ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

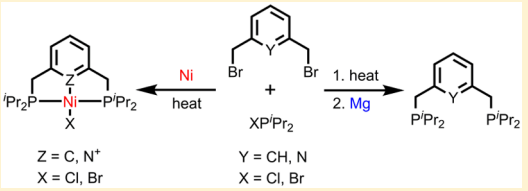
One-Pot Synthesis of 1,3-Bis(phosphinomethyl)arene PCP/PNP Pincer Ligands and Their Nickel Complexes

Wei-Chun Shih and Oleg V. Ozerov*

Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, Texas 77842, United States

Supporting Information

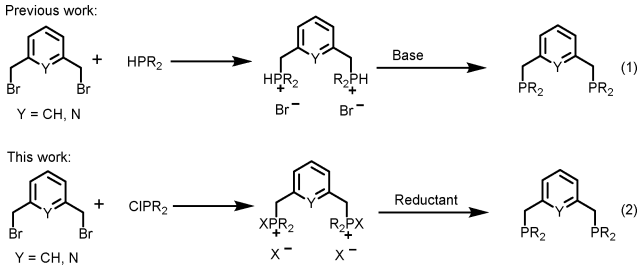
ABSTRACT: A one-pot synthesis of arene-based PCP/PNP ligands has been developed. The reaction of 1,3-bis(bromomethyl)benzene or 2,6-bis(bromomethyl)pyridine with various chlorophosphines in acetonitrile afforded bis-phosphonium salts. These salts can then be reduced by magnesium powder to yield PCP or PNP ligands. In comparison to traditional synthetic methods for making PCP/PNP ligands involving the use of secondary phosphines, this new alternative method allows for the use of chlorophosphines, which are cheaper, safer to handle, and have a broader range of commercially available derivatives. This is especially true for the chlorophosphines with less bulky alkyl groups. Moreover, the one-pot procedure can be extended to allow for the direct synthesis of PCP/PNP nickel complexes. By using nickel powder as the reductant, the resulting nickel halide was found to directly undergo metalation with the PCP or PNP ligand to generate nickel complexes in high yields.



INTRODUCTION

Pincer ligands are broadly used in organometallic chemistry.[1,2] They are typically defined as ligands that preferentially bind to transition metals in a tridentate, meridional fashion. Pincer complexes often possess exceptional thermal stability, which may permit homogeneous catalysis at unusually high temperatures.[3] They are also prized for the opportunity to position the desired types of donors about the metal center in a predictable and persistent fashion. Among the many families of pincers, PCP and PNP ligands based on the bis(phosphinomethyl)-benzene or -pyridine (Scheme 1, eq 1, simply PCP and PNP from here on) frameworks hold a particularly venerated place. This is in part due to their historical significance,[4] but also to the number of groundbreaking discoveries in which they have been instrumental.[5]

Scheme 1. Synthesis of PCP or PNP Ligands



The traditional synthesis of these ligands involves an S_N2 reaction of a secondary phosphine (HPR_2) with bis-(bromomethyl)benzene or -pyridine, followed by deprotonation of the resultant bis(phosphonium) salt (Scheme 1, eq 1).[1,6−9] This type of synthesis works very well, but the reliance on the HPR_2 starting material is not ideal. Secondary phosphines of modest molecular weight are pyrophoric liquids, and the selection of commercially available secondary phosphines is rather limited. An equally reliable PCP/PNP synthesis utilizing chlorodiorganyl phosphines ($ClPR_2$) would be preferable because $ClPR_2$ are generally not pyrophoric (although still quite air- and moisture-sensitive), because a somewhat large variety of $ClPR_2$ compounds is commercially available, and because $ClPR_2$ compounds tend to be cheaper than their HPR_2 counterparts. The latter is understandable since most HPR_2 compounds are prepared by $LiAlH_4$ reduction of $ClPR_2$,[10] a rather hazardous procedure on many counts.

We surmised that if $ClPR_2$ could successfully undergo an S_N2 reaction with halomethylarenes, then there should be a practical way to reduce the resultant halophosphonium salt to the desired phosphine (Scheme 1, eq 2). $ClPR_2$ should possess reduced nucleophilicity compared to HPR_2, but the reaction still appeared plausible. This report describes its successful implementation leading to a reliable method of preparation of a series of PCP/PNP pincer ligands that obviates the need for secondary phosphines. We also describe the incorporation of this method into one-pot synthesis of PCP and PNP nickel complexes, inspired by the one-pot synthesis of related POCOP complexes of Ni by Zargarian et al.[11]

RESULTS AND DISCUSSION

Synthesis of Benzylphosphonium Salts (3-X_2) and Benzylphosphines (3). To the best of our knowledge, the only precedent for the preparation of quaternary phosphonium salts by reactions of halodiorganyl phosphines with alkyl halides is the succinct report of Kabachnik et al.,[12] in which

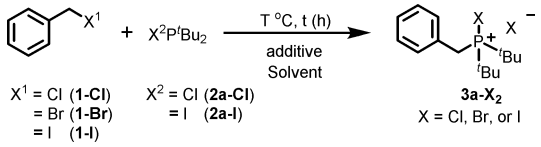
Received: August 3, 2015

DOI: 10.1021/acs.organomet.5b00671
Organometallics XXXX, XXX, XXX−XXX

iododiisopropylphoshine was shown to react with methyl, allyl, and benzyl halides. That work reported that chloro- and bromodialkylphosphines did not react, but without providing any details. We were eager to explore this reaction in greater depth in the context of the proposed phosphine ligand synthesis. Although alkyl chlorides are typically less expensive, many simple alkyl bromides and iodides are also commercially available. On the other hand, iododialkylphosphines are not, and the ability to use chlorodialkylphosphines would be strongly advantageous.

