2.03 (s, 24H) ($ArCH_3$). EI-MS (*m*/*z*): 1404 (10, $[M - (py\text{-}d_5)]^+$), 1320 (15, $[M - 2(py\text{-}d_5)]^+$), 541 (100, $\{[NPN]^*H_2 - Me\}^+$).

$\{[NPN]^*Zr(py)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}^{15}N_2)$ (2-$^{15}N_2$). Using the procedure outlined above, pyridine (0.24 g, 0.25 mL, 3.0 mmol) was added to **1-$^{15}N_2$** (0.150 g, 0.102 mmol) in C_6H_6 (3 mL), and a dark-green powder was isolated upon workup (0.129 g, 0.087 mmol, 85%). The ^1H NMR spectrum was the same as that of **2**. $^{31}P\{^1H\}$ NMR (C_6D_6, 161 MHz): $\delta = 6.0$ (AX_2 triplet, $^2J_{PN} = 7$ Hz). $^{15}N\{^1H\}$ NMR (C_6D_6, 40 MHz): $\delta = 118.2$ (AA′XX′ multiplet, $^2J_{NP} = 7$ Hz, $^2J_{NP'} = 7$s Hz, $^1J_{NN'} = 6$ Hz). EI-MS (*m*/*z*): 1322 (10, $[M - 2py]^+$), 541 (100, $\{[NPN]^*H_2 - Me\}^+$).

$\{[NPN]^*Zr(PMe_3)\}(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)\{Zr[NPN]^*\}$ (3). To a solution of **1** (0.320 g, 0.221 mmol) in Et_2O (5 mL) was added PMe_3 (0.52 g, 0.60 mL, 6.9 mmol). The mixture turned clear bright green instantly. After 30 min the reaction mixture was taken to dryness to obtain a green powder (0.306 g, 0.219 mmol, 99%). A sample of **3** for microanalysis was recrystallized from toluene, with a few drops of PMe_3 added, layered with $(Me_3Si)_2O$ (HMDSO) at −35 °C. The supernatant liquid was decanted, and the microcrystalline solid was rinsed with pentane and dried under vacuum for 5 min ^1H NMR (C_6D_6, 400 MHz): $\delta = 7.82$ (m, 4H), 7.56 (d, 2H, 8 Hz), 7.37 (d, 2H, 8 Hz), 7.27 (t, 2H, 8 Hz), 7.18 (t, 1H, 7 Hz), 7.13 (t, 1H, 7 Hz), 7.01 (t, 2H, 7 Hz), 6.94 (t, 2H, 7 Hz), 6.78 (d, 4H, 7 Hz), 6.77 (s, 2H), 6.74 (s, 2H), 6.66 (s, 2H), 6.13 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), and 5.78 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz) (ArH), 2.31 (s, 6H), 2.23 (s, 6H), 2.17 (s, 6H), 2.11 (s, 6H), 2.00 (s, 6H), 1.92 (s, 6H), 1.68 (s, 6H), and 1.43 (s, 6H) ($ArCH_3$), 0.27 (d, 9H, $J_{HP} = 6$ Hz, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): $\delta = 5.1$ (d, 1P, $^2J_{PP} = 44$ Hz), 2.5 (s, 1P), −33.1 (d, 1P, $^2J_{PP} = 44$ Hz, PMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz): $\delta = 162.8$ (d, 29 Hz), 159.6 (d, 25 Hz), 143.0, 141.8, 137.7, 137.1, 135.8, 134.9, 134.3, 134.1, 133.9, 133.6, 133.2, 130.7, 130.0, 129.7, 129.6, 129.3, 129.0, 128.8, 128.7, 128.6, 128.5, 128.1, 127.9, 127.0, 125.7 (d, 5 Hz), 125.6, 118.0, 117.6, 114.7 (d, 9 Hz), and 113.5 (d, 11 Hz) (ArC), 21.0, 20.9, 20.5, 20.3, 19.8, 19.7, 17.7, and 16.0 ($ArCH_3$), 15.4 (d, 13 Hz, PMe_3). Anal. Calcd for **3**·$(HMDSO)_{0.67}$, $C_{83}H_{99}N_6P_3Zr_2Si_{1.33}O_{0.67}$: C, 66.27; H, 6.63; N, 5.59. Found: C, 66.38; H, 6.90; N, 5.22.

