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Reversible Orthopalladation of Phosphinimine−Imine Dichloropalladium(II) Complexes

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The synthesis and characterization of triphenylphosphinimine−arylimine bidentate ligands (aryl = 2,4,6-trimethylphenyl or 4-methylphenyl) along with their dichloropalladium(II) complexes are reported. These complexes form tridentate orthopalladated species upon heating in the presence of sodium acetate. The reverse reaction occurs upon addition of $HCl \cdot Et_2O$. The rate of orthopalladation and reprotonation is highly dependent on the steric bulk of the ligand. Related cationic species were also synthesized and characterized and found to be inert in the presence of 1-hexene and styrene.

Introduction

In the past decade bidentate phosphinimine ligands have received significant attention as versatile supports for late transition metals.[1] There have been reports on bidentate phosphinimine systems incorporating pyridine, imidazole, and pyrazole moieties, many of which have been used in catalytic reactions with varying degrees of success.[2,3] In most of these systems the phosphinimine moiety plays only a structural role, either as a bulky substituent or as part of the ligand backbone.

Orthopalladation of phosphinimines offers a facile route to asymmetric pincer complexes and, in circumstances where the orthopalladation can be controlled, allows the facile transformation of a bidentate to a tridentate ligand.[4] These complexes are usually obtained directly via reaction of a proligand with a palladium salt; direct orthopalladation of phosphinimines upon reaction with $Pd(OAc)_2$ has recently been studied in detail by Urriolabeitia et al.[4,5] To the best of our knowledge, orthopalladation of a discrete complex bearing a bidentate phosphinimine−imine ligand has not been reported. We have explored a family of palladium complexes bearing bidentate phosphinimine−imine ligands and have developed a controlled method for their orthopalladation. We have also elucidated the direct and controlled reverse reaction. Herein we report the results of our findings.

Results and Discussion

Synthesis and Characterization of Proligands and Metal Complexes. The triphenylphosphinimine−arylimine compounds, L_{Ar} (Ar = Mes, 2,4,6-$Me_3C_6H_2$; Tol, 4-MeC_6H_4), were synthesized in four steps from 2-aminobenzophenone (Scheme 1).[6] The phosphinimine and imine moieties are installed via sequential Staudinger and condensation reactions, respectively. The ^{31}P NMR spectra of L_{Mes} and L_{Tol} show singlets at 1.2 and 0.87 ppm, and the IR spectra show the ν(PN) stretches at 1358 and 1360 cm^{-1}, respectively; both are characteristic of phosphinimine compounds.[2,3] The ^1H NMR spectrum of L_{Mes} shows two broad signals for the ortho mesityl CH_3 groups at 2.03 and 2.24 ppm, indicating hindered rotation in the compound. L_{Tol} had one characteristic singlet at 2.21 ppm. The molecular structure of L_{Mes}, determined by single-crystal X-ray crystallography, illustrates the origin of the hindered rotation (Figure 1). In the solid state streric hindrance directs the N-mesityl group away from the phosphinimine moiety. The $PN_{phosphinimine}$ and CN_{imine} bond lengths are consistent with similar compounds.[4]

Reaction of L_{Mes} and L_{Tol} with $(PhCN)_2PdCl_2$ in dichloromethane at room temperature forms the corresponding air- and moisture-stable, orange dichloropalladium(II) complexes, $L_{Mes}PdCl_2$ (**1**) and $L_{Tol}PdCl_2$ (**2**) (Scheme 2). Complexes **1** and **2** show ^{31}P NMR signals shifted significantly downfield of the proligands (37 and 34 ppm) and

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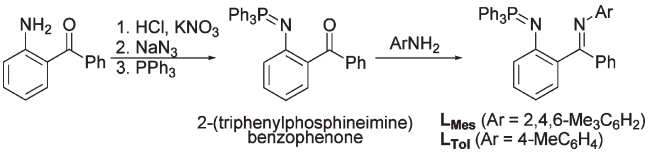
Scheme 1. Synthesis of Proligands L_{Mes} and L_{Tol}



IR stretches at significantly lower frequencies (ν(PN) = 1270 and 1251 cm^{-1}), indicative of a decrease in the P−N bond order and characteristic of bidentate phosphinimine-based dichloropalladium(II) complexes.[1,2,3] The ^1H NMR spectrum of **1** shows two sharp signals for the ortho mesityl CH_3 groups at 1.72 and 2.36 ppm, indicating that the hindered rotation observed in L_{Mes} is conserved.

The molecular structures of **1** and **2** were determined by single-crystal X-ray crystallography (Figures 2 and 3). Although complex **1** has square-planar geometry around the palladium atom, the molecule itself is not planar. The ligand bond lengths and angles are similar to those of the proligand L_{Mes}; however, there is a slight twist in the ligand and the backbone aryl group tilts away from the plane of the molecule by 65°. This twist creates a Pd1−N2−C7−C6 torsion angle of 0.42°, which is smaller than the torsion angle of 4.3° reported by Stephan et al. in an analogous phosphinimine−pyridine system.[2] The Pd−Cl bond lengths in **1** suggest a similar trans influence for the phosphinimine and imine donors (Pd−Cl(1) = 2.301(1) Å, Pd−Cl(2) = 2.305(1) Å).[2,3]

There are two independent palladium complexes in the molecular structure of $L_{Tol}PdCl_2$: **2** and **2′**. Structural analysis of **2** and **2′** indicates that the two structures may be a result of a greater degree of freedom associated with the Pd−N_{imine} bond compared to the more hindered analogue **1**. In **2** the Pd(1)−N(2)−C(7)−C(6) torsion angle is 0.90° (0.42° in **1**), whereas the analogous torsion angle in **2′** is 3.82°. In contrast the torsion angles at the phosphinimine nitrogen atom are nearly identical for **2** and **2′**. Other bond distances and angles are similar to **1**.

Reversible Orthopalladation of $L_{Mes}PdCl_2$ and $L_{Tol}PdCl_2$. Orthopalladation of complexes **1** and **2** can be induced thermally and catalyzed chemically by addition of base (Scheme 3). When **1** is refluxed in chlorobenzene for 3 days, the initially orange suspension is converted to a yellow solution of the orthopalladated product $L'_{Mes}PdCl$, **3** (L'_{Mes} = $(C_6H_4)(Ph)_2PN(C_6H_4)C(Ph)(=NMes)$). The accepted mechanism for this reaction is electrophilic substitution followed by HCl formation and thus may be base-catalyzed.[5a] Accordingly, addition of 1.1 equiv of sodium acetate reduces the reaction time to 2 days in refluxing chloroform. The ^{31}P NMR spectrum of **3** shows a signal at 41 ppm, and the IR spectrum shows a ν(PN) stretch at 1234 cm^{-1}; both are characteristic of orthopalladated phosphinimines.[5,8] The ^1H NMR spectrum (CD_2Cl_2) of **3** shows one sharp signal at 1.99 ppm corresponding to six protons of the ortho-methyl groups of the mesityl

