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

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C–H Activation of Benzene by a Photoactivated NiIII(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 \([\text{Ni}(N_3)(PNP)]\) \((PNP = 2,2’-di(isopropylphosphino)-4,4’-ditylylamine)\) in neat benzene produces diamagnetic complex 3 \([\text{Ni}(Ph)(PNP)]\), which is crystallographically characterized. DFT calculations support photoinitiated \(N_3\)-loss of the azido complex to generate a rare, transient NiIII nitrido species, which bears significant nitridyl radical character. Subsequent trapping of this nitrido through insertion into the Ni–P bond generates a coordinatively unsaturated NiIII imidophosphorane P=N donor. This species shows unprecedented reactivity toward 1,2-addition of a C=C bond of benzene to form 3. The structurally characterized chlorido complex 4 \([\text{Ni}(Cl)-(PNP)]\) 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. 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. 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.” Notwithstanding the challenges associated with the preparation of these species, their potential application in for example, C–N bond formation or as intermediates in alternative routes for \(N_2\) fixation warrants 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 \(N_2\). Progress in the generation of Group 9 nitrides and open-shell nitridyl radical analogues demonstrate the feasibility of this approach. 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.

Studies on the activation of terminal metal azides to generate M≡N species with Group 10 metals are very scarce, particularly for nickel and no bona fide (transient) nickel nitrido has been reported to date. Photo-, thermal, or redox-induced release of \(N_2\) 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 or

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[*] 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, John Hopkins University
3400 N Charles Street, Baltimore, MD 21218 (USA)

[*] J. I. van der Vlugt
Supramolecular Catalysis
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

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* Corresponding author.

Figure 1. Strategies toward and reactivity with “trapped” transient nitrido species of Group 9 (previous work) and Group 10 metals (Ni, this work; aren C–H).
As part of our ongoing program to utilize reactive ligands with (first-row) late transition metals for bond activation, 
we became interested in the preparation of nitrido species for 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.
Based on the latter observation, we decided to switch to C₆H₆ 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 ³¹P nucleus (confirmed by selective ³¹P decoupling of the ¹H NMR spectrum). The ¹⁵N-enriched material gave an additional splitting of the doublet with a large coupling constant (J₉¹ 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. Close-up inspection of the IR spectrum of ³⁰ (product from photolysis in C₆D₆) revealed the presence of an N–D vibration at ν 2493 cm⁻¹. In the corresponding ¹⁵N 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 Ni²⁺-complex ³ (Figure 3) confirms the formal insertion of an -NH fragment into the Ni₃=P₃ bond, thus creating a parent iminophosphorane, with a P₁=N₁ bond length of 1.5970(20) Å, which is typical for a P=N double bond.¹⁷ The angles ∠N₁=N₂=N₃ (93.98(8)° vs. 83.83(4)° for ∠N₁=N₂=N₃ in ²) and ∠N₂=N₃=N₁ (177.48(7)° vs. 167.38(1)° for ∠P₂=N₁=P₃ in ²) illustrate the expanded coordination sphere around Ni upon transformation of the PNP-donor into a 5,6'-chelating PNP²⁺ 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.¹³ 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 [D₆]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 E₁/₂ = −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 (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 N₂ proceeds via a high-energy transition state T₃ on all calculated surfaces and is therefore considered as a nonthermal, photochemical step. The reaction pathway after N₂ loss from ² can either follow photochemical or thermal steps or a combination thereof. The meta-stable "N₃⁻-nitrilo" intermediate B is most stable in its triplet configuration (B'), both at the BP86 and at the b₃-lyp level.

