ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

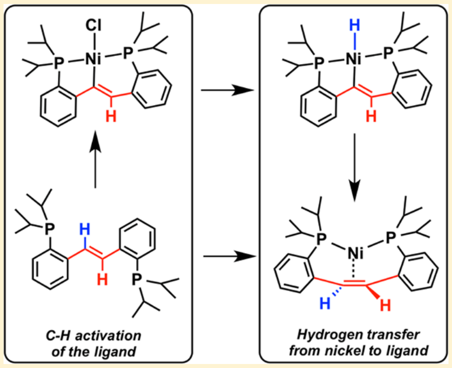
Group 10 Metal Complexes Supported by Pincer Ligands with an Olefinic Backbone

Brittany J. Barrett and Vlad M. Iluc*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

S *Supporting Information*

ABSTRACT: The coordination chemistry of 2,2′-bis(di-*iso*-propylphosphino)-*trans*-stilbene (*t*PCH═CHP) with group 10 metal centers in a variety of oxidation states is reported; different coordination modes were observed depending on the oxidation state of the metal. With metal centers in the 0 or +1 oxidation state ((*t*PCH═CHP)Ni, $[(tPCH{=}CHP)Pd]_2$, (*t*PCH═CHP)NiCl, (*t*PCH═CHP)NiI), η^2 coordination of the olefin occurs, whereas, with metals in the +2 oxidation state, C−H activation of the backbone, followed by rapid H−X reductive elimination, was observed, leading to an η^1 coordination of the backbone in (*t*PC═CHP)MCl (M = Ni, Pd, Pt). Employing the methyl-substituted analogue, 2,2′-bis(di-*iso*-propylphosphino)-*trans*-diphenyl-1,2-dimethylethene (*t*PCMe═CMeP), forced an η^2 coordination of the olefin in $[(tPCMe{=}CMeP)NiCl]_2[NiCl_4]$. The synthesis of the hydride complex (*t*PC═CHP)NiH was attempted, but, instead, led to the formation of (*t*PCH═CHP)Ni, indicating that the vinyl form of the backbone can function as a hydrogen acceptor. All metal complexes were characterized by multinuclei NMR spectroscopy, X-ray crystallography, and elemental analysis.



■ INTRODUCTION

Group 10 metal complexes hold a privileged status in organometallic chemistry because of their high and diverse activity in catalysis.[1,2] Olefin complexes have been known for a long time, Zeise's salt, $K[Cl_3Pt(CH_2{=}CH_2)]$,[3−5] being the first reported transition-metal organometallic complex; recently, this moiety has been successfully incorporated into ancillary ligands.[6−11] Given the versatility of group 10 metal olefin complexes in catalysis,[6,12−14] we became interested in determining whether including such a fragment in the backbone of a supporting ligand will engender new properties for the resulting metal complexes.

Pincers represent a versatile class of ligands, with various examples of group 10 metal complexes reported.[15−17] In general, the metal complexes tend to be stable and robust, properties conferred by the special pincer architecture.[18,19] Many examples include a central, anionic, strong σ donor flanked by two neutral donors.[2,20,21] However, deviations from this motif, in which the central chelating moiety is neutral, have been introduced and typically include a pyridine or a phosphine moiety.[22,23] The coordination mode of these ligands has been studied, and it has been shown that it can change in response to various factors such as their electronic and steric properties.

Neutral pincer ligands including an alkene as the central chelating moiety, PCH═CHP, are not numerous. Bennett and co-workers initially reported 2,2′-bis(diphenylphosphino)-*trans*-stilbene and observed that group 10 metals form monoanionic κ^3-PCP complexes in the +2 oxidation state (Figure 1).[24−26] However, the choice of an olefinic backbone allows various options, such as noncoordination and η^2-coordination in the neutral form, and η^1-coordination in the vinyl form, when the backbone could function as a hydrogen atom reservoir. Herein, we report an in depth investigation of the coordination chemistry of 2,2′-bis(di-*iso*-propylphosphino)-*trans*-stilbene (*t*PCH═CHP) by studying group 10 metal centers in a variety of oxidation states. Complementary to the results reported previously by the Bennett group, who only studied the +2 oxidation state, we observe more than one coordination mode with a metal center depending on its oxidation state. In order to probe the ability of the olefinic backbone to switch between various coordination modes, we also replaced the olefinic protons with methyl groups and studied the coordination chemistry of 2,2′-bis(di-*iso*-propylphosphino)-*trans*-diphenyl-1,2-dimethylethene (*t*PCMe═CMeP). Furthermore, reactivity studies indicate that the vinyl backbone is noninnocent and can function as a hydrogen acceptor.

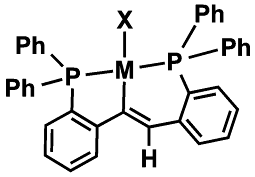


Figure 1. Coordination of 2,2′-bis(diphenylphosphino)-*trans*-stilbene to group 10 metals (M = Pd, Pt).

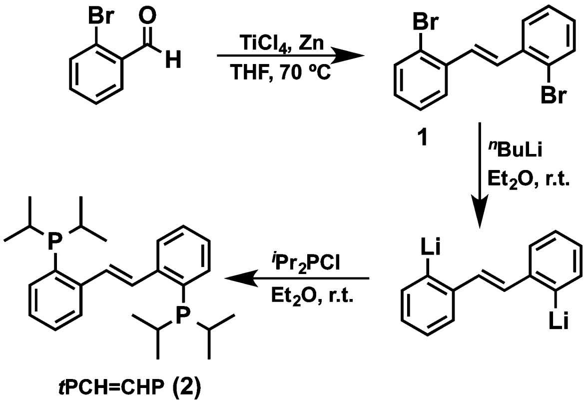
Received: March 10, 2014
Published: May 13, 2014

dx.doi.org/10.1021/om500256r | *Organometallics* 2014, 33, 2565−2574

RESULTS AND DISCUSSION

Synthesis and Characterization of Metal Complexes. We hypothesized that replacing the phenyl phosphine groups with *iso*-propyls would lead to increased solubility of the resulting metal complexes. This characteristic may prove important in allowing us to survey various oxidation states of the same metal. The precursor *o,o′-trans*-dibromostilbene (1) was prepared via a McMurry aldehyde coupling reaction as previously described (Scheme 1).[27] A lithium halogen exchange reaction then led to *o,o′-trans*-dilithiostilbene, which, in turn, reacted with the desired phosphine chloride to generate 2,2′-bis(di-*iso*-propylphosphino)-*trans*-stilbene (*t*PCH═CHP, **2**). The product was isolated as a pure crystalline material in good yield by recrystallization from *n*-pentane. ^{1}H NMR spectroscopy shows equivalent environments for all methine protons and only two environments for the *iso*-propyl methyl protons. The olefin protons exhibited a downfield resonance as a singlet at 8.53 ppm. The product *t*PCH═CHP (**2**) was also characterized by ^{31}P NMR spectroscopy as a singlet at −6.52 ppm and by single-crystal X-ray diffraction (Figure 2). The C(1)−C(1)# distance corresponding to the alkene carbon atoms is 1.330(4) Å, supporting C═C double bond character.

Scheme 1. Synthesis of *t*PCH═CHP (2)



With the diphosphine in hand, we decided to survey its coordination mode. Metal d^8 complexes (PC═CHP)NiCl (**3**), (PC═CHP)PdCl (**4**), and (PC═CHP)PtCl (**5**) form readily upon the addition of **2** to the appropriate metal precursor (Scheme 2), similarly to what Bennett observed for the phenyl derivative.[25,28] Uniquely, the reaction involving the nickel precursor leads to two products: **3**, which is analogous to the previously characterized nickel complex (*o*-Ph_2P-C_6H_4-C═CH-C_6H_4-PPh_2-*o*)NiCl, and another product, which was not characterized because of its insolubility in common organic solvents. Compounds **3**, **4**, and **5** result from the C−H activation of the backbone, followed by rapid reductive elimination of HCl. All three d^8 metals tend to favor the anionic form of the backbone consistently, a notion supported by Bennett and Clark's observations with the phenyl analogue of the ligand.[25] Bennett and Clark observed a similar behavior when reacting bdps (bdps = bis(diphenylphosphino)-*trans*-stilbene) with (cod)MCl_2 (M = Pd, Pt) and (cod)Pt$(CH_3)_2$. Ni(II) vinyl complexes are usually isolated as the insertion products of alkynes into nickel aryl bonds,[29,30] by oxidative addition of vinyl chloride to Ni(I)[31] and by cyclization reactions.[32] Palladium(II) salts have been known to remove vinylic hydrogens from olefins.[33] Other vinyl Pd(II) complexes were isolated by oxidative addition of a C−Cl bond to a Pd(0) center[34] or rearrangement of Pd(II) allyl complexes.[35] A similar behavior of Pt(II) was observed by Shaw et al. for (^{t}Bu$_2$P(CH$_2$)$_5$P^{t}Bu$_2$)PtCl$_2$, where, after several C−H activations, a similar complex, (^{t}Bu$_2$P(CH$_2$)$_2$-C═CH-P^{t}Bu$_2$)PtCl, was isolated, invoking an η^2 olefin intermediate.[36]

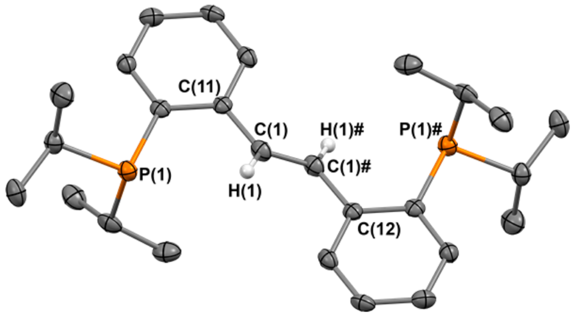
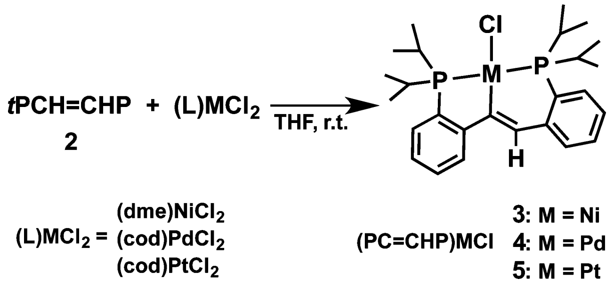


Figure 2. Thermal-ellipsoid (50% probability level) representation of *t*PCH═CHP (**2**). Most hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): C(1) −C(1)# = 1.330(4), P(1)−C(11) = 1.848(2), P(1)−C(22) = 1.870(2), P(1)−C(21) = 1.852(2), C(1)#1−C(1)−C(12) = 125.6(2), C(11)−P(1)−C(22) = 101.16(9), C(11)−P(1)−C(22) = 102.81(9).