Instead of the bis(halomethyl)arenes required for pincer synthesis, we chose to explore benzyl halides ($PhCH_2X$, **1-X**) as simpler model substrates. We initially focused on their reactions[13] with di-*tert*-butylchlorophosphine (**2a-Cl**), which we expected to be more challenging compared to smaller dialkylhalophosphines (Table 1). Gratifyingly, the reaction of

Table 1. Screening and Optimization of the Reaction of Benzyl Halide with Halodi-*tert*-butylphosphine[a]



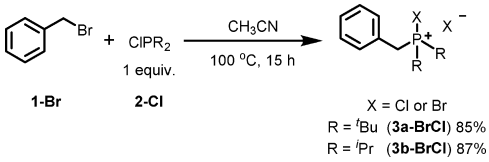
entry	X^1	X^2	additive	T (°C)	t (h)	solvent	**3a-X_2** (%)[b]
1	Br	Cl		50	15	C_6D_6	22
2	Br	Cl		50	15	CD_3CN	90
3	Cl	Cl		50	15	CD_3CN	2
4	I	Cl		50	15	CD_3CN	100
5	I	I		rt	15	CD_3CN	100
6	Br	Cl		100	15	CD_3CN	100
7[c]	Cl	Cl	NaI	50	15	CD_3CN	86
8[d]	Cl	Cl	NaI	50	15	CD_3CN	100
9[e]	Cl	Cl	NaI	50	20	CD_3CN	26
10[c]	Cl	Cl	LiBr	50	15	CD_3CN	66

[a]The reaction was carried out using **1-X** (0.2 mmol) and **2a-X** (0.2 mmol) in C_6D_6 or CD_3CN in a J. Young NMR tube. [b]The conversion was determined by ^{31}P NMR and ^1H NMR. [c]1.0 equiv of additive was added. [d]2.0 equiv of additive was added. [e]0.1 equiv of additive was added.

$PhCH_2Br$ (**1-Br**) with **2a-Cl** proceeded to give the product of S_N2 addition in both CD_3CN and C_6D_6 as solvents (entries 1 and 2). The product formation was accelerated in the more polar acetonitrile (consistent with Hughes–Ingold rules for S_N2 reactions),[14] and further optimization was conducted in this solvent. Using benzyl chloride (**1-Cl**) as substrate resulted in a much lower conversion than with benzyl bromide (**1-Br**) or benzyl iodide (**1-I**) (entries 2–4). The highest reactivity can be achieved by the reaction of benzyl iodide (**1-I**) with di-*tert*-butyliodophosphine (**2a-I**)[15] to afford 100% conversion in 15 h at room temperature (entry 5). By using commercially available **1-Br** and **2a-Cl**, the reaction can be brought to completion in 15 h at 100 °C (entry 6). Addition of 1 equiv of sodium iodide or lithium bromide accelerated the reaction between **1-Cl** and **2a-Cl**, leading to 86% or 66% conversion (entries 7 and 10) vs 2% without additives (entry 3). The use of 2 equiv of sodium iodide further improved the conversion under the same conditions to 100% (entry 8). Addition of 0.1 equiv of sodium iodide gave lower conversion, but the observed 26% yield (entry 9) indicated that NaI accelerates the reaction as a catalyst. Both chlorides **1-Cl** and **2a-Cl** can undergo halide exchange with sodium iodide to form iodo-substituted compounds **1-I** and **2a-I**. Since **1-I** is a better S_N2 electrophile, access to it and regeneration of iodide anion upon S_N2 substitution is likely the mechanism of acceleration.

On the preparative scale (2 mmol), thermolysis of **1-Br** and **2a-Cl** for 15 h at 100 °C led to **3a-BrCl** in 85% isolated yield. Analogously, the reaction of **1-Br** with diisopropylchlorophosphine **2b-Cl** under the same conditions led to **3b-BrCl** in 87% isolated yield (Scheme 2). Available literature evidence

Scheme 2. Synthesis of Phosphonium Salts (3-X_2) from Chlorodialkylphosphines (2-Cl)

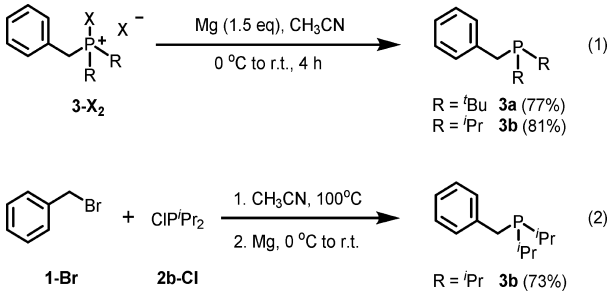


indicates that R_3PX_2 (R = alkyl and X = Cl, Br, or I) are ionic compounds as $[R_3PX][X]$ with approximately tetrahedral phosphonium centers.[16] We assume **3a-BrCl** and **3b-BrCl** are also ionic because of their poor solubility in benzene, toluene, diethyl ether, and THF.

3a-BrCl showed two resonances at 115.8 and 117.1 ppm in a 1:9 ratio in the ^{31}P NMR spectrum, which are presumed to be isomeric products with either a bromine or chlorine atom attached to the phosphorus atom. **3b-BrCl** showed only one broad resonance at 111.2 ppm. This may be due to a stronger preference for one halide or a more rapid halide exchange. The observation of doublet signals for the benzylic protons of **3a-BrCl** (δ 4.69 ppm, $^2J_{P-H}$ = 7.3 Hz) and **3b-BrCl** (δ 4.86 ppm, $^2J_{P-H}$ = 10 Hz) in the ^1H NMR spectra was in agreement with the formation of benzyl C–P bonds.

Pure **3a-BrCl** and **3b-BrCl** were reduced by the reactions of **3-X_2** with magnesium powder in acetonitrile at 0 °C for 2 h. The reactions were allowed to stir at room temperature for another 2 h, affording benzyldialkylphosphines **3a** and **3b** in 77% and 81% isolated yields, respectively (Scheme 3, eq 1). A

Scheme 3. Synthesis of Benzyldialkylphosphines (3) from Phosphonium Salts (3-X_2)

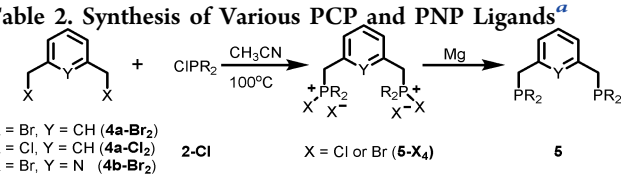


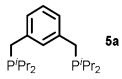
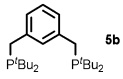
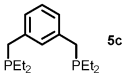
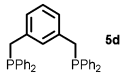
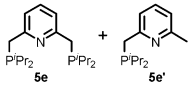
73% overall isolated yield of **3b** was obtained by the reaction of **1-Br** with **2b-Cl** followed by reduction in situ (Scheme 3, eq 2), showing that isolation of pure **3a-BrCl**/**3b-BrCl** was not necessary. Pure products **3a** and **3b** were obtained simply by pentane extraction from the crude mixture in acetonitrile. Two immiscible layers were formed, and the acetonitrile layer fortuitously retained not only magnesium halides but also the small amounts of various unidentified side products.

