UvA-DARE (Digital Academic Repository)

C-H Activation of Benzene by a Photoactivated NiII(azide): Formation of a Transient Nickel Nitrido Complex

Vreeken, V.; Siegler, M.A.; de Bruin, B.; Reek, J.N.H.; Lutz, M.; van der Vlugt, J.I.

DOI

[10.1002/anie.201501437](https://doi.org/10.1002/anie.201501437)
[10.1002/ange.201501437](https://doi.org/10.1002/ange.201501437)

Publication date

2015

Document Version

Final published version

Published in

Angewandte Chemie, International Edition

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Vreeken, V., Siegler, M. A., de Bruin, B., Reek, J. N. H., Lutz, M., & van der Vlugt, J. I. (2015). C-H Activation of Benzene by a Photoactivated Ni^{II}(azide): Formation of a Transient Nickel Nitrido Complex. *Angewandte Chemie, International Edition*, 54(24), 7055-7059. <https://doi.org/10.1002/anie.201501437>, <https://doi.org/10.1002/ange.201501437>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

C–H Activation of Benzene by a Photoactivated Ni^{II}(azide): Formation of a Transient Nickel Nitrido Complex**

Vincent Vreeken, Maxime A. Siegler, Bas de Bruin, Joost N. H. Reek, Martin Lutz, and Jarl Ivar van der Vlugt*

In memory of Greg Hillhouse

Abstract: Photochemical activation of nickel-azido complex **2** [Ni(N₃)(PNP)] (PNP = 2,2'-di(isopropylphosphino)-4,4'-ditolylamine) in neat benzene produces diamagnetic complex **3** [Ni(Ph)(PN^PN^H)], which is crystallographically characterized. DFT calculations support photoinitiated N₂-loss of the azido complex to generate a rare, transient Ni^{IV} nitrido species, which bears significant nitridyl radical character. Subsequent trapping of this nitrido through insertion into the Ni–P bond generates a coordinatively unsaturated Ni^{II} imidophosphorane P=N donor. This species shows unprecedented reactivity toward 1,2-addition of a C–H bond of benzene to form **3**. The structurally characterized chlorido complex **4** [Ni(Cl)(PN^PN^H)] is generated by reaction of **3** with HCl or by direct photolysis of **2** in chlorobenzene. This is the first report of aromatic C–H bond activation by a trapped transient nitrido species of a late transition metal.

Transition metal complexes with terminal multiple bonds to main-group elements (e.g. C, O, N) play critical roles in various chemical and biological processes, including but not limited to nitrogen fixation, water splitting, and metathesis.^[1] However, ligands based on multiple-bonded heteroatoms (e.g. imido or nitrido) typically exhibit strong π -donor character. For stable multiple bonding to occur between a transition metal and a strong π -donor main-group element, one or more empty metal d-orbitals of suitable symmetry and

matching energy levels should be available on the metal center to accommodate the additional π -electron density.^[2] Hence, complexes with Group 9–11 metals featuring multiple-bonded E-fragments are either rare or elusive, a situation sometimes referred to as “the oxo-wall dilemma”.^[3] Notwithstanding the challenges associated with the preparation of these species, their potential application in for example, C–N bond formation^[4] or as intermediates in alternative routes for N₂ fixation warrant continued investigation, even when using “abiological” non-Group 8 metals.

Metal azides offer access to the interesting chemistry of nitrido complexes, as thermal, photolytic, or oxidative activation may result in the expulsion of N₂. Progress in the generation of Group 9 nitrides and open-shell nitridyl radical analogues demonstrate the feasibility of this approach.^[5] However, these studies are dominated by the use of the second- and third-row transition metals. Only very recently the first low-temperature characterization of a cobalt nitrido intermediate was reported, which highlights the potential for late first-row transition metal nitrido chemistry.^[6]

