ORGANOMETALLICS-

Synthesis and Structures of Nickel Complexes with a PN-Chelate Phosphaalkene Ligand

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S Supporting Information

ABSTRACT: Phosphaalkenes with a P=C bond possess extremely strong π -accepting ability, often providing transition metal complexes with interesting structures and properties. This paper describes unique structures of nickel complexes coordinated with a PN-chelate phosphaalkene ligand (PEP = 2-[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine). The PEP ligand combines with [NiBr₂(dme)] (dme = 1,2-dimethoxyethane) in toluene to afford [Ni(Br)(μ -Br)(PEP)]₂ (1), which reacts with R₂Mg(thf)₂ in Et₂O or THF to form three types of nickel complexes depending on the R groups and reaction conditions. The reaction with Ph₂Mg(thf)₂ produces a Ni(I) dimer bridged with two μ -Br



ligands, $[Ni(\mu-Br)(PEP)]_2$ (2). Treatment of 1 with $R_2Mg(thf)_2$ (R = Me, Me_3SiCH₂) at -35 °C leads to dialkyl complexes $[NiR_2(PEP)]$ (3 and 4), with a significantly distorted square planar configuration. DFT calculations support the occurrence of effective π -back-bonding between Ni to PEP to cause the structural distortion. On the other hand, the reaction of 1 with $R_2Mg(thf)_2$ (R = Me_3SiCH₂) conducted at a low temperature of -78 °C forms an aryl bromide complex of the formula $[Ni(Mes^*)(Br)(PEP^*)]$ (5; Mes* = 2,4,6-^tBu₃C₆H₂), in which the Mes* group originally bonded to the phosphorus atom of PEP is shifted to nickel; instead, the phosphorus atom is substituted with the R group to form the PEP* ligand. The temperature-dependent formation of 4 or 5 is rationalized by considering a common five-coordinate intermediate.

INTRODUCTION

Phosphaalkenes with a P=C double bond possess an extremely low-lying π^* orbital, thereby serving as effective π -acceptors toward transition metals.¹ We have demonstrated that this particular ligand property often provides interesting structures and reactivities in late transition metal complexes. For example, 1,2-diaryl-3,4-diphosphinidenecyclobutene causes highly efficient catalysis in conjunction with group 8–10 metals.^{2,3} 2,6-Bis(phosphaethenyl)pyridine effectively stabilizes coordinatively unsaturated complexes of 3d metals.^{4,5} Moreover, the P=C bond installed in a PNP-pincer type iridium complex remarkably enhances the reactivity toward N–H bond activation of ammonia and amines via metal–ligand cooperation.⁶

This paper deals with novel nickel complexes with a PNchelate phosphaalkene ligand, 2-[1-phenyl-2-(2,4,6-tri-*tert*butylphenyl)-2-phosphaethenyl]pyridine (PEP) (Scheme 1). Thus far, nickel complexes have been extensively studied using tertiary phosphine ligands and have proven to be useful for catalytic organic transformations.⁷ In this context, phosphaalkene complexes of nickel should also be attractive; however, only three papers have documented their isolation using CO and π -allyl ligands.⁸

In this study, we prepared $[Ni(Br)(\mu-Br)(PEP)]_2$ (1) and examined its reactions with $R_2Mg(thf)_2$ (R = Ph, Me,

Scheme 1. Reactions of $[Ni(Br)(\mu-Br)(PEP)]_2$ (1) with Diorganomagnesiums



 Me_3SiCH_2). The resultant complexes displayed notable structural variations depending on R groups and reaction conditions as summarized in Scheme 1. The reaction with $Ph_2Mg(thf)_2$ forms a Ni(I) bromide complex (2).⁹ Treatment

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of 1 with dialkylmagnesiums leads to dialkyl complexes of the formula [NiR₂(PEP)] (3 and 4) with a significantly distorted square planar configuration. On the other hand, treatment of 1 with R₂Mg(thf)₂ (R = Me₃SiCH₂) at low temperature (-78 °C) results in the formation of Mes* complex 5 (Mes* = 2,4,6-^tBu₃C₆H₂) via the exchange of Me₃SiCH₂ and Mes* groups between Ni and P atoms.

