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A Phosphine-ß-diketiminate Nickel(I)-Complex for Small Molecule Activation

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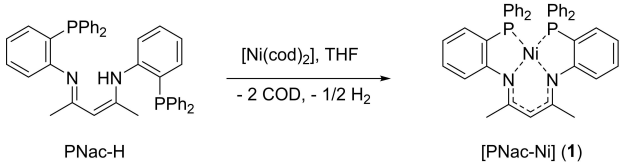
A bis(diphenyl)-phosphine functionalized ß-diketimine ligand (PNac-H) was applied for the synthesis of a subvalent Ni(I) complex [PNac-Ni]. Here, the Ni(I) center is stabilized by a tetradentate PNNP-type pocket, forming a square planar coordination sphere. Subsequently, the Ni(I) complex was investigated with regard to its reactivity and the activation of small molecules. The reductive potential of Ni(I) enabled an activation of different substrate classes, such as CH_2X_2 (X=Br, I), I_2 or Ph_2E_2 (E=S, Se). The ligand's design allows a stabilization of the reactive Ni(I) species while at the same time enabling activation processes due to a hemilabile coordination behavior and accessible axial coordination sites. The activation products have been characterized by single crystal X-ray diffraction, NMR and IR spectroscopy as well as elemental analysis.

Introduction

The majority of investigations in current nickel chemistry focus on nickel in its most common oxidation states 0 and +2. However, in recent years Ni(I) compounds have generated extensive interest, mainly due to their unique reactivity and magnetic properties.[1,2] In particular, nickel(I) species have indicated great potential regarding catalytic transformations of organic substrates,[3,4] aiming for a replacement of expensive palladium and platinum, and the activation of small molecules.[5] For this purpose, a better understanding in relation to the role of nickel in catalytic reactions, *e.g.* the involvement of different cycles such as Ni(0)/Ni(II), Ni(I)/Ni(II) or a radical mechanism Ni(0)/Ni(I)/Ni(II), will help for understanding future catalyst design.[4,6–8] In addition, nickel(I) has been discovered to play a key role in several catalytic cycles proposed for nickel-containing enzymes.[5,9–14] Despite the often proclaimed instability, Ni(I) complexes have been known for over a century.[1,15,16] However, since the isolation of the first Ni(I) complex $K_4[Ni_2(CN)_6]$ by Bellucci and Corelli in 1914,[17] exhibiting two planar $Ni(CN)_3$ units connected by a short Ni–Ni bond,[18] it took many decades until Ni(I) chemistry received further attention.[15] Nowadays more than 300 structurally characterized Ni(I) complexes are known, which are stabilized by different ligand systems with coordination numbers ranging from 2 to 6.[1,19]

Recently our group reported the synthesis of a phosphine functionalized *ß*-diketimine (PNac-H; Scheme 1), combining two of the most commonly applied ligand systems in coordination chemistry.[20,21] The popularity of *ß*-diketimines is mainly based on the convenient synthetic accessibility and adjustability, allowing a fine tuning of the ligand's electronic and steric properties.[20,22–31] Hence, a high degree of control for task-specific adjustments, *e.g.* kinetic stabilization of sub-valent metal species via sterically demanding substituents, is facilitated.[31] The introduction of additional phosphorous donor sites to a *ß*-diketimine scaffold enables the extension to more complex coordination motifs and a higher degree of metal stabilization. As a result, a series of transition metal and main group complexes, including metal ions in subvalent oxidation states, was realized applying the PNac ligand system.[32,33] In this manner, the isolation of a Ni(I) species [PNac-Ni] was achieved (Scheme 1).

Herein, we investigate the Ni(I) complex [PNac-Ni] (**1**) with regard to the activation of small molecules. The reductive potential of a Ni(I) species combined with a hemilabile coordination behavior of the bifunctional ligand system and accessible axial coordination sites should allow an effectual reactivity of the nickel(I) center.



PNac-H [PNac-Ni] (**1**)

Scheme 1. Synthesis of the Ni(I) complex **1** via reaction of PNac-H and $[Ni(cod)_2]$.