Studies on the activation of terminal metal azides to generate M≡N species with Group 10 metals are very scarce, particularly for nickel^[7–9] and no bona fide (transient) nickel nitrido has been reported to date. Photo-, thermal, or redox-induced release of N₂ would convert the monoanionic azido ligand into a trivalent nitrido (N^{3–}) ligand, which raises the formal oxidation state of the metal platform by two (Figure 1). Hence, stabilization of such (transient) species could potentially benefit from electron-donating or redox-active ligands. Terminal nitrido ligands on Group 9 metals are often too reactive to be isolated, and “trapping” these sought-after transient species by insertion into ligand C–H^[10] or

[*] V. Vreeken, Prof. Dr. B. de Bruin, Prof. Dr. J. N. H. Reek, Dr. Ir. J. I. van der Vlugt
Homogeneous, Bioinspired & Supramolecular Catalysis
van't Hoff Institute for Molecular Sciences
University of Amsterdam
Science Park 904, 1098 XH Amsterdam (The Netherlands)
E-mail: j.i.vandervlugt@uva.nl

Dr. M. Lutz
Department of Chemistry, Utrecht University
Padualaan 8, 3584 CH Utrecht (The Netherlands)

Dr. M. A. Siegler
Department of Chemistry, Johns Hopkins University
3400 N Charles Street, Baltimore, MD 21218 (USA)

[**] Research funded by the European Research Council (ERC Starting Grant 279097 to J.I.v.d.V.). We thank Ed Zuidinga (MS), Jan-Meine Ernsting (¹⁵N NMR), Dr. Wojciech Dzik and Esther Schippers for experimental assistance and EU COST Network CARISMA CM1205 members for scientific discussions.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201501437>.

Figure 1. Strategies toward and reactivity with “trapped” transient nitrido species of Group 9 (previous work) and Group 10 metals (Ni, this work; arene C–H).

metal–ligand^[5,11] bonds is an attractive strategy. However, to the best of our knowledge, well-defined reactivity of a “trapped” nitrido species toward intermolecular arene C–H bond activation has not been reported to date.

As part of our ongoing program to utilize reactive ligands with (first-row) late transition metals for bond activation,^[12] we became interested in the preparation of nitrido species for nonligand C–H bond functionalization. Inspired by the recent examples with Group 9 metals,^[5,6] we set out to explore this chemistry with Group 10 congeners. Herein, we report on the photolytic activation of a Ni(N₃)(PNP) complex, which results in a transient nitrido species that is trapped as parent imidophosphorane by an intramolecular insertion reaction. This species facilitates unexpected follow-up aromatic C–H bond activation of benzene. DFT calculations on the mechanism and reactivity of the photolysis product are presented. The combined data provide insight into the chemical reactivity of a transient Ni-bound “nitrido” ligand.

Our starting point was the previously reported chlorido complex Ni(Cl)(PNP) (**1**; PNP = 2,2′-di(isopropylphosphino)-4,4′-ditolylamide).^[13] This species cleanly reacted through salt metathesis with excess NaN₃ in THF to generate azido complex Ni(N₃)(PNP) (**2**, Scheme 1) in high yield, as con-

Scheme 1. Synthesis and reactivity of complex **2**, (PNP)Ni(N₃), including reaction with CO to generate **A**, photolytic activation to species **3**, and subsequent reaction with HCl to product **4**.

firmed by multinuclear NMR (³¹P: singlet δ 36.3) and IR spectroscopy (ν 2051 cm^{−1}; ¹⁵N-labeled isotopomer: ν 2040 cm^{−1}). The compound absorbs strongly at λ 345 nm (ϵ = 32 000 L mol^{−1} cm^{−1}) and at λ 316 nm (ϵ = 24 000 L mol^{−1} cm^{−1}), as deduced from UV/Vis spectroscopy. Complex **2** exhibits local C₂-symmetry according to ¹H NMR spectroscopy. The X-ray structure of **2** was determined by X-ray diffraction on single crystals grown from toluene/pentane.

