

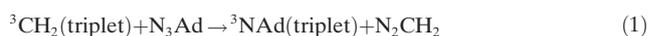
Divergent Pathways Involving 1,3-Dipolar Addition and N–N Bond Splitting of an Organic Azide across a Zirconium Methylidene

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Abstract: The zirconium methylidene (PNP)Zr=CH₂(OAr) (**1**) reacts with N₃Ad to give two products (PNP)Zr=NAd(OAr) (**2**) and (PNP)Zr(η²-N=NAd)(N=CH₂)(OAr) (**3**), both resulting from a common cycloaddition intermediate (PNP)Zr(CH₂N₃Ad)(OAr) (**A**). Using a series of control experiments in combination with DFT calculations, it was found that **2** results from a nitrene by a carbene metathesis reaction in which N₂ acts as a delivery vehicle and forms N₂CH₂ as a side product. In the case of **3**, N–N bond splitting of the azide at the α-position allowed the isolation of a rare example of a parent ketimide complex of zirconium. Isotopic labeling studies and solid-state X-ray analysis are presented for **2** and **3**, in addition to an independent synthesis for the former.

Diazomethane (N₂CH₂) is a highly reactive molecule with rich history owing to its ability to readily perform methylenation reactions, that is, CH₂-group transfer, to organic substrates.^[1] This small, but often explosive and toxic, molecule is generally prepared thermally and under basic conditions from reactive N-methyl-nitroso precursors that have a leaving group.^[2,3] Given our interest in metal-mediated group-transfer processes with metal–ligand multiple bonds, we questioned whether a high-energy molecule such as diazomethane could be alternatively prepared by a cross-metathesis reaction involving an early-transition-metal methylidene and an organic azide (N₃R). The M=CH₂ fragment is highly reactive and formation of the strong M=NR bond should provide an additional driving force. This unprecedented reaction would constitute a methylidene for nitrene cross-metathesis in which the N₂ unit of the azide acts as the delivery vehicle, and is not released in the process. Indeed, calculations using ³CH₂ with an organic azide N₃Ad (Ad = 1-adamantyl) reveal such a process to be exergonic

with a free energy of formation (ΔG_f^o) of –23 kcal mol^{–1} [Eq. (1)].^[4]



To test this hypothesis, we decided to explore the mononuclear zirconium methylidene complex (PNP)Zr=CH₂(OAr) (**1**) (PNP[–] = N[2-PⁱPr₂-4-methylphenyl]₂[–], Ar = 2,6-ⁱPr₂C₆H₃)^[3] with N₃Ad and report herein two divergent reactions that result from the formation of N₂CH₂ along with the imide (PNP)Zr=NAd(OAr) (**2**); the latter species could be prepared independently by oxidation of (PNP)Zr(η²-H₂CCH₂)(OAr) (**5**) with N₃Ad. In the formation of **2** from **1** and N₃Ad, another product, a parent ketimide (PNP)Zr(η²-N=NAd)(N=CH₂)(OAr) (**3**), also resulted from N–N splitting of the azide. Computational studies established that the products **2** and **3** share a common intermediate, the 1,3-addition product of **1** with N₃Ad, namely [(PNP)Zr(CH₂N₃Ad)(OAr)] (**A**), which can undergo retrocycloaddition: N–N bond splitting at the β-γ position or N–N bond splitting at the α-β position of the formal azide moiety.

Few stable examples of mononuclear group 4 methylidene complexes exist^[5,6] and when complex **1**^[5] is treated with N₃Ad in toluene at –35 °C over 15 minutes, the ³¹P NMR spectrum reveals two products (2:3 ratio)^[4] both possessing inequivalent phosphorus groups for the PNP supporting ligand. Combined, these species are formed in over 95% yield. Fortunately, these two species possess remarkably different solubility that allows for some separation in *n*-hexane. Accordingly, the zirconium imide complex **2** could be isolated in approximately 80% purity given its lower solubility in this hydrocarbon solvent. Complex **2** is remarkably stable and the ¹H NMR spectrum shows characteristic features for an adamantyl group in addition to the asymmetric PNP ligand. A solid-state structure of **2** (Figure 1, left) confirms the formation of the terminal and nearly linear imide moiety (Zr–N, 1.8476(19) Å, Zr=N–C, 175.30(17)°),^[7] and the Zr metal is confined to a nearly perfect square pyramidal geometry (τ₅ = 0.06).^[8]

