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FULL PAPER

Amido PNP pincer complexes of palladium(II) and platinum(II): Synthesis, structure, and reactivity

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The synthesis of a series of divalent palladium and platinum complexes containing amido PNP pincer ligands of the type $[N(o\text{-}C_6H_4PR_2)_2]^-$ (R = Ph (**1a**), *i*Pr (**1b**)) is reported. Metathetical reactions of [**1a–b**]PdCl or [**1a–b**]PtCl with a variety of alkyl Grignard reagents or $LiHBEt_3$ in ethereal or arene solutions generate their corresponding alkyl or hydride complexes [**1a**]PdR^1 (R^1 = Me, Et, *n*Bu), [**1b**]PdR^1 (R^1 = Me, Et, H), [**1a**]PtR^1 (R^1 = Me, Et, *n*Bu, *n*Hexyl, H), and [**1b**]PtR^1 (R^1 = Me, H). Although these organometallic complexes are all thermally stable, including those containing β-hydrogen atoms even at elevated temperatures, compounds [**1a**]PdH and [**1b**]PtR^1 (R^1 = Et, *n*Bu, *n*Hexyl) are not isolable due to facile decomposition. The stability and reactivity of these complexes are discussed. The chloro [**1a**]PdCl is a superior catalyst precursor to [**1b**]PdCl, [**1a**]PtCl, and [**1b**]PtCl in Kumada couplings, affording, for instance, *n*-butyl arenes nearly quantitatively. The X-ray structures of [**1b**]PtCl, [**1b**]PtMe, [**1b**]PdEt, [**1a**]Pt*n*Bu, [**1b**]PdH, and [**1b**]PtH are presented.

KEYWORDS
amido PNP pincer, Kumada coupling, olefin insertion, β-hydrogen elimination

1 | INTRODUCTION

Both β-hydrogen elimination and olefin insertion play important roles in organometallic chemistry,[1–3] particularly transition metal-mediated organic synthesis and catalysis.[4–10] These reactions coexist in equilibrium, with one being the reverse of the other. Understanding and effective manipulation of these reactions have been the essential core of a number of chemical transformations.

Pincer complexes have received considerable attention in the last decades in organometallic chemistry, catalysis, and materials science.[11–18] It is known that organonickel complexes of amido PNP pincer ligands of the type $[N(o\text{-}C_6H_4PR_2)_2]^-$ (R = Ph (**1a**), *i*Pr (**1b**)) are thermally stable, including those containing β-hydrogen atoms.[19,20] No β-hydrogen elimination occurs for these complexes even at elevated temperatures. Olefins, such as ethylene, 1-hexene, cycloocta-1,5-diene, norbornene, and methyl acrylate, readily insert into the Ni–H bond of [**1a**]NiH, but similar reactions involving [**1b**]NiH occur only for electronically activated olefins.[21] Consistent with the insertion reactivity, the hydrocarbyl complexes derived from these reactions are also thermally stable and do not undergo β-hydrogen elimination at elevated temperatures.

We are interested in reaction chemistry employing amido phosphine complexes.[22–26] Whereas [**1a**]NiCl and [**1b**]NiCl are catalytically active for Kumada couplings[20] and [**1a**]PdCl is active for Heck,[27] Suzuki,[28] and Sonogashira couplings,[29] [**1a**]PtMe and [**1b**]NiH are capable of arene C–H bond cleavage at room temperature in the presence of Lewis acids.[30,31] In an effort to expand the reaction chemistry of group 10 complexes of

amido PNP,[32,33] we aim in this contribution to demonstrate the synthetic possibilities of a series of organopalladium and organoplatinum complexes of **1a** and **1b** and evaluate their compatibilities in catalytic Kumada couplings, particularly alkyl that contains β-hydrogen atoms.

2 | EXPERIMENTAL

2.1 | General procedures

Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. Compounds H[**1a**],[19,20] H[**1b**],[20] [**1a**]Li(THF)$_2$,[19,20] [**1b**]Li(THF),[20] [**1a**]PdCl,[27] [**1b**]PdCl,[29] [**1a**]PtCl,[30] [**1a**]PtMe,[30] and $PtCl_2(SMe_2)_2$[34] were prepared following reported procedures. All other chemicals were obtained from commercial vendors and used as received. Unless otherwise noted, all NMR spectra were recorded at room temperature in specified solvents on Varian Unity or Bruker AV instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane. Coupling constants (*J*) are listed in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6. ^{13}C NMR spectra are referenced using the internal solvent peak at δ 128.39 for C_6D_6. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. Kumada coupling reactions were analyzed by GC on a Varian chrompack CP-3800 instrument equipped with a CP-Sil 5 CB chrompack capillary column. Conversions and yields were calculated versus *n*-dodecane as the internal standard.

2.2 | X-ray crystallography

Data were collected on a diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full matrix least squares procedures against F^2 using SHELXL-97[35] or SHELXL-2014.[36] All full-weight non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions except the hydride ligand in [**1b**]PtH that was found in the difference map. CCDC 2031162–2031167 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif).

2.3 | Synthesis of [1a]PtCl

Method 1: To a THF solution (3 ml) of H[**1a**] (13.4 mg, 0.025 mmol) at −35°C was added *n*BuLi (0.01 ml, 2.5 M in *n*-hexane, 0.025 mmol). The reaction solution was stirred at room temperature for 30 min and added to a THF suspension (1 ml) of K_2PtCl_4 (10.4 mg, 0.025 mmol). The reaction vessel was sealed with a Teflon cap. The reaction mixture was heated with stirring in an oil bath at 110°C for 20 h. After being cooled to room temperature, the reaction mixture was evaporated to dryness under reduced pressure. Benzene (5 ml) was added. The benzene solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure to afford the product as a yellow solid; yield 16.1 mg (84%). Method 2: To a THF solution (10 ml) of H[**1a**] (295.8 mg, 0.55 mmol) at room temperature was added yellow powder $PtCl_2(SMe_2)_2$ (216.1 mg, 0.55 mmol, cis/trans ratio approximately 1:2). The reaction vessel was sealed with a Teflon cap. The reaction mixture was heated with stirring in an oil bath at 80°C for 3 h. After being cooled to room temperature, the reaction mixture was evaporated to dryness under reduced pressure. The solid residue was triturated with *n*-hexane (2 ml × 3). Dichloromethane (80 ml) was added. The dichloromethane solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure. The solid residue was washed with diethyl ether (3 ml × 3) to afford the product as a yellow solid; yield 414.8 mg (98%). The NMR spectra are all identical to those reported previously.[30]

