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Synthesis and Reactivity of New Ni, Pd, and Pt 2,6-Bis(di-*tert*-butylphosphinito)pyridine Pincer Complexes

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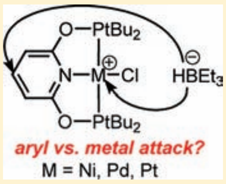
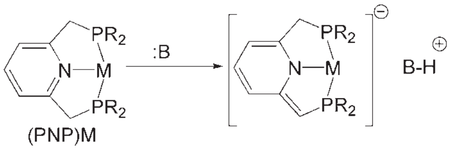
Supporting Information

ABSTRACT: Synthesis and characterization of new (PONOP) [2,6-bis(di-*tert*-butylphosphinito)-pyridine] metal (Ni, Pd, Pt) complexes are reported. Surprisingly, these compounds [(PONOP)-MCl]Cl in the presence of 1 equiv of superhydride ($LiEt_3BH$) formed a new class of complexes (H-PONOP)MCl, in which the pyridine ring in the PONOP ligand lost its aromaticity as a result of hydride attack at the *para* position of the ring. The new Ni−H compound [(H-PONOP)NiH] was synthesized by reacting (H-PONOP)NiCl with 1 equiv of superhydride. Analogous Pd and Pt compounds were prepared. Reactivity of these new pincer complexes toward MeLi and PhLi also has been studied. These Ni complexes catalyzed the hydrosilylation of aldehyde. In some cases characterization of new (PONOP)M complexes was difficult because of high instability due to degradation of the P−O bond.



INTRODUCTION

There has been a great deal of interest in pincer metal complexes in recent years following Moulton and Shaw's first report on PCP pincer complexes 35 years ago,[1] and a wide variety of transition metal complexes having pincer ligands have been reported in the literature.[2] These complexes play an important role in different types of bond activation,[3b−f,j−l,t] synthesis,[3a,h,n,q,w] and catalysis.[3g,i,m,o,p,r,s,u,v] Among these pincer ligands, PNP (PNP = 2,6-bis-(di-*tert*-butylphosphinomethyl)-pyridine) is one example of a neutral ligand, and catalytic activity of many PNP transition metal complexes are known.[4] One special property of these PNP complexes is that in the presence of base, dearomatization of the pyridine core can take place via deprotonation of the methylene side arm (eq 1). Milstein and coworkers studied and explored this property in many complexes of PNP and the analogous PNN pincer ligands.[4i,5] They found that the non-innocent ligand allowed for the catalytic reaction of primary alcohols with primary and secondary amines to give imines and amides with the release of H_2. The non-innocent ligand allowed for the shuttling of hydrogen from the metal to the ligand to generate the required unsaturation at carbon. van der Vlugt also saw dearomatization due to methylene deprotonation in several Cu(PNP) derivatives.[4n,o] This behavior was also noted with other metals,[2m,p] indicating the potential for non-innocence of pincer ligands.[2d,e]



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This kind of deprotonation can be avoided if oxygen is present instead of CH_2 in the side arm of the pincer ligand (PNP or PNN). This new class of neutral pincer ligand having oxygen is abbreviated PONOP, **1**. The synthesis and reactivity of (PONOP)M (M = Ru, Rh, and Ir) complexes have been reported by the Milstein and Brookhart groups.[6]

In this report, the synthesis and reactivity of new (PONOP)M (M = Ni, Pd, and Pt) complexes are examined. Reactions of these group 10 metal PONOP complexes with superhydride to provide new metal-hydrides are investigated. The synthesis and characterization of the derivatives of (^{tBu4}PONOP)M (M = Ni, Pd, and Pt) complexes proved to be difficult because of the instability of these complexes, even at room temperature under inert atmosphere.

RESULTS AND DISCUSSION

Synthesis of Nickel-PONOP Compounds. Treatment of $NiCl_2 \cdot 6H_2O$ with PONOP in EtOH at room temperature for 15 min afforded the complex [(PONOP)NiCl]Cl·EtOH (**2a**) in good yield (Scheme 1). Complex **2a** was isolated as a dark red solid and was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. One equivalent of EtOH was found to be present by NMR spectroscopy even after the solid was placed under vacuum for 3 days. Bound EtOH could be removed by sonication. Successful sonication in tetrahydrofuran (THF, 2 h) followed by hexane (2 h) produced a light red solid characterized as pure complex [(PONOP)NiCl]Cl (**3a**), characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. Although we were unable to obtain an X-ray structure of this material (the crystals were subject to diffuse scattering), a separate reaction using a slight excess of $NiCl_2.6H_2O$, provided crystals of $[(PONOP)NiCl]_2[NiCl_4]$ (**3a-NiCl$_4$**), which diffracted suitably to provide a structure (Figure 1). The molecule is almost perfectly planar and the P−Ni−N angles are slightly acute (∼84.4°).

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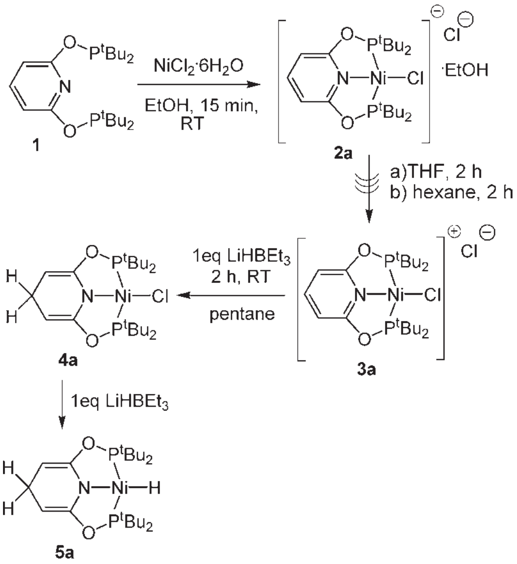
Scheme 1. Synthesis of (PONOP)Ni Complexes



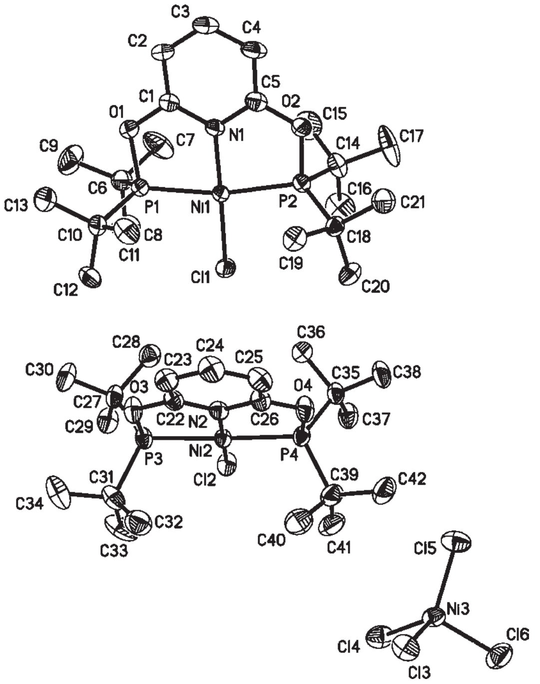


Figure 1. X-ray structure of [(PONOP)NiCl]$_2$[NiCl$_4$], **3a-NiCl$_4$**. Selected distances: Ni1−P1, 2.190(1); Ni1−P2, 2.195(1); Ni1−Cl1, 2.1463(9) Å; Ni1−N1, 1.878(3) Å; N1−C1, 1.356(4) Å;C1−C2, 1.362(5) Å; C2−C3, 1.373(5) Å; C3−C4, 1.381(5) Å; C4−C5, 1.379(5) Å; C5−N1, 1.350(4) Å. Ellipsoids are shown at the 50% level.

Synthesis of (H-PONOP)NiCl (4a). Dropwise treatment of the complex **3a** suspended in pentane with 1 equiv of superhydride in pentane at room temperature over 2 h produced a color change from red to deep green. The new product was identified as complex **4a**, in which the pyridine had undergone attack at the para position, losing its aromaticity (Scheme 1). This observation is in stark contrast to the analogous (PCP)NiCl complex which undergoes attack by hydride exclusively at the metal.[3q] Complex **4a** was characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and X-ray crystallography (Figure 2). In the ^{1}H NMR spectrum, no aromatic resonances were present and new resonances at δ 4.19 and 3.39 appeared, which clearly indicate that the pyridine ring of the complex had lost its aromaticity. The ^{13}C{^{1}H} NMR spectrum shows resonances for the pyridal ring carbons at δ 159.7, 72.2, and 39.3, also indicating a loss of aromaticity. Other hydride reducing reagents (lithium aluminum hydride or sodium borohydride) led to reduction to the Ni^I species (PONOP)NiCl rather than **4a** (see Experimental Section).[7] The X-ray structure of **4a** shows bond length alternation around the pyridyl ring, and the Ni−N distance (1.887(2) Å) is slightly longer than in **3a** (1.878(3) Å). The pyridyl ring, and the entire H-PONOP ligand for that matter, remain planar. The P−Ni−P angles remain acute (∼83.0°). Compound **4a** is most closely related to an analogous ruthenium-bisphosphinoacridine complex reported by Milstein, in which the C9 of the acridine can similarly be reduced by heating the chloro derivative with KOH and hydrogen.[8] Reduction of a bound pyridine is rare, but has been seen in yttrium hydride complexes[9,10] and a magnesium hydride complex.[11]

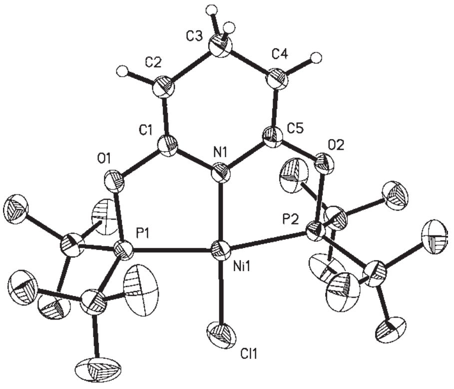
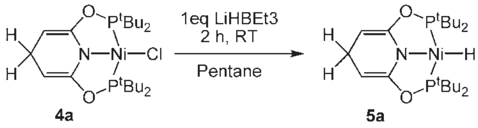


Figure 2. X-ray structure of **4a**. Selected distances: Ni1−P1, 2.1914(6); Ni1−P2, 2.1936(6); Ni1−Cl1, 2.1755(7) Å; Ni1−N1, 1.8876(16) Å; N1−C1, 1.379(2) Å;C1−C2, 1.332(3) Å; C2−C3, 1.479(3) Å; C3−C4, 1.479(3) Å; C4−C5, 1.335(3) Å; C5−N1, 1.378(3) Å. Ellipsoids are shown at the 50% level.

