# A Modular Approach to Achiral and Chiral Nickel(II), Palladium(II), and Platinum(II) PCP Pincer Complexes Based on Diaminobenzenes

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The synthesis and characterization of a series of nickel, palladium, and platinum complexes containing new achiral and chiral PCP pincer ligands based on 1,3-diaminobenzene, 5-trifluoromethyl-1,3-diaminobenzene, and 3,5-diamino-4-chloroisobutylbenzoate are reported. The new PCP ligands are prepared conveniently in high yield by treatment of the respective diaminobenzene with 2 equiv of a variety of achiral and chiral $R_2PCl$ compounds in the presence of base. PCP complexes of Ni(II), Ni(PCP)Cl, were synthesized by the reaction of $NiCl_2 \cdot 6H_2O$ with 1 equiv of a PCP ligand. In similar fashion, treatment of $M(COD)X_2$ (M = Pd, Pt; X = Cl, Br) with 1 equiv of a PCP ligand yields the square-planar complexes M(PCP)X. Palladium PCP complexes featuring a coordinated TFA ligand (TFA = $CF_3COO^-$) are obtained by the reaction of $Pd(TFA)_2$ with 1 equiv of a PCP ligand. Alternatively, palladium PCP complexes can also be generated via an oxidative addition route. Addition of 2 equiv of PCP ligands based on 3,5-diamino-4-chloroisobutylbenzoate to $Pd_2(dba)_3$ affords the respective Pd(PCP)Cl pincer complexes in high yields. X-ray structures of representative Ni, Pd, and Pt PCP complexes have been determined. Finally, the use of the palladium complexes as catalysts for the Suzuki−Miyaura coupling of some aryl bromides and phenyl boronic acid has been examined.

## Introduction

Tridentate PCP ligands comprising an anionic aryl ring that is ortho,ortho-disubstituted with $-CH_2PR_2$ units are widely utilized ligands in transition metal chemistry and catalysis.[1,2−9] In this family of ligands steric, electronic, and stereochemical parameters can be manipulated by modifications of the benzylic positions and/or phosphino R groups so as to control the reactivity at the metal center. Stereochemical parameters, however, are comparatively difficult to modify and often require tedious multistep syntheses and expensive starting materials.[3,5a,10−12] As part of our effort to create novel pincer ligands in which the steric, electronic, and stereochemical properties can be easily modulated, we have designed a synthetic route for the high-yield synthesis of a new generation of PCP ligands, based on 1,3-diaminobenzenes and $R_2PCl$, which contain dialkyl or diaryl phosphines as well as various P−O bond-containing achiral and chiral phosphite units.[13] This methodology has recently been applied to the preparation of several PNP pincer-type ligands based on 2,6-diaminopyridine.[14] The new PCP ligands are applied to the synthesis of a series of square-planar Ni(II), Pd(II), and Pt(II) PCP complexes. In addition, preliminary investigations of the Suzuki−Miyaura coupling of aryl and alkyl bromides and phenylboronic acid catalyzed by some palladium PCP complexes are also presented.

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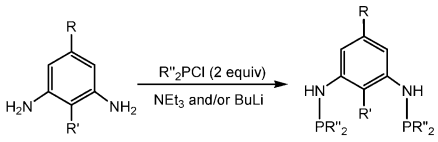
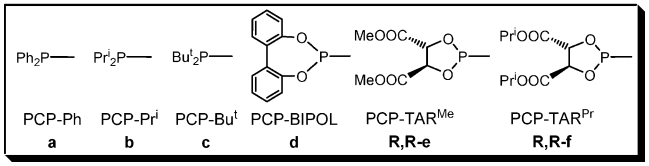
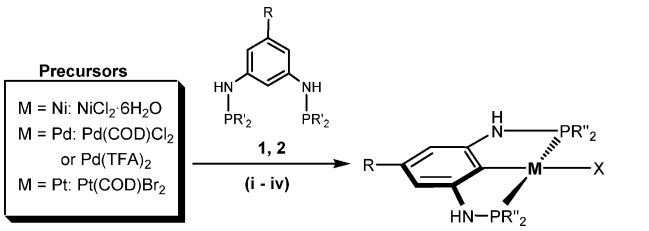
**Scheme 1**




**1a - f** R = R' = H
**2a, 2d, 2e** R = $CF_3$, R' = H
**3a, 3e** R = $COOBu^i$, R' = Cl



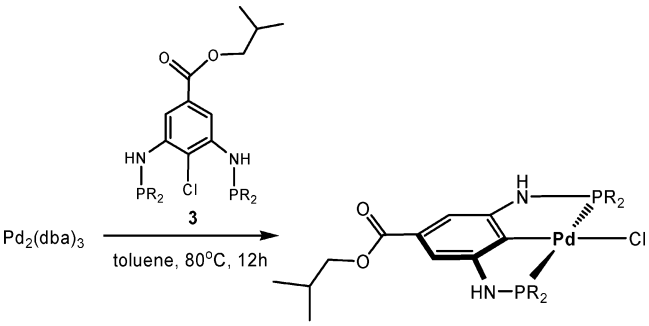

**Scheme 2**[a]




**4a - c** M =Ni, X = Cl, R = H
**5a - c** M = Pd, X = Cl, R = H
**6a, 6d, 6e** M = Pd, X = Cl, R = $CF_3$
**7a - c** M = Pt, X = Br, R = H
**8a - d** M = Pd, X = TFA, R = H

[a] (i) $NiCl_2·6H_2O$, EtOH, reflux, 12 h, (ii) $Pd(COD)Cl_2$, toluene, 110 °C, 5 h; (iii) $Pt(COD)Br_2$, $NEt_3$ (1 equiv), toluene, 110 °C, 5 h; (iv) $Pd(TFA)_2$, THF, rt, 3 h.

**Scheme 3**




**9a, 9e**

## Results and Discussion

The new PCP ligands **1**, **2**, and **3** are conveniently prepared by treatment of 1,3-diaminobenzene, 5-trifluoromethyl-1,3-diaminobenzene, and 3,5-diamino-4-chloroisobutylbenzoate, respectively, with the respective $R_2PCl$ (2 equiv) in the presence of $NEt_3$ and/or *n*-BuLi (Scheme 1). All PCP ligands are air stable in the solid state and in oxygen-free solutions. They have been characterized by $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Most diagnostic is the $^{31}P\{^1H\}$ NMR spectrum, exhibiting one singlet in the range of 27.0 to 146.7 ppm.

From the array of PCP ligands **1**−**3** we exemplarily tested some for the complexation with various Ni, Pd, and Pt precursors as shown in Schemes 2 and 3. The PCP complexes of Ni(II) (**4a**−**c**) were prepared by the reaction of $NiCl_2·6H_2O$ with the ligands **1a**−**c** according to Scheme 2. It is important to note that small amounts of water apparently do not cause hydrolysis resulting in cleavage of the P−N bonds of the PCP ligands. Palladium PCP complexes **5a**−**f**, **6a**, **6d**, and **6e** are easily prepared by treatment of $Pd(COD)Cl_2$ with 1 equiv of the corresponding ligands **1** and **2**, respectively, according to Scheme 2. The analogous platinum PCP complexes **7a**−**c** were prepared in similar fashion by treatment of $Pt(COD)Br_2$ with ligands **1a**−**c** in the presence of 1 equiv of $NEt_3$. Palladium PCP complexes **8a**−**d**, featuring a coordinated TFA ligand (TFA = $CF_3COO^-$), are obtained by the reaction of $Pd(TFA)_2$ with 1 equiv of **1a**−**d** in THF at room temperature for 3 h. Surprisingly, in the case of **1e** and **1f** the corresponding PCP complexes turned out to be unstable, and decomposition to several intractable materials took place.