To establish the stability of species **2** and in particular the robustness of the azide group, we conducted a series of experiments. The azide complex exhibited fully reversible one-electron oxidation chemistry in cyclic voltammetry, with a $E_{1/2}$ of 0.03 V versus Fe⁰/Fe⁺ (in THF). Oxidation of precursor **1** has been shown by DFT calculations to occur predominantly at the nitrogen of the PNP backbone (ΔE = −0.10 V vs. **2**), making this a redox-active ligand.^[14] Chemical oxidation with AgBF₄ in acetone resulted in the blue cationic derivative [Ni(N₃)(PNP)]BF₄ (**2**⁺)BF₄, which contained an

intact azide fragment as deduced from IR spectroscopy. Surprisingly, the azide band of the oxidized species was found at the same wavenumber as for its neutral analogue (ν 2051 cm^{−1}). Species **2** also proved thermally stable up to 200 °C as a solid and no sign of decomposition was observed after five days in refluxing toluene. The azide fragment cleanly converted to the corresponding isocyanate under five bars of CO, as confirmed by NMR (³¹P: singlet δ 37.7) and IR spectroscopy (ν 2240 cm^{−1}) and by independent synthesis of the isocyanate species **A** [Ni(NCO)(PNP)] (Scheme 1; for details, see the Supporting Information, SI). This reaction occurred both in the absence and presence of light, implying the direct (intramolecular) attack of CO onto the azide with expulsion of N₂.^[15] Addition of PMe₃ or PPh₃ to a solution of **2** in THF did not result in any appreciable reactivity.

Interestingly, in contrast to the thermal and oxidative stability of species **2**, photolysis of a [D₆]benzene solution of **2** (10.4 mM) using a 500 W Hg/Xe lamp with a cut-off filter at 305 nm resulted in a clear color change from green to yellow and complete conversion of the azide complex, according to IR spectroscopy. Multinuclear NMR spectroscopy suggested the quantitative formation of one well-defined diamagnetic species. The ¹H NMR spectrum (Figure 2) showed complete preservation of all hydrogen atoms within the ligand scaffold,

Figure 2. ¹H NMR spectra before (top), after irradiation of **2** in C₆D₆ (middle), and after irradiation in C₆H₆ (bottom). The insert is showing an additional (−NH) doublet at 0.22 ppm for the irradiation in C₆H₆.

hence excluding ligand-based intramolecular C–H activation as a potential reaction pathway. Furthermore, complete loss of the C₂ symmetry is observed, with two signals for the −CH₃ groups of the ditolylamine backbone and eight non-equivalent −CH₃ signals from the PiPr₂ groups present. Notably, the ³¹P NMR spectrum contains two doublets at δ 45.9 and 48.5 with a small coupling constant J_{PP} of 6.4 Hz, excluding a direct *trans*-coordination of the P moieties. Irradiation of the corresponding ¹⁵N-labeled isotopomer of **2** resulted in two new doublets-of-doublets in the ³¹P NMR spectrum. Remarkably, both J_{PN} coupling constants are almost identical at 29.2 and 30.5 Hz, whereas the J_{PP} coupling is 6.5 Hz. This confirmed the presence of the azide N α -atom and suggested that the two P-atoms are chemically inequivalent, but both couple to the ¹⁵N nucleus. Further analysis of the species by cold-spray ionization (CSI) MS spectrometry revealed the presence of a perdeuterophenyl fragment in the generated complex.

Based on the latter observation, we decided to switch to C_6H_6 as the solvent for the photolysis reaction. In line with the MS data, this resulted in the appearance of additional aromatic signals in the 1H NMR spectrum and, markedly, also a doublet at δ 0.22, coupled to a ^{31}P nucleus (confirmed by selective ^{31}P decoupling of the 1H NMR spectrum). The ^{15}N -enriched material gave an additional splitting of the doublet with a large coupling constant (J_{NH} 73.2 Hz), which suggests a direct bond between a hydrogen of the activated benzene and a nitrogen originating from the decomposed azide group. The existence of an N–H fragment was additionally confirmed by the appearance of a weak N–H vibration (ν 3365 cm^{-1}) in the IR spectrum. Closer inspection of the IR spectrum of **3^D** (product from photolysis in C_6D_6) revealed the presence of an N–D vibration at ν 2493 cm^{-1} . In the corresponding ^{15}N HSQC NMR spectrum a triplet was observed at δ –365.

