Supporting Information

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

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SUPPORTING INFORMATION
1) General methods

All reactions were carried out under an atmosphere of argon or dinitrogen using standard Schlenk techniques. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. (PNP)Ni(Cl) (1) was synthesized according to literature procedures.\(^{51}\) Toluene, THF, pentane and diethyl ether were distilled from sodium benzophenone ketyl. CH\(_2\)Cl\(_2\) was distilled from CaH\(_2\). NMR spectra (\(^1\)H, \(^1\)H\{\(^{31}\)P\}, \(^{13}\)C\{\(^1\)H\}, \(^{31}\)P\{\(^1\)H\} and \(^{15}\)N (HSQC)) were measured on a Bruker DRX 500, Bruker AV 400, Bruker DRX 300 or on a Bruker AV 300 spectrometer at room temperature, unless noted otherwise. Infrared spectra were recorded on a Thermo Nicolet Nexus FT-IR spectrometer. High resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP Mass spectrometer using cold spray ionization (CSI) and electron spray ionization (ESI) and on a JEOL AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer using field desorption (FD). A Shimadzu UV 2700 spectrophotometer was used to record UV/vis spectra. Elemental analyses were carried out by Mikroanalytisches Laboratorium Kolbe. Cyclic voltammetry measurements were performed in THF containing N(n-Bu)\(_4\)PF\(_6\) (0.1 M) at room temperature under an argon atmosphere using a platinum disk working electrode, a platinum coil counter electrode and a silver coil reference electrode. All redox potentials are referenced to Fe/Fe\(^+\). For the irradiation experiments a 500 W Hg/Xe lamp (Hamamatsu Photonics L8288) with a 305 nm cut-off filter was used.
2) Synthesis of new compounds

Synthesis of Ni(N₃)(PNP) (complex 2):

To a solution of 1 (750 mg, 1.43 mmol) in THF (15 mL) was added NaN₃ (466 mg, 7.2 mmol). The dark-green mixture was stirred for 20 hours, resulting in a gradual fading of color from green to moss-green. Upon complete conversion, based on ³¹P NMR spectroscopy, the volatiles were removed in vacuo. The product was extracted with toluene and filtered over Celite. Evaporation of toluene yielded the desired complex as a green-brown powder (749 mg, 99%). Single crystals suitable for X-ray diffraction were grown from a toluene/pentane mixture at -20 °C.

¹H NMR (400 MHz, C₆D₆, ppm): δ 7.45 (dt, J = 8.6, 2.3 Hz, 2H), 6.86-6.82 (m, 2H), 6.69 (dd, J = 8.5, 2.0 Hz, 2H), 2.19-2.12 (m, 4H), 2.10 (s, 6H), 1.47 (q, J = 8.8, 7.2 Hz, 12H), 1.17 (q, J = 8.0, 7.2 Hz, 12H);

¹³C {¹H} NMR (101 MHz, C₆D₆, ppm): δ 162.2 (t, J = 13.0 Hz), 132.6 (s), 132.0 (s), 125.4 (t, J = 3.2 Hz), 119.4 (t, J = 19.5 Hz), 116.7 (t, J = 5.4 Hz), 23.4 (t, J = 11.4 Hz), 20.4 (s), 18.4 (t, J = 2.5 Hz), 17.7 (s).

³¹P {¹H} NMR (162 MHz, C₆D₆, ppm): 36.3.

FT-IR (CH₂Cl₂, cm⁻¹): ν 2051 (N₃, strong).

HR-MS (CSI) calcd for [M]⁺ C₂₆H₄₀N₄NiP₂ m/z: 528.20817; found: 528.21033.


Synthesis of ¹⁵N enriched (complex ¹⁵/¹⁴N-2):

¹⁵/¹⁴N-2 was synthesized by adding Na¹⁵N¹⁴N₂ (75 mg, 1.14 mmol) to a solution of 1 (150 mg, 0.29 mmol) in THF (10 mL). The mixture was stirred for 66 hours, during which the green color slightly faded. Completion of the reaction was confirmed by ³¹P NMR spectroscopy, then the volatiles were removed in vacuo. The resulting solid was extracted with toluene and filtered over Celite. Removal of solvent yielded the product as a green-brown solid, which was recrystallized from a toluene/pentane mixture at -20 °C.

FT-IR (CH₂Cl₂, cm⁻¹): ν 2040 cm⁻¹ (N₃, strong).
Figure S1. $^{31}$P$^1$H NMR spectrum of complex 2 (C₆D₆, 298 K, 162 MHz)

Figure S2. $^1$H NMR spectrum of complex 2 (C₆D₆, 298 K, 400 MHz)
Synthesis of [Ni(N3)(PNP)][BF4] (complex (2')BF4)

To a Schlenk charged with 2 (26.1 mg, 0.049 mmol) and AgBF4 (9.1 mg, 0.047 mmol) was added 2 mL acetone. The solution immediately colored intense blue and was stirred for 2 hours. The volatiles were then removed in vacuo. The residue was triturated with 2 × 1.5 mL toluene and 2 × 2 mL pentane. The desired complex was then dissolved in CH2Cl2 and filtered by cannula. Evaporation of the solvent resulted in a dark blue/purple solid (28 mg, 97%).

μeff: 2.047 μB (CDCl3, 25°C, Evans method)

HR-MS (FD) calcd for [M]+ C26H40N4NiP2 m/z: 528.20817; found: 528.20797.