2.4 | Synthesis of [1b]PtCl

Method 1: Solid $PtCl_2(SMe_2)_2$ (90 mg, 0.23 mmol, cis/trans ratio approximately 1:2) was suspended in THF (3 ml) and cooled to −35°C. To this was added dropwise a solution of [**1b**]Li(THF) (109.1 mg, 0.23 mmol) in THF (20 ml) at −35°C. After being stirred at room temperature overnight, the reaction mixture was stripped to dryness in vacuo. The residue thus obtained was triturated with pentane (2 ml × 2), and CH_2Cl_2 (6 ml) was added. The CH_2Cl_2 solution was filtered through a pad of Celite, which was further washed with CH_2Cl_2 (2 ml) until the washings became colorless. The filtrate and washings were combined and evaporated to dryness under reduced pressure. The solid thus obtained was gently washed with pentane (2 ml × 2) and dried in vacuo to give the product as a yellow solid; yield 123.7 mg (99%). Method 2:

Procedures were similar to those of Method 1 in the synthesis of [**1a**]PtCl; yield 87%. Method 3: Procedures were similar to those of Method 2 in the synthesis of [**1a**]PtCl; yield 98%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.78 (d, 2, J = 8.50, Ar), 6.96 (m, 2, Ar), 6.90 (t, 2, J = 7.50, Ar), 6.48 (t, 2, J = 7.25, Ar), 2.48 (m, 4, C*H*Me$_2$), 1.40 (dd, 12, J = 16.50 and 6.60, CH*Me*$_2$), 1.08 (dd, 12, J = 15.75 and 7.00, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz) δ 41.48 ($^{1}J_{PPt}$ = 2662). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 164.40 (t, J_{CP} = 9.17, C), 133.45 (s, CH), 131.71 (s, CH), 120.50 (t, J_{CP} = 23.0, C), 118.22 (t, J_{CP} = 3.77, CH), 116.93 (t, J_{CP} = 4.65, CH), 25.54 (t, $^{1}J_{CP}$ = 14.58, *C*HMe$_2$), 18.57 (s, CH*Me*$_2$), 18.17 (s, CH*Me*$_2$). Anal. Calcd for $C_{24}H_{36}ClNP_2Pt$: C, 45.68; H, 5.75; N, 2.22. Found: C, 45.47; H, 5.98; N, 2.18.

2.5 | General procedures for the synthesis of alkyl complexes

The corresponding chloro complex (0.10 mmol) was dissolved in THF or diethyl ether (5 ml) and cooled to −35°C. To this was added Grignard reagent (1 equiv).The reaction mixture was stirred at room temperature for a specified period of time and evaporated to dryness under reduced pressure. Benzene (5 ml) was added, and the solution was filtered through a pad of Celite. Solvent was removed in vacuo. The resulting solid was washed with diethyl ether (1 ml × 2) and dried in vacuo to afford the final product.

2.6 | Synthesis of [1a]PdMe

The reaction was complete in 10 min, affording the product as a yellowish orange solid; yield 93%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.96 (t, 1, J = 3.00, Ar), 7.94 (t, 1, J = 2.75, Ar), 7.64 (td, 8, J = 6.00 and 1.50, Ar), 7.11 (m, 2, Ar), 6.98 (m, 14, Ar), 6.45 (t, 2, J = 7.00, Ar), 0.99 (t, 3, $^{3}J_{HP}$ = 5.5, PdCH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz) δ 28.46. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 162.00 (t, J_{CP} = 11.80, C), 136.21 (s, CH), 134.23 (t, J_{CP} = 7.28, CH), 133.06 (t, J_{CP} = 22.72, C), 132.50 (s, CH), 130.52 (s, CH), 129.25 (t, J_{CP} = 4.52, CH), 124.02 (t, J_{CP} = 22.59, C), 117.22 (t, J_{CP} = 3.64, CH), 116.75 (t, J_{CP} = 5.40, CH), −10.29 (t, J_{CP} = 5.52, PdCH_3). Anal. Calcd for $C_{37}H_{31}NPdP_2$: C, 67.54; H, 4.75; N, 2.13. Found: C, 67.41; H, 4.65; N, 2.09.

2.7 | Synthesis of [1b]PdMe

The reaction was complete in 30 min, affording the product as a yellowish orange solid; yield 99%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.89 (d, 2, J = 8.50, Ar), 7.03 (m, 4, Ar), 6.52 (t, 2, J = 7.25, Ar), 2.15 (m, 4, C*H*Me$_2$), 1.19 (dd, 12, J = 16.25 and 7.00, CH*Me*$_2$), 1.05 (dd, 12, J = 14.50 and 7.00, CH*Me*$_2$), 0.64 (t, 3, $^{3}J_{HP}$ = 5.50, PdMe). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz) δ 42.03. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 163.22 (t, J_{CP} = 10.38, C), 133.44 (s, CH), 131.65 (s, CH), 121.72 (t, J_{CP} = 18.38, C), 116.25 (t, J_{CP} = 5.19, CH), 115.94 (t, J_{CP} = 3.06, CH), 25.16 (t, $^{1}J_{CP}$ = 11.50, *C*HMe$_2$), 19.34 (t, $^{2}J_{CP}$ = 2.88, CH*Me*$_2$), 18.57 (s, CH*Me*$_2$), −20.49 (t, $^{2}J_{CP}$ = 7.06, PdMe). Anal. Calcd for $C_{25}H_{39}NP_2Pd$: C, 57.53; H, 7.53; N, 2.68. Found: C, 57.52; H, 7.29; N, 2.43.

2.8 | Synthesis of [1b]PtMe

The reaction was complete overnight, affording the product as a yellowish orange solid; yield 83%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.94 (d, 2, J = 9.00, Ar), 7.05 (m, 4, Ar), 6.52 (t, 2, J = 7.25, Ar), 2.33 (m, 4, C*H*Me$_2$), 1.20 (dd, 12, J = 16.00 and 7.00, CH*Me*$_2$), 1.16 (t, 3, $^{3}J_{HP}$ = 5.5, PtCH_3), 1.05 (dd, 12, J = 14.50 and 7.50, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz) δ 41.72 ($^{1}J_{PPt}$ = 2837). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 164.10 (t, J_{CP} = 8.79, C), 133.73 (s, CH), 131.63 (s, CH), 122.08 (t, J_{CP} = 22.46, C), 116.69 (t, J_{CP} = 4.89, CH), 116.57 (t, J_{CP} = 3.89, CH), 25.53 (t, $^{1}J_{CP}$ = 6.90, *C*HMe$_2$), 18.89 (s, CH*Me*$_2$), 18.44 (s, CH*Me*$_2$), −31.35 (t, $^{2}J_{CP}$ = 6.90, $^{1}J_{CPt}$ = 588.94, Pt*C*H$_3$). Anal. Calcd for $C_{25}H_{39}NP_2Pt$: C, 49.18; H, 6.44; N, 2.29. Found: C, 48.97; H, 6.22; N, 2.24.