DOI: 10.1021/acs.organomet.5b00671
Organometallics XXXX, XXX, XXX–XXX

Synthesis of PCP and PNP Ligands (5). Having optimized the synthesis of benzyldialkylphosphines, we set out to tackle the one-pot synthesis of PCP or PNP pincer ligands from chlorophosphines **2-Cl** (Table 2). The reaction of

Table 2. Synthesis of Various PCP and PNP Ligands[a]



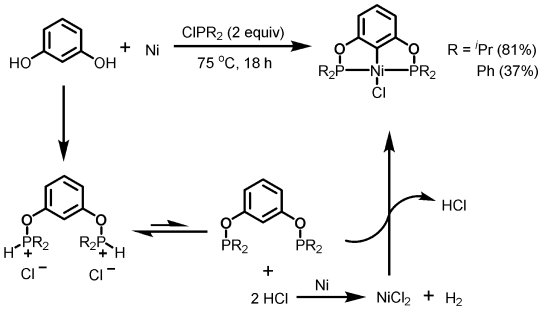
Entry	5	2	Product	Yield (%)[b]
1	**4a-Br$_2$**	ClP^{i}Pr$_2$ **2b-Cl**	 **5a**	70
2[c]	**4a-Cl$_2$**	ClP^{t}Bu$_2$ **2a-Cl**	 **5b**	64 (52)[d]
3	**4a-Br$_2$**	ClPEt$_2$ **2c-Cl**	 **5c**	78
4	**4a-Br$_2$**	ClPPh$_2$ **2d-Cl**	 **5d**	42
5	**4b-Br$_2$**	**2b-Cl**	 **5e** **5e′**	72:7

[a]General conditions: a mixture of **4** (2.0 mmol) and **2-Cl** (4.0 mmol) in CH_3CN was stirred at 100 °C for 15 h, and then Mg powder (4.0–5.0 mmol) was added to the mixture. See Experimental Section for procedure details. [b]Isolated yield. [c]Sodium iodide (8.0 mmol) was added. [d]Larger scale preparation: a mixture of **4a-Cl$_2$** (20.0 mmol) and **2a-Cl** (40.0 mmol) in CH_3CN with NaI was refluxed for 15 h, and then Mg powder (40.0 mmol) was added to the mixture. See Experimental Section for procedure details.

1,3-bis(bromomethyl)benzene (**4a-Br$_2$**) with **2b-Cl** in acetonitrile at 100 °C for 15 h produced a copious amount of a poorly soluble product, which is assumed to be the corresponding bis-phosphonium salt **5a-Br$_2$Cl$_2$**; it resonated at a frequency (δ 110.9 ppm) similar to **3b-BrCl** by ^{31}P NMR spectroscopy. Reduction of this bis-phosphonium salt with magnesium powder in situ at 0 °C followed by gradual warming to ambient temperature gave the ^{iPr}(PCP)H ligand **5a** in 70% overall isolated yield (entry 1). The analogous synthesis of the bulkier ^{tBu}(PCP)H (**5b**) from **4a-Br$_2$** and **2a-Cl** afforded a yellow, viscous oil in 76% yield, but only with ~75% purity.[17] Attempts to purify **5b** by chromatography or recrystallization were unsuccessful. However, reaction of **4a-Cl$_2$** and **2a-Cl** with 4 equiv of sodium iodide followed by reduction with Mg led to a pure off-white powder of **5b** in 64% isolated yield (entry 2, 0.5 g scale). On a larger scale, analogous preparation yielded 4.1 g as a 52% isolated yield of **5b**. The less sterically imposing ligand ^{Et}(PCP)H (**5c**) was successfully isolated in 78% yield starting from **4a-Br$_2$** and **2c-Cl** (entry 3). Benzyl C–P bond cleavage was observed in the synthesis of ^{Ph}(PCP)H **5d** and ^{iPr}(PNP) **5e**, which gave rise to the formation of (3-methylbenzyl)diphenylphosphine (**5d′**) and **5e′** as side products.[17] The oily nature of **5e** and **5e′** precluded their separation (entry 5), but it proved possible to obtain pure **5d** in 42% yield by recrystallization (entry 4). The lower isolated yield of **5d** is due to lower conversion to **5d** and the need for an extra workup step to separate it from **5d′**.

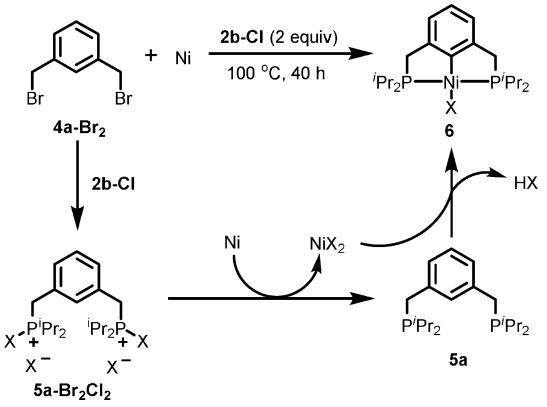
Synthesis of PCP and PNP Nickel Complexes (6 and 7). We envisaged that metallic powders other than Mg might be suitable for reduction of phosphonium salts and through it generate precursors for the formation of pincer complexes. This line of thought was inspired by the similar one-pot concept of synthesis of P°C^{O}P-type nickel complexes from metallic nickel powder, resorcinol, and **2b-Cl** reported by the Zargarian group (Scheme 4).[11] In the Zargarian synthesis, the interaction of the

Scheme 4. Proposed Mechanism of (P°C^{O}P)NiCl Formation in the Study by Zargarian et al.[11]



ligand precursors can be viewed to produce HCl equivalents, which react with Ni(0) to give $NiCl_2$ for the metalation. On the other hand, our syntheses (Scheme 5) here can be viewed to produce formal dihalogen (X_2) equivalents that then give rise to NiX_2.