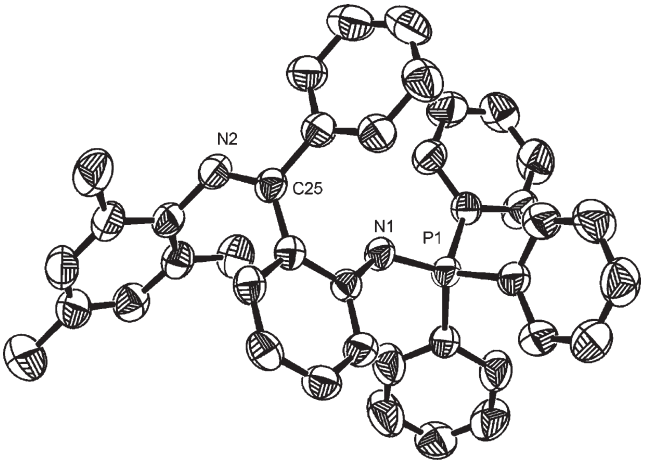
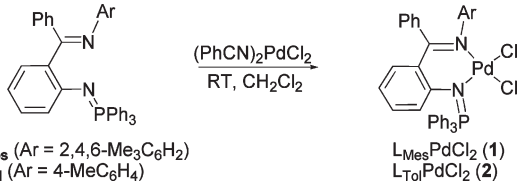


Figure 1. Molecular structure of L_{Mes} (depicted with 35% probability ellipsoids, H atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): P(1)−N(1) = 1.5689(2), P(1)−C(19) = 1.380(2); C(25)−N(2) = 1.282(2); C(32)−N(2) = 1.416(3); C(19)−N(1)−P(1) = 127.5(1); C(25)−N(2)−C(32) = 122.1(2); N(2)−C(25)−C(24) = 124.1(2); N(1)−C(19)−C(24) = 117.8(2).

Scheme 2. Synthesis of $L_{Ar}PdCl_2$, Ar = Mes (1), Tol (2)



substituent and indicates a relief of steric hindrance observed for L_{Mes} and **1**. The $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) shows a characteristic doublet for the orthopalladated carbon atom at 157.6 ppm (J_{CP} = 19.4 Hz).

A similar reaction with the less hindered $L_{Tol}PdCl_2$ requires more forcing conditions. Orthopalladation of **2** under strictly thermal conditions is achieved after 8 days in refluxing chlorobenzene; an orange solution of **2** becomes a yellow solution of the orthopalladated complex $L'_{Tol}PdCl$ (**4**) (L'_{Tol} = $(C_6H_4)(Ph)_2PN(C_6H_4)C(Ph)(=NTol)$). Addition of 1.1 equiv of sodium acetate reduced the reaction time to 2 days in refluxing chlorobenzene. The NMR and IR spectra of **4** are similar to those of **3**. Our findings are consistent with ligand-induced orthopalladation due to steric repulsion reported for other phosphinimine and phosphorus ylide systems:[6,9] increasing the steric bulk at the imine moiety increases the susceptibility of the complexes to undergo orthopalladation. A closer structural analysis of **1** and **2** supports this hypothesis: the distance between the nearest ortho carbon atom on the phenyl ring and the palladium center is 0.1 Å shorter in **1** than it is in **2** (3.457 Å for **2** and 3.510 Å for **1**) (Figures 2 and 3).

The molecular structures of **3** and **4** show a slightly distorted square-planar geometry around the palladium center similar to the dichloropalladium(II) complexes (Figure 4). The N_{imine}−Pd bond lengths in **3** and **4**, 2.148(1) and 2.105(19) Å, respectively, are longer than those for **1** (2.054(2) Å) and **2** (2.016(5) Å) likely due to the trans influence of the newly formed Pd−C_{aryl}

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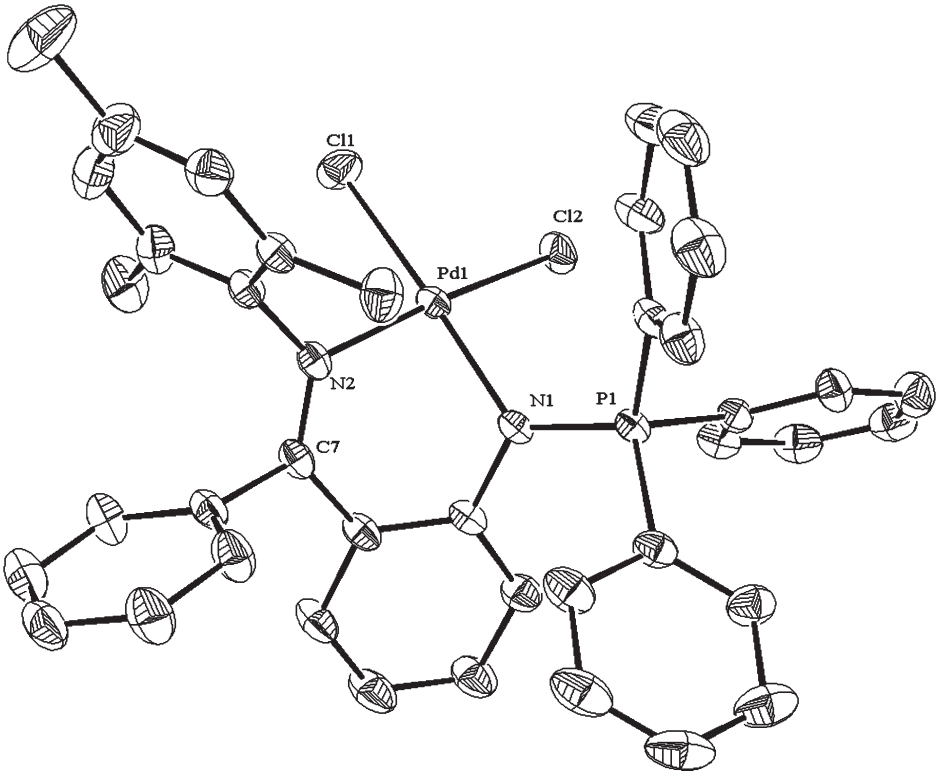


Figure 2. Molecular structure of **1** (left) (depicted with 35% probability ellipsoids, H atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): P(1)−N(1) = 1.6267(16), C(7)−N(2) = 1.293(2); Pd(1)−N(1) = 2.0504(15); Pd(1)−N(2) = 2.0543(15); Pd(1)−Cl(1) = 2.3009(6); Pd(1)−Cl(2) = 2.3047(5); N(1)−Pd(1)−N(2) = 85.67(6); N(1)−Pd(1)−Cl(1) = 178.15(4); N(2)−Pd(1)−Cl(2) = 175.18(4); Cl(1)−Pd(1)−Cl(2) = 89.34(2).

