2-Indolylphosphines, a New Class of Tunable Ligands: Their Synthesis, Facile Derivatization, and Coordination to Palladium(II)

Joanne O. Yu, Edmond Lam, Julie L. Sereda, Nicole C. Rampersad, Alan J. Lough, C. S. Browning,* and David H. Farrar

Davenport Chemical Research Building, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

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The generation of new metal complexes with potentially interesting properties provides the motivation for designing novel polydentate bridging ligands. Herein we report the syntheses of tertiary indolylphenylphosphines **L**, where **L** = diphenyl(3-methyl-2-indolyl)-phosphine ($P(C_6H_5)_2(C_9H_8N$, **1**), phenylbis(3-methyl-2-indolyl)phosphine ($P(C_6H_5)(C_9H_8N)_2$, **2**), and bis(1*H*-3-indolyl)methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{17}H_{12}N_2)$, **3**). Ligands **1**−**3** were functionalized at the indolyl nitrogen with a variety of both electron-withdrawing and electron-donating groups. The solid-state structures of **1**, **2**, and N-functionalized indolylphosphines diphenyl(3-methyl-1-benzyl-2-indolyl)phosphine ($P(C_6H_5)_2(C_9H_7N(CH_2C_6H_5))$, ***N*-Bz-1**) and bis[1-($CH_2C_6F_5$)-3-indolyl]methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{17}H_{10}N_2[CH_2C_6F_5]_2$), **(*N*-$F_5$Bz)$_2$-3**), are reported. The reaction of ligands **1**−**3** with 1 equiv of $Pd(COD)Cl_2$ led to the formation of Pd(II) complexes of the type $[Pd(\mathbf{L})Cl(\mu\text{-}Cl)]_2$ (**4**, **L** = **1**; **5, L** = **2**; **6, L** = **3**). The products were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, and elemental analysis. X-ray crystallography established the dimeric structure of the products and confirmed the ability of the ligands to serve, in the absence of base, as monodentate P-donors in reaction with a transition metal. The indolyl NH groups of the complexes **4**−**6** demonstrate a marked propensity for hydrogen bonding in the solid state.

Introduction

Phosphines with aromatic heterocyclic substituents are interesting ligands in coordination chemistry because they offer several potential modes of coordination to transition metals. The most frequently studied of these polydentate ligands are the pyridinylphosphines, in which the pyridinyl substituents are bound to phosphorus at the 2-position (Figure 1). Mono-, bis-, and tris-(2-pyridinyl)phosphines have been prepared,[1,2] and their coordination chemistry remains an area of considerable activity,[1,2] in part because of the difference in character between the two centers of Lewis basicity. As a softer σ-donor and stronger π-acceptor than the nitrogen atom,[2] the phosphorus center of diphenylpyridinylphosphine preferentially coordinates to transition metals in obtaining mononuclear complexes.[2,3]

The bound diphenylpyridinylphosphine ligand may bridge to an additional metal atom through the uncoordinated nitrogen atom to generate binuclear homo- and heterometallic complexes.[1,2,4] The small separation between the bridged metal atoms, induced by the geometry and rigidity of the ligand, can yield metal−metal interactions.[2,4] These bridged complexes have received considerable attention because of their interesting structural features as well as their potential as catalysts. Although four-membered metallacycles occasionally form through P,N-chelation of the ligand, these are observed less frequently than the above coordination modes because of their inherent ring strain.[2,3,5] In all cases, the phosphorus center and the pyridinyl nitrogen atoms of diphenylpyridinylphosphine serve as classic two-electron donors in their coordination chemistry.

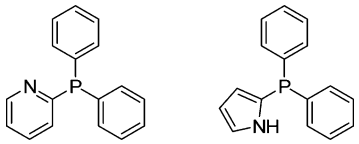

Figure 1. (a) 2-Pyridynylphosphine, a common ligand used in coordination chemistry. (b) 2-Pyrrolylphosphine, also used in coordination chemistry, although less frequently compared to 2-pyridynylphosphine.