$\{[NPN]^*Zr(PMe_2Ph)\}(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)\{Zr[NPN]^*\}$ (4). To a stirred blue-green suspension of **1** (0.410 g, 0.280 mmol) in toluene (10 mL) was added PMe_2Ph (0.250 g, 1.81 mmol). The suspension turned bright green and was stirred at room temperature for 30 min to obtain a clear, emerald green solution. The reaction mixture was taken to dryness to obtain a green residue that was triturated and taken to dryness, first with toluene (5 mL), then with hexanes (3 × 5 mL). The deep green solids obtained were suspended in pentane (5 mL), and the mixture was chilled to −35 °C overnight. The solids were collected on a frit, rinsed with hexanes (5 mL), and dried for 1 h to obtain a bright green powder (0.335 g, 0.229 mmol, 82%). Small crystals of **4** suitable for microanalysis were grown by slow evaporation of a benzene/HMDSO solution of the complex. Crystals of **4** suitable for X-ray analysis were grown by slow evaporation of a concentrated hexanes solution of the compound. ^1H NMR (C_6D_6, 400 MHz): $\delta = 7.79$ (t, 2H, 9 Hz), 7.74 (t, 2H, 9 Hz), 7.51 (d, 2H, 7 Hz), 7.38 (d, 2H, 8 Hz), 7.25−7.15 (m, 3H), 6.98 (m, 2H), 6.91 (t, 2H, 7 Hz), 6.79−6.65 (m, 16H), 6.12 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6.5$ Hz), and 5.77 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6.5$ Hz) (ArH), 2.28 (s, 6H), 2.19 (s, 6H), 2.16 (s, 6H), 1.98 (s, 12H), 1.92 (s, 6H), 1.67 (s, 6H), and 1.48 (s, 6H) ($ArCH_3$), 0.80 (d, 6H, $J_{HP} = 6$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): $\delta = 7.3$ (d, 1P, $^2J_{PP} = 46$ Hz), 1.9 (s, 1P), −22.5 (d, 1P, $^2J_{PP} = 46$ Hz, PMe_2Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz): $\delta = 162.9$ (d, 31 Hz), 159.4 (d, 26 Hz), 141.4, 137.8, 137.5 (d, 4 Hz), 136.1, 135.4, 135.0, 134.7, 134.3, 134.2, 133.9, 133.7, 133.6, 133.5, 133.4, 133.3, 131.7, 131.4, 131.3, 130.8 (d, 8 Hz), 129.7 (d, Hz), 129.2, 129.0, 128.7 (d, 3 Hz), 128.6 (d, 3 Hz), 127.9, 127.4 (d, 7.5 Hz), 127.1 (d, 5 Hz), 125.8 (d, 5 Hz), 118.1, 117.8, 117.6, 117.2, 114.5 (d, 9 Hz), and 113.6 (d, 11 Hz) (ArC), 21.1, 21.0, 20.5, 20.3, 19.5, 19.1, 17.9, and 16.1 ($ArCH_3$), 15.6 (d, 13 Hz, $PPh(CH_3)_2$). EI-MS (*m*/*z*): 1320 (8, $[M - PMe_2Ph]^+$), 541 (100, $[[NPN]^*H_2 - Me]^+$). Anal. Calcd for **4**·$(C_6H_6)(HMDSO)_{1.5}$, $C_{99}H_{122}N_6O_{1.5}Si_3P_3Zr_2$: C, 66.81; H, 6.91; N, 4.72. Found: C, 67.21; H, 6.86; N, 4.35. UV−vis (toluene) λ_{max} (ϵ) = 363 (1.1×10^4), 699 (9.7×10^3) nm (L mol^{-1} cm^{-1}).