Dropwise treatment of the complex **4a** in pentane with a second equivalent of superhydride at room temperature for 2 h afforded the complex (H-PONOP)NiH (**5a**), with reduction now occurring at the metal (eq 2). An immediate color change occurred from deep green to light brown-green. Complex **5a** was characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The nickel hydride appeared as triplet at δ −16.49 ($J_{\mathrm{P-H}}$ = 62.0 Hz) in the ^{1}H NMR spectrum. The ^{31}P{^{1}H} NMR spectrum of complex **5a** displayed a singlet at δ 194.3, while the selectively coupled (by hydride) ^{31}P NMR spectrum displayed a doublet at δ 194.3 ($J_{\mathrm{P-H}}$ = 62.0 Hz), clearly indicating the presence of a nickel hydride. NMR data for the pyridyl ring continued to be consistent with dearomatization. Crystallization of complex **5a** was not successful as it slowly decomposed in hexane after 5 days at room temperature to yield an unusual Ni$_2$(P^{t}Bu$_2$)$_4$ species (see Supporting Information for structure).[12]



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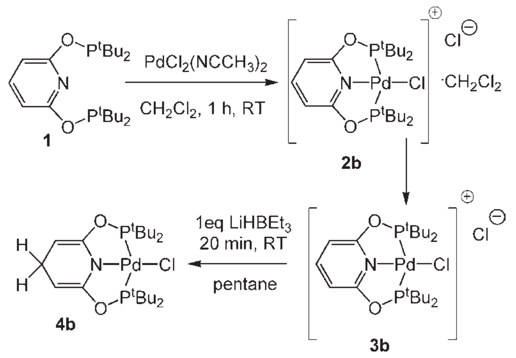
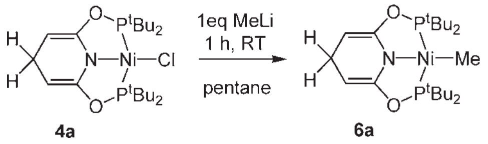
Scheme 2. Synthesis of (PONOP)Pd Complexes



Reaction of Complex 4a with MeLi and PhLi. When complex **4a** was treated with 1 equiv of MeLi at room temperature, complex **6a** formed after 1 h, which was isolated as light brown solid (eq 3). The nickel(II) methyl complex was characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The Ni-CH$_3$ appeared as a triplet at δ −0.36 ($J_{\text{P-H}}$ = 9.2 Hz) in the ^{1}H NMR spectrum and a triplet at δ −27.8 ($J_{\text{P-C}}$ = 30.0 Hz) in the ^{13}C{^{1}H} NMR spectrum. Crystallization of complex **6a** was not successful as it slowly decomposed in hexane after 4 days at room temperature. Under similar reaction conditions, treatment of complex **4a** with 1 equiv of PhLi at room temperature did not produce the analogous phenyl derivative cleanly. Many products along with complex **4a** as the major species were observed by ^{31}P NMR spectroscopy (from the mixture of products (H-PONOP)-NiPh was identified by X-ray crystallography. See Supporting Information).



(3)

Synthesis of [(PONOP)PdCl]Cl (3b) and (H-PONOP)PdCl (4b). Treatment of PdCl$_2$(NCCH$_3$)$_2$ with PONOP ligand in CH$_2$Cl$_2$ at room temperature for 1 h afforded the complex **2b** in good yield (Scheme 2). Complex **2b** was isolated as a light yellow solid and characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and elemental analysis. When the same reaction was carried out in CH$_3$CN as solvent, the reaction was not clean and many unknown products were observed. Bound CH$_2$Cl$_2$ was removed by sonication in THF followed by hexane. The solid was dried overnight in vacuum yielding pure complex **3b**. Complex **3b** was characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.

In a similar fashion to the Ni complex, treatment of complex **3b** slurried in pentane with 1 equiv of superhydride at room temperature for 20 min afforded the complex **4b** (Scheme 2). An immediate color change from light yellow to pink was observed. Complex **4b** was characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and X-ray crystallography (Figure 3). The molecule is again planar with acute P−Pd−N angles of ~80.8°, larger than in nickel complex **4a** because of the larger palladium metal. The ^{1}H NMR spectrum was similar to that of the Ni complex. New resonances at δ 4.18 and 3.37 were seen, which clearly indicate that the pyridine ring had lost its aromaticity. Similar changes in the ^{13}C{^{1}H} spectrum were observed.

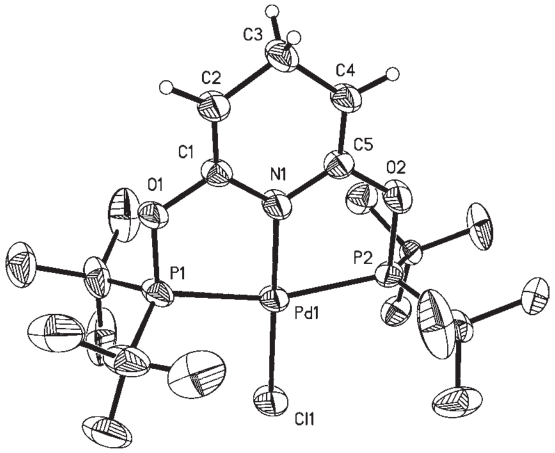
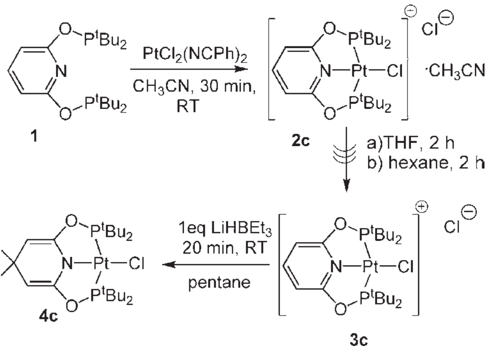


Figure 3. X-ray structure of **4b**. Selected distances: Pd1−Cl1, 2.3169(12) Å; Pd1−N1, 1.989(4) Å; N1−C1, Å;C1−C2, 1.373(6) Å; C2−C3, 1.504(7) Å; C3−C4, 1.495(7) Å; C4−C5, 1.303(6) Å; C5−N1, 1.374(6) Å. Ellipsoids are shown at the 50% level.

Scheme 3. Synthesis of (PONOP)Pt Complexes



Synthesis of [(PONOP)PtCl]Cl (3c) and (H-PONOP)PtCl (4c). Treatment of PtCl$_2$(NCPh)$_2$ with PONOP in CH$_3$CN at room temperature for 30 min afforded complex **2c** in good yield (Scheme 3). Complex **2c** was isolated as a white solid and characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and elemental analysis. The bound CH$_3$CN was removed by sonication in THF followed by hexane. The white solid was dried overnight in vacuum yielding pure complex **3c**. Complex **3c** was characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.

Dropwise treatment of a slurry of complex **3c** in pentane with 1 equiv of superhydride at room temperature over 20 min afforded complex **4c** (Scheme 3). An immediate color change from colorless to light yellow was observed. Complex **4c** was characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, elemental analysis, and X-ray crystallography (Figure 4). The molecule is again planar with acute P−Pt−N angles of ~81.0°, similar to those in palladium complex **4b**. The ^{1}H NMR spectra displayed no aromatic resonances and new resonances at δ 4.24 and 3.44 appeared, indicating loss of aromaticity of the pyridine ring. The ^{31}P NMR spectrum of **4c** shows a singlet at δ 157.9 with $J_{\text{Pt-P}}$ = 2799 Hz, which is 264 Hz larger than in **3c** or **2c**. This is consistent with the notion that the more electron-withdrawing the substituent (i.e., chloride > hydride), the smaller the $^{1}J_{\text{Pt-P}}$ in platinum(II) complexes.[13]

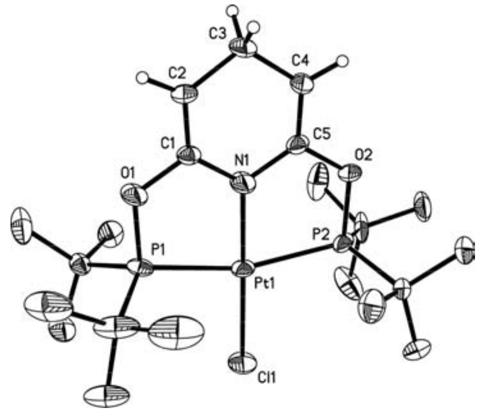
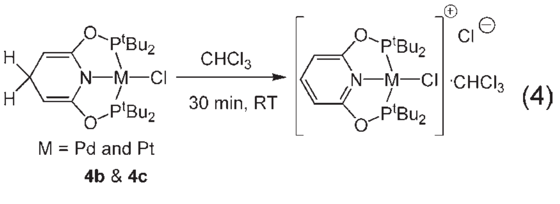


Figure 4. X-ray structure of **4c**. Selected distances: Pt1−Cl1, 2.3275(9) Å; Pt1−N1, 1.991(3) Å; N1−C1, 1.368(5) Å;C1−C2, 1.325(5) Å; C2−C3, 1.500(5) Å; C3−C4, 1.503(5) Å; C4−C5, 1.323(5) Å; C5−N1, 1.394(5) Å. Ellipsoids are shown at the 50% level.

Unlike the Ni complex **4a**,, treatment of the complexes **4b** or **4c** with 1 equiv of superhydride or $LiAlH_4$ did not generate the corresponding metal hydrides (**5b** and **5c**). Instead both complexes decomposed as the reaction was stirred at room temperature for a longer time under nitrogen atmosphere. From the palladium reaction, a known[14] dimeric bis-μ-chloro complex was obtained in which the PONOP ligand had been cleaved at the pyridyl-oxygen bonds, $[Pd(\mu\text{-}Cl)(^tBu_2PO\cdots H\cdots OP^tBu_2)]_2$ (See Experimental Section). Also, reaction of **3c** with KOH and dihydrogen under the conditions employed by Milstein did not result in the formation of **4c**.[8]

To further prove the structure of complex **4c** and **4b**, the complexes were stirred at room temperature in $CHCl_3$. After 30 min, both solutions changed color and the complexes **3c·CHCl₃** and **3b·CHCl₃** were generated accordingly, as confirmed by NMR spectroscopy. Both complexes have very similar NMR spectra compared to pure **3c** and **3b** (eq 4). Conversions of metal hydrides to metal halides by adding haloforms are well-known in the literature,[15] presumably initiated via electron transfer to the haloform, and may be operative in this case also.