2.9 | Synthesis of [1a]PdEt

The reaction was complete in 30 min, affording the product as a yellowish orange solid; yield 99%. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.92 (m, 2, Ar), 7.64 (m, 8, Ar), 7.10 (m, 2, Ar), 7.00 (m, 14, Ar), 6.43 (t, 2, J = 7.25, Ar), 2.00 (m, 2, PdCH_2), 1.25 (m, 3, PdCH$_2$CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz) δ 27.54. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz) δ 161.84 (t, J_{CP} = 11.80, C), 136.03 (s, CH), 134.17 (t, J_{CP} = 7.28, CH), 133.13 (t, J_{CP} = 21.71, C), 132.43 (s, CH), 130.48 (s, CH), 129.28 (t, J_{CP} = 5.40, CH), 124.37 (t, J_{CP} = 22.59, C), 117.06 (t, J_{CP} = 3.64, CH), 116.66 (t, J_{CP} = 5.52, CH), 18.79 (t, J_{CP} = 2.70, PdCH$_2$CH$_3$), 5.78 (t, J_{CP} = 2.76, PdCH_2). Anal. Calcd for $C_{38}H_{33}NPdP_2$: C, 67.91; H, 4.95; N, 2.08. Found: C, 67.72; H, 4.82; N, 1.99.

2.10 | Synthesis of [1b]PdEt

The reaction was complete in 20 min, affording the product as a yellowish orange solid; yield 97%. ^{1}H NMR

(C_6D_6, 500 MHz) δ 7.86 (d, 2, J = 8.50, Ar), 7.04 (t, 2, J = 7.00, Ar), 7.01 (m, 2, Ar), 6.51 (t, 2, J = 7.25, Ar), 2.19 (m, 4, C*H*Me_2), 1.87 (m, 2, PdCH_2), 1.56 (tt, 3, J = 7.75 and 2.25, $PdCH_2CH_3$), 1.22 (dd, 12, J = 15.75 and 8.00, CHMe_2), 1.04 (dd, 12, J = 14.50 and 7.00, CHMe_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ 37.55. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 163.11 (t, J_{CP} = 10.25, C), 133.48 (s, CH), 131.62 (s, CH), 121.23 (t, J_{CP} = 18.44, C), 116.19 (t, J_{CP} = 4.81, CH), 115.76 (t, J_{CP} = 3.19, CH), 24.88 (t, $^1J_{CP}$ = 11.19, *C*HMe$_2$), 19.17 (t, $^2J_{CP}$ = 3.00, CH*Me*$_2$), 19.03 (s, $PdCH_2CH_3$), 18.25 (s, CH*Me*$_2$), −6.25 (t, $^2J_{CP}$ = 4.56, $PdCH_2CH_3$). Anal. Calcd for $C_{26}H_{41}NP_2Pd$: C, 58.26; H, 7.71; N, 2.61. Found: C, 58.19; H, 7.65; N, 2.50.

2.11 | Synthesis of [1a]PtEt

The reaction was complete in 48 h, affording the product as a yellow solid; yield 94%. ^1H NMR (C_6D_6, 300 MHz) δ 7.95 (d, 2, J = 8.37, Ar), 7.73 (m, 8, Ar), 7.13 (t, 2, J = 5.70, Ar), 6.99 (m, 14, Ar), 6.44 (t, 2, J = 7.14, Ar), 2.12 (q, 2, $^3J_{HH}$ = 6.99, $^2J_{HPt}$ = 74.76, $PtCH_2$), 1.36 (t, 3, $^3J_{HH}$ = 7.53, $^3J_{HPt}$ = 54.03, $PtCH_2CH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) δ 30.85 ($^1J_{PPt}$ = 3130). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 162.25 (t, J_{CP} = 10.19, C), 135.79 (t, J_{CP} = 9.83, CH), 133.89 (t, J_{CP} = 6.45, CH), 132.60 (t, J_{CP} = 26.74, C), 132.05 (s, CH), 130.38 (s, CH), 128.79 (t, J_{CP} = 4.81, CH), 124.47 (t, J_{CP} = 27.75, C), 117.38 (t, J_{CP} = 3.91, CH), 116.85 (t, J_{CP} = 3.83, CH), 19.65 (s, $PtCH_2CH_3$), −8.81 (t, $^2J_{CP}$ = 4.16, $^1J_{CPt}$ = 612.67, $PtCH_2CH_3$).

2.12 | Synthesis of [1a]Pd*n*Bu

The reaction was complete in 30 min, affording the product as a yellowish brown solid; yield 90%. ^1H NMR (C_6D_6, 500 MHz) δ 7.92 (t, 1, J = 2.50, Ar), 7.91 (t, 1, J = 2.75, Ar), 7.67 (m, 8, Ar), 7.10 (m, 2, Ar), 7.00 (m, 14, Ar), 6.43 (t, 2, J = 7.50, Ar), 1.98 (m, 2, $PdCH_2$), 1.51 (m, 2, $PdCH_2CH_2CH_2CH_3$), 1.24 (m, 2, $PdCH_2CH_2CH_2CH_3$), 0.69 (t, 3, J = 7.50, $PdCH_2CH_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ 27.95. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 161.85 (t, J_{CP} = 10.79, C), 135.96 (s, CH), 134.16 (t, J_{CP} = 7.28, CH), 133.19 (t, J_{CP} = 21.71, C), 132.44 (s, CH), 130.50 (s, CH), 129.21 (t, J_{CP} = 5.40, CH), 124.45 (t, J_{CP} = 23.59, C), 117.07 (t, J_{CP} = 3.64, CH), 116.66 (t, J_{CP} = 5.52, CH), 36.97 (t, J_{CP} = 2.76, CH_2), 28.37 (t, J_{CP} = 2.64, CH_2), 14.60 (s, CH_3), 13.81 (t, J_{CP} = 1.76, CH_2). Anal. Calcd for $C_{40}H_{37}NPdP_2$: C, 68.62; H, 5.33; N, 2.00. Found: C, 68.37; H, 5.11; N, 1.92.

