**Supporting Information**

# pH-dependent reduction potentials and proton-coupled electron transfer mechanisms in hydrogen-producing nickel molecular electrocatalysts

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# Table of Contents

## COMPUTATIONAL METHODS

**Reaction free energies for ET and PT.** A number of issues arise when calculating free energies of molecules optimized in dielectric continuum solvent. Standard electronic structure programs use gas-phase partition functions when evaluating the contributions to the free energy from the translational, rotational, and vibrational degrees of freedom. The vibrational contributions to the free energy are often orders of magnitude larger than the translational and rotational contributions. As the stationary points were obtained in solution, the frequency analyses must also be performed in solution. This treatment of the vibrational contributions to the free energy has been shown to be reliable.[1] The gas-phase translational contributions to the partition function become the solution-phase liberation free energy and therefore should be included.[1,2] The transformation of gas-phase free rotations into solution-phase hindered rotations (i.e., librations), however, can present serious problems.[1,3] As discussed in the literature, inclusion or exclusion of one or more of these terms can lead to significant errors. For cases where the number and type of molecules do not change in the reaction, such as in calculating reduction potentials by using isodesmic reactions or in calculating PT reaction free energies ($\Delta G^0_{\mathrm{PT}}$), these errors should approximately cancel. For other cases, such as in calculating association reaction free energies ($\Delta G^0_{\mathrm{assoc}}$) or activation free energies, these errors could be on the order of several kcal/mol.[1] In the present work, the translational, rotational, and vibrational contributions were included for the calculation of all free energy differences except $\Delta G^0_{\mathrm{assoc}}$, for which only the rotational contributions were excluded as recommended by Truhlar and coworkers.[1]

As was mentioned in the main text, we calculated the free energies of association, $\Delta G^0_{\mathrm{assoc}}$, before and after reduction for the *endo* isomer. The results are reported in Table 2 of the main text as well as in Tables S2 and S3. For cases where the free energies of association are positive, $(\Delta G^0_{\mathrm{assoc}} > 0)$, the effect of bringing two positively charged species in close proximity to one another is

thermodynamically unfavorable. However, when both the translational and rotational contributions are excluded, some of the association reaction free energies are negative ($\Delta G^0_{\text{assoc}} < 0$). In these cases, association of the acid is thermodynamically favorable. Regardless of the sign of $\Delta G^0_{\text{assoc}}$, the acid association is more favorable for stronger acids and after reduction.

**Thermodynamic scheme.** In Figures 3 and S1, we present the completed thermodynamic scheme for the (Ph,Bn) catalyst. All of the values are free energies in MeCN and are derived from experimental and calculated thermodynamic data. The thermodynamic schemes represent different states in which the (Ph,Bn) complex may exist, most of which have been observed experimentally.[4,5] The species in gray have not been directly observed, and their relative stabilities are therefore determined from the calculations presented herein. Within these schemes, vertical transitions represent changes in the number of hydrogen atoms (expressed as solution bond dissociation free energies associated with hydrogen atom transfer, as depicted by blue arrows in Figures 3 and S1), horizontal transitions represent changes in charge (black arrows), and diagonal transitions represent combinations of both vertical and horizontal transitions. These diagonal transitions can be either p$K_a$ values ($H\cdot - e^-$, associated with proton transfer, as depicted by red arrows) or free energies for $H^-$ cleavage ($H\cdot + e^-$, associated with hydride transfer, as depicted by green arrows). Note that the charge and number of hydrogen atoms specifies only composition, not structure (i.e., notation does not distinguish between protonated pendent amine or Ni-hydride). As discussed in the text of the main paper, completion of these schemes utilizes reaction free energies related to hydrogen in MeCN, such as $H^+ + e^- \rightarrow H\cdot$ and/or $H^- \rightarrow H\cdot + e^-$. A table of these reaction free energies is provided in Table S8.

**Calculated Pourbaix diagram.** The calculated Pourbaix diagrams[6] are representations of the relative free energies of the nine species shown in Figures 3 and S1. The relative free energies depend on the pH and potential ($E^0$), as well as the six p$K_a$'s of the protonated species and the $Ni^{II/I}$ and $Ni^{I/0}$ reduction potentials of the unprotonated species. Eq (S1) provides the expressions for the free energies relative to

the $[Ni^{II}N]^{2+}$ species. These values are given explicitly in Table S6 but are also available in Figure 3 for the associated Pourbaix diagram in Figure 4 and in Figure S1 for the associated Pourbaix diagram in Figure S2.

$$
\begin{aligned}
\Delta G[Ni^{II}N]^{2+} &= 0.0 \\
\Delta G[Ni^{II}NH]^{3+} &= -RT\ln(10)(pK_a^{[Ni^{II}NH]^{3+}} - pH) \\
\Delta G[Ni^{I}N]^{+} &= -nF(E_{1/2}^{Ni^{II/I}} - E^0) \\
\Delta G[Ni^{II}NH_2]^{4+} &= -RT\ln(10)(pK_a^{[Ni^{II}NH_2]^{4+}} - pH) + \Delta G[Ni^{II}NH]^{3+} \\
\Delta G[Ni^{I}NH]^{2+} &= -RT\ln(10)(pK_a^{[Ni^{I}NH]^{2+}} - pH) + \Delta G[Ni^{I}N]^{+} \qquad \text{(S1)} \\
\Delta G[Ni^{0}N] &= -nF(E_{1/2}^{Ni^{I/0}} - E^0) + \Delta G[Ni^{I}N]^{+} \\
\Delta G[Ni^{I}NH_2]^{3+} &= -RT\ln(10)(pK_a^{[Ni^{I}NH_2]^{3+}} - pH) + \Delta G[Ni^{I}NH]^{2+} \\
\Delta G[Ni^{0}NH]^{+} &= -RT\ln(10)(pK_a^{[Ni^{0}NH]^{+}} - pH) + \Delta G[Ni^{0}N] \\
\Delta G[Ni^{0}NH_2]^{2+} &= -RT\ln(10)(pK_a^{[Ni^{0}NH_2]^{2+}} - pH) + \Delta G[Ni^{0}NH]^{+}
\end{aligned}
$$

As noted in the main text, we use standard relationships to convert between pH units, $E^0$ (volts vs. $Fc^+/Fc$), and $\Delta G$ (kcal/mol).[7] For the expressions given in eq (S1), $R$ is the gas law constant, $T$ is the temperature in Kelvin, $n$ is the number of electrons transferred ($n$ = 1 for these systems), and $F$ is Faraday's constant. Note that in eq (S1), all free energies are given relative to the unprotonated $Ni^{II}$ species, $[Ni^{II}N]^{2+}$, which therefore has a value of zero. The lines separating regions in the Pourbaix diagram arise when the free energy difference between the two species on each side of the line vanishes, indicating that the free energies of the two species are the same along the line. Similarly, points on the diagram indicate that more than two species have the same free energy. Thus, the lines and points denote regions in which more than one species coexists for a given pH and/or $E^0$ value.

## EXPERIMENTAL METHODS

**Redetermination of p$K_a$ for $[Ni(P_2^{Ph}HN_2^{Bn})_2]^{4+}$ in the presence of electrolyte.** The average p$K_a$ for the double deprotonation of $[Ni(P_2^{Ph}HN_2^{Bn})_2]^{4+}$ to generate $[Ni(P_2^{Ph}N_2^{Bn})_2]^{2+}$ was redetermined in the presence of electrolyte to check for ionic strength effects that would distinguish the previous NMR spectroscopy and electrochemical experiments. The previously reported method was used,[4] except for the addition of 0.2 M $NEt_4BF_4$ in the current work. The analyte solution was prepared by dissolving 9.7 mg of $[Ni(P_2^{Ph}N_2^{Bn})_2]_2(BF_4)_2$ (7.8 μmol) and 26.0 mg of $NEt_4BF_4$ (120 μmol) in 0.5 mL of $CD_3CN$. A separate solution of acid was prepared using 21.7 mg of *p*-cyanoanilinium $BF_4$ (105 μmol) in 0.5 mL of $CD_3CN$. Following acquisition of initial $^1H$ and $^{31}P$ NMR spectra, 50 μL of the solution of acid (1.3 equivalents relative to the nickel complex) were added to the analyte solution, and the spectra recollected. This was repeated after total additions of 100 μL and 150 μL of the acid solution. The corresponding spectra were used to determine the average p$K_a$ value for the double deprotonation of $[Ni(P_2^{Ph}N_2^{Bn})_2]_2(BF_4)_2$ giving an average of 6.8 ± 0.5 for three measurements, for which the error is twice the standard deviation for the three measurements. Note that the newly obtained values are in quantitative agreement with those reported previously:[4] 6.7 ± 0.4.

**Estimation of kinetic potential shift.** Digital simulations were performed using DigiElch (version 6F) to estimate the magnitude of the shift in potential that could result from a diffusion-controlled exergonic proton transfer (PT) reaction following reduction. The concentration (parameter "Canal") of the oxidized complex (A) was set to 0.001 M, and the concentration of the acid (C) was set as 0.10 M, as these concentrations are similar to the concentrations typically used in the previously reported cyclic voltammetry experiments.[4] The concentrations of the products (B and D) were set to 0 M. $E^0$ was arbitrarily set to 0.0 V such that the potential of the resulting wave would be equivalent to the difference between the observed wave and $E^0$ (the choice of potential is unimportant for the intended purpose).

Default diffusion coefficients ($10^{-5}$ $cm^2 \cdot s^{-1}$), α values (0.5), and electron transfer rates (10,000 $cm \cdot s^{-1}$) were used. Additional parameters used for the simulations are given in Table S7.

The resulting simulations indicated that the potential at half-current ($E_{p/2}$) would be observed approximately 270 mV positive of $E^0$ in the presence of this subsequent PT reaction. The utilized $K_{eq}$ is approximately equal to the largest difference in p$K_a$ values between the acids and the resulting nickel complexes. Increasing $K_{eq}$ further did not have an appreciable effect on the resulting $E_{p/2}$ value. Given that a diffusion-controlled rate constant of $2 \times 10^9$ $M^{-1} \cdot s^{-1}$ was assumed for this subsequent PT reaction, a shift of 270 mV or less from $E^0$ would be expected. Any lower rate constant or higher reaction order would be expected to result in a smaller shift in potential.

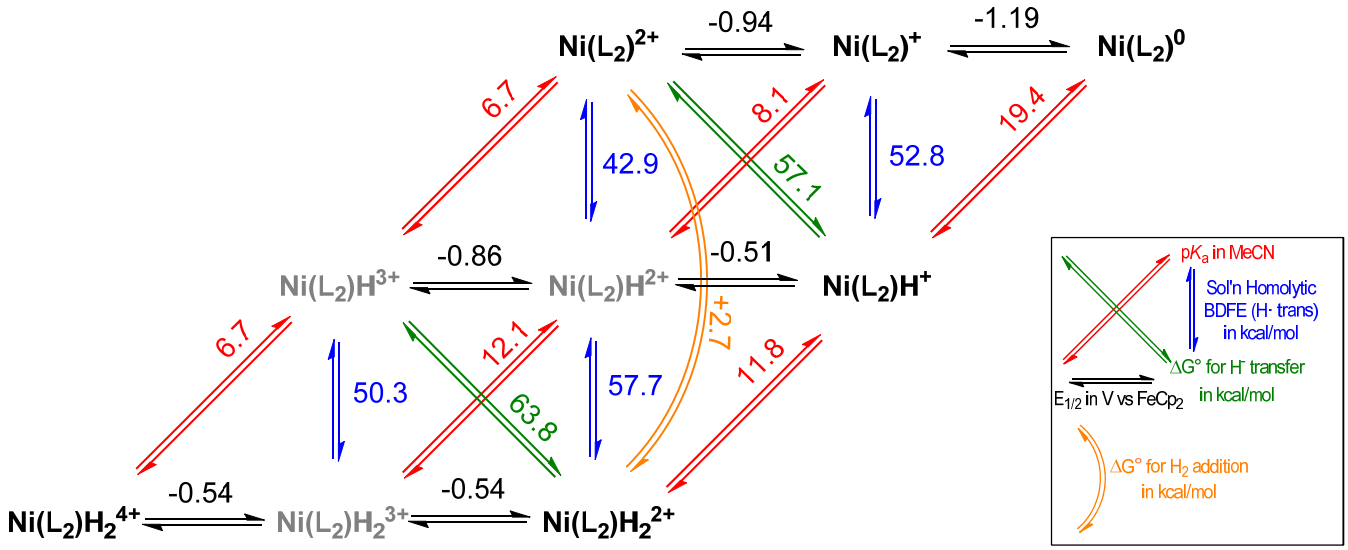


**FIGURE S1.** Experimental and calculated thermodynamic data for the (Ph,Bn) catalyst, where the $P_2N_2$ ligand is denoted by L. The thermodynamic scheme shows the relationships among the species in terms of $E_{½}$, p$K_a$, homolytic solution bond dissociation free energy (BDFE), $\Delta G^0_{H^-}$, and $\Delta G^0_{H_2}$ values. Formulas are intended to indicate only composition and not structure (i.e., notation does not distinguish between nickel hydrides and protonated pendant amines). The species in gray have not been directly observed experimentally, and their relative stabilities are therefore determined from the calculations presented herein. A version this scheme was reported previously;[4] however, since all thermodynamic relationships have been determined, the scheme is presented here in its entirety. Some of the quantities required to complete this scheme are provided in Table S8.

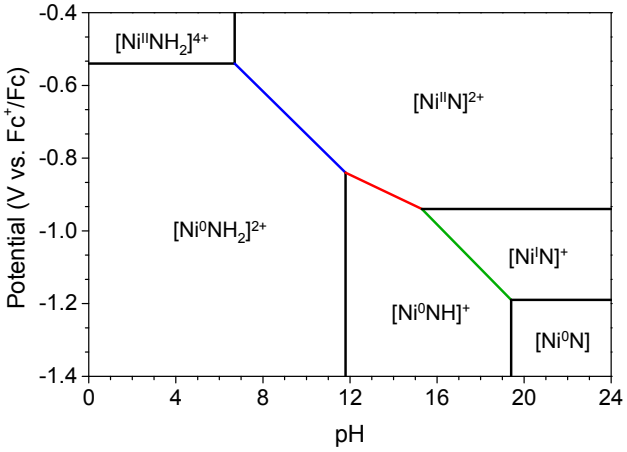


**FIGURE S2.** Pourbaix diagram for the (Ph,Bn) catalyst calculated from the thermodynamic scheme in Figure S1. The horizontal and vertical lines are the reduction potentials and p$K_a$'s, respectively, of various protonated and unprotonated forms of the catalyst in MeCN. The red line has a slope of ~29.5 mV/pH unit and corresponds to a $2e^-$–$1H^+$ process. The blue line has a slope of ~59 mV/pH unit and corresponds to a $2e^-$–$2H^+$ process. The green line has a slope of ~59 mV/pH unit and corresponds to a $1e^-$–$1H^+$ process. Note that $[Ni^0NH]^+$ corresponds to the $Ni^{II}$-hydride species.

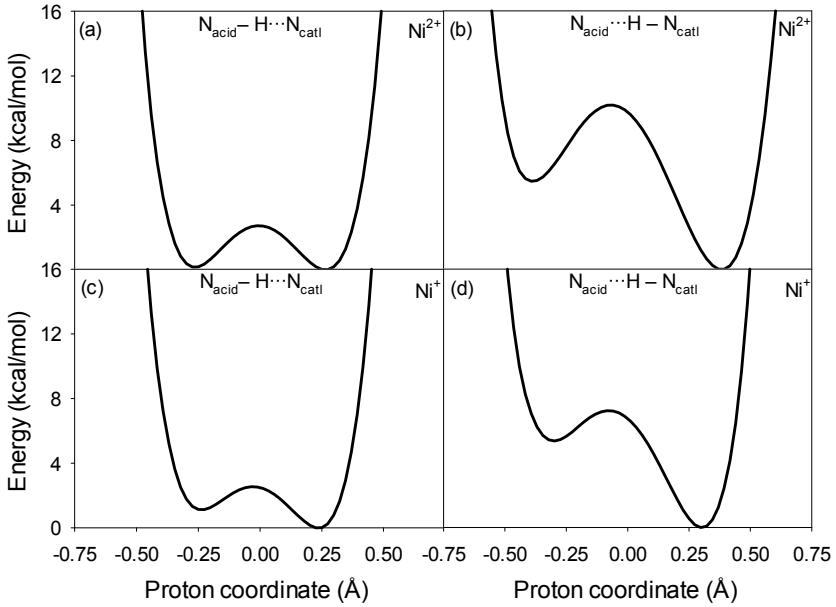


**FIGURE S3.** Proton potential energy curves for the four charge transfer states associated with the first PCET process for the $[Ni(P_2^{Ph}N_2^{Bn})_2]^{2+}$ complex with *p*-anisidine: (a) oxidized species with the proton on the acid; (b) oxidized species with the proton on the catalyst; (c) reduced species with the proton on the acid; and (d) reduced species with the proton on the catalyst. Each proton potential is generated for the fixed optimized geometry of the hydrogen-bonded acid–catalyst complex corresponding to that state. All nuclei remain fixed except for the transferring hydrogen nucleus, which is moved along a one-dimensional grid to generate the proton potential energy curve. As expected, the proton potentials are asymmetric with the well on the catalyst side lower for (b) and (d). The well on the catalyst side is lower in energy for (a) and (c) because the geometry is only a local minimum on the potential energy surface, and there is another lower-energy minimum corresponding to the species with the proton on the catalyst.

**TABLE S1.** Selected geometric parameters of catalyst complexes.

| species | | $R(N_{MeCN} - Ni)$ [Å] | $r(N_{acid} - H)$ [Å] | $r(N_{catl} - H)$ [Å] | $R(N - N)$ [a,b] [Å] | $\Theta(N_{acid} - H - N_{catl})$ [°] |
|---|---|---|---|---|---|---|
| $[Ni^{II}N]^{2+}$ | | 2.03 | | | | |
| $[N^{II}NH]^{3+}$ | *endo* | 2.03 | | 1.03 | | |
| | *exo* | 2.03 | | 1.07 | 2.68 | |
| $[N^{II}NH_2]^{4+}$ | *endo-endo* | 2.02 | | 1.02/1.03 | | |
| | *exo-exo* | 2.00 | | 1.06/1.06 | 2.68/2.72 | |
| $[N^{I}NH]^{2+}$ | *endo* | | | 1.03 | | |
| | *exo* | | | 1.08 | 2.64 | |
| $[N^{I}NH_2]^{3+}$ | *endo-endo* | | | 1.03/1.03 | | |
| | *exo-exo* | | | 1.06/1.07 | 2.64/2.73 | |
| $[Ni^{II}N\cdots HAsd]^{3+}$ [c] | *endo* | 2.12 | 1.11 | 1.61 | 2.71 | 172.2 |
| $[Ni^{II}NH\cdots Asd]^{3+}$ [c] | *endo* | 2.08 | 1.84 | 1.06 | 2.84 | 154.1 |
| $[Ni^{I}N\cdots HAsd]^{2+}$ [c] | *endo* | | 1.12 | 1.57 | 2.69 | 175.0 |
| $[Ni^{I}NH\cdots Asd]^{2+}$ [c] | *endo* | | 1.72 | 1.08 | 2.77 | 164.2 |
| $[Ni^{II}NH\cdots Anl]^{3+}$ [d] | *endo* | 2.08 | 2.05 | 1.04 | 2.97 | 146.8 |
| $[Ni^{I}NH\cdots Anl]^{2+}$ [d] | *endo* | | 1.82 | 1.06 | 2.85 | 162.6 |

[a]N–N distance is between the two nitrogens on the same $P_2N_2$ ligand in pinched configuration for *exo* and *exo-exo* species. [b]N–N distance is between nitrogen on the acid and nitrogen on the catalyst: $N_{acid} - N_{catl}$. [c]Asd = *p*-anisidine. [d]Anl = *p*-cyanoaniline.

**TABLE S2.** Calculated $Ni^{II/I}$ reduction potentials for various protonated species using different methods.[a]

| species | direct method [b] | | | Born-Haber method [c] | |
|---|---|---|---|---|---|
| | 4-coord. $Ni^{II}$ & $Ni^{I}$ [d] | 5-coord. $Ni^{II}$ & 4-coord. $Ni^{I}$ [e,f] | 5-coord. $Ni^{II}$ & $Ni^{I}$ [g] | 4-coord. $Ni^{II}$ & $Ni^{I}$ [d] | 5-coord. $Ni^{II}$ & 4-coord. $Ni^{I}$ [e] |
| *endo* | – 0.64 | – 0.79 | – 0.66 | – 0.49 | – 0.48 |
| *exo* | – 0.50 | – 0.86 | – 0.80 | – 0.62 | – 0.70 |
| *endo-endo* | – 0.28 | – 0.57 | – 0.32 | – 0.16 | – 0.25 |
| *exo-exo* | – 0.25 | – 0.57 | – 0.39 | – 0.40 | – 0.56 |

[a]Units of volts (V) vs. $Fc^{+}$/Fc couple in acetonitrile. [b]Optimizations performed in solution (MeCN). [c]Optimizations performed in gas-phase and solvated at the gas-phase optimized geometry.[8] [d]No MeCN ligand is explicitly included for the $Ni^{II}$ or $Ni^{I}$ species. [e]MeCN ligand is explicitly included for the $Ni^{II}$ but not for the $Ni^{I}$ species. [f]Same as values reported in Table 2. [g]MeCN ligand is explicitly included for both the $Ni^{II}$ and $Ni^{I}$ species.