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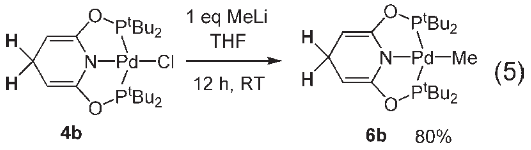
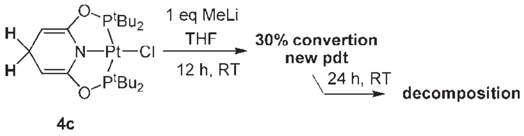
Reaction of Complex 4b and 4c with MeLi. In a similar fashion to the Ni complex (**4a**), freshly prepared complex **4b** was reacted with 1 equiv of MeLi in THF at room temperature. After 12 h, a new product **6b** was observed (~ 80%) by ^{31}P NMR spectroscopy (eq 5). Compound **6b** was not very stable. It slowly decomposed in solution after a few days even at −20 °C. Compound **6b** appeared as a singlet at δ 168.4 in the ^{31}P NMR spectrum. The Pd-CH_3 moiety appeared as a triplet at δ 0.52 (J_{P-H} = 5.4 Hz) in the ^1H NMR spectrum, and a triplet at δ −20.4 (J_{P-C} = 6.8 Hz) in the ^{13}C NMR spectrum, indicating attachment of the methyl group to the Pd center. Crystallization of complex **6b** was not successful as it slowly decomposed in hexane after 4 days at room temperature.



(5)

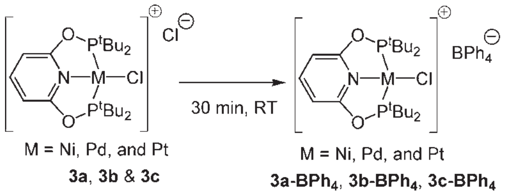
Likewise, freshly prepared complex **4c** was reacted with 1 equiv of MeLi in THF at room temperature. After 12 h a new product was observed (~ 30%) by ^{31}P NMR spectroscopy while unreacted **4c** remained in the solution. Further stirring (24 h) of this solution at room temperature led to decomposition (eq 6). The new unidentified product was highly unstable and appeared as singlet at δ 198.4 (J_{Pt-P} = 2790 Hz) in the ^{31}P NMR spectrum and displayed a Pt−H resonance which appeared as a triplet at δ −10.51 (J_{Pt-H} = 989 Hz, J_{P-H} = 10.0 Hz) in the ^1H NMR spectrum. From both ^{31}P and ^1H NMR spectra, it was clear that this new compound was not the (H-PONOP)Pt(Me) complex **6c**, but that cleavage of the PONOP ligand had occurred.



(6)

Reaction of Complexes 3b and 3c with MeLi. In an attempt to see if the metal and/or the pyridyl ring could be alkylated in an analogous fashion to the reaction with superhydride, methyllithium was added to **3b** or **3c**. Reactions of complex **3b** or **3c** with 2 equiv of MeLi in THF at room temperature were not clean. In case of Pd complex **3b**, four unidentified compounds were observed by ^{31}P NMR spectroscopy (ratio: 1:2:4:7). These complexes decomposed in hexane after 7 days. In the case of Pt complex **3c**, two unknown compounds were observed by ^{31}P NMR spectroscopy (ratio: 1:1.25) after 30 min. One example of alkylation of a pyridinediimine ligand has been reported using $Ca[CH(TMS)_2]_2$.[16]

Reaction Complexes 3a, 3c, and 3b with NaBPh₄. As we were unable to obtain an X-ray structure of complexes **3a**, **3b**, and **3c** (crystals formed but were subject to diffuse scattering), substitution of chloride anion with the large BPh_4 anion was carried out by reacting complexes **3a**, **3c**, and **3b** with 10 equiv of $NaBPh_4$ in methanol at room temperature (eq 7). Reactions were clean and after 30 min at room temperature the corresponding BPh_4 anion substituted complexes **3a-BPh₄**, **3b-BPh₄**, and **3c-BPh₄** were generated, which were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and X-ray crystallography. Crystals of these salts diffracted suitably to provide the structures (Figure 5). The structural parameters for **3a-BPh₄** are comparable to those of **3a-NiCl₄**, although the N1−Ni1−Cl1 angle is slightly bent (171.8°, but linear in Pd or Pt compounds). The C−C distances around the pyridyl rings are essentially equivalent, indicating delocalization.



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Reaction of Complex 5a with Different Substrates. The chemical properties of complex **5a** were tested by reaction with

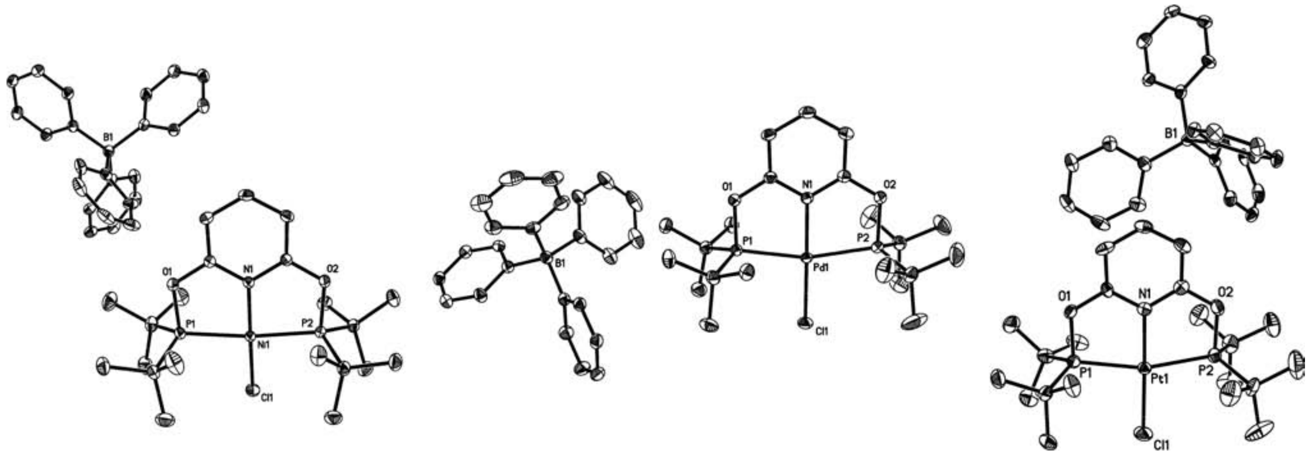
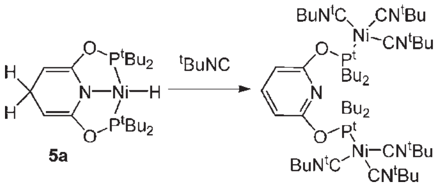


Figure 5. X-ray structures of **3a-BPh$_4$**, **3b-BPh$_4$**, and **3c-BPh$_4$**. Selected distances for **3a-BPh$_4$**: Ni1−P1, 2.1841(3); Ni1−P2, 2.1809(3); Ni1−Cl1, 2.1433(3) Å; Ni1−N1, 1.871(1) Å; N1−C1, 1.3565(13) Å;C1−C2, 1.3749(15) Å; C2−C3, 1.3870(16) Å; C3−C4, 1.3822(16) Å; C4−C5, 1.3772(15) Å; C5−N1, 1.3565(13) Å. Selected distances for **3b-BPh$_4$**: Pd1−Cl1, 2.2914(4) Å; Pd1−N1, 2.0057(12) Å; N1−C1, 1.3526(18) Å; C1−C2, 1.376(2) Å; C2−C3, 1.386(2) Å; C3−C4, 1.385(2) Å; C4−C5, 1.373(2) Å; C5−N1, 1.3526(19) Å. Selected distances for **3c-BPh$_4$**: Pt1−Cl1, 2.2890(16) Å; Pt1−N1, 2.000(4) Å; N1−C1, 1.345(7) Å;C1−C2, 1.376(7) Å; C2−C3, 1.372(9) Å; C3−C4, 1.371(8) Å; C4−C5, 1.380(8) Å; C5−N1, 1.348(7) Å. Ellipsoids are shown at the 50% level.

several substrates (Scheme 4). This new Ni−H complex did not lose H_2 easily and did not react with carbon monoxide or isocyanides at room temperature. Heating complex **5a** in the presence of excess of isocyanide (20 equiv) led to decomposition, and one compound was isolated as a crystalline solid (eq 8, Figure 6). Complex **5a** did not hydrogenate or bind with imine, ethylene, or 1-octene, although in case of 1-octene isomerization was observed in the ^{1}H NMR spectrum. No free H_2 was observed by NMR spectroscopy. Complex **5a** also did not show H/D exchange with C_6D_6 or D_2 at room temperature. When benzaldehyde reacted with complex **5a**, no benzyl alcohol was observed. Instead benzoin was formed, which was confirmed by comparison with an authentic sample. The benzoin condensation is typically carried out using a nucleophile that adds reversibly to benzaldehyde, but it is not clear how **5a** could act in this fashion. As complex **5a** decomposes during this reaction, it is difficult to tell exactly how it effects the condensation.



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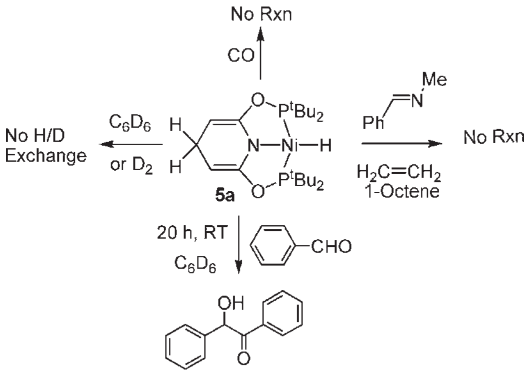
Hydrosilylation of PhCHO Using Complex 4a and 5a. Many organic transformations using Ni complexes have been known for decades.[17] Recently, hydrosilylation of carbonyl functional groups using a Ni-hydride catalyst has been reported by several other groups.[3s,18] The system reported by Guan[3s] uses the benzene analogue (POCOP)NiH, and is most similar to the compound reported here. We wanted to test the catalytic activity of both complex **4a** and **5a** in the hydrosilylation of benzaldehyde as a benchmark for comparison with other catalysts. Complex **5a** catalyzed the hydrosilylation of PhCHO in the presence of $PhSiH_3$. After 10 h at room temperature, all of the benzaldehyde was consumed, and hydrosilylation products were observed, as confirmed by ^{1}H NMR spectroscopy and GC-MS (eq 9).

