DOI: 10.1002/ange.201402401

Photochemical Nitrogen Reduction

Photochemically Induced Reductive Elimination as a Route to a Zirconocene Complex with a Strongly Activated N_2 Ligand**

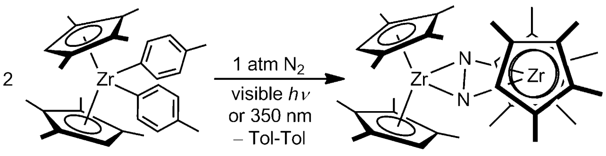
*Grant W. Margulieux, Scott P. Semproni, and Paul J. Chirik**

Abstract: *The zirconocene dinitrogen complex* $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ *was synthesized by photochemical reductive elimination from the corresponding zirconium bis(aryl) or aryl hydride complexes, providing a high-yielding, alkali metal-free route to strongly activated early-metal* N_2 *complexes. Mechanistic studies support the intermediacy of zirconocene arene complexes that in the absence of sufficient dinitrogen promote C–H activation or undergo comproportion to formally* Zr^{III} *complexes. When* N_2 *is in excess arene displacement gives rise to strong dinitrogen activation.*

Reduced early transition metal complexes are of interest due to their ability to activate, cleave and functionalize the otherwise inert dinitrogen molecule.[1] Zirconocene and hafnocene complexes with strongly activated dinitrogen ligands are exemplary offering diverse reactivity ranging from N_2 hydrogenation to ammonia[2] to the synthesis of organic molecules including substituted oxamides,[3] formamide,[4] unsymmetrical ureas,[5] and carbodiimides[5] using CO-induced dinitrogen cleavage as the N–C bond forming strategy.[6] Preparation of the metal complexes bearing activated dinitrogen ligands requires alkali metal reduction of a suitable halide precursor, conditions often incompatible with catalytic turnover.[7] Reductive elimination of dihydrogen or alkanes is an attractive alternative[8] and has recently been postulated as a key step for the activation of the FeMoCo cluster in molybdenum-containing nitrogenases.[9] With zirconocene compounds, both H–H[10] and C–H reductive elimination[11,12] have been reported as routes to dinitrogen complexes. Unfortunately, the electron-withdrawing cyclopentadienyl substituents required to enable thermal reductive elimination inhibit N_2 activation as only weakly activated dinitrogen complexes with $[N_2]^0$ or $[N_2]^{2-}$ ligands have been prepared by this route.

Recently, Evans and co-workers described photochemical activation of mixed-ring tris(cyclopentadienyl) lanthanide compounds as a route to lanthanocene dinitrogen complexes with $[N_2]^{2-}$ ligands.[13] These findings, in combination with Erker's seminal report of photochemically induced biaryl coupling from $[(\eta^5\text{-}C_5H_5)_2Zr(Tol)_2]$ (Tol = 4-Me-C_6H_4)[14] suggested that photochemical reductive elimination may overcome the barrier of thermal methods and provide a convenient and alkali metal-free route to strongly activated early transition metal dinitrogen complexes. Here we describe successful application of this concept with visible light to the synthesis of $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$, a zirconocene complex with a strongly activated dinitrogen ligand known to undergo hydrogenation and CO-induced N_2 cleavage. The scope and mechanism of the reaction were also investigated.

Based on Erker's precedent,[14] $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ was synthesized in 66% yield and crystallographically characterized (Figure S1 in the Supporting Information) from straightforward diarylation of the corresponding zirconocene dichloride. Exposure of a benzene solution of the bis(aryl) zirconocene to visible light (from a commercially available compact fluorescent light source; $\lambda = 285$ to 700 nm) resulted in a color change to dark purple in 2 h, signaling formation of $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$. This observation is somewhat misleading because of the high extinction coefficient of the complex as only small quantities of the product are formed at this time interval; complete conversion was achieved after 3 days of continued irradiation [Eq. (1)]. A quantitative amount of 4,4′-dimethylbiphenyl was observed by ^1H NMR spectroscopy and confirmed by mass spectrometry. Improved reaction times of 3 h were obtained using 350 nm light in a UV photoreactor. Using this procedure, $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ was isolated in 77% yield, higher than previously reported alkali metal reduction route.[2c] Notably, using shorter wavelength light of 254 or 300 nm resulted in decomposition of the starting zirconocene to unidentified products.