**TABLE S3.** Relative free energies ($\Delta\Delta G$) for solvated protonated species using various computational approaches.[a]

| $Ni^{II}$ species | B3P86/ 6–31G* [b,c] | B3P86/ 6–31+G* [b,d] | $\omega$B97X-D/ 6–31G* [d,e] |
|---|---|---|---|
| *endo* | 0.0 | 0.0 | 0.0 |
| *exo* | – 2.7 | – 2.4 | – 0.7 |
| | | | |
| *endo-endo* | 0.0 | 0.0 | 0.0 |
| *exo-exo* | – 6.9 | – 6.0 | – 4.4 |

[a]Relative energies of 4-coordinate singly and doubly protonated species (i.e., no explicit MeCN ligand) in units of kcal/mol. Monoprotonated species are relative to each other, and diprotonated species are relative to each other. All energies are calculated at the geometry optimized at B3P86/6–31G*. Because these geometries are not stationary points for the $\omega$B97X-D functional or 6–31+G* basis set, the thermal and zero point energy corrections are not included in any of these values, so a portion of the free energy is omitted for all cases. For all methods/basis sets examined, the *exo* or *exo-exo* species is lower in energy. [b]Functional parameters from Becke[9] and Perdew.[10] [c]Basis set: 6–31G** on the transferring hydrogen(s) and 6–31G* on all other atoms, excluding Ni. [d]Basis set that includes diffuse functions: 6–31+G** on the transferring hydrogen(s) and 6–31+G* on all other atoms, excluding Ni.[11] [e]Dispersion-corrected functional of Chai and Head-Gordon.[12-14]

**TABLE S4.** Calculated reaction free energies for acid association of *p*-anisidinium (HB) to Ni catalyst using various approaches.

| association reaction | terms contributing to free energy included | excluded | $\Delta G^0_{assoc}$ (eV) [a] |
|---|---|---|---|
| $[Ni^{II}N]^{2+} + [HB]^{+} \rightarrow [Ni^{II}N\cdots HB]^{3+}$ | vib + trans + rot | (none) | 1.07 |
| | vib + trans | rot | 0.75 [b] |
| | vib | trans + rot | 0.27 |
| $[Ni^{II}N]^{2+} + [HB]^{+} \rightarrow [Ni^{II}NH\cdots B]^{3+}$ | vib + trans + rot | (none) | 0.97 |
| | vib + trans | rot | 0.65 [b] |
| | vib | trans + rot | 0.17 |
| $[Ni^{I}N]^{+} + [HB]^{+} \rightarrow [Ni^{I}N\cdots HB]^{2+}$ | vib + trans + rot | (none) | 0.59 |
| | vib + trans | rot | 0.26 [b] |
| | vib | trans + rot | –0.21 |
| $[Ni^{I}N]^{+} + [HB]^{+} \rightarrow [Ni^{I}NH\cdots B]^{2+}$ | vib + trans + rot | (none) | 0.56 |
| | vib + trans | rot | 0.24 [b] |
| | vib | trans + rot | –0.24 |

[a]Reaction free energy, $\Delta G^0_{assoc}$, obtained from free energies of optimized solvated reactant and product structures. $\Delta G^0_{assoc}$ does not account for basis set superposition error (BSSE). [b]Values are the same as those reported in Table 2.

**TABLE S5.** Calculated reaction free energies for acid association of *p*-cyanoanilinium (HB) to Ni catalyst using various approaches.

| association reaction | terms contributing to free energy included | excluded | $\Delta G^0_{assoc}$ (eV) [a] |
|---|---|---|---|
| $[Ni^{II}N]^{2+} + [HB]^{+} \rightarrow [Ni^{II}NH\cdots B]^{3+}$ | vib + trans + rot | (none) | 0.76 |
| | vib + trans | rot | 0.44 [b] |
| | vib | trans + rot | –0.04 |
| $[Ni^{I}N]^{+} + [HB]^{+} \rightarrow [Ni^{I}NH\cdots B]^{2+}$ | vib + trans + rot | (none) | 0.39 |
| | vib + trans | rot | 0.06 [b] |
| | vib | trans + rot | –0.42 |

[a]Reaction free energy, $\Delta G^0_{assoc}$, obtained from free energies of optimized solvated reactant and product structures. $\Delta G^0_{assoc}$ does not account for basis set superposition error (BSSE). [b]Values are the same as those reported in Table 2.

**TABLE S6.** Reduction potentials and p$K_a$'s of (Ph,Bn) catalyst and related species.

| parameter | Fig. 4 | Fig. S2 |
|---|---|---|
| $E_{1/2}^{Ni^{II/I}}$ | – 0.94 | – 0.94 |
| $E_{1/2}^{Ni^{I/0}}$ | – 1.19 | – 1.19 |
| $pK_a^{[Ni^{II}NH_2]^{4+}}$ | 5.9 | 6.7 |
| $pK_a^{[Ni^{II}NH]^{3+}}$ | 7.5 | 6.7 |
| $pK_a^{[Ni^{I}NH_2]^{3+}}$ | 10.3 | 12.1 |
| $pK_a^{[Ni^{I}NH]^{2+}}$ | 9.4 | 8.1 |
| $pK_a^{[Ni^{0}NH_2]^{2+}}$ | 11.8 | 11.8 |
| $pK_a^{[Ni^{0}NH]^{+}}$ | 19.4 | 19.4 |

**TABLE S7.** Parameters used in simulations of cyclic voltammetry experiments.

| parameter | value | |
|---|---|---|
| scan rate | 0.05 | V/s |
| $K_{eq}$ | $1\times10^{6}$ | $M^{-1}$ |
| $k_f$ | $2\times10^{9}$ | $M^{-1}\cdot s^{-1}$ |
| $k_r$ [a] | $2\times10^{3}$ | $s^{-1}$ |

[a] as defined by $K_{eq} = k_f / k_r$ .

**TABLE S8.** Reaction free energies related to hydrogen in MeCN.

| reaction | $\Delta G^{0\,a}$ |
|---|---|
| $H_2 \rightarrow H^+ + H^-$ | 76.0 |
| $H_2 \rightarrow 2H\cdot$ | 103.6 |
| $H^+ + 2e^- \rightarrow H^-$ | 79.6 |
| $H^+ + e^- \rightarrow H\cdot$ | 53.6 |
| $H\cdot + e^- \rightarrow H^-$ | 26.0 |

[a]Units of kcal/mol. Values reported previously.[15,16]

**TABLE S9.** Cartesian coordinates of the optimized structure of $[Ni^{II}(P_2^{Ph}N_2^{Bn})_2(MeCN)]^{2+}$ (i.e., $[Ni^{II}N]^{2+}$ with an MeCN ligand).

(– 4222.77366416 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| Ni | 1.418362 | 18.949401 | 9.338545 |
| N | 2.786037 | 21.828655 | 7.224306 |
| N | 2.159313 | 21.884574 | 10.845383 |
| N | 0.270139 | 15.732970 | 11.058995 |
| N | -0.789966 | 19.152116 | 11.930148 |
| N | 1.963853 | 17.783356 | 7.772909 |
| P | 3.336470 | 20.003963 | 9.219628 |
| P | 0.639751 | 20.949147 | 8.688626 |
| P | 1.724631 | 18.042961 | 11.355567 |
| P | -0.489632 | 17.876282 | 9.490342 |
| C | 4.913420 | 17.688211 | 9.306664 |
| H | 3.997108 | 17.152191 | 9.085215 |
| C | 6.118949 | 16.999616 | 9.418389 |
| H | 6.138606 | 15.924154 | 9.280835 |
| C | 7.293127 | 17.689338 | 9.711489 |
| H | 8.230788 | 17.151472 | 9.800544 |
| C | 7.263207 | 19.070907 | 9.894548 |
| H | 8.175400 | 19.609139 | 10.128412 |
| C | 6.063456 | 19.766041 | 9.772258 |
| H | 6.056759 | 20.843568 | 9.901624 |
| C | 4.880493 | 19.074796 | 9.480806 |
| C | 3.602657 | 20.664416 | 7.506258 |
| H | 4.654413 | 20.961136 | 7.459759 |
| H | 3.449144 | 19.833903 | 6.798780 |
| C | 3.289303 | 22.525534 | 6.034167 |
| H | 3.111481 | 21.931731 | 5.122721 |
| H | 4.374436 | 22.606997 | 6.156344 |
| C | 2.199946 | 24.289826 | 4.608752 |
| H | 2.168793 | 23.564781 | 3.800273 |
| C | 1.742592 | 25.589425 | 4.396454 |
| H | 1.350390 | 25.869276 | 3.424174 |
| C | 1.780837 | 26.520478 | 5.431622 |
| H | 1.424145 | 27.532224 | 5.270126 |
| C | 2.278907 | 26.141756 | 6.679039 |
| H | 2.315061 | 26.860890 | 7.491327 |
| C | 2.744069 | 24.846118 | 6.885324 |
| H | 3.150727 | 24.565433 | 7.852069 |
| C | 2.710842 | 23.905118 | 5.850114 |
| C | 1.372329 | 21.527587 | 7.085289 |
| H | 1.174819 | 20.767906 | 6.311396 |
| H | 0.858683 | 22.450884 | 6.800664 |
| C | -1.709602 | 21.474489 | 7.216528 |
| H | -1.098313 | 21.434872 | 6.322675 |

| | | | |
|---|---|---|---|
| C | -3.075585 | 21.722110 | 7.096572 |
| H | -3.506482 | 21.875605 | 6.113089 |
| C | -3.882276 | 21.777630 | 8.230227 |
| H | -4.944616 | 21.972457 | 8.131292 |
| C | -3.320799 | 21.579709 | 9.490874 |
| H | -3.943535 | 21.615501 | 10.378054 |
| C | -1.958006 | 21.328218 | 9.615637 |
| H | -1.527988 | 21.143761 | 10.595947 |
| C | -1.139860 | 21.284589 | 8.479804 |
| C | 1.167970 | 22.299098 | 9.864178 |
| H | 1.493857 | 23.152867 | 9.250232 |
| H | 0.267811 | 22.598637 | 10.407022 |
| C | 2.311392 | 22.896973 | 11.910777 |
| H | 1.333964 | 22.997856 | 12.393826 |
| H | 3.003846 | 22.476795 | 12.647077 |
| C | 4.177364 | 24.518640 | 11.360767 |
| H | 4.892319 | 23.759816 | 11.664824 |
| C | 4.632692 | 25.755254 | 10.907403 |
| H | 5.698697 | 25.948727 | 10.846848 |
| C | 3.720616 | 26.744452 | 10.541942 |
| H | 4.072632 | 27.711873 | 10.200301 |
| C | 2.352831 | 26.491611 | 10.638313 |
| H | 1.637172 | 27.262640 | 10.372809 |
| C | 1.902083 | 25.252405 | 11.089809 |
| H | 0.835944 | 25.066503 | 11.180180 |
| C | 2.807000 | 24.249714 | 11.453746 |
| C | 3.447622 | 21.521472 | 10.276437 |
| H | 4.124889 | 21.280984 | 11.100295 |
| H | 3.901544 | 22.320073 | 9.670122 |
| C | 4.226784 | 17.380543 | 12.452585 |
| H | 4.130491 | 16.429169 | 11.943286 |
| C | 5.367626 | 17.632686 | 13.210495 |
| H | 6.140906 | 16.875301 | 13.279725 |
| C | 5.514077 | 18.847734 | 13.875526 |
| H | 6.403753 | 19.042027 | 14.464505 |
| C | 4.514459 | 19.814504 | 13.781530 |
| H | 4.621982 | 20.762978 | 14.296623 |
| C | 3.375057 | 19.570429 | 13.019386 |
| H | 2.612688 | 20.338950 | 12.935877 |
| C | 3.219526 | 18.347306 | 12.354531 |
| C | 1.624211 | 16.188881 | 11.318042 |
| H | 2.347378 | 15.810589 | 10.577094 |
| H | 1.925654 | 15.825635 | 12.304731 |
| C | 0.145022 | 14.287078 | 11.301549 |
| H | 0.859270 | 13.722553 | 10.680512 |
| H | -0.860771 | 14.004549 | 10.975845 |
| C | -0.572593 | 14.357332 | 13.720511 |
| H | -1.388062 | 15.012643 | 13.429165 |
| C | -0.434236 | 13.963875 | 15.048358 |
| H | -1.139413 | 14.319304 | 15.792592 |
| C | 0.604574 | 13.109756 | 15.421793 |
| H | 0.708979 | 12.798978 | 16.456021 |
| C | 1.503747 | 12.655213 | 14.460116 |

| | | | |
|---|---|---|---|
| H | 2.314160 | 11.991485 | 14.743010 |
| C | 1.362962 | 13.052882 | 13.130992 |
| H | 2.058769 | 12.690762 | 12.379815 |
| C | 0.324790 | 13.903840 | 12.746755 |
| C | -0.200735 | 16.057658 | 9.726626 |
| H | -1.174869 | 15.582625 | 9.574321 |
| H | 0.472058 | 15.714021 | 8.924351 |
| C | -1.219507 | 18.240680 | 6.800472 |
| H | -0.201695 | 18.580949 | 6.644722 |
| C | -2.108969 | 18.174421 | 5.730108 |
| H | -1.778136 | 18.460538 | 4.737893 |
| C | -3.419821 | 17.750091 | 5.932762 |
| H | -4.111451 | 17.705348 | 5.098297 |
| C | -3.844048 | 17.379454 | 7.208424 |
| H | -4.862814 | 17.045137 | 7.370336 |
| C | -2.956629 | 17.431384 | 8.279133 |
| H | -3.293042 | 17.133445 | 9.266755 |
| C | -1.640755 | 17.868820 | 8.080092 |
| C | -1.504914 | 18.312016 | 10.977137 |
| H | -2.374678 | 18.864515 | 10.613097 |
| H | -1.850054 | 17.369106 | 11.430999 |
| C | -1.744768 | 19.566072 | 12.976877 |
| H | -2.085351 | 18.688905 | 13.550704 |
| H | -2.618011 | 19.970639 | 12.456134 |
| C | -1.012293 | 21.923818 | 13.523966 |
| H | -1.225730 | 22.205624 | 12.497082 |
| C | -0.576493 | 22.888694 | 14.428886 |
| H | -0.439856 | 23.913708 | 14.099962 |
| C | -0.334669 | 22.541919 | 15.758682 |
| H | -0.002168 | 23.294724 | 16.465734 |
| C | -0.524680 | 21.226764 | 16.175182 |
| H | -0.341776 | 20.949950 | 17.208216 |
| C | -0.957918 | 20.263513 | 15.264685 |
| H | -1.118775 | 19.240529 | 15.591682 |
| C | -1.209283 | 20.599996 | 13.932427 |
| C | 0.348287 | 18.474519 | 12.537083 |
| H | 0.059169 | 17.535803 | 13.038569 |
| H | 0.773880 | 19.141610 | 13.289521 |
| C | 2.273810 | 17.097265 | 6.893234 |
| C | 2.667804 | 16.230993 | 5.804577 |
| H | 1.897991 | 15.473985 | 5.642925 |
| H | 3.610075 | 15.738586 | 6.054791 |
| H | 2.797200 | 16.816539 | 4.892461 |

**TABLE S10.** Cartesian coordinates of the optimized structure of $[Ni^{I}(P_2^{Ph}N_2^{Bn})_2]^+$ (i.e., $[Ni^{I}N]^+$).

(– 4089.78151322 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | 9.330705 | 5.986863 | 8.448388 |
| H | 9.198260 | 5.052258 | 9.000937 |
| H | 10.144749 | 5.836922 | 7.719488 |
| C | 9.989187 | 8.314120 | 8.820370 |
| H | 10.806283 | 8.209418 | 8.086921 |
| H | 10.343012 | 8.961454 | 9.628353 |
| C | 10.667398 | 6.583780 | 10.335349 |
| H | 11.640712 | 6.508552 | 9.822245 |
| H | 10.396032 | 5.569870 | 10.648486 |
| C | 10.822990 | 7.449522 | 11.559899 |
| C | 12.089558 | 7.886286 | 11.954360 |
| H | 12.952407 | 7.633444 | 11.344726 |
| C | 12.259141 | 8.625495 | 13.124679 |
| H | 13.252087 | 8.951721 | 13.416224 |
| C | 11.156474 | 8.945532 | 13.913138 |
| H | 11.284121 | 9.520667 | 14.824225 |
| C | 9.885918 | 8.520009 | 13.523458 |
| H | 9.018796 | 8.766822 | 14.127711 |
| C | 9.721406 | 7.775260 | 12.359046 |
| H | 8.731111 | 7.436908 | 12.070256 |
| C | 7.219850 | 9.045511 | 9.281365 |
| H | 7.690632 | 8.815177 | 10.249023 |
| H | 6.765196 | 10.036993 | 9.358065 |
| C | 6.584109 | 6.709055 | 8.893888 |
| H | 5.692000 | 6.101566 | 8.721345 |
| H | 7.044788 | 6.383334 | 9.839022 |
| C | 4.950148 | 8.306592 | 9.705003 |
| H | 4.195723 | 7.623921 | 9.302673 |
| H | 4.611494 | 9.330344 | 9.515220 |
| C | 5.093928 | 8.092377 | 11.195448 |
| C | 4.922204 | 6.824330 | 11.762128 |
| H | 4.642394 | 5.987571 | 11.128956 |
| C | 5.076416 | 6.628390 | 13.133324 |
| H | 4.927412 | 5.640515 | 13.557044 |
| C | 5.406843 | 7.700581 | 13.960887 |
| H | 5.521615 | 7.550434 | 15.029366 |
| C | 5.575881 | 8.969870 | 13.409382 |
| H | 5.820544 | 9.813457 | 14.046637 |
| C | 5.420046 | 9.160610 | 12.037874 |
| H | 5.536139 | 10.155155 | 11.617337 |
| C | 7.247372 | 4.644393 | 6.975253 |
| C | 6.861760 | 4.439604 | 5.645377 |
| H | 6.903970 | 5.265433 | 4.935974 |
| C | 6.416964 | 3.183942 | 5.230898 |

| | | | |
|---|---|---|---|
| H | 6.118101 | 3.032356 | 4.199096 |
| C | 6.356837 | 2.129727 | 6.139568 |
| H | 6.011961 | 1.152711 | 5.818000 |
| C | 6.741078 | 2.328025 | 7.465646 |
| H | 6.693736 | 1.508604 | 8.175307 |
| C | 7.185484 | 3.579100 | 7.883650 |
| H | 7.476802 | 3.723119 | 8.919334 |
| C | 9.047293 | 10.936823 | 8.085603 |
| C | 10.393012 | 11.312926 | 8.183629 |
| H | 11.171473 | 10.558998 | 8.228222 |
| C | 10.749000 | 12.659591 | 8.231500 |
| H | 11.795117 | 12.934175 | 8.315669 |
| C | 9.768035 | 13.647135 | 8.184715 |
| H | 10.046711 | 14.694315 | 8.231435 |
| C | 8.427255 | 13.282003 | 8.070650 |
| H | 7.657135 | 14.045308 | 8.027900 |
| C | 8.067995 | 11.938311 | 8.014313 |
| H | 7.020041 | 11.672587 | 7.912713 |
| C | 8.459442 | 6.857795 | 2.937053 |
| H | 8.811189 | 7.371595 | 2.030290 |
| H | 8.729192 | 5.801336 | 2.854378 |
| C | 10.128233 | 9.095544 | 3.680150 |
| H | 10.588246 | 9.676887 | 4.496513 |
| H | 10.923484 | 8.792591 | 2.993033 |
| C | 6.303831 | 6.043051 | 2.184791 |
| H | 5.250438 | 6.042859 | 2.481937 |
| H | 6.697726 | 5.034264 | 2.345797 |
| C | 6.418956 | 6.416728 | 0.723655 |
| C | 7.499729 | 5.976217 | -0.048997 |
| H | 8.237094 | 5.313053 | 0.392928 |
| C | 7.629532 | 6.361633 | -1.381852 |
| H | 8.470900 | 6.003979 | -1.966881 |
| C | 6.674631 | 7.193376 | -1.965512 |
| H | 6.770053 | 7.489185 | -3.004995 |
| C | 5.588235 | 7.630801 | -1.209018 |
| H | 4.832619 | 8.266614 | -1.658718 |
| C | 5.464599 | 7.245352 | 0.124580 |
| H | 4.609835 | 7.581050 | 0.704774 |
| C | 8.150364 | 10.524814 | 3.746860 |
| H | 7.560269 | 11.176467 | 3.096549 |
| H | 8.595870 | 11.152259 | 4.537643 |
| C | 6.459188 | 8.281739 | 3.099739 |
| H | 5.372038 | 8.190253 | 3.172279 |
| H | 6.689934 | 8.833291 | 2.175287 |
| C | 9.833789 | 10.843177 | 2.061822 |
| H | 10.653683 | 10.312185 | 1.567078 |
| H | 10.286885 | 11.653880 | 2.656660 |
| C | 8.929366 | 11.439686 | 1.013691 |
| C | 8.233282 | 10.616469 | 0.121115 |
| H | 8.325633 | 9.537980 | 0.207232 |
| C | 7.431664 | 11.168794 | -0.873399 |
| H | 6.900007 | 10.516051 | -1.558040 |
| C | 7.318762 | 12.554293 | -0.995156 |

| | | | |
|---|---|---|---|
| H | 6.696429 | 12.983801 | -1.773356 |
| C | 8.009478 | 13.381672 | -0.113403 |
| H | 7.925812 | 14.460073 | -0.200607 |
| C | 8.807390 | 12.824479 | 0.885728 |
| H | 9.344647 | 13.471352 | 1.573063 |
| C | 10.853041 | 6.445907 | 4.544554 |
| C | 12.139576 | 6.984055 | 4.682687 |
| H | 12.291612 | 8.057178 | 4.642455 |
| C | 13.239608 | 6.149814 | 4.872668 |
| H | 14.229743 | 6.581884 | 4.971377 |
| C | 13.069701 | 4.768783 | 4.929529 |
| H | 13.925675 | 4.118119 | 5.071647 |
| C | 11.792327 | 4.225005 | 4.798867 |
| H | 11.652914 | 3.150048 | 4.842443 |
| C | 10.689604 | 5.054843 | 4.614777 |
| H | 9.700684 | 4.614426 | 4.531320 |
| C | 5.525019 | 10.351886 | 4.911694 |
| C | 4.969267 | 11.207567 | 3.951391 |
| H | 5.413902 | 11.291213 | 2.964555 |
| C | 3.835042 | 11.956657 | 4.252420 |
| H | 3.409097 | 12.615181 | 3.503045 |
| C | 3.244560 | 11.856638 | 5.512155 |
| H | 2.358404 | 12.437666 | 5.745262 |
| C | 3.791643 | 11.007711 | 6.471214 |
| H | 3.335126 | 10.927626 | 7.452193 |
| C | 4.928216 | 10.256776 | 6.174598 |
| H | 5.354112 | 9.591612 | 6.923837 |
| N | 9.619006 | 7.036863 | 9.413225 |
| N | 6.171773 | 8.105926 | 8.906937 |
| N | 7.014940 | 6.933220 | 3.119554 |
| N | 9.153880 | 9.867229 | 2.925084 |
| Ni | 8.025003 | 8.060496 | 6.105823 |
| P | 7.766286 | 6.316728 | 7.495605 |
| P | 8.555793 | 9.176157 | 7.984462 |
| P | 9.392119 | 7.536094 | 4.403818 |
| P | 6.991187 | 9.319178 | 4.564546 |

**TABLE S11.** Cartesian coordinates of the optimized structure of $[Ni^{II}(P_2^{Ph}N_2^{Bn})_2(H\text{-}Asd)(MeCN)]^{3+}$ (i.e., $[Ni^{II}N\cdots HAsd]^{3+}$ with an MeCN ligand).