2.13 | Synthesis of [1a]Pt*n*Bu

The reaction was complete overnight, affording the product as a yellow solid; yield 74%. ^1H NMR (C_6D_6, 500 MHz) δ 7.95 (dt, 2, J = 4.25 and 2.50, Ar), 7.74 (m, 6, Ar), 7.14 (t, 4, J = 5.50, Ar), 7.00 (m, 10, Ar), 6.96 (t, 4, J = 8.00, Ar), 6.43 (t, 2, J = 7.25, Ar), 2.09 (m, 2, $^2J_{HPt}$ = 78.50, $PtCH_2$), 1.55 (m, 2, CH_2), 1.28 (m, 2, CH_2), 0.72 (t, 3, J = 7.50, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ 31.55 ($^1J_{PPt}$ = 3126). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 162.55 (t, J_{CP} = 10.42, C), 136.09 (s, CH), 134.20 (t, J_{CP} = 6.90, CH), 132.93 (t, J_{CP} = 26.86, C), 132.39 (s, CH), 130.74 (s, CH), 129.09 (t, J_{CP} = 5.27, CH), 124.85 (t, J_{CP} = 27.74, C), 117.73 (t, J_{CP} = 4.39, CH), 117.15 (t, J_{CP} = 4.39, CH), 38.27 (s, CH_2), 29.04 (s, CH_2), 14.71 (s, CH_3), 0.17 (t, $^2J_{CP}$ = 5.15, $^1J_{CPt}$ = 619.47, $PtCH_2$). Anal. Calcd for $C_{40}H_{37}NP_2Pt$: C, 60.91; H, 4.73; N, 1.78. Found: C, 60.62; H, 5.02; N, 1.49.

2.14 | Synthesis of [1a]Pt*n*Hexyl

The reaction was complete overnight, affording the product as a yellowish orange solid; yield 75%. ^1H NMR (C_6D_6, 500 MHz) δ 7.94 (d, 2, J = 8.50, Ar), 7.74 (m, 8, Ar), 7.14 (m, 2, Ar), 7.00 (m, 14, Ar), 6.43 (t, 2, J = 7.00, Ar), 2.09 (m, 2, $^2J_{HPt}$ = 79.5, $PtCH_2$), 1.55 (m, 2, CH_2), 1.24 (m, 2, CH_2), 1.12 (m, 2, CH_2), 1.07 (q, 2, J = 7.00, CH_2), 0.81 (t, 3, J = 7.25, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ 31.50 ($^1J_{PPt}$ = 3128). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 162.56 (t, J_{CP} = 10.04, C), 136.11 (s, CH), 134.20 (t, J_{CP} = 6.53, CH), 132.96 (t, J_{CP} = 26.86, C), 132.38 (s, CH), 130.73 (s, CH), 129.09 (t, J_{CP} = 5.27, CH), 124.84 (t, J_{CP} = 28.24, C), 117.73 (t, J_{CP} = 4.39, CH), 117.16 (t, J_{CP} = 4.77, CH), 36.01 (s, CH_2), 35.96 (s, CH_2), 32.67 (s, CH_2), 23.45 (s, CH_2), 14.80 (s, CH_3), 0.59 (t, $^2J_{CP}$ = 5.27, $^1J_{CPt}$ = 613.82, $PtCH_2$). Anal. Calcd for $C_{42}H_{41}NP_2Pt$: C, 61.76; H, 5.06; N, 1.71. Found: C, 61.45; H, 4.75; N, 1.49.

2.15 | Synthesis of [1a]PdH

Method 1: To a C_6D_6 solution (0.35 ml) of [**1a**]PdCl (3.4 mg, 5.0 μmol) at room temperature was added $LiHBEt_3$ (5.0 μl, 1.0 M in THF, 5.0 μmol). The solution was transferred to an NMR tube, and the reaction was examined in 10 min by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy that showed quantitative formation of [**1a**]PdH. Method 2: A similar reaction employing 100 equiv of $NaBH_4$ in THF at room temperature also afforded [**1a**]PdH quantitatively in 1 h as indicated by the $^{31}P\{^1H\}$ NMR spectrum of reaction aliquots. ^1H NMR (C_6D_6,

300 MHz) δ 7.99 (dt, 2, J = 8.52 and 2.55, Ar), 7.70 (qd, 8, J = 5.85 and 1.71, Ar), 7.04 (t, 2, J = 8.04, Ar), 6.95 (m, 14, Ar), 6.47 (t, 2, J = 7.25, Ar), −9.78 (t, 1, $^2J_{HP}$ = 3.53, PdH). $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) δ 34.10.

2.16 | Synthesis of [1b]PdH

To a red solution of [**1b**]PdCl (50 mg, 0.092 mmol) in toluene (5 ml) at −35°C was added $LiHBEt_3$ (0.1 ml, 1.0 M in THF, 0.1 mmol). The reaction mixture was stirred at room temperature for 1 h to result in a yellow solution. All volatiles were removed in vacuo. The residue was triturated with pentane (1 ml) twice. Diethyl ether (6 ml) was added. The diethyl ether solution was filtered through a pad of Celite and evaporated to dryness under reduced pressure to afford the product as a yellow solid; yield 45.8 mg (98%). ^1H NMR (C_6D_6, 500 MHz) δ 8.06 (d, 2, J = 8.50, Ar), 7.20 (t, 2, J = 7.50, Ar), 7.13 (m, 2, Ar), 6.65 (t, 2, J = 7.50, Ar), 2.13 (m, 4, C*H*Me_2), 1.30 (dd, 12, J = 16.75 and 7.50, CH*Me*$_2$), 1.05 (dd, 12, J = 15.00 and 7.00, CH*Me*$_2$), −10.29 (t, 1, $^2J_{HP}$ = 6.50, PdH). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ 60.03. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 163.29 (t, J_{CP} = 10.25, C), 134.09 (s, CH), 131.98 (s, CH), 122.64 (t, J_{CP} = 17.75, C), 116.00 (t, J_{CP} = 5.00, CH), 115.98 (t, J_{CP} = 2.25, CH), 24.65 (t, $^1J_{CP}$ = 12.75, *C*HMe_2), 20.15 (t, $^2J_{CP}$ = 4.06, CH*Me*$_2$), 18.75 (s, CH*Me*$_2$). Anal. Calcd for $C_{24}H_{37}NP_2Pd$: C, 56.75; H, 7.34; N, 2.76. Found: C, 56.94; H, 7.45; N, 2.52.

2.17 | Synthesis of [1a]PtH

Procedures were similar to those of [**1b**]PdH except employing [**1a**]PtCl (200 mg, 0.26 mmol) in THF (8 ml) with heating at 100°C in a Teflon-sealed reaction vessel for 24 h, affording the product as yellowish orange crystals; yield 112.5 mg (59%). ^1H NMR (C_6D_6, 500 MHz) δ 8.02 (d, 2, J = 8.50, Ar), 7.76 (q, 8, J = 5.50, Ar), 7.19 (q, 2, J = 6.00, Ar), 7.01 (t, 2, J = 7.75, Ar), 6.94 (m, 12, Ar), 6.46 (t, 2, J = 7.50, Ar), −11.31 (t, $^2J_{HP}$ = 14.5, $^1J_{HPt}$ = 1052). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ 34.79 ($^1J_{PPt}$ = 2902). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 162.84 (t, J_{CP} = 10.04, C), 136.57 (s, CH), 134.57 (t, J_{CP} = 7.30, CH), 134.11 (t, J_{CP} = 28.36, C), 132.41 (s, CH), 130.79 (s, CH), 129.08 (t, J_{CP} = 5.40, CH), 124.69 (t, J_{CP} = 26.50, C), 117.93 (t, J_{CP} = 3.60, CH), 117.160 (t, J_{CP} = 4.50, CH). Anal. Calcd for $C_{36}H_{37}NP_2Pt$: C, 58.37; H, 5.03; N, 1.89. Found: C, 58.09; H, 5.00; N, 2.01.