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Results and Discussion

The phosphine functionalized ß-diketimine ligand (PNac-H) was obtained by a two-step synthesis route, as previously reported by our group.[32,33] Subsequent treatment with Ni(0) precursor [Ni(cod)$_2$] resulted in the formation of nickel(I) complex [PNac-Ni] (**1**) by a redox reaction (Scheme 1). In complex **1** the metal ion is surrounded by a tetradentate PNNP type pocket, which effectively protects the subvalent Ni(I) center.[34]

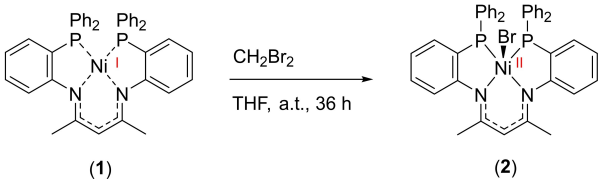
A molecular structure of **1** in the solid state was previously reported by us (see SI, Figure S1).[33] Here, the Ni(I) center is arranged in a square planar coordination sphere, which according to crystal field theory seems advantageous for a d^9 electron system such as Ni(I).[35] In addition, the steric demand of the triarylphosphine groups most likely helps to prohibit a dimerization, *via* formation of a Ni–Ni bond, which in some cases is observed as a stabilization process.[36,37] Applying the Evans NMR method,[38,39] a paramagnetic susceptibility of **1** was observed, which is consistent with a complex containing a single unpaired electron, in line with a Ni(I) d^9 species.[33]

Despite the fact that the square planar PNNP pocket of the PNac ligand stabilizes the nickel center in its uncommon oxidation state +1,[1,40] the reactive metal center is axially unprotected and therefore seems accessible for smaller molecules. Thus, the reductive Ni(I) complex [PNac-Ni] (**1**) was subsequently investigated regarding its potential for the activation of small molecules. In prior studies we have already shown that [PNac-Ni] (**1**) exhibited a distinct reactivity towards dichloromethane (CH_2Cl_2), resulting in the formation of a divalent nickel species [PNac-NiCl].[33]

In a first study [PNac-Ni] (**1**), synthesized *in situ* by reaction of PNac-H with [Ni(cod)$_2$], was added to a solution of CH_2Br_2 (in excess) and stirred overnight at ambient temperature (Scheme 2). The incipiently dark red color of the solution, characteristic of a nickel(I) complex, changed to dark green throughout the reaction. Such a color change indicates the formation of a Ni(II) species, caused by a radical reaction of nickel(I) with the bromine containing substrate.[34]

Dark green single crystals of **2**, suitable for X-ray analysis, were obtained from slow diffusion of *n*-pentane into a DCM solution. Complex **2** crystallizes in the triclinic space group $P\bar{1}$, with one molecule in the asymmetric unit. The molecular structure in the solid state (Figure 1) confirms the formation of a Ni(II) species [PNac-NiBr] (**2**), which is in line with a formal oxidation of the Ni center.

The molecular structure reveals a square pyramidal coordination geometry around the Ni(II) center,[41] consisting of the ligand's tetradentate PNNP unit and a bromide. Here, the PNNP



(**1**) (**2**)

Scheme 2. Activation of dibromomethane (CH_2Br_2) applying [PNac-Ni] (**1**).

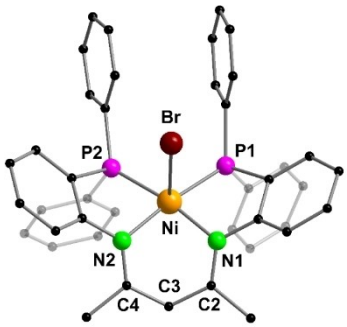


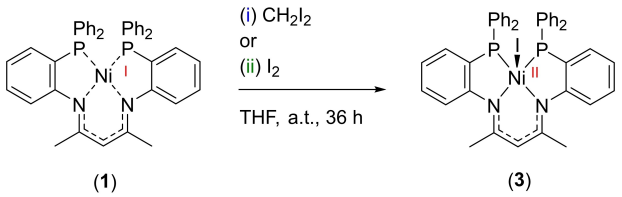
Figure 1. Molecular structure of **2** in the solid state. Hydrogen atoms and solvent molecules (DCM) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–Br 2.8097(8), Ni–P1 2.1556(12), Ni–P2 2.1762(12), Ni–N1 1.938(3), Ni–N2 1.932(3), N1–C2 1.329(5), C2–C3 1.400(5), C3–C4 1.392(5), N2–C4 1.326(5); P1–Ni–Br 90.81(4), P1–Ni–P2 101.95(4), P2–Ni–Br 94.15(4), N1–Ni–Br 93.89(9), N1–Ni–P1 83.20(9), N2–Ni–Br 95.52(10), N2–Ni–P2 81.47(10), N1–Ni–N2 92.51(13), N1–C2–C3 123.0(3), C2–C3–C4 126.4(3), N2–C4–C3 121.8(3).