Scheme 2. Synthesis of Complexes 3−5



The nonsymmetrical coordination mode of *t*PC═CHP in **3**, **4**, and **5** is supported by the aspect of the aryl region in the corresponding ^{1}H and ^{31}P NMR spectra. All species are identified by two doublets in the ^{31}P NMR spectrum and exhibit *trans* phosphorus couplings of 288, 387, and 382 Hz, respectively. The platinum satellites for compound **5** are also observed in the ^{31}P NMR spectrum. In addition, compound **3** displays a broad singlet at 6.83 ppm in the ^{1}H NMR spectrum assigned to the olefinic proton. The broadness of this peak is attributed to unresolved coupling with the phosphorus atoms. The olefinic proton for compound **4** is lost in the aryl region of the spectrum, while compound **5** contains a doublet at 7.63 ppm along with Pt satellites at 7.74 and 7.51 ppm, respectively (J_{PtH} = 48 Hz).

The structures of compounds **3** and **4** were obtained by single-crystal X-ray diffraction and show a square-planar coordination environment around the respective metal center (Figures 3 and 4). Although the data obtained for **5** was of relatively low quality (Figure SX44 in the Supporting Information), connectivity information could be obtained and the structure is similar to that of **3** and **4**. The C(1)−C(2) bond is in the typical range of a C−C double bond (1.351(3) Å for **3** and 1.329(4) Å for **4**). The Ni(II) complex is a more distorted form a square-planar geometry (Figure 3); the angle P(1)−Ni−P(2) is 165.91(3)° compared to 173.59(3)° for the

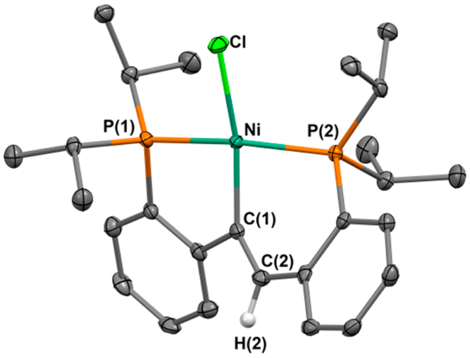


Figure 3. Thermal-ellipsoid (50% probability level) representation of **3**. Most hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Ni−P(1) = 2.1891(6), Ni−P(2) = 2.1884(6), Ni−Cl = 2.2127(6), Ni−C(1) = 1.930(2), C(1)−C(2) = 1.351(3), P(1)−Ni−P(2) = 165.91(3), Cl−Ni−P(1) = 99.13(2), Cl−Ni−P(2) = 99.72(2), C(1)−Ni−P(1) = 90.13(2), C(1)−Ni−P(2) = 87.01(6), C(1)−Ni−Cl = 167.63(7).

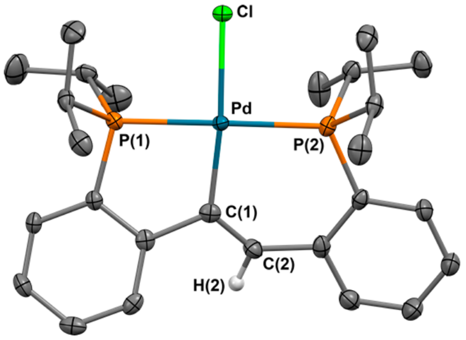
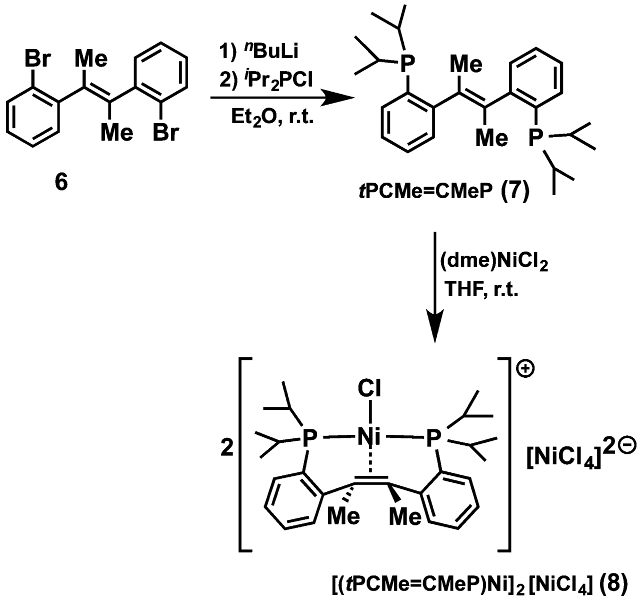


Figure 4. Thermal-ellipsoid (50% probability level) representation of **4**. Most hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Pd−P(1) = 2.2942(7), Pd−P(2) = 2.3160(7), Pd−Cl = 2.3919(7), Pd−C(1) = 2.033(3), C(1)−C(2) = 1.329(4), Cl−Pd−P(1) = 90.35(3), Cl−Pd−P(2) = 90.99(3), P(1)−Pd−P(2) = 173.59(3), C(1)−Pd−P(1) = 83.74(8), C(1)−Pd−Cl = 170.46(8).

Scheme 3. Synthesis of *t*PCMe═CMeP (7) and Complex 8



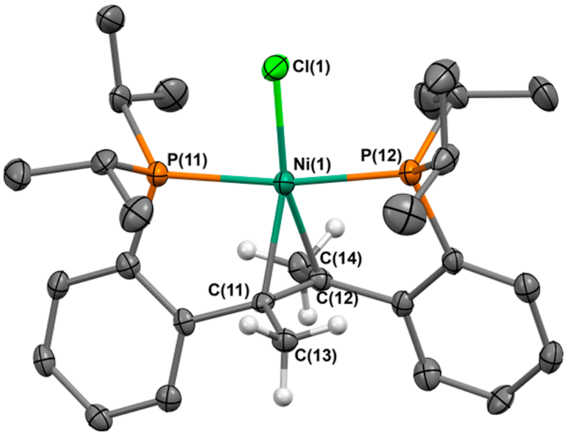


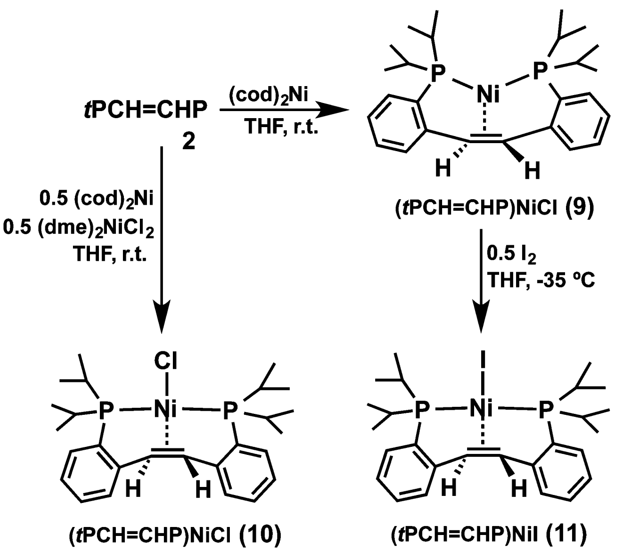
Figure 5. Thermal-ellipsoid (50% probability level) representation of **8**. Only one of the two crystallographically independent molecules is shown. Most hydrogen atoms and the counterion were omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)−Cl(1) = 2.1695(9), Ni(1)−P(11) = 2.2283(8), Ni(1)−P(12) = 2.2272(8), C(11)−C(12) = 1.398(3), Cl(1)−Ni(1)−P(11) = 85.53(3), Cl(1)−Ni(1)−P(12) = 85.56(3), Cl(1)−Ni(1)−P(11) = 105.58(7), P(12)−Ni(1)−P(11) = 171.10(3).

corresponding Pd(II) complex (Figure 4). In both cases, the two phenylene rings of the ligand are not coplanar, possibly to avoid the steric interaction between the vinylic and aromatic hydrogen atoms.

Since the deprotonation of the olefinic backbone is rather unusual, we decided to study the reactions of 2,2′-bis(di-*iso*-propylphosphino)-*trans*-diphenyl-1,2-dimethylethene (*t*PCMe═CMeP, **7**), in which methyl groups replace the olefinic protons. A McMurry coupling reaction can be performed on 2′-bromoacetophenone to generate bis(2-bromophenyl)-2-butene (**6**).[37] This particular reaction generates a higher yield of the *cis* (91%) than *trans* product (9%). Trituration of the crude product with *n*-hexane led to the isolation of the clean *trans* isomer since its solubility properties are different than those of the *cis* isomer. From bis(2-bromophenyl)-2-butene (**6**), the same synthetic procedure used to generate **2** can be used to produce *t*PCMe═CMeP (**7**).

Reaction of 2 equiv of *t*PCMe═CMeP (**7**) with 3 equiv of (dme)$NiCl_2$ generates [(*t*PCMe═CMeP)NiCl]$_2$[$NiCl_4$], **8** (Scheme 3). Interestingly, η^2 coordination is observed in **8** (Figure 5) instead of the previously observed C−H activation with *t*PCH═CHP (**2**). The forced η^2 coordination of the olefin in **8** causes the formation of a cationic species, with $NiCl_4^{2-}$ as a counteranion (Figure 5), which broadens the ^1H NMR spectra. The methyl groups in the backbone of *t*PCMe═CMeP (**7**) are equivalent with a shift at 2.08 ppm, similar to the shift found in the free ligand, at 2.12 ppm. The phosphines in this complex are also equivalent and show up as a singlet at 64.40 ppm in the corresponding ^{31}P NMR spectra. The solid-state molecular structure (Figure 5) also indicates a square-planar coordination environment at the metal center and an elongated olefinic C−C distance (1.398(3) Å), consistent with the presence of π-backbonding in **8**. The formation of **8** indicates that the absence of olefinic protons in *t*PCMe═CMeP renders the ligand analogous to previously reported PNP systems, in which the nitrogen donor is neutral and the corresponding nickel(II) complexes are cationic, such as [(PONOP)NiCl][Cl] (PONOP = 2,6-bis(di-*tert*-butylphosphinito)-pyridine),[38] [(PNHP^{Cy})NiBr][Br] (PNHP^{Cy} = HN[$CH_2CH_2P(Cy)_2$]$_2$),[39] and [(PNP^{tBu})Ni(NCMe)][BF$_4$] (PNP^{tBu} = 2,6-bis[(di-*tert*-butylphosphino)methyl]pyridine).[40]