(1)

Other diaryl zirconocenes, $[(\eta^5\text{-}C_5Me_4H)_2Zr(C_6H_5)_2]$ and $[(\eta^5\text{-}C_5Me_4H)_2Zr(C_6H_5\text{-}4\text{-}R)_2]$ (R = Et, Ph) were also competent reductive elimination precursors to the desired dinitrogen compound. Likewise, irradiation of $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ in benzene solution with 350 nm light in the presence of excess carbon monoxide or bis(trimethylsilyl)acetylene[15] yielded $[(\eta^5\text{-}C_5Me_4H)_2Zr(CO)_2]$[16] and $[(\eta^5\text{-}C_5Me_4H)_2Zr(\eta^2\text{-}Me_3SiCCSiMe_3)]$[15b] respectively.[17]

When the photolysis of $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ was performed with insufficient mixing or at reduced pressures of dinitrogen, intense ink blue solutions were observed. In addition to reduced yields of $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}$

---

[*] G. W. Margulieux, S. P. Semproni, Prof. Dr. P. J. Chirik
Department of Chemistry, Princeton University
292 Frick Laboratory, Princeton, NJ 08544 (USA)
E-mail: pchirik@princeton.edu

[**] We thank the Department of Energy, Basic Energy and Sciences (DE-SC0006498) for financial support. Dr. Carsten Milsmann is also acknowledged for assistance with TD-DFT.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201402401.

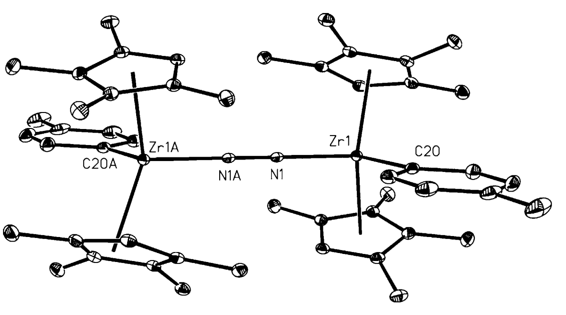


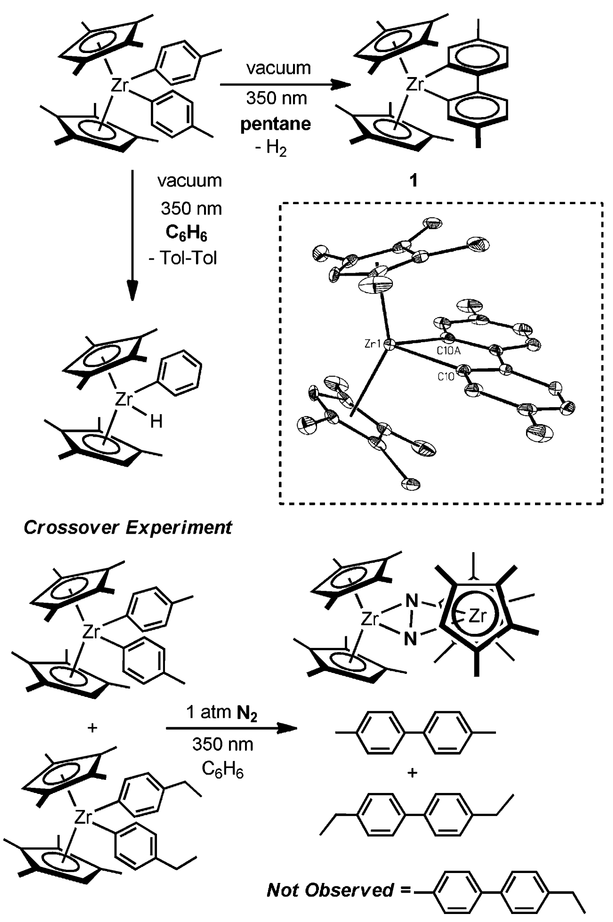
Figure 1. Representation of the molecular structure of [{(η^5-$C_5Me_4H)_2Zr(Tol)\}_2(\mu_2,\eta^1,\eta^1$-$N_2$)] at 30% probability ellipsoids.[24] Hydrogen atoms omitted for clarity; d(N−N) = 1.179(3) Å.