* To whom correspondence should be addressed. E-mail: sbrownin@chem.utoronto.ca.

(1) Newkome, G. R. *Chem. Rev.* **1993**, *93*, 2067.
(2) Zhang, Z.-Z.; Cheng, H. *Coord. Chem. Rev.* **1996**, *147*, 1.
(3) (a) Kuo, C. Y.; Fuh, Y. S.; Shiue, J. Y.; Yu, S. J.; Lee, G. H.; Peng, S. M. *J. Organomet. Chem.* **1999**, *588*, 260. (b) Jones, N. D.; MacFarlane, K. S.; Smith, M. B.; Schutte, R. P.; Rettig, S. J.; James, B. R. *Inorg. Chem.* **1999**, *38*, 3956. (c) Nicholson, T.; Hirsch-Kuchma, M.; Shellenbarger-Jones, A.; Davison, A.; Jones, A. *Inorg. Chim. Acta* **1998**, *267*, 319. (d) Schutte, R. P.; Rettig, S. J.; Joshi, A. M.; James, B. R. *Inorg. Chem.* **1997**, *36*, 5809. (e) Baird, I. R.; Smith, M. B.; James, B. R. *Inorg. Chim. Acta* **1995**, *235*, 291.
(4) Zhang, G.; Zhao, J.; Raudaschl-Sieber, G.; Herdtweck, E.; Kuhn, F. E. *Polyhedron* **2002**, *21*, 1737.
(5) (a) Wasserman, H. J.; Moody, D. C.; Paine, R. T.; Ryan, R. R.; Salazar, K. V. *Chem. Commun.* **1984**, 533. (b) Arean, C. G.; Rotondo, E.; Faraone, F. *Organometallics* **1991**, *10*, 3877. (c) Inoguchi, Y.; Mahrla, B. M.; Neugebauer, D.; Jones, P. G.; Schimdbaur, H. *Chem. Ber.* **1983**, *116*, 1487. (d) Olmstead, M. M.; Maisonnat, A.; Farr, J. P.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 4060. (e) Jain, V. K.; Jakkal, V. S.; Bohra, R. *J. Organomet. Chem.* **1990**, *389*, 417.

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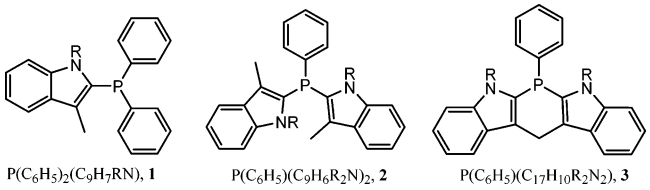
Chart 1. Novel C2-Bound Indolylphosphine Ligands. Parent Ligands with R = H, Diphenyl(3-methyl-2-indolyl)phosphine ($P(C_6H_5)_2(C_9H_8N)$, 1), Phenylbis(3-methyl-2-indolyl)phosphine ($P(C_6H_5)(C_9H_8N)_2$, 2), and Bis(1*H*-3-indolyl)methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{17}H_{12}N_2)$, 3)[a]



$P(C_6H_5)_2(C_9H_7RN)$, **1** $P(C_6H_5)(C_9H_6R_2N)_2$, **2** $P(C_6H_5)(C_{17}H_{10}R_2N_2)$, **3**

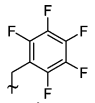
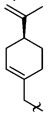
[a] Refer to Table 1 for N-functionalized indolylphosphine ligands where R ≠ H.

In principle, diphenyl(2-pyrrolyl)phosphine (Figure 1) should provide a similarly rich and varied chemistry in reaction with transition metals upon deprotonation of its pyrrolyl nitrogen center. However, its low-yielding synthesis[6] and its propensity for complicated and unpredictable behavior in metal coordination have rendered diphenyl(2-pyrrolyl)phosphine a rarely used ligand in reaction with transition metals.[7,8]