RESULTS AND DISCUSSION

Synthesis of $[Ni(Br)(\mu-Br)(PEP)]_2$ (1). The PEP ligand was prepared from 2-benzoylpyridine and Mes*PH₂ by the phospha-Peterson reaction.¹⁰ A crude product of PEP, which contained a small amount of Mes*H, was subjected to the reaction with $[NiBr_2(dme)]$ (dme = 1,2-dimethoxyethane) in toluene at 60 °C for 17 h to form 1, which was isolated as a reddish-brown solid in 74% yield. Complex 1 was a paramagnetic compound unable to be characterized by NMR spectroscopy; however, its dimeric structure with Ni(II) centers could be confirmed by X-ray diffraction analysis.

Figure 1 shows the crystal structure, which consists of two NiBr₂(PEP) units connected by two μ -Br ligands (Br1 and



Figure 1. Molecular structure of $1 \cdot CH_2Cl_2$ with 50% probability ellipsoids. Hydrogen atoms and a crystal solvent (CH_2Cl_2) are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni-P 2.3218(15), Ni-N 2.061(4), Ni-Br1 2.5119(10), Ni-Br1' 2.5316(10), Ni-Br2 2.3997(9), P-C6 1.691(5), P-Ni-N 80.51(12), P-Ni-Br1' 97.78(4), N-Ni-Br1 87.44(11), Br1-Ni-Br1' 84.18(3), P-Ni-Br1 110.80(4), N-Ni-Br1' 170.23(12).

Br1'). Each unit has a trigonal bipyramidal configuration around Ni. The Br1, Br2, and P atoms are located at the equatorial positions, whereas the N and Br1' atoms are at the apical positions. The bond distances of Ni–N (2.061(4) Å) and Ni–P (2.3218(15) Å) are comparable to those of a phosphinebased PN-chelate analogue.¹¹ The P–C6 distance (1.691(5) Å) is in a typical range of P-coordinated phosphaalkenes in late transition metal complexes.^{4–6,8}

Reaction with Ph₂Mg(thf)₂. Treatment of 1 with Ph₂Mg(thf)₂ in a 1:2 molar ratio in Et₂O at -35 °C formed a Ni(I) bromide dimer, $[Ni(\mu-Br)(PEP)]_2$ (2), which was isolated as a dark blue crystalline solid in 91% yield and characterized by elemental analysis and X-ray crystallography. Complex 2 is likely to be formed by comproportionation of $[NiBr_2(PEP)]$ and [Ni(PEP)], the latter of which is generated by reductive elimination of biphenyl from $[NiPh_2(PEP)]$ formed by transmetalation. The formation of biphenyl was confirmed by GC-MS analysis of the reaction solution.

Figure 2 shows the crystal structure of **2**. Nearly half of the molecules (46%) are paired with a crystal solvent (Et_2O). The



Figure 2. Molecular structure of $2 \cdot (Et_2O)_{0.46}$ with 50% probability ellipsoids. Hydrogen atoms, disordered carbon atoms (Ph), and a crystal solvent (Et₂O) are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni1–P1 2.1334(17), Ni1–N1 1.961(5), Ni1–Br1 2.4456(10), Ni1–Br2 2.4160(10), P1–C6 1.691(6), Ni2–P2 2.1472(16), Ni2–N2 1.966(4), Ni2–Br1 2.4220(10), Ni2–Br2 2.4481(10), P2–C36 1.703(6), P1–Ni1–N1 83.52(14), Br1–Ni1–Br2 95.28(3), P2–Ni2–N2 83.76(14), Br1–Ni2–Br2 95.07(3), Ni1–Br1–Ni2 80.60(3), Ni1–Br2–Ni2 80.67(3).

other half does not involve the solvent molecule, but instead the phenyl group on the C6 atom is tilted to compensate for the vacant space. The core structures are identical to one another irrespective of the presence or absence of Et_2O .

The Ni1 and Ni2 atoms are bridged by μ -Br ligands (Br1 and Br2). The complex has a quasi- $C_{2\nu}$ symmetry, and the PEP ligands are associated with the Ni₂(μ -Br)₂ core in a *syn*-orientation. The bond distances of Ni–N (1.961(5) and 1.966(4) Å) and Ni–P (2.1334(17) and 2.1472(16) Å) are clearly shorter than those of the Ni(II) dimer (1) in a high-spin state. The P=C bond distances (1.691(6) and 1.703(6) Å) are comparable to that of 1 (1.691(5) Å).