2.18 | Synthesis of [1b]PtH

Procedures were similar to those of [**1b**]PdH except employing [**1b**]PtCl (100 mg, 0.185 mmol) in THF (8 ml) with heating at 110°C in a Teflon-sealed reaction vessel for 24 h, affording the product as yellowish orange crystals; yield 81.3 mg (87%). ^1H NMR (C_6D_6, 500 MHz) δ 8.00 (d, 2, J = 9.00, Ar), 7.08 (t, 2, J = 7.50, Ar), 7.03 (m, 2, Ar), 6.54 (t, 2, J = 7.00, Ar), 2.10 (m, 4, C*H*Me_2), 1.20 (dd, 12, J = 16.75 and 7.50, CH*Me*$_2$), 0.96 (dd, 12, J = 15.00 and 7.50, CH*Me*$_2$), −12.25 (t, 1, $^2J_{HP}$ = 14.5, $^1J_{HPt}$ = 1027, Pt*H*). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz) δ 59.64 ($^1J_{PPt}$ = 2780). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 164.30 (t, J_{CP} = 9.54, J_{CPt} = 44.80, C), 134.38 (t, J_{CP} = 17.44, CH), 131.98 (s, CH), 123.00 (t, J_{CP} = 22.34, C), 116.61 (t, J_{CP} = 3.64, CH), 116.40 (t, J_{CP} = 4.64, CH), 25.50 (t, $^1J_{CP}$ = 16.06, $^2J_{CPt}$ = 44.93, *C*HMe_2), 20.00 (t, $^2J_{CP}$ = 3.26, $^3J_{CPt}$ = 23.34, CH*Me*$_2$), 18.71 (s, $^3J_{CPt}$ = 27.36, CH*Me*$_2$). Anal. Calcd for $C_{24}H_{37}NP_2Pt$: C, 48.32; H, 6.25; N, 2.35. Found: C, 48.62; H, 6.34; N, 2.05.

2.19 | Synthesis of [1b]PtD

Procedures were similar to those of [**1b**]PdH except employing [**1b**]PtCl (72.0 mg, 0.114 mmol) and $LiAlD_4$ (11.0 mg, 0.262 mmol, 2.3 equiv) in THF (4 ml), affording the product as yellowish orange crystals; yield 35.4 mg (52%). ^2H NMR (C_6H_6, 61 MHz) δ −12.19 ($^1J_{DPt}$ = 156).

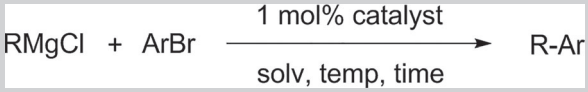
2.20 | General procedures for catalytic Kumada couplings (Table 1)

A heavy wall Schlenk flask was charged with aryl bromide (1.0 equiv), Grignard reagent (1.1 equiv), 1 mol% [**1a–b**]MCl (M = Pd, Pt; 1.0 mg for each single experiment), solvent (2 ml), and a magnetic stir bar. The flask was sealed with a Teflon stopper and heated with stirring in an oil bath at a prescribed temperature for a specified period of time. After being cooled to room temperature, the reaction mixture was quenched with deionized water and the product was extracted with diethyl ether. The diethyl ether solution was separated from the aqueous layer, dried over $MgSO_4$, and subject to GC-FID analysis with *n*-dodecane as an internal standard or flash column chromatography on silica gel with *n*-hexane as an eluent.

2.21 | Synthesis of *n*-butylbenzene (Table 1, entry 12)

Isolated yield 91%. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.24 (m, 2, Ar), 7.16 (m, 3, Ar), 2.59 (t, 2, J = 7.61, CH_2), 1.59 (m, 2, CH_2), 1.35 (m, 2, CH_2), 0.93 (t, 3, J = 7.22, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 142.76 (C), 128.45 (CH), 128.29 (CH), 125.66 (CH), 35.86 (CH_2), 33.86 (CH_2), 22.52 (CH_2), 14.01 (CH_3).

TABLE 1 Catalytic Kumada couplings



Entry	Catalyst	R	Ar	Solvent	Temp	Time	Conv[a]	R–Ar/Ar–Ar selectivity[a]
1	[**1a**]PdCl	*n*Bu	Ph	Et_2O	60	12	69	99/1
2	[**1a**]PdCl	*n*Bu	Ph	THF	60	12	94	86/14
3	[**1a**]PdCl	*n*Bu	Ph	DME	60	12	72	78/22
4	[**1a**]PdCl	*n*Bu	Ph	1,4-Dioxane	60	12	45	97/3
5	[**1a**]PdCl	*n*Bu	Ph	*n*-Hexane	60	12	97	48/52
6	[**1a**]PdCl	*n*Bu	Ph	Benzene	60	12	100	54/46
7	[**1a**]PdCl	*n*Bu	Ph	Toluene	60	12	100	57/43
8	[**1a**]PdCl	*n*Bu	Ph	Et_2O	28	40	31	100/0
9	[**1a**]PdCl	*n*Bu	Ph	Et_2O	40	40	50	100/0
10	[**1a**]PdCl	*n*Bu	Ph	Et_2O	40	84	91	99/1
11	[**1a**]PdCl	*n*Bu	Ph	Et_2O	60	24	90	99/1
12	[**1a**]PdCl	*n*Bu	Ph	Et_2O	60	36	100	99/1
13	[**1b**]PdCl	*n*Bu	Ph	Et_2O	60	36	98	90/10
14	[**1a**]PtCl	*n*Bu	Ph	Et_2O	60	36	19	100/0
15	[**1b**]PtCl	*n*Bu	Ph	Et_2O	60	36	0	NA
16	[**1a**]PdCl	*n*Bu	4-FC_6H_4	Et_2O	60	36	100	99/1
17	[**1a**]PdCl	*n*Bu	4-$MeOC_6H_4$	Et_2O	60	36	100	100/0
18	[**1a**]PdCl	4-Tolyl	Ph	Et_2O	60	36	83	100/0
19[b]	[**1a**]NiCl	*n*Bu	Ph	THF	60	12	97	44/56
20[b]	[**1b**]NiCl	*n*Bu	Ph	THF	60	12	57	46/54

Note: Unless otherwise noted, all reactions were carried out with 1 equiv of aryl bromide and 1.1 equiv of Grignard reagent in the presence of 1 mol% catalyst (1.0 mg) in 2-ml solvent; temperature in °C, time in hour, conversion in %.