Yellow-colored single crystals, suitable for X-ray diffraction, were obtained by slow evaporation of a dichloromethane/cyclopentane mixture. The X-ray structure of square-planar Ni^{II} -complex **3** (Figure 3) confirms the formal insertion of an –NH fragment into the Ni_1 – P_1 bond, thus creating a parent iminophosphorane, with a P_1 – N_2 bond length of 1.5970(20) Å, which is typical for a P=N double bond.^[17] The angles $\angle N_1$ – Ni_1 – N_2 (93.98(8)° vs. (83.83(4)° for $\angle N_1$ – Ni_1 – P_1 in **2**) and $\angle N_2$ – Ni_1 – P_2 (177.48(7)° vs. 167.38(1)° for $\angle P_1$ – Ni_1 – P_2 in **2**) illustrate the expanded coordination sphere around Ni upon transformation of the PNP-donor into a 5,6'-chelating PN^2N^H donor in **3**. Furthermore, C–H bond activation of benzene has resulted in the introduction of a phenyl ligand, with hydrogen transfer to the nitrogen originating from the azide precursor.^[18] Variable temperature NMR studies suggest that the phenyl ligand exhibits hindered rotation at room temperature, causing the broadening of the *ortho*- and *meta*-H signals in the 1H NMR spectrum (Figure 2). Decreasing the temperature of a sample in $[D_8]toluene$ to –20°C gave rise to splitting of these broad signals into four well-defined peaks. Species **3** still displays well-behaved redox chemistry, as illustrated by cyclic voltammetry, with a reversible one-electron oxidation event occurring at $E_{1/2}$ –0.34 V, which is significantly more negative (ΔE –0.41 V) than that for azide **2**.

To gain more insight into the mechanism of the formation of complex **3**, DFT calculations were performed. For computational ease, a simplified model of complex **2** was used, with phenyl instead of tolyl rings for the backbone and Me-substituents at the phosphorus atoms. We investigated routes at different (excited-state) spin states, both at the hybrid b3-lyp level (Scheme 2) and the pure GGA BP86 DFT functional (Scheme S3, SI). Open-shell singlet

Figure 3. ORTEP plots (50% probability level) for **2** (left), **3** (middle), and **4** (right). Hydrogen atoms are omitted for clarity, except for hydrogen on N_2 and hydrogens on exogenous phenyl ring.^[16] Selected bond lengths [Å] and angles [°], for **2**: Ni_1 – P_1 2.1956(4); Ni_1 – N_1 1.8970(8); Ni_1 – P_2 2.1988(4); Ni_1 – N_2 1.9004(10); N_2 – N_3 1.1826(17); P_1 – Ni_1 – P_2 167.376(11); P_1 – Ni_1 – N_1 83.82(4); P_1 – Ni_1 – N_2 96.63(5); N_1 – Ni_1 – N_2 177.08(6); Ni_1 – N_2 – N_3 120.59(10); C_6 – N_1 – C_{12} 121.97(9). For **3**: Ni_1 – N_1 1.9770(17); Ni_1 – P_2 2.1259(6); Ni_1 – N_2 1.8923(18); Ni_1 – C_{27} 1.893(2); N_2 – P_1 1.597(2); P_2 – Ni_1 – N_2 177.48(7); N_1 – Ni_1 – N_2 93.98(8); N_1 – Ni_1 – P_2 85.92(5); N_1 – Ni_1 – C_{27} 177.74(8); Ni_1 – N_2 – P_1 123.39(11); C_6 – N_1 – C_{12} 117.99(17). For **4**: Ni_1 – N_1 1.930(3); Ni_1 – P_2 2.112(2); Ni_1 – N_2 1.893(3); Ni_1 – Cl_1 2.1951(11); N_2 – P_1 1.587(3); P_2 – Ni_1 – N_2 176.80(13); N_1 – Ni_1 – N_2 94.05(13); N_1 – Ni_1 – P_2 86.03(11); N_1 – Ni_1 – Cl_1 173.74(9); Ni_1 – N_2 – P_1 129.7(2); C_6 – N_1 – C_{12} 116.8(3).