FT-IR (CH2Cl2, cm⁻¹): ν 2051 (strong, N3 stretch)

Synthesis of Ni(Ph)(PNN) (complex 3):

A J-Young NMR tube was charged with 2 (3 mg, 5.2 μmol) dissolved in benzene (0.5 mL). The dark-green solution was irradiated for 30 minutes, during which the color of the solution changed to yellow. Removal of volatiles in vacuo resulted in a yellow solid that was used for analysis in NMR experiments. Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH2Cl2/cyclopentane mixture.
\(^1\)H NMR (400 MHz, \(\text{CD}_6\), ppm): \(\delta\) 7.92 (br. s, 2H), 7.68 (dd, \(J = 8.6, 5.0\) Hz, 1H), 7.26 (dd, \(J = 8.4, 4.2\) Hz, 1H), 7.16 (s, 2H), 7.02 (t, \(J = 7.2\) Hz, 1H), 6.96–6.91 (m, 2H), 6.84 (d, \(J = 8.6\) Hz, 1H), 6.69 (dd, \(J = 12.0, 2.1\) Hz, 1H), 2.28–2.20 (m, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.11–1.97 (m, 2H), 1.85–1.75 (m, 1H), 1.54 (dd, \(J = 17.1, 7.1\) Hz, 3H), 1.39 (dd, \(J = 16.9, 6.9\) Hz, 3H), 1.21 (dd, \(J = 16.4, 7.3\) Hz, 3H), 1.00 (dd, \(J = 16.6, 7.3\) Hz, 3H), 0.94 (dd, \(J = 10.8, 6.9\) Hz, 3H), 0.65 (dd, \(J = 14.4, 6.9\) Hz, 3H), 0.56 (dd, \(J = 14.6, 7.1\) Hz, 3H), 0.33 (dd, \(J = 13.7, 7.1\) Hz, 3H), 0.22 (d, \(J = 6.5\) Hz, 1H).

\(^{13}\)C\(^{\text{\scriptsize{[\text{\text{[H}}}]}\text{NMR (101 MHz, \([\text{CD}_6]\text{, ppm):} \quad \delta\) 164.4 (d, \(J = 22.0\) Hz), 158.1 (s), 156.6 (d, \(J = 44.7\) Hz), 139.3 (bs), 133.0 (d, \(J = 2.0\) Hz), 132.4 (d, \(J = 2.1\) Hz), 130.9 (d, \(J = 1.1\) Hz), 130.1 (d, \(J = 8.7\) Hz), 126.0 (bs), 124.5 (d, \(J = 5.4\) Hz), 123.7 (s), 123.6 (d, \(J = 4.7\) Hz), 122.2 (s), 120.9 (d, \(J = 36.3\) Hz), 118.4 (d, \(J = 10.0\) Hz), 115.3 (s), 114.3 (s), 27.9 (d, \(J = 58.5\) Hz), 22.2 (d, \(J = 19.2\) Hz), 21.4 (d, \(J = 33.2\) Hz), 21.3 (d, \(J = 53.5, 3.0\) Hz), 20.8 (s), 20.7 (s), 19.7 (d, \(J = 6.3\) Hz), 17.8 (d, \(J = 4.7\) Hz), 17.0 (d, \(J = 1.2\) Hz), 16.9 (d, \(J = 1.3\) Hz), 16.7 (d, \(J = 2.8\) Hz), 15.7 (d, \(J = 6.9\) Hz), 15.7 (d, \(J = 1.8\) Hz), 15.4 (d, \(J = 1.0\) Hz).

\(^{31}\)P\(^{\text{\scriptsize{[\text{\text{[H}}}]}\text{NMR (162 MHz, \([\text{CD}_6]\text{, \(\delta\) 48.5 (d, \(J = 6.4\) Hz), 45.9 (d, \(J = 6.4\) Hz).}}\)

FT-IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): \(\nu\) 3365 (weak, NH stretch).

HR-MS (CSI) calced for [M+H]\(^+\)\(\text{C}_2\text{H}_8\text{N}_2\text{NiP}_2\) \(m/z\): 579.25679; found: 579.25263.

El. Anal. Calc. for \(\text{C}_2\text{H}_8\text{N}_2\text{NiP}_2\): C 66.22; H 8.16; N 4.83. Found: C 66.31; H 7.99; N 4.92.

**Isotopic labelling experiments:**

Enriched \(^{15/14}\)N-3 was prepared by irradiation of a \(J\)-Young NMR tube charged with a solution of \(^{15/14}\)N-2 in benzene. Photolysis for 30 minutes using a 305 nm cut-off filter yielded the 50% \(^{15}\)N-enriched product \(^{15/14}\)N-3.

\(^{1}\)H NMR (500 MHz, \(\text{CD}_6\), ppm): \(\delta\) 7.91 (s, 2H), 7.66 (dd, \(J = 8.6, 5.0\) Hz, 1H), 7.24 (dd, \(J = 8.5, 4.2\) Hz, 1H), 7.16 (s, 2H), 7.01 (t, \(J = 7.2\) Hz, 1H), 6.93 (td, \(J = 7.6, 6.7, 2.1\) Hz, 2H), 6.84 (d, \(J = 8.5\) Hz, 1H), 6.70 (dd, \(J = 11.8, 2.2\) Hz, 1H), 2.32 – 2.19 (m, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.14 – 1.97 (m, 2H), 1.88 – 1.77 (m, 1H), 1.54 (dd, \(J = 17.2, 7.2\) Hz, 3H), 1.39 (dd, \(J = 16.9, 6.9\) Hz, 3H), 1.22 (dd, \(J = 16.4, 7.3\) Hz, 3H), 1.01 (dd, \(J = 16.6, 7.2\) Hz, 3H), 0.94 (dd, \(J = 10.8, 6.9\) Hz, 3H), 0.66 (dd, \(J = 14.4, 7.0\) Hz, 3H), 0.57 (dd, \(J = 14.6, 7.2\) Hz, 3H), 0.34 (dd, \(J = 13.7, 7.1\) Hz, 3H), 0.21 (d, \(J = 6.4\) Hz, 0.5H), 0.21 (dd, \(J = 73.2, 6.4\) Hz, 0.5H).