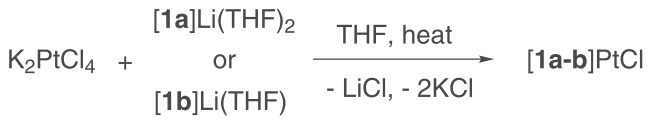
[a]Determined by GC, based on aryl bromide, average of two runs.

[b]Reference Liang et al.[20]

3 | RESULTS AND DISCUSSION

3.1 | Synthesis of chloro complexes

Chloro complexes are convenient starting materials for subsequent derivatization. Scheme S1 illustrates the synthetic strategies to prepare [**1a–b**]PdCl and [**1a–b**]PtCl. The synthesis of [**1a**]PdCl,[27] [**1b**]PdCl,[29] and [**1a**]PtCl[30] was reported previously. In addition to these known methods that take advantage of the enhanced reactivity of MCl_2L_2 (M = Pd, L = PhCN; M = Pt, L = SMe_2), we found that the most convenient entry to the synthesis of [**1a**]PtCl and [**1b**]PtCl perhaps involves heating a THF suspension of K_2PtCl_4 in the presence of in situ prepared lithium complexes of **1a** and **1b**, respectively (Scheme 1). No reaction was found without heating or prior lithiation of the protio ligands. Complex [**1b**]PtCl



SCHEME 1 A facile entry to the synthesis of [**1a**]PtCl and [**1b**]PtCl

can be isolated in a nearly quantitative yield as a yellow crystalline solid.

3.2 | Synthesis of alkyl and hydride complexes

Treating [**1a**]PdCl in THF at −35°C with R^1MgCl leads to their corresponding alkyl complexes [**1a**]PdR^1

(R^1 = Me, Et, *n*Bu) quantitatively in 30 min (Scheme 2). Similar reactions employing [**1b**]PdCl, [**1a**]PtCl, or [**1b**]PtCl generate successfully [**1b**]PdR^1 (R^1 = Me, Et), [**1a**]PtR^1 (R^1 = Me, Et, *n*Bu, *n*Hexyl), or [**1b**]PtMe, respectively, though it requires >12 h to produce high yields of organoplatinum complexes [**1a**]PtR^1 and [**1b**]PtMe. As a result, the alkylation of palladium complexes [**1a**]PdCl and [**1b**]PdCl with Grignard reagents proceeds much faster than that of platinum complexes [**1a**]PtCl and [**1b**]PtCl. In contrast to their **1a** counterparts, no reaction occurs in attempts to prepare higher homologs of [**1b**]PtMe under otherwise identical conditions. Attempts to accelerate reactions of [**1b**]PtCl with R^1MgCl (R^1 = Et, *n*Bu, *n*Hexyl) by increasing reaction temperatures, for example, 80°C, led inevitably to a mixture of [**1b**]PtH (vide infra) and the presumed [**1b**]PtR^1 in a ratio of approximately 4:1 as indicated by the $^{31}P\{^1H\}$ NMR spectra of reaction aliquots. The formation of [**1b**]PtH in these alkylation reactions is ascribed to β-hydrogen elimination of their presumed alkyl precursors. In contrast, alkyls that contain β-hydrogen atoms such as [**1a**]PdEt, [**1b**]PdEt, and [**1a**]PtEt are all thermally stable in C_6D_6 (approximately 21 mM) at 80°C for >30 h as evidenced by their ^1H and $^{31}P\{^1H\}$ NMR spectra. The fact that no β-hydrogen elimination occurs for [**1a**]PdEt, [**1b**]PdEt, or [**1a**]PtEt but for in situ prepared [**1b**]PtEt is surprising. Attempts to selectively isolate [**1b**]PtEt, [**1b**]Pt*n*Bu, or [**1b**]Pt*n*Hexyl have so far been unsuccessful.

Addition of one equivalent of $LiHBEt_3$ or an excess amount of $NaBH_4$ to an arene or THF solution of [**1a**]PdCl at room temperature leads to [**1a**]PdH quantitatively in 10 min or 1 h, respectively, as indicated by the ^1H and $^{31}P\{^1H\}$ NMR spectra of reaction aliquots. Attempts to isolate this hydride complex, however, were hampered by its facile decomposition upon workup where the solution darkened significantly to give intractable materials. Similar reactions employing [**1b**]PdCl, [**1a**]PtCl, or [**1b**]PtCl afford successfully their corresponding hydride complexes in high isolated yields though those involving platinum again proceed much slower than palladium. For instance, the reaction of [**1b**]PdCl with $LiHBEt_3$ is complete in 1 h, but those of [**1a**]PtCl or [**1b**]PtCl requires >12 h.

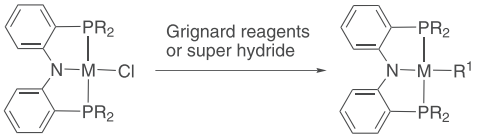
3.3 | Structural characterization

Solution structures of [**1b**]PtCl and organometallic complexes illustrated in Scheme 2 were all characterized by multinuclear NMR spectroscopy. Table S1 summarizes their selected data, along with those of their protio ligands, nickel congeners, and in situ prepared [**1a**]PdH and [**1b**]PtR^1 (R^1 = Et, *n*Bu, *n*Hexyl). Similar to their nickel derivatives,[19–21,37–39] these palladium and platinum complexes are all C_{2v} symmetric in solution on the NMR timescale, having the coordination geometry about the metal center being square planar as evidenced by virtual triplet resonances observed in their $^{13}C\{^1H\}$ NMR spectra for the *o*-phenylene carbon atoms in these complexes.

The ^{31}P resonances of these 4d and 5d complexes are all shifted relatively downfield as compared with those of their 3d analogs or protio ligands. The ^{31}P–^{195}Pt coupling constants of **1a** derivatives are consistently larger than those of **1b** counterparts, indicating slightly stronger P–Pt bonds for the former. These results are in line with what one expects for a phenyl-substituted phosphine being a better π acid than an isopropyl-substituted phosphine. The observed chemical shifts of Hα and Cα in alkyl complexes and their corresponding coupling constants with ^{31}P and ^{195}Pt, if not hampered by overlaps with other signals, are all typical.[40–43] The hydride complexes exhibit a diagnostic triplet[44] resonance at approximately −10 ppm for the hydride ligand in palladium derivatives and approximately −12 ppm for platinum derivatives, values that are both downfield shifted from those of their nickel analogs.