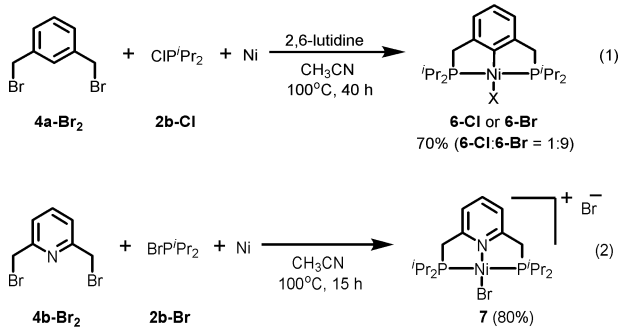
Scheme 5. Proposed Mechanism of (PCP)NiX Formation



When the mixture of **4a-Br$_2$**, **2b-Cl**, and metallic nickel powder in acetonitrile was heated at 100 °C for 40 h, the metalated products **6-Cl**[18] and **6-Br**[19] were isolated in 50% combined yield. The reaction yield was increased to 70% by the addition of 1.0 equiv of 2,6-lutidine as base to the mixture of **5a**, **2c**, and Ni prior to thermolysis (Scheme 6, eq 1). The ratio of **6-Br** and **6-Cl** was ca. 9:1 based on the ^{31}P NMR spectrum (**6-Br**: δ 61.7 ppm, **6-Cl**: δ 60.6 ppm). The mixture could be fully converted to **6-Br** by treatment with 2 equiv of lithium bromide in toluene at room temperature overnight. Most likely, the bis(halophosphonium) salt **5a-Br$_2$Cl$_2$** is formed first and then was reduced by Ni metal to give rise to **5a**, which undergoes metalation to **6** with NiX_2 formed in the reduction of **5a-Br$_2$Cl$_2$** (Scheme 5). The analogous [^{iPr}(PNP)NiBr][Br] complex **7** was also synthesized by the reaction of **4b-Br$_2$** and **2b-Br**[20] without

DOI: 10.1021/acs.organomet.5b00671
Organometallics XXXX, XXX, XXX–XXX

Scheme 6. Synthesis of ^{iPr}(PCP)NiX (6) and [^{iPr}(PNP)NiBr][Br] (7)



base (Scheme 6, eq 2). In control experiments, Ni powder did not react with **2b-Cl** in CD_3CN (100 °C, 15 h) and gave only ca. 30% conversion of **4a-Br$_2$** under analogous conditions to benzyl radical coupling products containing Ar−CH_2−CH_2−Ar moieties (as evidenced by ^{1}H NMR resonances in the 2.8−3.0 ppm region). These products were not observed in the one-pot syntheses of **6**. It is worth noting that Ni powder can be added to the reaction mixture from the start, while Mg has to be added only after the formation of halophosphonium salts is allowed to take place.

CONCLUSION

The synthesis of PCP- and PNP-type pincer ligands and their nickel complexes was achieved via utilization of inexpensive and commercially available chlorophosphines. Due to the electron-withdrawing nature of the chlorine atom on the phosphorus, chlorophosphines are weaker nucleophiles but safer reactants than secondary phosphines, particularly for the phosphines containing less sterically imposing alkyl groups. Moreover, we discovered metallic nickel powder was not only a suitable reagent for the reduction of halophosphonium salts to phosphine ligands but also the nickel precursor for the formation of PCP and PNP nickel complexes. This synthetic strategy permits one-pot synthesis of PCP and PNP nickel complexes from commercially available, nonpyrophoric[21] materials.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all manipulations were performed under argon, using standard glovebox or Schlenk line techniques. Screw-cap culture tubes with PTFE-lined phenolic caps were used to perform reactions. Toluene, THF, pentane, and diethyl ether were dried and deoxygenated (by purging) using a solvent purification system (Innovative Technology Pure Solv MD-5 solvent purification system) and stored over molecular sieves in an Ar-filled glovebox. C_6D_6 was dried over NaK/Ph_2CO/18-crown-6, distilled, and stored over molecular sieves in an Ar-filled glovebox. Acetonitrile, CD_3CN, $CDCl_3$, CH_2Cl_2, CD_2Cl_2, and 2,6-lutidine were dried over CaH_2, distilled or vacuum transferred, and stored over molecular sieves in an Ar-filled glovebox. Benzyl chloride, benzyl bromide, and benzyl iodide were degassed by freeze−pump−thaw and stored over molecular sieves in an Ar-filled glovebox. Sodium iodide was purified by recrystallization in acetone and dried under vacuum at 70 °C for 12 h. Celite and silica gel were dried at 200 °C overnight under vacuum and then stored inside a glovebox. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian Inova 300, Mercury 300 (^{1}H NMR, 299.952 MHz; ^{13}C NMR, 75.421 MHz; ^{31}P NMR, 121.422 MHz), and Inova NMR 500 (^{1}H NMR, 499.703 MHz; ^{13}C NMR, 125.697 MHz; ^{31}P NMR, 202.265 MHz) spectrometers. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR, the residual solvent peak was used to reference the spectra (^{1}H NMR: δ 7.16 for C_6D_6, 7.26 for $CDCl_3$, 5.32 for CD_2Cl_2, and 1.94 for CD_3CN; ^{13}C NMR: δ 128.06 for C_6D_6, 77.16 for $CDCl_3$, 53.84 for CD_2Cl_2, and 118.26 for CD_3CN).

Synthesis of Di-*tert*-butyliodophosphine (2a-I). Method 1: In a 25 mL Schlenk flask, to the toluene solution (10 mL) of di-*tert*-butylchlorophosphine (**2a-Cl**, 1.80 g, 10.0 mmol) was added sodium iodide (3.00 g, 20.0 mmol), and the reaction mixture was stirred at room temperature for 24 h. After the solution was qucikly filtered through a short pad of Celite and silica gel, the filtrate was collected and the volatiles were removed under vacuum, yielding a yellow liquid that appeared ca. 95% pure by NMR spectroscopy. Isolated yield: 2.24 g, 82%. Method 2: In a 10 mL Schlenk flask, to the pentane solution (1 mL) of di-*tert*-butylchlorophosphine (**2a-Cl**, 90 mg, 0.50 mmol) was added trimethylsilyl iodide (200 mg, 1.00 mmol), and the reaction mixture was stirred at room temperature for 10 min. After the solution was filtered through a pad of Celite, the filtrate was collected and the volatiles were removed under vacuum, yielding a yellow liquid (129 mg, 95%) that appeared >98% pure by NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6): δ 1.19 (d, J_{H-P} = 12.0 Hz, 18 H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 33.1 (d, J_{P-C} = 47.0 Hz), 29.7 (d, J_{P-C} = 16.4 Hz). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 135.8.

Synthesis of Bromodiisopropylphosphine (2b-Br). In a 25 mL Schlenk flask, to the toluene solution (10 mL) of chlorodiisopropylphosphine (**2b-Cl**, 1.53 g, 10.0 mmol) was added lithium bromide (1.74 g, 20.0 mmol), and the reaction mixture was stirred at room temperature for 24 h. After the solution was filtered through a pad of Celite and silica gel, the filtrate was collected and the volatiles were removed under vacuum, yielding a colorless liquid. Isolated yield: 1.58 g, 80%. ^{1}H NMR (500 MHz, C_6D_6): δ 1.70 (m, 2 H), 0.98 (dd, J_{H-H} = 13 Hz, J_{H-P} = 6.8 Hz, 12 H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 28.1 (d, J_{P-C} = 34 Hz), 18.6 (d, J_{P-C} = 14 Hz). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 134.7. HRMS (ESI): calcd for $C_6H_{14}BrLiP$ $(M + Li)^+$ 203.0177, found 203.0178.