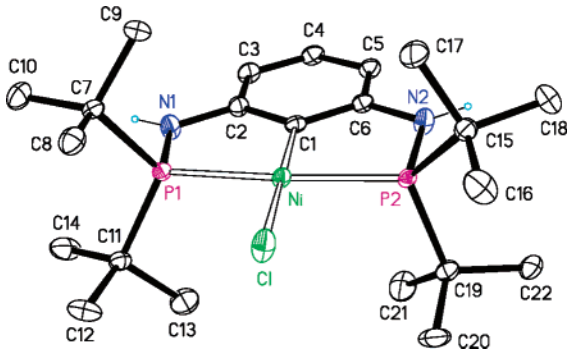



**Figure 1.** Structural view of Ni(PCP-$Bu^t$)Cl (**4c**) showing 50% thermal ellipsoids (C-bonded H atoms are omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Ni−C(1) 1.912(2), Ni−P(1) 2.213(1), Ni−P(2) 2.201(1), Ni−Cl 2.232(1), P(1)−Ni−P(2) 166.82(3), C(1)−Ni−P(1) 84.0(1), C(1)−Ni−P(2) 83.5(1), Cl−Ni−P(1) 96.46(2), Cl−Ni−P(2) 96.15(2).

Alternatively, palladium PCP complexes could also be generated via an oxidative addition route. Accordingly, addition of 2 equiv of ligands **3a** and **3e** to $Pd_2(dba)_3$ in toluene at 80 °C for 12 h afforded complexes **9a** and **9e**, respectively, in high isolated yields (Scheme 3). Due to the introduction of a COO-*i*-Bu substituent into the arene ring, these palladium PCP complexes exhibit very high solubility in most organic solvents, including $CH_2Cl_2$ and $Et_2O$.

All these complexes are thermally stable and can be handled in air. They have been characterized by a combination of elemental analysis and $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. In addition, the solid-state structures of Ni(PCP-Ph)Cl (**4a** as the solvate **4a**·$^1/_2C_6H_6$), Ni(PCP-$Bu^t$)Cl (**4c**), Pd(PCP-Ph)Cl (**5a** as the solvate **5a**·2DMF), Pd($PCP^F$-Ph)Cl (**6a** as the solvate **6a**·$CH_3CN$), Pt(PCP-Ph)Cl (**7a** as the cocrystal **7a**·$[NEt_3H]Br·CH_2Cl_2$; this compound crystallized spontaneously when the reaction of $Pt(COD)Br_2$ with *N*,*N*′-bis(diphenylphosphino)-1,3-benzenediamine and triethylamine was carried out in dichloromethane), Pd(PCP-$Pr^i$)(TFA) (**8b**), and Pd(PCP-BIPOL)(TFA) (**8d** as the solvate **8d**·$2Et_2O$) were determined by single-crystal X-ray diffraction. ORTEP diagrams of **4c**, **6a**, **8b**, and **8d** are depicted in Figures 1−4, with selected bond distances and angles reported in the captions. Structural views of **4a**, **5a**, and **7a** are given in the Supporting Information, Figures S1−S3. The molecular structures of all these compounds show the metal in a typical distorted-square-planar conformation with the PCP ligands coordinated to the metal center in a tridentate meridional mode. The aminophosphine nitrogen atoms are typically active hydrogen bond donors to suitable acceptor atoms, e.g., an $Et_2O$ solvent oxygen in the case of **8d**·$2Et_2O$, as shown in Figure 4. It is remarkable that the complex Pd(PCP-$Pr^i$)(TFA) (**8b**) (Figure 3) is stabilized in the solid state by a clear-cut intramolecular donor coordination between the TFA oxygen O(2) and the phosphine atom P(1).[15] The corre-

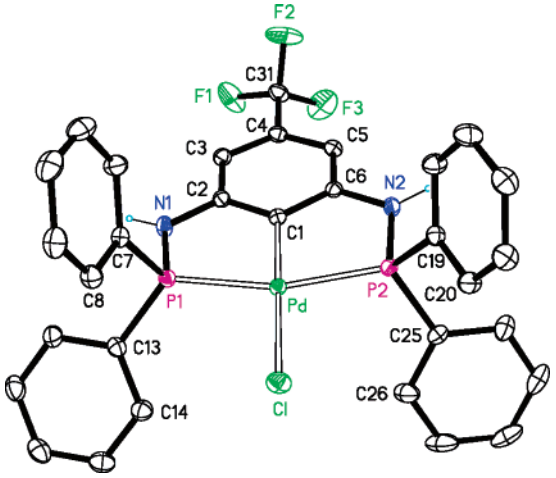



**Figure 2.** Structural view of Pd(PCP$^{F}$-Ph)Cl·$CH_3CN$ (**6a**·$CH_3CN$) showing 50% thermal ellipsoids (C-bonded H atoms and $CH_3CN$ omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Pd−C(1) 2.000(2), Pd−P(1) 2.2768(3), Pd−P(2) 2.2831(3), Pd−Cl 2.3950(3), P(1)−Pd−P(2) 163.18(1), C(1)−Pd−P(1) 81.63(3), C(1)−Pd−P(2) 81.97(3), Cl−Pd−P(2) 98.42(1), Cl−Pd−P(2) 98.16(1).

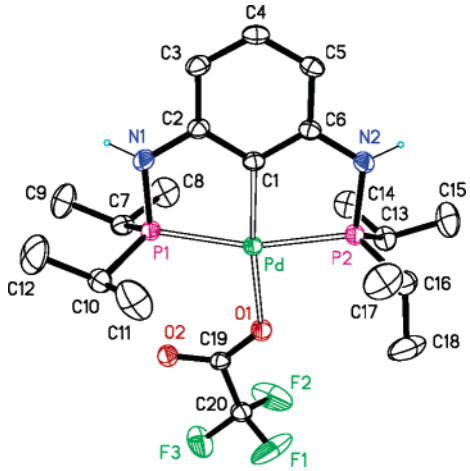



**Figure 3.** Structural view of Pd(PCP-Pr$^{i}$)(TFA) (**8b**) showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Pd−C(1) 1.988(1), Pd−P(1) 2.2988(4), Pd−P(2) 2.2830(4), Pd−O(1) 2.131(1), P(1)−N(1) 1.685(1), P(2)−N(2) 1.676(1), P(1)−Pd−P(2) 164.45(2), C(1)−Pd−P(1) 82.34(5), C(1)−Pd−P(2) 82.30(5), O(1)−Pd−P(1) 103.40(3), O(1)−Pd−P(2) 91.79(3); donor interaction O(2)···P(1) 3.114(1).

sponding distance P(1)−O(2) = 3.114(1) Å is shorter than the distance limit of 3.35 Å given by Holmes (2004).[15] This behavior is at variance with complex **8d** (Figure 4), where phosphorus is more polarized by one P−N and two P−O bonds and less prone to such interaction with the result that the TFA group points away from phosphorus and adopts an orientation inclined to the PCP main plane.