\(^{31}\)P\(^{\text{\scriptsize{[\text{\text{[H}}}]}\text{NMR (162 MHz, \([\text{CD}_6]\text{, \(\delta\) 48.5 (dd, \(J_{NP} = 30.5\) Hz, \(J_{pp} = 6.5\) Hz), 48.5 (d, \(J_{pp} = 6.5\) Hz), 45.8 (dd, \(J_{NP} = 29.2\) Hz, \(J_{pp} = 6.5\) Hz), 45.8 (d, \(J_{pp} = 6.5\) Hz).}}\)

\(^{15}\)N\(^{\text{\scriptsize{[\text{\text{[H}}}]}\text{NMR (50.7 MHz, \([\text{CD}_6]\text{, \(\delta\) -364.8 (t, \(J = 30.2\) Hz).}}\)

Deuterium-labelled \(^3\)H was prepared by dissolving 2 in \(\text{CD}_6\). A \(J\)-Young NMR tube was filled with the solution and irradiated using a 305 nm cut-off filter. After 30 minutes the color had changed from green to yellow and the deuterium-labelled product \(^3\)H had formed.

\(^{1}\)H NMR (400 MHz, \([\text{CD}_6]\), ppm): \(\delta\) 7.68 (dd, \(J = 8.7, 5.0\) Hz, 1H), 7.26 (dd, \(J = 8.4, 4.1\) Hz, 1H), 6.93 (td, \(J = 7.9, 7.0, 2.2\) Hz, 2H), 6.86 – 6.83 (m, 1H), 6.69 (dd, \(J = 11.9, 2.1\) Hz, 1H), 2.28 – 2.20 (m,
1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.13-1.95 (m, 2H), 1.86-1.73 (m, 1H), 1.54 (dd, $J = 17.2$, 7.2 Hz, 3H), 1.39 (dd, $J = 16.8$, 6.9 Hz, 3H), 1.21 (dd, $J = 16.3$, 7.3 Hz, 3H), 1.00 (dd, $J = 16.8$, 6.9 Hz, 3H), 0.94 (dd, $J = 10.8$, 6.9 Hz, 3H), 0.65 (dd, $J = 14.4$, 7.0 Hz, 3H), 0.56 (dd, $J = 14.6$, 7.1 Hz, 3H), 0.32 (dd, $J = 13.6$, 7.0 Hz, 3H).

FT-IR (CH$_2$Cl$_2$, cm$^{-1}$): $\nu$ 2493.

**Figure S4.** $^{31}$P($^1$H) NMR spectrum of complex 3 (C$_6$D$_6$, 298 K, 162 MHz)
Figure S5. $^1$H NMR spectrum of complex 3 ($C_6D_6$, 298 K, 400 MHz)

Figure S6. $^{13}$C($^1$H) NMR spectrum of complex 3 ($C_6D_6$, 298 K, 101 MHz), * = residual peak for THF
Figure S7. $^1$H NMR spectrum of complex $^{15/14}$N-3 (C₆D₆, 298 K, 500 MHz)

Figure S8. $^{15}$N{$^1$H} NMR spectrum of complex $^{15/14}$N-3 (C₆D₆, 298 K, 50.7 MHz)
Figure S9. $^1$H NMR spectrum of complex 3$^0$ (C$_6$D$_6$, 298 K, 400 MHz)

Figure S10. Stacked $^1$H NMR spectra of complex 3 at different temperatures from 203 K (bottom) to 273 K (top) (C$_7$D$_8$, 298 K, 500 MHz)
Synthesis of Ni(NCO)(PNP) (complex A)

Method A: A solution of 2 (3.0 mg, 5.7 µmol) in C₆D₆ (0.6 mL) was put in a J-Young NMR tube. The tube was pressurized with CO to 5 bar. It was then covered with aluminum foil. The reaction was complete after 18 hours, with a color change to bright-green. Method B: To a Schlenk charged with 1 (104 mg, 0.20 mmol) and KNCO (161.4 mg, 1.98 mmol) was added THF (10 mL). The mixture was stirred for 68 hours. The color changed to bright-green during this period and completion of the reaction was confirmed by ³¹P NMR spectroscopy. The volatiles were evaporated and the residue was extracted with toluene and filtered over Celite. Toluene was removed in vacuo, yielding a green crystalline solid (98.1 mg, 93%).

¹H NMR (400 MHz, C₆D₆, ppm): δ 7.43 (dt, J = 8.6, 2.2 Hz, 2H), 6.82 (q, J = 3.6 Hz, 2H), 6.68 (dd, J = 8.5, 2.1 Hz, 2H), 2.09 (s, 6H), 2.07 – 1.96 (m, 4H), 1.40 (q, J = 8.8, 7.6 Hz, 12H), 1.13 (q, J = 7.6, 7.2 Hz, 12H).

¹³C {¹H} NMR (100.6 MHz, CD₂Cl₂, ppm): δ 162.0 (t, J = 13.2 Hz), 132.3 (s), 132.1 (s), 125.9 (t, J = 3.3 Hz), 119.2 (t, J = 19.6 Hz), 116.5 (t, J = 5.6 Hz), 24.0 (t, J = 11.6 Hz), 20.3 (s), 18.5 (t, J = 2.1 Hz), 17.9 (s).