moiety coordinates square planarly, as indicated by the respective angles (*e.g.* N1–Ni–N2 92.51(13)°, N1–Ni–P1 83.20(9)° or P1–Ni–P2 101.95(4)°). The angles are in close agreement with those obtained for [PNac-Ni] (**1**).[33] The bromide is located orthogonally to this plane, as confirmed by the angles P1–Ni–Br 90.81(4)°, P2–Ni–Br 94.15(4)°, N1–Ni–Br 93.89(9)° and N2–Ni–Br 95.52(10)°. The nickel phosphorous (Ni–P1 2.1556(12), Ni–P2 2.1762(12) Å) and nitrogen (Ni–N1 1.938(3), Ni–N2 1.932(3) Å) bond lengths confirm the ligand's symmetric arrangement in the solid state. However, the bond lengths are significantly shorter (approx. 0.1 Å) in comparison to [PNac-Ni] (**1**), which is mainly due to the higher charge of the Ni(II) center and the consequential difference in ionic radii.[42] A similar effect has been observed for the isostructural chloride complex.[33]

Furthermore, compound **2** was analyzed by NMR and IR spectroscopy as well as elemental analysis. In contrast to paramagnetic Ni(I) complex **1**, interpretable NMR spectra of **2** were obtained, confirming the formation of a diamagnetic Ni(II) species. In the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) a singlet resonance at $\delta = 35.4$ ppm is detected, indicating a symmetric phosphine nickel coordination in solution. The resonance is significantly downfield shifted in comparison to ligand PNac-H ($\delta = -14.5$ ppm).[33] Accordingly, characteristic resonances for the PNac ligand system are observed in the respective ^1H and $^{13}C\{^1H\}$ NMR spectra of **2**.

In a second attempt, [PNac-Ni] (**1**) was reacted with an excess of diiodomethane (CH_2I_2) applying similar reaction conditions as before (Scheme 3).[34]

Dark green single crystals of **3**, suitable for X-ray analysis, were obtained from slow diffusion of *n*-pentane into a DCM solution. As expected, complex **3** crystallizes isostructural to complex **2** in the triclinic space group $P\bar{1}$. Accordingly, the Ni(II) center of [PNac-NiI] (**3**) lies in a square pyramidal coordination sphere, consisting of the ligand's tetradentate PNNP unit and an iodide (Figure 2). The respective bond length and angles are



Scheme 3. Activation of diiodomethane (CH_2I_2) or molecular I_2 applying [PNac-Ni] (**1**).

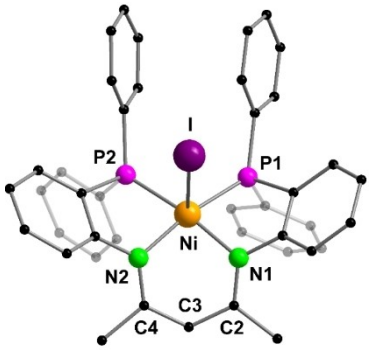


Figure 2. Molecular structure of **3** in the solid state. Hydrogen atoms and solvent molecules (DCM) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–I 2.9616(6), Ni–P1 2.1777(10), Ni–P2 2.1564(8), Ni–N1 1.922(2), Ni–N2 1.926(2), N1–C2 1.333(2), C2–C3 1.391(3), C3–C4 1.396(3), N2–C4 1.396(3); P1–Ni–I 95.87(4), P2–Ni–I 91.39(3), P2–Ni–P1 102.23(3), N1–Ni-I 96.78(5), N1–Ni–P1 81.33(5), N1–Ni–N2 92.19(7), N2–Ni–I 94.56(6), N2–Ni–P2 82.79(6), N1–C2–C3 121.3(2), C2–C3–C4 126.4(2), N2–C4–C3 122.8(2).

similar to those observed for the bromide containing complex **2**.