As a phosphine substituent, the electron-rich heteroaromatic indole, like pyrrole, also offers further modes of coordination through its nitrogen atom in a potentially polydentate ligand. The required deprotonation of the indolyl nitrogen center provides the opportunity to control secondary N-coordination and yields a stronger ligand of transition metals than the nitrogen center of pyridinylphosphines. We reasoned that the lesser reactivity of indole relative to pyrrole,[7,8] however, might permit an easier synthesis of mono- and disubstituted indolylphenylphosphines and that these ligands may provide a rich and interesting coordination chemistry that is based upon their expected polydenticity rather than the propensity for ligand fragmentation[7] and other complications[7,8] observed upon coordination of diphenyl(2-pyrrolyl)phosphine. The only report to date of an indolylphenylphosphine involved the synthesis of diphenyl-2,2′-biindolylphosphine and its subsequent coordination through phosphorus to a palladium(II) center to generate a seven-membered metallacycle.[9]

This manuscript outlines the syntheses of three new C2-bound indolylphosphines: diphenyl(3-methyl-2-indolyl)phosphine ($P(C_6H_5)_2(C_9H_8N)$, **1**), phenylbis(3-methyl-2-indolyl)phosphine ($P(C_6H_5)(C_9H_8N)_2$, **2**), and bis(1*H*-3-indolyl)methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{17}H_{12}N_2)$, **3**) (Chart 1). Several N-substituted derivatives of each are also reported to demonstrate the facility with which a variety of electron-withdrawing, electron-donating, and chiral groups may be introduced at the indolyl nitrogen to vary the electronic and steric properties of the ligands (see Table 1). In addition, the complexation of equimolar $Pd(COD)Cl_2$ with **1**−**3** is reported, illustrating the ability of the ligand to serve as a monodentate P-donor in generating dimeric coordination complexes of the type $[Pd(\mathbf{L})Cl(\mu\text{-}Cl)]_2$.

Table 1. ^{31}P NMR Signals (ppm)[a] and Product Yields for N-Functionalized Ligands of 1−3

R	1	2	3
-H	-33.1 (96%)	-59.3 (71%)	-56.0 (87%)
	-30.1 (89%)	-65.1 (51%)	-61.9 (53%)
$-CH_3$	-33.1 (48%)	-53.3 (38%)	-64.4 (82%)
	-32.0 (52%)	-53.6 (46%)	-66.3 (84%)
	-30.8 (56%)	-52.3 (32%)	-67.3 (92%)
	-31.9 (42%)	-55.2 (40%)	-66.8 (81%)

[a] At 25 °C in $CDCl_3$.

Experimental Section

General Comments. All reactions and manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise stated. Dimethylmethyleneammonium chloride, 3-methylindole, dichlorophenylphosphine, chlorodiphenylphosphine, 1.6 M *n*-butyllithium, sodium borohydride, sodium hydride, iodomethane, benzyl bromide, 2,3,4,5,6-pentafluorobenzyl bromide, (1*R*)-(−)-myrtenol, and phosphorus tribromide (Aldrich), bis(1*H*-3-indolyl)methane (ChemPacific), hydrochloric acid (Fisher Scientific), and acetonitrile and triethylamine (ACP Chemicals) were used without further purification. Dichloromethane, hexanes, ethanol, and methanol (Caledon) were used as received. The solvents tetrahydrofuran and diethyl ether were distilled from dark purple solutions of sodium benzophenone ketyl under a dinitrogen atmosphere. (1*R*)-(−)-Myrtenyl bromide[10a] and $Pd(COD)Cl_2$[10b] were prepared according to literature methods. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian XL 400 and Varian Mercury 300 spectrometers and referenced to $SiMe_4$ (TMS) and 85% H_3PO_4 in $CDCl_3$, respectively.