Scheme 4. Synthesis of Complexes 9−11



Metal d^{10} complexes were also synthesized. Compound (*t*PCH=CHP)Ni (**9**) was obtained readily from the reaction of **2** with (cod)$_2$Ni in THF (Scheme 4). The product was isolated as a pure crystalline material in good yield by recrystallization from *n*-pentane. The ^{1}H NMR spectrum of **9** shows a C_2 symmetric compound, as indicated by the two environments for the four isopropyl methine positions at 2.14 and 1.90 ppm, respectively. The olefinic protons are represented as a singlet at 4.62 ppm. This upfield shift indicates that π-backbonding takes place in this complex, the formulation also supported by the elongated C(11)−C(12) distance of 1.406(5) Å (Figure 6).[41,42] The olefin does not approach a perpendicular orientation to the plane defined by P(1), Ni(1), and P(2) (dihedral angle of 29°). This is attributed to the pseudotrigonal-planar geometry observed around nickel, which prevents the olefin from twisting out of plane. The trigonal-planar geometry of this complex has been observed for other Ni(0) complexes; however, few examples of Ni(0) species supported solely by a chelating ligand itself exist.[43] Agapie and co-workers reported a diphosphine arene pincer system, which is capable of stabilizing the metal center by coordinating in an η^2 fashion to the arene group along with the phosphine arms and generates a trigonal-planar complex similar to **9**.[44,45] Other systems have shown the need for an additional ligand to stabilize the metal, such as the previously reported {RN(CH$_2$-P^{i}Pr$_2$)$_2$}Ni(C$_2$H$_4$) (R = Me, ^{i}Pr), in which the amine functionality remains dissociated from the metal center. In that example, an olefin is present to donate electron density to the metal.[46]

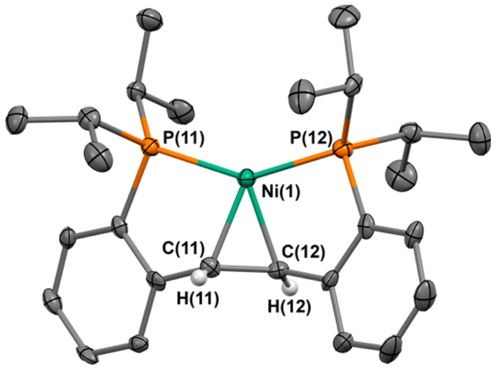
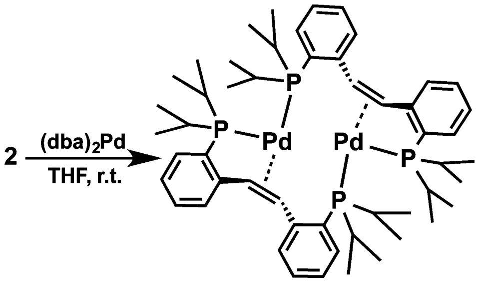


Figure 6. Thermal-ellipsoid (50% probability level) representation of **9**. Only one of the two crystallographically independent molecules is shown. Most hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)−P(12) = 2.1385(13), Ni(1)−P(11) = 2.1463(13), Ni(1)−C(12) = 1.968(4), Ni(1)−C(11) = 1.968(4), C(11)−C(12) = 1.406(5), P(11)−Ni(1)−P(12) = 146.35(5).

A comproportionation reaction[47−49] was then attempted with in situ generated nickel(II) and nickel(0) complexes in order to generate a nickel(I) species (Scheme 4). Two solutions were made, one containing **2** and (cod)$_2$Ni and the other **2** and (dme)NiCl$_2$, which were stirred separately for 30 min. The mixtures were then combined and stirred for an additional hour. An NMR spectrum of the crude reaction mixture showed the presence of multiple products, of which (*t*PCH=CHP)NiCl (**3**) was dominant. Because of the fast C−H activation of the ligand (vide supra), we were unable to optimize the reaction conditions to avoid the side products. X-ray quality crystals were obtained from a concentrated toluene solution of the reaction mixture. The solid-state molecular structure of **10** (Figure 7) shows the presence of a tetrahedral Ni(I) species in which the ligand coordinates through the phosphines and the olefinic backbone.

The analogous iodide, (*t*PCH=CHP)NiI (**11**), could be obtained on a large scale by adding a chilled THF solution of a half an equivalent of I$_2$ dropwise to a chilled solution of (*t*PCH=CHP)Ni (**9**) (Scheme 4). The ^{1}H NMR spectrum of the resulting product showed broad peaks, consistent with the presence of a paramagnetic product, whereas the corresponding ^{31}P NMR spectrum showed no peaks. Crystals suitable for X-ray diffraction were obtained from a concentrated solution of diethyl ether (Figure 7). The solid-state molecular structure is analogous to that of (*t*PCH=CHP)NiCl (**10**) and indicates a tetrahedral geometry around the metal center with angles ranging from 108.275(16) to 124.78(2)°. In general, monomeric Ni(I) species have a trigonal-planar geometry,[49−51] such as (^{i}Pr$_3$P)$_2$NiX (X = Cl, Br, I),[47] while reported tetrahedral Ni(I) species are dimers, such as [(dtbpe)NiCl]$_2$;[52] thus, the presence of the olefinic backbone in **10** and **11** helps stabilize the metal center in its tetrahedral form, allowing it to maintain its monomeric nature.

A palladium(0) compound was synthesized by stirring **2** with bis(dibenzylideneacetone)palladium(0) (Pd(dba)$_2$) for 1 h (eq 1). Single-crystal X-ray diffraction (Figure 8) indicated the



(1)

[(*t*PCH=CHP)Pd]$_2$ (12)

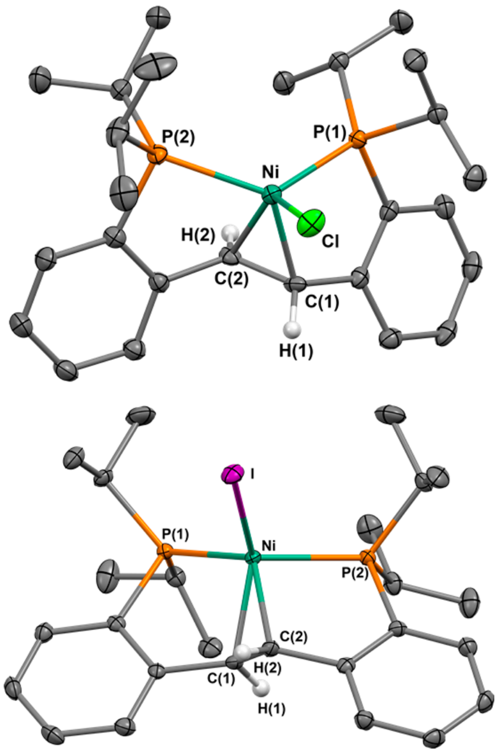


Figure 7. Thermal-ellipsoid (50% probability level) representation of **10** (top) and **11** (bottom). Most hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): For **10**: Ni−Cl = 2.2498(7), Ni−P(1) = 2.2569(7), Ni−P(2) = 2.2905(7), C(1)−C(2) = 1.394(3), Cl−Ni−P(1) = 110.46(3), P(1)−Ni−P(2) = 125.10(3), Cl−Ni−P(2) = 107.24(3). For **11**: I−Ni = 2.5717(4), Ni−P(1) = 2.3039(6), Ni−P(2) = 2.2521(7), C(1)−C(2) = 1.390(3), P(1)−Ni−P(2) = 124.78(2), P(1)−Ni−I = 112.000(18), P(2)−Ni−I = 108.275(16).

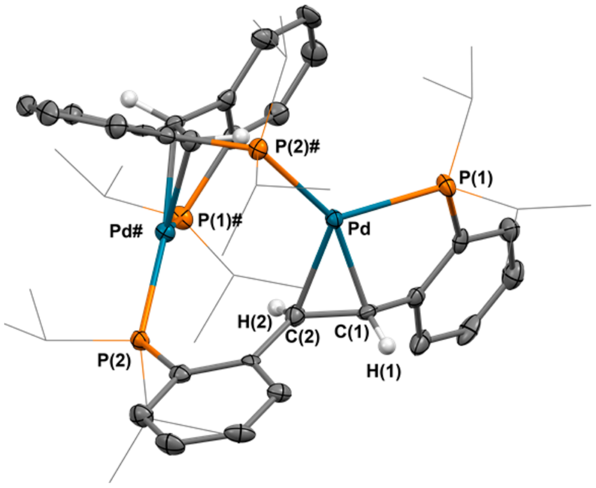
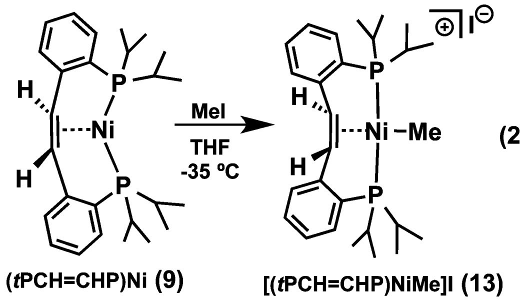


Figure 8. Thermal-ellipsoid (50% probability level) representation of **12**. Most hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Pd−P(1) = 2.3145(11), Pd−P(2)# = 2.3510(11), C(1)−C(2) = 1.398(5), P(1)−Pd−P(2)# = 122.74(4).

formation of a dimer, **12**, in which each ligand binds to one palladium through one phosphine and the olefin and to the other through the other phosphine. Each palladium center exhibits a pseudotrigonal-planar geometry with a P−Pd−P angle of 122.74(4)°. The ^{1}H NMR spectrum of **12** shows the olefinic protons at 5.91 ppm, shifted upfield compared to the corresponding protons of the free ligand. All four methine positions are equivalent and appear as a broad multiplet at 2.15 ppm. Evaluation of the corresponding ^{31}P NMR spectrum shows equivalent phosphorus atoms, as indicated by the presence of a sharp singlet at 55.28 ppm. Both ^{1}H and ^{31}P NMR spectra indicated that **12** is found as a monomer in solution. We propose that, in solution, the dimer dissociates and forms a monomeric species similar to that observed for the nickel(0) complex **9**.

Reactivity Studies. Given the various coordination modes of *t*PCH═CHP observed especially with nickel complexes, we decided to initiate a reactivity study to determine whether the ligand changes its coordination depending on the reaction conditions. Two compounds were targeted: (*t*PCH═CHP)Ni (**9**), which shows an η^2-olefinic backbone, and (*t*PC═CHP)NiCl (**3**), which contains an η^1-vinyl backbone.

Reaction of (*t*PCH═CHP)Ni (**9**) with 1 equiv of MeI (eq 2) led to the formation of the cationic methyl nickel complex,



(2)

[(*t*PCH═CHP)NiMe]I (**13**), with no change in the coordination mode of the olefinic backbone. The formation of a cationic species upon the addition of MeI to nickel(0) has been previously observed for an amine-based PNP nickel(0) complex, (PNHP)Ni (PNHP = HN(CH$_2$CH$_2$NHP^{i}Pr$_2$)$_2$).[53,54] Compound **13** was characterized by ^{1}H and ^{31}P NMR spectroscopy in solution, and by X-ray crystallography in the solid state. ^{1}H NMR spectroscopy indicates that the olefinic protons appear as a singlet at 5.87 ppm, consistent with a bound olefin experiencing π-backbonding with the metal center. The new methyl ligand is found at 0.9 ppm, and its signal is overlapping with those corresponding to the methyl *iso*-propyl groups. ^{31}P NMR spectroscopy shows two equivalent environments for the phosphine atoms, which appear as a singlet at 59.68 ppm, again, supporting the η^2-coordination mode of the olefinic backbone. Comparison of the solid-state molecular structure (Figure 9) with that of (*t*PCH═CHP)Ni (**9**) shows elongation of the Ni−C distances between the metal and the olefin from 1.968(4)−1.972(4) Å to 2.1148(19)−2.1355(19) Å. The addition of a new ligand to the coordination sphere also has the effect of shortening the C−C distance of the backbone from 1.406(5) to 1.383(3) Å, as expected in the presence of a more electron-deficient metal center.