(OSS) configurations for all investigated stationary points could only be located at the hybrid b3-lyp level. At the BP86 level only closed-shell singlet (CSS) configurations were found. As a starting point the activation of the azide was investigated. The release of N_2 proceeds via a high-energy transition state **TS1** on all calculated surfaces and is therefore considered as a nonthermal, photochemical step. The reaction pathway after N_2 loss from **2** can either follow photochemical or thermal steps or a combination thereof. The *meta*-stable “ Ni^{IV} -nitrido” intermediate **B** is most stable in its triplet configuration (**³B**), both at the BP86 and at the b3-lyp level.

Scheme 2. Proposed pathway for the formation of **3** upon irradiation of **2** in C_6H_6 based on DFT calculations (b3-lyp, def2-TZVP). Energies in $kcal\ mol^{-1}$ relative to CSS state of compound **A**.

Figure 4. Spin density plot of triplet intermediate **3B** (b3-lyp, def2-TZVP) and a schematic representation of the metal–nitrido π -bonding scheme.

The spin density predominantly resides on the N-atom (b3-lyp: 89 %, BP86: 81 %), resulting in significant nitridyl radical character (Figure 4), similar to previously reported systems.^[5b,d,f,6] The unusual electronic structure of **3B** is perhaps best described with contributions from the following resonance structures: $\text{Ni}^{\text{IV}}(\text{N}^{3-}) \leftrightarrow \text{Ni}^{\text{III}}(\text{N}^{2-}) \leftrightarrow \text{Ni}^{\text{II}}(\cdot\text{N}^-)$. The CSS and the OSS configurations of singlet **1B** collapse via a virtually barrierless transition state **TS2** to the coordinatively unsaturated $\text{Ni}^{\text{II}}(\text{PN}^{\text{P}}\text{N})$ intermediate **C**, featuring two anionic N-donor atoms (i.e. the PNP-nitrogen and the “nitrido” nitrogen). In fact, the barrier from **1B** to **1C** at the closed-shell singlet BP86 configuration is so low that **1B** converges spontaneously to **1C**. Conversion of **3B** to **3C** on the triplet surface also has quite a low barrier (both at the BP86 and the b3-lyp level) and thus might well proceed thermally (although photoexcitation to the singlet surface cannot be excluded).

The relative spin-state energies of intermediate **C** at the CSS, OSS, and triplet surface are quite similar. While the triplet configuration of **C** is most stable at the b3-lyp level, the CSS configuration of **C** is most stable at the BP86 level. The reaction from **C** via **TS3** to **D** may follow a thermal or photochemical pathway. Thermal conversion at the triplet surface has a prohibitively high barrier at room temperature, but spin cross-over from the triplet to the CSS surface might facilitate the overall process. A pathway involving H-atom abstraction from benzene followed by a radical rebound reaction was found to be less likely, due to a higher energy barrier. At the CSS and OSS surfaces, direct thermal conversion from **1C** to **1D** is energetically possible at room temperature. The alternative scenarios of outer-sphere C–H activation prior to the N-insertion step, with formation of a five-coordinate $\text{Ni}(\text{PNP})(\text{NH})(\text{Ph})$ imido-species intermediate, were also investigated but found to be less favorable.

Based on these computational data, several attempts to trap the postulated intermediate **B** were undertaken. Photolysis of **2** in benzene in the presence of Me_3NO , 50 equiv PMe_3 , or in pure 1,4-cyclohexadiene did not generate $\text{Ni}(\text{NO})(\text{PNP})$, $\text{Ni}(\text{N}=\text{PMe}_3)(\text{PNP})$, or $\text{Ni}(\text{NH}_2)(\text{PNP})$, respectively, based on IR and NMR spectroscopic analysis. The use of H_2 as trapping agent did not lead to the parent Ni-amido species, but instead the known $\text{Ni}(\text{H})(\text{PNP})$ complex^[13] was observed. NH_3 was detected by ^{15}N NMR spectroscopy and spectrophotometric assay analysis (SI). Use of D_2 resulted in ND_3 . The NH_3 and the Ni-hydride may originate from reaction of H_2 with the transient nitrido, but other pathways for their formation cannot be excluded at this