³¹P {¹H} NMR (162 MHz, C₆D₆, ppm): δ 37.7 (s).

FT-IR (CH₂Cl₂, cm⁻¹): ν 2240 (strong, NCO band).

HR MS (FD) calcd for [M]⁺ C₉H₄₀N₂NiOP₂ m/z: 528.19693; found: 528.19819.

Figure S11. ³¹P {¹H} NMR spectrum of complex A (C₆D₆, 298 K, 162 MHz)
Figure S12. $^1$H NMR spectrum of complex A (C$_6$D$_6$, 298 K, 400 MHz), * = residual peak for silicon grease.

Figure S13. $^{13}$C{$_^1$H} NMR spectrum of complex A (CD$_2$Cl$_2$, 298 K, 400 MHz), * = residual peak for silicon grease.
Synthesis of Ni(Cl)(PNN) (complex 4):

A solution of 3 (10 mg, 17.3 µmol) in 2 mL THF was prepared. A small excess of HCl (1M in Et₂O) was added and the mixture was stirred for 2.5 h. During this period the color of the solution changed from yellow to green. All volatiles were removed in vacuo. The resulting solid was redissolved in pentane and filtered via cannula. After evaporation of the solvent a green powder remained as product (6.2 mg, 67%).

¹H NMR (400 MHz, C₆D₆, ppm): δ 7.50 (dd, J = 8.8, 4.8 Hz, 1H), 6.97-6.90 (m, 2H), 6.81 (dd, J = 8.8, 0.8 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 12 Hz, 1H), 2.40 (septet, J = 7.2 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.07-1.95 (m, 1H), 1.86-1.71 (m, 2H), 1.74 (dd, J = 15.2, 7.2 Hz, 3H), 1.63-1.53 (m, 6H), 1.28 (dd, J = 16.0, 7.2 Hz, 3H), 1.07 (dd, J = 13.8, 7.2 Hz, 3H), 0.85-0.75 (m, 6H), 0.55 (dd, J = 15.2, 7.2 Hz, 3H), 0.35 (d, J = 4.5 Hz, 1H).

¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂, ppm): δ 165.0 (s), 164.7 (s), 156.7 (s), 132.9 (d, J = 2.3 Hz), 132.5 (d, J = 2.3 Hz), 130.9 (d, J = 1.0 Hz), 130.4 (d, J = 8.5 Hz), 126.7 (d, J = 12.3 Hz), 126.2 (d, J = 8.4 Hz), 125.8 (d, J = 5.9 Hz), 120.6 (d, J = 41.8 Hz), 119.5 (d, J = 11.0 Hz), 28.0 (d, J = 56.5 Hz), 25.2 (d, J = 20.3 Hz), 23.1 (d, J = 3.8 Hz), 22.8 (s), 22.1 (dd, J = 55.0, 3.2 Hz), 20.7 (s), 20.3 (s), 19.0 (d, J = 4.1 Hz), 18.4 (d, J = 1.8 Hz), 18.1 (s), 17.4 (d, J = 1.8 Hz), 16.9 (s), 16.8 (s), 15.7 (d, J = 1.0 Hz).

³¹P{¹H} NMR (162 MHz, C₆D₆, ppm): δ 46.8 (d, J = 8.1 Hz), 45.3 (d, J = 8.1 Hz).

HR MS (FD) calcd for [M]⁺ C₂₆H₄₁ClN₂NiP₂ m/z: 536.17807; found: 536.17904.
Figure S14. $^{31}$P{H} NMR spectrum of complex 4 (C$_6$D$_6$, 298 K, 162 MHz), * = residual peak of 1, † = unidentified byproduct

Figure S15. $^1$H NMR spectrum of complex 4 (C$_6$D$_6$, 298 K, 400 MHz)
Figure S16. $^{13}$C NMR spectrum of complex 4 (CD$_2$Cl$_2$, 298 K, 100 MHz), * = residual peaks for silicon and H grease
3) Irradiation experiments using other solvents

For a typical experiment, 3 mg (5.7 µmol) of 2 was dissolved in 0.6 mL of the chosen solvent. A J-Young NMR tube was charged with the solution. The solution in the NMR tube was irradiated until the starting material was completely converted, based on in-situ $^{31}$P NMR spectroscopy.

Irradiation of 2 in toluene

![NMR spectrum of irradiated toluene solution of 2](image)

Figure S17. $^{31}$P{${}^1$H} NMR spectrum of an irradiated toluene solution of 2 (toluene, 298 K, 162 MHz)
Figure S18. $^{31}P\{^1H\}$ NMR spectrum of an irradiated toluene solution of 2 (CD$_2$Cl$_2$, 298 K, 162 MHz), * = doublet for chlorinated complex (4), probably due to presence of traces HCl in CD$_2$Cl$_2$.

HR MS (CSI) calcd for [M]$^+$ C$_{26}$H$_{41}$ClN$_2$NiP$_2$ m/z: 592.26462; found: 592.26839.
**Irradiation of 2 in chlorobenzene:**

Irradiating a chlorobenzene solution of 2 for 1.5 hours resulted in 80% conversion and the formation of both NiCl(PNP) complex 1 (resulting from direct substitution of the N₃ group for a Cl ligand), and two sets of doublets, resulting from photolysis of 2. These are attributed to an intermediate of unknown composition (doublets at 48.6 and 46.8 ppm) and the final product of photolysis NiCl(PN₃N'H), complex 4 (doublets at 46.1 and 44.5 ppm) (Figure S19). After 4 hours of irradiation, complex 2 has been fully converted resulting in a mixture of only 1 and 4 (Figure S20). Analysis of the final reaction mixture by GC-MS shows traces of mono-chlorobiphenyl, indicating splitting of the Ph-Cl bond. This is most likely the source of chloride for the formation of the chlorido-complexes.