When isolated, complex **2** was accompanied by traces of the other species when recrystallized; therefore, we sought a clean and alternative route to this zirconium imide moiety for unambiguous characterization. Using the dichloride precursor (PNP)ZrCl₂(OAr) (**4**) reported previously,^[9] an ethylene ligand was installed by a transmetallation and β- abstraction route with two equivalents of the ethyl Grignard (H₃CCH₂MgCl) in toluene/Et₂O at –35 °C over 1 hour (Scheme 1). As a result, the ethylene complex (PNP)Zr(η²-H₂CCH₂)(OAr) (**5**) was isolated in 95% yield concurrent with

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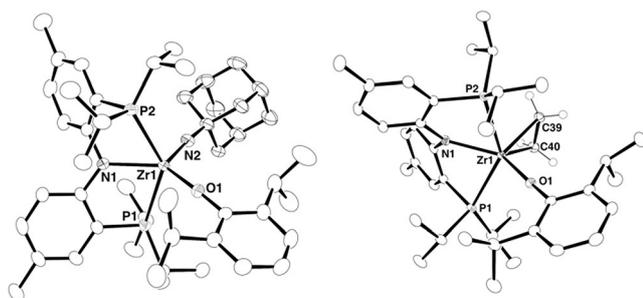
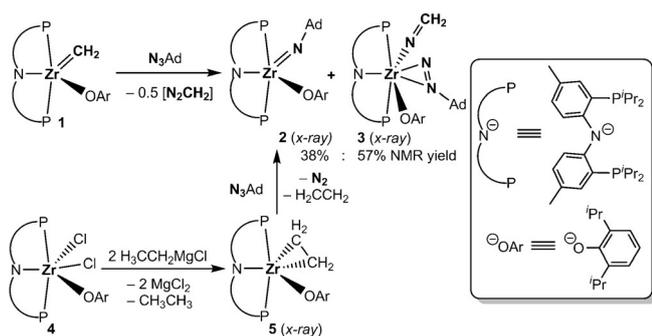


Figure 1. Molecular structures of complexes **2** (left) and **5** (right) showing thermal ellipsoids at the 50% probability level. Solvent (*n*-pentane) and hydrogen atoms with the exception of the ethylene hydrogen atoms on **5** have been omitted for clarity.



Scheme 1. Synthesis of complexes **2** and **3** from the reaction of **1** and N_3Ad and the independent synthesis of **2** from N_3Ad oxidation of **5**.

$MgCl_2$ precipitation and ethane elimination (Scheme 1). The most prominent feature for **5** in the 1H NMR spectrum is the bound ethylene resonances at 1.23 and 1.29 ppm correlated to ^{13}C NMR resonances at 43.4 and 41.0 ppm, respectively, via an HMQC experiment.^[4] Likewise, the ^{31}P NMR spectrum reveals the expected pair of doublets with $^2J_{PP}=37$ Hz. A solid-state structure of **5** also confirms the presence of the ethylene moiety, being oriented approximately along the P–Zr–P vector (Figure 1, right). Similar systems to **5** have been reported previously and cationic versions are often sought as models for olefin polymerization reactions.^[10–12]

Gratifyingly, complex **5** is a Zr^{II} synthon because treatment with N_3Ad in toluene resulted in rapid effervescence from ethylene and N_2 ejection, and workup of the reaction mixture allowed for an independent synthesis of complex **2**. More notably, this synthesis occurred in a clean manner and without the presence of the second species involving the reaction of N_3Ad with **1** (see above, Scheme 1). It should be noted that the addition of N_3Ad to **5** must be done slowly to avoid formation of a tetraazadiene complex $(PNP)Zr(NAdNNNAd)(OAr)$ resulting from cycloaddition of a second equivalent of N_3Ad to **2**.^[4,7g,13]

To isolate the second species formed from the reaction of **1** with N_3Ad , fractional crystallization of the filtrate collected after separation of **2** (see above) allowed us to identify this species as the parent ketimide complex $(PNP)Zr(\eta^2-N=NAd)(N=CH_2)(OAr)$ (**3**) on the basis of 1H , ^{13}C , and ^{31}P NMR spectroscopy as well as single-crystal X-ray diffraction analysis.^[4] The most salient spectroscopic feature of **3** is