(– 4626.52422520 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | 7.628383 | 5.766896 | 8.378306 |
| H | 7.050944 | 5.098029 | 9.021784 |
| H | 7.825255 | 5.240550 | 7.432908 |
| C | 9.788402 | 6.839182 | 8.232208 |
| H | 10.028424 | 6.313518 | 7.292631 |
| H | 10.713223 | 6.960565 | 8.801980 |
| C | 9.471756 | 4.952529 | 9.695919 |
| H | 9.879278 | 4.269034 | 8.934545 |
| H | 8.674904 | 4.418185 | 10.222152 |
| C | 10.559441 | 5.325210 | 10.670556 |
| C | 11.870265 | 4.887034 | 10.473654 |
| H | 12.104209 | 4.287232 | 9.598778 |
| C | 12.876594 | 5.213422 | 11.382712 |
| H | 13.889714 | 4.863339 | 11.214779 |
| C | 12.579219 | 5.986932 | 12.501802 |
| H | 13.358708 | 6.240753 | 13.212349 |
| C | 11.271769 | 6.428969 | 12.707762 |
| H | 11.028224 | 7.022613 | 13.582896 |
| C | 10.269054 | 6.098222 | 11.800857 |
| H | 9.251675 | 6.437242 | 11.972347 |
| C | 8.692136 | 9.206807 | 9.505131 |
| H | 9.234107 | 8.590176 | 10.240169 |
| H | 9.107460 | 10.217315 | 9.540611 |
| C | 6.554831 | 8.042526 | 9.748748 |
| H | 5.514197 | 8.243763 | 10.013921 |
| H | 6.952011 | 7.297004 | 10.454435 |
| C | 6.961710 | 10.137467 | 10.916321 |
| H | 5.874135 | 10.254465 | 10.946488 |
| H | 7.401393 | 11.121601 | 10.724521 |
| C | 7.459242 | 9.613921 | 12.245119 |
| C | 6.695737 | 8.710766 | 12.993418 |
| H | 5.716833 | 8.410591 | 12.631803 |
| C | 7.165902 | 8.215785 | 14.208394 |
| H | 6.557280 | 7.524662 | 14.782353 |
| C | 8.407582 | 8.623053 | 14.694898 |
| H | 8.767882 | 8.248748 | 15.647115 |
| C | 9.175378 | 9.525929 | 13.960801 |
| H | 10.137739 | 9.854008 | 14.339495 |
| C | 8.702368 | 10.014809 | 12.744511 |
| H | 9.296840 | 10.728724 | 12.182119 |
| C | 4.888220 | 6.461942 | 7.988724 |
| C | 4.749911 | 5.125423 | 7.590536 |
| H | 5.622001 | 4.532566 | 7.337809 |

| | | | |
|---|---|---|---|
| C | 3.494829 | 4.522719 | 7.553499 |
| H | 3.407937 | 3.485762 | 7.248768 |
| C | 2.362971 | 5.247142 | 7.917999 |
| H | 1.384887 | 4.778965 | 7.895103 |
| C | 2.492781 | 6.573264 | 8.324176 |
| H | 1.616382 | 7.140190 | 8.618421 |
| C | 3.744697 | 7.181279 | 8.355990 |
| H | 3.819841 | 8.216944 | 8.665511 |
| C | 10.675887 | 9.489358 | 7.454783 |
| C | 11.939021 | 8.888788 | 7.414160 |
| H | 12.052164 | 7.819076 | 7.537648 |
| C | 13.077110 | 9.664188 | 7.202609 |
| H | 14.050214 | 9.186352 | 7.175292 |
| C | 12.968114 | 11.041017 | 7.029771 |
| H | 13.857293 | 11.641011 | 6.870277 |
| C | 11.712259 | 11.644552 | 7.061714 |
| H | 11.616565 | 12.716665 | 6.929041 |
| C | 10.572279 | 10.875115 | 7.271824 |
| H | 9.601354 | 11.354022 | 7.295512 |
| C | 7.832331 | 7.578307 | 3.123155 |
| H | 7.711758 | 8.259689 | 2.271840 |
| H | 8.617302 | 6.857186 | 2.886241 |
| C | 8.277784 | 10.311688 | 3.739631 |
| H | 8.527367 | 11.081860 | 4.485208 |
| H | 8.988362 | 10.389854 | 2.911794 |
| C | 6.281285 | 5.953920 | 2.201064 |
| H | 5.438462 | 5.331330 | 2.513793 |
| H | 7.144453 | 5.299680 | 2.053415 |
| C | 5.935808 | 6.648123 | 0.908553 |
| C | 6.935957 | 7.036747 | 0.009037 |
| H | 7.978384 | 6.854307 | 0.250904 |
| C | 6.605178 | 7.620230 | -1.211589 |
| H | 7.391420 | 7.909030 | -1.900915 |
| C | 5.267780 | 7.812242 | -1.555811 |
| H | 5.010343 | 8.256241 | -2.511704 |
| C | 4.263503 | 7.423546 | -0.670737 |
| H | 3.220508 | 7.559018 | -0.936319 |
| C | 4.597973 | 6.849279 | 0.553960 |
| H | 3.813007 | 6.525497 | 1.231222 |
| C | 5.877059 | 10.445165 | 4.170782 |
| H | 4.928906 | 10.599985 | 3.648041 |
| H | 5.976512 | 11.236240 | 4.929071 |
| C | 5.431767 | 7.603252 | 3.747287 |
| H | 4.667218 | 6.897283 | 4.080913 |
| H | 5.035245 | 8.156340 | 2.884309 |
| C | 6.892426 | 11.686656 | 2.378567 |
| H | 7.730398 | 11.626890 | 1.675708 |
| H | 7.064384 | 12.572165 | 3.012075 |
| C | 5.608389 | 11.873103 | 1.613043 |
| C | 5.146326 | 10.895675 | 0.725006 |
| H | 5.699111 | 9.968052 | 0.609980 |
| C | 3.988217 | 11.109248 | -0.017878 |
| H | 3.640418 | 10.342299 | -0.701861 |

| | | | |
|---|---|---|---|
| C | 3.280110 | 12.304410 | 0.110661 |
| H | 2.379497 | 12.470217 | -0.471293 |
| C | 3.732760 | 13.282805 | 0.992292 |
| H | 3.188165 | 14.214906 | 1.101803 |
| C | 4.888375 | 13.063092 | 1.740626 |
| H | 5.242405 | 13.826387 | 2.427240 |
| C | 10.272720 | 8.274034 | 4.379579 |
| C | 11.205119 | 9.226721 | 3.958184 |
| H | 10.906433 | 10.251008 | 3.767972 |
| C | 12.537793 | 8.861543 | 3.776773 |
| H | 13.253253 | 9.604029 | 3.440695 |
| C | 12.947271 | 7.551853 | 4.011779 |
| H | 13.983327 | 7.270858 | 3.857968 |
| C | 12.022656 | 6.602379 | 4.446563 |
| H | 12.336146 | 5.581708 | 4.635036 |
| C | 10.692018 | 6.961419 | 4.635069 |
| H | 9.978219 | 6.215862 | 4.973453 |
| C | 3.997748 | 9.137749 | 5.763148 |
| C | 2.852562 | 8.582685 | 5.182025 |
| H | 2.926199 | 7.878924 | 4.361673 |
| C | 1.590463 | 8.941107 | 5.650578 |
| H | 0.710177 | 8.501806 | 5.195071 |
| C | 1.460059 | 9.862745 | 6.686808 |
| H | 0.474705 | 10.142724 | 7.042716 |
| C | 2.598147 | 10.423069 | 7.263599 |
| H | 2.505112 | 11.141877 | 8.070309 |
| C | 3.862069 | 10.058017 | 6.810122 |
| H | 4.742792 | 10.485859 | 7.275031 |
| N | 8.845524 | 6.127687 | 9.070235 |
| N | 7.269258 | 9.300385 | 9.747633 |
| N | 6.611379 | 6.814633 | 3.379661 |
| N | 6.941131 | 10.456768 | 3.185945 |
| P | 6.538071 | 7.248920 | 8.061811 |
| P | 9.166794 | 8.530705 | 7.828849 |
| P | 8.492868 | 8.642271 | 4.516695 |
| P | 5.670815 | 8.842753 | 5.101522 |
| C | 7.913972 | 1.305413 | 2.334177 |
| C | 8.936795 | 2.189124 | 2.692671 |
| C | 8.656614 | 3.268318 | 3.528292 |
| C | 7.367380 | 3.458766 | 4.003208 |
| C | 6.343122 | 2.581277 | 3.656064 |
| C | 6.617330 | 1.507159 | 2.824599 |
| H | 9.946378 | 2.047419 | 2.329979 |
| H | 9.450689 | 3.952757 | 3.807754 |
| H | 5.338907 | 2.733274 | 4.036650 |
| H | 5.835497 | 0.811687 | 2.543062 |
| N | 7.075844 | 4.598140 | 4.862740 |
| H | 6.909562 | 5.552378 | 4.327652 |
| H | 6.235192 | 4.428654 | 5.416820 |
| H | 7.836836 | 4.760876 | 5.523692 |
| O | 8.081400 | 0.234890 | 1.525499 |
| C | 9.381808 | 0.002091 | 1.002745 |
| H | 10.105824 | -0.165211 | 1.805583 |

| | | | |
|---|---|---|---|
| H | 9.302600 | -0.892769 | 0.388507 |
| H | 9.714108 | 0.843332 | 0.386734 |
| Ni | 7.401327 | 8.607101 | 6.472644 |
| N | 7.210576 | 10.645391 | 7.009430 |
| C | 7.105771 | 11.766749 | 7.279751 |
| C | 6.969502 | 13.162853 | 7.631586 |
| H | 6.283369 | 13.262909 | 8.474744 |
| H | 7.944782 | 13.569674 | 7.907120 |
| H | 6.578730 | 13.721015 | 6.778130 |

**TABLE S12.** Cartesian coordinates of the optimized structure of $[Ni^{I}(P_2^{Ph}N_2^{Bn})_2(H\text{-}Asd)]^{2+}$ (i.e., $[Ni^{I}N\cdots HAsd]^{2+}$).

(– 4493.55375180 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | 8.381646 | 5.604346 | 8.673103 |
| H | 7.945484 | 4.882915 | 9.369930 |
| H | 8.821594 | 5.040864 | 7.833891 |
| C | 10.183995 | 7.254838 | 8.571735 |
| H | 10.688743 | 6.697430 | 7.765463 |
| H | 10.954193 | 7.698828 | 9.209900 |
| C | 10.210982 | 5.516953 | 10.225164 |
| H | 10.917080 | 4.946043 | 9.600117 |
| H | 9.544452 | 4.789416 | 10.699182 |
| C | 10.975250 | 6.256439 | 11.293810 |
| C | 12.354451 | 6.083263 | 11.425060 |
| H | 12.876544 | 5.439436 | 10.723008 |
| C | 13.059000 | 6.718214 | 12.447767 |
| H | 14.130321 | 6.571450 | 12.539120 |
| C | 12.388692 | 7.542462 | 13.348176 |
| H | 12.934656 | 8.036290 | 14.145265 |
| C | 11.011387 | 7.726400 | 13.221795 |
| H | 10.480565 | 8.367379 | 13.918185 |
| C | 10.310407 | 7.085571 | 12.204331 |
| H | 9.237323 | 7.225092 | 12.114666 |
| C | 8.359363 | 9.356031 | 9.326942 |
| H | 8.903059 | 9.009007 | 10.218845 |
| H | 8.483149 | 10.441211 | 9.263418 |
| C | 6.569405 | 7.679333 | 9.527762 |
| H | 5.483420 | 7.627258 | 9.645671 |
| H | 7.028882 | 7.196697 | 10.402631 |
| C | 6.249050 | 9.937604 | 10.358987 |
| H | 5.175978 | 9.745972 | 10.256524 |
| H | 6.432528 | 10.973680 | 10.058673 |
| C | 6.670606 | 9.750768 | 11.799292 |
| C | 6.083418 | 8.764752 | 12.600745 |
| H | 5.289533 | 8.146621 | 12.192840 |
| C | 6.487474 | 8.586270 | 13.922368 |
| H | 6.017983 | 7.822041 | 14.533327 |
| C | 7.483367 | 9.397847 | 14.464596 |
| H | 7.792309 | 9.266445 | 15.496287 |
| C | 8.072321 | 10.386734 | 13.677987 |
| H | 8.838593 | 11.030301 | 14.097578 |
| C | 7.667600 | 10.558988 | 12.355623 |
| H | 8.116375 | 11.341584 | 11.750533 |
| C | 5.592763 | 5.477877 | 7.910123 |
| C | 5.794667 | 4.093846 | 7.817679 |
| H | 6.794604 | 3.678148 | 7.877845 |

| | | | |
|---|---|---|---|
| C | 4.709499 | 3.233764 | 7.647814 |
| H | 4.880426 | 2.164835 | 7.578944 |
| C | 3.415069 | 3.741061 | 7.570211 |
| H | 2.573541 | 3.068412 | 7.445967 |
| C | 3.206320 | 5.117183 | 7.661065 |
| H | 2.200673 | 5.519975 | 7.607114 |
| C | 4.285684 | 5.980162 | 7.820849 |
| H | 4.111599 | 7.050857 | 7.877845 |
| C | 10.484496 | 9.886485 | 7.431702 |
| C | 11.824451 | 9.525573 | 7.246546 |
| H | 12.142441 | 8.499208 | 7.392871 |
| C | 12.765957 | 10.483308 | 6.871980 |
| H | 13.801597 | 10.191558 | 6.735096 |
| C | 12.382595 | 11.808447 | 6.683256 |
| H | 13.117794 | 12.552389 | 6.395822 |
| C | 11.049264 | 12.175384 | 6.862000 |
| H | 10.743556 | 13.205688 | 6.715745 |
| C | 10.104302 | 11.220525 | 7.226354 |
| H | 9.067751 | 11.518650 | 7.354274 |
| C | 7.770714 | 7.551166 | 2.809937 |
| H | 7.741230 | 8.358742 | 2.068777 |
| H | 8.339770 | 6.716503 | 2.394001 |
| C | 8.804569 | 9.982779 | 3.896865 |
| H | 9.224919 | 10.504751 | 4.772954 |
| H | 9.497274 | 10.118458 | 3.061650 |
| C | 5.853184 | 6.334872 | 1.938976 |
| H | 4.944354 | 5.837943 | 2.290161 |
| H | 6.576607 | 5.560645 | 1.670995 |
| C | 5.535855 | 7.189394 | 0.737193 |
| C | 6.520357 | 7.503131 | -0.207154 |
| H | 7.525206 | 7.111316 | -0.085419 |
| C | 6.217007 | 8.290075 | -1.316503 |
| H | 6.988204 | 8.513478 | -2.045876 |
| C | 4.920269 | 8.768016 | -1.500323 |
| H | 4.678042 | 9.365028 | -2.373288 |
| C | 3.929304 | 8.453388 | -0.571813 |
| H | 2.914985 | 8.810012 | -0.716220 |
| C | 4.238169 | 7.671736 | 0.539430 |
| H | 3.462464 | 7.419651 | 1.256068 |
| C | 6.539306 | 10.578597 | 4.571902 |
| H | 5.655992 | 11.104011 | 4.198275 |
| H | 6.916331 | 11.134858 | 5.447194 |
| C | 5.481088 | 8.070260 | 3.595355 |
| H | 4.532582 | 7.561052 | 3.786026 |
| H | 5.308063 | 8.832780 | 2.825345 |
| C | 7.692641 | 11.834541 | 2.878401 |
| H | 8.477540 | 11.720793 | 2.122958 |
| H | 8.061882 | 12.564898 | 3.617626 |
| C | 6.449058 | 12.380307 | 2.225714 |
| C | 5.787576 | 11.666023 | 1.220381 |
| H | 6.157100 | 10.687513 | 0.928109 |
| C | 4.668474 | 12.205047 | 0.591289 |
| H | 4.168885 | 11.640878 | -0.189628 |

| | | | |
|---|---|---|---|
| C | 4.197060 | 13.467181 | 0.955033 |
| H | 3.330212 | 13.887710 | 0.456183 |
| C | 4.848873 | 14.184908 | 1.954678 |
| H | 4.489747 | 15.167284 | 2.243041 |
| C | 5.965609 | 13.639528 | 2.586820 |
| H | 6.472607 | 14.197306 | 3.368951 |
| C | 10.414140 | 7.565644 | 3.933344 |
| C | 11.135431 | 7.983262 | 2.807159 |
| H | 10.713004 | 8.709229 | 2.119994 |
| C | 12.401253 | 7.462421 | 2.553443 |
| H | 12.951821 | 7.790362 | 1.678146 |
| C | 12.957457 | 6.518314 | 3.416225 |
| H | 13.943066 | 6.112590 | 3.214210 |
| C | 12.244383 | 6.093777 | 4.534649 |
| H | 12.673073 | 5.359902 | 5.208292 |
| C | 10.978432 | 6.616105 | 4.791835 |
| H | 10.421518 | 6.290457 | 5.665619 |
| C | 4.346624 | 9.369915 | 5.903981 |
| C | 3.214910 | 9.589962 | 5.107699 |
| H | 3.271052 | 9.471564 | 4.030292 |
| C | 2.008682 | 9.968277 | 5.691083 |
| H | 1.136080 | 10.129263 | 5.067258 |
| C | 1.923369 | 10.140495 | 7.072042 |
| H | 0.982707 | 10.430229 | 7.528462 |
| C | 3.048911 | 9.936080 | 7.867289 |
| H | 2.985624 | 10.072535 | 8.941798 |
| C | 4.256581 | 9.546900 | 7.289294 |
| H | 5.137567 | 9.389675 | 7.910385 |
| N | 9.362025 | 6.391049 | 9.404389 |
| N | 6.930469 | 9.080922 | 9.373703 |
| N | 6.425993 | 7.048617 | 3.118537 |
| N | 7.510165 | 10.511046 | 3.493288 |
| Ni | 7.683268 | 7.949309 | 6.297894 |
| P | 6.987438 | 6.657839 | 8.019999 |
| P | 9.200005 | 8.646081 | 7.817698 |
| P | 8.725426 | 8.163073 | 4.299260 |
| P | 5.967432 | 8.907210 | 5.191378 |
| C | 6.887853 | 1.280192 | 2.628686 |
| C | 8.069929 | 2.006645 | 2.797359 |
| C | 8.048595 | 3.209942 | 3.499493 |
| C | 6.858262 | 3.684416 | 4.032769 |
| C | 5.675001 | 2.966314 | 3.866809 |
| C | 5.690936 | 1.770379 | 3.167196 |
| H | 9.005889 | 1.649189 | 2.388164 |
| H | 8.969980 | 3.767691 | 3.631493 |
| H | 4.747369 | 3.330300 | 4.295008 |
| H | 4.780762 | 1.198029 | 3.031370 |
| N | 6.835201 | 4.948210 | 4.751242 |
| H | 6.623354 | 5.841246 | 4.105620 |
| H | 6.140051 | 4.930521 | 5.502687 |
| H | 7.730863 | 5.138799 | 5.204501 |
| O | 6.805283 | 0.103092 | 1.967685 |
| C | 7.999883 | -0.419664 | 1.404402 |

| | | | |
|---|---|---|---|
| H | 8.749376 | -0.609593 | 2.178422 |
| H | 7.721251 | -1.356730 | 0.925478 |
| H | 8.416533 | 0.263796 | 0.658359 |

**TABLE S13.** Cartesian coordinates of the optimized structure of $[Ni^{II}(P_2^{Ph}N_2^{Bn})(P_2^{Ph}HN_2^{Bn})(Asd)(MeCN)]^{3+}$ (i.e., $[Ni^{II}NH\cdots Asd]^{3+}$ with an MeCN ligand).