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 N₂ and hydrogens on exogenous phenyl ring.¹⁴ Selected bond lengths [Å] and angles [°], for ²: Ni₁=P₁ 2.1956(4); Ni₁=N₁ 1.8970(8); Ni₂=P₂ 2.1908(4); Ni₁-N₂ 1.9004(10); N₁-N₂ 1.1826(17); P₁-N₁-P₂ 167.376(11); P₁-N₁-N₃ 83.82(4); P₁-N₂-N₃ 96.63(5); N₁-N₃=N₃ 177.08(6); N₁-N₂-N₃ 120.59(10); C₁-N₃-C₂ 121.97(9). For ³: Ni₁=P₁ 1.9770(17); Ni₁-P₂ 2.1259(6); Ni₁=N₃ 1.8923(18); Ni₂-C₃ 1.893(2); N₁–N₃ 1.597(2); P₂-N₁-N₃ 177.48(7); Ni₂-N₃-N₃ 93.98(8); N₁-N₁-P₂ 85.92(5); N₁=N₂-N₃ 177.74(8); N₂-N₃-P₂ 123.39(11); C₂-N₃-C₃ 117.99(17). For ⁴: Ni₁=N₁ 1.930(3); Ni₁–P₂ 2.112(2); Ni₁–N₃ 1.893(3); N₁–C₃ 2.1951(11); Ni₁–P₂ 1.587(3); P₂-N₁-N₃ 176.80(13); N₂-N₃-N₄ 94.05(13); N₁-N₁-P₂ 86.03(11); N₁-N₂-C₃ 173.74(9); Ni₁-N₂-P₂ 129.7(2); C₃-N₃-C₄ 116.8(3).

Scheme 2. Proposed pathway for the formation of ³ upon irradiation of ² in C₆H₆ based on DFT calculations (b₃-lyp, def2-TZVP). Energies in kcal mol⁻¹ relative to CSS state of compound A.
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.[3b,d,f,6] The relative electronic structure of ¹B is perhaps best described with contributions from the following resonance structures: \( \text{Ni}^{\text{III}}(\text{N}^3) \rightarrow \text{Ni}^{\text{II}}(\text{N}^2) \rightarrow \text{Ni}^{\text{II}}(\text{N}^1) \). The CSS and OSS configurations of singlet ¹B collapse via a virtually barrierless transition state TSS2 to the coordinatively unsaturated Ni^{II}(PNP=PNP) intermediate C, featuring two anionic N-donor atoms (i.e., the PNP-nitrogen and the “nitrido” nitrogen). In fact, the barrier from ¹B to C at the closed-shell singlet BP86 configuration is so low that ¹B converges spontaneously to C. Conversion of ¹B to C 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 TSS3 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 ³D is energetically possible at room temperature. The alternative scenarios of outer-sphere C–H activation prior to the N-insertion step, with the formation of a five-coordinate Ni(PNP)(NH)(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. Photoysis of 2 in benzene in the presence of Me$_2$NO, 50 equiv PMe$_3$, or in pure 1,4-cyclohexadiene did not generate Ni(NO)(PNP), Ni(N=PMe$_3$)(PNP), or Ni(NH$_2$)(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 Ni(H)(PNP) complex[10] was observed. NH$_3$ was detected by $^{15}$N NMR spectroscopy and spectrophotometric assay analysis (SI). Use of D$_2$ resulted in ND$_2$. 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. Photoysis of 2 in toluene led to four sets of doublets by in situ $^{31}$P NMR spectroscopy, suggesting that C$_n$H$_{2n-1}$ and C$_n$H$_{2n+1}$ bond activation may be competitive processes. Photoysis of 2 in neat cyclohexane or heptane resulted in a myriad of unidentified species in the $^{31}$P NMR spectrum. Photoysis in 1,3,5-trideuterobenzene was thwarted by trace amounts of chlorobenzene (detected by MS), culminating in the presence of two doublets at $\delta$ 46.8 and 45.3 in the $^{31}$P NMR spectrum, attributed to be the chlorido derivative of 3. NiCl(PNP=PNP) (4).

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 disopropiolamide (LDA) in the presence of benzene did not result in aren 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 P=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 Ni^{II}(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 PNP=NH ligand in the coordination sphere of Ni^{III}. DFT calculations support the intermediacy of a rare transient formal Ni^{III} 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

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[15] CCDC 1043360 (1), 1043865 (3), and 1044848 (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] Activation of C=H 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.

[18] This includes potential pathways for photoactivated reaction of 2 with H2 to generate Ni(H)(PNP) and HN2. The latter can be decomposed to NH2 under photolytic conditions: M. van Thiel, G. C. Pimentel, *J. Chem. Phys.* 1960, 32, 133–140.

[19] Next to 4, species 1 was also observed. Photolysis of 2 in neat chlorobenzene generated the same two compounds.