1-[(Dimethylamino)methyl]-3-methylindole. Dimethylmethyleneammonium chloride (14.05 g, 150 mmol) and 3-methylindole (9.95 g, 75.9 mmol) were added to tetrahydrofuran (300 mL). The mixture was stirred for 24 h at ambient temperature, gradually forming a white suspension. Triethylamine (21 mL, 151 mmol) was added to the mixture, and stirring was continued for 2 h. The solvent was removed in vacuo, affording a white residue. The residue was suspended in water (200 mL), and the product was extracted with dichloromethane (2 × 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo to afford the product as a cream-colored oil (10.43 g, 73%). ^1H NMR ($CDCl_3$, δ, ppm): 7.52 (d, 1H, C8H), 7.36 (d, 1H, C4H), 7.17 (t, 1H, C7H), 7.07 (t, 1H, C6H), 6.86 (s, 1H, C2H), 4.61 (s, 2H, $-NCH_2N-$), 2.30 (s, 3H, CH_3 on indole), 2.24 (s, 6H, $-N(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ,

(6) Arce, A. J.; Deeming, A. J.; De Sanctis, Y.; Joahl, S. K.; Martin, C. M.; Shinhmar, M.; Speel, D. M.; Vassos, A. *Chem. Commun.* **1998**, 233.
(7) Deeming, A. J.; Shinhmar, M. K. *J. Organomet. Chem.* **1999**, *592*, 235.
(8) Allen, D. W.; Charlton, J. R.; Huntley, B. G. *Phosphorus* **1976**, *6*, 191.
(9) Berens, U.; Brown, J. M.; Long, J.; Selke, R. *Tetrahedron: Asymmetry* **1996**, *7*, 285.
(10) (a).Harwood: L. M.; Julia, M. *Synthesis* **1980**, *6*, 456−457. (b) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 348.

ppm): 137.4, 129.0, 126.3, 121.8, 119.0, 118.9, 110.7, 109.9, 68.6, 42.8, and 9.7. EI-MS: *m/z* 188 [M^+, 46], 144 [$M^+ - N(CH_3)_2$, 42], 130 [$M^+ - CH_2N(CH_3)_2$, 33], 58 [$CH_2N(CH_3)_2^+$, 100].

Diphenyl(3-methyl-2-indolyl)phosphine ($P(C_6H_5)_2(C_9H_8N)$, 1). To a degassed solution of 1-[(dimethylamino)-methyl]-3-methylindole (2.02 g, 10.7 mmol) in diethyl ether (50 mL) was added 1.6 M *n*-BuLi (7.05 mL, 11.3 mmol) dropwise over 10 min at ambient temperature. Upon addition of *n*-BuLi, the white opaque solution became a turbid orange solution. The solution was stirred for 4 h. The resultant mixture was cooled to −78 °C, and chlorodiphenylphosphine (1.94 mL, 10.7 mmol) was added dropwise over 10 min. The beige mixture was stirred for 24 h. To quench the reaction, methanol (2 mL) was added to the mixture. Volatile solvents were removed in vacuo, affording $P(C_6H_5)_2(C_{12}H_{15}N_2)$ as a brown residue (3.99 g, 89%). HRMS (EI) for $C_{24}H_{25}N_2P$ (M^+): calcd, 372.1755; found, 372.1764. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −30.1. ^1H NMR ($CDCl_3$, δ, ppm): 7.25−7.37 (m, 14H), 4.95 (s, 2H, N−CH_2), 2.09 (s, 6H, N−CH_3), and 1.80 (s, 3H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 138.9, 135.8, 132.4, 130.3, 129.2, 128.4, 128.0, 123.0, 121.3, 119.1, 110.4, 66.8, 42.1, and 10.5. EI-MS: *m/z* 372 [M^+, 100] and 58 [$Me_2NCH_2^+$, 100]. The brown $P(C_6H_5)_2(C_{12}H_{15}N_2)$ residue was suspended in degassed aqueous 0.1 M HCl (50 mL) and extracted with degassed dichloromethane (2 × 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo to afford an orange residue. The product was obtained as a white powder from recrystallization with methanol (3.24 g, 96%). Crystals suitable for single-crystal X-ray diffraction were obtained from slow evaporation of the ligand in a toluene solution. Anal. Calcd for $C_{21}H_{18}NP$ (315.4): C, 80.0; H, 5.8; N, 4.4. Found: C, 80.0; H, 5.9; N, 4.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −33.1. ^1H NMR ($CDCl_3$, δ, ppm): 8.21 (s, 1H, NH), 7.08−7.62 (m, 14H), 2.46 (s, 3H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 139.3, 137.4, 134.3, 129.3, 128.9, 128.8, 127.2, 123.1, 122.2, 119.4, 119.3, 111.0, and 9.9. EI-MS: *m/z* 315 [M^+, 100], 238 [M^+ − Ph, 27], 130 [(3-methylindole)$^+$, 7], 77 [Ph^+, 8]. Mp: 147−148 °C.