$\{[NPN]^*Zr(PPhMe_2)\}(\mu\text{-}\eta^2{:}\eta^2\text{-}^{15}N_2)\{Zr[NPN]^*\}$ (4-$^{15}N_2$). Complex **4-$^{15}N_2$** (74 mg, 51 μmol, 97%) was prepared in an analogous fashion to **4** from **1-$^{15}N_2$** (77 mg, 53 μmol) in toluene (1 mL) and PMe_2Ph (73 mg, 53 μmol). The ^1H NMR spectrum was identical to that observed for **4**. $^{31}P\{^1H\}$ NMR (toluene-d_8, 162 MHz, 253 K): $\delta = 7.3$ (ddd, 1P, $^2J_{PP} = 46$ Hz, $^2J_{PN} = 4$ Hz, $^2J_{PN} = 7$ Hz), 1.9 (s, 1P), −22.5 (dd, 1P, $^2J_{PP} = 46$ Hz, $^2J_{PN} = 7$ Hz). $^{15}N\{^1H\}$ NMR (toluene-d_8, 40 MHz, 253 K): $\delta = 119.0$ (AA′XX′ multiplet, 1N, $^1J_{NN} = 8$ Hz, $^2J_{NP} = 7$ Hz, $^2J_{NP} = 4$ Hz), 118.0 (AA′XX′ multiplet, 1N, $^1J_{NN} = 8$ Hz, $^2J_{NP} = 7$ Hz, $^2J_{NP} = 4$ Hz). EI-MS (*m*/*z*): 1322 (15, $[M - PMe_2Ph]^+$), 541 (100, $[[NPN]^*H_2 - Me]^+$).

$\{[NPN]^*Zr(PMe_3)\}(\mu\text{-}H)(\mu\text{-}NNH)\{Zr[NPN]^*\}$ (5). Complex **3** (0.400 g, 0.287 mmol) was dissolved in toluene (10 mL), and PMe_3 (0.010 g, 0.132 mmol) was added. The solution was transferred to a Teflon-sealed bomb and degassed by three freeze−pump−thaw cycles. At room temperature, the flask was filled with 1 atm of H_2 gas and sealed, and the contents of the flask were stirred vigorously for 6 weeks. Over 2−3 weeks, the bright green solution became light yellow-green, and after 5−6 weeks an orange precipitate formed. In the glovebox, the precipitate was collected on a frit, rinsed with pentane (10 mL), and dried under vacuum for 10 min to obtain a yellow-orange powder (0.224 g, 0.160 mmol, 56%). The filtrate was stored under H_2 (1 atm) in a Teflon-sealed bomb for 1 week to obtain yellow crystals that were collected on a frit and dried under vacuum (0.105 g, 0.075 mmol, 26%). Although samples of **5** decompose over days at 25 °C in a N_2-filled glovebox, at −35 °C no decomposition is observed over 1 month. At 25 °C, toluene solutions of **5** with added PMe_3 (∼10 mg per 1 mL of toluene) can be stored for weeks without decomposition. Small yellow-orange crystals were grown from toluene/HMDSO at −35 °C. The amount of cocrystallized HMDSO was consistent with the results of ^1H NMR spectroscopy performed on crystalline samples dissolved in C_6D_6. Orange single crystals suitable for X-ray analysis were grown in an NMR tube under H_2 by vapor diffusion of pentane into a C_6H_6 solution of the compound with ∼10 mg PMe_3 added per 1 mL of benzene. ^1H NMR (C_6D_6, 400 MHz, 298 K): $\delta = 7.98$ (bt, 4H, 5 Hz), 7.45−7.25 (m, 4H), 7.14−7.00 (m, 4H), 6.91−6.68 (m, 12H), 6.07 (dd, 1H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), 6.01 (dd, 1H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), 5.86 (bs, 1H), 5.83 (s, 1H), 5.71 (bs, 1H), and 5.47 (bs, 1H) (ArH), 4.83 (t, 1H, $^2J_{HP} = 11$ Hz, ZrHZr), 4.78 (bs, 1H, NNH), 2.41 (s, 3H), 2.39 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H), 2.16 (s, 3H), 2.13 (s, 6H), 1.99 (s, 6H), 1.97 (s, 6H), 1.94 (s, 3H), 1.93 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), and 1.59 (s, 3H) ($ArCH_3$), 0.19 (d, 9H, $J_{HP} = 5$ Hz,