The interatomic distance between Ni1 and Ni2 is 3.15 Å; this value is apparently too large for a direct bonding interaction, but is somewhat smaller than the sum of the van der Waals radii of Ni atoms (3.22 Å). Therefore, we carried out SQUID measurement of **2** in the solid state. The magnetic moment (μ_{eff}) ranging from 2.17 to 2.80 μ_{B} at 5–300 K demonstrated the S = 1 ground state, and the χ^{-1} –T plot exhibited a good linear correlation (see Figure S1). Thus, we concluded the absence of a notable spin–spin interaction between the Ni atoms.

On the other hand, the magnetic moment of a solution of **2** in toluene was determined to be 1.68 $\mu_{\rm B}$ at 25 °C by the Evans method (calculated for the monomer). This value corresponds to the S = 1/2 ground state and indicates the occurrence of dissociation of **2** into the monomeric species [NiBr(PEP)] in solution.

Reactions with R_2Mg(thf)_2 (R = Me, Me_3SiCH_2). Unlike the reaction with $Ph_2Mg(thf)_2$, the reactions of 1 with 2 molar quantities of dialkylmagnesiums in Et_2O formed dialkyl complexes of the formula $[NiR_2(PEP)]$ (R = Me (3), Me_3SiCH_2 (4)) in 55% and 83% isolated yields, respectively. Dimethyl complex 3 was relatively unstable in solution and gradually decomposed even at -35 °C. On the other hand, complex 4, with bulky Me_2SiCH_2 ligands, was fairly stable at room temperature. Complexes 3 and 4 are diamagnetic compounds displaying their NMR signals in a normal region. The ¹H NMR spectrum of 3 measured in THF- d_8 exhibited two sets of doublets at δ 0.47 (${}^{3}J_{\rm PH} = 5.2$ Hz) and 0.79 (${}^{3}J_{\rm PH} = 13.2$ Hz), which are assignable to the Me ligands *cis* and *trans* to the phosphorus atom, respectively, based on the ${}^{3}J_{\rm PH}$ values. Similarly, the methylene proton signals of Me₃SiCH₂ ligands in 4 at the *cis* and *trans* positions of the phosphorus atom appeared at δ 0.48 (${}^{3}J_{\rm PH} = 7.6$ Hz) and 0.86 (${}^{3}J_{\rm PH} = 12.4$ Hz), respectively.

Figure 3 presents the X-ray crystal structure of 3. One of the most remarkable features is a significantly distorted square



Figure 3. Molecular structure of 3 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–P 2.1339(10), Ni–N 1.972(3), Ni–C1 1.943(4), Ni–C2 1.931(4), P–C8 1.692(3), P–Ni–N 82.69(8), P–Ni–C1 155.28(17), N–Ni–C2 172.59(15).

planar geometry with a bent P–Ni–C1 bond (155.28(17)°), whereas the N–Ni–C2 axis retains linearity (172.59(15)°). Complex 4 adopts a similar geometry around Ni (P–Ni–C1 = 154.69(7)°; see Figure S2). Furthermore, the phosphorus atom is slightly pyramidalized to the opposite side of the Ni–C1 axis; the sum of the bond angles around phosphorus is 353.6° .

To explore the cause of the structural distortion, DFT calculations were carried out for the model compound [NiMe₂(pep)] (3a), in which the 2,4,6^{-t}Bu₃C₆H₂ group (Mes*) on the phosphorus atom was replaced by the 2,4,6- $Me_3C_6H_2$ group (Mes); see the Supporting Information for details of the computation. The optimized structure of 3a given in Figure 4a successfully reproduces the distorted square planar configuration of 3. The P-Ni-C1 bond is bent to 148.1°, and the bond angles around the phosphorus atom are 342.0° in total. The distorted structure proved to be 4.9 kcal/mol more stable than the square planar geometry with the fixed P-Ni-C1 angle of 180° (3a' in Figure 4b). On the other hand, phosphine analogue 3b, having a saturated MesP(H)CHPh group at the 2-position of pyridine (Figure 4c), was optimized with a square planar configuration, which was located 4.3 kcal/ mol lower in energy than the distorted one with the fixed P-Ni–C1 angle of 148° (3b' in Figure 4d).