Palladium complexes containing PCP ligands have been found to be excellent catalysts for various C−C bond forming reactions including the Heck reaction[16] and the Suzuki−Miyaura coupling.[17] Accordingly, the catalytic activity of some of the palladium PCP complexes (**5a**, **5d**, **8a**, and **8d**) was tested in

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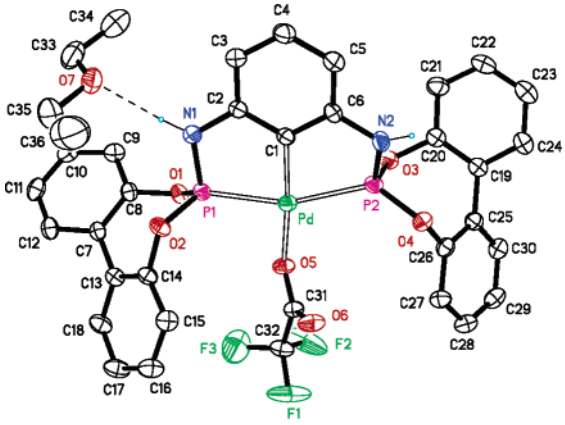
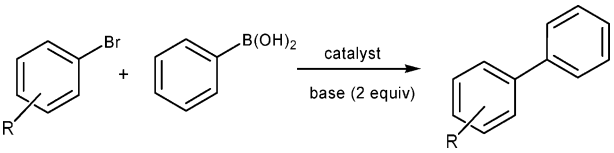



**Figure 4.** Structural view of Pd(PCP-BIPOL)(TFA)·$2Et_2O$ (**8d**·$2Et_2O$) showing 50% thermal ellipsoids (C-bonded H atoms and second $Et_2O$ omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Pd−C(1) 2.003(3), Pd−P(1) 2.262(1), Pd−P(2) 2.299(1), Pd−O(5) 2.124(2), P(1)−N(1) 1.630(3), P(2)−N(2) 1.631(3), P(1)−Pd-P(2) 159.20(3), C(1)−Pd−P(1) 80.5(1), C(1)−Pd−P(2) 79.4(1), O(5)−Pd−P(1) 95.3(1), O(5)−Pd−P(2) 104.4(1); hydrogen bonds N(1)···O(7) 2.893(4), N(2)···O(6′) 2.868(3) (not shown).

**Table 1. Yields of the Suzuki−Miyaura Cross Coupling of Aryl Bromides with Phenyl Boronic Acid Catalyzed by 5a, 5d, 8a, and 8d**[a]




| entry | R | catalyst | yield (%) | TON |
|---|---|---|---|---|
| 1 | 4-COMe | **5a** (0.01) | >99 | $9.9 \times 10^5$ |
| 2 | 4-COMe | **5a** (0.0001) | >99 | $9.9 \times 10^5$ |
| 3 | 4-COMe | **5a** (0.00001) | 97 | $9.7 \times 10^6$ |
| 4 | 4-OMe | **5a** (0.01) | 94 | 9900 |
| 5 | 4-OMe | **5a** (0.001) | 77 | $7.7 \times 10^4$ |
| 6 | 4-OMe | **5a** (0.0001) | 18 | $1.8 \times 10^5$ |
| 7 | 4-Me | **5a** (0.01) | >99 | 9900 |
| 8 | 4-Me | **5a** (0.001) | 72 | $7.2 \times 10^4$ |
| 9 | 4-Me | **5a** (0.0001) | 44 | $4.4 \times 10^5$ |
| 10 | 4-$NO_2$ | **5a** (0.01) | 81 | 8100 |
| 11 | 2-Et | **5a** (0.01) | 65 | 6500 |
| 12 | 2-bromopyridine | **5a** (0.01) | 68 | 6800 |
| 13 | 1-bromododecane | **5a** (0.01) | 74 | 7400 |
| 14 | 4-COMe | **5d** (0.01) | >99 | 9900 |
| 15 | 4-OMe | **5d** (0.01) | >99 | 9900 |
| 16 | 4-COMe | **8a** (0.01) | >99 | 9900 |
| 17 | 4-COMe | **8a** (0.001) | 15 | $1.5 \times 10^4$ |
| 18 | 4-Me | **8a** (0.01) | 70 | 7000 |
| 19 | 4-OMe | **8a** (0.1) | 88 | 880 |
| 20 | 4-COMe | **8d** (0.01) | >99 | 9900 |
| 21 | 4-COMe | **8d** (0.001) | 36 | 3600 |

[a] Reaction conditions: 1.0 mmol of bromide, 1.5 mmol of $PhB(OH)_2$, 2.0 mmol of $K_2CO_3$, 5 mL of toluene, 110 °C, reaction time is 16 h, yields represent isolated yields (average of at least three experiments) of compounds estimated to be ≥95% pure as judged by $^1H$ NMR.

the Suzuki−Miyaura coupling of aryl and alkyl bromides and phenylboronic acid. These complexes show high activity in the catalytic coupling of aryl and alkyl bromides with phenylboronic acid (Table 1). The catalyst remains highly active after the reaction is complete, and upon addition of more substrates, catalysis is resumed, leading to the coupled product in quantitative yield at essentially the same rate. In general, the chloro complexes **5a** and **5d** are better catalysts than the respective TFA complexes **8a** and **8d**. The reaction of 4-bromoacetophenone

with phenylboronic acid and **5a** as catalyst proceeds with 97% isolated yield even with 0.00001 mol % catalyst (TON = $9.7 \times 10^6$), while the electronically deactivated and thus more challenging substrate 4-bromoanisole can still be coupled in 18% yield with a catalyst loading of 0.0001 mol % (TON = $1.8 \times 10^5$). These conditions have not been optimized, and thus tuning of steric and electronic properties by ligand variations is expected to result in more enhanced catalytic reactivity.

## Concluding Remarks

In sum, we have shown that both achiral and chiral PCP ligands are conveniently generated by reacting readily available parent 1,3-diaminobenzene or derivatives thereof with a series of $R_2PCl$ compounds. These new ligands form very stable square-planar Ni(II), Pd(II), and Pt(II) PCP complexes. The palladium complexes are efficient catalysts for the coupling of aryl and alkyl bromides and phenylboronic acid. In some instances TONs in the range of $10^5-10^6$ have been achieved that are among the highest reported thus far. We are currently studying our new PCP ligands in conjunction with other transition metals including Mo, W, Fe, Ru, Rh, and Ir. These studies will be reported in due course.

## Experimental Section

**General Procedures.** All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. The solvents were purified according to standard procedures.[18] The starting materials $PPh_2Cl$, $PPr^i_2Cl$, and $PBu^t_2Cl$, 1,3-diaminobenzene, 5-triflouromethyl-1,3-diaminobenzene, and 3,5-diamino-4-chloroisobutylbenzoate were purchased from Aldrich and used without further purification. 2-Chlorodibenzo[*d*,*f*][1,3,2]dioxaphosphepine,[19] S-2-chlorodinaphtho[2,1-*d*:1′2′-*f*][1,3,2]dioxaphosphepine,[20] 2-chloro-(4*R*,5*R*)-dicarbomethoxy-1,3,2-dioxaphospholane, and 2-chloro-(4*R*,5*R*)-dicarboisopropoxy-1,3,2-dioxaphospholane[21] were prepared according to the literature. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE-250 spectrometer and were referenced to $SiMe_4$ and $H_3PO_4$ (85%), respectively. $^1H$ and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by $^1H$-COSY, 135-DEPT, and HMQC-($^1H-^{13}C$) experiments.