point.^[19] Initial experiments to broaden the reactivity “scope” of the trapped nitrido species **C** were also performed. Photolysis of **2** in toluene led to four sets of doublets by in situ ^{31}P NMR spectroscopy, suggesting that $\text{C}_{\text{sp}^2}\text{--H}$ and $\text{C}_{\text{sp}^3}\text{--H}$ bond activation may be competitive processes. Photolysis of **2** in neat cyclohexane or heptane resulted in a myriad of unidentified species in the ^{31}P NMR spectrum. Photolysis in 1,3,5-trideutero benzene was thwarted by trace amounts of chlorobenzene (detected by MS), culminating in the presence of two doublets at δ 46.8 and 45.3 in the ^{31}P NMR spectrum, attributed to be the chlorido derivative of **3**, $\text{NiCl}(\text{PN}^{\text{P}}\text{N}^{\text{H}})$ (**4**).^[20] Complex **4** was also prepared independently by reaction of **3** with HCl (Scheme 1) and fully characterized by NMR spectroscopy, mass spectrometry, and X-ray crystallography (see Figure 3 for X-ray structure). The structural parameters for **4** are very similar to those observed for **3** (Figure 3). Deprotonation of **4** with lithium diisopropylamide (LDA) in the presence of benzene did not result in arene C–H activation. We are currently exploring the reactivity of **3** and **4**, both to understand the unique structural features of these species and to deduce whether the parent iminophosphorane $\text{P}=\text{NH}$ unit shows promising ligand reactivity.

In summary, we herein report the first example of a trapped transient nickel nitrido species, making use of a well-defined $\text{Ni}^{\text{II}}(\text{PNP})$ platform. Irradiation of the nickel-azido precursor generates a nickel nitrido, which has significant nitridyl radical character, that is efficiently trapped by insertion of the nitrogen into a Ni–P bond. This trapped intermediate undergoes follow-up intermolecular C–H bond activation of aromatic solvent, with the activated exogenous phenyl fragment incorporated in the final complex **3**, which bears a unique tridentate phosphino-amido-iminophosphorane $\text{PN}^{\text{P}}\text{N}^{\text{H}}$ ligand in the coordination sphere of Ni^{II} . DFT calculations support the intermediacy of a rare transient formal Ni^{IV} nitrido species and subsequent 1,2-addition of the C–H bond. Substitution of the Ph-ligand for Cl is facile, generating **4**, which is likely amenable to follow-up chemistry.

Keywords: azides · C–H activation · iminophosphoranes · nickel · nitridyl radical

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 7055–7059
Angew. Chem. **2015**, *127*, 7161–7165

- [1] a) K. M. Lancaster, M. Roemelt, P. Ettenhuber, Y. Hu, M. W. Ribbe, F. Neese, U. Bergmann, S. DeBeer, *Science* **2011**, *334*, 974–977; b) S. Friedle, E. Reisner, S. J. Lippard, *Chem. Soc. Rev.* **2010**, *39*, 2768–2779; c) C. Krebs, D. G. Fujimori, C. T. Walsh, J. M. Bollinger, *Acc. Chem. Res.* **2007**, *40*, 484–492.
- [2] J. F. Berry, *Comments Inorg. Chem.* **2009**, *30*, 28–66.
- [3] K. Ray, F. Heims, F. F. Pfaff, *Eur. J. Inorg. Chem.* **2013**, 3784–3807.
- [4] A. I. Olivos Suarez, V. Lyaskovskyy, J. N. H. Reek, J. I. van der Vlugt, B. de Bruin, *Angew. Chem. Int. Ed.* **2013**, *52*, 12510–12529; *Angew. Chem.* **2013**, *125*, 12740–12760.
- [5] a) J. Schöffel, A. Y. Rogachev, S. DeBeer George, P. Burger, *Angew. Chem. Int. Ed.* **2009**, *48*, 4734–4738; *Angew. Chem.* **2009**, *121*, 4828–4832; b) M. G. Scheibel, B. Askevold, F. W. Heinemann, E. J. Reijerse, B. de Bruin, S. Schneider, *Nat. Chem.* **2012**, *4*, 552–558; c) D. Sieh, P. Burger, *J. Am. Chem. Soc.* **2013**, *135*, 3971–3982; d) M. G. Scheibel, Y. Wu, A. C. Stückl, L.