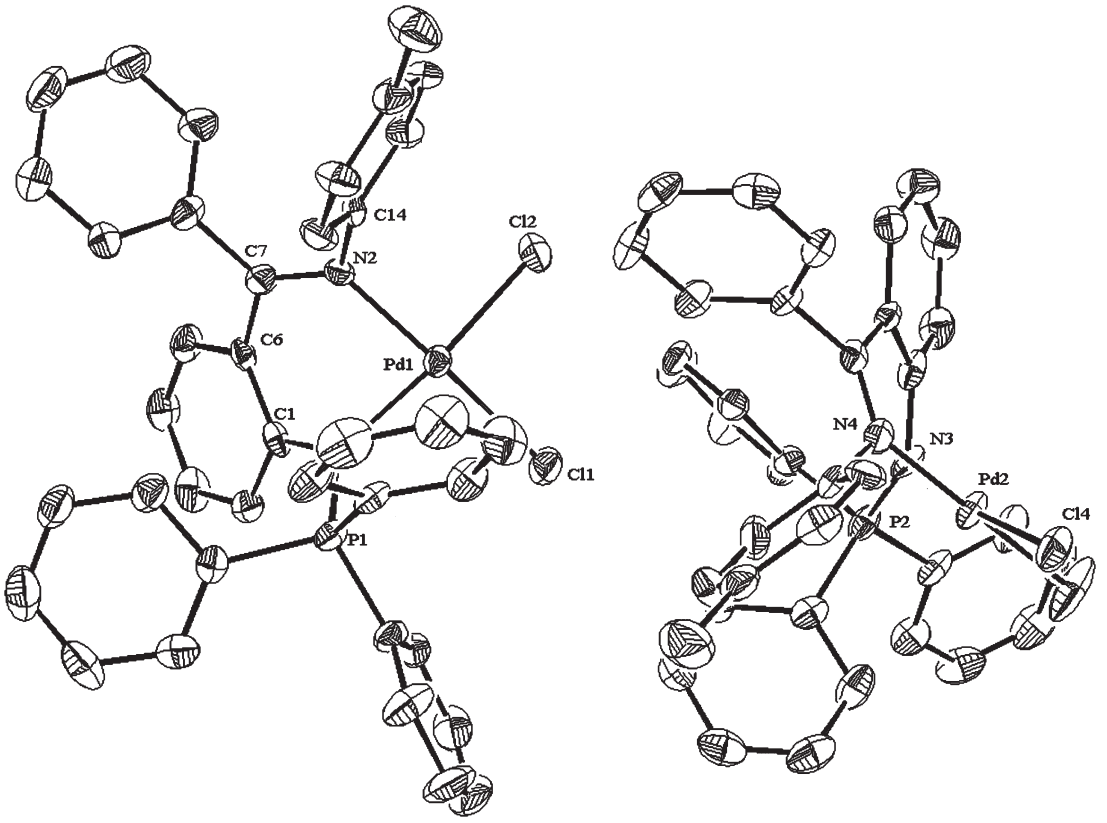


Figure 3. Molecular structure of **2** and **2′**. There are two Pd complexes in the asymmetric unit, in addition to four solvent CH_2Cl_2 molecules (depicted with 35% probability ellipsoids, solvent molecules and H atoms are omitted for clarity). Selected bond distances (Å) and angles (deg) for **2**: P(1)−N(1) = 1.615(5); C(7)−N(2) = 1.296(8); Pd(1)−N(1) = 2.044(5); Pd(2)−N(2) = 2.016(5); Pd(1)−Cl(1) = 2.2933(17); Pd(1)−Cl(2) = 2.3003(19); N(1)−Pd(1)−N(2) = 83.80(2); N(1)−Pd(1)−Cl(2) = 170.34(15); N(2)−Pd(1)−Cl(1) = 175.77(16); Cl(1)−Pd(1)−Cl(2) = 90.32(7).

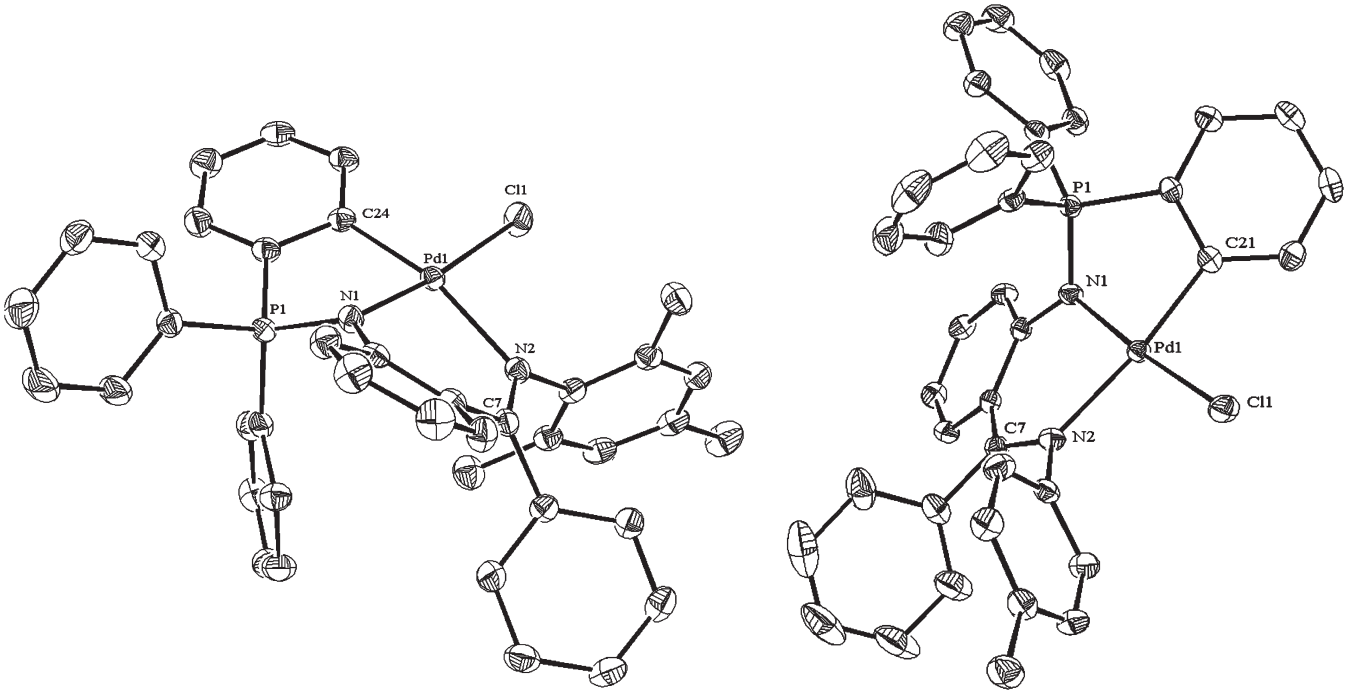
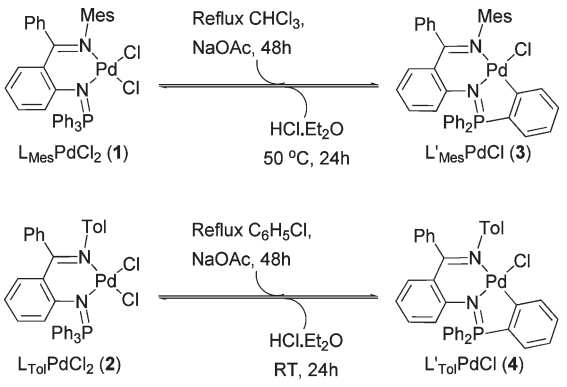
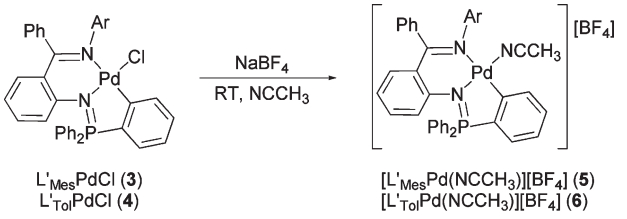