***N*,*N*′-Bis(diphenylphosphino)-1,3-benzenediamine (PCP-Ph) (1a).** To a suspension of 1,3-diaminobenzene (5.0 g, 46 mmol) in toluene (75 mL) was added triethylamine (11.2 mL, 92 mmol). The mixture was then cooled to 0 °C, $PPh_2Cl$ (16.5 mL, 92 mmol) was added in a dropwise fashion, and the solution was allowed to reach room temperature and stirred overnight at 80 °C. After that, the solution was filtered and the solvent was removed under vacuum. The remaining yellow oil was recrystallized from toluene/*n*-hexane (1:1). Yield: 13.2 g (84%). Anal. Calcd for $C_{30}H_{26}N_2P_2$: C, 75.62; H, 5.50; N, 5.88. Found: C, 75.24; H, 5.16; N, 6.15. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 7.43−7.32 (m, 20H, PPh), 6.99 (t, $J$ = 8.0 Hz, 1H, $Ph^4$), 6.72 (t, $J$ = 2.1 Hz, 1H, $Ph^{ipso}$), 6.50 (d, $J$ = 8.0 Hz, 2H, $Ph^{3,5}$), 4.39 (d, $J$ = 8.2 Hz, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 147.7 (d, $J$ = 16.5 Hz, $C^{Ph}$), 140.2 (d, $J$ = 11.9 Hz, $C^{PPh}$), 131.3 (d, $J$ = 20.7 Hz, $C^{PPh}$), 130.1 ($C^{Ph}$), 129.1 ($C^{PPh}$), 128.6 (d, $J$ = 6.5 Hz, $C^{PPh}$), 107.3 (d, $J$ = 13.8 Hz, $C^{Ph}$), 103.3 (t, $J$ = 13.4 Hz, $C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 28.6.

***N*,*N*′-Bis(diisopropylphosphino)-1,3-benzenediamine (PCP-Pr$^i$) (1b).** This ligand has been prepared analogously to **1a** with triethylamine (8.0 mL, 66 mmol), 1,3-diaminobenzene (3.6 g, 33 mmol), and $PPr^i_2Cl$ (10.0 g, 66 mmol) as the starting materials. Yield: 8.8 g (79%). Anal. Calcd for $C_{18}H_{33}N_2P_2$: C, 63.70; H, 9.80; N, 8.25. Found: C, 63.24; H, 10.01; N, 8.15. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 6.92 (t, $J$ = 8.0 Hz, 1H, $Ph^4$), 6.64 (t, $J$ = 2.2 Hz, 1H, $Ph^{ipso}$), 6.37 (d, $J$ = 8.0 Hz, 2H, $Ph^{3,5}$), 3.63 (d, $J$ = 10.5 Hz, 2H, N*H*), 1.75−1.68 (m, 4H, C*H*$(CH_3)_2$), 1.12−1.02 (m, 24H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 149.6 (d, $J$ = 17.2 Hz, $C^{Ph}$), 129.5 ($C^{Ph}$), 106.5 (d, $J$ = 12.1 Hz, $C^{Ph}$), 103.4 (t, $J$ = 12.4 Hz, $C^{Ph}$), 26.6 (d, $J$ = 9.8 Hz, *C*H$(CH_3)_2$), 18.7 (d, $J$ = 20.1 Hz, CH(*C*H$_3)_2$), 17.1 (d, $J$ = 7.5 Hz, CH(*C*H$_3)_2$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 48.9.

***N*,*N*′-Bis(di-*tert*-butylphosphino)-1,3-benzenediamine (PCP-Bu$^t$) (1c).** Triethylamine (6.0 mL, 42 mmol) was added to a solution of 1,3-diaminobenzene (0.6 g, 5.3 mmol) in THF; the reaction mixture was then cooled to 0 °C, and $PBu^t_2Cl$ (2.0 mL, 10.5 mmol) was added. Upon cooling to −80 °C, *n*-BuLi (10.5 mmol, 5.0 mL of a 2.1 M solution in hexane) was added and the reaction was allowed to reach room temperature and stirred overnight. After that, the solution was filtered and the solvent was removed under vacuum; the white solid obtained was used without further purification. Yield: 2.0 g (96%). Anal. Calcd for $C_{22}H_{42}N_2P_2$: C, 66.64; H, 10.68; N, 7.06. Found: C, 67.11; H, 10.43; N, 10.45. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 6.89 (t, $J$ = 7.9 Hz, 1H, $Ph^4$), 6.73 (t, $J$ = 2.3 Hz, 1H, $Ph^{ipso}$), 6.36 (d, $J$ = 7.9 Hz, 2H, $Ph^{3,5}$), 3.96 (d, $J$ = 11.0 Hz, 2H, N*H*), 1.12 (d, $J$ = 11.9 Hz, 36H, C(C*H*$_3)_3$). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 150.1 (d, $J$ = 16.7 Hz, $C^{Ph}$), 129.6 ($C^{Ph}$), 106.5 (d, $J$ = 12.1 Hz, $C^{Ph}$), 103.5 (t, $J$ = 11.2 Hz, $C^{Ph}$), 34.2 (d, $J$ = 19.0 Hz, *C*$(CH_3)_3$), 28.1 (d, $J$ = 14.9 Hz, C(*C*H$_3)_3$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 59.3.

***N*,*N*′-Bis(dibenzo[*d*,*f*][1,3,2]dioxaphosphepine)-1,3-benzenediamine (PCP-BIPOL) (1d).** 1,3-Diaminobenzene (0.4 g, 4.0 mmol) and triethylamine (1.2 mL, 8.0 mmol) were dissolved in THF (25 mL), and the solution was cooled to 0 °C. 2-Chlorodibenzo-[*d*,*f*][1,3,2]dioxaphosphepine (2.0 g, 8.0 mmol) was then added dropwise under ice cooling, and a white precipitate was formed immediately. The mixture was stirred at 50 °C for 16 h. The precipitate of triethylammonium chloride was removed by filtration, the solvent evaporated, and the residue dried in under vacuum. Yield: 1.94 g (91%). Anal. Calcd for $C_{30}H_{22}N_2O_4P_2$: C, 67.17; H, 4.13; N, 5.22. Found: C, 67.24; H, 4.16; N, 5.13. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 7.50−7.10 (m, 16H, Biph), 7.03 (t, $J$ = 7.9 Hz, 1H, $Ph^4$), 6.67 (d, $J$ = 6.5 Hz, $Ph^{3,5}$), 6.37 (d, $J$ = 7.8 Hz, $Ph^{ipso}$), 5.25 (d, $J$ = 4.9 Hz, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 149.5 ($C^{Biph}$), 142.8, ($C^{Ph}$) 142.5 ($C^{Ph}$), 131.7 ($C^{Biph}$), 131.6 ($C^{Biph}$), 130.5 ($C^{Ph}$), 129.8 ($C^{Biph}$), 129.3 ($C^{Biph}$), 125.3 ($C^{Biph}$), 122.3 ($C^{Biph}$), 111.2 (d, $J$ = 13.9 Hz, $C^{Ph}$), 107.5 (t, $J$ = 12.2 Hz, $C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 146.7.

***N*,*N*′-Bis(4*R*,5*R*-dicarbomethoxy-1,3,2-dioxaphospholane)-1,3-diaminobenzene (PCP-TAR$^{Me}$) (*R*,*R*-1e).** To a solution of 1,3-diaminobenzene (446 mg, 4.12 mmol) and triethylamine (1.2 mL, 8.6 mmol) in THF (12 mL) was added dropwise 2-chloro-(4*R*,5*R*)-dicarbomethoxy-1,3,2-dioxaphospholane (2.0 g, 8.24 mmol) under ice cooling. The mixture was stirred for 16 h at room temperature. The precipitate of triethylammonium chloride was removed by filtration, the solvent evaporated, and the residue dried in under vacuum. The product was a highly viscous yellow oil, which solidified after a few days of storage in the refrigerator. Yield: 2.09 g (98%). Anal. Calcd for $C_{18}H_{22}N_2O_{12}P_2$: C, 41.55; H, 4.26; N, 5.38. Found: C, 42.06; H, 4.36; N, 5.45. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 7.05 (t, $J$ = 7.7 Hz, $Ph^4$), 6.63 (s, 2H, $Ph^{3,5}$), 6.59 (s, 1H, $Ph^{ipso}$), 6.28 (d, $J$ = 3.2 Hz, 2H, N*H*), 4.97 (t, $J$ = 3.4 Hz, 2H,

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C*H*), 4.81 (d, $J$ = 4.3 Hz, 1H, G*H*), 4.76 (d, $J$ = 4.4 Hz, 1H, C*H*), 3.87 (s, 6H, C$H_3$), 3.85 (s, 6H, C$H_3$). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 171.5, (*C*O) 169.2 (*C*O), 142.3 (d, $J$ = 17.3 Hz, $C^{Ph}$), 131.0 ($C^{Ph}$), 111.5 (d, $J$ = 13.9 Hz, $C^{Ph}$), 107.4 (t, $J$ = 12.5 Hz, $C^{Ph}$), 76.8 (*C*H), 76.7 (*C*H), 76.3 (*C*H), 76.1 (*C*H), 53.4, (C$H_3$), 53.1 (C$H_3$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 145.2.