Scheme 4. Reaction Complex 5a with Different Substrates



The catalytic activity of complex **5a** was not good, as ∼60% of the complex had decomposed after 10 h at room temperature (measured by ^{31}P NMR spectroscopy). Under the same reaction conditions complex **4a** showed similar hydrosilylation products by ^{1}H NMR spectroscopy and GC-MS. The reaction was much slower in case of complex **4a** compared to **5a**, taking 2 days to consume all of the benzaldehyde. However, even after 2 days no decomposition of complex **4a** was observed by ^{31}P NMR spectroscopy. In comparison to **5a**, the (POCOP)NiH catalyst reported by Guan et al.[3s] resulted in an 80% yield of alcohol (following workup with aqueous base) after only 2 h at room temperature using 0.2 mol % catalyst.

To test the scope of this hydrosilylation reaction using complex **4a**, 4-chlorobenzaldehyde was used as the hydrosilylation substrate under the same reaction conditions. After 2 days at room temperature most of the aldehyde was consumed and hydrosilylation products were detected by ^{1}H NMR spectroscopy with no decomposition of complex **4a**. One notable observation was that no hydrosilylation products were detected when the tertiary silane Et_3SiH was used instead of the primary silane $PhSiH_3$ under the same reaction conditions (3 days at room

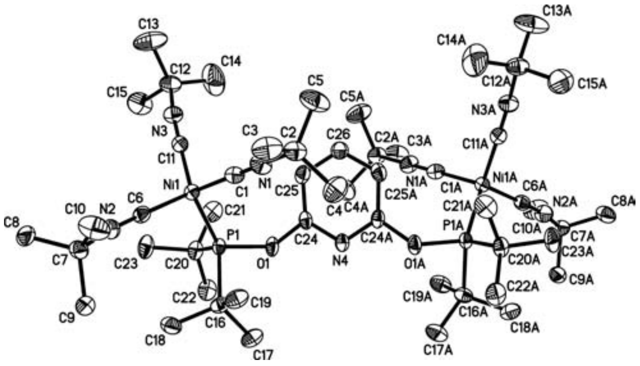
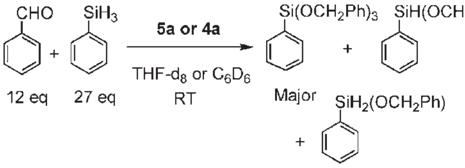


Figure 6. Structure of Ni isocyanide complex. Ellipsoids are shown at the 50% level.

temperature). To test whether complex **4a** catalyzed this hydrosilylation by insertion of aldehyde to the metal hydride bond as reported in the literature,[3s] complex **4a** was reacted with benzaldehyde in the absence of silane. No insertion of benzaldehyde was observed after 2 days at room temperature, as confirmed by ^{1}H NMR spectroscopy (eq 10). When this mixture was heated at 100 °C for 1 h, it decomposed to some paramagnetic complexes and one diamagnetic complex. The ^{31}P NMR spectrum showed only one signal with low intensity at δ 50.56, and the ^{1}H NMR spectrum showed broad signals at δ 25.80, 16.53, and 9.36 and 2.49. Crystals were grown by slow evaporation from the hexane solution of this decomposition mixture. X-ray crystallography provided the structure of the diamagnetic decomposition product (Figure 7), showing degradation of the PONOP ligand. Nickel—phosphorus and nickel—carbon distances are comparable to those in **3a** and **3a-BPh$_4$**. This unusual compound is somewhat reminiscent of Nieke's PNPN macrocycle,[19] although the pentavalent phosphorus here results in a planar structure compared with Nieke's tetravalent phosphorus macrocycle complex of copper, which is folded.[20]



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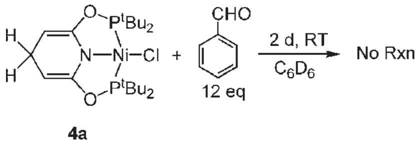

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To gain insight into the mechanism more clearly (D-PONOP)NiCl (**4a-d_1**) was synthesized by reacting complex **3a** with deuterated superhydride (eq 11). Reaction of **4a-d_1** with benzaldehyde and PhSiH$_3$ under similar reaction conditions did not show deuterium incorporation in the hydrosilylation products. It is not clear how this reaction proceeds, but a radical pathway is possible, although there is no direct evidence for this. When complex **4a** in C_6D_6 was heated for 30 min at 100 °C, it decomposed, and several paramagnetic complexes and one diamagnetic complex were detected by ^{1}H and ^{31}P NMR spectroscopy, as determined by the broad range of chemical shifts. Consequently, the mechanism of this hydrosilylation reaction catalyzed by complex **4a** remains unknown.

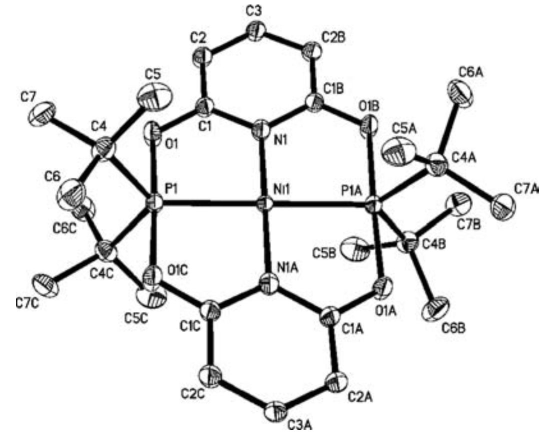
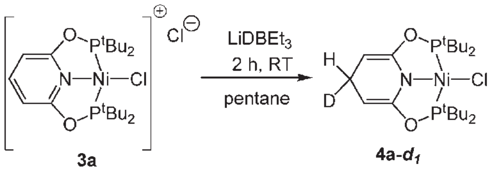


Figure 7. Structure of Ni(c-PONOPONO) from the decomposition of product **6**. Selected bond distances (Å): Ni1—N1, 1.864(4); Ni1—P1, 2.233(1); P1—O1, 1.862(3); N1—C1, 1.353(4); C1—C2, 1.395(4); 1.380(4). Ellipsoids are shown at the 50% level.



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CONCLUSIONS

The synthesis and characterization of new class of group 10 metal pincer complexes has been established. The side arm of these complexes has no proton to lose in the presence of base (particularly hydride), compared to other known PNP or PNN pincer complexes. These (PONOP)M (M = Ni, Pd, Pt) complexes showed some unique properties. When the (PONOP)-MCl$_2$ (M = Ni, Pd, Pt) complexes were reacted with 1 equiv of superhydride, a new class of pincer complex [(H-PONOP)MCl (M = Ni, Pd, Pt)] formed in which the pyridine was reduced. Reactivity of these complexes toward MeLi was also examined, and (H-PONOP)Ni(Me) was prepared. These pincer nickel complexes catalyzed the hydrosilylation of aldehydes, although the mechanism of this reaction was not established. Characterization and crystallization of these complexes were difficult in most of the cases, particularly with Pd and Pt metals, because of their high instability.

EXPERIMENTAL SECTION

General Procedures and Materials. Unless otherwise stated, all reactions and manipulations were carried out in dry glassware using standard Schlenk and glovebox techniques, under a nitrogen atmosphere. THF-d_8, p-xylene-d_{10}, and C_6D_6 were purchased from Cambridge Isotope Laboratories and dried using Na/K and collected by vacuum transfer. All other reagents were purchased from Aldrich, Strem, or VWR chemical company and used without any further purification. All NMR spectra were recorded on Bruker Avance 400 and 500 MHz spectrometers. ^{31}P NMR chemical shifts (δ in ppm) are relative to an external 85% solution of H_3PO_4 in the appropriate solvent. Elemental analyses were obtained from CENTC Elemental Analysis Facility at the University of Rochester. GC-MS spectra were recorded on a SHIMADZU QP2010 GCMS

Improved Synthesis of PONOP, [1,3-$C_5H_3N(OP^tBu_2)_2$] (1). Synthesis of this tridentate ligand has been reported by the Brookhart (57%) and Milstein (75%) groups.[6a,c] This ligand can be synthesized in higher yield (85%) and purity (99%) by combining aspects of both of their methods (i.e., Milstein employed TMEDA and NEt_3 as base for 20 h at 65 °C, whereas Brookhart used only NEt_3 and heated to 65 °C for 1 week). In a 500 mL Schlenk flask, 2,6-dihydroxypyridine hydrochloride (1.0 g, 6.8 mmol), *N,N,N,N*-tetramethylethylenediamine (13.6 mmol, 2.00 mL), triethylamine (41.6 mmol, 5.80 mL), $(^tBu)_2PCl$ (2.70 g, 14.9 mmol), and 60 mL of THF were combined under a nitrogen atmosphere. The reaction mixture was heated with stirring at 75 °C for 1 week. The volatiles were removed under vacuum, leaving a yellow solid. The solid was extracted into benzene and filtered under a nitrogen atmosphere. The solvent was then removed under vacuum, leaving an oily material which solidified to a white solid in few minutes (yield, 2.01 g, 85%).^{1}H NMR (400 MHz, C_6D_6): δ 7.13 (t, J_{H-H} = 7.8 Hz, 1H), 6.46 (d, J_{H-H} = 8.0 Hz, 2H), 1.18 (d, J_{P-H} = 11.2 Hz, 36H). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 151.3 (s).

Synthesis of [(PONOP)NiCl]Cl·EtOH (2a). In a 500 mL Schlenk flask PONOP (500 mg, 1.25 mmol), $NiCl_2.6H_2O$ (297.3 mg, 1.25 mmol), and 75 mL of anhydrous EtOH were combined under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 15 min. Volatiles were removed under vacuum (overnight), leaving a dark red solid **2a** (yield: 95%). **2a** was found to contain a bound EtOH. ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of complex **2a** were very similar to those of complex **3a** (see below) except for the presence of the bound EtOH resonances. ^{1}H NMR (400 MHz, CD_3OD): δ 8.19 (t, J_{H-H} = 8.2 Hz, 1H), 7.07 (d, J_{H-H} = 8.0 Hz, 2H), 3.60 (q, J_{H-H} = 5.6 Hz, 2H), 1.67 (vt, J_{P-H} = 8.0 Hz, 36H), 1.78 (d, J_{H-H} = 5.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ 167.4 (t, J_{P-C} = 5.0 Hz), 150.9 (s), 106.9 (s), 43.2 (t, J_{P-C} = 5.1 Hz), 28.5 (s). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3OD): δ 184.3 (s).