Figure 4. Molecular structure of **3** (left) and **4** (right) (depicted with 35% probability ellipsoids, H atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): For **3** P(1)−N(1) = 1.6171(15); C(7)−N(2) = 1.293(2); Pd(1)−N(1) = 2.0483(14); Pd(1)−N(2) = 2.1481(14); Pd(1)−Cl(1) = 2.3083(5); Pd(1)−C(24) = 1.9911(17); N(1)−Pd(1)−N(2) = 89.66(5); N(1)−Pd(1)−Cl(1) = 172.19(4); Cl(1)−Pd(1)−C(24) = 91.90(5); C(24)−Pd(1)−N(2) = 165.27(6). For **4** P(1)−N(1) = 1.6222(19); C(7)−N(2) = 1.295(3); Pd(1)−N(1) = 2.0433(17); Pd(1)−N(2) = 2.1053(19); Pd(1)−Cl(1) = 2.3027(6); Pd(1)−C(21) = 1.976(2); N(1)−Pd(1)−N(2) = 88.62(7); N(1)−Pd(1)−Cl(1) = 175.01(5); Cl(1)−Pd(1)−C(21) = 90.34(6); C(21)−Pd(1)−N(2) = 173.00(8).

Scheme 3. Reversible Orthopalladation of $L_{Ar}PdCl_2$, Ar = Mes (1), Tol (2)



Scheme 4. Formation of $[L'_{Ar}Pd(NCCH_3)][BF_4]$, Ar = Mes (5), Tol (6)



bonds. A closer inspection of the structures illustrates a more severe distortion for **3**, demonstrated by the N2−Pd−C24 angle of 165.2(6)° compared to 173.0(8)° for the analogous angle in **4**. The top hemispheres of the molecules are sterically protected by one of the free P-bound phenyl groups; however, the Pd−C_{ipso} bond length is significantly longer for **3** than the less bulky **4** (3.78 vs 3.40 Å).

The orthopalladated complexes **3** and **4** can be converted back to **1** and **2**, respectively, by the dropwise addition of 1.1 equiv $HCl \cdot Et_2O$ at room temperature. The steric bulk on the imine moiety effects the ability of the orthopalladated complexes to convert back to the bidentate dichloropalladium(II) complex. Upon addition of the acid, a yellow solution of **3** immediately reverts to orange; the ^{31}P NMR spectrum of the reaction mixture after 15 min shows ca. 50% reversion to complex **1**. The reaction is complete after heating at 50 °C for 18 h. In a similar reaction with **4**, however, the ^{31}P NMR spectrum of the reaction mixture after 15 min shows ca. 70% reversion to complex **2** and the conversion is complete after stirring at room temperature for 18 h. Complexes **1** and **2** were isolated in ca. 80% yield, and their identities were confirmed by spectroscopic means. Hence, increasing the steric bulk at the imine moiety favors the tridentate orthopalladated complex, whereas decreasing the steric bulk favors the bidentate dichloropalladium complex.

Reactivity of the Orthopalladated Complexes. The chloride ligand can be abstracted from **3** and **4** upon reaction with $NaBF_4$ in the presence of excess acetonitrile to generate $[L'_{Mes}Pd(NCCH_3)][BF_4]$ (**5**) and $[L'_{Tol}Pd(NCCH_3)][BF_4]$ (**6**), respectively; both were isolated as an air-stable yellow solids in 86% yield (Scheme 4). The ^{31}P NMR spectra of **5** and **6** show signals at 51 and 50 ppm, respectively, while the $^{13}C\{^1H\}$ NMR spectra shows Pd-bound carbon atoms as doublets at 155.4 ppm (J_{CP} = 20.3 Hz) and 153.9 ppm (J_{CP} = 20.2 Hz), respectively. The ^1H NMR spectrum of **5** shows equivalent ortho-methyl groups for the mesityl moiety, indicating free rotation of the group on the

Table 1. Selected Crystallographic Data for Compounds L_{Mes}, 1, 2 3, 4, and 5

	L_{Mes}	1	2	3	4	5
empirical formula	$C_{40}H_{35}N_2P$	$C_{41}H_{37}N_2PCl_4Pd$	$C_{40}H_{35}N_2PCl_6Pd$	$C_{40}H_{34}N_2PClPd$	$C_{38}H_{30}N_2PClPd$	$C_{42}H_{37}N_3PBF_4Pd$
fw	574.67	836.9	893.77	715.51	687.46	807.93
T (K)	173	173	173	173	173	173
a (Å)	13.343(4)	11.759(2)	18.1562(12)	9.7151(8)	12.2462(10)	9.4453(9)
b (Å)	15.022(4)	15.851(3)	22.9851(17)	12.7851(11)	21.9905(18)	12.2825(12)
c (Å)	16.788(4)	20.681(4)	20.5796(17)	14.0233(11)	12.1611(10)	16.3277(17)
α (deg)	90	90	90	98.186(3)	90	73.756
β (deg)	107.07(1)	96.746(7)	111.516(3)	99.256(3)	112.617(3)	8.209(5)
γ (deg)	90	90	90	103.113(4)	90	86.4117(6)
volume (Å^3)	3217(2)	3828.0(12)	6848.2(2)	1645.1(2)	3023.1(4)	1808.1(3)
Z	4	4	8	2	4	2
cryst syst	monoclinic	monoclinic	monoclinic	tirclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
d_{calc} (g/cm^3)	1.167	1.452	1.486	1.444	1.51	1.484
μ(Mo Kα) (cm^{-1})	1.16	8.38	9.37	7.26	7.86	6.14
$2\theta_{max}$ (deg)	56.8	55.1	45.1	55	56.2	56.5
absorp corr (T_{min}, T_{max})	0.836, 0.966	0.775, 0.889	0.810, 0.954	0.823, 0.890	0.808, 0.882	0.865, 0.976
total no. of reflns	41 185	35 421	42 250	28 275	36 270	40 233
no. of indep reflns (R_{int})	7770 (0.056)	8813 (0.025)	10498 (0.075)	7474 (0.028)	7364 (0.041)	8817 (0.030)
residuals (refined on F^2, all data): R_1[a]; wR_2[b]	0.050; 0.117	0.035; 0.066	0.098; 0.126	0.028; 0.059	0.051; 0.069	0.043; 0.086
GOF	1	1.03	1.01	1.03	1.02	1.05
no. observations [$I > 2\sigma(I)$]	4334	7429	6986	6780	5648	7545
residuals (refined on F): R_1; wR_2	0.108; 0.143	0.026; 0.062	0.053; 0.109	0.024; 0.057	0.030; 0.061	0.032; 0.079