***N,N′*-Bis(4*R*,5*R*-dicarboisopropoxy-1,3,2-dioxaphospholane)-1,3-benzenediamine (PCP-TAR$^{Pr}$) (*R,R*-1f).** This ligand has been prepared analogously to ***R,R*-1e** with 1,3-diaminobenzene (362 mg, 3.35 mmol), 2-chloro-(4*R*,5*R*)-dicarboisopropoxy-1,3,2-dioxaphospholane (2.0 g, 6.7 mmol), and triethylamine (1.0 mL, 7.0 mmol) as the starting materials. Yield: 2.1 g (99%). Anal. Calcd for $C_{26}H_{38}O_{12}N_2P_2$: C, 49.37; H, 6.05; N, 4.43. Found: C, 49.46; H, 6.26; N, 4.31. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 7.03 (t, $J$ = 8.0 Hz, 1H, $Ph^4$), 6.59 (s, 2H, $Ph^{3,5}$), 6.56 (s, 1H, $Ph^{ipso}$), 6.32 (d, $J$ = 4.4 Hz, 2H, N*H*), 5.13 (m, 4H, C*H*(C$H_3$)$_2$), 4.83 (m, 2H, C*H*), 4.63 (d, $J$ = 5.1 Hz, 2H, C*H*), 4.59 (d, $J$ = 5.1 Hz, 2H, C*H*) 1.31 (m, 24H, CH(C$H_3$)$_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 170.8 (*C*O), 168.1 (*C*O), 142.5 (d, $J$ = 17.2 Hz, $C^{Ph}$), 130.0 ($C^{Ph}$), 111.1 (d, $J$ = 13.8 Hz, $C^{Ph}$), 106.92 (t, $J$ = 12.4 Hz, $C^{Ph}$), 76.8 (*C*H), 76.7 (*C*H), 70.8 (*C*H(C$H_3$)$_2$), 70.3 (*C*H(C$H_3$)$_2$), 21.6 (m, CH(*C*$H_3$)$_2$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 144.1.

***N,N′*-Bis(diphenylphosphino)-5-(trifluoromethyl)-1,3-benzenediamine (PCP$^F$-Ph) (2a).** Triethylamine (0.4 mL, 2.84 mmol) was added to a solution of 5-(trifluoromethyl)-1,3-benzenediamine (250 mg, 1.42 mmol) in THF; the reaction mixture was then cooled to 0 °C and $PPh_2Cl$ (0.5 mL, 2.84 mmol) was added, whereupon a white solid immediately precipitated. The mixture was stirred overnight at room temperature. Insoluble materials were then removed by filtration. The solvent was removed under vacuum, yielding a colorless oil. Yield: 725 mg (94%). Anal. Calcd for $C_{31}H_{24}F_3N_2P_2$: C, 68.51; H, 4.45; N, 5.15. Found: C, 68.59; H, 4.36; N, 5.35. $^1H$ NMR ($\delta$, $CDCl_3$, 20°C): 7.81−7.75 (m, 2H, PPh), 7.63−7.57 (m, 2H, PPh), 7.43−7.24 (m, 16H, PPh), 6.88 (s, 1H, $Ph^{ipso}$), 6.76 (s, 1H, $Ph^{3,5}$), 4.56 (d, $J$ = 8.2 Hz, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 148.2 (d, $J$ = 18.3 Hz, $C^{Ph}$), 139.5 (d, $J$ = 11.4 Hz, $C^{PPh}$), 131.2 (d, $J$ = 20.85 Hz, $C^{PPh}$), 130.3 ($C^{Ph}$), 129.3 ($C^{PPh}$), 128.6 (t, $J$ = 5.4 Hz, $C^{PPh}$), 105.5 (t, $J$ = 16.4 Hz, $C^{Ph}$), 103.7 (t, $J$ = 4.4 Hz, $C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 27.0.

***N,N′*-Bis(dibenzo[*d,f*][1,3,2]dioxaphosphepine)-5-(trifluoromethyl)-1,3-benzenediamine (PCP$^F$-BIPOL) (2d).** This ligand has been prepared analogously to **2a** with 5-(trifluoromethyl)-1,3-benzenediamine (250 mg, 1.42 mmol), 2,2′-biphenylylenephosphochloridite (712 mg, 2.84 mmol), and triethylamine (0.4 mL, 3.0 mmol) as the starting materials. Toluene instead of THF was used as the solvent. Yield: 760 mg (89%). Anal. Calcd for $C_{31}H_{21}F_3N_2O_4P_2$: C, 61.60; H, 3.50; N, 4.63. Found: C, 61.64; H, 3.70; N, 4.65. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 7.52−7.20 (m, 16H, Biph), 6.87 (s, 2H, $Ph^{3,5}$), 6.81 (s, 1H, $Ph^{ipso}$), 5.42 (s, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 149.6 ($C^{Biph}$), 148.2 ($C^{Ph}$), 143.8 ($C^{Ph}$), 143.6 ($C^{Ph}$), 131.8 ($C^{Biph}$), 130.5 ($C^{Biph}$), 129.7 ($C^{Biph}$), 125.8 ($C^{Biph}$), 122.1 ($C^{Biph}$), 109.4 (t, $J$ = 11.4 Hz, $C^{Ph}$), 107.5 (d, $J$ = 12.1 Hz, $C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 145.1.

***N,N′*-Bis(4*R*,5*R*-dicarbomethoxy-1,3,2-dioxaphospholane)-5-(trifluoromethyl)-1,3-benzenediamine (PCP$^F$-TAR$^{Me}$) (*R,R*-2e).** This ligand was prepared analogously to **2a** with 5-(trifluoromethyl)-1,3-phenylenediamine (250 mg, 1.42 mmol), 2-chloro-(4*R*,5*R*)-dicarbomethoxy-1,3,2-dioxaphospholane (688 mg, 2.84 mmol), and triethylamine (0.4 mL, 3.0 mmol) as the starting materials. Yield: 670 mg (80%). Anal. Calcd for $C_{19}H_{21}F_3N_2O_{12}P_2$: C, 38.79; H, 3.60; N, 4.76. Found: C, 38.88; H, 3.77; N, 4.81. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 6.80 (s, 2H, $Ph^{3,5}$), 6.54 (s, 2H, N*H*), 6.47 (s, 1H, $Ph^{ipso}$), 4.96 (m, 2H, C*H*), 4.83−4.77 (m, 2H, C*H*), 3.87 (s, 6H, C$H_3$), 3.84 (s, 6H, C$H_3$). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 171.6 (*C*O), 168.6 ($C^{Ph}$), 148.0 ($C^{Ph}$), 109.1 (t, $J$ = 14.4 Hz, $C^{Ph}$), 105.0 ($C^{Ph}$), 76.9 (*C*H), 76.8 (*C*H), 76.3 (*C*H), 76.2 (*C*H), 53.5 (C$H_3$), 53.2 (C$H_3$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 144.9.