[(PONOP)NiCl]Cl (3a). In a 500 mL Schlenk flask complex **2a** (500 mg) and 100 mL of THF were combined under a nitrogen atmosphere. The mixture was sonicated for 2 h, and THF was removed by cannula, leaving a solid at the bottom of the flask. A 100 mL portion of hexane was added, and the solid was sonicated again for 2 h. Hexane was removed by cannula while the light red solid remain at the bottom of the flask. The solid was dried overnight in vacuum yielding pure complex **3a** (85%). ^{1}H NMR (400 MHz, CD_3OD): δ 8.19 (t, J_{H-H} = 8.2 Hz, 1H), 7.07 (d, J_{H-H} = 8.0 Hz, 2H), 1.67 (vt, J_{P-H} = 8.0 Hz, 36H). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ 167.4 (t, J_{P-C} = 5.0 Hz), 150.9 (s), 106.9 (s), 43.2 (t, J_{P-C} = 5.1 Hz), 28.5 (s). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3OD): δ 184.3 (s). Anal. Calcd (found) for $C_{21}H_{39}Cl_2NNiO_2P_2$: % C, 47.67 (47.71); % H, 7.43 (7.56); % N, 2.65 (2.70).

(H-PONOP)NiCl (4a). In a 250 mL Schlenk flask complex **3a** (200 mg, 0.38 mmol) and 100 mL of pentane were combined under a nitrogen atmosphere. A 0.38 mL portion of $LiHBEt_3$ (0.38 mmol, 1 M in THF) was added dropwise at room temperature. An immediate color change from red to deep green was observed. The reaction mixture was stirred at room temperature for 2 h. The solution was filtered under a nitrogen atmosphere using a cannula, and the volatiles were then removed under vacuum yielding pure dark green complex **4a** (95%). Crystals of complex **4a** were grown by slow evaporation from a hexane solution. ^{1}H NMR (400 MHz, C_6D_6): δ 4.19 (t, J_{H-H} = 3.2 Hz, 2H), 3.39 (t, J_{H-H} = 3.2 Hz, 2H), 1.45 (vt, J_{P-H} = 7.2 Hz, 36H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 159.7 (t, J_{P-C} = 5.7 Hz), 72.2 (t, J_{P-C} = 3.1 Hz), 39.3 (t, J_{P-C} = 7.4 Hz), 27.4 (s), 24.6 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 165.1 (s). Anal. Calcd (found) for $C_{21}H_{40}ClNNiO_2P_2$: % C, 50.99 (49.65); % H, 8.15 (8.17); % N, 2.83 (2.40).

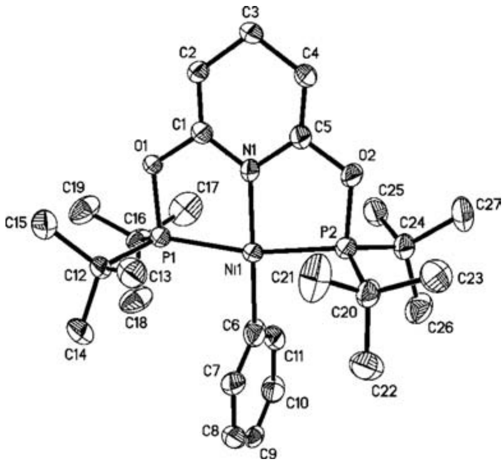

Figure 8. X-ray structure of (H-PONOP)NiPh. Selected distances: Ni1−C6, 1.959(4) Å; Ni1−N1, 1.877(3) Å; N1−C1, 1.376(5) Å; C1−C2, 1.326(5) Å; C2−C3, 1.501(5) Å; C3−C4, 1.512(6) Å; C4−C5, 1.309(6) Å; C5−N1, 1.387(5) Å. Ellipsoids are shown at the 50% level.

(H-PONOP)NiH (5a). In a 100 mL Schlenk flask complex **4a** (100 mg, 0.20 mmol) and 40 mL of pentane were combined under a nitrogen atmosphere. A 0.20 mL portion of $LiHBEt_3$ (0.20 mmol, 1 M in THF) was added dropwise at room temperature. An immediate color change from deep green to light brown was observed. The reaction mixture was stirred at room temperature for 1 h, and the solution was filtered under nitrogen atmosphere using a cannula. The volatiles were then removed under vacuum yielding sticky light brown complex **5a** (82%). ^{1}H NMR (400 MHz, C_6D_6): δ 4.28 (t, J_{H-H} = 3.0 Hz, 2H), 3.72 (t, J_{H-H} = 3.0 Hz, 2H), 1.25 (vt, J_{P-H} = 7.2 Hz, 36H), −16.49 (t, J_{P-H} = 62.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 159.3 (t, J_{P-C} = 6.0 Hz), 68.5 (t, J_{P-C} = 2.9 Hz), 37.4 (t, J_{P-C} = 9.5 Hz), 27.4 (s), 26.3 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 194.3 (s).

(H-PONOP)Ni(Me) (6a). In a 50 mL Schlenk flask complex **4a** (20 mg, 0.04 mmol) and 5 mL of pentane were combined under a nitrogen atmosphere. Twenty-five microliters of MeLi (0.04 mmol, 1.66 M in THF) was added dropwise at room temperature. An immediate color change from deep green to light brown was observed. The reaction mixture was stirred at room temperature for 1 h, and the solution was filtered through Celite. The volatiles were then removed under vacuum yielding complex **6a** (purity 70% by ^{31}P NMR spectroscopy) along with some decomposition products. ^{1}H NMR (400 MHz, C_6D_6): δ 4.21 (t, J_{H-H} = 2.6 Hz, 2H), 3.68 (t, J_{H-H} = 2.6 Hz, 2H), 1.29 (vt, J_{P-H} = 6.8 Hz, 36H), −0.36 (t, J_{P-H} = 9.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 159.7 (t, J_{P-C} = 4.8 Hz), 69.2 (t, J_{P-C} = 2.6 Hz), 39.6 (t, J_{P-C} = 7.6 Hz), 28.4 (s), 26.7 (s), −27.8 (t, J_{P-C} = 30.0 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 169.9 (s).

Reaction of 4a with PhLi. In a 50 mL Schlenk flask complex **4a** (20 mg, 0.04 mmol) and 5 mL of pentane were combined under a nitrogen atmosphere. Twenty-three microliters of PhLi (0.04 mmol, 1.8 M in THF) were added dropwise at room temperature. An immediate color change from deep green to light brown was observed. The reaction mixture was stirred at room temperature for 1 h, and the solution was filtered under nitrogen atmosphere using a cannula. The volatiles were then removed under vacuum yielding a light brown solid. The ^{31}P NMR spectrum showed many peaks, some of them were the result of breaking apart of the PONOP ligand. From the mixture of products, (H-PONOP)-NiPh was identified by X-ray crystallography (Figure 8). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 165.1 (s, **4a**), 164.9 (s), 164.8 (s), 164.4 (s), 164.2(s), 59.5 (s), 35.4 (s).

Synthesis of [(PONOP)PdCl]Cl·CH$_2$Cl$_2$ (2b). In a 500 mL Schlenk flask PONOP ligand (500 mg, 1.25 mmol), PdCl$_2$(NCCH$_3$)$_2$ (324 mg, 1.25 mmol), and 100 mL of anhydrous CH$_2$Cl$_2$ were combined under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 60 min. The volatiles were removed under vacuum (overnight), leaving a light yellow solid which was washed with hexane and benzene and dried under vacuum yielding complex **2c** (87%). When this reaction was carried out in CH$_3$CN as solvent, some decomposition of the PONOP ligand was observed. ^{1}H NMR (500 MHz, CD$_3$OD): δ 8.28 (t, J_{H-H} = 8.3 Hz, 1H), 7.28 (d, J_{H-H} = 8.5 Hz, 2H), 2.01(s, 2H), 1.57 (vt, J_{P-H} = 8.0 Hz, 36H). ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$): δ 163.8 (s), 150.9 (s), 106.7 (s), 42.3 (t, J_{P-C} = 5.2 Hz), 27.5 (t, J_{P-C} = 2.5 Hz). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 192.6 (s). Anal. Calcd (found) for C$_{22}$H$_{41}$Cl$_4$NO$_2$P$_2$Pd: % C, 39.93 (40.25); % H, 6.24 (6.32); % N, 2.12 (2.13).

[(PONOP)PdCl]Cl (3b). In a 500 mL Schlenk flask complex **2b** (500 mg) and 100 mL of THF were combined under a nitrogen atmosphere. The mixture was sonicated for 2 h and then THF was removed by cannula leaving the solid at the bottom of the flask. A 100 mL portion of hexane was added, and the solid sonicated again for 2 h. Hexane was removed by cannula leaving the solid at the bottom of the flask. The solid was dried overnight under vacuum yielding pure complex **3b** (83%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.65 (t, J_{H-H} = 7.6 Hz, 1H), 7.28 (d, J_{H-H} = 8.0 Hz, 2H), 1.50 (vt, J_{P-H} = 8.0 Hz, 36H). ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$): δ 163.8 (s), 150.9 (s), 106.7 (s), 42.3 (t, J_{P-C} = 5.2 Hz), 27.5 (t, J_{P-C} = 2.5 Hz). ^{31}P{^{1}H} NMR (162 MHz, CD$_2$Cl$_2$): δ 192.6 (s).

(H-PONOP)PdCl (4b). In a 250 mL Schlenk flask, complex **3b** (100 mg, 0.17 mmol) and 70 mL of pentane were combined under a nitrogen atmosphere. A 0.17 mL portion of LiHBEt$_3$ (0.17 mmol, 1 M in THF) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 20 min. The solution was filtered under a nitrogen atmosphere using a cannula, and the volatiles were removed under vacuum yielding complex **4b** (79%). Crystals of complex **4b** were grown by slow evaporation from a benzene solution. Complex **4b** was more stable than **4c** and slowly decomposed after a few days in solution. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 4.18 (t, J_{H-H} = 2.8 Hz, 2H), 3.37 (t, J_{H-H} = 3.2 Hz, 2H), 1.34 (vt, J_{P-H} = 7.6 Hz, 36H). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ 159.7 (s), 71.3 (t, J_{P-C} = 4.4 Hz), 39.8 (t, J_{P-C} = 7.8 Hz), 26.9 (s), 25.1 (s). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ 173.1 (s).