the presence of a rare and parent ketimide ligand (1H NMR: 7.94 ppm, ^{13}C NMR: 146.3 ppm),^[4] which is comparable to that of the reported parent ketimide complex $(tBuArN)_3Mo(N=CH_2)$ ($Ar=3,5-(CH_3)_2C_6H_3$) by Cummins and co-workers.^[14] To further characterize **3**, we prepared the ^{13}C -enriched isotopologue $(PNP)Zr(\eta^2-N=NAd)(N=^{13}CH_2)(OAr)$ (**3- ^{13}C**) from $(PNP)Zr=^{13}CH_2(OAr)$ (**1- ^{13}C**).^[4] Accordingly, the 1H NMR spectral resonance of the parent ketimide ligand in **3- ^{13}C** resolves into a doublet ($^1J_{CH}=167$ Hz), indicating that the methylene moiety in $[N=CH_2]^-$ is delivered from the zirconium methylene. A solid-state structure confirms the binding mode of the Zr– $N=CH_2$ (κ^1) ligand along with the presence of a side-on diazoadamantyl group (Zr– N_{α} : 2.228(3) Å; Zr– N_{β} : 2.104(2) Å). The grip of the pincer ligand is still enforced, which is corroborated by the ^{31}P NMR spectrum (13.0 and 19.2 ppm, $^2J_{PP}=78$ Hz), and as a result, the Zr center in **3** is overall seven coordinate as depicted in Figure 2.

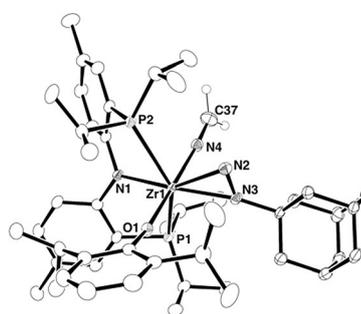
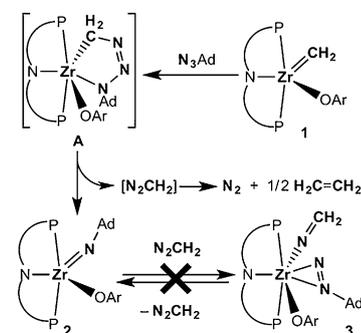


Figure 2. Molecular structure of complex **3** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms with the exception of those of the parent ketimide have been omitted for clarity.

The formation of **2** from **1** and N_3Ad implies that a CH_2 for NAd metathesis has taken place in which the side product should conceivably be N_2CH_2 . Monitoring the formation of **2** and **3** from **1** and N_3Ad in C_6D_6 intermittently by 1H NMR spectroscopy reveals only formation of $H_2C=CH_2$ (Scheme 2), as well as $H_2^{13}C=^{13}CH_2$ when using **1- ^{13}C** .^[4] Attempts to trap elusive N_2CH_2 have been unsuccessful given the reactivity of **1** or N_3Ad with phosphines or low-coordinate metal centers, which both react with N_2CH_2 . Complex **1** could in principle react with N_2CH_2 to form $H_2C=CH_2$, therefore, we explored



Scheme 2. Attempted reactions of **2** with N_2CR_2 ($CR_2=CPh_2$ or $CHSiMe_3$) to form **3** and proposed pathway leading to **2** and ethylene.

the reactivity of **1** with various diazo reagents. It was found, however, that the reaction of **1** with diazoalkane reagents N_2CR_2 ($CR_2 = CPh_2$, $CHSiMe_3$) does not result in any formation of the corresponding olefin ($H_2C=CR_2$).^[4] The almost quantitative formation of **2** and **3** from **1** and N_3Ad also suggests that this pathway does not likely occur. Regardless, the bimolecular conversion of N_2CH_2 to ethylene and N_2 (under more forcing conditions), albeit rare, has been documented and we propose that such a transformation is likely being facilitated by the metal complexes herein.^[15]

Although the formation of **2** and N_2CH_2 from **1** and N_3Ad seems intuitive based on a cross-metathesis reaction, the production of **3** is not because a $N=N$ bond is broken and a $C=N$ bond is formed. In a recent study, Zi and co-workers reported an unprecedented reaction involving a thorium imide with 9-diazo fluorene to yield a ketimide and diazoaryl species.^[16] N_2CH_2 is very likely formed in our reaction mixture, therefore, we questioned whether this substrate would further react with **2** to yield **3**. However, multiple attempts involving **2** with various diazoalkane reagents resulted in no reaction, thus raising the question of how complex **3** is formed. Likewise, thermolysis of **3** did not result in formation of **2** (Scheme 2).