Synthesis of 3a-BrCl. In a screw-cap culture tube, to the acetonitrile solution (10 mL) of benzyl bromide (342 mg, 2.00 mmol) was added **2a-Cl** (361 mg, 2.00 mmol), and the reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, the volatiles were removed under vacuum, and the product was washed with pentane, yielding a white solid. Isolated yield: 597 mg, 85%. The product was a mixture of two isomers in ca. 9:1 ratio based on ^{31}P NMR (117.1 and 115.8 ppm) and ^{1}H NMR spectra. The spectroscopic data for the major isomer follow. ^{1}H NMR (500 MHz, CD_3CN): δ 7.61 (m, 2 H), 7.41 (m, 3 H), 4.69 (d, J_{P-H} = 7.3 Hz, 2 H), 1.52 (d, J_{P-H} = 19 Hz, 18 H). ^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 132.2 (d, J_{P-C} = 5.7 Hz), 130.0 (s), 129.7 (m), 129.5 (d, J_{P-C} = 11 Hz), 42.3 (d, J_{P-C} = 23 Hz), 29.5 (d, J_{P-C} = 27 Hz), 27.0 (d, J_{P-C} = 4.8 Hz). ^{31}P{^{1}H} NMR (202 MHz, CD_3CN): δ 117.1. HRMS (MALDI): calcd for $C_{15}H_{25}ClP$ $(M - Br)^+$ 271.1376, found 271.1360.

Synthesis of 3b-BrCl. In a screw-cap culture tube, to the acetonitrile solution (10 mL) of benzyl bromide (342 mg, 2.00 mmol) was added **2b-Cl** (305 mg, 2.00 mmol), and the reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, the volatiles were removed under vacuum, and the product was washed with pentane, yielding a white solid. Isolated yield: 560 mg, 87%. ^{1}H NMR (500 MHz, CD_3CN): δ 7.57 (m, 2 H), 7.40 (m, 3 H), 4.86 (d, J_{P-H} = 10 Hz, 2 H), 3.43 (m, 2 H), 1.32 (dd, J_{P-H} = 21 Hz, J_{H-H} = 7.0 Hz, 12 H). ^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 131.8 (d, J_{P-C} = 5.9 Hz), 130.2 (d, J_{P-C} = 2.7 Hz), 129.8 (m), 128.4 (d, J_{P-C} = 10 Hz), 31.4 (d, J_{P-C} = 32 Hz), 28.4 (d, J_{P-C} = 33 Hz), 16.5 (s). ^{31}P{^{1}H} NMR (202 MHz, CD_3CN): δ 111.2 (br s).

Synthesis of PhCH$_2$P^{t}Bu$_2$ (3a). In a screw-cap culture tube, to the acetonitrile solution (5 mL) of **3a-BrCl** (352 mg, 1.00 mmol) was added magnesium powder (37 mg, 1.50 mmol), and the reaction mixture was stirred at 0 °C for 2 h. The reaction was allowed to warm to room temperature and stirred for another 2 h. The product was extracted with pentane (3 × 10 mL), and the volatiles were removed under vacuum, yielding a yellow oil. Isolated yield: 191 mg, 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, J_{H-H} = 7.5 Hz, 2 H), 7.21 (t, J_{H-H} = 7.6 Hz, 2 H), 7.09 (t, J_{H-H} = 7.2 Hz, 1 H), 2.83 (d, J_{P-H} = 3.0

DOI: 10.1021/acs.organomet.5b00671
Organometallics XXXX, XXX, XXX−XXX

Hz, 2 H), 1.12 (d, J_{P-H} = 11 Hz, 18 H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 141.5 (d, J_{P-C} = 12 Hz), 129.5 (d, J_{P-C} = 8.5 Hz), 128.2, 125.3 (d, J_{P-C} = 2.1 Hz), 31.8 (d, J_{P-C} = 22 Hz), 29.8 (d, J_{P-C} = 13 Hz), 28.5 (d, J_{P-C} = 24 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 35.9. NMR spectroscopic data were consistent with those previously reported in the literature.[8,22]

Synthesis of $PhCH_2P^iPr_2$ (3b). In a screw-cap culture tube, to the acetonitrile solution (5 mL) of **3b-BrCl** (324 mg, 1.00 mmol) was added magnesium powder (37 mg, 1.50 mmol), and the reaction mixture was stirred at 0 °C for 2 h. The reaction was allowed to warm to room temperature and stirred for another 2 h. The product was extracted with pentane (3 × 5 mL), and the volatiles were removed under vacuum, yielding a colorless oil. Isolated yield: 161 mg, 77%. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.29 (m, 4 H), 7.17 (m, 1 H), 2.82 (d, J_{P-H} = 1.6 Hz, 2 H), 1.78 (dsp, J_{P-H} = 2.0 Hz, J_{H-H} = 7.1 Hz, 2 H), 1.09 (m, 12 H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 141.0 (d, J_{P-C} = 8.5 Hz), 129.8 (d, J_{P-C} = 6.9 Hz), 128.7 (d, J_{P-C} = 0.8 Hz), 125.8 (d, J_{P-C} = 2.2 Hz), 30.1 (d, J_{P-C} = 21 Hz), 23.9 (d, J_{P-C} = 15 Hz), 20.0 (d, J_{P-C} = 14 Hz), 19.5 (d, J_{P-C} = 11 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 12.2. NMR spectroscopic data were consistent with those previously reported in the literature.[23]

One-Pot Synthesis of $PhCH_2P^iPr_2$ (3b). In a screw-cap culture tube, to the acetonitrile solution (10 mL) of benzyl bromide (342 mg, 2.00 mmol) was added **2b-Cl** (305 mg, 2.00 mmol), and the reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, magnesium powder (73 mg, 3.00 mmol) was added under argon, and the reaction mixture was stirred at 0 °C for 2 h. The reaction was allowed to warm to room temperature and stirred for another 2 h. The product was extracted by pentane (3 × 20 mL), and the volatiles were removed under vacuum, yielding a yellow oil. Isolated yield: 305 mg, 73%. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.29 (m, 4 H), 7.17 (m, 1 H), 2.82 (d, J_{P-H} = 1.6 Hz, 2 H), 1.78 (dsp, J_{P-H} = 2.0 Hz, J_{H-H} = 7.1 Hz, 2 H), 1.09 (m, 12 H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 141.0 (d, J_{P-C} = 8.5 Hz), 129.8 (d, J_{P-C} = 6.9 Hz), 128.7 (d, J_{P-C} = 0.8 Hz), 125.8 (d, J_{P-C} = 2.2 Hz), 30.1 (d, J_{P-C} = 21 Hz), 23.9 (d, J_{P-C} = 15 Hz), 20.0 (d, J_{P-C} = 14 Hz), 19.5 (d, J_{P-C} = 11 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 12.2. NMR spectroscopic data were consistent with those previously reported in the literature.[23]