Attempted Synthesis of (H-PONOP)PdH (5b). In a 100 mL Schlenk flask, complex **4b** (50 mg, 0.09 mmol) and 10 mL of pentane were combined under a nitrogen atmosphere. A 0.09 mL portion of LiHBEt$_3$ (0.09 mmol, 1 M in THF) was added dropwise at room temperature. The reaction mixture was stirred at room temperature and monitored by ^{31}P NMR spectroscopy over time. No Pd−H complex was observed. With longer stirring times complex **4b** slowly decomposed. From the decomposed mixture, one compound was isolated as crystalline solid, [Pd(μ-Cl)(^{t}Bu$_2$PO···H···OP^{t}Bu$_2$)]$_2$ (Figure 9), which is a known catalyst for the cross-coupling reactions of vinyl and aryl chlorides with arylboronic acids, arylzinc reagents, and thiols.[14,21]

Synthesis of [(PONOP)PtCl]Cl·CH$_3$CN (2c). In a 500 mL Schlenk flask, PONOP (500 mg, 1.25 mmol), PtCl$_2$(NCPh)$_2$ (534 mg, 1.25 mmol), and 100 mL of anhydrous CH$_3$CN were combined under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min. The volatiles were removed under vacuum (overnight), leaving a white solid which was washed with hexane and benzene and dried under vacuum yielding complex **2c** (84%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 8.67 (t, J_{H-H} = 8.4 Hz, 1H), 7.32 (d, J_{H-H} = 8.0 Hz, 2H), 1.98 (s, 3H), 1.11 (vt, J_{P-H} = 8.0 Hz, 36H). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 164.0 (t, J_{P-C} = 5.5 Hz), 148.3 (s), 106.3 (s), 42.4 (t, J_{P-C} = 9.4 Hz), 27.0 (t, J_{P-C} = 2.5 Hz). ^{31}P{^{1}H} NMR (162 MHz, CD$_3$CN): δ 175.0 (s, J_{Pt-P} = 2535 Hz). Anal. Calcd (found) for C$_{23}$H$_{42}$Cl$_2$N$_2$O$_2$P$_2$Pt: % C, 39.10 (39.20); % H, 5.99 (5.95); % N, 3.96 (3.76).

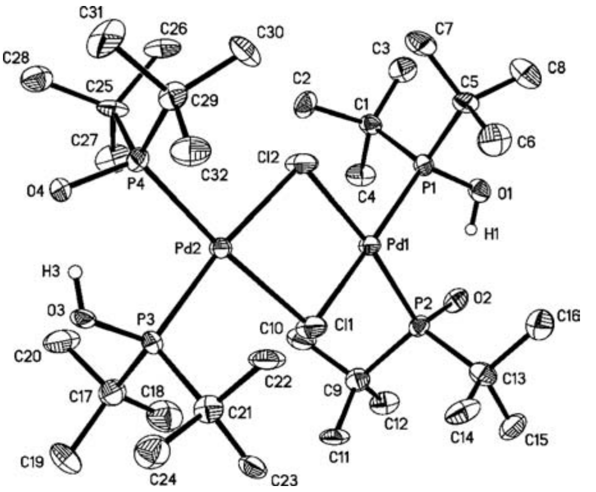

Figure 9. X-ray structure of the decomposition product [Pd(μ-Cl)(^{t}Bu$_2$PO···H···OP^{t}Bu$_2$)]$_2$. Ellipsoids are shown at the 50% level.

[(PONOP)PtCl]Cl (3c). In a 500 mL Schlenk flask, complex **2c** (500 mg) and 100 mL of THF were combined under a nitrogen atmosphere. The mixture was sonicated for 2 h, and then THF was removed by cannula while the solid remained at the bottom of the flask. A 100 mL portion of hexane was added, and the solid sonicated again for 2 h. Hexane was removed by cannula leaving solid at the bottom of the flask. The solid was dried overnight under vacuum yielding pure complex **3c** (83%). The ^{1}H, ^{13}C, and ^{31}P NMR spectra of complex **3c** were very similar to those of complex **2c**, except for the absence of a bound CH$_3$CN resonance. ^{1}H NMR (500 MHz, CD$_3$OD): δ 8.32 (t, J_{H-H} = 8.0 Hz, 1H), 7.29 (d, J_{H-H} = 8.0 Hz, 2H), 1.55 (vt, J_{P-H} = 8.0 Hz, 36H). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 164.0 (t, J_{P-C} = 5.5 Hz), 148.3 (s), 106.3 (s), 42.4 (t, J_{P-C} = 9.4 Hz), 27.0 (t, J_{P-C} = 2.5 Hz). ^{31}P{^{1}H} NMR (162 MHz, CD$_3$CN): δ 175.0 (s, J_{Pt-P} = 2535 Hz). Anal. Calcd (found) for C$_{21}$H$_{39}$Cl$_2$NO$_2$P$_2$Pt: % C, 37.90 (38.29); % H, 5.91 (5.85); % N, 2.10 (2.31).

(H-PONOP)PtCl (4c). In a 250 mL Schlenk flask, complex **3c** (100 mg, 0.15 mmol) and 70 mL of pentane were combined under a nitrogen atmosphere. A 0.15 mL portion of LiHBEt$_3$ (0.15 mmol, 1 M in THF) was added dropwise at room temperature. An immediate color change from colorless to light yellow was observed. The reaction mixture was stirred at room temperature for 20 min. The solution was filtered under a nitrogen atmosphere using a cannula, and the volatiles were then removed under vacuum yielding pure light yellow complex **4c** (81%). Complex **4c** was not stable in solution, as stirring the solution for 4 h led to a color change from yellow to colorless because of decomposition. Crystals of complex **4c** were grown by slow evaporation from a benzene solution. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 4.24 (t, J_{H-H} = 3.0 Hz, 2H), 3.44 (t, J_{H-H} = 3.4 Hz), 1.33 (vt, J_{P-H} = 7.6 Hz, 36H). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 159.4 (s), 70.8 , 40.8 (t, J_{P-C} = 12.1 Hz), 27.8 (t, J_{P-C} = 2.5 Hz), 25.6 (s). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ 157.9 (s, J_{Pt-P} = 2799 Hz). Anal. Calcd (found) for C$_{21}$H$_{40}$ClNO$_2$P$_2$Pt: % C, 39.97 (40.10); % H, 6.39 (6.42); % N, 2.22 (2.43).

Attempted Synthesis of (H-PONOP)PtH (5c). In a 100 mL Schlenk flask, complex **4c** (50 mg, 0.08 mmol) and 10 mL of pentane were combined under a nitrogen atmosphere. A 0.08 mL portion of LiHBEt$_3$ (0.08 mmol, 1 M in THF) was added dropwise at room temperature. The reaction mixture was stirred at room temperature and monitored by ^{31}P NMR spectroscopy over time. No Pt−H complex was observed. With longer stirring times complex **4c** decomposed. From the decomposed mixture, one compound was isolated as crystalline solid, and the unit cell was similar to that obtained in an analogous reaction with the Pd complex (vide infra, Figure 9), but no X-ray data were collected.

Reaction of the Complex 4c and 4b with $CHCl_3$. In a 50 mL Schlenk flask complexes **4b** or **4c** (20 mg) and 0.5 mL of $CHCl_3$ were combined under a nitrogen atmosphere. The reaction mixture was stirred at room temperature. After 30 min both solutions changed color. The volatiles were removed under vacuum, and complex **3c·CHCl$_3$** or **3b·CHCl$_3$** had been generated accordingly along with some decomposition, as confirmed by NMR spectroscopy. **3c·CHCl$_3$**: ^{1}H NMR (400 MHz, CD_3CN): δ 7.86 (t, J_{H-H} = 8.2 Hz, 1H), 7.26 (s, 1H), 6.80 (d, J_{H-H} = 8.0 Hz, 2H), 1.11 (vt, J_{P-H} = 8.0 Hz, 36H). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ 175.0 (s, J_{Pt-P} = 2535 Hz). **3b·CHCl$_3$**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.54 (t, J_{H-H} = 7.6 Hz, 1H), 7.36 (s, 1H), 7.28 (d, J_{H-H} = 8.0 Hz, 2H), 1.50 (vt, J_{P-H} = 8.0 Hz, 36H). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 192.6 (s).

Reaction of the Complex 4b with MeLi. In a 50 mL Schlenk flask, freshly prepared complex **4b** (20 mg, 0.037 mmol) and 3 mL of THF were combined under a nitrogen atmosphere. Twenty-two microliters of MeLi (0.037 mmol, 1.66 M in THF) were added dropwise at room temperature. The reaction mixture was stirred at room temperature for 12 h, and the solution filtered through Celite. The volatiles were then removed under vacuum yielding complex **6b** (80% purity). Compound **6b** was not very stable. It slowly decomposed in solution over several days even in the freezer at −20 °C. Crystallization of complex **6b** was not successful as it slowly decomposed in hexane after 4 d at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 4.16 (s, 2H), 3.74 (s, 2H), 1.23 (vt, J_{P-H} = 7.2 Hz, 36H), 0.52 (t, J_{P-H} = 5.4 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 159.1 (s), 67.9 (t, J_{P-C} = 3.3 Hz), 39.8 (t, J_{P-C} = 8.1 Hz), 28.0 (s), 27.1 (s), −20.4 (t, J_{P-C} = 6.8 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 168.4 (s).

Reaction of the Complex 4c with MeLi. In a 50 mL Schlenk flask, freshly prepared complex **4c** (20 mg, 0.03 mmol) and 3 mL of THF were combined under a nitrogen atmosphere. Eighteen microliters of MeLi (0.03 mmol, 1.66 M in THF) were added dropwise at room temperature. The reaction mixture was stirred at room temperature and monitored by ^{31}P NMR spectroscopy over time. After 12 h, a new product (highly unstable) was observed (30%) by ^{31}P NMR spectroscopy while unreacted **4c** remained in the solution. Further stirring (24 h) of this solution at room temperature led to decomposition as determined by the observation of many peaks in the ^{31}P NMR spectrum. ^{1}H NMR (400 MHz, C_6D_6) (12 h RT): δ −10.51 (t, J_{Pt-H} = 989 Hz, J_{P-H} = 10.0 Hz) and many unidentified peaks. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) (12 h RT): δ 198.4 (s, J_{Pt-P} = 2790 Hz), 157.9 (s, J_{Pt-P} = 2799 Hz, **4c**). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) (24 h RT, major peaks): δ 182.8 (s, J_{Pt-P} = 2263 Hz), 180.1 (s, J_{Pt-P} = 2256 Hz), 173.8 (s, J_{Pt-P} = 2831 Hz).

Reaction of the Complexes 3c and 3b with MeLi. In a 50 mL Schlenk flask, complexes **3c** or **3b** (20 mg) and 1 mL of THF were combined under a nitrogen atmosphere. Two equivalents of MeLi (1.66 M in THF) were added dropwise at room temperature. The reaction mixture was stirred at room temperature for 30 min, and the solution was filtered through Celite. The volatiles were then removed under vacuum, and an NMR spectrum was recorded. Neither reaction was clean. Crystal structures of these unknown compounds were unsuccessful as they decomposed in hexane after 7 d. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) (**3c**): δ 163.1 (s, J_{Pt-P} = 2207 Hz), 161.4 (s, J_{Pt-P} = 2235 Hz) in: 1.25:1 ratio. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) (**3b**): δ 174.4 (s), 172.5 (s), 170.5 (s), 168.3 (s) in 1:2:4:7 ratio.