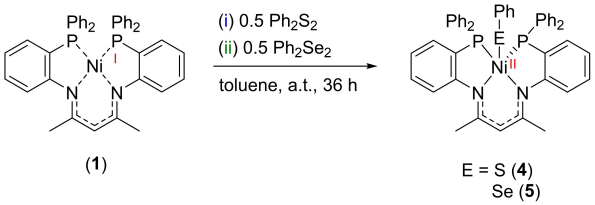
Compound **3** was further analyzed by NMR and IR spectroscopy as well as elemental analysis. The NMR data is in agreement with the isostructural bromide compound **2**. For instance, a resonance at $\delta = 35.6$ ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **3** (in comparison **2**: $\delta = 35.4$ ppm), which can be attributed to the symmetrically coordinating phosphine moieties.

Hence, [PNac-Ni] (**1**) proved to be highly reactive regarding the dihalogenide methanes CH_2Cl_2, CH_2Br_2 and CH_2I_2. In each case, the activation of the substrate goes along with an oxidation of the Ni(I) center. In the process a Ni(II) halogenide complex is formed as activation product, in which the square planar coordination sphere of [PNac-Ni] (**1**) is extended to a pyramidal polyhedron. In an additional study the activation of molecular iodine I_2 has been investigated, applying [PNac-Ni] (Scheme 3). Here, an analogous formation of Ni(II) iodide complex [PNac-NiI] (**3**) was observed and confirmed by X-ray analysis and NMR spectroscopy. Therefore, the monovalent Ni(I) species seems to exhibit a similar reactivity towards CH_2I_2 and I_2, resulting in the corresponding activation product **3**.

Investigating a completely different substance class, we aimed at the activation of diphenyldichalcogenides (Ph_2E_2 ; E=S, Se). These substrates exhibit a S–S or Se–Se bond, which can be cleaved reductively and therefore allow a meaningful determination with regard to the reactivity of a reducing agent.[43] In both cases [PNac-Ni] (**1**) was synthesized *in situ* and successively reacted with half an equivalent of diphenyldisulfide or diphenyldiselenide, respectively (Scheme 4). Similar to the reactions with CH_2Br_2 and CH_2I_2, a color change of the solution to dark green indicated an oxidation of the Ni(I) species during the activation process.[34]

Single crystals of the activation products **4** and **5**, suitable for X-ray analysis, were obtained from slow diffusion of *n*-pentane into a toluene solution of the respective complex. Both complexes (**4**, **5**) crystallize in the monoclinic space group $P2_1/c$, each with one molecule in the asymmetric unit. The molecular structures, displayed in Figure 3, confirm the successful activation of both Ph_2S_2 and Ph_2Se_2. The S-S and Se–Se bonds are cleaved by the reductive Ni(I) center, forming Ni(II) chalcogenides in the process.

The resulting Ni(II) center of the activation products [PNac-NiSPh] (**4**) and [PNac-NiSePh] (**5**) is in between a square pyramidal and a square planar coordination sphere with a loose Ni–P interaction, consisting of the ligand's PNNP moiety and a phenyl-sulfide (SPh) or phenyl-selenide (SePh) group. In contrast to **2** and **3**, the square planar coordination sphere is not formed by the PNNP pocket, yet one phosphine group is replaced by the respective chalcogenide moiety (SPh or SePh).



Scheme 4. Activation of diphenyldisulfide (Ph_2S_2) and diphenyldiselenide (Ph_2Se_2) applying [PNac-Ni] (**1**).