Density functional theory (DFT) calculations were performed to shed light on the mechanism of how the two different products are formed. The most likely pathways are illustrated in Figure 3 and other plausible pathways that were considered and rejected are summarized in the Supporting Information.^[4] We first examined the reaction of **1** with N_3Ad that yielded **2** with diazomethane. In such a process, the first step involves a [2+3] cycloaddition of azide across the

$Zr=CH_2$ bond to form the five-membered intermediate complex **A**, traversing the transition state **1-TS** with a barrier of $18.2 \text{ kcal mol}^{-1}$. Next, diazomethane is extruded from intermediate **A** to give the final imido product **2** with an overall driving force of $-39.5 \text{ kcal mol}^{-1}$. The calculated free-energy profile suggests that intermediate **A** has a short lifetime for this step, because the formation of **2** from **A** is associated with a low-energy transition state **A-TS** of only $17.2 \text{ kcal mol}^{-1}$. Therefore, it is not surprising that intermediate **A** cannot be detected in the reaction conditions that lead to **2**.

Interestingly, the formation of product **3**, a species isolated as one of two products from the reaction of **1** with N_3Ad , involves a more complicated reaction mechanism consisting of a four-membered metallatriazacyclo intermediate **B** originating from the common intermediate **A**. Conversion of **A** into **B** via a transition state **A'-TS**, however, must traverse through a slightly higher barrier of $19.4 \text{ kcal mol}^{-1}$ by breaking the $Zr-C$ bond but without breaking the $N_\beta-N_\gamma$ bond. Intermediate **B** is thermodynamically favored by $8.2 \text{ kcal mol}^{-1}$ from intermediate **A**. Figure 3 shows how **B** finally converts into the diazenido product complex via the metallatriazanido cyclobutene transition state **B-TS** with a barrier of only $12.3 \text{ kcal mol}^{-1}$. Therefore, the reaction profile shown in Figure 3 is consistent with the formation of **2** always being accompanied by the formation of **3** given their similar transition states originating from the common intermediate **A** ($\Delta\Delta G^\ddagger \approx 2.3 \text{ kcal mol}^{-1}$). Also, we have considered independent reactions involving the conversion of **3** from **2** and diazomethane and found these to possess prohibitively high activation barriers.^[4]

In conclusion, we have demonstrated how a CH_2 group can be transferred from a Zr center to the N_2 unit of an organic azide, N_3Ad , to transiently generate a reactive molecule such as N_2CH_2 . Formation of **2** and **3** very likely share a common intermediate, **A**. In a divergent pathway, N_3Ad can also serve as an N-atom source to the methyldiene to form both $\bar{N}=CH_2$ and $\bar{N}=NAd$ units. These transformations greatly contrast earlier reports involving alkylidene reactivity of $(nacnac)Ti=CH^tBu(OTf)$ ($nacnac^- = [ArNC(CH_3)_2CH^-]$) with N_2CPh_2 and N_3Ad .^[17]

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Conflict of interest

The authors declare no conflict of interest.

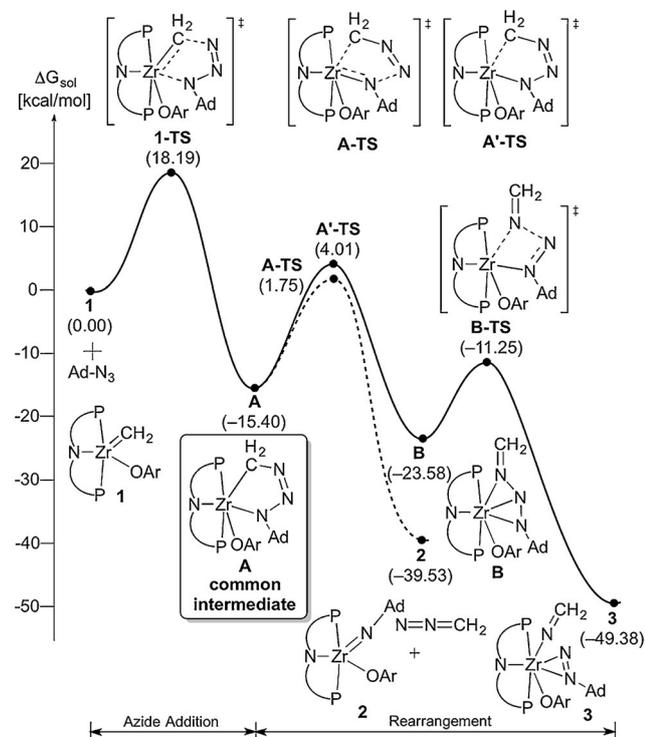


Figure 3. The free-energy profile for the independent formation of **2** and **3** from the reaction of **1** and N_3Ad .

Keywords: azides · diazomethane · imides · methyldiene · zirconium

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