(PONOP)NiCl(BPh_4) (3a-BPh_4). In a 50 mL Schlenk flask, complex **3a** (30 mg, 0.057 mmol) and 1 mL of MeOH were combined under a nitrogen atmosphere. A solution of $NaBPh_4$ (194 mg, 0.57 mmol) in MeOH (2 mL) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 20 min, and a red solid precipitated from solution. The solvent was removed by syringe, and the solid was washed 2 times with MeOH and dried under vacuum yielding pure complex **3a-BPh$_4$** (88%). Crystals of complex **3a-BPh$_4$** were grown by slow evaporation from a THF/C_6H_6 solution. ^{1}H NMR (500 MHz, THF-d_8): δ 7.54 (t, J_{H-H} = 8 Hz, 1H), 7.33 (m, 8H), 6.87 (t, J_{H-H} = 6.8 Hz, 8H), 6.73 (t, J_{H-H} = 6.5 Hz, 4H), 6.63 (d, J_{H-H} = 8 Hz, 2H), 1.62 (vt, J_{P-H} = 7.8 Hz, 36H). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8): δ 166.2 (t, J_{P-C} = 4.0 Hz), 165.8 (q, J_{B-C} = 49.1 Hz), 150.9 (s), 137.8 (s), 126.4 (m), 122.5 (s), 106.5 (s), 42.6 (t, J_{P-C} = 4.8 Hz), 28.1 (s). ^{31}P{^{1}H} NMR (202 MHz, THF-d_8): δ 183.5 (s). Anal. Calcd (found) for $C_{45}H_{59}BClNNiO_2P_2$: % C, 66.49 (65.97); % H, 7.32 (7.37); % N, 1.72 (1.79).

(PONOP)PtCl(BPh_4) (3c-BPh_4). In a 50 mL Schlenk flask, complex **3c** (30 mg, 0.045 mmol) and 1 mL of MeOH were combined under a nitrogen atmosphere. A solution of $NaBPh_4$ (153 mg, 0.45 mmol) in MeOH (2 mL) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 20 min, and a colorless solid precipitated from solution. The solvent was removed by syringe, and the solid was washed 2 times with MeOH and dried under vacuum yielding pure complex **3c-BPh$_4$** (89%). Crystals of complex **3c-BPh$_4$** were grown by slow evaporation from a THF/C_6H_6 solution. ^{1}H NMR (500 MHz, THF-d_8): δ 7.58 (t, J_{H-H} = 8 Hz, 1H), 7.34 (m, 8H), 6.88 (t, J_{H-H} = 7.3 Hz, 8H), 6.74 (m, 6H), 1.52 (vt, J_{P-H} = 8.3 Hz, 36H). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8): δ 165.8 (q, J_{B-C} = 49.1 Hz), 164.2 (s), 149.6 (s), 137.8 (s), 126.4 (m), 122.5 (s), 106.7 (s), 43.1 (t, J_{P-C} = 9.2 Hz), 27.6 (s). ^{31}P{^{1}H} NMR (202 MHz, THF): δ 174.8 (s, J_{Pt-P} = 2535 Hz). Anal. Calcd (found) for $C_{51}H_{65}BClNO_2P_2Pt$: % C, 59.62 (59.94); % H, 6.38 (6.29); % N, 1.36 (1.18).

(PONOP)PdCl(BPh_4) (3b-BPh_4). In a 50 mL Schlenk flask, complex **3b** (30 mg, 0.051 mmol) and 1 mL of MeOH were combined under a nitrogen atmosphere. A solution of $NaBPh_4$ (173 mg, 0.51 mmol) in MeOH (2 mL) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 20 min, and a light yellow solid precipitated from solution. The solvent was removed by syringe, and the solid was washed 2 times with MeOH and dried under vacuum yielding pure complex **3b-BPh$_4$** (86%). Crystals of complex **3b-BPh$_4$** were grown by slow evaporation from a THF/C_6H_6 solution. ^{1}H NMR (500 MHz, THF-d_8): δ 7.53 (t, J_{H-H} = 8.3 Hz, 1H), 7.34 (m, 8H), 6.88 (t, J_{H-H} = 7.3 Hz, 8H), 6.74 (m, 6H), 1.52 (vt, J_{P-H} = 8.5 Hz, 36H). ^{13}C{^{1}H} NMR (125 MHz, THF-d_8): δ 166.1 (q, J_{B-C} = 49.1 Hz), 164.8 (s), 150.9 (s), 138.1 (s), 126.7 (m), 122.8 (s), 107.2 (s), 43.2 (t, J_{P-C} = 5.4 Hz), 27.9 (s). ^{31}P{^{1}H} NMR (202 MHz, THF-d_8): δ 192.1 (s, J_{Pt-P} = 2535 Hz). Anal. Calcd (found) for $C_{51}H_{65}BClNO_2P_2Pd$: % C, 65.25 (65.05); % H, 6.98 (7.06); % N, 1.49 (1.34).

Reaction Complex 5a with Different Substrates. In a J-Young tube 10 mg of complex **5a**, 5 equiv of substrate (*N*-benzylidenemethylimine, 1-octene, ^{t}BuNC, or PhCHO), and 0.5 mL of C_6D_6 were combined. The reactions were monitored by both ^{1}H and ^{31}P NMR spectroscopy at room temperature. In the case of gaseous substrates (CO, D_2 and ethylene), 1 atm substrate was added under the same reaction conditions. In the case of benzaldehyde, benzoin was formed, which was confirmed by ^{1}H NMR spectroscopy and GC-MS using an authentic sample. In the case of 1-octene after 2 days at room temperature, mostly isomerized 2-trans and 2-cis octene were observed by ^{1}H NMR spectroscopy. In the case of excess of ^{t}BuNC: ^{31}P{^{1}H} NMR (202 MHz, THF-d_8): δ 186.6 (s), 145.5 (s), 53.2 (s), 11.0(s).

(D-PONOP)NiCl (4a-*d$_1$*). In a 50 mL Schlenk flask, complex **3a** (20 mg, 0.038 mmol) and 10 mL of pentane were combined under a nitrogen atmosphere. A 0.038 mL portion of $LiDBEt_3$ (0.038 mmol, 1 M in THF) was added dropwise at room temperature. An immediate color change from red to deep green was observed. The reaction mixture was stirred at room temperature for 2 h. The solution was filtered under a nitrogen atmosphere using a cannula, and the volatiles were then removed under vacuum yielding a dark green complex **4a-*d$_1$*** (90%). ^{1}H NMR (400 MHz, C_6D_6): δ 4.19 (2H), 3.39 (m, 1H), 1.45 (vt, J_{P-H} =

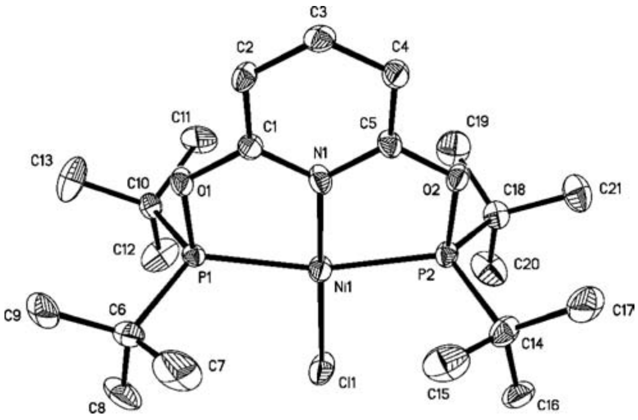

Figure 10. X-ray structure of (PONOP)NiCl. Selected distances: Ni1−Cl1, 2.3469(18) Å; Ni1−N1, 2.042(3) Å; N1−C1, 1.345(5) Å; C1−C2, 1.374(5) Å; C2−C3, 1.376(5) Å; C3−C4, 1.385(5) Å; C4−C5, 1.369(5) Å; C5−N1, 1.349(5) Å.

7.2 Hz, 36H). ^{2}H NMR (400 MHz, C_6H_6): δ 3.39 (m). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 165.1 (s).

When the reaction was carried out using $LiAlD_4$ or $NaBD_4$ under the same reaction conditions complex **4a-*d₁*** was not observed. No phosphorus signal was observed by ^{31}P NMR spectroscopy. A crystal was grown by slow evaporation from hexane solution, and formation of the paramagnetic complex (PONOP)Ni^ICl was confirmed (Figure 10). It is not clear why two different types of product form upon changing the hydride source.

Hydrosilylation of PhCHO Using Complex 5a. In a J-Young tube complex **5a** (5 mg, 0.0108 mmol), PhCHO (13 μL, 0.129 mmol), $PhSiH_3$ (36 μL, 0.291 mmol), and 0.5 mL of C_6D_6 were combined, and the reaction was monitored by both ^{1}H and ^{31}P NMR spectroscopy at room temperature. After 10 h at room temperature all of the benzaldehyde was consumed, and hydrosilylation products were observed, as confirmed by ^{1}H NMR spectroscopy and GC-MS. $PhSi(OCH_2Ph)_3$: ^{1}H NMR (400 MHz, C_6D_6) (selective part of the spectra): δ 5.22 (s, OCH_2Ph). GC-MS: $m/z = 425$ $[M]^+$. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) (Reaction mixture, 10 h): δ 165.1 (s), 14.7 (s).

Hydrosilylation Reaction Using Complex 4a. In a J-Young tube complex **4a** (5 mg, 0.0101 mmol), PhCHO (12.3 μL, 0.121 mmol), $PhSiH_3$ (34 μL, 0.273 mmol), and 0.5 mL of C_6D_6 were combined, and the reaction was monitored by both ^{1}H and ^{31}P NMR spectroscopy at room temperature. ^{1}H NMR (400 MHz, C_6D_6) (selective part of the spectra): δ 5.22 (s, OCH_2Ph, $PhSi(OCH_2Ph)_3$), 4.85 (s), 4.74 (s), 4.61 (s), 4.49 (s), 4.23 (s, free $PhSiH_3$).