In order to determine whether the vinyl backbone maintains its coordination mode in the presence of a hydride ligand, the nickel(II) hydride complex (*t*PC═CHP)NiH (**14**) was targeted from the corresponding chloride, (*t*PC═CHP)NiCl (**3**) (Scheme 5). Reaction with Li[HBEt$_3$] led to the desired complex, as indicated by a characteristic hydride signal in the ^{1}H NMR spectrum of the crude reaction mixture. However, after 1 h of stirring, when full conversion to (*t*PC═CHP)NiH (**14**) was determined by ^{1}H NMR spectroscopy, and during the

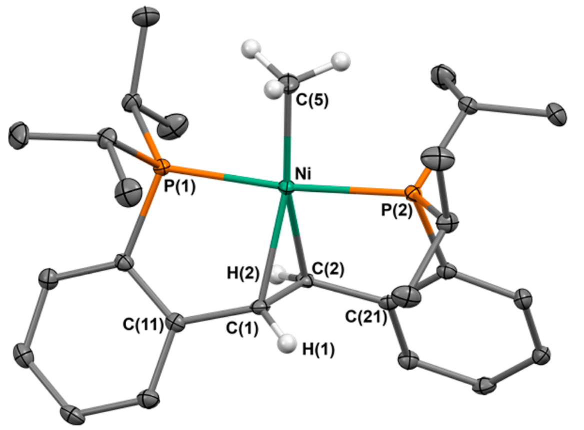
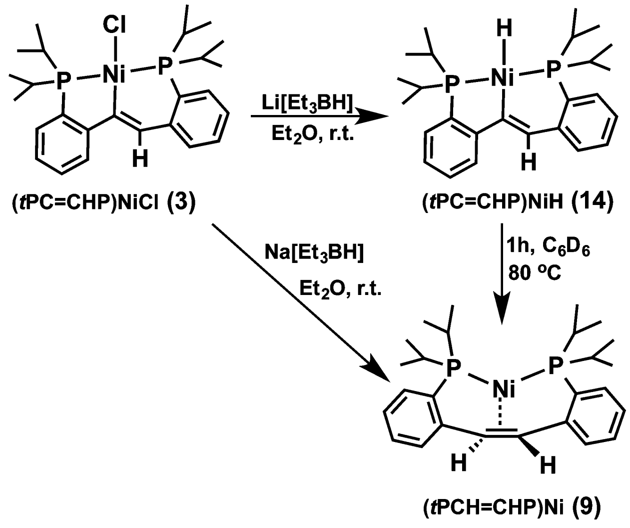


Figure 9. Thermal-ellipsoid (50% probability level) representation of **13**. Most hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Ni−P(1) = 2.2062(6), Ni−P(2) = 2.2095(6), Ni−C(5) = 1.982(2), Ni−C(1) = 2.1355(19), Ni−C(2) = 2.1148(19), C(1)−C(2) = 1.383(3), P(1)−Ni−P(2) = 174.07(2), P(1)−Ni−C(5) = 87.45(7), P(2)−Ni−C(5) = 87.48(7).

Scheme 5. Synthesis of Complex 14



reaction workup, the presence of the nickel(0) complex (*t*PCH═CHP)Ni (**9**) was observed. Heating of the crude reaction mixture to 80 °C for 1 h led to clean conversion to **9**. Reaction of **3** with 1 equiv of Na[HBEt$_3$] led to the exclusive formation of the nickel(0) complex **9**. Hydrogen transfer from ruthenium to a supporting pincer ligand has been invoked by the Milstein group in an interesting water oxidation reaction and in amine formation from alcohols.[55,56] Relevant to the hydrogen transfer described here are the reactions reported by the Agapie group with cationic diphosphine arene pincer nickel(II) complexes, which transfer the hydride from the metal to the arene backbone.[44] Moreover, it is important to note that the lack of hydrogen acceptor ability for the supporting ligand can lead to decomposition reactions, as observed by Hu's group with (^{Me}N$_2$N)Ni-H, where ^{Me}N$_2$N is a pincer bis(amino)amide ligand, which underwent intramolecular decomposition and led to the formation of nickel particles and (^{Me}N$_2$N)H by reductive elimination.[57] The findings described for the nickel hydride complex (*t*PC═CHP)NiH (**14**) may have applications in nickel(0)/nickel(II) catalytic cycles that would bypass nickel(I) or nickel(III) oxidation states and mimic palladium(0)/palladium(II) catalytic cycles more efficiently than what has been reported so far.[58−61]

DFT Calculations. In order to compare the electronic structures of metal complexes containing a coordinated olefinic backbone, models for the two diamagnetic nickel complexes (*t*PCH═CHP)Ni (**9**) and [(*t*PCH═CHP)NiMe]I (**13**), which contain nickel in the +2 and 0 oxidation states, respectively, were investigated. Calculations were carried out with Gaussian 03, and the phosphine *iso*-propyls were replaced by methyl groups. A good agreement was found between the optimized and the experimental structures (Figures SX31 and SX33, Supporting Information). The results of DFT calculations support the experimental findings described above: both complexes feature σ donation from the olefinic π orbital and π backdonation from the metal to the olefin π* orbital (Figure 10). The amount of π backdonation between the two nickel complexes varies, as expected, according to the d electron count of the metal, with the nickel(0) compound featuring the largest contribution of the olefin π* orbital (Figure 10). In addition, DFT calculations support the assignment of the nickel(I) formulation in (*t*PCH═CHP)NiCl (**10**) and (*t*PCH═CHP)NiI (**11**), with the unpaired electron residing primarily in the d$_{z2}$ orbital (Figures SX37 and SX40, Supporting Information).

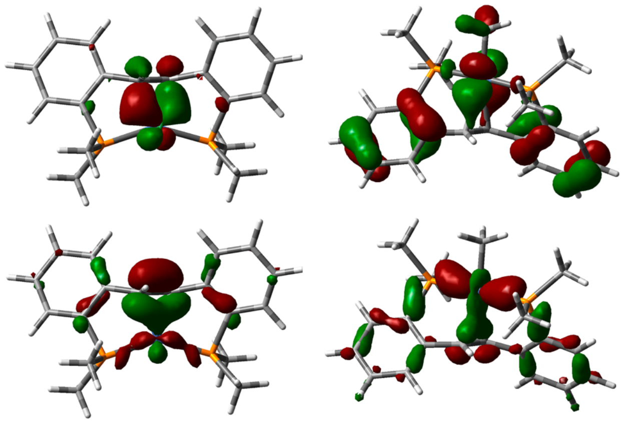


Figure 10. σ- and π-bonding interactions for (*t*PCH═CHP)^{Me}Ni (**9′**, left) and [(*t*PCH═CHP)^{Me}NiMe$^+$] (**13′**, right).

■ CONCLUSIONS

A neutral *t*PCH═CHP (**2**) pincer and its dimethyl analogue, *t*PCMe═CMeP (**7**), were synthesized and their coordination chemistry with group 10 metal centers was studied. The backbone olefinic moiety is versatile and responds to the electronic requirements of the metal. With metal centers in the 0 or +1 oxidation state ((*t*PCH═CHP)Ni (**9**), [(*t*PCH═CHP)Pd]$_2$ (**12**), (*t*PCH═CHP)NiCl (**10**), (*t*PCH═CHP)NiI (**11**)), η^2 coordination of the olefin occurred, whereas, with metals in the +2 oxidation state, C−H activation of the backbone, followed by rapid H−X reductive elimination, was observed, leading to an η^1 coordination of the backbone in (*t*PC═CHP)MCl (M = Ni (**3**), Pd (**4**), Pt (**5**)). This reactivity mode likely responds to subtle changes in the coordination environment because employing the methyl-substituted olefinic backbone analogue, (*t*PCMe═CMeP, **7**), forced an η^2 coordination of the olefin in [(*t*PCMe═CMeP)NiCl]$_2$[NiCl$_4$] (**8**). Reactivity studies with two nickel complexes, (*t*PCH═CHP)Ni (**9**), which shows an η^2-olefinic backbone, and (*t*PC═

CHP)NiCl (**3**), which contains an η^1-vinyl backbone, indicate that, while the η^2-coordination at nickel(0) is unperturbed by reactions with electrophiles ([(*t*PCH═CHP)NiMe]I (**13**)), the vinyl backbone acts as a hydrogen acceptor at the anionic carbon when the synthesis of (*t*PC═CHP)NiH (**14**) is attempted, leading, ultimately, to the nickel(0) complex (*t*PCH═CHP)Ni (**9**). The various coordination modes observed show that this ligand class is versatile and accommodates different coordination geometries that could enable new reactivity behavior for group 10 metal centers.

■ EXPERIMENTAL SECTION

All manipulations of air- and water-sensitive compounds were performed under a dry nitrogen atmosphere using a drybox. Glassware, vials, and stirring bars were dried in an oven at 120 °C overnight and evacuated for 24 h in the antechamber before being brought into the drybox. All solvents were dried by passing through a column of activated alumina, followed by storage over molecular sieves and sodium. Deuterated solvents were purchased from Cambridge Isotope Laboratories. C_6D_6 was dried by stirring over CaH_2, followed by filtration. $CDCl_3$ was dried over molecular sieves. All other chemicals were commercially available and used as received. NMR spectra were obtained on Bruker 400 and Bruker 500 spectrometers at ambient temperature. Chemical shift values are reported in parts per million (ppm) relative to residual internal protonated solvent or to a tetramethylsilane standard while using $CDCl_3$ for ^{1}H and ^{13}C{^{1}H} experiments. Coupling constants are reported in Hz. Magnetic moments were determined by the Evans method[62−64] using capillaries containing trimethoxybenzene in C_6D_6 as a reference and trimethoxybenzene in the sample solution. CHN analyses were performed on a CE-440 Elemental Analyzer or by Midwest Microlab, LLC. Gaussian 03 (revision D.02) was used for all reported calculations. The B3LYP (DFT) method was used to carry out the geometry optimizations on model compounds specified in the text using the LANL2DZ basis set. The validity of the true minima was checked by the absence of negative frequencies in the energy Hessian.