Thus, we concluded that the phosphaalkene unit causes the structural distortion found in **3** and **3a**. Figure 5 shows a schematic view of the orbital interaction along the P–Ni–C1 bond in **3**, which corresponds to the π -back-bonding between the Ni atom and the P=C bond. Bending the P–Ni–C1 bond causes an antibonding interaction between the d (Ni) and σ (Me) orbitals, thereby increasing the d orbital level. As a result, the π -back-donation is facilitated and the distorted structure is stabilized. In fact, the Mayer bond order of the P=C bond of **3a** (1.39) was lower than that of **3a**' (1.49).



Figure 4. Optimized structures for 3a, 3a', 3b, and 3b'. The structures of 3a' and 3b' were optimized under the constraints of the fixed bond angles of $P-Ni-C1 = 180^{\circ}$ (3a'), 148° (3b').



Figure 5. Schematic view of an orbital interaction causing structural distortion of 3.

Reaction with $R_2Mg(thf)_2$ ($R = Me_3SiCH_2$) at Low Temperature. The above-mentioned reaction of 1 with $R_2Mg(thf)_2$ ($R = Me_3SiCH_2$) to give dialkyl complex 4 was conducted at -35 °C. On the other hand, the same reaction performed at -78 °C afforded the Mes* complex [Ni(Mes*)-(Br)(PEP*)] (5), in which the Mes* substituent on phosphorus was replaced by a Me_3SiCH_2 group. Complex 5 was exclusively formed when a 1:1 molar ratio of 1 and $R_2Mg(thf)_2$ was employed (R/Ni = 1:1). Furthermore, even with a 2 molar quantity of $R_2Mg(thf)_2$ (R/Ni = 2), complex 5 was formed as the major product (71%), along with 4 (29%), as confirmed by ³¹P NMR spectroscopy.

Figure 6 shows the X-ray crystal structure of 5, which adopts a square planar configuration around nickel, as generally observed for 16e complexes with a low-spin state d^8 metal center. The Mes* and Br ligands are located *trans* to the N and P atoms, respectively. This ligand arrangement is in accordance with the order of *trans*-influence.

Scheme 2 presents a plausible reaction process for the formation of $[Ni(Mes^*)(Br)(PEP^*)]$ (5). The first step is transmetalation of 1 with $R_2Mg(thf)_2$ ($R = Me_3SiCH_2$) via five-coordinate intermediate A, in which the $Ni(R)Br_2(PEP)$ moiety is very likely to be associated with the MgR(thf) moiety. Although there are several possibilities of the aggregation form, the doubly bridged structure with two μ -Br ligands is illustrated as a probable one. When the reaction temperature is relatively high (-35 °C), the MgR(thf) moiety is eliminated from A,



Figure 6. Molecular structure of 5 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–P 2.0702(7), Ni–N 2.025(2), Ni–Br 2.3502(4), Ni–C17 1.912(3), P–C6 1.682(2), P–Ni–N 83.41(6), P–Ni–Br 174.12(3), N–Ni–C17 171.11(10).





along with the μ -Br ligand, to form monoalkyl complex D, which subsequently undergoes transmetalation with alkylmagnesium to afford dialkyl complex 4.

On the other hand, when the five-coordinate intermediate **A** is reluctant to eliminate the MgR(Br)(thf)₂ moiety at a low temperature of -78 °C, the R ligand becomes capable of migrating to the phosphorus atom, affording **B**. This reaction requires a parallel orientation of the Ni–R bond against the π^* orbital of the P=C bond. The five-coordinate structure of **A** having the R ligand at the apical position realizes an ideal situation. Recently, we have demonstrated a similar migration process for an Fe(I) mesityl complex by DFT calculations.¹² Then, complex **B** undergoes migration of the Mes* group from

phosphorus to nickel, and the subsequent elimination of $MgR(Br)(thf)_2$ from C produces the mesityl complex 5.