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

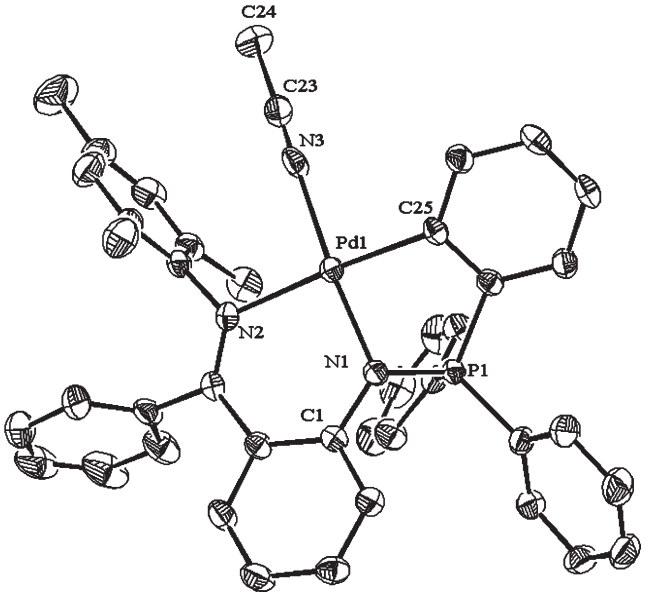


Figure 5. Molecular structure of **5** (depicted with 35% probability ellipsoids, BF_4 anion and H atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): P(1)−N(1) = 1.6361(19), C(7)−N(2) = 1.287(3); Pd(1)−N(1) = 2.0058(18); Pd(1)−N(2) = 2.1068(18); Pd(1)−N(3) = 2.042(2); Pd(1)−C(25) = 1.985(2); N(1)−Pd(1)−N(2) = 90.54(7); N(1)−Pd(1)−N(3) = 175.01(8); N(2)−Pd(1)−C(25) = 171.16(8); N(3)−Pd(1)−C(25) = 89.32(8).

NMR time scale. The ^{1}H NMR spectra of both **5** and **6** show the methyl signal for the coordinated acetonitrile at 1.80 and 1.87 ppm, respectively. The molecular structure of **5** shows a slightly distorted square-planar geometry at the Pd center. The Pd−N bonds in **5** are ca. 0.04 Å shorter than the analogous bonds in **3**, which is indicative of the positive charge now associated at the palladium center. Other bond lengths and bond angles of **5** are similar to those of the parent complex **3** and similar literature compounds.[3,5]

The Pd−C bonds in the cationic complexes are inert toward insertion of olefins. The bond in [L'_{Mes}Pd($NCCH_3$)][BF_4] (**5**) is also inert toward reactions with excess amounts of 1-hexene or styrene at room temperature or in refluxing acetonitrile for 48 h. If the abstraction of a chloride ligand in **5** using $NaBF_4$ is carried out in the presence of 1-hexene (instead of acetonitrile), no reaction is observed and there is no evidence for a coordinated olefin. Reactions of **5** and **6** with acid do not result in protonation of the Pd-bound aryl group and reversion to **1** and **2**, respectively. Complex **5** does not revert to **1** upon addition of $HCl\cdot Et_2O$ at elevated temperatures; instead it slowly degrades to unidentified materials. Upon addition of $HCl\cdot Et_2O$ at room temperature, the sterically accessible [L'_{Tol}Pd($NCCH_3$)][BF_4] (**6**) decomposes to an insoluble orange powder, unidentifiable by NMR spectroscopy.

Conclusions

We have synthesized bidentate triphenylphosphinimine−arylimine proligands, L_{Mes} and L_{Tol}, and their dichloropalladium(II) complexes $L_{Mes}PdCl_2$ (**1**) and $L_{Mes}PdCl_2$ (**2**). Complexes **1** and **2** can undergo orthopalladation under thermal or chemical conditions to form $L'_{Mes}PdCl$ (**3**) and $L'_{Tol}PdCl$ (**4**), although more forcing conditions are required for the less hindered tolyl analogue. This process is reversible via addition of $HCl\cdot Et_2O$ and is more facile for the less hindered complex **4**. Complexes **3** and **4** are readily converted to the cationic complexes [L'_{Mes}Pd($NCCH_3$)][BF_4] (**5**) and [L'_{Tol}Pd($NCCH_3$)][BF_4] (**6**), which are inert toward olefins but degrade upon reaction with acid.

Synthesis of the proligands is facile and allows the possibility of a family of ligands with varied steric and electronic properties by varying the substituents on the imine moiety. The controlled reversibility of the orthopalladation may be promising for developing a system where a switch from a bidentate to a tridentate ligand system (L_{Mes} to L'_{Mes}) can be triggered cleanly without decomposition of compounds or formation of Pd black. In particular, the inertness of the Pd−C bond in the cationic species to olefins makes the compounds promising as catalysts for coupling

and insertion reactions. We are currently expanding this work to include a family of ligands and other late transition metal centers, and we also intend to explore the versatility of this ligand system with Lewis acidic metals such as zinc.

Experimental Section

General Procedures. Unless otherwise specified, all procedures were carried out using standard Schlenk techniques. A Bruker Avance 300 MHz spectrometer and Bruker Avance 400dir MHz spectrometer were used to record the ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR spectra. ^{1}H NMR chemical shifts are given in ppm versus residual protons in deuterated solvents as follows: δ 5.32 for CD_2Cl_2, and δ 7.27 for $CDCl_3$. ^{13}C{^{1}H} NMR chemical shifts are given in ppm versus residual ^{13}C in solvents as follows: δ 54.00 for CD_2Cl_2, and δ 77.23 for $CDCl_3$. ^{31}P{^{1}H} NMR chemical shifts are given in ppm versus 85% H_3PO_4 set at 0.00 ppm. A Waters/Micromass LCT mass spectrometer equipped with an electrospray (ESI) ion source and a Kratos-50 mass spectrometer equipped with an electron impact ionization (EI) source were used to record low-resolution and high-resolution spectra. A Nicolet 4700 FT-IR spectrometer was used to record infrared spectra. All solvents were degassed and dried using 3 Å molecular sieves in an mBraun solvent purification system. The THF was further dried over Na/benzophenone and distilled under N_2. CD_2Cl_2 and $CDCl_3$ were dried over CaH_2 and degassed through a series of freeze−pump−thaw cycles. $(PhCN)_2PdCl_2$ was purchased from Strem Chemicals and used without further purification. All other chemicals were obtained from Aldrich and used without further purification.

2-(Triphenylphosphinimine)benzophenone. HCl (100 mL, 12 M) was added to a stirred suspension of 2-aminobenzophenone (23.19 g, 100 mmol) in 95% ethanol (500 mL) at 0 °C. Potassium nitrite (12.75 g, 150 mmol) in distilled water (150 mL) was added dropwise to the suspension. The reaction mixture was warmed to room temperature over 1 h while stirring. Over 15 min, a cooled solution of sodium azide (13.66 g, 210 mmol, 150 mL of H_2O) was added to the reaction mixture at room temperature. The reaction mixture was stirred for 45 min, then extracted with ether (3 × 125 mL), the organic phase was washed with water (125 mL) and dried over magnesium sulfate, and the solvent was removed to yield a viscous, yellow-orange oil of 2-azidobenzophenone, which was used without further purification. *(Note: Azidobenzophenone is a possible explosive hazard and should not be isolated/stored.)* Triphenylphosphine (7.5 g, 33 mmol) was added to 2-azidobenzophenone (6.96 g, 30 mmol) in toluene (500 mL) at 0 °C. The reaction mixture was stirred for 1.5 h, after which ether (20 mL) was added to precipitate out a light yellow solid. The solid was filtered and dried *in vacuo* to yield 2-(triphenylphosphinimine)benzophenone as a milky, yellow solid (11.25 g, 82%). ^{1}H NMR (300.1 MHz; $CDCl_3$): δ 6.45 (d, J_{H-H} = 8.1 Hz, 1H, Ar-*H*); 6.72 (td, J_{H-H} = 6.9, 0.6 Hz, 1H, Ar-*H*); 6.99 (td, J_{H-H} = 7.5, 1.8 Hz, 1H, Ar-*H*); 7.53−7.26 (m, 19H, Ar-*H*); 7.90−7.86 (m, 2H, Ar-*H*). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 117.46 (s, CH); 122.25 (d, J_{C-P} = 10.8 Hz, CH); 128.49 (s, CH); 129.01 (s, CH); 129.13 (s, CH); 130.34 (s, CH); 130.47 (s, C); 131.16 (s, CH); 131.47 (s, C); 132.27 (d, J_{C-P} = 2.8 Hz, CH); 132.86 (s, CH); 132.95 (s, CH); 139.73 (s, C); 150.51 (s, C); 200.91 (s, C). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 2.60 (s). IR (Nujol, cm^{-1}): 1650 (ν_{CO}), 1325 (ν_{NP}). Anal. Calcd for $C_{31}H_{24}NOP$ (457.50): C, 81.38; H, 5.29; N, 3.06. Found: C, 81.06; H, 5.24; N, 3.38. MS (ESI, *m*/*z*): calcd mass 458.1660; obsd mass 458.1674 (M^+).