N_2)], a second diamagnetic compound, identified as [{(η^5-$C_5Me_4H)_2Zr(Tol)\}_2(\mu_2,\eta^1,\eta^1$-$N_2$)], was observed by NMR spectroscopy. A more rational and straightforward synthesis of the compound was achieved from reduction of [(η^5-$C_5Me_4H)_2Zr(Tol)Cl$] with one equivalent of sodium naphthalenide under 1 atm of N_2. The product proved stable to N_2 loss under vacuum and was readily isolated in the solid state. The observed diamagnetism of the formally Zr^{III}-Zr^{III} complex can be accounted for either by antiferromagnetic coupling or two electron reduction of the N_2 ligand.

The solid-state structure of [{(η^5-$C_5Me_4H)_2Zr(Tol)\}_2(\mu_2,\eta^1,\eta^1$-$N_2$)] (Figure 1) confirms the identity of the molecule and establishes the *transoid* disposition of the aryl groups across the dimer. The tolyl rings are nearly coplanar with the idealized metallocene wedge and the N−N bond distance of 1.179(3) Å is consistent with weak activation. The observed magnetism arises from antiferromagnetic coupling rather than two-electron reduction of the bridging N_2 ligand. Importantly, photolysis of [{(η^5-$C_5Me_4H)_2Zr(Tol)\}_2(\mu_2,\eta^1,\eta^1$-$N_2$)] with 254, 300 or 350 nm light for extended periods under an N_2 atmosphere produced no change demonstrating that this compound is not a competent intermediate in the formation of [{(η^5-$C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2$-$N_2$)].

Additional studies were conducted to gain insight into the mechanism of photoinduced reductive elimination. Irradiation of a benzene solution of [(η^5-$C_5Me_4H)_2Zr(Tol)_2$] with 350 nm light under vacuum or argon resulted in loss of 4,4′-dimethylbiphenyl along with complete conversion to [(η^5-$C_5Me_4H)_2Zr(Ph)H$] after 3 h (Scheme 1). Repeating this procedure in pentane solution in the absence of N_2 resulted in isolation of [(η^5-$C_5Me_4H)_2Zr$(4,4′-dimethylbiphenyl)] (**1**) arising from reductive coupling and formal loss of H_2 (Scheme 1). This product was characterized by X-ray diffraction and the solid-state data confirms selective C−C coupling at the position adjacent to the site of metalation.

A crossover experiment was conducted to gain insight into the molecularity of the photoinduced reductive elimination reaction. A benzene solution containing an equimolar mixture of [(η^5-$C_5Me_4H)_2Zr(Tol)_2$] and [(η^5-$C_5Me_4H)_2Zr(C_6H_4$-4-Et$)_2$] was irradiated with 350 nm light for 3 h under 4 atm of N_2 and [{(η^5-$C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2$-$N_2$)] was identified as the exclusive organometallic product. Analysis of the organic byproducts by NMR spectroscopy and mass spectrometry established formation of 4,4′-dimethylbiphenyl and 4,4′-diethylbiphenyl. Importantly, no 4-methyl-4′-ethylbiphenyl was observed as judged by comparison of the experimental data to authentic samples. These results support a unimolecular, classical two-electron reductive elimination pathway.



Scheme 1. Photolysis of [(η^5-$C_5Me_4H)_2Zr(Tol)_2$] under vacuum in benzene and pentane solution. The solid state structure of **1** at 30% probability ellipsoids.[24] Hydrogen atoms omitted for clarity.