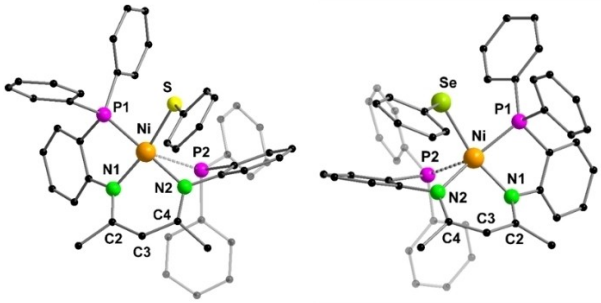


Figure 3. Molecular structures of **4** (left) and **5** (right) in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **4**: Ni–S 2.2030(12), Ni–P1 2.1260(12), Ni–P2 3.2216(13), Ni–N1 1.921(3), Ni–N2 1.954(3), N1–C2 1.352(5), C2–C3 1.396(5), C3–C4 1.410(6), N2–C4 1.318(5); S–Ni-P1 85.62(5), S–Ni-P2 98.15(4), P1–Ni–P2 114.37(4), N1–Ni–S 169.80(10), N1–Ni–P1 85.23(10), N1–Ni–P2 89.75(10), N1–Ni–N2 93.55(13), N2–Ni–S 95.75(10), N2–Ni–P2 63.60(10), N1–C2–C3 122.1(4), C2–C3–C4 126.3(4), N2–C4–C3 122.8(4). Selected bond lengths [Å] and angles [°] for **5**: Se–Ni 2.3582(4), Ni–P1 2.1217(8), Ni–P2 2.6285(8), Ni–N1 1.934(2), Ni–N2 1.949(2), N1–C2 1.339(4), C2–C3 1.391(4), C3–C4 1.413(4), N2–C4 1.326(4); Se-Ni–P1 84.48(2), Se-Ni–P2 93.01(2), P1–Ni–P2 118.25(3), N1–Ni–Se 164.37(7), N1–Ni–P1 83.45(7), N1–Ni–P2 101.44(7), N1–Ni–N2 93.27(10), N2–Ni–Se 95.87(7), N2–Ni–P2 76.62(7), N1–C2–C3 122.3(3), C2–C3–C4 127.0(3), N2–C4–C3 121.9(3).

The substituted triarylphosphine (P2) is aligned orthogonally to the square plane. In complex **4** the respective phosphorous nickel bond length P2–Ni is 3.2216(13) Å and therefore significantly longer than P1–Ni (2.1260(12) Å), indicating a merely weak phosphine coordination. A similar trend, although not as extensive, is observed in complex **5** (P1–Ni: 2.1217(8) Å; P2–Ni: 2.6285(8) Å). Hence, the molecular structures indicate that the PNac ligand enables a decoordination of the phosphines from the nickel center when a new substrate is added. On the other hand, the coordination of the *ß*-diketiminate moiety remains unchanged, as indicated by the nitrogen nickel distances (**4**: Ni–N1 1.921(3), Ni–N2 1.954(3) Å; **5**: Ni–N1 1.934(2), Ni-N2 1.949(2) Å), which are in the same range as observed for **2** and **3**. Hence, the *ß*-diketiminate unit provides a monoanionic, bidentate support for the nickel species, whereas the phosphine moieties allow partial replacement if necessary.[20]

In addition, activation products **4** and **5** were analyzed by NMR and IR spectroscopy as well as elemental analysis. In the respective $^{31}P\{^1H\}$ NMR spectrum (C_6D_6) of **4** two broad resonances are observed at $\delta = -15.1$ and 20.3 ppm. Hence, the two phosphine moieties do not behave equally in solution, which is in accordance to the information obtained from the solid state structure. Here, the resonance at $\delta = -15.1$ ppm can be attributed to a non-coordinated phosphorous species, which is in agreement to ligand PNac-H ($\delta = -14.5$ ppm).[33] The resonance at $\delta = 20.3$ ppm represents a phosphorous nickel species, which is slightly upfield shifted in comparison to the complexes **2** ($\delta = 35.4$ ppm) and **3** ($\delta = 35.6$ ppm). Analogously, the $^{31}P\{^1H\}$ NMR spectrum of complex **5** exhibits two broad resonances at $\delta = -14.4$ and 22.3 ppm. It closely matches the spectrum obtained for compound **4**, indicating a similar behavior of both complexes in solution. The broad signals observed in the $^{31}P\{^1H\}$ NMR spectra of **4** and **5** suggest an exchange equilibrium in solution, in which the phosphines coordinate and respectively decoordinate to the nickel center. Additionally, ^1H and $^{31}P\{^1H\}$ VT-NMR studies confirm this behavior, showing a coalescence point at around 330 K in the $^{31}P\{^1H\}$ NMR spectrum (see SI, Figure S19). Hence, [PNac-Ni] (**1**) proves to be an effective reducing agent for diphenyldichalcogenides, enabling activation with the help of the ligand's hemilabile coordination behavior. This effect is mainly due to the diverging functionalities of the PNac ligand, exhibiting hard *ß*-ketiminate and soft phosphine donor centers.[44,45] A ligand's hemilabile coordination behavior is an important characteristic for activation processes as well as potential catalytic applications, as free coordination sites can be unclosed for substrates to attach.