***N,N′*-Bis(diphenylphosphino)-3,5-diamino-4-chloroisobutylbenzoate (PCP$^E$-Ph) (3a).** Triethylamine (0.3 mL, 2.10 mmol) was added to a solution of 3,5-diamino-4-chloroisobutylbenzoate (250 mg, 1.03 mmol) in THF; the reaction mixture was then cooled to 0 °C and $PPh_2Cl$ (0.4 mL, 2.10 mmol) was added, whereupon a white solid immediately precipitated. The mixture was stirred overnight at 50 °C and filtered, and the solvent was removed under vacuum, yielding a white solid. Yield: 486 mg (82%). Anal. Calcd for $C_{35}H_{33}ClN_2O_2P_2$: C, 64.80; H, 5.44; N, 4.58. Found: C, 64.84; H, 5.56; N, 4.39. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 7.61−7.36 (m, 23H, PPh, $Ph^{3,5}$ and $Ph^{ipso}$), 5.10 (d, $J$ = 7.3 Hz, 2H, N*H*), 4.02 (q, $J$ = 6.7 Hz, 2H, C$H_2$), 2.0 (m, $J$ = 6.7 Hz, 1H, C*H*(C$H_3$)$_2$), 0.95 (d, $J$ = 6.7 Hz, 6H, CH(C$H_3$)$_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 166.3 (*C*O), 143.4 (t, $J$ = 19.6 Hz, $C^{Ph}$), 139.4 (d, $J$ = 12.6 Hz, $C^{PPh}$), 131.2 (d, $J$ = 20.9 Hz, $C^{PPh}$), 130.3 ($C^{Ph}$), 129.3 ($C^{PPh}$), 128.6 (t, $J$ = 6.3 Hz, $C^{PPh}$), 107.2 ($C^{Ph}$), 106.4 ($C^{Ph}$), 70.9 (*C*$H_2$), 27.8 (*C*H(C$H_3$)$_2$), 19.1 (CH(*C*$H_3$)$_2$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 30.6.

***N,N′*-Bis(4*R*,5*R*-dicarbomethoxy-1,3,2-dioxaphospholane)-3,5-diamino-4-chloroisobutylbenzoate (PCP$^E$-Tar$^{Me}$) (*R,R*-3e).** This ligand has been prepared analogously to **3a** with 3,5-diamino-4-chloroisobutylbenzoate (250 mg, 1.03 mmol), 2-chloro-(4R,5R)-dicarbomethoxy-1,3,2-dioxaphospholane (500 mg, 2.06 mmol), and triethylamine (0.4 mL, 3.0 mmol) as the starting materials. Yield: 660 mg (98%). Anal. Calcd for $C_{23}H_{29}ClN_2O_{14}P_2$: C, 42.18; H, 4.46; N, 4.28. Found: C, 41.98; H, 4.66; N, 4.19. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 6.89 (d, $J$ = 3.5 Hz, $Ph^{3,5}$), 6.81 (d, $J$ = 3.6 Hz, 2H, N*H*), 5.00 (m, 2H, C*H*), 4.83−4.77 (m, 2H, C*H*), 4.04 (t, $J$ = 6.3 Hz, 2H, C$H_2$$^i$Bu), 3.87(s, 6H, C$H_3$) 3.84 (s, 6H, C$H_3$), 2.06 (m, 1H, C*H*$^i$Bu), 0.98 (d, $J$ = 6.8 Hz, 6H, CH$_3$$^i$Bu). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 171.2 (*C*OOCH$_3$), 168.8 (*C*OOCH$_3$), 165.6 (*C*O$^i$Bu), 143.7 ($C^{Ph}$), 139.7 ($C^{Ph}$), 139.4 ($C^{Ph}$), 133.4 ($C^{Ph}$), 109.6 ($C^{Ph}$), 77.0 (*C*H), 76.8 (*C*H), 76.7 (*C*H), 76.4 (*C*H), 71.1 (*C*H$_2$$^i$Bu), 53.5 (*C*H$_3$), 53.2 (*C*H$_3$), 27.8 (*C*H$^i$Bu), 19.2 (*C*H$_3$$^i$Bu). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 143.7.

**Ni(PCP-Ph)Cl (4a).** To a suspension of **1a** (300 mg, 0.63 mmol) in ethanol (10 mL) was added $NiCl_2 \cdot 6H_2O$ (78 mg, 0.63 mmol), whereupon the solution turned orange. The mixture was refluxed overnight, and the precipitated orange solid was collected on a glass frit, washed twice with pentane, and dried under vacuum. Yield: 316 mg (88%). Anal. Calcd for $C_{30}H_{25}ClN_2NiP_2$: C, 63.25; H, 4.42; N, 4.92. Found: C, 63.04; H, 4.32; N, 5.10. $^1H$ NMR ($\delta$, $C_6D_6$, 20 °C): 8.08 (d, $J$ = 5.5 Hz, 2H, N*H*), 7.56 (q, $J$ = 6.3 Hz, 8H, Ph), 7.07−7.04 (m, 12H, Ph), 6.90 (s, 1H, $Ph^4$), 6.39 (d, $J$ = 7.6 Hz, 2H, $Ph^{3,5}$). $^{13}C\{^1H\}$ NMR ($\delta$, $C_6D_6$, 20 °C): 159.2 (t, $J$ = 17.0 Hz, $C^{Ph}$), 134.2 (t, $J$ = 23.9 Hz, $C^{PPh}$), 132.5 (t, $J$ = 6.9 Hz, $C^{PPh}$), 131.8 (d, $J$ = 2.3 Hz, $C^{PPh}$), 130.7 (d, $J$ = 11.5 Hz, $C^{Ph}$), 128.5 (t, $J$ = 12.4 Hz, $C^{PPh}$), 103.0 (t, $J$ = 8.3 Hz, $C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $C_6D_6$, 20 °C): 77.8.

**Ni(PCP-Pr$^i$)Cl (4b).** This complex has been prepared analogously to **4a** with $NiCl_2 \cdot 6H_2O$ (137 mg, 0.58 mmol) and **1b** (200 mg, 0.58 mmol) as the starting materials. Yield: 181 mg (72%). Anal. Calcd for $C_{18}H_{33}ClN_2NiP_2$: C, 49.86; H, 7.67; N, 6.46. Found: C, 49.74; H, 7. 50; N, 7.02. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 6.61 (s, 1H, $Ph^4$), 5.94 (s, 2H, $Ph^{3,5}$), 3.95 (s, 2H, N*H*), 2.22 (s, 4H, C*H*(CH$_3$)$_2$, 1.36 (s, 24H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 160.7 ($C^{Ph}$), 131.1 ($C^{Ph}$), 127.3 ($C^{Ph}$), 101.1 ($C^{Ph}$), 26.3 (*C*H(CH$_3$)$_2$), 17.8 (CH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 110.8.