Attempts were also made to follow the course of the photolysis of [(η^5-$C_5Me_4H)_2Zr(Tol)_2$] by EPR spectroscopy. Recording X-band spectra during photolysis of a [D_6]benzene solution of the compound with 350 nm light at 23 °C in the presence of 1 atm of N_2 produced a spectrum with a large isotropic signal at $g = 1.980$, consistent with [(η^5-$C_5Me_4H)_2ZrTol$] (Figure S2).[18] Notably, an additional weak-intensity 1:1:1 triplet was also observed at $g = 1.961$, consistent with formation of [(η^5-$C_5Me_4H)_2ZrTol(N_2)$]. The confines of a narrow EPR tube and poor gas mixing in the cavity of the spectrometer likely inhibit formation of [{(η^5-$C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2$-$N_2$)] (see below). Repeating the experiment under vacuum resulted in disappearance of this signal and performing the reaction with $^{15}N_2$ produced a doublet, consistent with coupling to the $I = {}^1\!/_2$ nitrogen nucleus. Alkyl zirconocene(III) dinitrogen complexes were first proposed by Lappert[19] but subsequent studies from our laboratory have established, using X-ray crystallography and EPR spectroscopy, that these compounds are in fact the anionic zirconocene dinitrogen complexes.[20] The spectra observed in Figure S2 and the conditions of the synthesis used here eliminate the possibility of anionic compounds and support formation of neutral Zr^{III} N_2 derivatives. Unfortunately, these species have proven extremely reactive and attempts to observe or isolate them on preparative scale have been unsuccessful.

The scope of the photoinduced reductive elimination reaction to prepare the strongly activated zircononcene dinitrogen compound was explored by systematic variation of the X-type ligand in the metallocene wedge. Replacement of one of the aryl ligands with hydride also resulted in productive chemistry as irradiation of $[(\eta^5\text{-}C_5Me_4H)_2Zr(Ar)H]$ (Ar = Ph, Tol) with 350 nm light cleanly yielded $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ in good yields. In contrast, zirconocenes with sp^3 hybridized alkyl ligands proved unreactive as photolysis of $[(\eta^5\text{-}C_5Me_4H)_2ZrMe_2]$ for extended periods with 254, 300 or 350 nm light produced no change. Notably, $[(\eta^5\text{-}C_5Me_4H)_2ZrBn_2]$ or $[(\eta^5\text{-}C_5Me_4H)_2Zr(Bn)H]$, isomers of compounds that undergo successful reductive elimination, were also unsuccessful as the former was unreactive while the latter yielded toluene and a mixture of unidentified products. A similar outcome was observed with $[(\eta^5\text{-}C_5Me_4H)_2ZrH_2]$.

To determine the origin of the differential reactivity, the UV/Vis spectra of $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ and $[(\eta^5\text{-}C_5Me_4H)_2ZrMe_2]$ were recorded in pentane solution and are presented in Figure 2. The spectrum of $[(\eta^5\text{-}C_5Me_4H)_2ZrBn_2]$ was also obtained under identical conditions and is reported in the Supporting Information. The spectrum of $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ exhibits two bands at $\lambda_{max} = 244$ ($\varepsilon = 22761\,\text{M}^{-1}\text{cm}^{-1}$) and 345 nm ($\varepsilon = 3345\,\text{M}^{-1}\text{cm}^{-1}$). To aid spectral assignment, TD-DFT calculations were conducted, the details of which are reported in the Supporting Information. The intense transition at 244 nm is an LMCT band, a result of high oscillator strength excitations from the HOMO and HOMO−1 to the LUMO+1 and LUMO+2 excited states. While we recognize that electronic transitions occur rigorously between states, it is most convenient to discuss electron transfer between constituent molecular orbitals. The occupied orbitals are best described as linear combinations of π-symmetry orbitals on both the cyclopentadienyl and aryl ligands. The unoccupied orbitals are primarily metal in character (Figure S4). Because these transitions are principally cyclopentadienyl in origin, it is likely that the observed decomposition when using shorter wavelength light is a result of photoinduced cyclopentadienyl dissociation.[21] Importantly, this region of the spectrum is not the origin of the observed photochemical reductive elimination.