Synthesis of 2,2′-Bis(di-*iso*-propylphosphino)-*trans*-stilbene (*t*PCH═CHP, 2). The precursor *o*,*o*′-*trans*-dibromostilbene (**1**, 2.9 g, 8.63 mmol, 63.9%) was synthesized via a McMurry coupling reaction as reported in the literature.[27] ^{1}H NMR peaks agree with literature values.[65] Compound **1** was then brought into the glovebox and dissolved in 75 mL of diethyl ether. The solution was allowed to cool in a −35 °C freezer for 30 min, followed by the addition of *n*-butyllithium (10.8 mL, 17.3 mmol) via syringe. The mixture was allowed to warm to room temperature and then stirred for 1.5 h. The resulting solution was cooled in a −35 °C freezer for an additional 30 min before the addition of di-*iso*-propyl phosphine chloride via syringe (2.8 mL, 17.3 mmol), affording a cloudy yellow solution. After stirring overnight, the reaction was quenched with 1 mL of a degassed 10% solution of NH_4Cl. The solution was then dried over Na_2SO_4, followed by filtration through a frit padded with Celite. The volatiles were removed under reduced pressure, leaving behind the crude residue of *t*PCH═CHP (**2**, 2.76 g, 6.70 mmol, 78.15%), which was recrystallized from *n*-pentane. ^{1}H NMR (400 MHz, C_6D_6) δ: 0.88 (dd, J_{PH} = 12 Hz, J_{HH} = 8 Hz, 12H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.02 (dd, J_{PH} = 12 Hz, J_{HH} = 8 Hz, 12H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.95 (m, 4H, $\mathrm{C}H(\mathrm{CH}_3)_2$), 7.03 (td, J_{HH} = 8 Hz, J_{PH} = 1.6 Hz, 2H, Ar*H*), 7.11 (td, J_{HH} = 8 Hz, J_{PH} = 1.2 Hz, 2H, Ar*H*), 7.29 (dt, J_{HH} = 8 Hz, J_{PH} = 1.6 Hz, Ar*H*), 7.95 (ddd, J_{HH} = 6.8 Hz, J_{HH} = 4 Hz, J_{PH} = 0.8 Hz, 2H, Ar*H*), 8.52 (d, J_{HH} = 4 Hz, 2H, C*H*═C*H*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: −6.52 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 19.17 (d, J_{PC} = 10 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 20.33 (d, J_{PC} = 19 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 23.82 (d, J_{PC} = 14 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 126.24 (d, J_{PC} = 4 Hz, Ar*C*), 126.68 (s, Ar*C*), 129.16 (s, Ar*C*), 129.65 (dd, J_{PC} = 34 Hz, J_{PC} = 3 Hz, Ar*C*), 132.67 (d, J_{PC} = 3 Hz, CH═CH), 134.55 (d, J = 22 Hz, Ar*C*), 145.59 (d, J_{PC} = 22 Hz, Ar*C*). MS (QTOF) *m*/*z*: $C_{26}H_{39}P_2^+$, 413.25 (expected: $C_{26}H_{38}P_2$, 412.24).

Synthesis of (*t*PC═CHP)NiCl (3). Compound **2** (100 mg, 0.242 mmol) was dissolved in THF along with nickel(II) chloride dimethoxyethane ((dme)$NiCl_2$, 52.6 mg, 0.242 mmol), and the resulting solution was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure, followed by extraction with *n*-pentane. The orange extract was set to crystallize at −34 °C (69.9 mg0.138 mmol, 57%). ^{1}H NMR (400 MHz, C_6D_6) δ: 1.15 (dd, J_{PH} = 15 Hz, J_{HH} = 10 Hz, 6H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.36 (dd, J_{PH} = 15 Hz, J_{HH} = 5 Hz, 6H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.44 (app m, 12H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 2.55 (m, 2H, $\mathrm{C}H(\mathrm{CH}_3)_2$), 2.63 (m, 2H, $\mathrm{C}H(\mathrm{CH}_3)_2$), 6.86 (br s, 1H, C*H*═C), 6.92 (t, J_{HH} = 4 Hz, 1H, Ar*H*), 7.01 (t, J_{HH} = 8 Hz, 1H, Ar*H*), 7.11 (m, 2H, Ar*H*), 7.13 (t, J_{HH} = 4 Hz, 1H, Ar*H*), 7.30 (t, J_{HH} = 4 Hz, 1H, Ar*H*), 7.55 (d, J_{HH} = 8 Hz, 1H, Ar*H*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: 29.23 (d, J_{PP} = 221.9 Hz), 61.09 (d, J_{PP} = 221.9 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 18.20 (d, J_{PC} = 1 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 19.18 (s, $\mathrm{CH}(\mathrm{CH}_3)_2$), 19.22 (d, J_{PC} = 2 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 19.27 (s, $\mathrm{CH}(\mathrm{CH}_3)_2$), 24.97 (dd, J_{PC} = 2 Hz, J_{PC} = 21 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 25.56 (dd, J_{PC} = 2 Hz, J_{PC} = 21 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 120.67 (d, J_{PC} = 32 Hz, Ar*C*), 123.51 (d, J_{PC} = 16 Hz, Ar*C*), 127.29 (d, J_{PC} = 5 Hz, Ar*C*), 130.18 (d, J_{PC} = 1 Hz, Ar*C*), 130.74 (d, J_{PC} = 1 Hz, Ar*C*), 130.81 (d, J_{PC} = 3 Hz, Ar*C*), 131.54 (d, J_{PC} = 3 Hz, Ar*C*), 130.02 (s, Ar*C*), 132.40 (d, J_{PC} = 8 Hz, Ar*C*), 134.89 (d, J_{PC} = 5 Hz, Ar*C*),147.63 (d, J_{PC} = 16 Hz, Ar*C*), 154.89 (dd, J_{PC} = 5 Hz, J_{PC} = 19 Hz, *C*═CH), 165.10 (d, J_{PC} = 43 Hz, CH═*C*). Anal. Calcd for $C_{26}H_{37}ClNiP_2$: C, 61.76; H, 7.38. Found C, 61.82; H, 7.39.

Synthesis of (*t*PC═CHP)PdCl (4). A mixture containing *t*PCH═CHP (**2**, 100 mg, 0.242 mmol) and dichloro(1,5-cyclooctadiene)-palladium ((cod)$PdCl_2$, 69.1 mg, 0.242 mmol) in THF was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure, and the remaining yellow residue was triturated with *n*-pentane. The resulting powder was dissolved in diethyl ether and allowed to crystallize at −35 °C (63.1 mg, 0.114 mmol, 47%). ^{1}H NMR (400 MHz, C_6D_6) δ: 1.01 (dd, J_{PH} = 8 Hz, J_{HH} = 4 Hz, 6H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.17 (dd, J_{PH} = 8 Hz, J_{HH} = 4 Hz, 6H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.40 (m, 12H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 2.62 (m, 2H, $\mathrm{C}H(\mathrm{CH}_3)_2$), 2.80 (m, 2H, $\mathrm{C}H(\mathrm{CH}_3)_2$), 6.95 (t, J_{HH} = 8 Hz, 1H, Ar*H*), 6.98 (t, J_{HH} = 8 Hz, 1H, Ar*H*), 7.19 (app m, 5H, Ar*H*), 7.32 (t, J_{HH} = 4 Hz, 1H, Ar*H*), 7.69 (d, J_{HH} = 8 Hz, 1H, Ar*H*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: 35.14 (d, J_{PP} = 382 Hz), 66.92 (d, J_{PP} = 382 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 18.35 (d, J_{CP} = 2 Hz, $\mathrm{CH}(\mathrm{CH}_2)_2$), 18.90 (s, $\mathrm{CH}(\mathrm{CH}_3)_2$), 19.15 (d, J_{PC} = 5 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 19.32 (d, J_{PC} = 4 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 25.42 (dd, J_{PC} = 18 Hz, J_{PC} = 2 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 26.00 (dd, J_{PC} = 18 Hz, J_{PC} = 2 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 119.76 (d, J_{PC} = 35 Hz, Ar*C*), 124.58 (d, J_{PC} = 17 Hz, Ar*C*), 127.53 (d, J_{PC} = 5 Hz, Ar*C*), 130.90 (app t, J_{PC} = 2 Hz, Ar*C*), 131.21 (d, J_{PC} = 4 Hz, Ar*C*), 131.58 (d, J_{PC} = 2 Hz, Ar*C*), 131.62 (app d, J_{PC} = 1 Hz, Ar*C*), 131.78 (app d, J_{PC} = 1 Hz, Ar*C*),131.74 (br s, Ar*C*), 132.10 (br s, Ar*C*), 133.55 (d, J_{PC} = 9 Hz, Ar*C*), 148.60 (d, J_{PC} = 10 Hz, Ar*C*), 153.06 (q, J_{PC} = 4 Hz, CH═*C*), 163.62 (d, J_{PC} = 43 Hz, CH═C). Anal. Calcd for $C_{26}H_{37}ClP_2Pd$: C, 56.43; H, 6.74. Found C, 56.78; H, 6.71.

Synthesis of (*t*PC═CHP)PtCl (5). A THF solution containing *t*PCH═CHP (**2**, 25 mg, 0.061 mmol) and dichloro(1,5-cyclooctadiene)platinum ((cod)$PtCl_2$, 22.8 mg, 0.061 mmol) was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure, and the resulting residue was triturated with *n*-pentane, leading to the formation of a powder (36.4 mg, 0.057 mmol, 93%). Dissolving this powder in toluene and layering this solution with *n*-pentane at −35 °C led to the isolation of analytically pure **5**. ^{1}H NMR (400 MHz, C_6D_6) δ: 1.03 (dd, J_{PH} = 8 Hz, J_{HH} = 4 Hz, 6 Hz, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.14 (dd, J_{PH} = 8 Hz, J_{HH} = 4 Hz, 6 Hz, $\mathrm{CH}(\mathrm{C}H_3)_2$), 1.43 (m, 12H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 2.81 (m, 2H, $\mathrm{C}H(\mathrm{CH}_3)_2$), 3.12 (m, 2H, $\mathrm{CH}(\mathrm{CH}_3)_2$), 7.00 (app q, J_{HH} = 8 Hz, 2H, Ar*H*), 7.15 (br m, 2H, Ar*H*), 7.25 (m, 2H, Ar*H*), 7.41 (t, J_{HH} = 8 Hz, 1H, Ar*H*), 7.63 (d with platinum satellites, J_{HH} = 4 Hz, J_{HPt} = 48 Hz, 1H, C*H*═C), 7.86 (dd, J_{HH} = 4 Hz, J_{PH} = 1 Hz, 1H, Ar*H*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: 31.46 (d with platinum satellites, J_{PP} = 306.2 Hz, J_{PPt} = 1017.4 Hz), 62.29 (d with platinum satellites, J_{PP} = 302.9 Hz, J_{PPt} = 1165.6 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 18.16 (d with platinum satellites, J_{PtC} = 12 Hz, J_{PC} = 2 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 18.62 (d with platinum satellites, J_{PtC} = 10 Hz, J_{PC} = 2 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 19.00 (d, J_{PC} = 4 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 19.13 (d, J_{PC} = 3 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 25.14 (dd with platinum satellites, J_{PtC} = 13 Hz, J_{PC} = 28 Hz, J_{CC} = 3 Hz, $\mathrm{CH}(\mathrm{CH}_3)_2$), 26.39 (dd with platinum satellites, J_{PtC} = 8 Hz, J_{PC} = 29 Hz, J_{CC} = 2 Hz, $CH(CH_3)_2$), 117.46 (dd, J_{PC} = 40 Hz, J_{PC} = 2 Hz, ArC), 124.42 (d with platinum satellites, J_{PtC} = 17 Hz, J_{PC} = 15 Hz, ArC), 125.96 (d, J_{PC} = 6 Hz, ArC), 127.45 (d, J_{PC} = 6 Hz, ArC), 128.67 (d with platinum satellites, J_{PtC} = 12 Hz, J_{PC} = 12 Hz, CH═C), 130.59 (d with platinum satellites, J_{PtC} = 14 Hz, J_{PC} = 2 Hz, ArC), 131.28 (dd, J_{PC} = 27 Hz, J_{CC} = 3 Hz, ArC), 131.28 (d, J = 4 Hz, ArC), 133.38 (d, J = 9 Hz, ArC), 139.59 (d, J = 7 Hz, ArC), 149.62 (d, J = 16 Hz, ArC), 164.47 (d, J = 32 Hz, ArC). Anal. Calcd for $C_{26}H_{37}ClP_2Pt$: C, 48.64; H, 5.81. Found C, 48.37; H, 5.71.