(– 4626.52884326 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | 7.403313 | 5.964718 | 8.304071 |
| H | 6.761239 | 5.321939 | 8.911996 |
| H | 7.542260 | 5.481843 | 7.326997 |
| C | 9.660175 | 6.849926 | 8.230487 |
| H | 9.880693 | 6.347979 | 7.274538 |
| H | 10.578935 | 6.878314 | 8.823806 |
| C | 9.165786 | 4.873583 | 9.496848 |
| H | 9.516435 | 4.254082 | 8.655914 |
| H | 8.317510 | 4.349574 | 9.948623 |
| C | 10.268145 | 5.004725 | 10.515931 |
| C | 11.481041 | 4.337877 | 10.329790 |
| H | 11.643297 | 3.774824 | 9.415481 |
| C | 12.476511 | 4.380334 | 11.305667 |
| H | 13.411137 | 3.852830 | 11.144650 |
| C | 12.271441 | 5.103352 | 12.478219 |
| H | 13.042628 | 5.137142 | 13.241144 |
| C | 11.067519 | 5.783579 | 12.667477 |
| H | 10.895984 | 6.345550 | 13.579868 |
| C | 10.073163 | 5.733671 | 11.694626 |
| H | 9.132247 | 6.250883 | 11.857422 |
| C | 8.750903 | 9.227488 | 9.603898 |
| H | 9.200513 | 8.510487 | 10.309649 |
| H | 9.277440 | 10.179121 | 9.709028 |
| C | 6.516537 | 8.275409 | 9.771786 |
| H | 5.498203 | 8.555961 | 10.046923 |
| H | 6.843475 | 7.470744 | 10.448137 |
| C | 7.111234 | 10.240151 | 11.065745 |
| H | 6.045825 | 10.488402 | 11.088908 |
| H | 7.670658 | 11.174380 | 10.960979 |
| C | 7.504812 | 9.546902 | 12.350491 |
| C | 6.602629 | 8.707907 | 13.014043 |
| H | 5.596489 | 8.589515 | 12.623195 |
| C | 6.971969 | 8.041784 | 14.180589 |
| H | 6.257025 | 7.399035 | 14.683817 |
| C | 8.253094 | 8.210172 | 14.704544 |
| H | 8.539716 | 7.699424 | 15.617990 |
| C | 9.158317 | 9.049598 | 14.056901 |
| H | 10.151352 | 9.198601 | 14.467889 |
| C | 8.785229 | 9.711590 | 12.888372 |
| H | 9.489201 | 10.377904 | 12.398428 |
| C | 4.766594 | 6.899325 | 7.860696 |
| C | 4.569573 | 5.796561 | 7.018686 |
| H | 5.403602 | 5.368879 | 6.475086 |

| | | | |
|---|---|---|---|
| C | 3.304968 | 5.233278 | 6.872968 |
| H | 3.174458 | 4.374072 | 6.224714 |
| C | 2.219124 | 5.771423 | 7.559757 |
| H | 1.233528 | 5.332296 | 7.451404 |
| C | 2.405442 | 6.876027 | 8.387800 |
| H | 1.565571 | 7.300441 | 8.926770 |
| C | 3.668817 | 7.442344 | 8.535814 |
| H | 3.781777 | 8.303402 | 9.182181 |
| C | 10.733853 | 9.469823 | 7.547232 |
| C | 11.943775 | 8.784419 | 7.390924 |
| H | 11.980129 | 7.702284 | 7.418080 |
| C | 13.126673 | 9.493911 | 7.193753 |
| H | 14.059266 | 8.953191 | 7.076822 |
| C | 13.114007 | 10.885331 | 7.145554 |
| H | 14.038533 | 11.431368 | 6.992474 |
| C | 11.910283 | 11.572639 | 7.292768 |
| H | 11.891169 | 12.656215 | 7.256232 |
| C | 10.725448 | 10.870800 | 7.490801 |
| H | 9.795765 | 11.416121 | 7.606992 |
| C | 7.808508 | 7.642864 | 3.228562 |
| H | 7.545212 | 8.253676 | 2.362522 |
| H | 8.584595 | 6.927521 | 2.957130 |
| C | 8.235413 | 10.399711 | 3.648839 |
| H | 8.471161 | 11.218826 | 4.344717 |
| H | 8.935897 | 10.445705 | 2.810988 |
| C | 6.247484 | 5.872705 | 2.483752 |
| H | 5.506105 | 5.205635 | 2.925481 |
| H | 7.159363 | 5.302963 | 2.304299 |
| C | 5.731030 | 6.493216 | 1.221275 |
| C | 6.611174 | 6.888662 | 0.206969 |
| H | 7.681179 | 6.775201 | 0.346879 |
| C | 6.120544 | 7.391471 | -0.995496 |
| H | 6.810721 | 7.684528 | -1.778948 |
| C | 4.745478 | 7.493792 | -1.201336 |
| H | 4.364682 | 7.867647 | -2.145475 |
| C | 3.861673 | 7.096860 | -0.199650 |
| H | 2.791147 | 7.164560 | -0.358782 |
| C | 4.352456 | 6.599343 | 1.004539 |
| H | 3.662716 | 6.264056 | 1.772797 |
| C | 5.854118 | 10.528148 | 4.121275 |
| H | 4.887844 | 10.638782 | 3.621814 |
| H | 5.971995 | 11.371856 | 4.820307 |
| C | 5.414243 | 7.617723 | 4.019231 |
| H | 4.734704 | 6.912001 | 4.501099 |
| H | 4.942335 | 8.006649 | 3.113627 |
| C | 6.795996 | 11.639669 | 2.211147 |
| H | 7.627358 | 11.550489 | 1.504234 |
| H | 6.948131 | 12.574838 | 2.773611 |
| C | 5.498311 | 11.726530 | 1.452903 |
| C | 5.092625 | 10.700354 | 0.592352 |
| H | 5.701004 | 9.805790 | 0.492879 |
| C | 3.918307 | 10.823906 | -0.145001 |
| H | 3.618877 | 10.018934 | -0.808428 |

| | | | |
|---|---|---|---|
| C | 3.135913 | 11.974055 | -0.035906 |
| H | 2.223161 | 12.068525 | -0.614799 |
| C | 3.531866 | 12.999816 | 0.818780 |
| H | 2.930149 | 13.897957 | 0.909139 |
| C | 4.705757 | 12.871604 | 1.559517 |
| H | 5.020539 | 13.672959 | 2.221622 |
| C | 10.293032 | 8.461096 | 4.296372 |
| C | 11.178010 | 9.474308 | 3.913003 |
| H | 10.835081 | 10.495772 | 3.798422 |
| C | 12.516568 | 9.173305 | 3.670050 |
| H | 13.193101 | 9.963269 | 3.363636 |
| C | 12.980002 | 7.867461 | 3.807528 |
| H | 14.021023 | 7.636713 | 3.608760 |
| C | 12.103279 | 6.858265 | 4.202929 |
| H | 12.457237 | 5.839375 | 4.312647 |
| C | 10.766669 | 7.152766 | 4.451532 |
| H | 10.095393 | 6.358472 | 4.759982 |
| C | 4.041188 | 9.361728 | 5.886744 |
| C | 2.869880 | 8.849846 | 5.317741 |
| H | 2.905555 | 8.133497 | 4.504974 |
| C | 1.630004 | 9.270379 | 5.794183 |
| H | 0.725632 | 8.869809 | 5.350342 |
| C | 1.551304 | 10.209368 | 6.820420 |
| H | 0.582102 | 10.538875 | 7.177971 |
| C | 2.716856 | 10.722149 | 7.385540 |
| H | 2.662270 | 11.451454 | 8.186422 |
| C | 3.959297 | 10.294651 | 6.927586 |
| H | 4.864927 | 10.684346 | 7.379724 |
| N | 8.650533 | 6.163125 | 9.014536 |
| N | 7.340585 | 9.465299 | 9.832643 |
| N | 6.615575 | 6.842346 | 3.606277 |
| N | 6.888974 | 10.475595 | 3.109319 |
| P | 6.460349 | 7.550559 | 8.060961 |
| P | 9.171186 | 8.597673 | 7.897138 |
| P | 8.514723 | 8.788260 | 4.531743 |
| P | 5.691950 | 9.019144 | 5.198655 |
| C | 8.472663 | 1.364582 | 2.275025 |
| C | 9.466066 | 2.269640 | 2.652335 |
| C | 9.162240 | 3.310444 | 3.531208 |
| C | 7.877709 | 3.459128 | 4.051241 |
| C | 6.885536 | 2.550246 | 3.663120 |
| C | 7.179558 | 1.515305 | 2.788401 |
| H | 10.476339 | 2.175174 | 2.274188 |
| H | 9.946126 | 4.002435 | 3.823687 |
| H | 5.880411 | 2.650862 | 4.060898 |
| H | 6.412743 | 0.807451 | 2.493500 |
| N | 7.564060 | 4.526204 | 4.938440 |
| H | 6.921496 | 6.149928 | 4.349774 |
| H | 6.824899 | 4.242521 | 5.573689 |
| H | 8.370222 | 4.773415 | 5.503723 |
| O | 8.663559 | 0.319084 | 1.425892 |
| C | 9.972104 | 0.128327 | 0.915107 |
| H | 10.693221 | -0.040598 | 1.721197 |

| | | | |
|---|---|---|---|
| H | 9.923005 | -0.753516 | 0.278444 |
| H | 10.296540 | 0.990010 | 0.322322 |
| Ni | 7.440577 | 8.829134 | 6.518750 |
| N | 7.355413 | 10.876356 | 6.930713 |
| C | 7.301318 | 12.009023 | 7.165183 |
| C | 7.234163 | 13.422813 | 7.463892 |
| H | 6.511769 | 13.594158 | 8.264152 |
| H | 8.217733 | 13.777295 | 7.778530 |
| H | 6.923639 | 13.970608 | 6.571880 |

**TABLE S14.** Cartesian coordinates of the optimized structure of $[Ni^{I}(P_2^{Ph}N_2^{Bn})(P_2^{Ph}HN_2^{Bn})(Asd)]^{2+}$ (i.e., $[Ni^{I}NH\cdots Asd]^{2+}$).

(– 4493.55875534 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | 8.406859 | 5.639889 | 8.749976 |
| H | 7.988701 | 4.914581 | 9.453519 |
| H | 8.848847 | 5.079792 | 7.909921 |
| C | 10.189750 | 7.305863 | 8.621198 |
| H | 10.693512 | 6.743863 | 7.817534 |
| H | 10.959934 | 7.765482 | 9.248044 |
| C | 10.240664 | 5.590660 | 10.298012 |
| H | 10.954087 | 5.022803 | 9.678635 |
| H | 9.583694 | 4.859135 | 10.778966 |
| C | 10.994655 | 6.348076 | 11.361624 |
| C | 12.373810 | 6.182509 | 11.503116 |
| H | 12.903493 | 5.535319 | 10.809869 |
| C | 13.068838 | 6.828171 | 12.525661 |
| H | 14.140105 | 6.686363 | 12.625137 |
| C | 12.388916 | 7.656168 | 13.415367 |
| H | 12.926904 | 8.158309 | 14.212679 |
| C | 11.011742 | 7.833174 | 13.278226 |
| H | 10.473253 | 8.476647 | 13.966453 |
| C | 10.320212 | 7.181587 | 12.261045 |
| H | 9.247085 | 7.315359 | 12.163717 |
| C | 8.348705 | 9.397051 | 9.365400 |
| H | 8.900324 | 9.064191 | 10.257646 |
| H | 8.462260 | 10.482401 | 9.288326 |
| C | 6.580569 | 7.704044 | 9.602667 |
| H | 5.497911 | 7.642452 | 9.741880 |
| H | 7.061145 | 7.240775 | 10.476547 |
| C | 6.231676 | 9.974149 | 10.390181 |
| H | 5.160164 | 9.776106 | 10.282654 |
| H | 6.412869 | 11.006477 | 10.076080 |
| C | 6.643671 | 9.808933 | 11.835816 |
| C | 6.047952 | 8.837235 | 12.648354 |
| H | 5.254022 | 8.216298 | 12.244736 |
| C | 6.444902 | 8.675321 | 13.974207 |
| H | 5.969122 | 7.921793 | 14.593515 |
| C | 7.442027 | 9.489929 | 14.509565 |
| H | 7.745833 | 9.371663 | 15.544377 |
| C | 8.038682 | 10.465493 | 13.712158 |
| H | 8.805488 | 11.111621 | 14.126751 |
| C | 7.640722 | 10.621467 | 12.385704 |
| H | 8.095280 | 11.393997 | 11.772098 |
| C | 5.611692 | 5.444417 | 8.074315 |
| C | 5.862353 | 4.069328 | 7.969760 |
| H | 6.880297 | 3.696048 | 7.940941 |

| | | | |
|---|---|---|---|
| C | 4.806862 | 3.159489 | 7.917199 |
| H | 5.017220 | 2.098021 | 7.843738 |
| C | 3.490487 | 3.610683 | 7.968566 |
| H | 2.670223 | 2.901549 | 7.937760 |
| C | 3.232303 | 4.977962 | 8.060369 |
| H | 2.209501 | 5.337381 | 8.098614 |
| C | 4.282116 | 5.891090 | 8.102761 |
| H | 4.065601 | 6.954072 | 8.165645 |
| C | 10.451534 | 9.921097 | 7.439329 |
| C | 11.792519 | 9.567185 | 7.248125 |
| H | 12.118075 | 8.544500 | 7.402319 |
| C | 12.725408 | 10.527786 | 6.859951 |
| H | 13.762158 | 10.241669 | 6.719586 |
| C | 12.332133 | 11.848855 | 6.663150 |
| H | 13.060737 | 12.595198 | 6.365274 |
| C | 10.997438 | 12.208522 | 6.846694 |
| H | 10.684230 | 13.235648 | 6.694186 |
| C | 10.060772 | 11.250444 | 7.224376 |
| H | 9.023293 | 11.542816 | 7.357596 |
| C | 7.763498 | 7.477175 | 2.901905 |
| H | 7.699261 | 8.246449 | 2.130765 |
| H | 8.298812 | 6.610762 | 2.511996 |
| C | 8.799038 | 9.928441 | 3.917378 |
| H | 9.223522 | 10.471212 | 4.778269 |
| H | 9.488140 | 10.040487 | 3.076264 |
| C | 5.790293 | 6.254794 | 2.051427 |
| H | 4.832427 | 5.874542 | 2.409250 |
| H | 6.461300 | 5.408260 | 1.896524 |
| C | 5.619175 | 7.055378 | 0.793854 |
| C | 6.625126 | 7.069342 | -0.179037 |
| H | 7.541770 | 6.513653 | -0.009394 |
| C | 6.450791 | 7.773071 | -1.368153 |
| H | 7.234971 | 7.768874 | -2.117996 |
| C | 5.264816 | 8.468203 | -1.598980 |
| H | 5.121426 | 9.005852 | -2.530229 |
| C | 4.254061 | 8.454221 | -0.639001 |
| H | 3.321936 | 8.976818 | -0.824854 |
| C | 4.429594 | 7.750510 | 0.550182 |
| H | 3.629937 | 7.722302 | 1.284174 |
| C | 6.547061 | 10.574137 | 4.594258 |
| H | 5.669016 | 11.103133 | 4.213345 |
| H | 6.947048 | 11.149513 | 5.445538 |
| C | 5.453220 | 8.079585 | 3.687785 |
| H | 4.496164 | 7.587346 | 3.866398 |
| H | 5.339828 | 8.802673 | 2.877866 |
| C | 7.692558 | 11.742655 | 2.832537 |
| H | 8.470443 | 11.587298 | 2.077465 |
| H | 8.077568 | 12.497837 | 3.537056 |
| C | 6.451801 | 12.275915 | 2.164352 |
| C | 5.731975 | 11.498716 | 1.250326 |
| H | 6.049035 | 10.480756 | 1.044834 |
| C | 4.619404 | 12.024254 | 0.599279 |
| H | 4.070970 | 11.408603 | -0.106215 |

| | | | |
|---|---|---|---|
| C | 4.216780 | 13.338022 | 0.841183 |
| H | 3.355218 | 13.745973 | 0.323118 |
| C | 4.928853 | 14.120105 | 1.747204 |
| H | 4.623146 | 15.142393 | 1.944750 |
| C | 6.036715 | 13.587520 | 2.405575 |
| H | 6.591404 | 14.197727 | 3.112753 |
| C | 10.393086 | 7.486204 | 4.027277 |
| C | 11.148306 | 7.895814 | 2.920960 |
| H | 10.759499 | 8.638673 | 2.232412 |
| C | 12.405241 | 7.343681 | 2.690098 |
| H | 12.982981 | 7.667252 | 1.830957 |
| C | 12.916277 | 6.376230 | 3.554958 |
| H | 13.895229 | 5.946894 | 3.369886 |
| C | 12.167772 | 5.959550 | 4.653236 |
| H | 12.562341 | 5.207778 | 5.327929 |
| C | 10.911565 | 6.513729 | 4.889281 |
| H | 10.328365 | 6.194687 | 5.748010 |
| C | 4.333169 | 9.395571 | 5.966932 |
| C | 3.228513 | 9.680753 | 5.153268 |
| H | 3.311930 | 9.621595 | 4.072572 |
| C | 2.014007 | 10.048723 | 5.724982 |
| H | 1.161732 | 10.261867 | 5.089060 |
| C | 1.896057 | 10.149110 | 7.110785 |
| H | 0.949350 | 10.434294 | 7.557292 |
| C | 2.995507 | 9.881805 | 7.923195 |
| H | 2.906943 | 9.967045 | 9.001098 |
| C | 4.210615 | 9.499222 | 7.356822 |
| H | 5.073188 | 9.297671 | 7.989221 |
| N | 9.380534 | 6.445248 | 9.468656 |
| N | 6.923627 | 9.106935 | 9.421871 |
| N | 6.385910 | 7.015607 | 3.223803 |
| N | 7.502573 | 10.447684 | 3.505898 |
| Ni | 7.659101 | 7.943092 | 6.363422 |
| P | 6.981306 | 6.660097 | 8.104548 |
| P | 9.184038 | 8.675480 | 7.859650 |
| P | 8.718026 | 8.124560 | 4.375392 |
| P | 5.958774 | 8.932959 | 5.271623 |
| C | 6.764632 | 1.575343 | 2.090805 |
| C | 7.939796 | 2.307871 | 2.266355 |
| C | 7.975652 | 3.353277 | 3.190089 |
| C | 6.853874 | 3.682085 | 3.950426 |
| C | 5.681648 | 2.936448 | 3.774651 |
| C | 5.638498 | 1.897705 | 2.856347 |
| H | 8.832477 | 2.068191 | 1.701589 |
| H | 8.896057 | 3.914819 | 3.320362 |
| H | 4.797203 | 3.176851 | 4.356523 |
| H | 4.730100 | 1.321048 | 2.720720 |
| N | 6.872013 | 4.803275 | 4.820158 |
| H | 6.490220 | 6.252213 | 3.974461 |
| H | 6.247765 | 4.687597 | 5.614923 |
| H | 7.802737 | 4.991431 | 5.180934 |
| O | 6.621915 | 0.541825 | 1.217933 |
| C | 7.767074 | 0.149334 | 0.480624 |

| | | | |
|---|---|---|---|
| H | 8.573553 | -0.181004 | 1.143761 |
| H | 7.448604 | -0.682335 | -0.146336 |
| H | 8.133926 | 0.965062 | -0.150942 |

**TABLE S15.** Cartesian coordinates of the optimized structure of $[Ni^{II}(P_2^{Ph}N_2^{Bn})(P_2^{Ph}HN_2^{Bn})(Anl)(MeCN)]^{3+}$ (i.e., $[Ni^{II}NH\cdots Anl]^{3+}$ with an MeCN ligand).

(– 4604.17708559 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | 7.404524 | 5.982295 | 8.272086 |
| H | 6.762993 | 5.329570 | 8.869948 |
| H | 7.545463 | 5.514364 | 7.287615 |
| C | 9.659846 | 6.872269 | 8.213889 |
| H | 9.883298 | 6.382327 | 7.252558 |
| H | 10.577520 | 6.895597 | 8.809180 |
| C | 9.167600 | 4.878651 | 9.453408 |
| H | 9.519226 | 4.269559 | 8.605175 |
| H | 8.320108 | 4.347757 | 9.898696 |
| C | 10.269915 | 5.000296 | 10.473725 |
| C | 11.482142 | 4.333519 | 10.283085 |
| H | 11.643856 | 3.775853 | 9.365352 |
| C | 12.478238 | 4.369910 | 11.258593 |
| H | 13.412442 | 3.842796 | 11.093888 |
| C | 12.274813 | 5.086927 | 12.435120 |
| H | 13.046813 | 5.116360 | 13.197402 |
| C | 11.071535 | 5.766981 | 12.628895 |
| H | 10.901092 | 6.324821 | 13.544025 |
| C | 10.076406 | 5.722814 | 11.656596 |
| H | 9.136144 | 6.240078 | 11.822762 |
| C | 8.747482 | 9.233696 | 9.614410 |
| H | 9.197810 | 8.510038 | 10.312912 |
| H | 9.272556 | 10.184909 | 9.730211 |
| C | 6.516157 | 8.274196 | 9.770644 |
| H | 5.497195 | 8.547706 | 10.050467 |
| H | 6.847257 | 7.462747 | 10.436617 |
| C | 7.105096 | 10.224445 | 11.088361 |
| H | 6.039371 | 10.471006 | 11.114157 |
| H | 7.663977 | 11.160290 | 10.996587 |
| C | 7.498674 | 9.514172 | 12.363784 |
| C | 6.595792 | 8.668299 | 13.017498 |
| H | 5.588758 | 8.557135 | 12.626707 |
| C | 6.965330 | 7.985665 | 14.174451 |
| H | 6.249665 | 7.338092 | 14.670369 |
| C | 8.247681 | 8.144310 | 14.698426 |
| H | 8.534901 | 7.621480 | 15.604863 |
| C | 9.153764 | 8.990128 | 14.060370 |
| H | 10.148033 | 9.130742 | 14.471386 |
| C | 8.780355 | 9.669014 | 12.901701 |
| H | 9.485043 | 10.340157 | 12.419475 |
| C | 4.765920 | 6.924630 | 7.839919 |
| C | 4.569045 | 5.833514 | 6.982818 |
| H | 5.404538 | 5.412493 | 6.436123 |