Conclusion

In summary, we present the investigation of a subvalent Ni(I) complex, utilizing a phosphine functionalized *ß*-diketimine ligand (PNac-H). The Ni(I) complex [PNac-Ni] was examined regarding its reactivity and activation potential of small molecules. Here, the reductive Ni(I) species, stabilized by a tetradentate, square planar PNNP pocket, enabled an activation of different substrate classes, e.g. CH_2X_2 (X=Br, I), I_2 or Ph_2E_2 (E=S, Se). The ligand's design allows a stabilization of the reactive Ni(I) species while at the same time enabling activation processes, due to a hemilabile coordination behavior of the ligand system and accessible axial coordination sites. Hence, monovalent [PNac-Ni] proves to be a promising and multipurpose metal complex for activation processes of small molecules.

Experimental Section

General procedures

All manipulations were performed under exclusion of moisture and oxygen in flame-dried Schlenk-type glassware or in an argon-filled *MBraun* glovebox. Prior to use, DCM was distilled under nitrogen from CaH_2. Hydrocarbon solvents (THF, toluene, *n*-pentane) were dried using an *MBraun* solvent purification system (SPS-800). THF was additionally distilled under nitrogen from potassium and benzophenone before storage over 4 Å molecular sieves. Deuterated solvents were obtained from Carl Roth GmbH (99.5 atom % D). Prior to use, $CDCl_3$ was stored over molecular sieves (4 Å), whereas C_6D_6 was stored over a Na/K alloy. NMR spectra were recorded on a Bruker Avance III 300 MHz or Avance Neo 400 MHz. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are referenced to the residual ^1H and ^{13}C resonances of the deuterated solvents and are reported relative to tetramethylsilane (TMS). $^{31}P\{^1H\}$ resonances are reported relative to external 85 % phosphoric acid. IR spectra were obtained on a *Bruker* Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit. Elemental analyses were carried out with a Micro Cube from *Elementar Analysensysteme GmbH.*

Synthesis[34]

General Information

PNac-H was prepared according to a literature procedure.[33] $[Ni(cod)_2]$ (98 %) was purchased from abcr. Diidomethane (99 %) and diphenyldiselenide (98 %) were purchased from Sigma Aldrich. Dibromomethane (99 %) and diphenyldisulfide (99 %) were purchased from Acros Organics. They were all used as received.

For the activation of CH_2Br_2, CH_2I_2, I_2, Ph_2S_2 and Ph_2Se_2 (synthesis of compounds **2**–**5**) the Ni(I) species [PNac-Ni] (**1**) has been formed *in situ* prior to the addition of the respective substrates. An isolation of complex **1** leads to the same results regarding the activation procedures. [PNac-Ni] (**1**) was prepared according to literature procedures.[33]

In the $^{13}C\{^1H\}$ NMR spectra of complexes **2** and **3** virtual triplet resonances (labelled: vt) are observed, due to specific C–P couplings. Such a fine structure splitting has previously been reported for organo-phosphorous metal complexes.[21,46]

[PNac-NiBr] (**2**): PNac-H (150.0 mg, 0.24 mmol, 1.0 eq.) and $[Ni(cod)_2]$ (67.0 mg, 0.24 mmol, 1.0 eq.) were dissolved in 10 mL of THF and stirred at ambient temperature for 16 hours. Subsequently, 2 mL of degassed dibromomethane (excess) were added to the dark red solution. After stirring for another 2 hours, whereupon a dark green solid precipitated, the solvent was removed under reduced pressure. The residue was washed with *n*-pentane (2 x 10 mL) and dissolved in DCM. Single crystals of **2** suitable for X-ray analysis

were obtained by slow diffusion of *n*-pentane into a DCM solution. Crystalline yield: 79.1 mg (43 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 2.08 (s, 6H, CH_3), 5.53 (s, 1H, CH_{NacNac}), 6.83–7.03 (m, 6H, CH_{Ar}), 7.21–7.60 (m, 22H, CH_{Ar}). – A quantitative integration of the aromatic proton resonances is hampered due to underlying solvent resonance. ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ [ppm] = 22.8 (CH_3), 115.6 (CH_{NacNac}), 123.8 (CH_{Ar}), 124.7 (vt, $^{1}J_{C,P}$ = 25.3 Hz, C_q), 125.1 (CH_{Ar}), 126.6 (vt, $^{1}J_{C,P}$ = 28.3 Hz, C_q), 129.6 (CH_{Ar}), 131.4 (CH_{Ar}), 132.3 (CH_{Ar}), 133.1 (CH_{Ar}), 133.3 (CH_{Ar}), 156.9 (vt, $^{2}J_{C,P}$ = 11.1 Hz, C_q), 160.4 (C_q). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ [ppm] = 35.4 (s). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3051 (w), 2975 (vw), 2922 (vw), 2855 (vw), 2869 (w), 1645 (w), 1584 (w), 1524 (w), 1481 (vw), 1435 (vs), 1351 (s), 1269 (w), 1187 (vw), 1151 (w), 1118 (m), 1098 (m), 1070 (vw), 1022 (vw), 996 (vw), 748 (m), 723 (m), 693 (s), 545 (m), 506 (w) 442 (vw). Elemental analysis calcd (%) for [$C_{41}H_{35}N_2NiP_2Br \cdot CH_2Cl_2$] (841.22 g mol^{-1}): C 59.97, H 4.43, N 3.33; found C 60.38, H 4.37, N 3.37.