Synthesis of (*Z*)-2,3-Bis(2-di-*iso*-propylphosphinephenyl)-2-butene (*t*PCMe═CMeP, 7). The precursor, (*Z*)-2,3-bis(2-bromophenyl)-2-butene (**6**), was synthesized as reported in the literature in 8.4% yield.[37] Compound **7** was generated via the same procedure as **2** (1.6878 g, 3.83 mmol, 72.4%). ^{1}H NMR (500 MHz, C_6D_6) δ: 0.95 (dd, J_{PH} = 10 Hz, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$, major), 1.03 (dd, J_{PH} = 10 Hz, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$, major), 1.17 (m, 12H, $CH(CH_3)_2$, major), 1.35 (dd, J_{PH} = 10 Hz, J_{HH} = 5 Hz, $CH(CH_3)_2$, minor), 1.94 (m, 4H, $CH(CH_3)_2$, major), 2.05 (s, CH_3C═CCH_3, minor) 2.12 (s, 6H, CH_3C═CCH_3, major), 7.11 (td, J_{HH} = 10 Hz, J_{PH} = 1 Hz, 2H, Ar*H*, major), 7.21 (t, J_{HH} = 10 Hz, 2H, Ar*H*, major), 7.41 (dt, J_{HH} = 10 Hz, J_{PH} = 1 Hz, 2H, Ar*H*, major), 7.47 (br d, J_{HH} = 5 Hz, Ar*H*, minor), 7.63 (ddd, J_{HH} = 5 Hz, J_{HH} = 5 Hz, J_{PH} = 1 Hz, 2H, Ar*H*, major). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: −3.09 (s, minor), −2.38 (s, major). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 20.44 (d, J_{PC} = 18 Hz, $CH(CH_3)_2$), 20.67 (d, J_{PC} = 13 Hz, $CH(CH_3)_2$), 20.77 (s, $CH(CH_3)_2$), 20.94 (d, J_{PC} = 15 Hz, $CH(CH_3)_2$), 24.99 (d, J_{PC} = 23 Hz, $-CH(CH_3)_2$), 25.29 (d, J_{PC} = 18 Hz, CH_3C═CCH_3), 25.96 (d, J_{PC} = 24 Hz, $CH(CH_3)_2$), 126.36 (s, ArC), 129.13 (s, CH_3C═CCH_3), 129.46 (s, ArC), 130.03 (d, J_{PC} = 11 Hz, ArC), 132.83 (d, J_{PC} = 7 Hz, ArC), 135.76 (d, J_{PC} = 32 Hz, ArC), 152.94 (d, J_{PC} = 49 Hz, ArC). MS (QTOF) *m*/*z*: $C_{28}H_{43}P_2^+$, 441.28 (expected: $C_{28}H_{42}P_2$, 440.28).

Synthesis of 2[(*t*PCMe═CMeP)NiCl]$_2$[NiCl$_4$] (8). A solution of THF containing *t*PCMe═CMeP (**7**, 25 mg, 0.057 mmol) and (dme)NiCl$_2$ (18.5 mg, 0.085 mmol) was stirred for 1 h at ambient temperature. The volatiles were then removed under reduced pressure; trituration with *n*-pentane produced a green powder (29.8 mg, 0.023 mmol, 83%). The powder was then recrystallized from a CH_2Cl_2 solution layered with *n*-pentane. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.54 (q, J_{PH} = 10 Hz, 6H, $CH(CH_3)_2$), 1.61 (q, 6H, J_{PH} = 10 Hz, $CH(CH_3)_2$), 1.74 (q, 12 H, J_{PH} = 10 Hz, $CH(CH_3)_2$), 2.08 (s, 6H, CH_3C═CCH_3), 3.00 (br s, 2H, $CH(CH_3)_2$), 3.24 (br m, 2H, $CH(CH_3)_2$), 7.94 (br s, 2H, Ar*H*), 8.05 (br s, 2H, Ar*H*), 9.04 (br s, 2H, Ar*H*), 9.29 (br s, 2H, Ar*H*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 64.40 (s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 18.74 (s, $CH(CH_3)_2$), 19.51 (s, $CH(CH_3)_2$), 20.43 (s, $CH(CH_3)_2$), 20.70 (s, $CH(CH_3)_2$), 26.85 (t, J_{PC} = 23 Hz, $CH(CH_3)_2$), 27.53 (t, J_{PC} = 21 Hz, $CH(CH_3)_2$), 33.15 (s, CH_3C═CCH_3), 123.83 (s, ArC), 128.94 (t, J_{PC} = 32 Hz, CH_3C═CCH_3), 131.23 (s, ArC), 132.08 (t, J_{PC} = 13 Hz, ArC), 132.65 (s, ArC), 137.42 (s, ArC), 151.93 (t, J_{PC} = 23 Hz, ArC). Anal. Calcd for $C_{56}H_{84}Cl_6Ni_3P_4\cdot CH_2Cl_2$: C, 50.53; H, 6.40. Found C, 50.52; H, 6.50.

Synthesis of (*t*PCH═CHP)Ni (9). A solution containing *t*PCH═CHP (**2**, 100 mg, 0.242 mmol) and nickel bis(cyclooctadiene), (cod)$_2$Ni, was stirred at room temperature for 1 h in THF. The volatiles were removed under reduced pressure, and the orange residue was dissolved in *n*-pentane and allowed to crystallize at −34 °C (79.0 mg, 0.168 mmol, 69%). ^{1}H NMR (500 MHz, C_6D_6) δ: 0.97 (app m, 6H, $CH(CH_3)_2$), 1.03 (dd, J_{PH} = 10 Hz, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$), 1.12 (dd, J_{PH} = 10 Hz, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$), 1.26 (dd, J_{PH} = 10 Hz, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$), 1.95 (m, 2H, $CH(CH_3)_2$), 2.19 (br m, 2H, $CH(CH_3)_2$), 4.65 (s, 2H, CH═CH), 7.07 (t, J_{HH} = 5 Hz, 2H, Ar*H*), 7.18 (m, 4H, Ar*H*), 7.69 (d, J_{HH} = 5 Hz, 2H, Ar*H*). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ: 57.85 (s). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ: 18.36 (s, $CH(CH_3)_2$), 18.92 (t, J_{PC} = 6.3 Hz, $CH(CH_3)_2$), 20.76 (t, J_{PC} = 6.3 Hz, $CH(CH_3)_2$), 21.20 (app m, $CH(CH_3)_2$), 26.44 (t, J_{PC} = 5.04 Hz, $CH(CH_3)_2$), 74.96 (t, J_{PC} = 8.82 Hz, CH═CH), 125.49 (s, ArC), 128.35 (t, J_{PC} = 7.6 Hz, ArC), 129.51 (t, J_{PC} = 7.56, ArC), 130.93 (s, ArC), 148.82 (t, J_{PC} = 21.42 Hz, ArC), 154.63 (t, J_{PC} = 15.1 Hz, ArC). Anal. Calcd for $C_{26}H_{38}NiP_2$: C, 66.27; H, 8.13. Found C, 65.81; H, 8.10.

Synthesis of (*t*PCH═CHP)NiCl (10). (cod)$_2$Ni (16.7 mg, 0.061 mmol) was mixed with **2** (25 mg, 0.061 mmol) in THF and stirred for 30 min. Concurrently, (dme)NiCl$_2$ (13.19 mg, 0.061 mmol) was mixed with **2** (25 mg, 0.061 mmol) in THF and stirred for 30 min. The two solutions were mixed and stirred for an additional 2 h. The volatiles were then removed under reduced pressure; a ^{1}H NMR spectrum of the crude reaction mixture indicated that multiple species were present, including complex **3**. Trituration with *n*-pentane, followed by recrystallization from toluene solution layered with *n*-pentane, led to the isolation of single crystals of (*t*PC═CP)NiCl (**10**), but because of the rapid formation of (*t*PC═CHP)NiCl (**3**), the sample was contaminated and all attempts to isolate pure **10** failed.[47,48]

Synthesis of (*t*PCH═CHP)NiI (11). A THF solution of **9** (25 mg, 0.053 mmol) was chilled to −35 °C, along with a THF solution of I_2 (6.7 mg, 0.026 mmol). After 30 min, the I_2 solution was added dropwise to the solution of **9** over the course of 5 min. The mixture was warmed to room temperature while stirring for 1 h. The volatiles were removed under reduced pressure, followed by trituration with *n*-pentane, which resulted in a dark yellow-green powder (24.4 mg, 0.043 mmol, 80%). The powder was then recrystallized from a concentrated diethyl ether solution. Magnetic moment: μ_{eff} = 1.63 μ_B. The ^{1}H NMR spectrum is broad (Figure SX22 in the Supporting Information). ^{1}H NMR (400 MHz, C_6D_6) δ: 2.97 ($\nu_{1/2}$ = 2080 Hz), 4.93 (($\nu_{1/2}$ = 1760 Hz), 6.16 ($\nu_{1/2}$ = 880 Hz), 7.83 ($\nu_{1/2}$ =360 Hz), 10.16 ($\nu_{1/2}$ = 120 Hz), 10.63 ($\nu_{1/2}$ = 312 Hz). Anal. Calcd for $C_{26}H_{38}INiP_2\cdot 2CHCl_3$: C, 40.19; H, 4.82. Found C, 40.58; H, 4.63.