| | | | |
|---|---|---|---|
| C | 3.303672 | 5.274838 | 6.826583 |
| H | 3.172542 | 4.425788 | 6.165219 |
| C | 2.217686 | 5.804482 | 7.519729 |
| H | 1.231816 | 5.367879 | 7.403749 |
| C | 2.404123 | 6.897019 | 8.363635 |
| H | 1.564148 | 7.314603 | 8.907809 |
| C | 3.667937 | 7.459893 | 8.520794 |
| H | 3.780948 | 8.311520 | 9.179516 |
| C | 10.729371 | 9.500738 | 7.557755 |
| C | 11.939333 | 8.817327 | 7.392654 |
| H | 11.976188 | 7.735013 | 7.409920 |
| C | 13.121297 | 9.529070 | 7.198387 |
| H | 14.053869 | 8.989958 | 7.073974 |
| C | 13.107651 | 10.920870 | 7.162127 |
| H | 14.031449 | 11.468776 | 7.011431 |
| C | 11.903945 | 11.606284 | 7.318422 |
| H | 11.884206 | 12.690140 | 7.292017 |
| C | 10.719990 | 10.902221 | 7.513758 |
| H | 9.790452 | 11.446035 | 7.638018 |
| C | 7.798788 | 7.666283 | 3.252052 |
| H | 7.529885 | 8.266237 | 2.380562 |
| H | 8.567209 | 6.941599 | 2.984686 |
| C | 8.236114 | 10.425212 | 3.644237 |
| H | 8.478283 | 11.250097 | 4.330941 |
| H | 8.933403 | 10.459720 | 2.803158 |
| C | 6.237069 | 5.874146 | 2.550900 |
| H | 5.488785 | 5.224114 | 3.005251 |
| H | 7.149153 | 5.298066 | 2.396342 |
| C | 5.733309 | 6.468539 | 1.270749 |
| C | 6.621670 | 6.846322 | 0.256941 |
| H | 7.690429 | 6.732870 | 0.405550 |
| C | 6.140443 | 7.333863 | -0.955498 |
| H | 6.836897 | 7.613368 | -1.738251 |
| C | 4.767009 | 7.437590 | -1.171633 |
| H | 4.393774 | 7.799518 | -2.123319 |
| C | 3.875335 | 7.055605 | -0.171108 |
| H | 2.806089 | 7.123719 | -0.338354 |
| C | 4.356541 | 6.574068 | 1.043282 |
| H | 3.661315 | 6.253108 | 1.812591 |
| C | 5.859089 | 10.576083 | 4.127900 |
| H | 4.891280 | 10.694698 | 3.633327 |
| H | 5.991966 | 11.423816 | 4.819057 |
| C | 5.399691 | 7.676356 | 4.029097 |
| H | 4.699367 | 6.981956 | 4.497065 |
| H | 4.959198 | 8.068219 | 3.109600 |
| C | 6.792711 | 11.648816 | 2.192456 |
| H | 7.622971 | 11.548206 | 1.485997 |
| H | 6.944410 | 12.593384 | 2.738913 |
| C | 5.493305 | 11.719504 | 1.435755 |
| C | 5.095351 | 10.682995 | 0.583994 |
| H | 5.712715 | 9.794081 | 0.489333 |
| C | 3.917526 | 10.789196 | -0.150320 |
| H | 3.623965 | 9.976654 | -0.807236 |

| | | | |
|---|---|---|---|
| C | 3.123713 | 11.932085 | -0.046441 |
| H | 2.208179 | 12.012994 | -0.622952 |
| C | 3.512044 | 12.968167 | 0.799258 |
| H | 2.901383 | 13.860755 | 0.884729 |
| C | 4.689936 | 12.857500 | 1.536455 |
| H | 4.999672 | 13.666844 | 2.191209 |
| C | 10.288417 | 8.481617 | 4.298900 |
| C | 11.177082 | 9.491962 | 3.916543 |
| H | 10.837472 | 10.514800 | 3.803582 |
| C | 12.514209 | 9.185945 | 3.672318 |
| H | 13.193962 | 9.973408 | 3.366676 |
| C | 12.972145 | 7.877978 | 3.807784 |
| H | 14.012146 | 7.643188 | 3.608455 |
| C | 12.091250 | 6.871329 | 4.200611 |
| H | 12.441205 | 5.850658 | 4.306792 |
| C | 10.755652 | 7.170240 | 4.449975 |
| H | 10.081119 | 6.376467 | 4.754354 |
| C | 4.039256 | 9.424735 | 5.905620 |
| C | 2.863940 | 8.927990 | 5.331287 |
| H | 2.893786 | 8.222229 | 4.509089 |
| C | 1.627457 | 9.351266 | 5.813691 |
| H | 0.719801 | 8.963672 | 5.364970 |
| C | 1.556107 | 10.278885 | 6.850836 |
| H | 0.589599 | 10.610713 | 7.213432 |
| C | 2.725602 | 10.777888 | 7.420117 |
| H | 2.676681 | 11.498856 | 8.228861 |
| C | 3.964798 | 10.346856 | 6.956661 |
| H | 4.873512 | 10.724374 | 7.412683 |
| N | 8.650282 | 6.173162 | 8.986930 |
| N | 7.336357 | 9.466343 | 9.844884 |
| N | 6.599654 | 6.879235 | 3.647074 |
| N | 6.887152 | 10.500184 | 3.110623 |
| P | 6.460044 | 7.570696 | 8.051094 |
| P | 9.168737 | 8.622979 | 7.901366 |
| P | 8.513560 | 8.820535 | 4.540498 |
| P | 5.685915 | 9.074657 | 5.212463 |
| C | 8.513243 | 1.294144 | 2.275799 |
| C | 9.497143 | 2.215698 | 2.667824 |
| C | 9.180473 | 3.238071 | 3.545337 |
| C | 7.879904 | 3.356007 | 4.060158 |
| C | 6.894697 | 2.442481 | 3.652099 |
| C | 7.206688 | 1.420609 | 2.773322 |
| H | 10.506909 | 2.121807 | 2.286885 |
| H | 9.946594 | 3.941414 | 3.854197 |
| H | 5.888126 | 2.531259 | 4.046345 |
| H | 6.444163 | 0.711942 | 2.472853 |
| N | 7.559395 | 4.384606 | 4.946490 |
| H | 6.884768 | 6.242482 | 4.420738 |
| H | 6.779279 | 4.146212 | 5.547563 |
| H | 8.350413 | 4.684719 | 5.503900 |
| Ni | 7.438200 | 8.868525 | 6.526175 |
| N | 7.360224 | 10.908875 | 6.941588 |
| C | 7.303372 | 12.043170 | 7.167252 |

| | | | |
|---|---|---|---|
| C | 7.230788 | 13.459182 | 7.453277 |
| H | 6.505830 | 13.635220 | 8.250185 |
| H | 8.212223 | 13.820368 | 7.766873 |
| H | 6.920772 | 13.997922 | 6.555512 |
| C | 8.842864 | 0.229765 | 1.391023 |
| N | 9.115014 | -0.642411 | 0.669188 |

**TABLE S16.** Cartesian coordinates of the optimized structure of $[Ni^{I}(P_2^{Ph}N_2^{Bn})(P_2^{Ph}HN_2^{Bn})(Asd)]^{2+}$ (i.e., $[Ni^{I}NH\cdots Anl]^{2+}$).

(– 4471.20746912 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | 8.390437 | 5.637373 | 8.747061 |
| H | 7.971252 | 4.910069 | 9.447894 |
| H | 8.828063 | 5.080147 | 7.902873 |
| C | 10.180466 | 7.297055 | 8.623971 |
| H | 10.682503 | 6.737486 | 7.817623 |
| H | 10.952036 | 7.751611 | 9.252829 |
| C | 10.227647 | 5.572554 | 10.291057 |
| H | 10.936160 | 5.003462 | 9.667135 |
| H | 9.568553 | 4.842631 | 10.771563 |
| C | 10.989343 | 6.323185 | 11.353874 |
| C | 12.368711 | 6.153237 | 11.487693 |
| H | 12.892779 | 5.506168 | 10.790096 |
| C | 13.070981 | 6.794962 | 12.507752 |
| H | 14.142381 | 6.650204 | 12.601301 |
| C | 12.398211 | 7.623180 | 13.402670 |
| H | 12.942168 | 8.122239 | 14.197864 |
| C | 11.020816 | 7.804319 | 13.273361 |
| H | 10.487973 | 8.448177 | 13.965577 |
| C | 10.322078 | 7.156627 | 12.258669 |
| H | 9.248865 | 7.293717 | 12.167091 |
| C | 8.349768 | 9.393051 | 9.379551 |
| H | 8.902708 | 9.055580 | 10.269290 |
| H | 8.467400 | 10.478172 | 9.305374 |
| C | 6.575780 | 7.706044 | 9.614821 |
| H | 5.493305 | 7.648116 | 9.756820 |
| H | 7.057122 | 7.236819 | 10.485096 |
| C | 6.239812 | 9.973275 | 10.415698 |
| H | 5.167176 | 9.778561 | 10.313829 |
| H | 6.421631 | 11.006504 | 10.104884 |
| C | 6.660410 | 9.801100 | 11.858033 |
| C | 6.067299 | 8.827842 | 12.670603 |
| H | 5.269777 | 8.209927 | 12.269470 |
| C | 6.470989 | 8.660978 | 13.993818 |
| H | 5.996978 | 7.906513 | 14.613348 |
| C | 7.472779 | 9.471742 | 14.526259 |
| H | 7.782009 | 9.349563 | 15.558993 |
| C | 8.067348 | 10.448403 | 13.728655 |
| H | 8.838077 | 11.091277 | 14.141041 |
| C | 7.662544 | 10.609424 | 12.404897 |
| H | 8.115346 | 11.383039 | 11.791366 |
| C | 5.589856 | 5.458681 | 8.080819 |
| C | 5.830341 | 4.081975 | 7.973761 |
| H | 6.845538 | 3.701362 | 7.942727 |

| | | | |
|---|---|---|---|
| C | 4.767935 | 3.179999 | 7.921681 |
| H | 4.970220 | 2.117142 | 7.846060 |
| C | 3.455056 | 3.640722 | 7.977182 |
| H | 2.629468 | 2.937822 | 7.946748 |
| C | 3.207136 | 5.009620 | 8.072701 |
| H | 2.187010 | 5.376060 | 8.114725 |
| C | 4.263652 | 5.914916 | 8.114230 |
| H | 4.055425 | 6.979325 | 8.180498 |
| C | 10.448996 | 9.916049 | 7.450257 |
| C | 11.788612 | 9.558893 | 7.255707 |
| H | 12.111665 | 8.534942 | 7.406795 |
| C | 12.723373 | 10.517892 | 6.867969 |
| H | 13.759036 | 10.229269 | 6.724796 |
| C | 12.333274 | 11.840431 | 6.674821 |
| H | 13.063254 | 12.585439 | 6.376984 |
| C | 11.000017 | 12.203397 | 6.862191 |
| H | 10.689305 | 13.231736 | 6.712825 |
| C | 10.061509 | 11.247099 | 7.239742 |
| H | 9.025195 | 11.542323 | 7.375774 |
| C | 7.747448 | 7.496753 | 2.914315 |
| H | 7.677225 | 8.270817 | 2.148958 |
| H | 8.276649 | 6.630861 | 2.515554 |
| C | 8.798961 | 9.938400 | 3.939433 |
| H | 9.218718 | 10.475485 | 4.805881 |
| H | 9.494800 | 10.051783 | 3.104244 |
| C | 5.764799 | 6.273824 | 2.071805 |
| H | 4.812268 | 5.889491 | 2.438822 |
| H | 6.439747 | 5.431876 | 1.910061 |
| C | 5.580167 | 7.076938 | 0.818403 |
| C | 6.578983 | 7.100135 | -0.161427 |
| H | 7.500248 | 6.549517 | -0.000966 |
| C | 6.390898 | 7.806677 | -1.346757 |
| H | 7.169270 | 7.809725 | -2.102568 |
| C | 5.198194 | 8.493811 | -1.566789 |
| H | 5.043665 | 9.032575 | -2.495585 |
| C | 4.194429 | 8.470510 | -0.599602 |
| H | 3.255961 | 8.984070 | -0.778276 |
| C | 4.383583 | 7.763968 | 0.585710 |
| H | 3.589868 | 7.727451 | 1.325621 |
| C | 6.544916 | 10.594622 | 4.601731 |
| H | 5.669864 | 11.121424 | 4.210445 |
| H | 6.940508 | 11.175914 | 5.450923 |
| C | 5.437412 | 8.106809 | 3.706609 |
| H | 4.479678 | 7.616709 | 3.887205 |
| H | 5.326745 | 8.826815 | 2.894013 |
| C | 7.692684 | 11.747738 | 2.835139 |
| H | 8.498026 | 11.599090 | 2.108169 |
| H | 8.036310 | 12.522279 | 3.539799 |
| C | 6.463903 | 12.237364 | 2.113653 |
| C | 5.802459 | 11.421010 | 1.190051 |
| H | 6.155393 | 10.408161 | 1.021348 |
| C | 4.706232 | 11.900353 | 0.478976 |
| H | 4.208609 | 11.250310 | -0.233777 |

| | | | |
|---|---|---|---|
| C | 4.261300 | 13.208511 | 0.672370 |
| H | 3.410970 | 13.583469 | 0.112282 |
| C | 4.915152 | 14.029366 | 1.587897 |
| H | 4.575127 | 15.047353 | 1.747076 |
| C | 6.006679 | 13.542744 | 2.306613 |
| H | 6.514452 | 14.184570 | 3.020815 |
| C | 10.380336 | 7.486775 | 4.032305 |
| C | 11.131613 | 7.896657 | 2.923361 |
| H | 10.741181 | 8.641170 | 2.237521 |
| C | 12.386336 | 7.342225 | 2.686371 |
| H | 12.961001 | 7.665436 | 1.825056 |
| C | 12.899173 | 6.372912 | 3.548068 |
| H | 13.876489 | 5.941894 | 3.358360 |
| C | 12.154508 | 5.956049 | 4.648857 |
| H | 12.550542 | 5.202657 | 5.320836 |
| C | 10.900061 | 6.511826 | 4.890674 |
| H | 10.319523 | 6.192476 | 5.751023 |
| C | 4.332556 | 9.426422 | 5.990824 |
| C | 3.224195 | 9.714175 | 5.183147 |
| H | 3.301496 | 9.655603 | 4.101964 |
| C | 2.013519 | 10.083700 | 5.761931 |
| H | 1.157871 | 10.298812 | 5.131202 |
| C | 1.903527 | 10.183203 | 7.148449 |
| H | 0.959712 | 10.469466 | 7.600417 |
| C | 3.006971 | 9.913742 | 7.954746 |
| H | 2.924361 | 9.998350 | 9.033147 |
| C | 4.218241 | 9.529207 | 7.381547 |
| H | 5.084009 | 9.324544 | 8.008793 |
| N | 9.369093 | 6.434902 | 9.467827 |
| N | 6.923770 | 9.108352 | 9.439445 |
| N | 6.367540 | 7.038558 | 3.240833 |
| N | 7.506440 | 10.459220 | 3.520167 |
| Ni | 7.648240 | 7.952706 | 6.373797 |
| P | 6.966797 | 6.666545 | 8.110966 |
| P | 9.178590 | 8.673177 | 7.869732 |
| P | 8.709758 | 8.132051 | 4.388201 |
| P | 5.952850 | 8.958903 | 5.287577 |
| C | 6.829508 | 1.613625 | 2.054022 |
| C | 7.994025 | 2.371462 | 2.255157 |
| C | 8.007717 | 3.384355 | 3.197925 |
| C | 6.862817 | 3.663383 | 3.961251 |
| C | 5.703714 | 2.895869 | 3.765367 |
| C | 5.685436 | 1.884053 | 2.821289 |
| H | 8.884423 | 2.155417 | 1.676718 |
| H | 8.910190 | 3.966275 | 3.353961 |
| H | 4.816252 | 3.103340 | 4.353619 |
| H | 4.785481 | 1.299339 | 2.672220 |
| N | 6.857648 | 4.740662 | 4.847515 |
| H | 6.464848 | 6.294791 | 3.986698 |
| H | 6.200340 | 4.647960 | 5.616561 |
| H | 7.775594 | 4.984710 | 5.204193 |
| C | 6.812038 | 0.576522 | 1.080753 |
| N | 6.799323 | -0.271361 | 0.282956 |

**TABLE S17.** Cartesian coordinates of the optimized structure of $[Ni^{II}(P_2^{Ph}N_2^{Bn})(P_2^{Ph}HN_2^{Bn})(MeCN)]^{3+}$ (i.e., $[Ni^{II}NH]^{3+}$ with an MeCN ligand) (*endo*).

(– 4223.22380378 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| Ni | 1.450985 | 18.968765 | 9.403437 |
| N | 2.776563 | 21.798272 | 7.226447 |
| N | 2.219716 | 21.991085 | 10.803228 |
| N | 0.245374 | 15.723344 | 11.011951 |
| N | -0.789745 | 19.119627 | 11.987130 |
| N | 2.037321 | 17.752167 | 7.891621 |
| P | 3.389156 | 19.999246 | 9.228059 |
| P | 0.646073 | 20.931527 | 8.691304 |
| P | 1.718000 | 17.999246 | 11.414695 |
| P | -0.479035 | 17.919940 | 9.509649 |
| C | 4.990119 | 17.719704 | 9.415890 |
| H | 4.076947 | 17.165152 | 9.232700 |
| C | 6.203905 | 17.048941 | 9.542654 |
| H | 6.232464 | 15.968904 | 9.452585 |
| C | 7.373719 | 17.762724 | 9.791042 |
| H | 8.317548 | 17.238747 | 9.894929 |
| C | 7.333321 | 19.151157 | 9.909558 |
| H | 8.243082 | 19.706933 | 10.107937 |
| C | 6.127306 | 19.830452 | 9.767117 |
| H | 6.115107 | 20.912921 | 9.843515 |
| C | 4.948324 | 19.112904 | 9.522794 |
| C | 3.620838 | 20.652815 | 7.504520 |
| H | 4.666121 | 20.967893 | 7.442234 |
| H | 3.472295 | 19.812361 | 6.809570 |
| C | 3.280201 | 22.528901 | 6.049312 |
| H | 3.182676 | 21.917111 | 5.139195 |
| H | 4.349072 | 22.689583 | 6.219919 |
| C | 1.915386 | 24.106297 | 4.641690 |
| H | 1.881008 | 23.336513 | 3.876188 |
| C | 1.290450 | 25.334105 | 4.426408 |
| H | 0.771452 | 25.520971 | 3.491965 |
| C | 1.331733 | 26.318597 | 5.410409 |
| H | 0.844818 | 27.273969 | 5.243793 |
| C | 2.008107 | 26.074137 | 6.606495 |
| H | 2.048679 | 26.838884 | 7.375504 |
| C | 2.636766 | 24.849682 | 6.816112 |
| H | 3.166949 | 24.663396 | 7.745800 |
| C | 2.593528 | 23.851961 | 5.835649 |
| C | 1.373682 | 21.456288 | 7.070501 |
| H | 1.202778 | 20.655419 | 6.334252 |
| H | 0.838272 | 22.351837 | 6.743358 |
| C | -1.733293 | 21.460875 | 7.284771 |
| H | -1.152524 | 21.374175 | 6.373911 |

| | | | |
|---|---|---|---|
| C | -3.094071 | 21.749007 | 7.202881 |
| H | -3.553639 | 21.885390 | 6.230304 |
| C | -3.856900 | 21.875409 | 8.361492 |
| H | -4.913962 | 22.107270 | 8.291729 |
| C | -3.260835 | 21.699604 | 9.609283 |
| H | -3.849622 | 21.792117 | 10.515088 |
| C | -1.905404 | 21.399182 | 9.698792 |
| H | -1.451200 | 21.232938 | 10.671298 |
| C | -1.132356 | 21.288911 | 8.536082 |
| C | 1.186818 | 22.346910 | 9.786650 |
| H | 1.584604 | 23.154177 | 9.170286 |
| H | 0.315351 | 22.697409 | 10.339364 |
| C | 2.411311 | 23.108941 | 11.829355 |
| H | 1.434961 | 23.227585 | 12.299520 |
| H | 3.106620 | 22.694833 | 12.560315 |
| C | 4.281154 | 24.645749 | 11.142731 |
| H | 4.992135 | 23.896072 | 11.475210 |
| C | 4.739132 | 25.861820 | 10.642486 |
| H | 5.805136 | 26.046590 | 10.567027 |
| C | 3.828165 | 26.842785 | 10.253378 |
| H | 4.182652 | 27.795155 | 9.875015 |
| C | 2.459183 | 26.606726 | 10.368635 |
| H | 1.748876 | 27.375069 | 10.083948 |
| C | 2.000804 | 25.388482 | 10.863371 |
| H | 0.935256 | 25.214819 | 10.973465 |
| C | 2.908304 | 24.396595 | 11.250186 |
| C | 3.525655 | 21.556006 | 10.228390 |
| H | 4.198163 | 21.377179 | 11.067226 |
| H | 3.907888 | 22.368968 | 9.609519 |
| C | 4.211865 | 17.288154 | 12.491310 |
| H | 4.124100 | 16.368825 | 11.924972 |
| C | 5.351368 | 17.503172 | 13.262924 |
| H | 6.128735 | 16.747080 | 13.288507 |
| C | 5.493366 | 18.679106 | 13.994797 |
| H | 6.384089 | 18.844594 | 14.590546 |
| C | 4.484162 | 19.640074 | 13.965071 |
| H | 4.579775 | 20.552594 | 14.542915 |
| C | 3.341861 | 19.427607 | 13.198617 |
| H | 2.558299 | 20.179287 | 13.201131 |
| C | 3.197507 | 18.251896 | 12.450810 |
| C | 1.603517 | 16.150225 | 11.294013 |
| H | 2.325560 | 15.797780 | 10.540086 |
| H | 1.897939 | 15.744881 | 12.266241 |
| C | 0.088589 | 14.274607 | 11.222325 |
| H | 0.794845 | 13.708449 | 10.594102 |
| H | -0.920877 | 14.020766 | 10.885308 |
| C | -0.646729 | 14.305153 | 13.636402 |
| H | -1.460819 | 14.964243 | 13.349722 |
| C | -0.513950 | 13.896038 | 14.960016 |
| H | -1.222633 | 14.242114 | 15.705289 |
| C | 0.523937 | 13.038326 | 15.327770 |
| H | 0.623771 | 12.714902 | 16.358531 |
| C | 1.427229 | 12.595199 | 14.364611 |

| | | | |
|---|---|---|---|
| H | 2.236419 | 11.928119 | 14.642959 |
| C | 1.292137 | 13.008536 | 13.039705 |
| H | 1.991743 | 12.656162 | 12.287431 |
| C | 0.255359 | 13.863914 | 12.661331 |
| C | -0.207153 | 16.092464 | 9.686218 |
| H | -1.182474 | 15.630644 | 9.506804 |
| H | 0.473876 | 15.777948 | 8.879299 |
| C | -1.044851 | 18.152104 | 6.778942 |
| H | 0.021895 | 18.296330 | 6.653045 |
| C | -1.879875 | 18.123101 | 5.665207 |
| H | -1.455980 | 18.240846 | 4.673991 |
| C | -3.253223 | 17.953250 | 5.823330 |
| H | -3.902269 | 17.935108 | 4.954730 |
| C | -3.793045 | 17.804285 | 7.099495 |
| H | -4.861077 | 17.668680 | 7.229086 |
| C | -2.963228 | 17.821068 | 8.216873 |
| H | -3.397116 | 17.685244 | 9.201878 |
| C | -1.582473 | 17.999413 | 8.061637 |
| C | -1.507247 | 18.338203 | 10.988590 |
| H | -2.345557 | 18.938710 | 10.627415 |
| H | -1.900848 | 17.391995 | 11.393196 |
| C | -1.752070 | 19.509245 | 13.036965 |
| H | -2.095320 | 18.619064 | 13.587879 |
| H | -2.620909 | 19.927540 | 12.520302 |
| C | -1.023678 | 21.853719 | 13.632419 |
| H | -1.241277 | 22.155880 | 12.611849 |
| C | -0.586937 | 22.801004 | 14.555342 |
| H | -0.451637 | 23.832419 | 14.246800 |
| C | -0.342457 | 22.428344 | 15.877674 |
| H | -0.009216 | 23.167519 | 16.598650 |
| C | -0.531825 | 21.105484 | 16.268970 |
| H | -0.347664 | 20.808838 | 17.296157 |
| C | -0.965775 | 20.159541 | 15.340416 |
| H | -1.125670 | 19.130362 | 15.648005 |
| C | -1.218628 | 20.522012 | 14.015459 |
| C | 0.326146 | 18.399323 | 12.584903 |
| H | 0.017787 | 17.445291 | 13.043865 |
| H | 0.745619 | 19.029828 | 13.371580 |
| C | 2.386452 | 17.028587 | 7.057987 |
| C | 2.818567 | 16.121245 | 6.019467 |
| H | 2.050325 | 15.362900 | 5.856141 |
| H | 3.747539 | 15.632968 | 6.321553 |
| H | 2.986854 | 16.673826 | 5.092929 |
| H | 1.845549 | 21.205621 | 11.345709 |

**TABLE S18.** Cartesian coordinates of the optimized structure of $[Ni^{I}(P_2^{Ph}N_2^{Bn})(P_2^{Ph}HN_2^{Bn})]^{2+}$ (i.e., $[Ni^{I}NH]^{2+}$) (*endo*).