CONCLUSION

In this study, we examined nickel complexes derived from $[Ni(Br)(\mu-Br)(PEP)]_2$ (1) with a PN-chelate phosphaalkene ligand (PEP). The complexes formed by the reactions of 1 with $R_2Mg(thf)_2$ (R = Ph, Me, Me_3SiCH₂) varied significantly with R groups and reaction conditions. The reaction with Ph₂Mg- $(thf)_2$ formed $[Ni(\mu-Br)(PEP)]_2$ (2) with significantly distorted coordination geometry around Ni(I) centers. Alkylmagnesiums provided dialkyl complexes $[NiR_2(PEP)]$ (R = Me (3), Me_3SiCH_2 (4)), with a bent P-Ni-R bond. On the other hand, treatment of 1 with $R_2Mg(thf)_2$ (R = Me₃SiCH₂) at low temperature (-78 °C) resulted in selective formation of $[Ni(Mes^*)(Br)(PEP^*)]$ (5; Mes^{*} = 2,4,6-^tBu₃C₆H₂). In this case, the Mes* group originally bonded to phosphorus was shifted to nickel, whereas the phosphorus atom was substituted with the R group instead. Apparently, the observed structures and reactivities are unique to the PEP complexes with a P=Cbond. Indeed, DFT calculations for 3 demonstrated the structural distortion caused by the phosphaalkene unit. The present results indicate the potential utility of phosphaalkene ligands in nickel chemistry.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glovebox. Toluene, hexane, CH_2Cl_2 , and Et_2O were purified by a solvent purification system (MBraun SPS-800). Other solvents (THF, benzene- d_{6} , toluene- d_8 , THF- d_8) were dried over sodium benzophenone ketyl and distilled. $R_2Mg(thf)_2$ (R = Ph, Me, Me₃SiCH₂) were prepared according to the literature.¹³

NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (¹H NMR, 400.13 MHz; ¹³C NMR, 100.62 MHz; ³¹P NMR, 161.98 MHz). Chemical shifts are reported in δ (ppm), referenced to ¹H (residual) and ¹³C signals of deuterated solvents as internal standards or the ³¹P signal of 85% H₃PO₄ as an external standard. Elemental analysis and FAB-MS were performed by the ICR Analytical Laboratory, Kyoto University. ESI-MS spectra were recorded on a Bruker micrOTOF I spectrometer. Solid-state magnetic moments were recorded using a Quantum Design SQUID magnetometer. Magnetization versus temperature data were recorded in a magnetic field of 10 000 G, using crystalline samples sealed in quartz tubes. An impurity correction was made by fitting experimental data to the formula $\chi_{impurity} = C/T$. GC-MS analysis was performed on a Shimadzu GC-MS QP2010 instrument (EI, 70 eV).

Synthesis of PEP. To a THF solution (20 mL) containing $Mes*PH_2$ (1.16 g, 4.16 mmol) was added *n*-BuLi (3.14 mL, 4.99 mmol, 1.59 M in hexane) at -78 °C. The mixture was stirred at room temperature for 30 min, and then Me_3SiCl (0.633 mL, 4.99 mmol) was added. After stirring for 30 min at room temperature, *n*-BuLi (3.14 mL, 4.99 mmol, 1.59 M in hexane) was added at -78 °C. The mixture was again stirred at room temperature for 30 min to give a solution of $Mes*P(Li)SiMe_3$.

The following procedure was carried out in the dark to avoid E/Z isomerization of P=C bonds. A solution of 2-benzoylpyridine (0.635 g, 3.47 mmol) in THF (13 mL) was prepared in another Schlenk tube and cooled to -78 °C. The solution of Mes*P(Li)SiMe₃ was added dropwise, and the mixture was stirred at room temperature for 15 h. Volatiles were removed under vacuum, and the residue was dissolved in toluene and filtered through a Celite pad. After drying under vacuum, PEP was obtained as a pale yellow sticky solid (0.81 g) containing a small amount of inseparable Mes*H.

PEP. ¹H NMR (C_6D_6 , 25 °C): δ 1.29 (s, 9H, ¹Bu), 1.57 (s, 18H, ¹Bu), 6.35 (d, ³J_{HH} = 7.7 Hz, 1H, 3-py), 6.79 (t, ³J_{HH} = 7.6 Hz, 1H, 5-py), 7.00–7.06 (m, 3H, 4-py and Ph), 7.12 (d, ³J_{HH} = 7.0 Hz, 1H, Ph),

7.33 (s, 2H, Mes^{*}), 7.64 (d, ${}^{3}J_{HH}$ = 6.8 Hz, 2H, Ph), 8.18 (d, ${}^{3}J_{HH}$ = 4.0 Hz, 1H, 6-py). ${}^{31}P{}^{1}H$ NMR (C₆D₆, 25 °C): δ 252.9 (s). HRMS (FAB): calcd for C₃₀H₃₈NP 443.2742 ([M]⁺); found 443.2739.