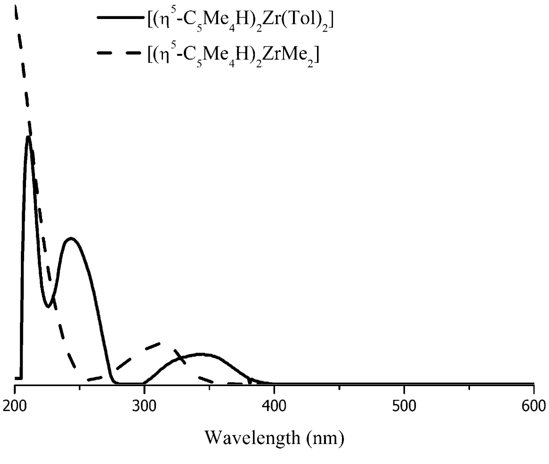


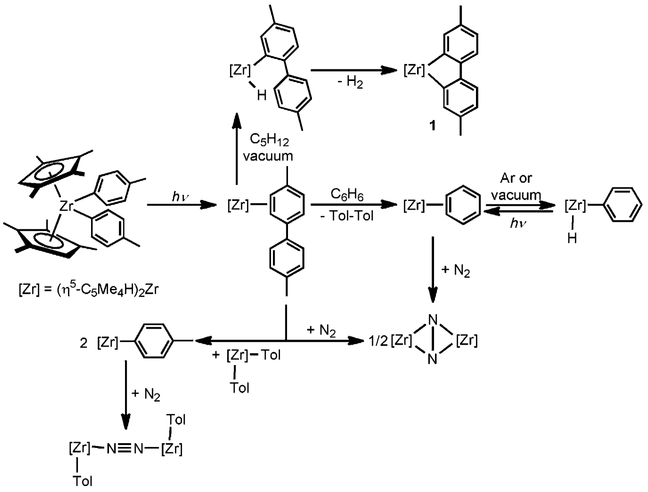
Figure 2. UV/Vis spectra of $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ and $[(\eta^5\text{-}C_5Me_4H)_2ZrMe_2]$ in benzene solution.

The less intense broad band centered at 345 nm is a result of a number of overlapping LMCT transitions. Excitations to the LUMO (Zr d orbital) from the HOMO−2 ($\eta^5\text{-}C_5Me_4H$), HOMO−1 ($\eta^5\text{-}C_5Me_4H$) and HOMO ($\eta^5\text{-}C_5Me_4H$) were calculated at 345, 350, and 370 nm, respectively.[19] As these transitions occur between states of similar parentage, meaning principally cyclopentadienyl-based orbitals, as the higher energy excitations at 244 nm, it is not immediately obvious how these LMCT events influence photochemical induced reductive elimination. Closer inspection of the TD-DFT calculations reveals a transition at 316 nm that arises from a linear combination of HOMO−3 and HOMO−9 (likely to a lesser extent) orbitals that have significant Zr−C bonding character to a metal-based LUMO.

Similar spectral features were observed with $[(\eta^5\text{-}C_5Me_4H)_2ZrMe_2]$, although the bands at 207 nm ($\varepsilon = 28593\,\text{M}^{-1}\text{cm}^{-1}$) and 314 nm ($\varepsilon = 3568\,\text{M}^{-1}\text{cm}^{-1}$) are blue-shifted relative to $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$. High oscillator strength bands were calculated at 307 and 323 nm and result from transitions from the HOMO−1 and HOMO, respectively, to an entirely metal-based LUMO. As with the bis(aryl) zirconocene, these high energy occupied orbitals have little to no Zr−C bonding character and are principally cyclopentadienyl in parentage. Three lower oscillator strength transitions at 298, 304, and 313 nm arise from HOMO−4, HOMO−3 and HOMO−2 based transitions with significant metal–carbon σ bonding character. In all cases these excitations terminate in the Zr-based LUMO. Thus, the experimental UV/Vis data in conjunction with the TD-DFT based assignments suggest little difference, aside from relative energetics, in the spectroscopic states of the two zirconocene complexes. What then is the origin of the disparate reactivity between the zirconocene bis(aryl) and dimethyl complexes?