(– 4090.24029147 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| Ni | -0.451626 | 0.079468 | 0.391750 |
| N | 2.116486 | -1.285979 | -1.199661 |
| N | 3.091509 | 0.345237 | 1.879812 |
| N | -3.931874 | 1.515527 | -0.422133 |
| N | -4.087185 | -1.098998 | -0.074929 |
| P | 0.990918 | -1.353375 | 1.352731 |
| P | 1.425632 | 1.187328 | -0.164528 |
| P | -1.826197 | -0.017372 | -1.370911 |
| P | -2.337961 | 0.356435 | 1.571460 |
| C | 2.194706 | -1.992453 | 0.071022 |
| H | 3.200640 | -1.982491 | 0.517456 |
| H | 1.919074 | -3.034889 | -0.111750 |
| C | 2.558491 | 0.102540 | -1.170560 |
| H | 2.521222 | 0.480311 | -2.196574 |
| H | 3.585349 | 0.233505 | -0.797330 |
| C | 2.471783 | 1.544945 | 1.336457 |
| H | 3.274682 | 2.217706 | 1.021049 |
| H | 1.855728 | 2.074715 | 2.081138 |
| C | 2.169209 | -0.556348 | 2.553105 |
| H | 1.592030 | -0.060019 | 3.350516 |
| H | 2.761144 | -1.352779 | 3.014365 |
| C | -2.973906 | 1.445244 | -1.532723 |
| H | -2.364649 | 2.355660 | -1.612435 |
| H | -3.550933 | 1.335159 | -2.455198 |
| C | -3.345602 | 1.786618 | 0.896198 |
| H | -4.173071 | 1.964017 | 1.588658 |
| H | -2.700446 | 2.675246 | 0.897227 |
| C | -3.552730 | -1.047717 | 1.318879 |
| H | -3.070156 | -1.997919 | 1.555363 |
| H | -4.414410 | -0.912300 | 1.975187 |
| C | -3.081588 | -1.397085 | -1.138816 |
| H | -3.636733 | -1.524095 | -2.069529 |
| H | -2.572897 | -2.330314 | -0.892761 |
| C | 4.190724 | 0.700666 | 2.789462 |
| H | 4.513232 | -0.229986 | 3.266898 |
| H | 3.837883 | 1.367196 | 3.593720 |
| C | 2.773366 | -2.035941 | -2.284393 |
| H | 2.312287 | -3.028254 | -2.311219 |
| H | 2.521233 | -1.525464 | -3.219460 |
| C | -5.293977 | -2.003596 | -0.177523 |
| H | -6.005085 | -1.615375 | 0.552594 |
| H | -5.694269 | -1.840317 | -1.178688 |
| C | -5.048261 | 2.444010 | -0.721236 |

| | | | |
|---|---|---|---|
| H | -5.514540 | 2.084056 | -1.641913 |
| H | -5.771034 | 2.330045 | 0.090346 |
| C | -4.656350 | 3.892951 | -0.872110 |
| C | -4.711862 | 4.770546 | 0.215929 |
| C | -4.226216 | 4.385179 | -2.109721 |
| C | -4.340966 | 6.106200 | 0.073088 |
| H | -5.061161 | 4.408463 | 1.178303 |
| C | -3.850132 | 5.718226 | -2.254899 |
| H | -4.205688 | 3.724354 | -2.970702 |
| C | -3.904753 | 6.582234 | -1.162315 |
| H | -4.398809 | 6.777095 | 0.923766 |
| H | -3.531197 | 6.086246 | -3.224387 |
| H | -3.622126 | 7.623321 | -1.276191 |
| C | -4.990853 | -3.452898 | 0.065619 |
| C | -4.645937 | -4.294672 | -0.997604 |
| C | -5.082134 | -3.989353 | 1.354637 |
| C | -4.383151 | -5.643921 | -0.775122 |
| H | -4.603696 | -3.898253 | -2.007034 |
| C | -4.819331 | -5.338629 | 1.577887 |
| H | -5.381691 | -3.355120 | 2.182832 |
| C | -4.468736 | -6.167906 | 0.513757 |
| H | -4.124058 | -6.286400 | -1.609683 |
| H | -4.900469 | -5.744100 | 2.580461 |
| H | -4.276550 | -7.221695 | 0.685609 |
| C | 4.275244 | -2.172123 | -2.170430 |
| C | 5.122880 | -1.252880 | -2.796902 |
| C | 4.847990 | -3.207526 | -1.422892 |
| C | 6.507375 | -1.360288 | -2.677434 |
| H | 4.694174 | -0.455819 | -3.397382 |
| C | 6.231311 | -3.317502 | -1.297941 |
| H | 4.204418 | -3.945291 | -0.953203 |
| C | 7.065369 | -2.392362 | -1.924615 |
| H | 7.150985 | -0.644089 | -3.177846 |
| H | 6.657367 | -4.131375 | -0.720317 |
| H | 8.142810 | -2.482743 | -1.834568 |
| C | 5.367461 | 1.335005 | 2.093545 |
| C | 6.031200 | 0.667124 | 1.057874 |
| C | 5.843896 | 2.581414 | 2.504415 |
| C | 7.144522 | 1.237494 | 0.447112 |
| H | 5.676921 | -0.307658 | 0.736843 |
| C | 6.962807 | 3.153240 | 1.899193 |
| H | 5.337352 | 3.104232 | 3.310386 |
| C | 7.614499 | 2.482633 | 0.867338 |
| H | 7.647592 | 0.707380 | -0.355263 |
| H | 7.319065 | 4.123408 | 2.229251 |
| H | 8.481437 | 2.926563 | 0.389628 |
| H | -4.389605 | -0.085707 | -0.274431 |
| C | 1.419557 | 2.778841 | -1.058831 |
| C | 1.670866 | 3.988286 | -0.399200 |
| C | 1.057904 | 2.801888 | -2.413269 |
| C | 1.571606 | 5.197099 | -1.086105 |
| H | 1.943305 | 3.996467 | 0.650489 |
| C | 0.967970 | 4.011047 | -3.096592 |

| | | | |
|---|---|---|---|
| H | 0.827786 | 1.876726 | -2.935208 |
| C | 1.222738 | 5.211831 | -2.434310 |
| H | 1.777037 | 6.127170 | -0.566643 |
| H | 0.693577 | 4.015058 | -4.146062 |
| H | 1.150835 | 6.153438 | -2.967757 |
| C | 0.454141 | -2.870832 | 2.214905 |
| C | 0.635008 | -3.064480 | 3.588978 |
| C | -0.230935 | -3.844769 | 1.473314 |
| C | 0.149187 | -4.217463 | 4.204222 |
| H | 1.150839 | -2.323226 | 4.188943 |
| C | -0.708712 | -4.996639 | 2.090359 |
| H | -0.394713 | -3.702259 | 0.408589 |
| C | -0.519079 | -5.185523 | 3.459239 |
| H | 0.299227 | -4.358991 | 5.269341 |
| H | -1.232856 | -5.742748 | 1.502926 |
| H | -0.889138 | -6.081960 | 3.944750 |
| C | -2.455434 | 0.645152 | 3.368851 |
| C | -3.682129 | 0.792069 | 4.030540 |
| C | -1.264830 | 0.778869 | 4.089397 |
| C | -3.709905 | 1.056979 | 5.396119 |
| H | -4.618153 | 0.707501 | 3.487527 |
| C | -1.295680 | 1.049336 | 5.455913 |
| H | -0.314621 | 0.673441 | 3.575362 |
| C | -2.517641 | 1.188810 | 6.108932 |
| H | -4.662201 | 1.169023 | 5.902910 |
| H | -0.366906 | 1.153435 | 6.005917 |
| H | -2.544485 | 1.399076 | 7.172749 |
| C | -1.312087 | -0.334939 | -3.091666 |
| C | -1.332139 | 0.674157 | -4.062417 |
| C | -0.833213 | -1.607041 | -3.433645 |
| C | -0.893153 | 0.407925 | -5.357909 |
| H | -1.694175 | 1.667308 | -3.820722 |
| C | -0.405371 | -1.868399 | -4.732235 |
| H | -0.791185 | -2.397367 | -2.690291 |
| C | -0.432931 | -0.862183 | -5.696927 |
| H | -0.917832 | 1.195395 | -6.103785 |
| H | -0.046268 | -2.859225 | -4.987662 |
| H | -0.096198 | -1.067534 | -6.707219 |

**TABLE S19.** Cartesian coordinates of the optimized structure of $[Ni^{II}(P_2^{Ph}N_2^{Bn})(P_2^{Ph}HN_2^{Bn})(MeCN)]^{3+}$ (i.e., $[Ni^{II}NH]^{2+}$ with an MeCN ligand) (*exo*).

(– 4223.22607729 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| Ni | 1.525048 | 19.036220 | 9.494900 |
| N | 2.914310 | 22.040639 | 7.496490 |
| N | 2.721864 | 22.654185 | 10.096972 |
| N | 0.290203 | 15.732238 | 10.960238 |
| N | -0.804763 | 19.083136 | 12.025319 |
| N | 2.110491 | 17.896906 | 7.921735 |
| P | 3.451655 | 20.087001 | 9.484548 |
| P | 0.749416 | 21.048469 | 8.930856 |
| P | 1.730345 | 18.006018 | 11.490480 |
| P | -0.402427 | 17.977639 | 9.516021 |
| C | 4.976096 | 17.754860 | 9.541994 |
| H | 4.038187 | 17.243146 | 9.358858 |
| C | 6.162939 | 17.031521 | 9.621107 |
| H | 6.143178 | 15.954105 | 9.501535 |
| C | 7.367410 | 17.689794 | 9.856665 |
| H | 8.291047 | 17.125164 | 9.920870 |
| C | 7.387552 | 19.075023 | 10.009920 |
| H | 8.323689 | 19.588894 | 10.197572 |
| C | 6.207488 | 19.806248 | 9.918743 |
| H | 6.246405 | 20.885079 | 10.023953 |
| C | 4.993669 | 19.145206 | 9.688869 |
| C | 3.782625 | 20.871259 | 7.825587 |
| H | 4.812454 | 21.233150 | 7.831076 |
| H | 3.670833 | 20.114651 | 7.047203 |
| C | 3.476630 | 22.727726 | 6.278621 |
| H | 3.564458 | 21.960798 | 5.507195 |
| H | 4.480637 | 23.040557 | 6.573478 |
| C | 2.426734 | 23.971294 | 4.397942 |
| H | 2.753140 | 23.162161 | 3.752207 |
| C | 1.786977 | 25.082958 | 3.854683 |
| H | 1.611685 | 25.134958 | 2.785623 |
| C | 1.371860 | 26.120344 | 4.685960 |
| H | 0.864187 | 26.983602 | 4.269209 |
| C | 1.599634 | 26.041296 | 6.059222 |
| H | 1.270004 | 26.843920 | 6.709904 |
| C | 2.252843 | 24.937257 | 6.600391 |
| H | 2.423591 | 24.890174 | 7.671666 |
| C | 2.676311 | 23.893313 | 5.770366 |
| C | 1.471898 | 21.698637 | 7.343895 |
| H | 1.368453 | 20.960890 | 6.545878 |
| H | 0.958865 | 22.620133 | 7.062749 |
| C | -1.603473 | 21.661743 | 7.496313 |
| H | -1.011141 | 21.631155 | 6.589461 |
| C | -2.963752 | 21.948399 | 7.409860 |

| | | | |
|---|---|---|---|
| H | -3.408960 | 22.139062 | 6.439749 |
| C | -3.746721 | 21.998144 | 8.560559 |
| H | -4.804044 | 22.227783 | 8.486658 |
| C | -3.170543 | 21.748945 | 9.804556 |
| H | -3.775243 | 21.780067 | 10.704103 |
| C | -1.814990 | 21.447687 | 9.898370 |
| H | -1.377952 | 21.210762 | 10.863042 |
| C | -1.021860 | 21.417950 | 8.744979 |
| C | 1.280974 | 22.380225 | 10.129419 |
| H | 0.759384 | 23.294105 | 9.835386 |
| H | 0.935602 | 22.092151 | 11.132929 |
| C | 3.001907 | 23.906014 | 10.839650 |
| H | 2.338029 | 24.664003 | 10.414946 |
| H | 2.731845 | 23.774693 | 11.896922 |
| C | 5.276552 | 24.311427 | 11.845422 |
| H | 4.890421 | 23.937852 | 12.788811 |
| C | 6.596284 | 24.752233 | 11.759736 |
| H | 7.234033 | 24.719935 | 12.636681 |
| C | 7.090527 | 25.240440 | 10.552496 |
| H | 8.114684 | 25.591541 | 10.484797 |
| C | 6.259834 | 25.284377 | 9.432766 |
| H | 6.636102 | 25.669847 | 8.491324 |
| C | 4.942009 | 24.846428 | 9.522950 |
| H | 4.297922 | 24.897146 | 8.650971 |
| C | 4.435211 | 24.353783 | 10.730517 |
| C | 3.532557 | 21.548254 | 10.613384 |
| H | 3.224449 | 21.226551 | 11.616852 |
| H | 4.569131 | 21.887317 | 10.667527 |
| C | 4.199711 | 17.290268 | 12.615332 |
| H | 4.139563 | 16.389005 | 12.017378 |
| C | 5.317397 | 17.498705 | 13.419425 |
| H | 6.104204 | 16.752450 | 13.442639 |
| C | 5.424867 | 18.655252 | 14.187380 |
| H | 6.298473 | 18.814198 | 14.809632 |
| C | 4.402352 | 19.601836 | 14.162650 |
| H | 4.471259 | 20.497815 | 14.769358 |
| C | 3.279307 | 19.395437 | 13.365927 |
| H | 2.483083 | 20.133373 | 13.372019 |
| C | 3.172342 | 18.240421 | 12.580227 |
| C | 1.629610 | 16.157848 | 11.320744 |
| H | 2.390450 | 15.822766 | 10.597710 |
| H | 1.873807 | 15.729858 | 12.297469 |
| C | 0.136284 | 14.278971 | 11.121211 |
| H | 0.905875 | 13.734486 | 10.550735 |
| H | -0.831513 | 14.020544 | 10.680392 |
| C | -0.743721 | 14.364307 | 13.484617 |
| H | -1.448996 | 15.123783 | 13.161044 |
| C | -0.753929 | 13.920310 | 14.803430 |
| H | -1.466663 | 14.336587 | 15.507854 |
| C | 0.143317 | 12.934595 | 15.217310 |
| H | 0.132053 | 12.583089 | 16.243642 |
| C | 1.052530 | 12.403235 | 14.306146 |
| H | 1.754026 | 11.637598 | 14.621146 |

| | | | |
|---|---|---|---|
| C | 1.063455 | 12.854475 | 12.986412 |
| H | 1.771350 | 12.436992 | 12.276061 |
| C | 0.165457 | 13.835465 | 12.561228 |
| C | -0.110079 | 16.147778 | 9.632477 |
| H | -1.070696 | 15.681616 | 9.394731 |
| H | 0.608758 | 15.877785 | 8.842517 |
| C | -0.985188 | 18.477857 | 6.812160 |
| H | 0.048494 | 18.791679 | 6.721885 |
| C | -1.813907 | 18.469604 | 5.692689 |
| H | -1.418063 | 18.774227 | 4.730190 |
| C | -3.143515 | 18.071999 | 5.809779 |
| H | -3.788050 | 18.067959 | 4.937604 |
| C | -3.645388 | 17.673770 | 7.047894 |
| H | -4.678756 | 17.359550 | 7.142947 |
| C | -2.820652 | 17.672102 | 8.168473 |
| H | -3.222619 | 17.355579 | 9.125316 |
| C | -1.484116 | 18.077420 | 8.054911 |
| C | -1.480698 | 18.326754 | 10.980053 |
| H | -2.319006 | 18.923871 | 10.611409 |
| H | -1.869940 | 17.359769 | 11.338143 |
| C | -1.799618 | 19.429691 | 13.059813 |
| H | -2.160834 | 18.516806 | 13.560268 |
| H | -2.651764 | 19.871794 | 12.534773 |
| C | -1.058564 | 21.736978 | 13.784475 |
| H | -1.227012 | 22.088535 | 12.771318 |
| C | -0.639470 | 22.634623 | 14.762968 |
| H | -0.471439 | 23.674954 | 14.504805 |
| C | -0.452860 | 22.202347 | 16.075986 |
| H | -0.132391 | 22.903592 | 16.839337 |
| C | -0.682374 | 20.868167 | 16.402826 |
| H | -0.542567 | 20.523990 | 17.422113 |
| C | -1.098542 | 19.971798 | 15.418805 |
| H | -1.285316 | 18.933055 | 15.675731 |
| C | -1.293372 | 20.394377 | 14.101272 |
| C | 0.301498 | 18.356302 | 12.629965 |
| H | -0.007452 | 17.384372 | 13.049347 |
| H | 0.693000 | 18.964030 | 13.448266 |
| C | 2.447765 | 17.211598 | 7.051768 |
| C | 2.865364 | 16.340065 | 5.976687 |
| H | 2.114975 | 15.560795 | 5.829423 |
| H | 3.820655 | 15.876590 | 6.232277 |
| H | 2.976644 | 16.914044 | 5.054903 |
| H | 2.980414 | 22.655318 | 8.365015 |

**TABLE S20.** Cartesian coordinates of the optimized structure of $[Ni^{I}(P_2^{Ph}N_2^{Bn})(P_2^{Ph}HN_2^{Bn})]^{2+}$ (i.e., $[Ni^{I}NH]^{2+}$) (*exo*).