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**Figure S19.** $^{31}$P{¹H} NMR spectrum irradiated chlorobenzene solution of 2 (80% conversion of the starting complex 2) (chlorobenzene, 298 K, 162 MHz)
Figure S20. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum irradiated chlorobenzene solution of 2 (100% conversion of the starting complex 2) (chlorobenzene, 298 K, 162 MHz)
**Irradiation experiments of 2 with nitrido trapping agents**

Experiments were conducted in an attempt to trap the postulated nitrido intermediate B, by carrying out the photolysis of 2 in the following ways:

- In a *J-Young* NMR tube, 2 (4 mg) was dissolved in degassed 1,4-cyclohexadiene (0.5 mL) and irradiated in the usual manner. The reaction was monitored by *in-situ* $^{31}$P NMR spectroscopy. When full conversion of the starting material was reached, all volatiles were removed *in vacuo*. The solid residue was dissolved in C$_6$D$_6$ and $^{31}$P and $^1$H NMR spectra were measured. The spectra showed no trace of Ni(NH$_2$)(PNP).

- In a *J-Young* NMR tube, 2 (4 mg, 7.6 µmol) was dissolved in C$_6$H$_6$ and 50 eq. of PMe$_3$ (39 µL, 380 µmol) was added. The mixture was irradiated in the usual manner. The reaction was monitored by *in-situ* $^{31}$P NMR spectroscopy. When full conversion of the starting material was reached, all volatiles were removed *in vacuo*. The solid residue was dissolved in C$_6$D$_6$ and $^{31}$P and $^1$H NMR spectra were measured. The spectra showed no trace of Ni(N=PM$_3$)(PNP).

- In a *J-Young* NMR tube, $^{15}$N enriched $^{15/14}$N-2 was dissolved in C$_6$D$_6$ and put under 5 bar H$_2$ pressure. The mixture was irradiated in the usual manner and when completion of the reaction was reached, $^{31}$P, $^1$H and $^{15}$N NMR spectra were measured. The spectra showed no trace of Ni(NH$_2$)(PNP). Instead, the main product was the known Ni(H)(PNP) complex. The presence of NH$_3$ was confirmed by $^1$H NMR (δ -0.30, br s) and $^{15}$N HSQC-NMR (-385.1 ppm, t) spectroscopy. After NMR analysis the organic phase was washed with 1 mL of a 1M H$_2$SO$_4$ (aq) solution. The presence of NH$_3$ in the aqueous phase was confirmed by the indophenol method and by a fluorometric ammonia assay. To exclude the involvement of 3 in the formation of NH$_3$, 3 was irradiated in the presence of H$_2$, which did not lead to formation of Ni(H)(PNP). To establish the origin of the hydrogen atoms in the formed NH$_3$ and Ni(H)(PNP), $^{15}$N enriched $^{15/14}$N-2 was dissolved in C$_6$H$_6$, put under 5 bar D$_2$ pressure and irradiated. The corresponding $^2$D NMR spectrum showed formation of ND$_3$ and Ni(D)(PNP).

- In a *J-Young* NMR tube 2 (3.3 mg, 6.2 µmol) and 18.7 eq. BPh$_3$ (28 mg, 116 µmmol) were dissolved in C$_6$H$_6$. The mixture was irradiated in the usual manner. After full conversion of the starting material, the $^{31}$P NMR spectrum of the solution showed a mixture of products, but the desired trapping product Ni(N-BPh$_3$)(PNP) could not be identified.

- In a *J-Young* NMR tube 2 (3.5 mg, 6.6 µmol) was dissolved in C$_6$D$_6$ and the solution was saturated with Me$_3$NO. The mixture was irradiated in the usual manner. After full conversion of the starting complex the $^{31}$P NMR spectrum showed a mixture of products. The IR spectrum of the resulting mixture did not show an indicative Ni-NO stretch.
Figure S2. $^{31}$P($^1$H) NMR spectrum of an irradiated 1,4-cyclohexadiene solution of 2 (C$_6$D$_6$, 298 K, 162 MHz)
Figure S22. $^{31}$P-$^1$H NMR spectrum of an irradiated C$_6$H$_6$ solution of 2 with 50 eq. PMe$_3$, after removal of volatiles (C$_6$D$_6$, 298 K, 162 MHz)

Figure S23. $^{31}$P-$^1$H NMR spectrum of an irradiated C$_6$D$_6$ solution of $^{15}$N-enriched $^{15/14}$N-2 with 5 bar H$_2$ (C$_6$D$_6$, 298 K, 162 MHz)
**Figure S24.** $^1$H NMR spectrum of an irradiated C$_6$D$_6$ solution of $^{15}$N-enriched $^{15/14}$N-2 with 5 bar H$_2$ (C$_6$D$_6$, 298 K, 400 MHz)

![NMR spectrum](image1.png)

**Figure S25.** $^{15}$N (HSQC) NMR spectrum of an irradiated C$_6$D$_6$ solution of $^{15}$N-enriched $^{15/14}$N-2 with 5 bar H$_2$ (C$_6$D$_6$, 298 K, 30 MHz)