A proposed mechanism to account for the observed photolysis chemistry with $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ is presented in Scheme 2. The sequence begins with two-electron chemistry—namely reductive coupling of the sp^2–sp^2 hybridized C−C bonds to yield a formally Zr^{II} arene complex.[22] In benzene solution, arene exchange is likely and the zirconocene benzene complex is formed. In the absence of N_2, C−H oxidative addition occurs forming $[(\eta^5\text{-}C_5Me_4H)_2Zr(Ph)H]$ consistent with the experimental observations when the photolysis was carried out under Ar or vacuum in [D$_6$]benzene. In the absence of arene solvent, the 4,4′-dimethylbiphenyl complex persists and undergoes C−H oxidative addition to initially form a putative zirconocene aryl hydride that ultimately undergoes a second, selective C−H activation to form the observed zirconocycle, **1**.

With sufficient N_2 pressure and efficient mixing, dinitrogen can displace the coordinated arenes, either 4,4′-dimethylbiphenyl or benzene and form the strongly activated zirconocene dinitrogen complex, $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$. Observations with CO and bis(trimethylsilyl)acetylene also support this hypothesis. When N_2 is deficient, comproportio-



Scheme 2. Summary of photochemical reductive elimination studies with $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$.

nation of the zirconocene arene intermediate with $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ yields $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)]$, which has been observed by EPR spectroscopy. Addition of N_2 to $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)]$ affords the observed zirconocene aryl complex with an end-on bridging N_2 ligand, $[\{(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)\}_2(\mu_2,\eta^1,\eta^1\text{-}N)]$.

Consistent with the observed crossover experiment, photolysis of $[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$ results in two-electron reductive coupling and formation of arene complexes that are key intermediates for resulting C−H and N_2 activation chemistry. The absence of similar reactivity with $[(\eta^5\text{-}C_5Me_4H)_2ZrMe_2]$ is likely a result of the higher barrier associated with sp^3–sp^3 reductive elimination prohibiting entry into reduced zirconocene chemistry.[23] It is also possible that introduction of saturated alkyl ligands into the coordination sphere of the metal reduces the quantum yield below the threshold necessary to initiate productive chemistry. We do note that introduction of benzyl ligands as in the case of $[(\eta^5\text{-}C_5Me_4H)_2ZrBn_2]$ ($Bn = CH_2C_6H_5$) does not enable photoinduced reductive elimination.

In summary, photoinduced C−C reductive elimination of biaryls has been identified as an effective, alkali metal-free route to zirconocene complexes with strongly activated dinitrogen ligands. The success of the reaction is dependent on the identity of the hydrocarbyl substituent on the zirconium. The application of this transformation to the preparation of new early transition metal complexes with strongly activated N_2 ligands is currently under investigation.

Received: February 13, 2014

Keywords: nitrogen fixation · photochemistry · reductive elimination · zirconium

[1] a) K. Macleod, P. Holland, *Nat. Chem.* **2013**, *5*, 559; b) Y. Tanabe, Y. Nishibayashi, *Coord. Chem. Rev.* **2013**, *257*, 2551; c) P. J. Chirik, *Organometallics* **2010**, *29*, 1500; d) M. D. Fryzuk, *Acc. Chem. Res.* **2009**, *42*, 127; e) P. J. Chirik, *Dalton Trans.* **2007**, 16; f) E. A. MacLachlan, M. D. Fryzuk, *Organometallics* **2006**, *25*, 1530; g) M. Shaver, M. Fryzuk, *Adv. Synth. Catal.* **2003**, *345*, 1061.

[2] a) W. H. Bernskoetter, A. V. Olmos, E. Lobkovsky, P. J. Chirik, *Organometallics* **2006**, *25*, 1021; b) W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2005**, *127*, 14051; c) J. A. Pool, E. Lobkovsky, P. J. Chirik, *Nature* **2004**, *427*, 527.