(– 4090.24056908 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| Ni | -0.451626 | 0.079468 | 0.391750 |
| N | 2.116486 | -1.285979 | -1.199661 |
| N | 3.091509 | 0.345237 | 1.879812 |
| N | -3.931874 | 1.515527 | -0.422133 |
| N | -4.087185 | -1.098998 | -0.074929 |
| P | 0.990918 | -1.353375 | 1.352731 |
| P | 1.425632 | 1.187328 | -0.164528 |
| P | -1.826197 | -0.017372 | -1.370911 |
| P | -2.337961 | 0.356435 | 1.571460 |
| C | 2.194706 | -1.992453 | 0.071022 |
| H | 3.200640 | -1.982491 | 0.517456 |
| H | 1.919074 | -3.034889 | -0.111750 |
| C | 2.558491 | 0.102540 | -1.170560 |
| H | 2.521222 | 0.480311 | -2.196574 |
| H | 3.585349 | 0.233505 | -0.797330 |
| C | 2.471783 | 1.544945 | 1.336457 |
| H | 3.274682 | 2.217706 | 1.021049 |
| H | 1.855728 | 2.074715 | 2.081138 |
| C | 2.169209 | -0.556348 | 2.553105 |
| H | 1.592030 | -0.060019 | 3.350516 |
| H | 2.761144 | -1.352779 | 3.014365 |
| C | -2.973906 | 1.445244 | -1.532723 |
| H | -2.364649 | 2.355660 | -1.612435 |
| H | -3.550933 | 1.335159 | -2.455198 |
| C | -3.345602 | 1.786618 | 0.896198 |
| H | -4.173071 | 1.964017 | 1.588658 |
| H | -2.700446 | 2.675246 | 0.897227 |
| C | -3.552730 | -1.047717 | 1.318879 |
| H | -3.070156 | -1.997919 | 1.555363 |
| H | -4.414410 | -0.912300 | 1.975187 |
| C | -3.081588 | -1.397085 | -1.138816 |
| H | -3.636733 | -1.524095 | -2.069529 |
| H | -2.572897 | -2.330314 | -0.892761 |
| C | 4.190724 | 0.700666 | 2.789462 |
| H | 4.513232 | -0.229986 | 3.266898 |
| H | 3.837883 | 1.367196 | 3.593720 |
| C | 2.773366 | -2.035941 | -2.284393 |
| H | 2.312287 | -3.028254 | -2.311219 |
| H | 2.521233 | -1.525464 | -3.219460 |
| C | -5.293977 | -2.003596 | -0.177523 |
| H | -6.005085 | -1.615375 | 0.552594 |
| H | -5.694269 | -1.840317 | -1.178688 |
| C | -5.048261 | 2.444010 | -0.721236 |

| | | | |
|---|---|---|---|
| H | -5.514540 | 2.084056 | -1.641913 |
| H | -5.771034 | 2.330045 | 0.090346 |
| C | -4.656350 | 3.892951 | -0.872110 |
| C | -4.711862 | 4.770546 | 0.215929 |
| C | -4.226216 | 4.385179 | -2.109721 |
| C | -4.340966 | 6.106200 | 0.073088 |
| H | -5.061161 | 4.408463 | 1.178303 |
| C | -3.850132 | 5.718226 | -2.254899 |
| H | -4.205688 | 3.724354 | -2.970702 |
| C | -3.904753 | 6.582234 | -1.162315 |
| H | -4.398809 | 6.777095 | 0.923766 |
| H | -3.531197 | 6.086246 | -3.224387 |
| H | -3.622126 | 7.623321 | -1.276191 |
| C | -4.990853 | -3.452898 | 0.065619 |
| C | -4.645937 | -4.294672 | -0.997604 |
| C | -5.082134 | -3.989353 | 1.354637 |
| C | -4.383151 | -5.643921 | -0.775122 |
| H | -4.603696 | -3.898253 | -2.007034 |
| C | -4.819331 | -5.338629 | 1.577887 |
| H | -5.381691 | -3.355120 | 2.182832 |
| C | -4.468736 | -6.167906 | 0.513757 |
| H | -4.124058 | -6.286400 | -1.609683 |
| H | -4.900469 | -5.744100 | 2.580461 |
| H | -4.276550 | -7.221695 | 0.685609 |
| C | 4.275244 | -2.172123 | -2.170430 |
| C | 5.122880 | -1.252880 | -2.796902 |
| C | 4.847990 | -3.207526 | -1.422892 |
| C | 6.507375 | -1.360288 | -2.677434 |
| H | 4.694174 | -0.455819 | -3.397382 |
| C | 6.231311 | -3.317502 | -1.297941 |
| H | 4.204418 | -3.945291 | -0.953203 |
| C | 7.065369 | -2.392362 | -1.924615 |
| H | 7.150985 | -0.644089 | -3.177846 |
| H | 6.657367 | -4.131375 | -0.720317 |
| H | 8.142810 | -2.482743 | -1.834568 |
| C | 5.367461 | 1.335005 | 2.093545 |
| C | 6.031200 | 0.667124 | 1.057874 |
| C | 5.843896 | 2.581414 | 2.504415 |
| C | 7.144522 | 1.237494 | 0.447112 |
| H | 5.676921 | -0.307658 | 0.736843 |
| C | 6.962807 | 3.153240 | 1.899193 |
| H | 5.337352 | 3.104232 | 3.310386 |
| C | 7.614499 | 2.482633 | 0.867338 |
| H | 7.647592 | 0.707380 | -0.355263 |
| H | 7.319065 | 4.123408 | 2.229251 |
| H | 8.481437 | 2.926563 | 0.389628 |
| H | -4.389605 | -0.085707 | -0.274431 |
| C | 1.419557 | 2.778841 | -1.058831 |
| C | 1.670866 | 3.988286 | -0.399200 |
| C | 1.057904 | 2.801888 | -2.413269 |
| C | 1.571606 | 5.197099 | -1.086105 |
| H | 1.943305 | 3.996467 | 0.650489 |
| C | 0.967970 | 4.011047 | -3.096592 |

| | | | |
|---|---|---|---|
| H | 0.827786 | 1.876726 | -2.935208 |
| C | 1.222738 | 5.211831 | -2.434310 |
| H | 1.777037 | 6.127170 | -0.566643 |
| H | 0.693577 | 4.015058 | -4.146062 |
| H | 1.150835 | 6.153438 | -2.967757 |
| C | 0.454141 | -2.870832 | 2.214905 |
| C | 0.635008 | -3.064480 | 3.588978 |
| C | -0.230935 | -3.844769 | 1.473314 |
| C | 0.149187 | -4.217463 | 4.204222 |
| H | 1.150839 | -2.323226 | 4.188943 |
| C | -0.708712 | -4.996639 | 2.090359 |
| H | -0.394713 | -3.702259 | 0.408589 |
| C | -0.519079 | -5.185523 | 3.459239 |
| H | 0.299227 | -4.358991 | 5.269341 |
| H | -1.232856 | -5.742748 | 1.502926 |
| H | -0.889138 | -6.081960 | 3.944750 |
| C | -2.455434 | 0.645152 | 3.368851 |
| C | -3.682129 | 0.792069 | 4.030540 |
| C | -1.264830 | 0.778869 | 4.089397 |
| C | -3.709905 | 1.056979 | 5.396119 |
| H | -4.618153 | 0.707501 | 3.487527 |
| C | -1.295680 | 1.049336 | 5.455913 |
| H | -0.314621 | 0.673441 | 3.575362 |
| C | -2.517641 | 1.188810 | 6.108932 |
| H | -4.662201 | 1.169023 | 5.902910 |
| H | -0.366906 | 1.153435 | 6.005917 |
| H | -2.544485 | 1.399076 | 7.172749 |
| C | -1.312087 | -0.334939 | -3.091666 |
| C | -1.332139 | 0.674157 | -4.062417 |
| C | -0.833213 | -1.607041 | -3.433645 |
| C | -0.893153 | 0.407925 | -5.357909 |
| H | -1.694175 | 1.667308 | -3.820722 |
| C | -0.405371 | -1.868399 | -4.732235 |
| H | -0.791185 | -2.397367 | -2.690291 |
| C | -0.432931 | -0.862183 | -5.696927 |
| H | -0.917832 | 1.195395 | -6.103785 |
| H | -0.046268 | -2.859225 | -4.987662 |
| H | -0.096198 | -1.067534 | -6.707219 |

**TABLE S21.** Cartesian coordinates of the optimized structure of $[Ni^{II}(P_2^{Ph}HN_2^{Bn})_2(MeCN)]^{4+}$ (i.e., $[Ni^{II}NH_2]^{4+}$ with an MeCN ligand) (*endo-endo*).

(– 4223.66929459 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| Ni | 1.482869 | 18.976010 | 9.367516 |
| N | 2.783694 | 21.852455 | 7.224683 |
| N | 2.273805 | 22.010229 | 10.811010 |
| N | 0.349306 | 15.714442 | 10.990730 |
| N | -0.785857 | 18.984749 | 11.981217 |
| N | 2.052656 | 17.816388 | 7.819354 |
| P | 3.414540 | 20.023674 | 9.191034 |
| P | 0.665678 | 20.977296 | 8.710853 |
| P | 1.814192 | 17.992232 | 11.375660 |
| P | -0.407960 | 17.844717 | 9.434837 |
| C | 4.991751 | 17.720096 | 9.325855 |
| H | 4.074273 | 17.174808 | 9.136536 |
| C | 6.200295 | 17.037684 | 9.438080 |
| H | 6.218858 | 15.958993 | 9.331642 |
| C | 7.377550 | 17.737658 | 9.690751 |
| H | 8.317240 | 17.204006 | 9.781312 |
| C | 7.349911 | 19.124340 | 9.829529 |
| H | 8.265165 | 19.669933 | 10.030610 |
| C | 6.149182 | 19.815988 | 9.704617 |
| H | 6.148576 | 20.897028 | 9.797966 |
| C | 4.962971 | 19.111885 | 9.456183 |
| C | 3.630766 | 20.705035 | 7.479322 |
| H | 4.675688 | 21.021597 | 7.418063 |
| H | 3.479966 | 19.874617 | 6.773156 |
| C | 3.274777 | 22.592536 | 6.047185 |
| H | 3.170781 | 21.985565 | 5.134676 |
| H | 4.344823 | 22.753686 | 6.209873 |
| C | 1.893492 | 24.174110 | 4.661522 |
| H | 1.850646 | 23.407183 | 3.893642 |
| C | 1.267648 | 25.403256 | 4.456897 |
| H | 0.739527 | 25.593771 | 3.528390 |
| C | 1.320560 | 26.384584 | 5.443455 |
| H | 0.833395 | 27.341188 | 5.285053 |
| C | 2.009729 | 26.135532 | 6.631253 |
| H | 2.060334 | 26.897898 | 7.401998 |
| C | 2.639167 | 24.909754 | 6.830329 |
| H | 3.179960 | 24.720672 | 7.753262 |
| C | 2.584342 | 23.915371 | 5.847160 |
| C | 1.381238 | 21.507465 | 7.082558 |
| H | 1.205427 | 20.710765 | 6.343864 |
| H | 0.836635 | 22.401686 | 6.767458 |
| C | -1.711193 | 21.376964 | 7.291083 |
| H | -1.130558 | 21.181927 | 6.397390 |

| | | | |
|---|---|---|---|
| C | -3.071497 | 21.650950 | 7.170623 |
| H | -3.525052 | 21.669148 | 6.185887 |
| C | -3.841736 | 21.903685 | 8.303125 |
| H | -4.899997 | 22.118191 | 8.203519 |
| C | -3.247394 | 21.882926 | 9.563502 |
| H | -3.834157 | 22.089823 | 10.451401 |
| C | -1.889370 | 21.608079 | 9.690898 |
| H | -1.448874 | 21.611189 | 10.683828 |
| C | -1.110187 | 21.354220 | 8.554878 |
| C | 1.240432 | 22.381514 | 9.801374 |
| H | 1.651332 | 23.175487 | 9.176253 |
| H | 0.383470 | 22.758455 | 10.358692 |
| C | 2.491108 | 23.130891 | 11.832502 |
| H | 1.520244 | 23.263449 | 12.310196 |
| H | 3.187850 | 22.709354 | 12.557683 |
| C | 4.373138 | 24.643468 | 11.128973 |
| H | 5.077504 | 23.885325 | 11.456136 |
| C | 4.841704 | 25.854440 | 10.626329 |
| H | 5.909159 | 26.026695 | 10.542763 |
| C | 3.939793 | 26.846832 | 10.245538 |
| H | 4.303418 | 27.795383 | 9.866424 |
| C | 2.568915 | 26.627620 | 10.370933 |
| H | 1.865754 | 27.405243 | 10.093670 |
| C | 2.099774 | 25.414273 | 10.867485 |
| H | 1.033135 | 25.253678 | 10.985706 |
| C | 2.998195 | 24.411116 | 11.246503 |
| C | 3.569509 | 21.555188 | 10.228444 |
| H | 4.236364 | 21.342367 | 11.063980 |
| H | 3.971860 | 22.371553 | 9.626829 |
| C | 4.296893 | 17.320794 | 12.468666 |
| H | 4.224151 | 16.405349 | 11.894502 |
| C | 5.430227 | 17.544821 | 13.245928 |
| H | 6.215886 | 16.797614 | 13.269245 |
| C | 5.554195 | 18.717142 | 13.986523 |
| H | 6.440504 | 18.889411 | 14.586743 |
| C | 4.533840 | 19.666131 | 13.959765 |
| H | 4.615556 | 20.575129 | 14.544846 |
| C | 3.396916 | 19.446675 | 13.187309 |
| H | 2.607481 | 20.191652 | 13.194070 |
| C | 3.271995 | 18.273976 | 12.431952 |
| C | 1.703719 | 16.140640 | 11.284699 |
| H | 2.436594 | 15.778648 | 10.547325 |
| H | 1.983561 | 15.756994 | 12.269867 |
| C | 0.160260 | 14.285809 | 11.293247 |
| H | 0.917667 | 13.672079 | 10.783062 |
| H | -0.813226 | 14.008543 | 10.879391 |
| C | -0.753270 | 14.578698 | 13.627955 |
| H | -1.473985 | 15.284633 | 13.225457 |
| C | -0.772410 | 14.257283 | 14.982052 |
| H | -1.505146 | 14.716937 | 15.636954 |
| C | 0.140138 | 13.334530 | 15.495909 |
| H | 0.120592 | 13.080160 | 16.550450 |
| C | 1.071852 | 12.739117 | 14.649703 |

| | | | |
|---|---|---|---|
| H | 1.784623 | 12.021818 | 15.043177 |
| C | 1.091219 | 13.067051 | 13.293928 |
| H | 1.815053 | 12.601826 | 12.631100 |
| C | 0.178878 | 13.984708 | 12.769533 |
| C | -0.066825 | 16.031268 | 9.641180 |
| H | -1.016753 | 15.530492 | 9.432683 |
| H | 0.655958 | 15.739275 | 8.864594 |
| C | -1.094132 | 18.250976 | 6.752871 |
| H | -0.069605 | 18.576903 | 6.616448 |
| C | -1.960236 | 18.196473 | 5.663695 |
| H | -1.602038 | 18.475842 | 4.679256 |
| C | -3.281112 | 17.791954 | 5.838715 |
| H | -3.955345 | 17.756177 | 4.990079 |
| C | -3.737968 | 17.428475 | 7.104625 |
| H | -4.764220 | 17.108921 | 7.244885 |
| C | -2.875496 | 17.465686 | 8.195425 |
| H | -3.243784 | 17.166657 | 9.170872 |
| C | -1.549515 | 17.884250 | 8.023104 |
| C | -1.461473 | 18.170439 | 10.926000 |
| H | -2.348519 | 18.722954 | 10.616556 |
| H | -1.744500 | 17.219555 | 11.381492 |
| C | -1.802194 | 19.317600 | 13.072021 |
| H | -2.042385 | 18.367681 | 13.550032 |
| H | -2.678603 | 19.682386 | 12.536617 |
| C | -1.404952 | 21.698987 | 13.756598 |
| H | -1.833325 | 22.010579 | 12.808271 |
| C | -0.987156 | 22.652039 | 14.681079 |
| H | -1.078997 | 23.707323 | 14.448953 |
| C | -0.477723 | 22.246867 | 15.914551 |
| H | -0.161732 | 22.988483 | 16.640286 |
| C | -0.383043 | 20.890656 | 16.219782 |
| H | 0.003850 | 20.577207 | 17.183028 |
| C | -0.795975 | 19.936597 | 15.292391 |
| H | -0.737354 | 18.880181 | 15.534214 |
| C | -1.306538 | 20.334825 | 14.053121 |
| C | 0.427186 | 18.344874 | 12.569097 |
| H | 0.115046 | 17.405463 | 13.028824 |
| H | 0.790293 | 19.023253 | 13.341173 |
| C | 2.366594 | 17.123863 | 6.946729 |
| C | 2.763974 | 16.250773 | 5.866664 |
| H | 1.996068 | 15.490079 | 5.712851 |
| H | 3.708203 | 15.764663 | 6.121659 |
| H | 2.890009 | 16.830311 | 4.950263 |
| H | 1.892619 | 21.235152 | 11.362611 |
| H | -0.497664 | 19.875749 | 11.561087 |

**TABLE S22.** Cartesian coordinates of the optimized structure of $[Ni^{I}(P_2^{Ph}HN_2^{Bn})_2]^{3+}$ (i.e., $[Ni^{I}NH_2]^{3+}$) (*endo-endo*).

(– 4090.69582659 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| Ni | 1.251359 | 19.347469 | 9.736960 |
| N | 2.611540 | 21.787251 | 7.073410 |
| N | 2.612849 | 22.170106 | 10.640993 |
| N | 0.676869 | 15.807993 | 11.045816 |
| N | -1.188631 | 18.708952 | 11.997395 |
| P | 3.291225 | 19.971294 | 9.048025 |
| P | 0.590036 | 21.320839 | 8.876933 |
| P | 1.583188 | 18.305753 | 11.706740 |
| P | -0.358827 | 17.814422 | 9.443516 |
| C | 4.606082 | 17.544413 | 9.050207 |
| H | 3.604872 | 17.134958 | 8.953133 |
| C | 5.709150 | 16.694126 | 9.063355 |
| H | 5.566353 | 15.623265 | 8.969840 |
| C | 6.990977 | 17.222246 | 9.200032 |
| H | 7.851079 | 16.561725 | 9.216442 |
| C | 7.169694 | 18.600445 | 9.313201 |
| H | 8.167686 | 19.012619 | 9.415156 |
| C | 6.071285 | 19.455273 | 9.285483 |
| H | 6.226624 | 20.526827 | 9.357051 |
| C | 4.779698 | 18.928578 | 9.159893 |
| C | 3.344379 | 20.551196 | 7.276603 |
| H | 4.396316 | 20.731289 | 7.038865 |
| H | 2.986738 | 19.722503 | 6.645113 |
| C | 3.033577 | 22.424829 | 5.817086 |
| H | 2.723676 | 21.826948 | 4.945260 |
| H | 4.128500 | 22.429748 | 5.826407 |
| C | 1.979356 | 24.236002 | 4.431052 |
| H | 1.871260 | 23.506456 | 3.633656 |
| C | 1.570792 | 25.553179 | 4.228494 |
| H | 1.142407 | 25.841944 | 3.274203 |
| C | 1.695852 | 26.487246 | 5.253831 |
| H | 1.371418 | 27.511302 | 5.102718 |
| C | 2.241329 | 26.096501 | 6.477041 |
| H | 2.349012 | 26.819746 | 7.278937 |
| C | 2.662247 | 24.783677 | 6.671496 |
| H | 3.113143 | 24.498237 | 7.617501 |
| C | 2.533030 | 23.836693 | 5.649610 |
| C | 1.168960 | 21.628825 | 7.130775 |
| H | 0.802687 | 20.810239 | 6.491472 |
| H | 0.710684 | 22.562695 | 6.794444 |
| C | -1.865358 | 22.089803 | 7.717338 |
| H | -1.421259 | 21.869594 | 6.753513 |
| C | -3.191773 | 22.513749 | 7.773101 |

| | | | |
|---|---|---|---|
| H | -3.754548 | 22.627159 | 6.852941 |
| C | -3.788636 | 22.795942 | 8.998720 |
| H | -4.819069 | 23.131535 | 9.037364 |
| C | -3.056712 | 22.648096 | 10.176645 |
| H | -3.515298 | 22.869746 | 11.134434 |
| C | -1.733558 | 22.221073 | 10.127099 |
| H | -1.174649 | 22.110435 | 11.052305 |
| C | -1.123509 | 21.946480 | 8.895843 |
| C | 1.512449 | 22.682781 | 9.763071 |
| H | 1.944470 | 23.384697 | 9.049800 |
| H | 0.811957 | 23.199710 | 10.419408 |
| C | 3.085168 | 23.238847 | 11.618107 |
| H | 2.192155 | 23.531316 | 12.171135 |
| H | 3.767261 | 22.722692 | 12.294390 |
| C | 5.117575 | 24.435296 | 10.734412 |
| H | 5.722220 | 23.583349 | 11.028558 |
| C | 5.723638 | 25.547516 | 10.156140 |
| H | 6.795574 | 25.551803 | 9.991815 |
| C | 4.956766 | 26.657786 | 9.808113 |
| H | 5.431802 | 27.526443 | 9.365374 |
| C | 3.582907 | 26.655809 | 10.043462 |
| H | 2.987472 | 27.525677 | 9.788272 |
| C | 2.976078 | 25.542026 | 10.618696 |
| H | 1.909182 | 25.552381 | 10.816966 |
| C | 3.736685 | 24.419056 | 10.962101 |
| C | 3.770301 | 21.546769 | 9.920841 |
| H | 4.512537 | 21.311863 | 10.684613 |
| H | 4.173706 | 22.286926 | 9.229925 |
| C | 4.042297 | 18.146032 | 13.055526 |
| H | 4.234152 | 17.249742 | 12.475849 |
| C | 5.017611 | 18.607032 | 13.938211 |
| H | 5.950145 | 18.062413 | 14.037507 |
| C | 4.794707 | 19.756283 | 14.692631 |
| H | 5.554420 | 20.113775 | 15.378948 |
| C | 3.591895 | 20.449140 | 14.560980 |
| H | 3.410772 | 21.344685 | 15.145104 |
| C | 2.615522 | 19.997669 | 13.677151 |
| H | 1.684649 | 20.550913 | 13.586651 |
| C | 2.830803 | 18.834848 | 12.924015 |
| C | 1.889973 | 16.481096 | 11.480062 |
| H | 2.725489 | 16.348837 | 10.776442 |
| H | 2.182999 | 16.068041 | 12.449197 |
| C | 0.759191 | 14.360964 | 11.293656 |
| H | 1.639041 | 13.923753 | 10.795945 |
| H | -0.125143 | 13.912255 | 10.830811 |
| C | -0.219066 | 14.467925 | 13.621825 |
| H | -1.008765 | 15.103439 | 13.231857 |
| C | -0.221751 | 14.098913 | 14.964214 |
| H | -1.007954 | 14.458756 | 15.619938 |
| C | 0.777741 | 13.262230 | 15.462693 |
| H | 0.772823 | 12.970046 | 16.507492 |
| C | 1.780846 | 12.803781 | 14.612286 |
| H | 2.563727 | 12.156250 | 14.993715 |

| | | | |
|---|---|---|---|
| C | 1.783440 | 13.179982 | 13.269302 |
| H | 2.564446 | 12.818132 | 12.606803 |
| C | 0.784229 | 14.010888 | 12.759521 |
| C | 0.306417 | 16.082147 | 9.669376 |
| H | -0.497489 | 15.398111 | 9.385137 |
| H | 1.134972 | 15.951957 | 8.955634 |
| C | -0.921685 | 18.172073 | 6.758389 |
| H | 0.017940 | 18.716831 | 6.745993 |
| C | -1.650429 | 18.003747 | 5.582608 |
| H | -1.276799 | 18.415177 | 4.651573 |
| C | -2.862121 | 17.317268 | 5.607588 |
| H | -3.430957 | 17.189674 | 4.692840 |
| C | -3.345198 | 16.792111 | 6.806205 |
| H | -4.287233 | 16.255095 | 6.825490 |
| C | -2.613880 | 16.945420 | 7.980236 |
| H | -2.984733 | 16.509701 | 8.902314 |
| C | -1.398229 | 17.640789 | 7.961597 |
| C | -1.604383 | 17.857031 | 10.832482 |
| H | -2.528928 | 18.293547 | 10.453849 |
| H | -1.794577 | 16.855176 | 11.219419 |
| C | -2.377939 | 18.863219 | 12.937184 |
| H | -2.643809 | 17.852100 | 13.247001 |
| H | -3.176637 | 19.270039 | 12.316167 |
| C | -2.043943 | 21.128369 | 13.992741 |
| H | -2.205148 | 21.585854 | 13.021201 |
| C | -1.803535 | 21.927940 | 15.106652 |
| H | -1.765079 | 23.006122 | 14.997335 |
| C | -1.629568 | 21.345018 | 16.361707 |
| H | -1.452048 | 21.970178 | 17.230090 |
| C | -1.695046 | 19.960362 | 16.500722 |
| H | -1.568246 | 19.503629 | 17.476224 |
| C | -1.924609 | 19.159659 | 15.384415 |
| H | -1.979445 | 18.080584 | 15.489864 |
| C | -2.098134 | 19.736287 | 14.122578 |
| C | 0.024369 | 18.222431 | 12.726195 |
| H | -0.168023 | 17.194776 | 13.040092 |
| H | 0.136875 | 18.861948 | 13.601446 |
| H | -0.970081 | 19.641731 | 11.629466 |
| H | 2.199598 | 21.428452 | 11.221157 |

**TABLE S23.** Cartesian coordinates of the optimized structure of $[Ni^{II}(P_2^{Ph}HN_2^{Bn})_2(MeCN)]^{4+}$ (i.e., $[Ni^{II}NH_2]^{4+}$ with an MeCN ligand) (*exo-exo*).