Yellow crystals of [**1b**]PtCl suitable for X-ray diffraction analysis were grown by layering pentane on a concentrated diethyl ether solution at −35°C whereas yellowish orange crystals of [**1b**]PtMe, [**1b**]PdEt, [**1a**]Pt*n*Bu, [**1b**]PdH, or [**1b**]PtH were grown from a concentrated diethyl ether or pentane solution at −35°C. Figures 1–3 and S1–S3 depict the structures of these complexes. Selected bond distances and angles are summarized in Tables S2 and S3, respectively, along with those of close analogs that were known previously.

As illustrated, the coordination geometry of these complexes is square planar, having the PNP ligand meridionally bound to palladium or platinum,



M = Pd, R = Ph, R^1 = Me, Et, *n*Bu
M = Pd, R = *i*Pr, R^1 = Me, Et, H
M = Pt, R = Ph, R^1 = Me, Et, *n*Bu, *n*Hexyl, H
M = Pt, R = *i*Pr, R^1 = Me, H

SCHEME 2 Synthesis of isolable palladium and platinum alkyl and hydride complexes of **1a** and **1b**

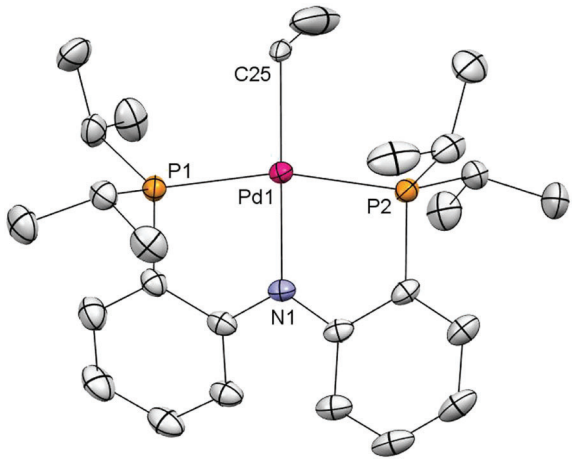


FIGURE 1 Molecular structure of [**1b**]PdEt with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity

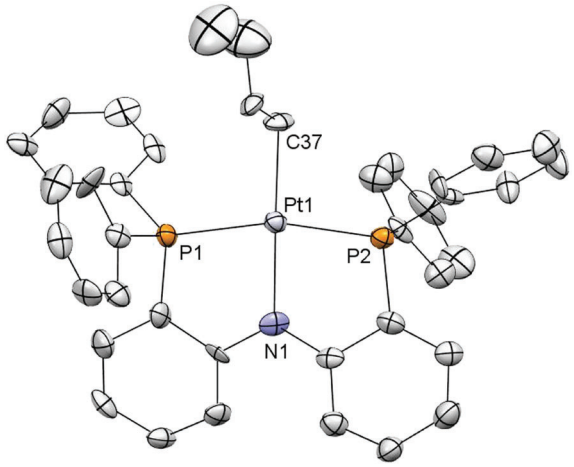


FIGURE 2 Molecular structure of [**1a**]Pt*n*Bu with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms are omitted for clarity

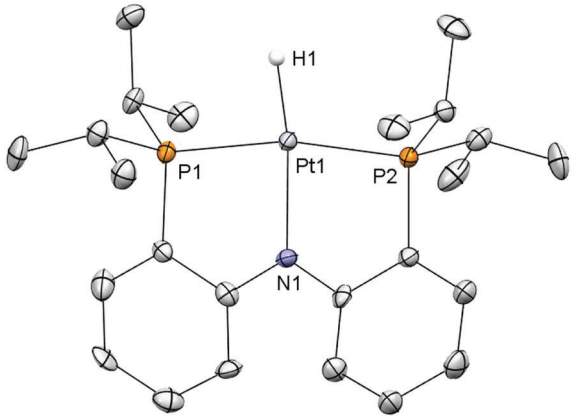


FIGURE 3 Molecular structure of [**1b**]PtH with thermal ellipsoids drawn at the 35% probability level. All hydrogen atoms except the hydride ligand are omitted for clarity

reminiscent of what was known for their nickel congeners. The bond distances and angles about the metal center are all comparable with those of amido or phosphine complexes of divalent group 10 metals.[40,44] Found in the difference map, the hydride ligand in [**1b**]PtH is anomalously bent from the ideal position in the square coordination plane. The reason why it is bent is not clear. The dihedral angle between the two *o*-phenylene planes in these complexes is approximately 40°, whereas that between the coordination plane and the C–N–C plane is approximately 22° (Table S4). The N–Pt bond distance of 2.084(6) Å in [**1b**]PtH is slightly longer than that in [**1b**]PtCl (2.029(7) Å) but somewhat shorter than that in [**1b**]PtMe (2.103(5) Å), consistent with the trans influence order of alkyl > H > Cl. Similar trends are also found for the N–Pd bond distances: [**1b**]PdEt (2.097(3) Å) > [**1b**]PdH (2.0881(18) Å) > [**1b**]PdCl (2.029(3) Å), the N–Pt bond distances: [**1a**]Pt*n*Bu (2.111(15) Å) > [**1a**]PtMe (2.09 (2) Å) > [**1a**]PtCl (2.024(6) Å), and the N–Ni bond distances: [**1b**]NiMe (1.945(3) Å) > [**1b**]NiH (1.920 (3) Å) > [**1b**]NiCl (1.9030(17) Å).

The magnitude of $^{31}P–^{195}Pt$ coupling constants observed from NMR spectroscopy has also been rationalized with s character involved in the corresponding P–Pt bond; the more s character, the larger coupling constant.[45] The larger C–P–C bond angles found for [**1b**]PtMe than [**1a**]PtMe (Table S3) imply less s character involved in the P–Pt bonds for the former, thus a smaller $^{31}P–^{195}Pt$ coupling constant (Table S1). Although this is in good agreement with our experimental data, [**1a**]PtCl instead shows larger C–P–C bond angles and a larger $^{31}P–^{195}Pt$ coupling constant than [**1b**]PtCl. Such inconsistency led us to analyze C–P–C bond angles of all structurally characterized compounds (Table S3) no matter if it is a platinum complex. These analyses consistently show larger C–P–C bond angles for all **1b** derivatives than their corresponding **1a** counterparts, as what is anticipated from the larger steric size of an isopropyl moiety than a phenyl group.[46] All in all, the consequence that [**1a**]PtCl has larger C–P–C bond angles than [**1b**]PtCl is the only exception.

Atomic radii of 4d metals are larger than those of their 3d counterparts for a larger principal quantum number but similar to those of their 5d congeners due to lanthanide contraction for the heavier elements. For instance, the ionic radius of divalent nickel in a square planar coordination geometry is 63 pm, whereas those of palladium and platinum are 78 and 74 pm, respectively.[47] As shown in Table S2, the M–N and M–P bond distances of the hydride complexes [**1b**]MH increase in the sequence of Ni < Pt < Pd. Similar trends are also found for the M–N and M–P bond distances of [**1a**]MCl, so are [**1b**]MCl, in spite of having one exception that the

M–N bond distances of [**1b**]PdCl and [**1b**]PtCl are coincidentally identical. The M–Cl bond distance of [**1a**]PdCl is similar to that of [**1a**]PtCl but significantly larger than that of [**1a**]NiCl. A similar phenomenon is also found for the M–Cl bond distances of [**1b**]MCl.