[3] D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 15340.

[4] S. P. Semproni, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2011**, *133*, 10406.

[5] S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2013**, *135*, 11373.

[6] a) D. J. Knobloch, S. P. Semproni, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2012**, *134*, 3377; b) D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *Nat. Chem.* **2010**, *2*, 30.

[7] For recent examples of catalytic N_2 functionalization using alkali metals as the stoichiometric reductant: a) J. S. Anderson, J. Rittle, J. C. Peters, *Nature* **2013**, *501*, 84; b) M. Yuki, H. Tanaka, Y. Miyake, K. Yoshizawa, Y. Nishibayashi, *Nat. Chem.* **2012**, *3*, 1254.

[8] J. Ballmann, R. F. Munhá, M. D. Fryzuk, *Chem. Commun.* **2010**, *46*, 1013.

[9] B. M. Hoffmann, D. Lukoyanov, D. R. Dean, L. C. Seefeldt, *Acc. Chem. Res.* **2013**, *46*, 587.

[10] P. J. Chirik, L. M. Henling, J. E. Bercaw, *Organometallics* **2001**, *20*, 534.

[11] J. A. Pool, E. Lobkovsky, P. J. Chirik, *Organometallics* **2003**, *22*, 2797.

[12] J. A. Pool, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2003**, *125*, 2241.

[13] M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2013**, *135*, 3804.

[14] G. Erker, *J. Organomet. Chem.* **1977**, *134*, 189.

[15] a) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2003**, *22*, 884; b) J. Hiller, U. Thewalt, M. Polasek, L. Petrusova, V. Varga, P. Sedmera, K. Mach, *Organometallics* **1996**, *15*, 3752.

[16] P. Courtot, V. Labed, R. Pichon, J. Y. Salaun, *J. Organomet. Chem.* **1989**, *359*, C9.

[17] M. J. Rausch, W. B. Boon, E. A. Mintz, *J. Organomet. Chem.* **1978**, *160*, 81.

[18] E. Samuel, P. Maillard, C. J. Giannotti, *J. Organomet. Chem.* **1977**, *142*, 289.

[19] a) M. J. S. Gynane, J. Jeffrey, M. F. Lappert, *J. Chem. Soc. Chem. Commun.* **1978**, 34; b) J. Jeffrey, M. F. Lappert, P. I. Riley, *J. Organomet. Chem.* **1979**, *181*, 25.

[20] S. P. Semproni, D. J. Knobloch, C. Milsmann, P. J. Chirik, *Angew. Chem.* **2013**, *125*, 5480; *Angew. Chem. Int. Ed.* **2013**, *52*, 5372.

[21] a) J. G. Lee, C. H. Brubaker, Jr., *Inorg. Chim. Acta* **1977**, *25*, 181; b) Z. Tsai, C. H. Brubaker, Jr., *J. Organomet. Chem.* **1979**, *166*, 199.

[22] a) H. S. Tung, C. H. Brubaker, *Inorg. Chim. Acta* **1981**, *52*, 197; b) L. E. Schock, C. P. Brook, T. J. Marks, *Organometallics* **1987**, *2*, 232; c) S. L. Buchwald, R. B. Nielsen, *Chem. Rev.* **1988**, *88*, 1047; d) G. Erker, M. Albrecht, *Organometallics* **1992**, *11*, 3517; e) E. Negishi, T. Takahashi, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755; f) W. D. Jones, *Inorg. Chem.* **2005**, *44*, 4475.

[23] a) J. J. Low, *J. Am. Chem. Soc.* **1984**, *106*, 8321; b) V. P. Ananikov, D. G. Musaev, K. Morokuma, *Organometallics* **2005**, *24*, 715; c) R. Ghosh, T. J. Emge, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2008**, *130*, 11317.

[24] CCDC 986587 ($[(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)_2]$), 986588 ($[\{(\eta^5\text{-}C_5Me_4H)_2Zr(Tol)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$), and 986589 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.