$P(CH_3)_3$). ^1H NMR (toluene-d_8, 500 MHz, 253 K): $\delta = 8.14$ (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 8$ Hz), 7.62 (d, 1H, 7 Hz), 7.48 (d, 1H, 8 Hz), 7.45 (d, 1H, 8 Hz), 7.34 (d, 1H, 9 Hz), 7.18 (m, 4H), 7.06 (m, 2H), 6.99 (m, 4H), 6.86 (d, 1H, 8.5 Hz), 6.80 (d, 1H, 8.5 Hz), 6.76 (bs, 3H), 6.72 (s, 1H), 6.67 (s, 2H), 6.57 (d, 2H, 8 Hz), 6.16 (dd, 1H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), 5.94 (dd, 1H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), 5.79 (dd, 1H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), and 5.70 (dd, 1H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz) (ArH), 4.84 (t, 1H, $^2J_{HP} = 11$ Hz, ZrHZr), 4.82 (bs, 1H, NNH), 2.65 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 2.14 (s, 6H), 2.08 (s, 6H), 2.01 (s, 3H), 1.99 (s, 6H), 1.95 (s, 3H), 1.94 (s, 3H), 1.80 (s, 3H), 1.69 (s, 3H), and 1.64 (s, 3H) ($ArCH_3$), 0.09 (bs, 9H, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (toluene-d_8, 202 MHz, 273 K): $\delta = 13.8$ (d, 1P, $^2J_{PP} = 56.7$ Hz), −2.2 (s, 1P), −34.5 (d, 1P, $^2J_{PP} = 56.7$ Hz). Anal. Calcd for **5**·$(HMDSO)_{0.67}$, $C_{83}H_{101}N_6P_3O_{0.67}Si_{1.33}Zr_2$: C, 66.19; H, 6.76; N, 5.58. Found: C, 65.98; H, 6.60; N, 5.50.

{[NPN]*Zr(PMe$_3$)}(μ-D)(μ-NND){Zr[NPN]*} (5-*d*$_2$). Complex **3** (0.300 g, 0.215 mmol) was dissolved in toluene (5 mL), and PMe_3 (0.010 g, 0.132 mmol) was added. The solution was transferred to a Teflon-sealed bomb and was degassed by three freeze−pump−thaw cycles. D_2 gas was added to the flask at 25 °C. The solution was stirred vigorously for 4 weeks to obtain a deep green solution with a small amount of a yellow-green precipitate. The flask was then refilled with D_2 at 77 K and allowed to warm to 25 °C (4 atm D_2 pressure) behind a blast shield. After the solution had been stirred vigorously for 4 weeks, the reaction mixture was a dark-orange suspension. The pressure was vented, and the reaction mixture was taken to dryness to obtain a dark-orange solid. The solid was triturated with hexanes to obtain an orange powder that was collected on a frit, washed with pentane (3 × 5 mL), and dried under vacuum (0.185 g, 0.132 mmol, 61%). A 10:1 mixture of **5-*d*$_2$** and **5** was obtained. The $^{31}P\{^1H\}$ NMR spectrum was identical to that of **5**. ^1H NMR (toluene-d_8, 400 MHz, 253 K): $\delta =$ same as for **5** except the resonances at δ 4.84 and 4.82 integrate to 0.1H each rather than 1H relative to one of the $ArCH_3$ resonances. EI-MS (*m*/*z*): 1396 (1, $[M]^+$), 541 (100, $[[NPN]^*H_2 - Me]^+$).