3.4 | Reactivity studies

Given the results that [**1a**]PdEt, [**1b**]PdEt, and [**1a**]PtEt do not undergo β-hydrogen elimination even at elevated temperatures, we examined the reactivity of their hydride analogs with respect to ethylene insertion. Neither [**1b**]PdH nor [**1a**]PtH reacts with an excess amount of ethylene (1 atm), even after heating at 80°C in C_6D_6 (29 mM) for >30 h. No reaction was found for [**1b**]PtH, either, under otherwise identical conditions. In contrast, in situ prepared [**1a**]PdH reacts with ethylene in C_6D_6 at room temperature to result in quantitative conversion of [**1a**]PdH in 10 h and formation of a mixture in which [**1a**]PdEt is one of the minor products (^{31}P NMR evidence). Attempts to isolate the major product (δ_P 7.1) of this reaction were not successful. Nevertheless, ethylene insertion into the Ni–H bond of [**1a**]PdH does occur though the reaction is complicated with either the facile decomposition of [**1a**]PdH or other prevailed pathways involving ethylene. The discrepancy in reactivity of these hydride complexes with ethylene highlights the difference in electrophilicity of their corresponding metal center. The consequence that [**1a**]PdH is active toward ethylene insertion but [**1b**]PdH is not is reminiscent of what was found for their nickel analogs.[21] Decomposition of in situ prepared [**1b**]PtEt, and its higher homologs, to give [**1b**]PtH, however, contrasts sharply with all other group 10 complexes of PNP.[19–21] In view of the principle of microscopic reversibility, β-hydrogen elimination of in situ prepared [**1b**]PtEt is therefore thermodynamically downhill, whereas that of [**1a**]PdEt is thermodynamically uphill.

To gain more insights, we prepared [**1b**]PtD and attempted its reaction with ethylene in order to probe the kinetic accessibility of [**1b**]PtEt-d_1 with which [**1b**]PtH and ethylene-d_1 might be observable after β-hydrogen elimination. Complex [**1b**]PtD can be synthesized by treating [**1b**]PtCl with $LiAlD_4$ in THF at room temperature in 1 h. Its ^{2}H NMR spectrum shows a diagnostic signal at −12 ppm with $^1J_{DPt}$ of 156 Hz. This coupling constant is in good agreement with that anticipated from $^1J_{HPt}$ in [**1b**]PtH and the magnetogyric ratios of these isotopes. No reaction was found, however, for [**1b**]PtD (23 mM in C_6D_6) with an excess amount of ethylene (1 atm) at 80°C for >30 h as evidenced by ^{1}H and ^{2}H NMR spectra, a result corroborating that ethylene does not insert into the Pt–D bond of [**1b**]PtD and [**1b**]PtEt-d_1 is not kinetically accessible.

Cross-coupling catalysis has made tremendous impacts on organic syntheses.[9,48,49] Nickel complexes of PNP are known catalyst precursors for Kumada couplings.[20] In this regard, the reactivity of their palladium and platinum analogs was investigated. Table 1 summarizes their catalytic activities.

We began with a survey of reaction parameters. Among seven solvents examined (entries 1–7), diethyl ether is superior to the others in the reaction of *n*-butylmagnesium chloride with phenyl bromide in the presence of 1 mol% [**1a**]PdCl at 60°C in 12 h in view of their corresponding selectivity of the desired cross-coupling product and turnover efficiency. An assessment of temperature and time in reaction run in diethyl ether (entries 8–12) gives an optimization of conversion and selectivity to produce *n*-butylbenzene in 99% yield at 60°C in 36 h (entry 12).

Under this optimized condition, [**1b**]PdCl shows virtually identical reactivity to [**1a**]PdCl but somewhat less satisfactory selectivity (entry 13). In contrast, the selectivity of the desired product derived from [**1a**]PtCl is excellent, but its reaction rate is too slow (entry 14). No catalytic reaction occurs, however, employing [**1b**]PtCl (entry 15). Collectively, [**1a**]PdCl outperforms [**1b**]PdCl, [**1a**]PtCl, and [**1b**]PtCl in Kumada coupling catalysis. The low activities of [**1a**]PtCl and [**1b**]PtCl in this catalysis are consistent with the slow reaction rates found for these platinum complexes in their stoichiometric reactions. The success in incorporating *n*-butyl that contains β-hydrogen atoms in cross-coupling catalyzed by [**1a**]PdCl, [**1b**]PdCl, and [**1a**]PtCl is in accordance with the consequence that no β-hydrogen elimination occurs for alkyl derivatives of these chloride precursors.

Both electronically activated and deactivated aryl bromide electrophiles are compatible in this catalysis to produce *n*-butyl arenes satisfactorily (entries 16–17). An aryl nucleophile such as 4-tolylmagnesium chloride also works successfully (entry 18). Notably, [**1a**]PdCl is superior to nickel complexes [**1a**]NiCl and [**1b**]NiCl (entries 19–20)[20] in view of its much higher selectivity of the desired cross-coupling product.

4 | CONCLUSIONS

We have prepared and structurally characterized a number of divalent palladium and platinum alkyl and hydride complexes of amido PNP pincer ligands **1a** and **1b**. Though the majority of these organometallic complexes are thermally stable, including alkyls that contain β-hydrogen atoms even at elevated temperatures, [**1a**]

PdH and [**1b**]PtR^1 (R^1 = Et, *n*Bu, *n*Hexyl) decompose either during synthesis or upon workup. Among the hydride complexes investigated in this study, [**1a**]PdH, though prepared in situ, is the only one that undergoes ethylene insertion. β-Hydrogen elimination of [**1a**]PdEt is therefore thermodynamically uphill, whereas that of in situ prepared [**1b**]PtEt is downhill. In addition to Heck, Suzuki, and Sonogashira couplings, [**1a**]PdCl is also competent in catalytic Kumada coupling. In terms of Kumada coupling catalysis, [**1a**]PdCl is superior to [**1b**]PdCl, [**1a**]PtCl, and [**1b**]PtCl, giving, for instance, *n*-butyl arenes nearly quantitatively.

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AUTHOR CONTRIBUTIONS

Mei-Hui Huang: Investigation. **Wei-Ying Lee:** Investigation. **Xue-Ru Zou:** Investigation. **Chia-Chin Lee:** Investigation. **Sheng-Bo Hong:** Investigation. **Lan-Chang Liang:** Funding acquisition; methodology; supervision.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article.

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