Synthesis of [(*t*PCH═CHP)Pd]$_2$ (12). Bis(dibenzylideneacetone)-palladium(0) (34.5 mg, 0.060 mmol) was mixed with *t*PCH═CHP (**2**, 25 mg, 0.061 mmol) in THF and stirred at room temperature for 12 h. The volatiles were removed under reduced pressure. The resulting residue was then dissolved in *n*-pentane and passed through a silica plug using a gradient elution of *n*-pentane, diethyl ether, and THF (3.3 mg, 0.006 mmol, 10.5%). ^{1}H NMR (400 MHz, C_6D_6) δ: 1.02 (dd, J_{PH} = 8 Hz, J_{HH} = 4 Hz, 12 H, $CH(CH)_3)_2$), 1.21 (dd, J_{PH} ~ J_{HH} = 8 Hz, 12H, $CH(CH_3)_2$), 2.16 (m, 4H, $CH(CH_3)_2$), 5.91 (s, 2H, CH═CH), 7.08 (t, J_{HH} = 4 Hz, 2H, Ar*H*), 7.17 (m, 2H, Ar*H*), 7.27 (d, J_{HH} = 8 Hz, 2H, Ar*H*), 7.60 (d, J_{HH} = 8 Hz, 2H, Ar*H*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: 55.28 (s). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6) δ: 19.45 (s, $CH(CH)_3)_2$), 20.47 (t, J_{PC} = 8 Hz, $CH(CH_3)_2$), 24.72 (br s, $CH(CH_3)_2$), 100.34 (t, J_{PC} = 7 Hz, CH═CH), 125.87 (t, J_{PC} = 2 Hz, ArC), 129.08 (s, ArC), 129.81 (t, J_{PC} = 8 Hz, ArC), 132.03 (s, ArC), 149.26 (t, J_{PC} = 18 Hz, ArC), 150.89 (t, J_{PC} = 15 Hz, ArC). Anal. Calcd for $C_{52}H_{76}P_4Pd_2$: C, 60.18; H, 7.38. Found C, 60.35; H, 7.42.

Synthesis of [(*t*PC═CHP)NiMe]I (13). A solution of (*t*PC═CP)Ni (**9**, 44.4 mg, 0.094 mmol) in THF was chilled in a −35 °C freezer for 30 min, along with a 1.6 M solution of iodomethane. Two equivalents of iodomethane (1.17 mL, 0.18 mmol) were added to the (*t*PC═CP)Ni (**9**) solution. The mixture was stirred for 5 min at ambient temperature until a yellow precipitate crashed out. The solvent was decanted, followed by trituration of the yellow powder with *n*-pentane (42.2 mg, 0.067 mmol, 71.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.01 (m, 9H, CH_3, $CH(CH_3)_2$), 1.32 (m, 12H, $CH(CH_3)_2$), 1.48 (app q, J_{PH} ~ J_{HH} = 8 Hz, 6 H, $CH(CH_3)_2$), 2.77 (br s, 2 H, $CH(CH_3)_2$), 2.90 (br s, 2H, $CH(CH_3)_2$), 5.66 (s, 2H, CH═CH), 7.42 (d, 2 H, J_{HH} = 8 Hz, Ar*H*), 7.68 (m, 6 H, Ar*H*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 60.18 (s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: −1.52 (t, J_{PC} = 23 Hz, CH_3), 16.69 (s, $CH(CH_3)_2$), 18.38 (s, $CH(CH_3)_2$), 19.37 (s, $CH(CH_3)_2$), 20.21 (s, $CH(CH_3)_2$), 23.75 (t, J_{PC} = 13 Hz, $CH(CH_3)_2$) 24.95 (t, J_{PC} = 11 Hz, $CH(CH_3)_2$), 116.21 (s, CH═CH), 125.76 (t, J_{PC} = 20 Hz, ArC), 127.38 (t, J_{PC} = 6 Hz, ArC), 129.64 (t, J_{PC} = 2 Hz, ArC), 131.53 (s, ArC), 132.72 (s, ArC), 148.62 (t, J_{PC} = 14 Hz, ArC). Anal. Calcd for $C_{27}H_{41}INiP_2$: C, 52.89; H, 6.74. Found C, 53.04; H, 6.82.

Synthesis of (*t*PC═CHP)NiH (14). To a solution of (*t*PC═CHP)NiCl (**3**, 20.4 mg, 0.043 mmol) in THF was added 0.04 mL of a 1 M Li[$(C_2H_5)_3BH$] (0.04 mmol) THF solution. The mixture was stirred at room temperature for 1 h, after which the volatiles were removed under reduced pressure. A NMR spectrum of the crude reaction mixture showed full conversion to **14**. The product was then extracted in *n*-pentane, and the resulting solution was filtered. NMR spectroscopy showed that the conversion to (*t*PCH═CHP)Ni (**9**) proceeded rapidly even at ambient temperature. Heating the NMR sample for 1 h at 80 °C showed full conversion to **9**. ^{1}H NMR (500 MHz, C_6D_6) δ: −10.65 (ddd, J_{HP} = 48 Hz, J_{HP} = 46 Hz, J_{HH} = 4 Hz, 1H, hydride), 0.98 (m, 12 H, $CH(CH_3)_2$), 1.19 (dd, J_{PH} = 12 Hz, J_{HH} = 4 Hz, 6 H, $CH(CH_3)_2$), 1.26 (dd, J_{PH} = 12 Hz, J_{HH} = 4 Hz, 6 H, $CH(CH_3)_2$), 2.20 (m, 2H, $CH(CH_3)_2$), 2.27 (m, 2H, $CH(CH_3)_2$), 7.03 (t, 1H, J_{HH} = 8 Hz, Ar*H*), 7.09 (t, J_{HH} = 4 Hz, 1H, Ar*H*), 7.32 (m, 4H, Ar*H*), 7.90 (m, 1H, Ar*H*), 8.05 (dd, J_{HH} = 8 Hz, J_{PH} = 4 Hz, 1H, Ar*H*). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: 57.53 (d, J_{PP} = 247 Hz), 84.17 (d, J_{PP} = 247 Hz). Because **14** is not stable for a reasonable amount of time at ambient temperature, an analytically pure sample suitable for elemental analysis could not be obtained. ^{1}H and ^{31}P NMR spectra for this complex can be found in the Supporting Information (Figures SX29 and SX30).

X-ray Crystal Structure of *t*PCH═CHP (2). X-ray quality single crystals were obtained from a concentrated solution of *n*-pentane solution at −34 °C in the glovebox. Crystal and refinement data for **2·C$_7$H$_8$**: Crystal data for $C_{33}H_{46}P_2$; M_r = 504.64; monoclinic; space group *C*2/*c*; *a* = 13.5186(11) Å; *b* = 12.0847(9) Å; *c* = 18.2230(14) Å; α = 90°; β = 93.335(2)°; γ = 90°; *V* = 2972.0(4) Å^3; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 0.165 mm^{-1}; d_{calc} = 1.128 g·cm^{-3}; 13 722 reflections collected; 1638 unique (R_{int} = 0.0504); giving R_1 = 0.0298, wR_2 = 0.0661 for 1390 data with $[I > 2\sigma(I)]$ and R_1 = 0.0406, wR_2 = 0.0711 for all 1638 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.141/−0.195.

X-ray Crystal Structure of (*t*PC═CHP)NiCl (3). X-ray quality single crystals were obtained from a concentrated CH_2Cl_2 solution layered with *n*-pentane at −35 °C in the glovebox. The resulting crystals were bright orange blocks. Crystal and refinement data for **3**: $C_{26}H_{37}ClNiP_2$; M_r = 505.66; monoclinic; space group *P*2(1)/*n*; *a* = 8.8598(10) Å; *b* = 9.8216(11) Å; *c* = 29.245(3) Å; α = 90°; β = 97.096(2)°; γ = 90°; *V* = 2525.3(5) Å^3; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 1.012 mm^{-1}; d_{calc} = 1.330 g·cm^{-3}; 22 334 reflections collected; 5171 unique (R_{int} = 0.0488); giving R_1 = 0.0345, wR_2 = 0.0695 for 4126 data with $[I > 2\sigma(I)]$ and R_1 = 0.0521, wR_2 = 0.0743 for all 5171 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.535/−0.283.

X-ray Crystal Structure of (*t*PC═CHP)PdCl (4). X-ray quality single crystals were obtained as pale yellow blocks from a concentrated diethyl ether solution at −35 °C in the freezer in the glovebox. Crystal and refinement data for **4**: $C_{26}H_{37}ClP_2Pd$; M_r = 553.35; orthorhombic; space group *Pca*2(1); *a* = 15.5062(11) Å; *b* = 11.0311(8) Å; *c* = 14.9547(11) Å; α = 90°; β = 90°; γ = 90°; *V* = 2558.0(3) Å^3; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 0.966 mm^{-1}; d_{calc} = 1.437 g·cm−3; 22 282 reflections collected; 5276 unique (R_{int} = 0.0346); giving R_1 = 0.0236, wR_2 = 0.0483 for 4899 data with $[I > 2\sigma(I)]$ and R_1 = 0.0280, wR_2 = 0.0496 for all 5276 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.652/−0.493.

X-ray Crystal Structure of [(*t*PCMe═CMeP)NiCl]$_2$[NiCl$_4$] (8). X-ray quality single crystals were obtained from a concentrated hexane layered CH_2Cl_2 solution at −35 °C in the glovebox. The resulting crystals where dichroic plates, appearing both green and orange. Crystal and refinement data for **8**: $C_{56}H_{84}Cl_6Ni_3P_4$; M_r = 1269.94; triclinic; space group $P\bar{1}$; *a* = 16.385(3) Å; *b* = 16.756(3) Å; *c* = 17.013(3) Å; α = 96.367(2)°; β = 116.335(2)°; γ = 114.271(2)°; *V* = 3561.9(10) Å^3; *Z* = 2; *T* = 120(2) K; λ = 0.71073 Å; μ = 1.129 mm^{-1}; d_{calc} = 1.184 g·cm^{-3}; 36 668 reflections collected; 12 540 unique (R_{int} = 0.0482); giving R_1 = 0.0334, wR_2 = 0.0685 for 8957 data with $[I > 2\sigma(I)]$ and R_1 = 0.0515, wR_2 = 0.0717 for all 12 540 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.431/−0.298.

X-ray Crystal Structure of (*t*PCH═CHP)Ni (9). X-ray quality single crystals were obtained readily as dark orange blocks from a concentrated *n*-pentane solution at −35 °C in the glovebox. Crystal and refinement data for **9**: $C_{26}H_{38}NiP_2$; M_r = 471.21; monoclinic; space group *P*2(1)/*c*; *a* = 15.245(2) Å; *b* = 10.7277(16) Å; *c* = 31.655(5) Å; α = 90°; β = 101.825(3)°; γ = 90°; *V* = 5067.1(13) Å^3; *Z* = 8; *T* = 120(2) K; λ = 0.71073 Å; μ = 0.902 mm^{-1}; d_{calc} = 1.235 g·cm^{-3}; 40 184 reflections collected; 8912 unique (R_{int} = 0.1426); giving R_1 = 0.0566, wR_2 = 0.0807 for 4771 data with $[I > 2\sigma(I)]$ and R_1 = 0.1361, wR_2 = 0.0931 for all 8912 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.711/−0.747.

X-ray Crystal Structure of (*t*PCH═CHP)NiCl (10). X-ray quality single crystals were obtained from a concentrated toluene solution at −35 °C in the glovebox. Crystal and refinement data for **10**: $C_{26}H_{38}ClNiP_2$; M_r = 506.66; monoclinic; space group *P*2(1)/*c*; *a* = 9.4899(9) Å; *b* = 20.450(2) Å; *c* = 13.0740(13) Å; α = 90°; β = 92.696(2)°; γ = 90°; *V* = 2534.4(4) Å^3; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 1.009 mm^{-1}; d_{calc} = 1.328 g·cm^{-3}; 35 899 reflections collected; 5182 unique (R_{int} = 0.0651); giving R_1 = 0.0362, wR_2 = 0.0694 for 4008 data with $[I > 2\sigma(I)]$ and R_1 = 0.0572, wR_2 = 0.0796 for all 5182 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.488/−0.323.