(Ph)$_3$NC(C$_6$H$_4$)C(Ph)(=N(2,4,6-Me$_3$C$_6$H$_2$)), L$_{Mes}$. A round-bottom flask was charged with a spatula head of *p*-toluidine sulfonic acid (0.1−0.2 g), 2-(triphenylphosphinimine)benzophenone (2.0 g, 4.6 mmol), 2,4,6-trimethylaniline (0.62 g, 4.6 mmol), and toluene (50 mL). A standard Dean−Stark apparatus topped with a Dryrite drying column was assembled, and the reaction mixture was refluxed for 48 h. Ether was added to the resulting dark yellow solution to precipitate a bright yellow solid. The solid was filtered and then dried *in vacuo*, yielding L_{Mes} as a pale yellow solid, which was recrystallized from CH_2Cl_2 (2.15 g, 86%). ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 2.03 (s, 3H, Mes *ortho*-C*H*$_3$); 2.19 (s, 3H, Mes *para*-C*H*$_3$); 2.24 (s, 3H, Mes-*ortho*-C*H*$_3$); 6.42 (qd, $^4J_{H-H}$ = 6.6 Hz, $^4J_{H-H}$ = 1.2 Hz, 2H, Mes *m*-CH); 6.83−6.64 (m, 4H, Ar-H); 7.53−7.26 (m, 18H, Ar-H); 7.89−7.86 (m, 2H, Ar-H). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 18.74 (s, σ *C*H$_3$); 19.04 (s, σ *C*H$_3$); 20.98 (s, *p*-*C*H$_3$); 116.50 (s, CH); 122.26 (d, J_{C-P} = 11.4 Hz, CH); 128.35 (s, CH); 128.92 (s, CH); 128.98 (s, CH); 129.04 (s, CH); 129.49 (s, CH); 129.75 (s, CH); 130.56 (s, C); 131.39 (s, C); 131.56 (s, C); 131.92 (s, C), 132.16 (d, J_{C-P} = 2.8 Hz, CH); 132.92 (s, CH); 133.02 (s, CH); 141.47 (s, C); 147.86 (s, C); 149.91 (s, C); 170.37 (s, C). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 1.16 (s). IR (Nujol, cm^{-1}): 1595 (ν_{CN}), 1339 (ν_{NP}). Anal. Calcd for $C_{40}H_{35}N_2P$ (574.69): C, 83.60; H, 6.14; N, 4.87. Found: C, 83.43; H, 6.12; N, 4.92. MS (ESI, *m*/*z*): calcd mass 575.2615; obsd mass 575.2600 (M^+).

(Ph)$_3$NC(C$_6$H$_4$)C(Ph)(=N(4-MeC$_6$H$_5$)), L$_{Tol}$. The proligand L_{Tol} was synthesized in an identical manner to L_{Mes}, except *p*-methylaniline (0.541 mL, 4.6 mmol) was used instead of 2,4,6-trimethylaniline, and the reaction was refluxed for 24 h. The reaction yielded L_{Tol} as a pale yellow solid (2.15 g, 86%). ^{1}H NMR (300.1 MHz; $CDCl_3$): δ 2.21 (s, 3H, C*H*$_3$); 6.36 (dt, J_{H-H} = 8.4, 0.9 Hz, 1H, Ar-*H*); 6.50 (td, J_{H-H} = 8.7, 1.2 Hz, 1H, Ar-*H*); 6.85−6.77 (m, 6H, Ar-*H*); 7.61−7.31 (m, 18H, Ar-*H*); 7.85−7.82 (m, 2H, Ar-*H*). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 21.15 (s, *C*H$_3$); 116.87 (s, CH); 121.00 (s, CH); 121.19 (d, J_{C-P} = 10.4 Hz, CH); 128.36 (s, CH); 128.87 (s, CH); 129.01 (s, CH); 129.13 (s, CH); 129.18 (s, CH); 129.24 (s, CH); 130.18 (s, CH); 130.86 (s, C); 131.85 (s, C); 132.21 (d, J_{C-P} = 2.8 Hz, CH); 132.60 (s, C); 132.90 (s, CH); 133.00 (s, CH); 141.00 (s, C); 150.46 (s, C); 150.57 (s, C); 170.95 (s, C). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 0.87 (s). IR (Nujol, cm^{-1}): 1624 (ν_{CN}), 1360 (ν_{NP}). Anal. Calcd for $C_{38}H_{31}N_2P$ (546.64): C, 83.49; H, 5.72; N, 5.12. Found: C, 83.09; H, 5.67; N, 5.06. MS (ESI, *m*/*z*): calcd mass 547.2307; obsd mass 547.2303 (M^+).

L$_{Mes}$PdCl$_2$ (1). A solution of L_{Mes} (0.28 g, 0.52 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $(PhCN)_2PdCl_2$ (0.22 g, 0.57 mmol) in CH_2Cl_2 (10 mL) and stirred for 22 h at room temperature. The resulting reddish solution was concentrated, and diethyl ether (10 mL) was added to precipitate an orange-red solid. Filtration and drying *in vacuo* yielded an orange solid, $L_{Mes}PdCl_2$ (**1**), which was recrystallized from CH_2Cl_2 (0.30 g, 76%). A single crystal of **1** suitable for X-ray crystallography was obtained by recrystallization from CH_2Cl_2 and hexane. ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 1.72 (s, 3H, CH_3); 2.11 (s, 3H, CH_3); 2.36 (s, 3H, CH_3); 6.48 (s, 1H, Ar); 6.74−6.67 (m, 3H, Ar); 6.97−6.89 (m, 5H, Ar); 7.29−7.17 (m, 3H, Ar); 7.97−7.38 (m, 14H, Ar). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 18.88 (s, *o*-CH_3); 20.92 (s, *p*-CH_3); 120.10 (s, CH); 125.33 (d, J_{C-P} = 6.0 Hz, CH); 126.97 (s, CH); 127.64 (s, CH); 127.93 (s, CH); 128.03 (s, CH); 129.41 (s, CH); 129.69 (s, CH); 131.67 (s, CH); 133.11 (s, CH); 133.71 (CH); 134.27 (s, C); 135.19 (s, C); 135.87 (s, C); 137.59 (s, C); 137.72 (s, C); 144.48 (s, C); 146.78 (s, C); 171.77 (s, C). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 37.91 (s). IR (Nujol, cm^{-1}): 1549 (ν_{CN}), 1245 (ν_{NP}). Anal. Calcd for $C_{40}H_{35}N_2PCl_2Pd$ (752.02): C, 63.89; H, 4.69; N, 3.73. Found: C, 64.12; H, 4.78; N, 3.72. MS (EI, *m*/*z*): calcd mass 712.11918; obsd mass 711.11884 ($(M - HCl)^+$).