**Pd(PCP-Ph)Cl (5a).** $Pd(COD)Cl_2$ (179 mg, 0.63 mmol) was added to a solution of **1a** (300 mg, 0.63 mmol) in toluene (15 mL), and the mixture was refluxed for 5 h, whereupon a yellow solid precipitated, which was collected on a glass frit and washed twice with $Et_2O$ (10 mL). Yield: 350 mg (90%). Anal. Calcd for $C_{30}H_{25}ClN_2P_2Pd$: C, 58.37; H, 4.08; N, 4.54. Found: C, 58.24; H, 4.06; N, 4.35. $^1H$ NMR ($\delta$, DMSO, 20 °C): 8.00 (s, 2H, N*H*), 7.87−7.83 (m, 6H, PPh), 7.50−7.48 (m, 14H, PPh), 6.77 (t, $J$ =

7.8 Hz, 1H, Ph[4]), 6.23 (d, $J$ = 7.8 Hz, 2H, Ph[3,5]). $^{13}C\{^1H\}$ NMR ($\delta$, DMSO, 20 °C): 156.9 (t, $J$ = 14.1 Hz, $C^{Ph}$), 135.1 (t, $J$ = 25.0 Hz, $C^{PPh}$), 131.8 (t, $J$ = 7.8 Hz, $C^{PPh}$), 131.4 ($C^{PPh}$), 129.2 ($C^{Ph}$), 129.0 (t, $J$ = 5.2 Hz, $C^{PPh}$), 103.2 (t, $J$ = 10.1 Hz, $C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, DMSO, 20 °C): 76.9.

**Pd(PCP-Pr$^i$)Cl (5b).** This complex has been prepared analogously to **4a** with $Pd(COD)Cl_2$ (208 mg, 0.73 mmol) and **1b** (250 mg, 0.73 mmol) as the starting materials. Yield: 434 mg (96%). Anal. Calcd for $C_{18}H_{32}ClN_2P_2Pd$: C, 45.02; H, 6.72; N, 5.83. Found: C, 45.11; H, 7.00; N, 5.75. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 6.76 (t, $J$ = 7.7 Hz, 1H, Ph[4]), 6.14 (t, $J$ = 7.7 Hz, 2H, Ph[3,5]), 3.91 (s, 2H, N*H*), 2.40−2.29 (m, 4H C*H*$(CH_3)_2$), 1.42−1.20 (m, 24H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 157.3 (t, $J$ = 12.1 Hz, $C^{Ph}$), 127.0 ($C^{Ph}$), 124.0 ($C^{Ph}$), 101.9 (t, $J$ = 7.9 Hz, $C^{Ph}$), 27.3 (t, $J$ = 12.7 Hz, *C*H$(CH_3)_2$), 18.1 (CH(*C*H$_3)_2$), 17.3 (CH(*C*H$_3)_2$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 114.3.

**Pd(PCP$^F$-Ph)Cl (6a).** This complex has been prepared analogously to **5a** with $Pd(COD)Cl_2$ (75 mg, 0.27 mmol) and **2a** (145 mg, 0.27 mmol) as the starting materials. Yield: 150 mg (81%). Anal. Calcd for $C_{31}H_{24}ClF_3N_2P_2Pd$: C, 54.33; H, 3.53; N, 4.09. Found: C, 54.34; H, 3.59; N, 4.15. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 7.89−7.81 (m, 8H, PPh), 7.55−7.49 (m, 12H, PPh), 6.57 (s, 2H, Ph[3,5]), 5.12 (s, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 151.3 ($C^{Ph}$), 139.7 ($C^{PPh}$), 133.8 ($C^{Ph}$), 131.8 ($C^{PPh}$), 131.4 ($C^{PPh}$), 128.9 ($C^{PPh}$), 100.9 ($C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 81.4.

**Pd(PCP$^F$-BIPOL)Cl (6b).** A solution of $Pd(COD)Cl_2$ (71 mg, 0.25 mmol) and **2d** (150 mg, 0.25 mmol) in THF (10 mL) was stirred at room temperature for 16 h. During that time the product precipitated as a yellow solid. The solvent was removed in a vacuum, and the residue was washed with $Et_2O$ (2 × 10 mL) and dried under vacuum. Yield: 160 mg (87%). Anal. Calcd for $C_{31}H_{20}ClF_3N_2O_4P_2Pd$: C, 49.96; H, 2.70; N, 3.76. Found: C, 50.04; H, 2.80; N, 3.77. $^1H$ NMR ($\delta$, DMSO-$d_6$, 20 °C): 7.70−7.27 (m, 16H, Biph), 6.56 (s, 2H, Ph[3,5]), 5.92(s, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, DMSO-$d_6$, 20 °C): 149.8 ($C^{Biph}$), 149.2 ($C^{Ph}$), 147.7 ($C^{Ph}$), 147.5 ($C^{Ph}$), 141.1 ($C^{Ph}$), 131.1 ($C^{Biph}$), 130.5 ($C^{Biph}$), 130.4 ($C^{Biph}$), 129.1 ($C^{Biph}$), 129.8 ($C^{Biph}$), 123.0 ($C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, DMSO, 20 °C): 145.5.

**Pt(PCP-Ph)Br (7a).** A mixture of $Pt(COD)Br_2$ (50 mg, 0.11 mmol) and **1a** (53 mg, 0.11 mmol) in toluene was heated to 80 °C, and triethylamine (20 $\mu$L, 0.13 mmol) was added. The mixture was refluxed overnight and then filtered while hot. The solvent was removed under vacuum, and the pale yellow product was precipitated with $Et_2O$, collected on a glass frit, and washed twice with $Et_2O$ (10 mL). Yield: 77 mg (93%). Anal. Calcd for $C_{30}H_{25}BrN_2P_2Pt$: C, 48.01; H, 3.36; N, 3.73. Found: C, 48.34; H, 3.42; N, 3.15. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 7.93−7.84 (m, 8H, Ph), 7.50−7.41 (m, 12H, Ph), 6.89 (t, $J$ = 7.8 Hz, 1H, Ph[4]), 6.42−6.33 (q, $J$ = 8.1 Hz, 2H, Ph[3,5]), 5.35 (t, $J$ = 38.8 Hz, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 153.7 (t, $J$ = 12.0 Hz, $C^{Ph}$), 133.9 ($C^{PPh}$), 132.3 (t, $J$ = 7.6 Hz, $C^{PPh}$), 131.3 ($C^{PPh}$), 128.6 (t, $J$ = 5.7 Hz, $C^{PPh}$), 127.3 (t, $J$ = 5.7 Hz, $C^{Ph}$), 103.0 (t, $J$ = 7.6 Hz, $C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 76.1 (t, $J$ = 1604.0 Hz).

**Pt(PCP-Pr$^i$)Br (7b).** This complex has been prepared analogously to **5a** with $Pt(COD)Br_2$ (50 mg, 0.11 mmol), **1b** (38 mg, 0.11 mmol), and triethylamine (20 $\mu$L, 0.13 mmol) as the starting materials. Yield: 61 mg (91%). Anal. Calcd for $C_{18}H_{33}BrN_2P_2Pt$: C, 35.19; H, 5.41; N, 4.56. Found: C, 35.32; H, 5.22; N, 4.62. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 6.77 (t, $J$ = 7.8 Hz, 1H, Ph[4]), 6.24−6.13 (q, $J$ = 7.6 Hz, 2H, Ph[3,5]), 4.35 (t, $J$ = 37.9 Hz, 2H, N*H*), 2.60−2.48 (m, $J$ = 7.5 Hz, 4H, C*H*$(CH_3)_2$, 1.27−1.18 (m, 24H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 155.2 (t, $J$ = 10.7 Hz, $C^{Ph}$), 128.5 ($C^{Ph}$), 125.2 ($C^{Ph}$), 101.6 (t, $J$ = 6.6 Hz, $C^{Ph}$), 27.9 (t, $J$ = 16.7 Hz, *C*H$(CH_3)_2$), 16.7 (CH(*C*H$_3)_2$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 106.6 (t, $J$ = 1555.6 Hz).