- Krause, E. Carl, D. Stalke, B. de Bruin, S. Schneider, *J. Am. Chem. Soc.* **2013**, *135*, 17719–17722; e) F. Angersbach-Bludau, C. Schulz, J. Schöffel, P. Burger, *Chem. Commun.* **2014**, *50*, 8735–8738; f) Y. Gloaguen, C. Rebreyend, M. Lutz, P. Kumar, M. I. Huber, J. I. van der Vlugt, S. Schneider, B. de Bruin, *Angew. Chem. Int. Ed.* **2014**, *53*, 6814–6818; *Angew. Chem.* **2014**, *126*, 6932–6936.
- [6] a) E. V. Zolnhofer, M. Käß, M. M. Khusniyarov, F. W. Heinemann, L. Maron, M. van Gastel, E. Bill, K. Meyer, *J. Am. Chem. Soc.* **2014**, *136*, 15072–15078; See also: b) X. Hu, K. Meyer, *J. Am. Chem. Soc.* **2004**, *126*, 16322–16323.
- [7] Photolysis of a Ni(Cl)(PMe₃)₂(N₃) complex led to a trimetallic nickel cluster containing bridging imido and imidophosphorane ligands, via a postulated nitrene intermediate: H.-F. Klein, S. Haller, H. König, M. Dartiguenave, Y. Dartiguenave, M.-J. Menu, *J. Am. Chem. Soc.* **1991**, *113*, 4673–4675. Irradiation of Ni(“P₂”)(N₃)₂-type complexes resulted in the formation of Ni(N₃)₂ and Ni⁰(“P₄”) products, leading to the proposal of a hypovalent nitrene intermediate, based on scavenging reactions: H. Henning, K. Hofbauer, K. Handke, R. Stich, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 408–410; *Angew. Chem.* **1997**, *109*, 373–375.
- [8] Irradiation of a tetrahedral Ni^{II}(BP₃)(N₃) complex gave no reaction, whereas thermolysis led to a myriad of products. N-atom transfer using dbabh (dbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]-hepta-2,5-diene) was also not successful. See: C. E. MacBeth, J. C. Thomas, T. A. Betley, J. C. Peters, *Inorg. Chem.* **2004**, *43*, 4645–4662.
- [9] The groups of Hillhouse and Warren have described a number of nickel(organoimido)Ni=NR species from low-coordinate Ni precursors using organic azides as the N-atom source: a) C. A. Laskowski, G. L. Hillhouse, *Organometallics* **2009**, *28*, 6114–6120; b) N. D. Harrold, R. Waterman, G. L. Hillhouse, T. R. Cundari, *J. Am. Chem. Soc.* **2009**, *131*, 12872–12873; c) C. A. Laskowski, G. L. Hillhouse, *Chem. Sci.* **2010**, *1*, 321–325; d) V. M. Iluc, G. L. Hillhouse, *J. Am. Chem. Soc.* **2010**, *132*, 15148–15150; e) V. M. Iluc, A. J. M. Miller, J. S. Anderson, M. J. Monreal, M. P. Mehn, G. L. Hillhouse, *J. Am. Chem. Soc.* **2011**, *133*, 13055–13063; f) C. A. Laskowski, A. J. M. Miller, G. L. Hillhouse, T. R. Cundari, *J. Am. Chem. Soc.* **2011**, *133*, 771–773; g) E. Kogut, H. L. Wiencko, L. Zhang, D. E. Cordeau, T. H. Warren, *J. Am. Chem. Soc.* **2005**, *127*, 11248–11249.
- [10] Co: a) C. C. Hojilla Atienza, A. C. Bowman, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 16343–16345; b) L. Zhang, Y. Liu, L. Deng, *J. Am. Chem. Soc.* **2014**, *136*, 15525–15528; U: c) R. K. Thomson, T. Cantat, B. L. Scott, D. E. Morris, E. R. Batista, J. L. Kiplinger, *Nat. Chem.* **2010**, *2*, 723–729.