Synthesis of ^{iPr}(PCP)H (5a). In a screw-cap culture tube, to the acetonitrile solution (10 mL) of *m*-xylylene dibromide (**4a-Br$_2$**) (528 mg, 2.00 mmol) was added **2b-Cl** (610 mg, 4.00 mmol), and the reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, magnesium powder (122 mg, 5.00 mmol) was added under argon, and the reaction mixture was stirred at 0 °C for 2 h. The reaction was allowed to warm to room temperature and stirred for another 2 h. The product was extracted with pentane (3 × 20 mL), and the volatiles were removed under vacuum, yielding a yellow oil. Isolated yield: 472 mg, 70%. ^1H NMR (300 MHz, C_6D_6): δ 7.47 (br s, 1 H), 7.18 (m, 3 H), 2.70 (br s, 4 H), 1.62 (dsp, J_{P-H} = 1.9 Hz, J_{H-H} = 7.1 Hz, 4 H), 1.04 (d, J_{H-H} = 7.0 Hz, 12 H), 1.00 (dd, J_{P-H} = 0.9 Hz, J_{H-H} = 7.0 Hz, 12 H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 140.5 (d, J_{P-C} = 7.4 Hz), 130.9 (vt, J_{P-C} = 7.0 Hz), 128.6 (s), 127.0 (dd, J_{P-C} = 7.2 Hz, J_{P-C} = 2.1 Hz), 30.3 (d, J_{P-C} = 22 Hz), 23.8 (d, J_{P-C} = 16 Hz), 19.9 (d, J_{P-C} = 14 Hz), 19.5 (d, J_{P-C} = 12 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 10.3. NMR spectroscopic data were consistent with those previously reported in the literature.[24]

Synthesis of ^{tBu}(PCP)H (5b). In a screw-cap culture tube, to the acetonitrile solution (10 mL) of *m*-xylylene dichloride (**4a-Cl$_2$**) (350 mg, 2.00 mmol) were added **2a-Cl** (723 mg, 4.00 mmol) and sodium iodide (1.20 g, 8.00 mmol), and the reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, magnesium powder (97 mg, 4.00 mmol) was added under argon, and the reaction mixture was stirred at room temperature for 36 h. The product was extracted with pentane (3 × 20 mL), and the volatiles were removed under vacuum, yielding an off-white solid. Isolated yield: 507 mg, 64%. ^1H NMR (500 MHz, C_6D_6): δ 7.59 (br s, 1 H), 7.26 (d, J_{P-H} = 7.5 Hz, 2 H), 7.14 (m, 1 H), 2.76 (d, J_{P-H} = 2.0 Hz, 4 H), 1.06 (d, J_{P-H} = 11 Hz, 36 H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 141.7 (d, J_{P-C} = 12 Hz), 131.5 (vt, J_{P-C} = 8.4 Hz), 128.4 (s), 127.2 (dd, J_{P-C} = 9.2 Hz, J_{P-C} = 1.8 Hz), 31.8 (d, J_{P-C} = 25 Hz), 30.1 (d, J_{P-C} = 14 Hz), 29.2 (d, J_{P-C} = 26 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 33.6. NMR spectroscopic data were consistent with those previously reported in the literature.[10a]

Larger Scale Preparation of ^{tBu}(PCP)H (5b). In a 250 mL Schlenk flask, to the acetonitrile solution (100 mL) of *m*-xylylene dichloride (**4a-Cl$_2$**) (3.50 g, 20.0 mmol) were added **2a-Cl** (7.23 g, 40.0 mmol) and sodium iodide (12.0 g, 80.0 mmol), and the reaction mixture was refluxed under argon for 15 h. After cooling to room temperature, magnesium powder (0.97 g, 40.0 mmol) was added under argon, and the reaction mixture was stirred at room temperature for 36 h. The reaction was filtered through a pad of silica gel, and the product was extracted with pentane (3 × 75 mL). The volatiles were removed under vacuum, yielding an off-white solid. Isolated yield: 4.10 g, 52%. ^1H NMR (500 MHz, C_6D_6): δ 7.59 (br s, 1 H), 7.26 (d, J_{P-H} = 7.5 Hz, 2 H), 7.14 (m, 1 H), 2.76 (d, J_{P-H} = 2.0 Hz, 4 H), 1.06 (d, J_{P-H} = 11 Hz, 36 H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 141.7 (d, J_{P-C} = 12 Hz), 131.5 (vt, J_{P-C} = 8.4 Hz), 128.4 (s), 127.2 (dd, J_{P-C} = 9.2 Hz, J_{P-C} = 1.8 Hz), 31.8 (d, J_{P-C} = 25 Hz), 30.1 (d, J_{P-C} = 14 Hz), 29.2 (d, J_{P-C} = 26 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 33.6. NMR spectroscopic data were consistent with those previously reported in the literature.[10a]

Synthesis of ^{Et}(PCP)H (5c). In a screw-cap culture tube, to the acetonitrile solution (10 mL) of **4a-Br$_2$** (528 mg, 2.00 mmol) was added diethylchlorophosphine (**2c-Cl**, 498 mg, 4.00 mmol), and the reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, magnesium powder (122 mg, 5.00 mmol) was added under argon, and the reaction mixture was stirred at 0 °C for 2 h. The reaction was allowed to warm to room temperature and stirred for another 2 h. The product was extracted with pentane (3 × 20 mL), and the volatiles were removed under vacuum, yielding a colorless oil. Isolated yield: 440 mg, 78%. ^1H NMR (500 MHz, C_6D_6): δ 7.11 (t, J_{H-H} = 8.0 Hz, 1 H), 7.08 (m, 1 H), 6.97 (m, 2 H), 2.61 (s, 4 H), 1.21 (m, 8 H), 0.96 (t, J_{H-H} = 7.1 Hz, 6 H), 0.93 (t, J_{H-H} = 7.1 Hz, 6 H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 138.8 (dd, J_{P-C} = 3.9 Hz, J_{P-C} = 1.2 Hz), 130.4 (vt, J_{P-C} = 5.4 Hz), 128.5 (vt, J_{P-C} = 1.0 Hz), 126.8 (dd, J_{P-C} = 5.3 Hz, J_{P-C} = 2.0 Hz), 34.3 (d, J_{P-C} = 19 Hz), 19.3 (d, J_{P-C} = 15 Hz), 10.0 (d, J_{P-C} = 14 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ −15.9. HRMS (ESI): calcd for $C_{16}H_{29}P_2$ $(M + H)^+$ 283.1745, found 283.1746.