X-ray Crystal Structure of (*t*PCH═CHP)NiI (11). X-ray quality single crystals were obtained as green plates from a concentrated diethyl ether solution at −35 °C in the glovebox. Crystal and refinement data for **11**: $C_{26}H_{38}INiP_2$; M_r = 598.11; monoclinic; space group *P*2(1)/*n*; *a* = 8.0612(15) Å; *b* = 15.333(3) Å; *c* = 21.312(4) Å; α = 90°; β = 91.438(3)°; γ = 90°; *V* = 2633.4(8) Å^3; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 2.042 mm^{-1}; d_{calc} = 1.509 g·cm^{-3}; 59 339 reflections collected; 6567 unique (R_{int} = 0.0531); giving R_1 = 0.0236, wR_2 = 0.0477 for 5501 data with $[I > 2\sigma(I)]$ and R_1 = 0.0352, wR_2 = 0.0512 for all 6567 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.604/−0.444.

X-ray Crystal Structure of [(*t*PCH═CHP)Pd]$_2$ (12). X-ray quality single crystals were obtained from a concentrated solution of *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **12**: $C_{52}H_{76}P_4Pd_2$; M_r = 1037.81; tetragonal; space group *P*4(1)2(1)2; *a* = 12.8344(11) Å; *b* = 12.8344(11) Å; *c* = 34.222(3) Å; α = 90°; β = 90°; γ = 90°; *V* = 5637.1(11) Å^3; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 0.781 mm^{-1}; d_{calc} = 1.223 g·cm^{-3}; 68 395 reflections collected; 4970 unique (R_{int} = 0.1171); giving R_1 = 0.0382, wR_2 = 0.0634 for 4420 data with $[I > 2\sigma(I)]$ and R_1 = 0.0485, wR_2 = 0.0659 for all 4970 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.302/−0.312.

X-ray Crystal Structure of [(*t*PCH═CHP)NiMe]I (13·2CH$_2$Cl$_2$). X-ray quality single crystals were obtained from a concentrated solution of dichloromethane at −35 °C in the glovebox. Crystal data for **13**: $C_{29}H_{45}Cl_4INiP_2$; M_r = 783.00; monoclinic; space group *P*2(1)/*c*; *a* = 12.3677(11) Å; *b* = 13.0174(11) Å; *c* = 21.8913(19) Å; α = 90°; β = 102.5694(11)°; γ = 90°; *V* = 3439.9(5) Å^3; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 1.883 mm^{-1}; d_{calc} = 1.512g·cm^{-3}; 36 026 reflections collected; 6051 unique (R_{int} = 0.0258); giving R_1 = 0.0214, wR_2 = 0.0509 for 5412 data with $[I > 2\sigma(I)]$ and R_1 = 0.0260, wR_2 = 0.0523 for all 6051 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.767/−0.464.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra for compounds **1**−**13**, crystallographic tables and details (CIF) for compounds **2**−**4** and **8**−**13**, a text file of all computed molecules' Cartesian coordinates in a format for convenient visualization. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: viluc@nd.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Allen Oliver and Dominic C. Babbini for crystallographic assistance. This work was partially supported by the University of Notre Dame. Acknowledgment is made to the Donors of the American Chemical Society Petroleum

Research Fund for partial support of this research (ACS PRF # 53536-DNI3).

■ REFERENCES

(1) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A. M.; Garg, N. K.; Percec, V. *Chem. Rev.* **2011**, *111*, 1346.
(2) Selander, N.; Szabo, K. J. *Chem. Rev.* **2011**, *111*, 2048.
(3) Zeise, W. C. *Ann. Phys.* **1831**, *97*, 497.
(4) Black, M.; Mais, R. H. B.; Owston, P. G. *Acta Crystallogr., Section B: Struct. Sci.* **1969**, *B 25*, 1753.
(5) Hartley, F. R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 596.
(6) Vogt, M.; de Bruin, B.; Berke, H.; Trincado, M.; Grutzmacher, H. *Chem. Sci.* **2011**, *2*, 723.
(7) Lyaskovskyy, V.; van Dijk-Moes, R. J. A.; Burck, S.; Dzik, W. I.; Lutz, M.; Ehlers, A. W.; Slootweg, J. C.; de Bruin, B.; Lammertsma, K. *Organometallics* **2013**, *32*, 363.
(8) Allen, S. R.; Green, M.; Moran, G.; Orpen, A. G.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1984**, 441.
(9) Bennett, M. A.; Clark, P. W.; Robertson, G. B.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1972**, 1011.
(10) Okamoto, K.; Omoto, Y.; Sano, H.; Ohe, K. *Dalton Trans.* **2012**, *41*, 10926.
(11) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27.
(12) Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1070.
(13) Wang, X.; Widenhoefer, R. A. *Organometallics* **2004**, *23*, 1649.
(14) Hartley, F. R. *Chem. Rev.* **1969**, *69*, 799.
(15) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423.
(16) Benito-Garagorri, D.; Kirchner, K. *Acc. Chem. Res.* **2008**, *41*, 201.
(17) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redón, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300–302*, 958.
(18) Jensen, C. M. *Chem. Commun.* **1999**, 2443.
(19) Ines, B.; SanMartin, R.; Moure, M. J.; Dominguez, E. *Adv. Synth. Catal.* **2009**, *351*, 2124.
(20) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.
(21) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759.
(22) van der Vlugt, J. I.; Pidko, E. A.; Vogt, D.; Lutz, M.; Spek, A. L.; Meetsma, A. *Inorg. Chem.* **2008**, *47*, 4442.
(23) Bauer, R. C.; Gloaguen, Y.; Lutz, M.; Reek, J. N. H.; de Bruin, B.; van der Vlugt, J. I. *Dalton Trans.* **2011**, *40*, 8822.
(24) Bennett, M. A.; Johnson, R. N.; Tomkins, I. B. *J. Organomet. Chem.* **1976**, *118*, 205.
(25) Bennett, M. A.; Clark, P. W. *J. Organomet. Chem.* **1976**, *110*, 367.
(26) Bennett, M. A.; Corlett, S.; Robertson, G. B.; Steffen, W. L. *Aust. J. Chem.* **1980**, *33*, 1261.
(27) Takimiya, K.; Shibata, Y.; Ohnishi, A.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Mater. Chem.* **1995**, *5*, 1539.
(28) Robertson, G. B.; Whimp, P. O. *Inorg. Chem.* **1974**, *13*, 2082.
(29) Muller, G.; Panyella, D.; Rocamora, M.; Sales, J.; Fontbardia, M.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1993**, 2959.
(30) Martinez, M.; Muller, G.; Panyella, D.; Rocamora, M. *Organometallics* **1995**, *14*, 5552.
(31) Marlier, E. E.; Tereniak, S. J.; Ding, K. Y.; Mulliken, J. E.; Lu, C. C. *Inorg. Chem.* **2011**, *50*, 9290.
(32) Yamamoto, A.; Suginome, M. *J. Am. Chem. Soc.* **2005**, *127*, 15706.
(33) Schuster, E. M.; Botoshansky, M.; Gandelman, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4555.
(34) Shaffer, A. R.; Schmidt, J. A. R. *Chem.—Eur. J.* **2009**, *15*, 2662.
(35) Imada, Y.; Ueno, K.; Kutsuwa, K.; Murahashi, S. I. *Chem. Lett.* **2002**, *31*, 140.
(36) Briggs, J. R.; Constable, A. G.; Mcdonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1225.
(37) Yamazaki, S.; Yoshimura, T.; Yamabe, S.; Arai, T.; Tamura, H. *J. Org. Chem.* **1990**, *55*, 263.
(38) Kundu, S.; Brennessel, W. W.; Jones, W. D. *Inorg. Chem.* **2011**, *50*, 9443.
(39) Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. *Eur. J. Inorg. Chem.* **2012**, 4898.
(40) van der Vlugt, J. I.; Lutz, M.; Pidko, E. A.; Vogt, D.; Spek, A. L. *Dalton Trans.* **2009**, 1016.
(41) Ohashi, M.; Shibata, M.; Saijo, H.; Kambara, T.; Ogoshi, S. *Organometallics* **2013**, *32*, 3631.
(42) Gareau, D.; Sui-Seng, C.; Groux, L. F.; Brisse, F.; Zargarian, D. *Organometallics* **2005**, *24*, 4003.
(43) Kelley, P.; Lin, S. B.; Edouard, G.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2012**, *134*, 5480.
(44) Lin, S. B.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2011**, *133*, 3828.
(45) Velian, A.; Lin, S. B.; Miller, A. J. M.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2010**, *132*, 6296.
(46) Kruckenberg, A.; Wadepohl, H.; Gade, L. H. *Organometallics* **2013**, *32*, 5153.
(47) Beck, R.; Shoshani, M.; Krasinkiewicz, J.; Hatnean, J. A.; Johnson, S. A. *Dalton Trans.* **2013**, *42*, 1461.
(48) Heimbach, P. *Angew. Chem., Int. Ed.* **1964**, *3*, 648.
(49) Herbert, D. E.; Lara, N. C.; Agapie, T. *Chem.—Eur. J.* **2013**, *19*, 16453.
(50) Anderson, J. S.; Iluc, V. M.; Hillhouse, G. L. *Inorg. Chem.* **2010**, *49*, 10203.
(51) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2010**, *132*, 15148.
(52) Mindiola, D. J.; Waterman, R.; Jenkins, D. M.; Hillhouse, G. L. *Inorg. Chim. Acta* **2003**, *345*, 299.
(53) Sgro, M. J.; Stephan, D. W. *Organometallics* **2012**, *31*, 1584.
(54) Sgro, M. J.; Stephan, D. W. *Dalton Trans.* **2012**, *41*, 6791.
(55) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790.
(56) Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, *324*, 74.
(57) Breitenfeld, J.; Scopelliti, R.; Hu, X. L. *Organometallics* **2012**, *31*, 2128.
(58) Chakraborty, S.; Krause, J. A.; Guan, H. *Organometallics* **2009**, *28*, 582.
(59) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. R. *J. Am. Chem. Soc.* **2010**, *132*, 8872.
(60) Fan, L.; Ozerov, O. V. *Chem. Commun.* **2005**, 4450.
(61) Liang, L. C.; Chien, P. S.; Lin, J. M.; Huang, M. H.; Huang, Y. L.; Liao, J. H. *Organometallics* **2006**, *25*, 1399.
(62) Bain, G. A.; Berry, J. F. *J. Chem. Educ.* **2008**, *85*, 532.
(63) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.
(64) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(65) Zhang, X. Y.; Yang, Y.; Liang, Y. *Tetrahedron Lett.* **2012**, *53*, 6406.