[PNac-NiI] (**3**): PNac-H (150.0 mg, 0.24 mmol, 1.0 eq.) and [Ni(cod)$_2$] (67.0 mg, 0.24 mmol, 1.0 eq.) were dissolved in 10 mL of THF and stirred at ambient temperature for 16 hours. Subsequently, 2 mL of degassed diiodomethane (excess) were added to the dark red solution. After stirring for another 2 hours, whereupon a dark green solid precipitated, the solvent was removed under reduced pressure. The residue was washed with *n*-pentane (2 x 10 mL) and dissolved in DCM. Single crystals of **3** suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a DCM solution. Crystalline yield: 141 mg (72 %). – Alternatively, complex **3** is formed, reacting [PNac-Ni] (**1**) *in situ* with molecular iodine I_2, applying similar reaction conditions. Here, half an equivalent of I_2 is used with regards to [PNac-Ni] (**1**).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.04 (s, 6H, CH_3), 5.31 (s, 1H, CH_{NacNac}), 6.81 – 6.96 (m, 6H, CH_{Ar}), 7.22–7.24 (m, 1H, CH_{Ar}), 7.27–7.29 (m, 3H, CH_{Ar}), 7.30–7.41 (m, 14H, CH_{Ar}), 7.43–7.52 (m, 4H, CH_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ [ppm] = 22.7 (CH_3), 115.6 (CH_{NacNac}), 123.7 (vt, $J_{C,P}$ = 6.1 Hz, CH_{Ar}), 124.5 (vt, $^{1}J_{C,P}$ = 26.0 Hz, C_q), 125.1 (vt, $J_{C,P}$ = 3.9 Hz, CH_{Ar}), 126.4 (vt, $^{1}J_{C,P}$ = 27.9 Hz, C_q), 128.4 (CH_{Ar}), 129.6 (vt, $J_{C,P}$ = 5.4 Hz, CH_{Ar}), 131.4 (CH_{Ar}), 132.3 (CH_{Ar}), 133.0 (vt, $J_{C,P}$ = 5.3 Hz, CH_{Ar}), 133.3 (CH_{Ar}), 156.9 (vt, $^{2}J_{C,P}$ = 11.6 Hz, C_q), 160.4 (C_q). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ [ppm] = 35.6 (s). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3048 (vw), 3008 (vw), 2955 (vw), 2913 (vw), 1597 (vw), 1576 (vw), 1524 (w), 1478 (vw), 1453 (vw), 1435 (m), 1368 (vw), 1343 (m), 1308 (m), 1234 (vs), 1188 (m), 1150 (s), 1134 (s), 1098 (s), 1067 (w), 1019 (vw), 982 (m), 944 (vw), 867 (vw), 808 (vw), 743 (m), 718 (w), 690 (m), 640 (vw), 566 (vw), 539 (w), 502 (m), 449 (vw), 415 (vw). Elemental analysis calcd (%) for [$C_{41}H_{35}N_2NiP_2I \cdot CH_2Cl_2$] (888.22 g mol^{-1}): C 56.79, H 4.20, N 3.15; found C 56.01, H 4.06, N 3.26.

[PNac-NiSPh] (**4**): PNac-H (150.0 mg, 0.24 mmol, 1.0 eq.) and [Ni(cod)$_2$] (67.0 mg, 0.24 mmol, 1.0 eq.) were dissolved in 10 mL toluene and stirred at ambient temperature for 16 hours. Subsequently, diphenyldisulfide (26.6 mg, 0.12 mmol, 0.50 eq.) was added and the solution stirred overnight. Single crystals of **4** suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a toluene solution. Crystalline yield: 32.0 mg (17 %).