L$_{Tol}$PdCl$_2$ (2). Complex **2** was synthesized in an identical manner to **1**, except using proligand L_{Tol} (0.30 g, 0.52 mmol) instead. Complex **2** was isolated as a yellow solid and recrystallized from dichloromethane and hexane (0.33 g, 81%). ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 2.20 (s, 3H, *p*Tol-C*H*$_3$); 6.87−6.75 (m, 7H, Ar-*H*); 6.95 (dt, J_{H-H} = 9.0, 1.8 Hz, 2H,

Ar-*H*); 7.27−7.06 (m, 4H, Ar-*H*); 7.60−7.53 (m, 6H, Ar-*H*); 7.64−7.68 (m, 3H, Ar-*H*); 7.98 (t, J_{H-H} = 9.0 Hz, 6H, Ar-*H*). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 21.00 (s, *C*H$_3$); 121.74 (s, CH); 125.31 (s, CH); 126.12 (s, C); 127.14 (s, C); 128.87 (s, CH); 128.34 (s, CH); 128.89 (s, CH); 129.02 (s, CH); 129.59 (s, CH); 129.88 (s, CH); 132.15 (s, CH); 133.39 (d, J_{C-P} = 4.0 Hz, CH); 134.35 (s, C); 134.73 (s, CH); 136.00 (s, CH); 146.59 (s, C); 146.81 (s, C); 154.21 (s, C); 175.26 (s, C). ^{31}P NMR (121.5 MHz; CD_2Cl_2): δ 34.28 (s). IR (Nujol, cm^{-1}): 1551 (ν_{CN}), 1251 (ν_{NP}). Anal. Calcd for $C_{38}H_{31}N_2PCl_2Pd$ (723.97): C, 63.04; H, 4.32; N, 3.87. Found: C, 61.94; H, 4.35; N, 3.78. MS (EI, *m*/*z*): calcd mass 684.08864; obsd mass 684.08754 ((M − HCl)$^+$).

L′$_{Mes}$PdCl (3). A round-bottomed flask was loaded with **1** (100 mg, 0.13 mmol) and NaOAc (16 mg, 1.5 equiv, 0.2 mmol). Chloroform (25 mL) was added, and the orange suspension was refluxed vigorously for 48 h. The resulting yellow solution was filtered through Celite, and hexane was (∼5 mL) added until a yellow solid began to precipitate. The mixture was then stirred for 18 h at room temperature and filtered, and the resulting yellow solid dried under vacuum, to yield complex **3** (70 mg, 74%). A single crystal suitable for X-ray crystallography was grown by slow diffusion of ether into a solution of **3** in CH_2Cl_2. ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 1.99 (s, 6H, Mes σ C*H*$_3$); 2.13 (s, 3H, Mes *p*-C*H*$_3$); 6.55−6.63 (m, 4H, Ar-H); 6.82 (m, 2H, Ar-H); 7.02 (m, 3H, Ar-H); 7.10 (t, J = 5.1 Hz, 1H, Ar-H); 7.12−7.25 (m, 4H, Ar-H); 7.60 (dt, ^dJ = 2.1 Hz, ^tJ = 5.7 Hz, 4H, Ar-H); 7.71−7.79 (m, 6H, Ar-H); 8.08 (d, J = 6.0 Hz, 1H, Ar-H). ^{13}C NMR (100.6 MHz; $CDCl_3$): δ 20.40 (s, σ *C*H$_3$); 21.82 (s, *p*-*C*H$_3$); 120.50 (s, CH); 128.16 (s, CH); 128.45 (s, CH); 128.61 (s, CH); 128.64 (s, CH); 129. 52 (s, CH); 130.00 (s, C); 130.17 (s, CH); 130.29 (S, CH); 130.67 (s, C); 130.69 (s, CH); 131.52 (s, C); 131.60 (d, J_{C-P} = 3.2 Hz, CH); 132.24 (s, CH); 133.63 (d, J_{C-P} = 11.3 Hz, CH); 134.14 (s, CH); 134.20 (s, CH); 134.23 (s, CH); 134.78 (s, C); 136.88 (s, CH); 137.36 (s, C); 139.66 (s, C); 147.12 (s, CH); 148.05 (d, J_{C-P} = 3.6 Hz, C); 157.62 (d, $^2J_{C-P}$ = 20 Hz, *C*-Pd); 171. 68 (s, C). ^{31}P NMR (121.5 MHz; CD_2Cl_2): δ 41.62 (s). IR (Nujol, cm^{-1}): 1546 (ν_{CN}), 1234 (ν_{NP}). Anal. Calcd for $C_{40}H_{34}N_2PClPd$ (715.57): C, 67.12; H, 4.79; N, 3.91. Found: C, 66.94; H, 4.81; N, 3.86. MS (EI, *m*/*z*): calcd mass 712.1186; obsd mass 712.1188 (M).

L′$_{Tol}$PdCl (4). A round-bottemed flask was loaded with complex **2** (100 mg, 0.13 mmol) and NaOAc (16 mg, 0.2 mmol). Chlorobenzene (25 mL) was added, and the orange suspension was refluxed vigorously for 24 h. The resulting yellow solution was filtered through Celite, and hexane was added until a yellow solid began to precipitate. The mixture was then stirred for 18 h at room temperature and filtered, and the resulting yellow solid dried *in vacuo* to yield complex **4** (70 mg, 74%). ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 1.99 (s, 3H, *p*Tol-C*H*$_3$); 6.38 (d, J = 8.4 Hz, 1H, Ar-H); 6.60 (t, J = 7.8 Hz, 1H, Ar-H); 6.68 (m, 2H, Ar-H); 6.84 (m, 4H, Ar-H); 7.17 (m, 8H, Ar-H); 7.63 (m, 4H, Ar-H); 7.74 (m, 2H, Ar-H); 7.87 (m, 4H, Ar-H); 7.99 (d, J = 7.5 Hz, 1H, Ar-H). ^{13}C NMR (100.6 MHz; $CDCl_3$): δ 21.51 (s, *p*-*C*H$_3$); 120.50 (s, CH); 123.26 (d, J_{C-P} = 7.6 Hz, CH); 124.87 (s, CH); 125.01 (s, CH); 128.59 (d, J_{C-P} = 10.1 Hz, CH); 129.22 (s, CH); 129.92 (s, CH); 130.23 (s, CH); 130.35 (s, CH); 131.20 (d, J_{C-P} = 3.7 Hz, CH); 132.65 (s, CH); 133.24 (d, J_{C-P} = 11.7 Hz, C); 134.13 (d, J_{C-P} = 10.3 Hz, CH); 134.46 (d, J_{C-P} = 2.7 Hz, CH); 134.81 (s, C); 136.69 (s, CH); 137.93 (s, C); 139.31 (s, C); 139.55 (s, CH); 139.60 (s, C); 139.70 (s, CH); 147.82 (s, C); 148.68 (s, C); 157.59 (d, $^2J_{C-P}$ = 19.4 Hz, *C*-Pd); 173.18 (s, C). ^{31}P NMR (121.5 MHz; CD_2Cl_2): δ 36.16 (s). IR (Nujol, cm^{-1}): 1543 (ν_{CN}), 1241 (ν_{NP}). Anal. Calcd. for $C_{38}H_{30}N_2PClPd\cdot CH_2Cl_2$ (772.44): C, 60.59; H, 4.18; N, 3.63. Found: C, 60.10; H, 3.82; N, 3.50. MS (EI, *m*/*z*): calcd mass 712.1186; obsd mass 712.1188 (M).