(– 4223.67878558 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| Ni | 1.574157 | 19.131085 | 9.421285 |
| N | 3.072396 | 22.084937 | 7.426357 |
| N | 2.978237 | 22.667541 | 10.086410 |
| N | 0.161790 | 15.943578 | 11.095494 |
| N | -0.956658 | 18.141507 | 12.143482 |
| N | 2.097450 | 17.970290 | 7.873053 |
| P | 3.551350 | 20.084843 | 9.392102 |
| P | 0.892186 | 21.209588 | 8.936177 |
| P | 1.733168 | 18.234740 | 11.470542 |
| P | -0.408330 | 18.168531 | 9.461199 |
| C | 4.925740 | 17.654080 | 9.460720 |
| H | 3.953781 | 17.193703 | 9.328983 |
| C | 6.069582 | 16.863274 | 9.522575 |
| H | 5.980829 | 15.786155 | 9.438050 |
| C | 7.318976 | 17.454361 | 9.693746 |
| H | 8.208522 | 16.836252 | 9.743335 |
| C | 7.427344 | 18.840090 | 9.797836 |
| H | 8.398296 | 19.303420 | 9.932393 |
| C | 6.290407 | 19.638478 | 9.724970 |
| H | 6.397045 | 20.715598 | 9.795927 |
| C | 5.031661 | 19.044735 | 9.560201 |
| C | 3.892664 | 20.876908 | 7.742069 |
| H | 4.936227 | 21.197481 | 7.736963 |
| H | 3.741855 | 20.131959 | 6.959073 |
| C | 3.631323 | 22.715873 | 6.162114 |
| H | 3.712069 | 21.902803 | 5.439229 |
| H | 4.632385 | 23.047448 | 6.440691 |
| C | 2.139273 | 23.633661 | 4.380655 |
| H | 2.181200 | 22.659321 | 3.904196 |
| C | 1.435334 | 24.673668 | 3.778443 |
| H | 0.925578 | 24.503229 | 2.836312 |
| C | 1.388930 | 25.925069 | 4.388343 |
| H | 0.839903 | 26.737576 | 3.924583 |
| C | 2.055844 | 26.133755 | 5.595486 |
| H | 2.028935 | 27.109620 | 6.068209 |
| C | 2.767440 | 25.096943 | 6.191159 |
| H | 3.295677 | 25.274939 | 7.121826 |
| C | 2.814714 | 23.835485 | 5.588158 |
| C | 1.608660 | 21.829675 | 7.333646 |
| H | 1.431662 | 21.104222 | 6.537602 |
| H | 1.137147 | 22.778804 | 7.075081 |
| C | -1.466396 | 21.774420 | 7.521173 |
| H | -0.925242 | 21.510497 | 6.620283 |

| | | | |
|---|---|---|---|
| C | -2.794720 | 22.178839 | 7.420557 |
| H | -3.262604 | 22.230971 | 6.443918 |
| C | -3.516514 | 22.514629 | 8.563743 |
| H | -4.549434 | 22.833839 | 8.480173 |
| C | -2.905011 | 22.447967 | 9.813857 |
| H | -3.455839 | 22.713119 | 10.709673 |
| C | -1.576187 | 22.047562 | 9.924237 |
| H | -1.110586 | 22.015358 | 10.903717 |
| C | -0.848770 | 21.712166 | 8.775227 |
| C | 1.527521 | 22.475832 | 10.148946 |
| H | 1.049240 | 23.423515 | 9.889471 |
| H | 1.189817 | 22.179148 | 11.152980 |
| C | 3.347525 | 23.877246 | 10.858629 |
| H | 2.710052 | 24.683045 | 10.483634 |
| H | 3.110451 | 23.725744 | 11.921100 |
| C | 5.670353 | 24.185894 | 11.795051 |
| H | 5.301311 | 23.829610 | 12.752076 |
| C | 7.001813 | 24.579690 | 11.665071 |
| H | 7.667351 | 24.523278 | 12.519785 |
| C | 7.474750 | 25.048980 | 10.441857 |
| H | 8.508521 | 25.361250 | 10.339834 |
| C | 6.610325 | 25.121986 | 9.349195 |
| H | 6.969022 | 25.491649 | 8.394645 |
| C | 5.281827 | 24.732335 | 9.484583 |
| H | 4.609243 | 24.805137 | 8.636325 |
| C | 4.795768 | 24.259437 | 10.708038 |
| C | 3.728651 | 21.504153 | 10.560503 |
| H | 3.415431 | 21.170349 | 11.560693 |
| H | 4.784763 | 21.778672 | 10.608646 |
| C | 4.178062 | 17.490398 | 12.622809 |
| H | 4.201893 | 16.686633 | 11.896544 |
| C | 5.194229 | 17.584664 | 13.568593 |
| H | 5.991610 | 16.849678 | 13.569400 |
| C | 5.180157 | 18.609149 | 14.512615 |
| H | 5.967383 | 18.672802 | 15.256111 |
| C | 4.153395 | 19.551066 | 14.501265 |
| H | 4.139215 | 20.350211 | 15.234473 |
| C | 3.131263 | 19.464004 | 13.558812 |
| H | 2.327501 | 20.192739 | 13.575124 |
| C | 3.134393 | 18.422755 | 12.621115 |
| C | 1.536454 | 16.379486 | 11.470022 |
| H | 2.245532 | 15.931264 | 10.772055 |
| H | 1.727241 | 16.000784 | 12.475561 |
| C | -0.025938 | 14.456683 | 11.295636 |
| H | 0.690285 | 13.961733 | 10.637577 |
| H | -1.036868 | 14.247658 | 10.943439 |
| C | -0.792384 | 14.396492 | 13.693001 |
| H | -1.659988 | 14.986397 | 13.410989 |
| C | -0.636457 | 13.979855 | 15.011389 |
| H | -1.373634 | 14.258752 | 15.756229 |
| C | 0.455905 | 13.189573 | 15.369957 |
| H | 0.570739 | 12.856925 | 16.395926 |
| C | 1.393779 | 12.820931 | 14.408317 |

| | | | |
|---|---|---|---|
| H | 2.243466 | 12.205726 | 14.683954 |
| C | 1.244621 | 13.248135 | 13.090621 |
| H | 1.972002 | 12.960440 | 12.338395 |
| C | 0.151756 | 14.037279 | 12.724137 |
| C | -0.244381 | 16.330614 | 9.714078 |
| H | -1.225505 | 15.889667 | 9.528232 |
| H | 0.473693 | 15.922539 | 9.001064 |
| C | -0.900333 | 18.658609 | 6.755542 |
| H | 0.117842 | 19.027074 | 6.721433 |
| C | -1.664144 | 18.615912 | 5.592709 |
| H | -1.234977 | 18.957614 | 4.657839 |
| C | -2.970939 | 18.136629 | 5.633204 |
| H | -3.567119 | 18.107101 | 4.727913 |
| C | -3.511403 | 17.687049 | 6.837005 |
| H | -4.528012 | 17.311660 | 6.872369 |
| C | -2.751510 | 17.716980 | 8.001571 |
| H | -3.194407 | 17.361463 | 8.925013 |
| C | -1.437822 | 18.204013 | 7.963698 |
| C | -1.497668 | 18.645022 | 10.881153 |
| H | -1.632737 | 19.733985 | 10.863288 |
| H | -2.472223 | 18.175829 | 10.724353 |
| C | -1.964037 | 18.165196 | 13.230606 |
| H | -1.521809 | 17.624450 | 14.071376 |
| H | -2.815421 | 17.582430 | 12.869218 |
| C | -3.496449 | 20.165418 | 13.035454 |
| H | -4.018759 | 19.658510 | 12.229665 |
| C | -3.925126 | 21.425488 | 13.448128 |
| H | -4.768313 | 21.895991 | 12.953652 |
| C | -3.282014 | 22.072276 | 14.502452 |
| H | -3.618738 | 23.050766 | 14.827806 |
| C | -2.210995 | 21.451568 | 15.142954 |
| H | -1.714001 | 21.943121 | 15.972588 |
| C | -1.784321 | 20.192048 | 14.727546 |
| H | -0.962683 | 19.706063 | 15.244938 |
| C | -2.419652 | 19.534664 | 13.668612 |
| C | 0.303931 | 18.764383 | 12.547903 |
| H | 0.534096 | 18.428799 | 13.561589 |
| H | 0.261334 | 19.861709 | 12.542896 |
| C | 2.400084 | 17.269964 | 7.002679 |
| C | 2.780675 | 16.384209 | 5.926163 |
| H | 2.006856 | 15.626309 | 5.788047 |
| H | 3.724691 | 15.894983 | 6.176176 |
| H | 2.900189 | 16.952748 | 5.002097 |
| H | 3.204244 | 22.714447 | 8.263096 |
| H | -0.480953 | 16.503011 | 11.732023 |

**TABLE S24.** Cartesian coordinates of the optimized structure of $[Ni^{I}(P_2^{Ph}HN_2^{Bn})_2]^{3+}$ (i.e., $[Ni^{I}NH_2]^{3+}$) (*exo-exo*).

(– 4090.70049226 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | 9.084455 | 5.845639 | 8.602552 |
| H | 8.852958 | 4.947024 | 9.177483 |
| H | 9.998467 | 5.674845 | 8.030828 |
| C | 9.747575 | 8.251694 | 9.034717 |
| H | 10.637152 | 8.113131 | 8.417315 |
| H | 9.996174 | 8.879466 | 9.890988 |
| C | 10.381871 | 6.398892 | 10.585071 |
| H | 11.207341 | 6.033640 | 9.972434 |
| H | 9.894675 | 5.549861 | 11.067130 |
| C | 10.877363 | 7.393406 | 11.592025 |
| C | 12.188135 | 7.870669 | 11.498819 |
| H | 12.818475 | 7.537851 | 10.680397 |
| C | 12.687957 | 8.752208 | 12.454468 |
| H | 13.708622 | 9.110527 | 12.377320 |
| C | 11.877686 | 9.166139 | 13.509430 |
| H | 12.267437 | 9.849904 | 14.256299 |
| C | 10.569074 | 8.694596 | 13.608401 |
| H | 9.936551 | 9.011618 | 14.430814 |
| C | 10.072921 | 7.806946 | 12.658269 |
| H | 9.056659 | 7.434855 | 12.748317 |
| C | 6.964299 | 8.924660 | 9.238301 |
| H | 7.203344 | 9.528199 | 10.117877 |
| H | 6.087735 | 9.367144 | 8.740679 |
| C | 6.319211 | 6.624057 | 8.621919 |
| H | 5.468664 | 6.996943 | 8.032554 |
| H | 6.020910 | 5.685703 | 9.095386 |
| C | 5.607567 | 7.579414 | 10.702433 |
| H | 5.278330 | 6.546574 | 10.832027 |
| H | 4.759454 | 8.151813 | 10.299012 |
| C | 6.007680 | 8.123965 | 12.047290 |
| C | 6.513802 | 7.255566 | 13.019965 |
| H | 6.639075 | 6.203550 | 12.781172 |
| C | 6.837785 | 7.720696 | 14.292023 |
| H | 7.221040 | 7.032024 | 15.037654 |
| C | 6.659680 | 9.067159 | 14.608595 |
| H | 6.902089 | 9.430913 | 15.601517 |
| C | 6.151998 | 9.940631 | 13.648534 |
| H | 5.996993 | 10.986660 | 13.891030 |
| C | 5.821565 | 9.469170 | 12.379087 |
| H | 5.394465 | 10.147743 | 11.646642 |
| C | 7.221196 | 4.538498 | 6.870599 |
| C | 7.093230 | 4.306823 | 5.498070 |
| H | 7.302627 | 5.108966 | 4.798287 |

| | | | |
|---|---|---|---|
| C | 6.687106 | 3.058884 | 5.030391 |
| H | 6.583874 | 2.892564 | 3.963562 |
| C | 6.407472 | 2.035826 | 5.932586 |
| H | 6.092315 | 1.063397 | 5.570461 |
| C | 6.535792 | 2.259445 | 7.303780 |
| H | 6.321232 | 1.464180 | 8.009047 |
| C | 6.939740 | 3.505282 | 7.773146 |
| H | 7.028791 | 3.666452 | 8.842637 |
| C | 8.789325 | 10.834955 | 8.114871 |
| C | 9.959919 | 11.345624 | 8.686697 |
| H | 10.693711 | 10.687552 | 9.137936 |
| C | 10.199687 | 12.718875 | 8.679965 |
| H | 11.109058 | 13.102488 | 9.129145 |
| C | 9.275097 | 13.591090 | 8.111839 |
| H | 9.460844 | 14.659634 | 8.114164 |
| C | 8.109277 | 13.086512 | 7.537130 |
| H | 7.385661 | 13.760682 | 7.092141 |
| C | 7.870921 | 11.715636 | 7.525159 |
| H | 6.969139 | 11.332401 | 7.055591 |
| C | 8.840388 | 6.837931 | 2.884859 |
| H | 9.651743 | 6.622641 | 2.184940 |
| H | 8.333256 | 5.894581 | 3.125128 |
| C | 10.297783 | 9.129211 | 3.805866 |
| H | 10.660837 | 9.740684 | 4.633626 |
| H | 11.126581 | 8.904469 | 3.132371 |
| C | 7.644674 | 7.420658 | 0.842213 |
| H | 8.606786 | 7.351569 | 0.327698 |
| H | 7.087954 | 8.253447 | 0.404334 |
| C | 6.880131 | 6.129588 | 0.683299 |
| C | 5.481390 | 6.110454 | 0.729821 |
| H | 4.935587 | 7.040321 | 0.857568 |
| C | 4.781429 | 4.914270 | 0.586923 |
| H | 3.696913 | 4.917181 | 0.617228 |
| C | 5.472539 | 3.718736 | 0.393772 |
| H | 4.928622 | 2.788144 | 0.270584 |
| C | 6.865608 | 3.726190 | 0.340868 |
| H | 7.407474 | 2.801440 | 0.171750 |
| C | 7.562364 | 4.924222 | 0.486542 |
| H | 8.646532 | 4.929155 | 0.424130 |
| C | 8.185073 | 10.500078 | 3.808729 |
| H | 7.619506 | 11.140345 | 3.128998 |
| H | 8.592372 | 11.109062 | 4.618538 |
| C | 6.732605 | 8.146779 | 2.994951 |
| H | 6.168610 | 7.259263 | 3.311136 |
| H | 6.092555 | 8.741916 | 2.338816 |
| C | 10.032884 | 10.990992 | 2.220549 |
| H | 10.853147 | 10.474161 | 1.720064 |
| H | 10.447116 | 11.694040 | 2.945543 |
| C | 9.150057 | 11.675171 | 1.218606 |
| C | 8.830636 | 11.036348 | 0.015382 |
| H | 9.214254 | 10.039792 | -0.182048 |
| C | 8.038573 | 11.677134 | -0.932315 |
| H | 7.798079 | 11.175534 | -1.863536 |

| | | | |
|---|---|---|---|
| C | 7.567144 | 12.967423 | -0.691667 |
| H | 6.954782 | 13.467535 | -1.434423 |
| C | 7.885221 | 13.612430 | 0.501422 |
| H | 7.525807 | 14.617940 | 0.690949 |
| C | 8.673027 | 12.967743 | 1.452980 |
| H | 8.931068 | 13.473572 | 2.378269 |
| C | 11.087933 | 6.505955 | 4.673407 |
| C | 12.351728 | 7.085711 | 4.840632 |
| H | 12.479239 | 8.161909 | 4.806569 |
| C | 13.468360 | 6.281138 | 5.058362 |
| H | 14.442525 | 6.741271 | 5.184087 |
| C | 13.334814 | 4.896112 | 5.112870 |
| H | 14.205641 | 4.271509 | 5.279007 |
| C | 12.077731 | 4.314452 | 4.954210 |
| H | 11.967111 | 3.236483 | 4.996486 |
| C | 10.956065 | 5.111595 | 4.742730 |
| H | 9.982342 | 4.644764 | 4.632766 |
| C | 5.495746 | 10.076708 | 4.733290 |
| C | 4.928443 | 10.832433 | 3.699436 |
| H | 5.425792 | 10.918203 | 2.738107 |
| C | 3.713316 | 11.481422 | 3.896155 |
| H | 3.281450 | 12.068871 | 3.093422 |
| C | 3.052923 | 11.374211 | 5.120388 |
| H | 2.104446 | 11.878568 | 5.271248 |
| C | 3.610013 | 10.619850 | 6.149435 |
| H | 3.096908 | 10.531355 | 7.100679 |
| C | 4.829054 | 9.972228 | 5.958293 |
| H | 5.258765 | 9.376495 | 6.757977 |
| N | 9.350463 | 6.927998 | 9.603219 |
| N | 6.699354 | 7.554882 | 9.694816 |
| N | 7.945983 | 7.806877 | 2.241372 |
| N | 9.312911 | 9.928017 | 3.015012 |
| Ni | 8.113206 | 7.964362 | 6.094196 |
| P | 7.688642 | 6.213479 | 7.418496 |
| P | 8.388390 | 9.058317 | 8.036653 |
| P | 9.588587 | 7.520004 | 4.458653 |
| P | 7.068504 | 9.178975 | 4.525270 |
| H | 8.417653 | 7.082401 | 10.076072 |
| H | 8.843958 | 9.212181 | 2.364889 |

**TABLE S25.** Cartesian coordinates of the optimized structure of *p*-anisidinium.

(– 403.77162493 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | -1.154272 | -0.053504 | 1.989940 |
| C | 0.098219 | -0.046392 | 1.399193 |
| C | 1.259795 | 0.007701 | 2.162286 |
| C | 1.157318 | 0.051971 | 3.542632 |
| C | -0.101581 | 0.045718 | 4.159648 |
| C | -1.259670 | -0.007144 | 3.377932 |
| N | 0.201485 | -0.073528 | -0.061666 |
| H | 1.025806 | -0.588886 | -0.376787 |
| H | -0.612028 | -0.520182 | -0.488681 |
| H | 2.234515 | 0.010179 | 1.686588 |
| H | 2.045857 | 0.086274 | 4.161416 |
| O | -0.097980 | 0.088530 | 5.508971 |
| H | -2.241244 | -0.014664 | 3.833550 |
| H | -2.052053 | -0.091055 | 1.382912 |
| C | -1.354043 | 0.079153 | 6.174826 |
| H | -1.128325 | 0.117907 | 7.238773 |
| H | -1.951832 | 0.950621 | 5.892068 |
| H | -1.909783 | -0.835383 | 5.947560 |
| H | 0.266856 | 0.866628 | -0.459784 |

**TABLE 26.** Cartesian coordinates of the optimized structure of *p*-cyanoanilinium.

(– 381.41040611 $E_h$)

| atom | X | Y | Z |
|---|---|---|---|
| C | -0.944548 | 1.328192 | 0.006912 |
| C | 0.441702 | 1.297233 | 0.010591 |
| C | 1.137619 | 2.499189 | 0.006221 |
| C | 0.428560 | 3.705902 | -0.001965 |
| C | -0.973438 | 3.715237 | -0.006220 |
| C | -1.665980 | 2.514307 | -0.001668 |
| H | 0.972218 | 0.352135 | 0.017099 |
| H | 2.220006 | 2.502348 | 0.009434 |
| H | -1.511788 | 4.654488 | -0.012196 |
| H | -2.749346 | 2.502021 | -0.004265 |
| C | 1.135188 | 4.947158 | -0.004885 |
| N | 1.698650 | 5.963619 | -0.006655 |
| N | -1.676796 | 0.062536 | 0.016437 |
| H | -2.269534 | -0.026785 | 0.846650 |
| H | -2.286065 | -0.031156 | -0.801099 |
| H | -1.040561 | -0.737642 | 0.011596 |

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