Synthesis of [Ni(Br)(\mu-Br)(PEP)]₂ (1). A Schlenk tube was charged with [NiBr₂(dme)] (160.7 mg, 0.520 mmol) and then with a toluene solution (60 mL) of PEP (209.9 mg, 0.473 mmol). The solution was heated to 60 °C for 17 h and then filtered while hot through a Celite pad. After drying under vacuum, the resulting reddish-brown solid was washed with hexane. Recrystallization from CH₂Cl₂ at -35 °C afforded orange crystals of 1 (241.2 mg, 0.182 mmol, 77%). Anal. Calcd for C₆₀H₇₆N₂P₂Ni₂Br₄: C, 54.42; H, 5.79; N, 2.12. Found: C, 54.22; H, 5.89; N, 2.27.

Reaction of 1 with Ph₂Mg(thf)₂. To an Et₂O solution (3.5 mL) of 1 (44.0 mg, 0.0332 mmol) was added an Et₂O suspension (4.0 mL) of Ph₂Mg(thf)₂ (25.8 mg, 0.0799 mmol) at -35 °C. 1,4-Dioxane (23 μ L) was added, and the solution was filtered through glass wool and concentrated to dryness to give a dark blue solid, which was dissolved in cooled toluene and filtered through a Celite pad. A crude product formed by concentration of the filtrate was recrystallized from Et₂O at -35 °C to give dark blue crystals of 2 (36.2 mg, 0.0302 mmol, 91%). Anal. Calcd for C₆₀H₇₆N₂P₂Ni₂Br₂·0.46(C₄H₁₀O): C, 61.97; H, 6.78; N, 2.34. Found: C, 62.37; H, 6.72; N, 2.26.

Reaction of 1 with R_2Mg(thf)_2 (R = Me, Me_3SiCH_2) at -35 °C. To an Et_2O solution (2.0 mL) of 1 (16.1 mg, 0.0122 mmol) was added an Et_2O suspension (1.0 mL) of Me_2Mg(thf)_2 (4.9 mg, 0.025 mmol) at -35 °C. 1,4-Dioxane (0.4 mL) was added, and the solution was filtered through glass wool and concentrated to dryness to give a deep blue solid. The solid was dissolved in cooled toluene and filtered through a Celite pad. The filtrate was concentrated, and the residue was recrystallized from Et_2O at -35 °C to give deep blue crystals of 3 (7.2 mg, 0.0135 mmol, 55%).

The reaction of 1 (37.6 mg, 0.0284 mmol) with $(Me_3SiCH_2)_2Mg_{(thf)_2}$ (22.0 mg, 0.0641 mmol) was similarly conducted in Et₂O (2 mL), and deep green crystals of 4 were obtained (32.2 mg, 0.0476 mmol, 83%).

3. ¹H NMR (THF- $d_{8^{}}$, -50 °C): δ 0.47 (d, ² J_{PH} = 5.2 Hz, 3H, Me), 0.79 (d, ² J_{PH} = 13.2 Hz, 3H, Me), 1.34 (s, 9H, p-⁴Bu), 1.50 (s, 18H, o-⁶Bu), 6.69 (d, ³ J_{HH} = 8.0 Hz, 1H, Ph), 6.97 (t, ³ J_{HH} = 7.6 Hz, 1H, Ph), 7.11 (t, ³ J_{HH} = 7.2 Hz, 2H, Ph), 7.36 (d, ³ J_{HH} = 8.0 Hz, 1H, py), 7.42 (s, 2H, Mes^{*}), 7.54 (m, 1H, py), 7.81 (d, ³ J_{HH} = 7.6 Hz, 1H, py), 9.23 (d, ³ J_{HH} = 5.6 Hz, 1H, py). ¹³C{¹H} NMR (THF- $d_{8^{}}$, -50 °C): δ 9.5 (s, Me), 10.5 (s, Me), 31.6 (s, p-C(CH₃)₃), 34.2 (s, o-C(CH₃)₃), 36.0 (s, p-C(CH₃)₃), 39.7 (s, o-C(CH₃)₃), 122.0 (s, *ipso*-Ph), 122.3 (s, 3-py), 123.4 (s, 5-py), 124.4 (s, *m*-Mes^{*}), 125.7 (d, ² J_{PC} = 21.7 Hz, 2-py), 127.2 (s, p-Ph), 128.4 (d, ³ J_{PC} = 6.7 Hz, o-Ph), 129.0 (s, *m*-Ph), 137.6 (s, 4-py), 139.8 (d, J = 13.8 Hz, *ipso*-Mes^{*}), 151.6 (s, 6-py), 153.5 (s, p-Mes^{*}), 154.3 (d, ¹ J_{PC} = 15.5 Hz, C==P), 157.2 (s, o-Mes^{*}). ³¹P{¹H</sup> NMR (THF- $d_{8^{}}$ -50 °C): δ 250.9 (s). Anal. Calcd for C₃₂H₄₄NPNi: C, 72.20; H, 8.33; N, 2.63. Found: C, 71.73; H, 8.50; N, 2.61.