Synthesis of ^{Ph}(PCP)H (5d). In a screw-cap culture tube, to the acetonitrile solution (10 mL) of **4a-Br$_2$** (528 mg, 2.00 mmol) was added diphenylchlorophosphine (**2d-Cl**, 882 mg, 4.00 mmol), and the reaction mixture was stirred at 100 °C for 20 h. After cooling to room temperature, magnesium powder (97.2 mg, 4.00 mmol) was added under argon, and the reaction mixture was stirred at 0 °C for 2 h. The reaction was allowed to warm to room temperature and stirred for another 2 h. The volatiles were removed under vacuum, and then the product was extracted with THF and filtered through Celite. The filtrate was layered with pentane and placed in the freezer (−35 °C) overnight, yielding a white crystalline solid. Isolated yield: 400 mg, 42%. ^1H NMR (500 MHz, C_6D_6): δ 7.35 (m, 8 H), 7.05 (m, 13 H), 6.87 (t, J_{H-H} = 7.5 Hz, 1 H), 6.80 (m, 2 H) 3.20 (s, 4 H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 139.2 (d, J_{P-C} = 17 Hz), 137.9 (dd, J_{P-C} = 8.2 Hz, J_{P-C} = 1.6 Hz), 133.3 (d, J_{P-C} = 19 Hz), 131.0 (vt, J_{P-C} = 7.1 Hz), 128.8 (s), 128.6 (d, J_{P-C} = 6.5 Hz), 128.4 (s), 127.4 (dd, J_{P-C} = 6.9 Hz, J_{P-C} = 2.5 Hz), 36.3 (d, J_{P-C} = 17 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ −9.9. NMR spectroscopic data were consistent with those previously reported in the literature.[25]

Synthesis of ^{iPr}(PNP) (5e). In a screw-cap culture tube, to the acetonitrile solution (10 mL) of 2,6-bis(bromomethyl)pyridine (**5b-Br$_2$**, 532 mg, 2.00 mmol) was added **2b-Cl** (610 mg, 4.00 mmol), and the reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, magnesium powder (97.2 mg, 4.00 mmol) was added under argon, and the reaction mixture was stirred at 0 °C for 2 h. The reaction was allowed to warm to room temperature and stirred for 2 h. The product was extracted with pentane (3 × 20 mL), and the volatiles were removed under vacuum, yielding a yellow oil. The product was a mixture of **5e** and **5e′**, and the ratio was about 9:1 based on the ^1H NMR spectrum. Total yield: 519 mg, 79%. The NMR spectroscopic data for **5e** follow. ^1H NMR (500 MHz, $CDCl_3$): δ 7.42 (t, J_{H-H} = 8.0 Hz, 1 H), 7.07 (d, J_{H-H} = 8.0 Hz, 2 H), 2.92 (d, J_{P-H} =

DOI: 10.1021/acs.organomet.5b00671
Organometallics XXXX, XXX, XXX−XXX

2.2 Hz, 4 H), 1.77 (dsp, J_{P-H} = 2.0 Hz, J_{H-H} = 7.0 Hz, 4 H), 1.03 (m, 24 H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 159.9 (d, J_{P-C} = 9.0 Hz), 136.2 (s), 120.5 (d, J_{P-C} = 7.7 Hz), 32.5 (d, J_{P-C} = 21 Hz), 23.6 (d, J_{P-C} = 14 Hz), 19.8 (d, J_{P-C} = 15 Hz), 19.2 (d, J_{P-C} = 11 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 12.7. NMR spectroscopic data were consistent with those previously reported in the literature.[26]

Synthesis of ^{iPr}(PCP)NiBr (6-Br). In a screw-cap culture tube, to the acetonitrile solution (10 mL) of **4a-Br$_2$** (528 mg, 2.00 mmol) were added nickel powder (294 mg, 5.00 mmol), **2b-Cl** (610 mg, 4.00 mmol), and 2,6-lutidine (214 mg, 2.00 mmol). The reaction mixture was stirred at 100 °C for 40 h. After cooling to room temperature, diethyl ether (3 × 10 mL) was added and the mixture was filtered through silica gel. The filtrate was collected, and the volatiles were removed under vacuum, yielding a yellow solid. Isolated yield: 659 mg, 70%. The product was a mixture of **6-Br** and **6-Cl**, and the ratio was about 9:1 based on the ^{31}P NMR spectrum (61.7 ppm for **6-Br** and 60.6 ppm for **6-Cl**). The mixture can be fully converted to **6-Br** by reacting the mixture with 2 equiv of lithium bromide in toluene at rt overnight. The NMR spectroscopic data for **6-Br** follow. ^1H NMR (500 MHz, CD_2Cl_2): δ 6.91 (br s, 3 H), 3.09 (vt, J_{P-H} = 4.0 Hz, 4 H), 2.37 (m, 4 H), 1.45 (dvt, $J_{H-H} \approx J_{P-H} \approx$ 7.8 Hz, 12 H), 1.18 (dvt, $J_{H-H} \approx J_{P-H} \approx$ 7.0 Hz, 12 H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 159.5 (vt, J_{P-C} = 16 Hz), 152.8 (vt, J_{P-C} = 13 Hz), 125.5 (s), 122.5 (vt, J_{P-C} = 8.9 Hz), 33.1 (vt, J_{P-C} = 13 Hz), 24.2 (vt, J_{P-C} = 11 Hz), 19.1 (s), 18.3 (s). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 61.7. NMR spectroscopic data were consistent with those previously reported in the literature.[19c]

