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

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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-bonding character. Stabilization of such 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 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. 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 M₂N 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 N₂ would convert the monoanionic azido C==N⁻⁻ into a trivalent nitrido (N³⁻) 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” such ligands after transient species by insertion into ligand C–H or...
metal–ligand\textsuperscript{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,\textsuperscript{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,\textsuperscript{5,6} we set out to explore this chemistry with Group 10 congeners. Herein, we report on the photolytic activation of a Ni(N\textsubscript{2})(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)-4,4,4-ditolylamide.\textsuperscript{13} This species cleanly reacted through salt metathesis with excess NaN\textsubscript{3} in THF to generate azido complex Ni(N\textsubscript{3})(PNP) (2, Scheme 1) in high yield, as confirmed by multinuclear NMR (\textsuperscript{\textit{13}P: singlet \(\delta \approx 36.3\)) and IR spectroscopy (\(\nu = 2051\) cm\(^{-1}\)). The compound absorbs strongly at \(\lambda = 345\) nm (\(\epsilon = 32000\) L mol\(^{-1}\) cm\(^{-1}\)) and at \(\lambda = 316\) nm (\(\epsilon = 24000\) L mol\(^{-1}\) cm\(^{-1}\)), as deduced from UV/Vis spectroscopy. Complex 2 exhibits local C\textsubscript{3v} symmetry according to \textsuperscript{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 \(E_{\text{oc}}\) of 0.03 V versus Fe\textsuperscript{3+/2+} (in THF). Oxidation of precursor 1 has been shown by DFT calculations to occur predominantly at the nitrogen of the PNP backbone (\(\Delta E = -0.10\) V vs. 2), making this a redox-active ligand.\textsuperscript{14} Chemical oxidation with AgBF\textsubscript{4} in acetone resulted in the blue cationic derivative [Ni(N\textsubscript{3})(PNP)]BF\textsubscript{4} (2') BF\textsubscript{4}, 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 (\(\nu = 2051\) 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 (\(\text{\textsuperscript{\textit{15}}}N\) : singlet \(\delta \approx 37.7\)) and IR spectroscopy (\(\nu = 2240\) 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 N\textsubscript{2}.\textsuperscript{15} Addition of PMe\textsubscript{3} or PPh\textsubscript{3} 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 [D\textsubscript{8}]-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 \textsuperscript{1H} NMR spectrum (Figure 2) showed complete preservation of all hydrogen atoms within the ligand scaffold, hence excluding ligand-based intramolecular C–H activation as a potential reaction pathway. Furthermore, complete loss of the C\textsubscript{2} symmetry is observed, with two signals for the -CH\textsubscript{3} groups of the ditolylamine backbone and eight non-equivalent -CH\textsubscript{3} signals from the PhPr\textsubscript{3} groups present. Notably, the \textsuperscript{31P} NMR spectrum contains two doublets at \(\delta \approx 45.9\) and 48.5 with a small coupling constant \(J_{PP} \approx 6.4\) Hz, excluding a direct trans-coordination of the P moieties. Irradiation of the corresponding \textsuperscript{15}N-labeled isotope of 2 resulted in two new doublets-of-doublets in the \textsuperscript{31P} NMR spectrum. Remarkably, both \(J_{PP}\) 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\textsubscript{2}-atom and suggested that the two P-atoms are chemically inequivalent, but both couple to the \textsuperscript{15}N 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 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 (Jₑ₋₋₀ 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 P₃ (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–P bond, thus creating a parent imino phosphorane, with a P–N bond length of 1.5970(20) Å, which is typical for a P=NP double bond.[17] The angles ∠Ni₂–Ni₃–Ni₄ (93.98(8)° vs. (83.83(4)° for ∠Ni₂–Ni₃–P₁, in 2) and ∠Ni₂–Ni₃–P₂ (177.48(7)° vs. 176.38(1)° for ∠P₁–Ni₄–P₁ in 2) illustrate the expanded coordination sphere around Ni upon transformation of the PNP-donor into a 5,6'-chelating PNP⁺⁺ 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 [D₈]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 TS₁ 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 “Ni²⁺-nitrido” intermediate B is most stable in its triplet configuration (³B), both at the BP86 and at the b3-lyp level.
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.[8a,9d,10] The unusual electronic structure of \( \mathbf{B} \) is perhaps best described with contributions from the following resonance structures: \( \text{Ni}^{\text{III}}(\text{N}^3) \rightarrow \text{Ni}^{\text{III}}(\text{N}^2) \rightarrow \text{Ni}^{\text{III}}(\text{N}^1) \). The CSS and the OSS configurations of singlet \( \mathbf{B} \) collapse via a virtually barrierless transition state \( \mathbf{TS2} \) to the coordinatively unsaturated \( \text{Ni}^{\text{III}}(\text{PNP}) \) intermediate \( \mathbf{C} \), featuring two anionic N-donor atoms (i.e. the PNP-nitrogen and the “nitrido” nitrogen). In fact, the barrier from \( \mathbf{B} \) to \( \mathbf{C} \) at the closed-shell singlet BP86 configuration is so low that \( \mathbf{B} \) converges spontaneously to \( \mathbf{C} \). Conversion of \( \mathbf{B} \) to \( \mathbf{C} \) on the triplet surface also has quite a low barrier (both at the BP86 level and the b3-lyp level) and thus might well proceed thermally (although photoexcitation to the singlet surface cannot be avoided). The spin density plot of triplet intermediate \( \mathbf{B} \) (b3-lyp, def2-TZVP) and a schematic representation of the metal–nitrido \( \pi \)-bonding scheme is shown in Figure 4.