4. ¹H NMR (THF- d_{8} , 25 °C): δ –0.21 (s, 9H, SiMe₃), 0.14 (s, 9H, SiMe₃), 0.48 (d, ³ J_{PH} = 7.6 Hz, 2H, CH₂), 0.86 (d, ³ J_{PH} = 12.4 Hz, 2H, CH₂), 1.34 (s, 9H, *p*-⁵Bu), 1.52 (s, 18H, *o*-⁵Bu), 6.57 (d, ³ J_{HH} = 6.4 Hz, 2H, Ph), 6.94 (t, ³ J_{HH} = 8.0 Hz, 1H, Ph), 7.08 (t, ³ J_{HH} = 6.8 Hz, 2H, Ph), 7.14 (d, ³ J_{HH} = 6.8 Hz, 1H, py), 7.40 (s, 2H, Mes*), 7.45 (t, ³ J_{HH} = 6.4 Hz, 1H, py), 7.69 (t, ³ J_{HH} = 7.6 Hz, 1H, py), 9.30 (d, ³ J_{HH} = 5.6 Hz, 1H, py), 7.69 (t, ³ J_{HH} = 7.6 Hz, 1H, py), 9.30 (d, ³ J_{HH} = 5.6 Hz, 1H, py), 1³C{¹H} NMR (THF- d_{8} , 25 °C): δ 2.7 (s, Si(CH₃)₃), 4.1 (s, Si(CH₃)₃), 15.4 (d, ² J_{PC} = 122 Hz, CH₂SiMe₃), 18.2 (d, ² J_{PC} = 84 Hz, CH₂SiMe₃), 31.8 (s, *p*-C(CH₃)₃), 34.8 (s, *o*-C(CH₃)₃), 36.0 (s, *p*-C(CH₃)₃), 39.6 (s, *o*-C(CH₃)₃), 121.8 (s, *ipso*-Ph), 121.9 (s, 3-py), 122.7 (s, 5-py), 123.9 (s, *m*-Mes*), 127.1 (s, *p*-Ph), 128.3 (d, ³ J_{PC} = 7.5 Hz, *o*-Ph), 128.8 (s, *m*-Ph), 129.2 (s, 2-py), 137.4 (s, 4-py), 140.3 (s, *ipso*-Mes*), 150.9 (s, 6-py), 153.7 (s, *p*-Mes*), 154.2 (s, C==P), 158.0 (s, *o*-Mes*). ³¹P{¹H} NMR (THF- d_{8} , 25 °C): δ 253.0 (s). HRMS (ESI): calcd for C₃₈H₆₀NPSi₂Ni 676.3462 ([M + H]⁺); found 676.3428.

Reaction of 1 with R_2Mg(thf)_2 (R = Me₃SiCH₂) at -78 °C. This reaction was initially examined in NMR scale at -78 °C in Et₂O using a 1:1 molar ratio of 1 and $(Me_3SiCH_2)_2Mg(thf)_2$, and the selective formation of $[Ni(Mes^*)(Br)(PEP^*)]$ (5) was confirmed by ${}^{31}P{}^{1}H$

NMR analysis. On the other hand, the reaction performed in CH_2Cl_2 was less selective, giving a mixture of 5 and 4 (6:4) even at -78 °C. The experimental procedure for a preparative-scale reaction is as follows. The reaction was carried out in THF to secure the solubility of product complex 5.