Reversible Orthopalladation: Conversion of 3 into 1. Dilute HCl·Et$_2$O (1.68M, 12 μL, 0.020) was added dropwise via syringe to a solution of **3** (15 mg, 0.021 mmol) in $CHCl_3$ (10 mL) at room temperature. The yellow solution immediately turned orange. The orange solution was heated at 50 °C for 18 h. Hexane (10 mL) was added to this solution to precipitate complex **1** as an orange solid, which was isolated by filtration and dried *in vacuo* (12.5 mg, 79%).

Conversion of 4 into 2. Dilute HCl·Et$_2$O (1.50 M, 11 μL, 0.023 mmol) was added dropwise via syringe to a solution of **4** (10 mg, 0.021 mmol) in $CHCl_3$ (10 mL) at room temperature. The yellow solution immediately turned orange. The orange solution was stirred at room temperature for 18 h. Hexane (10 mL) was added to this solution to precipitate complex **2** as an orange solid, which was isolated by filtration and dried *in vacuo* (9.0 mg, 85%).

[L′$_{Mes}$Pd(NCCH$_3$)][BF$_4$] (5). A Schlenk flask was loaded with **3** (100 mg, 0.14 mmol) and $NaBF_4$ (150 mg, 1.4 mmol). Dichloromethane (10 mL) and acetonitrile (1 mL) were added, and the reaction was stirred at room temperature for 18 h. Addition of hexane (2 mL) produced a yellow precipitate, which was filtered and dried *in vacuo* to yield **5** (97 mg, 86%). A single crystal of **5** suitable for X-ray crystallography was grown from slow evaporation from CH_2Cl_2 at room temperature ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 1.80 (s, 3H, C*H*$_3$CN); 1.99 (s, 6H, Mes σ C*H*$_3$); 2.13 (s, 3H, Mes *p*-C*H*$_3$); 6.69−6.77 (m, 4H, Ar-H); 6.96 (t, J = 9.9 Hz, 2H, Ar-H); 7.05 (d, J = 6.9 Hz, 2H, Ar-H); 7.15 (t, J = 8.4 Hz, 1H, Ar-H); 7.24−7.34 (m, 6H, Ar-H); 7.62−7.82 (m, 10H, Ar-H). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 3.19 (s, NC*C*H$_3$); 19.76 (s, σ *C*H$_3$); 21.54 (s, *p*-*C*H$_3$); 120.21 (s, N*C*CH$_3$); 121.90 (s, CH); 127.42 (s, CH); 128.31 (s, CH); 128.75 (s, CH); 129.43 (s, CH); 129.59 (s, CH); 129.61 (s, C); 129.86 (s, C); 130.58 (s, CH); 130.70 (s, CH); 130.76 (s, CH); 130.88 (s, CH); 131.30 (s, CH); 131.90 (d, J_{C-P} = 10.4 Hz, CH); 135.26 (d, J_{C-P} = 2.6 Hz, CH); 136.57 (s, C); 137.71 (s, CH); 137.96 (s, C); 138.15 (s, C); 146.60 (s, C); 146.79 (d, J_{C-P} = 3.3 Hz, C); 155.39 (d, J_{C-P} = 20.3 Hz, *C*-Pd); 173.46 (s, C). ^{31}P NMR (121.5 MHz; CD_2Cl_2): δ 51.16 (s). ^{11}B NMR (128.4 MHz, CD_2Cl_2): δ 1.22 (s). IR (Nujol, cm^{-1}): 1545 (νCN), 1228 (νNP). Anal. Calcd for $C_{42}H_{37}N_3PBF_4Pd$ (807.96): C, 62.43; H, 4.62; N, 5.20. Found: C, 61.96; H, 4.60; N, 5.20. MS (ESI, *m*/*z*): calcd mass 677.1500; obsd mass 677.1515 [(M − MeCN, − BF$_4$)].

[L′$_{Tol}$Pd(NCCH$_3$)][BF$_4$] (6). Complex **6** was made in an identical manner to **5**, using **4** (100 mg, 0.14 mmol) instead. The reaction yielded a dark yellow solid of **6** (97 mg, 86%). ^{1}H NMR (300.1 MHz; CD_2Cl_2): δ 1.87 (s, 3H, *CH*$_3$CN); 2.22 (s, 3H, *p*Tol-C*H*$_3$); 6.61 (d, J = 8.4 Hz, 1H, Ar-H); 6.72 (t, J = 8.0 Hz, 1H, Ar-H); 6.92 (t, J = 6.8 Hz, 1H, Ar-H); 6.99 (d, J = 8.4 Hz, 2H, Ar-H); 7.09 (m, 4H, Ar-H); 7.29 (m, 8H, Ar-H), 7.68 (m, 4H, Ar-H); 7,84 (m, 6H, Ar-H). ^{13}C NMR (100.6 MHz; CD_2Cl_2): δ 2.71 (s, NC*C*H$_3$); 20.84 (s, *p*-*C*H$_3$); 120.20 (s, N*C*CH$_3$); 120.77 (s, CH); 123.26 (s, CH); 127.49 (s, C); 128.21 (s, CH); 128.35 (s, C); 128.60 (s, CH); 128.73 (s, CH); 129.06 (s, CH); 129.84 (s, CH); 129.88 (s, CH); 130.01 (s, CH); 132.50 (s, CH); 132.71 (s, CH); 133.17 (d, J_{C-P} = 10.3 Hz, CH); 134.43 (d, J_{C-P} = 10.3 Hz, CH); 135.36 (s, C); 136.90 (s, CH); 137.11 (s, CH); 137.15 (s, C); 138.05 (s, C); 145.57 (s, C); 147.92 (s, C); 153.87 (d, J_{C-P} = 20.2 Hz, *C*-Pd); 173.69 (s, C). ^{31}P NMR (121.5 MHz; CD_2Cl_2): δ 49.71 (s). ^{11}B NMR (128.4 MHz, CD_2Cl_2): δ −1.04 (s). IR (Nujol, cm^{-1}): 1545 (ν_{CN}), 1221 (ν_{NP}). Anal. Calcd for $C_{40}H_{33}N_3PBF_4Pd$ (779.91): C, 61.60; H, 4.26; N, 5.39. Found: C, 61.63; H, 4.81; N, 4.96. MS (ESI, *m*/*z*): calcd mass 677.1500; obsd mass 677.1515 [(M − MeCN, − BF$_4$)].

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Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.