Based on these computational data, several attempts to trap the postulated intermediate \( \mathbf{B} \) were undertaken. Photolysis of \( \mathbf{2} \) in benzene in the presence of \( \text{Me}_2\text{NO} \), 50 equiv \( \text{PMe}_3 \), or in pure 1,4-cyclohexadiene did not generate \( \text{Ni}^{\text{III}}(\text{PNP}) \), \( \text{Ni}(\text{N}=\text{PMe}_3)(\text{PNP}) \), or \( \text{Ni}(\text{NH}_2)(\text{PNP}) \), respectively, based on IR and NMR spectroscopic analysis. The use of \( \text{H}_2 \) as trapping agent did not lead to the parent Ni-amiido species, but instead the known \( \text{Ni}(\text{H})(\text{PNP}) \) complex[10] was observed. \( \text{NH}_3 \) was detected by \( ^{15}\text{N} \) NMR spectroscopy and spectrophotometric assay analysis (SC). Use of \( \text{D}_2 \) resulted in \( \text{ND}_3 \). The \( \text{NH}_3 \) and the Ni-hydride may originate from reaction of \( \text{H}_2 \) 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 \( \mathbf{C} \) were also performed. Photolysis of \( \mathbf{2} \) in toluene led to four sets of doublets by in situ $^3\text{P}$ NMR spectroscopy, suggesting that \( \text{C}_0=\text{H} \) and \( \text{C}_0=\text{H} \) bond activation may be competitive processes. Photolysis of \( \mathbf{2} \) in neat cyclohexane or heptane resulted in a myriad of unidentified species in the $^3\text{P}$ NMR spectrum. Photolysis 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 $^3\text{P}$ NMR spectrum, attributed to be the chlorido derivative of \( \mathbf{3} \), \( \text{NiCl}(\text{PNP}) \).[4] Complex \( \mathbf{4} \) was also prepared independently by reaction of \( \mathbf{3} \) with \( \text{HCl} \) (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 \( \mathbf{4} \) are very similar to those observed for \( \mathbf{3} \) (Figure 3). Deprotonation of \( \mathbf{4} \) with lithium disopropylamide (LDA) in the presence of benzene did not result in arcene $\pi$–$\pi$ activation. We are currently exploring the reactivity of \( \mathbf{3} \) and \( \mathbf{4} \), both to understand the unique structural features of these species and to deduce whether the parent iminophosphorane \( \text{P}^{\text{III}}\text{N} \) 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 \( \text{Ni}^{\text{III}}(\text{PNP}) \) 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 $\mathbf{3}$. We are also developing nitrido species, which bears a unique tridentate phosphino-amiido-iminophosphorane \( \text{PN}^{\text{III}} \) ligand in the coordination sphere of \( \text{Ni}^{\text{III}} \). DFT calculations support the intermediacy of a rare transient formal \( \text{Ni}^{\text{III}} \) nitrido species and subsequent 1,2-addition of the C–H bond. Substitution of the Ph-ligand for Cl is facile, generating \( \mathbf{4} \), which is likely amenable to follow-up chemistry.

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

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[8] Irradiation of a tetrahedral Ni\(^{(3)}\)(BP\(_3\))(N\(_3\)) complex gave no reaction, whereas thermolysis led to a myriad of products. N-atom transfer using dbhh (dbhh = 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, 4645–4646.


[16] CCDC 1043360 (2), 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.


[18] Activation of CH\(_2\) by a Ni(PNP)-hydride species has been reported, but AlMe\(_3\) 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 H\(_2\) to generate Ni(H)(PNP) and H\(_2\). The latter can be decomposed to NH\(_2\) under photolytic conditions: M. van Thiel, G. C. Pimentel, J. Chem. Phys. 1960, 32, 133–140.

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