**Pd(PCP-Ph)(TFA) (8a).** $Pd(TFA)_2$ (100 mg, 0.30 mmol) was added to a solution of **1a** (144 mg, 0.30 mmol) in THF, and the mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum and the product precipitated with $Et_2O$, collected on a glass frit, and washed twice with $Et_2O$ (10 mL). Yield: 187 mg (91%). Anal. Calcd for $C_{32}H_{25}F_3N_2OP_2Pd$: C, 56.61; H, 3.71; N, 4.13. Found: C, 56.24; H, 3.89; N, 4.35. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 7.81−7.72 (m, 8H, PPh), 7.48−7.43 (m, 12H, PPh), 6.86 (t, $J$ = 7.9 Hz, 1H, Ph[4]), 6.26 (d, $J$ = 8.0 Hz, 2H, Ph[3,5]), 4.67 (s, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 156.0 (t, $J$ = 13.8 Hz, $C^{Ph}$), 133.5 (t, $J$ = 25.0 Hz, $C^{PPh}$), 131.9 (t, $J$ = 8.1 Hz, $C^{PPh}$), 131.4 ($C^{PPh}$), 128.7 (t, $J$ = 5.5 Hz, $C^{PPh}$), 128.2 ($C^{Ph}$), 103.5 (t, $J$ = 9.2 Hz, $C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 82.1.

**Pd(PCP-Pr$^i$)(TFA) (8b).** This complex has been prepared analogously to **8a** with $Pd(TFA)_2$ (86 mg, 0.26 mmol) and **1b** (88 mg, 0.26 mmol) as the starting materials. Yield: 124 mg (88%). Anal. Calcd for $C_{20}H_{32}F_3N_2OP_2Pd$: C, 44.34; H, 5.95; N, 5.17. Found: C, 44.11; H, 5.78; N, 5.23. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 6.76 (t, $J$ = 7.8 Hz, 1H, Ph[4]), 6.11 (t, $J$ = 8.0 Hz, 2H, Ph[3,5]), 3.91 (s, 2H, N*H*), 2.38−2.28 (m, 4H C*H*$(CH_3)_2$), 1.32−1.20 (m, 24 H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 157.7 ($C^{Ph}$), 127.3 ($C^{Ph}$), 124.0 ($C^{Ph}$), 102.1 ($C^{Ph}$), 27.4 (t, $J$ = 12.6 Hz, *C*H$(CH_3)_2$), 17.2 (CH(*C*H$_3)_2$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 114.5.

**Pd(PCP-BIPOL)(TFA) (8d).** A solution of $Pd(TFA)_2$ (124 mg, 0.37 mmol) and **1d** (200 mg, 0.37 mmol) in THF (10 mL) was stirred for 10 min under ice cooling. The solvent was then removed at reduced presure, and the remaining product was washed twice with pentane (10 mL) and dried under vacuum. Yield: 210 mg (75%). Anal. Calcd for $C_{32}H_{21}F_3N_2O_6P_2Pd$: C, 50.92; H, 2.80; N, 3.71. Found: C, 51.04; H, 2.96; N, 3.75. $^1H$ NMR ($\delta$, $CDCl_3$, 20 °C): 7.53−7.20 (m, 16H, Biph), 6.78 (t, $J$ = 9.4 Hz, 1H, Ph[4]), 6.31 (d, $J$ = 7.7 Hz, 2H, Ph[3,5]), 5.62 (s, 2H, N*H*). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 148.0 ($C^{Biph}$), 147.7 ($C^{Ph}$), 147.2 ($C^{Ph}$), 130.2 ($C^{Ph}$), 129.9 ($C^{Biph}$), 129.6 ($C^{Biph}$), 126.7 ($C^{Biph}$), 121.9 ($C^{Biph}$), 121.7 ($C^{Ph}$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$, 20 °C): 142.8.

**Pd(PCP$^E$-Ph)Cl (9a).** A suspension of $Pd_2(dba)_3$ (172 mg, 0.19 mmol) and **3a** (230 mg, 0.38 mmol) in toluene (10 mL) was stirred overnight at 80 °C. The resulting yellow solution was evaporated under vaccum and the product precipitated with $Et_2O$, collected on a glass frit, and washed twice with $Et_2O$. Yield: 245 mg (90%). Anal. Calcd for $C_{35}H_{33}ClN_2O_2P_2Pd$: C, 58.59; H, 4.64; N, 3.90. Found: C, 58.94; H, 4.77; N, 4.12. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 7.87−7.43 (m, 23H, PPh, Ph[3,5] and Ph[ipso]), 5.25 (s, 2H, N*H*), 4.00 (d, $J$ = 6.7 Hz, 2H, C*H*$_2$), 2.02 (m, $J$ = 6.7 Hz, 1H, C*H*$(CH_3)_2$), 0.99 (d, $J$ = 6.7 Hz, 6H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 166.1 (*C*O), 155.7 (t, $J$ = 13.9 Hz, $C^{Ph}$), 134.8 ($C^{PPh}$), 131.9 (t, $J$ = 7.9 Hz, $C^{PPh}$), 130.3 ($C^{PPh}$), 130.4 ($C^{Ph}$), 128.8 (t, $J$ = 5.7 Hz, $C^{PPh}$), 104.0 (t, $J$ = 9.5 Hz, $C^{Ph}$), 70.7 (*C*H$_2$), 27.9 (*C*H$(CH_3)_2$), 18.9 (CH(*C*H$_3)_2$). $^{31}P\{^1H\}$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 80.5.

**X-ray Structure Determination.** X-ray data for Ni(PCP-Ph)Cl·1/2$C_6H_6$ (**4a**·1/2$C_6H_6$), Ni(PCP-Bu$^t$)Cl (**4c**), Pd(PCP-Ph)Cl·2DMF (**5a**·2DMF), Pd(PCP$^F$-Ph)Cl·$CH_3CN$ (**6a**·$CH_3CN$), Pt(PCP-Ph)Br·$(Et_3NH)Br·CH_2Cl_2$ (**7a**·[$NEt_3H$]Br·$CH_2Cl_2$), Pd(PCP-Pr$^i$)(TFA) (**8b**), and Pd(PCP-BIPOL)(TFA)·2$Et_2O$ (**8d**·2$Et_2O$) were collected on a Bruker Smart CCD area detector diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) and 0.3° $\omega$-scan frames covering a hemisphere (**4a**·1/2$C_6H_6$, **4c**) or complete spheres (**5a**·2DMF, **6a**·$CH_3CN$, **7a**·[$NEt_3H$]Br·$CH_2Cl_2$, **8b**, and **8d**·2$Et_2O$) of the reciprocal space. Corrections for absorption, $\lambda$/2 effects, and crystal decay were applied.[22] The structures were solved by direct methods using the program SHELXS97.[23] Structure refinement on $F^2$ was carried out with the program SHELXL97.[23] All non-hydrogen atoms were refined

(22) Bruker programs: *SMART*, version 5.625; *SAINT*, version 6.36; *SADABS*, version 2.10; *XPREP*, version 6.1; *SHELXTL*, version 6.1 (Bruker AXS Inc.: Madison, WI, 2001).

anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Salient crystallographic data are given in the Supporting Information, Table S1; further details are given in the deposited CIF.

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(23) Sheldrick, G. M. *SHELX97*: Program System for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1997.

**Supporting Information Available:** Synthesis and spectroscopic data of **4c**, **5c**−**f**, **6e**, **7c**, **8c**, and **9e**. Complete crystallographic data and technical details in tabular and in CIF format for **4a**·1/2$C_6H_6$, **4c**, **5a**·2DMF, **6a**·$CH_3CN$, **7a**·[$NEt_3H$]Br·$CH_2Cl_2$, **8b**, and **8d**·2$Et_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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