![NMR spectrum](image2.png)
Figure S26. $^2$D NMR spectrum of an irradiated \text{C}_6\text{H}_6 solution of $^{15}$N-enriched $^{15/14}$N-2 with 5 bar D$_2$ (\text{C}_6\text{H}_6, 298 K, 61 MHz)

Figure S27. $^{31}$P NMR spectrum of an irradiated \text{C}_6\text{H}_6 solution of 2 and BPh$_3$ (\text{C}_6\text{D}_6, 298 K, 162 MHz)
**Figure S28.** $^{31}$P NMR spectrum of an irradiated C$_6$D$_6$ solution of 2 and Me$_3$NO (C$_6$D$_6$, 298 K, 162 MHz)
4) Redox-chemistry of 2 and 3 – cyclic voltammetry

0.006 M substrate, 0.1 M TBAF, 5 mL THF, working electrode: Pt disk, counter electrode: Pt coil, reference electrode: Ag coil

**Figure S29.** Cyclic voltammogram of 2 in THF, scan rate 0.1 V/s

**Figure S30.** Cyclic voltammogram of 3 in THF, scan rate 0.1 V/s
5) UV-Vis spectroscopy of 2

Figure S31. UV-Vis spectrum of 2 (CH₂Cl₂, 5·10⁻⁵ M)
6) DFT calculations

Geometry optimizations were carried out with the Turbomole program package\textsuperscript{55} coupled to the PQS Baker optimizer\textsuperscript{56} via the BOpt package,\textsuperscript{57} both at the BP86\textsuperscript{58} and at the DFT/b3-lyp\textsuperscript{59} level. We used the def2-TZVP basis set.\textsuperscript{510} All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The nature of the transition states was confirmed by IRC calculations.

The geometries for the open-shell singlet (singlet biradical) minima and transition states were evaluated employing the broken-symmetry protocol. The ‘real’ energy $\varepsilon_\alpha$ of the (multi-determinant) open-shell singlet species was estimated from the $\varepsilon_\alpha$ energies of the optimized single-determinant broken symmetry solutions and the $\varepsilon_\xi$ energies from a separate unrestricted triplet ($m_s = 1$) calculations at the same geometries with the same functional and basis set, using the approximate spin correction formula proposed by Noodleman and Yamagushi:\textsuperscript{511}

$$
\varepsilon_s \approx \frac{S_1^2 \varepsilon_0 - S_0^2 \varepsilon_1}{S_1^2 - S_0^2}
$$

The optimized geometries of all species are supplied as separate files in .pdb and .xyz format.

To decrease the required computation time the methyl groups on the ditolylamine backbone of 2 were omitted and the $i$-propyl groups on the phosphine arms were replaced by methyl groups.

Mechanistic considerations:

The b3-lyp functional as well as the BP86 functional was used for the geometry optimizations. The b3-lyp functional was used to enable optimization of geometries in the open-shell singlet (OSS) state. Although the calculated reaction pathway was found to be similar in the calculated for either functional (loss of N$_2$, insertion of N into a Ni-P bond, concerted C-H activation of benzene) discrepancies were found in the relative stability of the spin states (CSS and triplet) of several geometries. As a result, clear statements on the most stable spin states of intermediate and transition state structures in the envisioned mechanism are not possible. Furthermore, the CSS state of intermediate B could only be isolated using the b3-lyp functional, attempts with the BP-86 functional resulted in direct insertion into the Ni-P bond. A short discussion on the proposed pathway calculated using each will be given (\textit{vide infra}).

Using the b3-lyp functional (Scheme S1): the starting azide complex A is most stable in its closed-shell singlet (CSS) state, as expected. Attempts to optimize an open-shell singlet (OSS) state resulted in convergence to the CSS state, while the triplet (T) state was found to be 12.3 kcal mol$^{-1}$ higher in energy. Through (photochemical induced) expulsion of N$_2$ in TS1 intermediate B is formed, which is most stable in its triplet state. Insertion of the N into the Ni-P bond through TS2 leads to the low-energy intermediate C. Energies of the different spin states of C are close to one another, the triplet state is slightly preferred. Two scenarios were considered for the activation of benzene: a concerted pathway via TS3 involving a spin cross-over from the triplet to the singlet surface (see Scheme S1) or a hydrogen atom abstraction on the triplet or open-shell singlet surface via TS3$^\text{*}$ (see Scheme S2).
The concerted mechanism is deemed more likely because of the lower energy barrier TS3 poses opposed to TS3*. As expected, the product species D was found to be most stable in the CSS state.

Using the BP86 functional (Scheme S3): starting complex A was found to be most stable in the CSS state. Expulsion of N₂ in TS1 is followed by a barrierless insertion of N into a Ni-P bond in the CSS state leading to intermediate C. In the triplet state, intermediate B involving a ‘Ni-nitride’ could be isolated. A subsequent insertion of this ‘nitride’ into the Ni-P bond then also leads to intermediate C. A concerted C-H activation of benzene over the Ni-N moiety through TS3 leads to final product D.

Scheme S1. DFT calculated free energy profile (ΔG°298K in kcal mol⁻¹) of the proposed pathway from the starting azide complex A to the product of the photolysis D (b3-lyp, def2-TZVP).
Scheme S2. DFT calculated free energy profile ($\Delta G_{298K}^0$ in kcal mol$^{-1}$) for the alternative activation step of benzene via a hydrogen atom abstraction pathway (b3-lyp, def2-TZVP).