Heating Complex 4a. In a J-Young tube complex **4a** (5 mg, 0.0101 mmol), $PhSiH_3$ (34 μL, 0.273 mmol), and 0.5 mL of C_6D_6 were combined and heated at 100 °C for 1.5 h. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6) (selective part of the spectra): Broad signals at δ 25.80, 16.53, and 9.36 and 2.49. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 50.56 (s).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data for complexes (CCDC nos. 826970−826980, 839072), including CIF files and tables of coordinates, distances, and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

(2) (a) Jensen, C. M. *Chem. Commun.* **1999**, 2443. (b) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (c) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (d) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798. (e) Milstein, D. *Pure Appl. Chem.* **2003**, *75*, 445. (f) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (g) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (h) Benito-Garagorri, D.; Kirchner, K. *Acc. Chem. Res.* **2008**, *41*, 201. (i) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048. (j) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761. (k) Liang, L.-C. *Coord. Chem. Rev.* **2006**, *250*, 1152. (l) Whited, M. T.; Grubbs, R. H. *Acc. Chem. Res.* **2009**, *42*, 1607. (m) van der Vlugt, J. I.; Reek, J. N. H. *Ang. Chem. Int. Ed.* **2009**, *48*, 8832. (n) van der Vlugt, J. I.; Pidko, E. A.; Vogt, D.; Lutz, M.; Spek, A. L. *Inorg. Chem.* **2009**, *48*, 7513. (o) van der Vlugt, J. I. *Ang. Chem. Int. Ed.* **2010**, *49*, 252. (p) Askevold, B.; Khusniyarov, M. M.; Herdtweck, E.; Meyer, K.; Schneider, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7566. (q) Leonard, N. G.; Williard, P. G.; Bernskoetter, W. H. *Dalton Trans.* **2011**, *40*, 4300. (r) Jurca, T.; Gorelsky, S. I.; Korobkov, I.; Richeson, D. S. *Dalton Trans.* **2011**, *40*, 4394. (s) Lindner, R.; van der Bosch, B.; Lutz, M.; Reek, J. N. H.; van der Vlugt, J. I. *Organometallics* **2011**, *30*, 499.(t) Morales-Morales, D. , Jensen, C., Eds.; *The Chemistry of Pincer Compounds*; Elsevier: Amsterdam, The Netherlands, 2007.

(3) (a) Mcloughlin, M. A.; Flesher, R. J.; Kaska, W. C.; Mayer, H. A. *Organometallics* **1994**, *13*, 3816. (b) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (c) Gupta, M.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1997**, 461. (d) Xu, W. W.; Rosini, G. P.; Gupta, M.; Jensen, C. M.; Kaska, W. C.; KroghJespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273. (e) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H. J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596. (f) Kimmich, B. F. M.; Bullock, R. M. *Organometallics* **2002**, *21*, 1504. (g) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652. (h) Cámpora, J.; Palma, P.; del Río, D.; Conejo, M. M.; Álvarez, E. *Organometallics* **2004**, *23*, 5653. (i) Zhu, K. M.; Achord, P. D.; Zhang, X. W.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044. (j) Zhang, X. W.; Emge, T. J.; Ghosh, R.; Goldman, A. S. *J. Am. Chem. Soc.* **2005**, *127*, 8250. (k) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science* **2005**, *307*, 1080. (l) Ghosh, R.; Kanzelberger, M.; Emge, T. J.; Hall, G. S.; Goldman, A. S. *Organometallics* **2006**, *25*, 5668. (m) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. *Science* **2006**, *312*, 257. (n) Zhang, X. W.; Emge, T. J.; Ghosh, R.; Krogh-Jespersen, K.; Goldman, A. S. *Organometallics* **2006**, *25*, 1303. (o) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Organometallics* **2008**, *27*, 5723. (p) Bailey, B. C.; Schrock, R. R.; Kundu, S.; Goldman, A. S.; Huang, Z.; Brookhart, M. *Organometallics* **2009**, *28*, 355. (q) Boro, B. J.; Duesler, E. N.; Goldberg, K. I.; Kemp, R. A. *Inorg. Chem.* **2009**, *48*, 5081. (r) Castonguay, A.; Spasyuk, D. M.; Madern, N.; Beauchamp, A. L.; Zargarian, D. *Organometallics* **2009**, *28*, 2134. (s) Chakraborty, S.; Krause, J. A.; Guan, H. *Organometallics* **2009**, *28*, 582. (t) Choi, J.; Choliy, Y.; Zhang, X. W.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2009**, *131*, 15627. (u) Huang, Z.; Brookhart, M.; Goldman, A. S.; Kundu, S.; Ray, A.; Scott, S. L.; Vicente, B. C. *Adv. Synth. Catal.* **2009**, *351*, 188. (v) Kundu, S.; Choliy, Y.; Zhuo, G.; Ahuja, R.; Emge, T. J.; Warmuth, R.; Brookhart, M.;

Krogh-Jespersen, K.; Goldman, A. S. *Organometallics* **2009**, *28*, 5432. (w) Bonnet, S.; Lutz, M.; Spek, A. L.; van Koten, G.; Klein Gebbink, R. J. M. *Organometallics* **2010**, *29*, 1157.

(4) (a) Kawatsura, M.; Hartwig, J. F. *Organometallics* **2001**, *20*, 1960. (b) Stambuli, J. P.; Stauffer, S. R.; Shaughnessy, K. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 2677. (c) Kloek, S. M.; Heinekey, D. M.; Goldberg, K. I. *Organometallics* **2006**, *25*, 3007. (d) Pelczar, E. M.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *Organometallics* **2008**, *27*, 5759. (e) van der Vlugt, J. I.; Pidko, E. A.; Vogt, D.; Lutz, M.; Spek, A. L.; Meetsma, A. *Inorg. Chem.* **2008**, *47*, 4442. (f) Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14168. (g) van der Vlugt, J. I.; Siegler, M. A.; Janssen, M. l.; Vogt, D.; Spek, A. L. *Organometallics* **2009**, *28*, 7025. (h) Cucciolito, M. E.; D'Amora, A.; Vitagliano, A. *Organometallics* **2010**, *29*, 5878. (i) Gnanaprakasam, B.; Zhang, J.; Milstein, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 1468. (j) Hahn, C. *Organometallics* **2010**, *29*, 1331. (k) Khaskin, E.; Iron, M. A.; Shimon, L. J. W.; Zhang, J.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 8542. (l) Schwartsburd, L.; Iron, M. A.; Konstantinovski, L.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2010**, *29*, 3817. (m) Nakajima, Y.; Shiraishi, Y.; Tsuchimoto, T.; Ozawa, F. *Chem. Commun.* **2011**, *47*, 6332. (n) van der Vlugt, J. I.; Pidko, E. A.; Bauer, R. C.; Gloaguen, Y.; Rong, M. K.; Lutz, M. *Chem.—Eur. J.* **2011**, *17*, 3850. (o) van der Vlugt, J. I.; Pidko, E. A.; Vogt, D.; Lutz, M.; Spek, A. L. *Inorg. Chem.* **2009**, *48*, 7513.

(5) (a) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840. (b) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790. (c) van der Vlugt, J. I.; Lutz, M.; Pidko, E. A.; Vogt, D.; Spek, A. L. *Dalton Trans.* **2009**, 1016. (d) Feller, M.; Ben-Ari, E.; Iron, M. A.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Konstantinovski, L.; Milstein, D. *Inorg. Chem.* **2010**, *49*, 1615.

(6) (a) Bernskoetter, W. H.; Hanson, S. K.; Buzak, S. K.; Davis, Z.; White, P. S.; Swartz, R.; Goldberg, K. I.; Brookhart, M. *J. Am. Chem. Soc.* **2009**, *131*, 8603. (b) Bernskoetter, W. H.; Schauer, C. K.; Goldberg, K. I.; Brookhart, M. *Science* **2009**, *326*, 553. (c) Salem, H.; Shimon, L. J. W.; Diskin-Posner, Y.; Leitus, G.; Ben-David, Y.; Milstein, D. *Organometallics* **2009**, *28*, 4791. (d) Findlater, M.; Bernskoetter, W. H.; Brookhart, M. *J. Am. Chem. Soc.* **2010**, *132*, 4534.

(7) This observation is also in contrast to the chemistry of (PCP)NiCl, in which these reducing reagents also give (PCP)NiH.[3q]

(8) Gunanathan, C.; Gnanaprakasam, B.; Iron, M. A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 14763.

(9) Kirillov, E.; Lehmann, C. W.; Razavi, A.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2004**, 943.

(10) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 2896.

(11) Hill, M. S.; MacDougall, D. J.; Mahon, M. F. *Dalton Trans.* **2010**, *39*, 11129.

(12) Analogous zinc and mercury complexes, $Zn_2(P^tBu_2)_4$ and $Hg_2(P^tBu_2)_4$, have been reported. See: Scholz, S.; Bolte, M.; Wagner, M.; Lerner, H.-W. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1199.

(13) Cobley, C. J.; Pringle, P. G. *Inorg. Chim. Acta* **1977**, *265*, 107.

(14) Li, G. Y. *J. Org. Chem.* **2002**, *67*, 3643.

(15) For example, see: (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) Kao, S. C.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 646.

(16) Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G. *Organometallics* **2010**, *29*, 4203.

(17) (a) Gosser, L. W.; Parshall, G. W. *Tetrahedron Lett.* **1971**, *12*, 2555.(b) Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; Stevens, W. R. In *Advances in Catalysis*; D.D. Eley, H. P., Paul, B. W., Eds.; Academic Press: New York, 1985; Vol. 33. (c) Keim, W. *Angew. Chem., Int. Ed.* **1990**, *29*, 235. (d) Barber, D. E.; Lu, Z.; Richardson, T.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4709. (e) Sato, Y.; Takimoto, M.; Hayashi, K.; Katsuhara, T.; Takagi, K.; Mori, M. *J. Am. Chem. Soc.* **1994**, *116*, 9771. (f) Fan, L.; Krzywicki, A.; Somogyvari, A.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 4003. (g) Sato, Y.; Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2000**, *122*, 1624. (h) Frauenrath, H.; Brethauer, D.; Reim, S.; Maurer, M.; Raabe, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 177. (i) Jenkins, J. C.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 5827. (j) Kogut, E.; Zeller, A.; Warren, T. H.; Strassner, T. *J. Am. Chem. Soc.* **2004**, *126*, 11984. (k) Cuperly, D.; Petrignet, J.; Crévisy, C.; Grée, R. *Chem.—Eur. J.* **2006**, *12*, 3261.

(18) (a) Iyer, S.; Varghese, J. P. *J. Chem. Soc., Chem. Commun.* **1995**, 465. (b) Kong, Y. K.; Kim, J.; Choi, S.; Choi, S.-B. *Tetrahedron Lett.* **2007**, *48*, 2033. (c) Tran, B. L.; Pink, M.; Mindiola, D. J. *Organometallics* **2009**, *28*, 2234.

(19) Ekici, S.; Gudat, D.; Nieger, M.; Nyulaszi, L.; Niecke, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 3368.

(20) Ekici, S.; Nieger, M.; Glaum, R.; Niecke, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 435.

(21) The structure shown in Figure 9 is an isomorph of the reported structure.