{[NPN]*Zr(PMe$_2$Ph)}(μ-H)(μ-NNH){Zr[NPN]*} (6). Complex **4** (0.380 g, 0.261 mmol) and PMe_2Ph (0.010 g, 0.073 mmol) were dissolved in toluene (7 mL). The bright green solution was transferred to a Teflon-sealed bomb and degassed by three freeze−pump−thaw cycles. At room temperature the flask was filled with 1 atm of H_2 gas, the bomb was sealed, and the reaction mixture was stirred vigorously for 6 weeks. Over several weeks, the bright green solution gradually became light yellow-green and an orange precipitate formed. In the glovebox, the reaction mixture was taken to dryness, and pentane (10 mL) was added to obtain a yellow suspension that was chilled to −35 °C. The yellow solid was collected on a frit and dried (0.275 g, 0.188 mmol, 72%). Small yellow crystals were grown from toluene/HMDSO at −35 °C, and the amount of cocrystallized HMDSO was confirmed by ^1H NMR spectroscopy of samples of the crystals dissolved in C_6D_6. ^1H NMR (toluene-d_8, 400 MHz, 233 K): $\delta = 7.99$ (t, 2H, 8 Hz), 7.80 (t, 1H, 8 Hz), 7.49 (d, 1H, 7.5 Hz), 7.41 (d, 1H, 7.5 Hz), 7.32 (d, 1H, 7.5 Hz), 7.27 (d, 1H, 7.5 Hz), 7.09 (m, 2H), 7.05 (s, 1H), 6.97 (s, 2H), 6.89 (s, 2H), 6.81 (s, 1H), 6.64 (m, 10H), 6.54 (s, 1H), 6.49 (s, 1H), 6.36 (bm, 2H), 6.07 (dd, 2H, $J_{HH} = 8$ Hz, $J_{HP} = 6$ Hz), 5.89 (m, 2H), 5.70 (t, 1H, 7 Hz), 5.48 (t, 1H, 7 Hz) (ArH), 4.94 (s, 1H, NNH), 4.88 (bs, 1H, ZrHZr), 2.64 (s, 3H), 2.25 (s, 3H), 2.02 (s, 6H), 2.00 (s, 9H), 1.95 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H), 1.87 (s, 3H), 1.84 (s, 6H), 1.79 (s, 3H), 1.59 (s, 3H), 1.55 (s, 3H) ($ArCH_3$), 0.53 (bs, 3H), and 0.33 (bs, 3H) $(P(CH_3)_2Ph)$. $^{31}P\{^1H\}$ NMR (toluene-d_8, 162 MHz, 253 K): $\delta = 14.6$ (d, $^2J_{PP} = 57.4$ Hz, 1P), −2.3 (s, 1P), −24.6 (bs, 1P). Anal. Calcd for **6**·$(HMDSO)_{0.33}$, $C_{86}H_{97}N_6P_3O_{0.33}Si_{0.67}Zr_2$: C, 68.22; H, 6.46; N, 5.55. Found: C, 68.48; H, 6.62; N, 5.90.

{[NPN]*Zr(PMe$_2$Ph)}(μ-H)(μ-^{15}N^{15}NH){Zr[NPN]*} (6-^{15}N$_2$). Complex **6-^{15}N$_2$** (0.163 g, 0.112 mmol, 82%) was prepared in an analogous manner to **6** from **4-^{15}N$_2$** (0.200 g, 0.137 mmol), PMe_2Ph (0.010 g, 0.073 mmol), and H_2 in toluene (5 mL). ^1H NMR spectrum (toluene-d_8, 400 MHz, 233 K) is the same as that of **6**, but the resonance at δ 4.94 is a doublet (1H, $^1J_{HN} = 72$ Hz), and the resonance at δ 4.88 is a broad triplet (1H, $^2J_{HP} = 9.8$ Hz). $^1H\{^{31}P\}$ NMR (toluene-d_8, 400 MHz, 233 K): $\delta = 7.99$ (d, 2H, 7 Hz), 7.80 (d, 1H, 7.5 Hz), 7.49 (s, 1H), 7.41 (s, 1H), 7.32 (s, 1H), 7.27 (s, 1H), 7.09 (m, 2H), 7.05 (s, 1H), 6.97 (s, 2H), 6.89 (s, 2H), 6.81 (s, 1H), 6.64 (m, 10H), 6.54 (s, 1H), 6.49 (s, 1H), 6.36 (bm, 2H), 6.06 (d, 2H, 8 Hz), 5.89 (d, 2H, 8 Hz), 5.70 (d, 1H, 7 Hz), and 5.48 (d, 1H, 7 Hz) (ArH), 4.94 (d, 1H, $J_{HN} = 72$ Hz, NNH), 4.88 (bs, 1H, ZrHZr), 2.64 (s, 3H), 2.25 (s, 3H), 2.02 (s, 6H), 2.00 (s, 9H), 1.95 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H), 1.87 (s, 3H), 1.84 (s, 6H), 1.79 (s, 3H), 1.59 (s, 3H), and 1.55 (s, 3H) ($ArCH_3$), 0.53 (bs, 3H, $P(CH_3)_2Ph$), 0.33 (bs, 3H, $P(CH_3)_2Ph$). $^{31}P\{^1H\}$ NMR (toluene-d_8, 162 MHz, 253 K): $\delta = 14.6$ (d, 1P, $^2J_{PP} = 57.4$ Hz), −2.3 (s, 1P), −24.6 (bd, 1P, $^2J_{PP} = 51.5$ Hz). $^{15}N\{^1H\}$ NMR (toluene-d_8, 40 MHz, 298 K): $\delta = 143.9$ (s), 29.8 (d, $^2J_{NP} = 10$ Hz). EI-MS (*m*/*z*): 1320 (12, $[M - PMe_2Ph]^+$), 541 (100, $[[NPN]^*H_2 - Me]^+$).