Phenylbis(3-methyl-2-indolyl)phosphine ($P(C_6H_5)(C_9H_8N)_2$, 2). The preparation for **1** was followed, with the exceptions of using 1-[(dimethylamino)methyl]-3-methylindole (3.74 g, 19.9 mmol), 1.6 M *n*-BuLi (13.0 mL, 20.8 mmol), and dichlorophenylphosphine (1.00 mL, 7.4 mmol). The aminal-protected product was recrystallized from methanol to afford $P(C_6H_5)(C_{24}H_{30}N_4)_2$ as a white powder (1.39 g, 51%). HRMS (EI) for $C_{30}H_{35}N_4P$ (M^+): calcd, 482.2599; found, 482.2589. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −65.1. ^1H NMR ($CDCl_3$, δ, ppm): 7.05−7.65 (m, 13H), 4.25 (d, 2H, $^2J_{HH}$ = 13 Hz, N−CH_2), 4.15 (d, 2H, $^2J_{HH}$ = 13 z, N−CH_2), 2.63 (s, 6H, N−CH_3), 2.58 (s, 6H, N−CH_3), and 2.16 (s, 6H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 140.5, 139.0, 137.0, 130.8, 128.7, 128.1, 127.6, 126.8, 125.3, 123.8, 122.8, 122.7, 119.6, 119.6, 118.5, 111.2, 109.4, 65.2, 41.9, 10.9 and 9.9. EI-MS: *m/z* 482 [M^+, 1], 425 [$M^+ - Me_2NCH_2$, 32], and 58 [$Me_2NCH_2^+$, 100]. In a Schlenk vessel, the aminal-protected product, $P(C_6H_5)(C_{24}H_{30}N_4)_2$ (0.77 g, 1.6 mmol), and $NaBH_4$ (0.124 g, 3.3 mmol) were dissolved in a degassed ethanol−tetrahydrofuran solution (50 mL, 1:1 v/v). The solution was refluxed for 5 h at 85 °C. The solvent was removed in vacuo, affording a light yellow residue. The residue was suspended in degassed diluted HCl (100 mL) and extracted with degassed dichloromethane (2 × 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo to give the product as a white powder (0.42 g, 71%). Anal. Calcd for $C_{24}H_{21}N_2P\cdot H_2O$ (386.43): C, 74.6; H, 6.0; N, 7.3. Found: C, 74.5; H, 5.7; N, 7.3. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −59.3. ^1H NMR ($CDCl_3$, δ, ppm): 8.20 (s, 2H, NH, br), 7.20−7.33 (m, 13H), 2.43 (s, 6H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 138.3, 135.2, 132.1, 129.6, 129.1, 128.9, 126.2, 123.3, 122.0, 119.7, 119.5, 111.2, and 9.9. EI-MS: *m/z* 368 [M^+, 100], 238 [M^+ − 3-methylindole, 80], 130 [3-methylindole$^+$, 11]. Mp: 205−207 °C.