- [11] D. Adhikari, F. Basuli, H. Fan, J. C. Huffman, M. Pink, D. J. Mindiola, *Inorg. Chem.* **2008**, *47*, 4439–4441.
- [12] a) J. I. van der Vlugt, E. A. Pidko, D. Vogt, M. Lutz, A. L. Spek, *Inorg. Chem.* **2009**, *48*, 7513–7515; b) J. I. van der Vlugt, E. A. Pidko, M. Lutz, D. Vogt, A. L. Spek, *Dalton Trans.* **2009**, 1016–1023; c) J. I. van der Vlugt, E. A. Pidko, R. C. Bauer, Y. Gloaguen, M. K. Rong, M. Lutz, *Chem. Eur. J.* **2011**, *17*, 3850–3854; d) R. C. Bauer, Y. Gloaguen, M. Lutz, J. N. H. Reek, B. de Bruin, J. I. van der Vlugt, *Dalton Trans.* **2011**, *40*, 8822–8829; e) Y. Gloaguen, W. Jacobs, B. de Bruin, M. Lutz, J. I. van der Vlugt, *Inorg. Chem.* **2013**, *52*, 1682–1684; f) D. L. J. Broere, B. de Bruin, J. N. H. Reek, M. Lutz, J. I. van der Vlugt, *J. Am. Chem. Soc.* **2014**, *136*, 11574–11577; g) D. L. J. Broere, L. L. Metz, B. de Bruin, J. N. H. Reek, M. A. Siegler, J. I. van der Vlugt, *Angew. Chem. Int. Ed.* **2015**, *54*, 1516–1520; *Angew. Chem.* **2015**, *127*, 1536–1540; h) D. L. J. Broere, S. Demeshko, B. de Bruin, E. A. Pidko, J. N. H. Reek, M. A. Siegler, M. Lutz, J. I. van der Vlugt, *Chem. Eur. J.* **2015**, *21*, 5879–5886; i) L. S. Jongbloed, B. de Bruin, J. N. H. Reek, M. Lutz, J. I. van der Vlugt, *Chem. Eur. J.* **2015**, DOI: 10.1002/chem.201406463.
- [13] O. V. Ozerov, C. Guo, L. Fan, B. M. Foxman, *Organometallics* **2004**, *23*, 5573–5580.
- [14] D. Adhikari, S. Mossin, F. Basuli, J. C. Huffman, R. K. Szilagyi, K. Meyer, D. J. Mindiola, *J. Am. Chem. Soc.* **2008**, *130*, 3676–3682.
- [15] W. Beck, W. P. Fehlhammer, *Z. Anorg. Allg. Chem.* **2010**, *636*, 157–162.
- [16] CCDC 1043360 (**2**), 1043865 (**3**), and 1048448 (**4**) 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.
- [17] Review on iminophosphorane ligands: a) J. García-Álvarez, S. E. García-Garrido, V. Cadierno, *J. Organomet. Chem.* **2014**, *751*, 792–808. Relevant precedent for insertion of diphenyldiazomethane into Ni–P bond to generate a P=N bond: b) D. Adhikari, S. Mossin, F. Basuli, B. R. Dible, M. Chipara, H. Fan, J. C. Huffman, K. Meyer, D. J. Mindiola, *Inorg. Chem.* **2008**, *47*, 10479–10490.
- [18] Activation of C₆H₆ by a Ni(PNP)-hydride species has been reported, but AlMe₃ is required to promote this reaction: L.-C. Liang, P.-S. Chien, Y.-L. Huang, *J. Am. Chem. Soc.* **2006**, *128*, 15562–15563.
- [19] This includes potential pathways for photoactivated reaction of **2** with H₂ to generate Ni(H)(PNP) and HN₃. The latter can be decomposed to NH₃ under photolytic conditions: M. van Thiel, G. C. Pimentel, *J. Chem. Phys.* **1960**, *32*, 133–140.
- [20] Next to **4**, species **1** was also observed. Photolysis of **2** in neat chlorobenzene generated the same two compounds.

Received: February 13, 2015

Revised: March 27, 2015

Published online: April 29, 2015