Scheme S3. DFT calculated free energy profile ($\Delta G_{298K}^0$ in kcal mol$^{-1}$) of the proposed pathway from the starting azide complex A to the product of the photolysis D (BP86, def2-TZVP).
**Figure S32.** From left to right: closed-shell singlet (CSS) and triplet (T) optimized geometry for A (b3-lyp, def2-TZVP)

**Figure S33.** From left to right: closed-shell singlet (CSS), open-shell singlet (OSS) and triplet (T) optimized geometry for TS1 (b3-lyp, def2-TZVP)

**Figure S34.** From left to right: closed-shell singlet (CSS), open-shell singlet (OSS) and triplet (T) optimized geometry for B (b3-lyp, def2-TZVP)
**Figure S35.** From left to right: closed-shell singlet (CSS), open-shell singlet (OSS) and triplet (T) optimized geometry for **TS2** (b3-lyp, def2-TZVP)

**Figure S36.** From left to right: closed-shell singlet (CSS), open-shell singlet (OSS) and triplet (T) optimized geometry for **C** (b3-lyp, def2-TZVP)

**Figure S37.** From left to right: closed-shell singlet (CSS) and triplet (T) optimized geometry for **TS3** (b3-lyp, def2-TZVP)
**Figure S38.** From left to right: closed-shell singlet (CSS) and triplet (T) optimized geometry for D (b3-lyp, def2-TZVP)

**Figure S39.** From left to right: open-shell singlet (OSS) and triplet (T) optimized geometry for TS3* (b3-lyp, def2-TZVP)

**Figure S40.** Doublet (D) optimized geometry for E* (b3-lyp, def2-TZVP)
Table S1. Relative energies (kcal mol\(^{-1}\)) found for the optimized geometries (b3-lyp, def2-TZVP).

<table>
<thead>
<tr>
<th>Structure</th>
<th>ΔG</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (CSS)</td>
<td>0</td>
</tr>
<tr>
<td>A (T)</td>
<td>12.3</td>
</tr>
<tr>
<td>TS1 (CSS)</td>
<td>48.4</td>
</tr>
<tr>
<td>TS1 (OSS)</td>
<td>46.2</td>
</tr>
<tr>
<td>TS1 (T)</td>
<td>49.2</td>
</tr>
<tr>
<td>B (CSS)</td>
<td>28.7</td>
</tr>
<tr>
<td>B (OSS)</td>
<td>25.3</td>
</tr>
<tr>
<td>B (T)</td>
<td>9.7</td>
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<tr>
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<tr>
<td>TS2 (OSS)</td>
<td>28.1</td>
</tr>
<tr>
<td>TS2 (T)</td>
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<tr>
<td>C (CSS)</td>
<td>-20.8</td>
</tr>
<tr>
<td>C (OSS)</td>
<td>-22.7</td>
</tr>
<tr>
<td>C (T)</td>
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</tr>
<tr>
<td>TS3 (CSS)</td>
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</tr>
<tr>
<td>TS3 (T)</td>
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</tr>
<tr>
<td>D (CSS)</td>
<td>-36.1</td>
</tr>
<tr>
<td>D (T)</td>
<td>-20.3</td>
</tr>
<tr>
<td>TS3* (OSS)</td>
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</tr>
<tr>
<td>TS3* (T)</td>
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</tr>
<tr>
<td>E* (D)</td>
<td>0.1</td>
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</table>
Table S2. Relative energies (kcal mol$^{-1}$) found for the optimized geometries (BP86, def2-TVZP).

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (CSS)</td>
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<tr>
<td>A (T)</td>
<td>18.7</td>
</tr>
<tr>
<td>TS1 (CSS)</td>
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<td>TS1 (T)</td>
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<td>B (T)</td>
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</tr>
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<td>TS2 (T)</td>
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</tr>
<tr>
<td>C (CSS)</td>
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<tr>
<td>C (T)</td>
<td>-9.9</td>
</tr>
<tr>
<td>TS3 (CSS)</td>
<td>5.4</td>
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<tr>
<td>TS3 (T)</td>
<td>18.3</td>
</tr>
<tr>
<td>D (CSS)</td>
<td>-29.3</td>
</tr>
<tr>
<td>D (T)</td>
<td>-3.0</td>
</tr>
</tbody>
</table>

Figure S41. Spin density plot of the triplet geometry of B (b3-lyp, def2-TZVP), Ni: 0.14, N: 1.78

Figure S42. Schematic orbital representation for the triplet geometry of B
Figure S43. Spin density plots (from left to right: combined alpha and beta spin, alpha spin, beta spin) of the OSS geometry of B (b3-lyp, def2-TZVP), equal density of both alpha and beta set leading to a net density of zero on all atoms.

Figure S44. Schematic orbital representation for the open-shell singlet geometry of B.

Figure S45. Spin density plot of the triplet geometry of B (BP86, def2-TZVP), Ni: 0.29, N: 1.61.
Figure S46. Spin density plot of the doublet geometry of 2 (BP86, def2-TZVP)

Figure S47. Spin density plot of the doublet geometry of 3 (BP86, def2-TZVP)
7) Crystallographic information

2: C_{26}H_{40}N_4NiP_2 · C_7H_8, Fw = 621.40, black block, 0.51 x 0.35 x 0.21 mm³, monoclinic, Pn (no. 7), a = 11.3719(4), b = 10.0324(4), c = 14.3157(6) Å, β = 91.7827(11) °, V = 1632.45(11) Å³, Z = 2, D_x = 1.264 g/cm³, μ = 0.72 mm⁻¹. 30242 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of (sin θ/λ)_{max} = 0.71 Å⁻¹ at a temperature of 150(2) K. Intensities were integrated using the SAINT software.\(^{[S12]}\) Absorption correction and scaling based on multiple measured reflections was performed with SADABS\(^{[S13]}\) (0.70-0.75 correction range). 9601 Reflections were unique (R_{int} = 0.013), of which 9338 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using the program SHELXT.\(^{[S14]}\)