To a THF solution of 1 (62.8 mg, 0.0474 mmol) was added a THF solution (1.0 mL) of $(Me_3SiCH_2)Mg(thf)_2$ (16.3 mg, 0.0475 mmol) at -78 °C. After stirring the mixture for 1 h, the solution was concentrated to dryness under vacuum to afford a deep purple solid, which was extracted with toluene, filtered through a Celite pad, and concentrated. The resulting solid was recrystallized from Et₂O at -35 °C to afford reddish-purple crystals of **5** (52.5 mg, 0.0784 mmol, 82%).

5. ¹H NMR (THF- $d_{8^{2}}$ 25 °C): δ –0.36 (s, 9H, SiMe₃), 1.29 (s, 9H, p-^tBu), 1.36 (d, ² J_{PH} = 19.7 Hz, 2H, CH₂), 1.91 (s, 18H, o-^tBu), 6.97 (d, ³ J_{HH} = Hz, 1H, py), 7.22 (s, 2H, Mes^{*}), 7.29 (d, ³ J_{HH} = 7.0 Hz, 2H, o-Ph), 7.41–7.51 (m, 4H, py and m,p-Ph), 7.74 (t, J = 7.8 Hz, 1H, py), 10.0 (d, J = 5.7 Hz, 1H, py). ¹³C{¹H} NMR (THF- $d_{8^{2}}$ 25 °C): δ 0.69 (d, J = 2.1 Hz, SiMe₃), 11.0 (d, ¹ J_{CP} = 10.5 Hz, CH₂), 32.1, 32.3 (s, p-C(CH₃)₃), 34.9 (s, p-C(CH₃)₃), 35.8 (s, o-C(CH₃)₃), 39.5 (s, o-C(CH₃)₃), 119.8 (s, Ph), 120.0 (s, py), 123.8 (d, J = 7.1 Hz, py), 124.1 (s, Mes^{*}), 129.5 (s, o-Ph), 129.6 (s, Ph), 130.5 (s, Ph), 139.5 (s, py), 146.2 (s, Mes^{*}), 149.2 (s, py), 154.78 (s, Mes^{*}), 154.82 (s, Mes^{*}), 155.0 (s, py). The signal of C=P was not observed due to low intensity. ³¹P{¹H} NMR (THF- $d_{8^{2}}$ 25 °C): δ 232.2 (s). Anal. Calcd for C₃₄H₄₉NPSiNiBr: C, 61.00; H, 7.38; N, 2.09. Found: C, 61.14; H, 7.40; N, 2.13.

X-ray Crystal Structure Determination. The intensity data were collected on a Rigaku Mercury CCD diffractometer (for 1, 2, and 3) and a Rigaku VariMax diffractometer (for 4 and 5) with graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 70 Å). The data sets were corrected for Lorentz and polarization effects and absorption. The structures were solved by direct methods (SHELXS-97¹⁴ for 1, 2, 3; SIR-97¹⁵ for 4, 5) and refined by least-squares calculations on F^2 for all reflections (SHELXL-97)¹⁴ using Yadokari-XG 2009 software.¹⁶ Complexes 1 and 2 contained CH₂Cl₂ and Et₂O as crystal solvents, respectively. Anisotropic refinement was applied to all non-hydrogen atoms, expect for disordered groups. Hydrogen atoms were placed at calculated positions. The crystallographic data and the summary of solution and refinement are reported as Supporting Information (see Table S1).

Computational Details. The geometric optimization and NBO analysis were performed with the DFT method, where the B3LYP functional was used for exchange–correlation terms. These calculations employed the LANL2DZ basis set for Ni, 6-31G(d) for P, N, and C (Ni–Me), and 6-31G for C (non Ni–Me) and H. Core electrons of Ni (up to 2p) were replaced with effective core potentials.¹⁷ The Gaussian 09 program package was used for all calculations.¹⁸ Molecular orbitals were drawn with the GaussView 5 program package.¹⁹

ASSOCIATED CONTENT

S Supporting Information

SQUID magnetic data for 2; crystal structure of 4; crystal data for 1-5; Cartesian coordinates for the optimized structures of 3a, 3a', 3b, and 3b'; X-ray data (CIF) for 1-5. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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