^{1}H NMR (C_6D_6, 400 MHz): δ [ppm] = 1.52 (s, 6H, CH_3), 4.72 (s, 1H, CH_{NacNac}), 6.22–6.58 (m, 1H, CH_{Ar}), 6.62–6.75 (m, 2H, CH_{Ar}), 6.84–7.13 (m, 21H, CH_{Ar}), 7.38–8.08 (m, 7H, CH_{Ar}), 8.17–8.34 (m, 2H, CH_{Ar}). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ [ppm] = 22.1 (CH_3), 109.6 (CH_{NacNac}), 121.4 (CH_{Ar}), 126.9 (CH_{Ar}), 132.3 (CH_{Ar}), 133.6 (CH_{Ar}), 134.8 (CH_{Ar}), 148.4 (C_q), 158.7 (C_q). Due to resonance broadening and overlaying solvent not all carbon resonances can be observed and distinguished. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ [ppm] = −15.1 (s, *P*Ph_2Ar), 20.3 (s, Ni-*P*Ph_2Ar). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3366 (vw), 3050 (w), 3001 (vw), 2982 (vw), 1578 (w), 1548 (w), 1523 (w), 1465 (w), 1434 (vs), 1345 (vs), 1264 (m), 1185 (w), 1158 (vw), 1129 (vw), 1096 (w), 1067 (vw), 1022 (w), 998 (vw), 863 (vw), 838 (vw), 738 (s), 689 (vs), 628 (vw), 544 (vw), 495 (m), 483 (w), 448 (vw). Elemental analysis calcd (%) for [$C_{47}H_{40}N_2NiP_2S$] (785.55 g mol^{-1}): C 71.86, H 5.13, N 3.57, S 4.08; found C 70.47, H 4.73, N 3.70, S 4.48.

[PNac-NiSePh] (**5**): PNac-H (150.0 mg, 0.24 mmol, 1.0 eq.) and [Ni(cod)$_2$] (67.0 mg, 0.24 mmol, 1.0 eq.) were dissolved in 10 mL of toluene and stirred at ambient temperature for 16 hours. Subsequently, diphenyldiselenide (38.0 mg, 0.12 mmol, 0.50 eq.) was added and the solution stirred overnight. Single crystals of **5** suitable for X-Ray analysis were obtained by slow diffusion of *n*-pentane into a toluene solution. Crystalline yield: 88.0 mg (44 %).

^{1}H NMR (C_6D_6, 400 MHz): δ [ppm] = 1.57 (s, 6H, CH_3), 4.79 (s, 1H, CH_{NacNac}), 6.18–6.53 (m, 1H, CH_{Ar}), 6.53–6.78 (m, 2H, CH_{Ar}), 6.85–7.12 (m, 21H, CH_{Ar}), 7.51–7.90 (m, 7H, CH_{Ar}), 8.16–8.49 (m, 2H, CH_{Ar}). ^{13}C{^{1}H} NMR (C_6D_6, 101 MHz): δ [ppm] = 22.0 (CH_3), 110.2 (CH_{NacNac}), 122.9 (CH_{Ar}), 125.0 (CH_{Ar}), 132.2 (CH_{Ar}), 133.7 (CH_{Ar}), 134.6 (CH_{Ar}), 140.3 (CH_{Ar}), 158.8 (C_q).–Due to resonance broadening and overlaying solvent not all carbon resonances can be observed and distinguished. ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ [ppm] = −14.4 (s, *P*Ph_2Ar), 22.3 (s, Ni-*P*Ph_2Ar). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3050 (w), 2924 (vw), 1573 (w), 1545 (w), 1515 (w), 1474 (vw), 1432 (s), 1372 (vs), 1290 (vw), 1265 (s), 1228 (vw), 1183 (w), 1156 (vw), 1125 (vw), 1099 (w), 1064 (w), 1021 (w), 941 (vw), 874 (vw), 835 (vw), 755 (w), 735 (m), 689 (s), 625 (vw), 563 (vw), 542 (vw), 497 (m), 464 (m). Elemental analysis calcd (%) for [$C_{47}H_{40}N_2NiP_2Se$] (832.45 g mol^{-1}): C 67.81, H 4.48, N 3.37; found C 68.40, H 4.48, N 3.38.

X-ray crystallographic studies

Detailed XRD measurement description as well as crystal and structure refinement data are provided as Supporting Information (SI).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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