Reaction of 1 with H$_2$. A solution of **1** (0.365 g, 0.249 mmol) in toluene (10 mL) in a thick-walled Teflon-sealed bomb was degassed by three freeze−pump−thaw cycles. At 77 K the flask was filled with H_2. The solution was warmed slowly to 25 °C behind a blast shield. The deep green solution was stirred for 6 weeks. No change was observed visually or detected by $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of 2 with H$_2$. A solution of **2** (0.430 g, 0.291 mmol) in toluene (15 mL) was transferred to a thick-walled Teflon-sealed bomb and degassed by three freeze−pump−thaw cycles. At 77 K, the flask was filled with H_2 gas and allowed to warm slowly to 25 °C behind a blast shield. The solution was stirred vigorously for 8 weeks, and a gradual green to yellow color change was observed. The pressure was vented, and the yellow reaction mixture was taken to dryness to obtain a yellow hexanes-soluble solid. $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz): $\delta =$ −7.6 (s), −8.0 (s), −21.3 (s), −31.4 (s).

X-ray Crystal Structure Analyses. Selected crystals were coated in oil, mounted on a glass fiber, and placed under a N_2 stream. Measurements for compounds were made on a Bruker X8 Apex diffractometer with graphite-monochromated Mo Kα radiation ($\lambda =$ 0.71073 Å). The data were collected at a temperature of −100 ± 1 °C. Data were collected and integrated using the Bruker SAINT software package.[29] Data were corrected for absorption effects using the multiscan technique (SADABS)[30] and for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.[31] Anomalous dispersion effects were included in F_{calc};[32] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[33] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[34] All refinements were performed using the SHELXTL crystallographic software package of Bruker-AXS. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically using SHELXL-97. Except where noted, hydrogen atoms were included in fixed positions. Structures were solved and refined using the WinGX software package version 1.64.05. In the asymmetric unit of **1**, solvent that could be modeled as C_6H_6 + THF + 0.67(C_6H_{14}) appear. Residual electron density consistent with additional disordered solvent was also evident but could not be modeled successfully. Similarly, in the asymmetric units of **2** and **4** residual electron density consistent with disordered solvent was evident; however, no reasonable model could be established. For all three

(29) *SAINT*, version 6.02; Bruker AXS Inc.: Madison, WI, 1999.
(30) *SADABS*, V2.05; Bruker Nonius area detector scaling and absorption correction; Bruker AXS Inc.: Madison, WI.
(31) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.
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(35) Van der Sluys, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 40.

structures, the program SQUEEZE[35] was used to generate a data set that corrects for the scattering contribution from this disordered solvent.

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Supporting Information Available: UV−vis spectra for the dinitrogen complexes **1**, **2**, and **4**; X-ray crystal structure data (Table S1 and CIF files); ^{31}P NMR spectrum of complex **3**; low-resolution X-ray structure of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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