Synthesis of [^{iPr}(PNP)NiBr][Br] (7). In a screw-cap culture tube, to the acetonitrile solution (2 mL) of **4b-Br$_2$** (53 mg, 0.20 mmol) were added nickel powder (29 mg, 0.50 mmol) and **2b-Br** (90 mg, 0.40 mmol). The reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature, the volatiles were removed under vacuum, and the product was extracted with CH_2Cl_2 and filtered through Celite. The filtrate was collected, and the volatiles were removed under vacuum. The resulting residue was washed with THF and then dried under vacuum, yielding a brown solid. Isolated yield: 94 mg, 80%. ^1H NMR (500 MHz, CD_3CN): δ 8.09 (br, 1 H), 7.78 (d, J_{H-H} = 6.7 Hz, 2 H), 3.79 (s, 4 H), 2.50 (br s, 4 H), 1.53 (dvt, $J_{H-H} \approx J_{P-H} \approx$ 8.0 Hz, 12 H), 1.38 (dvt, $J_{H-H} \approx J_{P-H} \approx$ 7.3 Hz, 12 H). ^1H NMR (500 MHz, $CDCl_3$): δ 11.23 (br s, 2 H), 9.72 (br s, 1 H), 5.17 (br s, 4 H), 2.99 (br s, 4 H), 2.09 (br s, 12 H), 1.92 (br s, 12 H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.4, 147.5, 125.5, 36.2, 25.6 (vt, J_{P-C} = 13 Hz), 25.0, 20.3. $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN): δ 50.5. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): 50.3. NMR spectroscopic data were similar to [^{iPr}(PNP)NiCl][Cl] previously reported in the literature.[27]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00671.

Additional experimental details and pictorial NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ozerov@chem.tamu.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for the support of this research by the TAMU-Weizmann Collaborative Research Program, the U.S. National Science Foundation (grant CHE-1300299 to O.V.O.), the Welch Foundation (grant A-1717 to O.V.O.), and the Ministry of Education of Taiwan (Study Abroad Scholarship to W.-C.S.). We are grateful to Prof. David Milstein and Dr. Moran Feller of the Weizmann Institute of Science for insightful discussions.

■ REFERENCES

(1) (a) *The Chemistry of Pincer Compounds*; Morales-Morales, D.; Jensen, C. M., Eds.; Elsevier: Amsterdam, 2007. (b) *Organometallic Pincer Chemistry*; Van Koten, G.; Milstein, D., Eds.; Springer: Heidelberg, 2013.

(2) (a) Van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759−1792. (b) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761−1779. (c) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048−2076. (d) Gunanathan, C.; Milstein, D. *Science* **2013**, *341*, 1229712−1229712. (e) Gunanathan, C.; Milstein, D. *Chem. Rev.* **2014**, *114*, 12024−12087.

(3) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H.-J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596−3600.

(4) This report by Moulton and Shaw on some PCP complexes is often cited as containing the first recognizable pincer complex: Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020−1024.

(5) (a) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. *Science* **2006**, *312*, 257−261. (b) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699−701. (c) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 10840−10841.

(6) Montag, M.; Schwartsburd, L.; Cohen, R.; Leitus, G.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 1901−1904.

(7) Krogh-Jespersen, K.; Czerw, M.; Zhu, K.; Singh, B.; Kanzelberger, M.; Darji, N.; Achord, P. D.; Renkema, K. B.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 10797−10809.

(8) Rybtchinski, B.; Cohen, R.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 11041−11050.

(9) Hermann, D.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2002**, *21*, 812−818.

(10) (a) Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Y. *Organometallics* **2000**, *19*, 1734−1739. (b) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044−13053. (c) Meiners, J.; Friedrich, A.; Herdtweck, E.; Schneider, S. *Organometallics* **2009**, *28*, 6331−6338.

(11) Vabre, B.; Lindeperg, F.; Zargarian, D. *Green Chem.* **2013**, *15*, 3188−3194.

(12) Kabachnik, M. M.; Khomutova, Y. A.; Beletskaya, I. P. *Russ. J. Org. Chem.* **1999**, *35*, 26−27.

(13) Halophosphonium salts are easily hydrolyzed, trialkylphoshines are easily oxidized by dioxygen, and halodialkylphosphines are sensitive to both H_2O and O_2. Therefore all manipulations involving these materials were carried out under dry argon.

(14) Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1935**, 244−255.

(15) Di-*tert*-butyliodophosphine (**2a-I**) is not commercially available and was prepared from di-*tert*-butylchlorophosphine (**2a-Cl**) and sodium iodide. See Experimental Section.

(16) (a) Bricklebank, N.; Godfrey, S. M.; Lane, H. P.; McAuliffe, C. A.; Pritchard, R. G.; Moreno, J.-M. *J. Chem. Soc., Dalton Trans.* **1995**, 2421−2424. (b) Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sheffield, J. M.; Thompson, G. M. *J. Chem. Soc., Dalton Trans.* **1997**, 4823−4828. (c) Godfrey, S. M.; McAuliffe, C. A.; Mushtaq, I.; Pritchard, R. G.; Sheffield, J. M. *J. Chem. Soc., Dalton Trans.* **1998**, 3815−3818.

(17) See the Supporting Information.

(18) Boro, B. J.; Duesler, E. N.; Goldberg, K. I.; Kemp, R. A. *Inorg. Chem.* **2009**, *48*, 5081−5087.

(19) (a) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652−1655. (b) Castonguay, A.; Beauchamp, A. L.; Zargarian, D. *Organometallics* **2008**, *27*, 5723−5732. (c) Martínez-Prieto, L. M.; Melero, C.; del Río, D.; Palma, P.; Cámpora, J.; Álvarez, E. *Organometallics* **2012**, *31*, 1425−1438.

DOI: 10.1021/acs.organomet.5b00671
Organometallics XXXX, XXX, XXX−XXX

(20) Bromodiisopropylphosphine (**2b-Br**) needs to be separately prepared from Chlorodiisopropylphosphine (**2b-Cl**) and lithium bromide. See Experimental Section for procedure details.
(21) Very finely divided metal powders can be pyrophoric, but we were able to use Mg powder (40−80 mesh) and Ni powder (APS 2.2−3.0 μm), which are not pyrophoric.
(22) Ionkin, A. S.; Marshall, W. J.; Adelman, D. J.; Fones, B. B.; Fish, B. M.; Schiffhauer, M. F. *Organometallics* **2006**, *25*, 2978−2992.
(23) Holzhey, N.; Pitter, S. *J. Mol. Catal. A: Chem.* **1999**, *146*, 25−36.
(24) Rybtchinski, B.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786−3793.
(25) Arunachalampillai, A.; Loganathan, N.; Wendt, O. F. *Polyhedron* **2012**, *32*, 24−29.
(26) Jansen, A.; Pitter, S. *Monatsh. Chem.* **1999**, *130*, 783−794.
(27) Vogt, M.; Rivada-Wheelaghan, O.; Iron, M. A.; Leitus, G.; Diskin-Posner, Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **2013**, *32*, 300−308.

DOI: 10.1021/acs.organomet.5b00671
Organometallics XXXX, XXX, XXX−XXX