The crystal structure can be approximated in the higher symmetric space group P2/n (no. 13) with the metal complex on a twofold rotation axis and an inversion center in the crystal packing. The routine ADDSYM of the PLATON software\(^{[S15]}\) calculates an 82% fit for the
higher symmetry. Only the coordinated azide ligand and the non-coordinated toluene solvent molecule violate the higher symmetry, and force the structure to be in the lower symmetric space group Pn (no. 7). Refinement in space group Pn was done as an inversion twin, resulting in a twin fraction (Flack parameter \(^{S16}\)) of 0.496(5).

The SHELXL-97 software\(^{S17}\) was used for the least-squares refinement against \(F^2\) of all reflections. No correlation matrix element was larger than 0.5. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference-Fourier maps and refined with a riding model. 373 Parameters were refined with 2 restraints (floating origin restraints). R1/wR2 [I > 2σ(I)]: 0.0204 / 0.0554. R1/wR2 [all refl.]: 0.0215 / 0.0561. S = 1.054. Residual electron density between -0.22 and 0.37 e/Å\(^3\). Geometry calculations and checking for higher symmetry were performed with the PLATON program.\(^{S15}\)

CCDC 1043360 contains 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.
All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu Kα radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013S18 and was refined on $F^2$ with SHELXL-2013 (Sheldrick, 2013). Analytical numeric absorption corrections based on a multifaceted crystal model were applied. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times $U_{eq}$ of the attached C atoms. The H atom attached to N2 was found from difference Fourier map, and its coordinates and isotropic temperature factor were refined freely.

The structure is ordered. Prior to the final refinement, the occupancy factor of N2 was refined freely, and its value refines to 0.9983(99), which unambiguously shows that the
atom type for N2 has been correctly assigned. In the final refinement, one residual electron density peak of \( \text{ca.} \ 1.80 \ \text{e} \ \text{Å}^{-3} \) was found at 0.99 Å of Ni1, but has no chemical significance. A check for twinning was performed, but no applicable twin laws could be detected from Fobs/Fcalc analysis.

3: \( \text{C}_{32}\text{H}_{46}\text{N}_{2}\text{NiP}_{2}, \text{Fw} = 579.36, \) yellow-orange lath, 0.24 × 0.08 × 0.03 mm\(^3\), triclinic, \( P-1 \) (no. 2), \( a = 7.19620(17), b = 12.8613(3), c = 17.3310(3) \ \text{Å}, \ \alpha = 96.8179(17), \ \beta = 96.0094(17), \ \gamma = 105.721(2)^{\circ}, \ V = 1517.31(6) \ \text{Å}^{3}, \ Z = 2, \ D_{x} = 1.268 \ \text{g cm}^{-3}, \ \mu = 2.079 \ \text{mm}^{-1}, \ T_{\text{min}}-T_{\text{max}}: 0.706-0.941. \ 18773 \) Reflections were measured up to a resolution of (\( \sin \theta/\lambda \))\(_{\text{max}} = 0.62 \ \text{Å}^{-1}. \ 5948 \) Reflections were unique (\( R_{\text{int}} = 0.0503 \)), of which 5161 were observed [\( I > 2\sigma(I) \)]. 348 Parameters were refined. \( R1/wR2 \ [I > 2\sigma(I)]: 0.0432/0.1124. \ R1/wR2 \ [\text{all refl.}]: 0.0499/0.1169. S = 1.040. \) Residual electron density found between \(-0.48 \) and \( 1.80 \ \text{e} \ \text{Å}^{-3} \).
X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator ($\lambda = 0.71073$ Å). Diffraction data were collected at 150(2) K using a CMOS Photon 50 detector. Intensity data were integrated with Bruker APEX2 software.\textsuperscript{19} Absorption correction and scaling was performed with SADABS.\textsuperscript{11} The structures were solved using direct methods with SHELXL-13.\textsuperscript{18} Least-squares refinement was performed with SHELXL-2013\textsuperscript{18} against F2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Heteroatom bound hydrogen atoms were refined freely with an isotropic displacement parameter, all other hydrogen atoms were included at calculated positions using a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.\textsuperscript{15} Crystallographic data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
4: C_{26}H_{41}ClN_2NiP_2, Fw = 537.71, intense green diamond, 0.42 × 0.34 × 0.10 mm³, monoclinic, P2_1/c (no. 2), a = 16.9503(7), b = 10.1853(3), c = 15.9921(7) Å, β = 98.549(3)°, V = 2730.3(2) Å³, Z = 4, D_x = 1.308 g cm⁻³, μ = 0.942 mm⁻¹, T_{min}–T_{max}: 0.65–0.91. 26887 Reflections were measured up to a resolution of (sin θ/λ)_{max} = 0.75 Å⁻¹. 4803 Reflections were unique (R_{int} = 0.0503), of which 3576 were observed [I > 2σ(I)]. 336 Parameters were refined with 98 restraints. R1/wR2 [I > 2σ(I)]: 0.0446/0.0951. R1/wR2 [all refl.]: 0.0729/0.1089. S = 1.128. Residual electron density found between −0.50 and 0.63 e Å⁻³.
8) References


[S18] Bruker, APEX2 software, Madison, WI, USA, 2014.