1,1′-Bis[(dimethylamino)methyl]bis(1*H*-3-indolyl)-methane. Dimethylmethyleneammonium chloride (13.83 g, 148 mmol) and bis(1*H*-3-indolyl)methane (13.83 g, 56.2 mmol) were added to tetrahydrofuran (300 mL). The mixture was stirred for 24 h at ambient temperature, gradually forming a pink suspension. Triethylamine (21 mL, 151 mmol) was added to the solution, and the resultant mixture was stirred for 2 h. The solvent was removed in vacuo, affording a pink residue. The residue was suspended in water (200 mL) and extracted with dichloromethane (2 × 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo to give the product as a pink oil (16.4 g, 81%). ^1H NMR ($CDCl_3$, δ, ppm): 7.45 (d, 2H, C8H), 7.24 (d, 1H, C5H), 7.02 (t, 1H, C7H), 6.90 (t, 1H, C6H), 6.73 (s, 2H, C2H), 4.43 (s, 4H, −NCH_2N−), 4.07 (s, 2H, CH_2 bridge), 2.07 (s, 12H, −$N(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 137.5, 128.2, 126.8, 121.7, 119.4, 119.0, 114.6, 109.9, 68.6, 42.8, 21.2. EI-MS: *m/z* 360 [M^+, 25], 58 [$CH_2N(CH_3)_2^+$, 100].

Bis(1*H*-3-indolyl)methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{17}H_{12}N_2)$, 3). The preparation for **2** was followed, with the exceptions of using 1,1′-bis[(dimethylamino)methyl]-bis(1*H*-3-indolyl)methane (3.81 g, 10.5 mmol), 1.6 M *n*-BuLi (14.0 mL, 22.4 mmol), and dichlorophenylphosphine (1.00 mL, 7.4 mmol). The aminal-protected product was recrystallized from methanol to afford $P(C_6H_5)(C_{23}H_{26}N_4)$ as a white powder (1.80 g, 53%). HRMS (EI) for $C_{29}H_{31}N_4P$ (M^+): calcd, 466.2866; found, 466.2289. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −61.9. ^1H NMR ($CDCl_3$, δ, ppm): 6.71−7.34 (m, 13H), 4.22 (d, 2H, $^2J_{HH}$ = 12 Hz, N−CH_2), 4.19 (dd, 1H, $^2J_{HH}$ = 21 Hz, $^4J_{PH}$ = 3 Hz, CH_2 bridge), 4.10 (d, 2H, $^2J_{HH}$ = 12 Hz, N−CH_2), 4.04 (dd, 1H, $^2J_{HH}$ = 21 Hz, $^4J_{PH}$ = 3 Hz, CH_2 bridge), and 1.63 (s, 12H, N−CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 139.5, 138.1, 134.3, 131.5, 129.2, 128.7, 128.1, 127.7, 122.6, 119.4, 118.6, 116.8, 110.4, 67.4, 42.1, and 21.4. EI-MS: *m/z* 466 [M^+, 21], 408 [$M^+ - Me_2NCH_2$, 6], and 58 [$Me_2NCH_2^+$, 100]. The deprotection of the aminal product, $P(C_6H_5)(C_{23}H_{26}N_4)$, was achieved in the similar fashion as **2**, with the exceptions of using $P(C_6H_5)(C_{23}H_{26}N_4)$ (1.50 g, 3.2 mmol) and $NaBH_4$ (0.50 g, 13.2 mmol), to afford the product as a white powder (0.99 g, 87%). Anal. Calcd for $C_{12}H_{16}N_2$ (352.4): C, 78.4; H, 4.9; N, 8.0. Found: C, 78.4; H, 5.2; N, 7.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −56.0. ^1H NMR ($CDCl_3$, δ, ppm): 8.13 (s, 2H, NH, br), 7.27−7.76 (m, 13H), 4.57 (dd, 1H, $^2J_{HH}$ = 21 Hz, $^4J_{PH}$ = 3 Hz, CH_2 bridge), 4.41 (dd, 1H, $^2J_{HH}$ = 21 Hz, $^4J_{PH}$ = 3 Hz, CH_2 bridge). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 138.3, 137.0, 133.6, 131.7, 130.9, 128.8, 128.5, 123.0, 119.7, 118.8, 116.8, 111.0, 21.1. EI-MS: *m/z* 352 [M^+, 77], 275 [M^+ − Ph, 41]. Mp: 204−205 °C.

Representative N-Substitution in Diphenyl(1,3-methyl-2-indolyl)phosphine ($P(C_6H_5)_2(C_{19}H_8N)$): Reaction with Iodomethane. $P(C_6H_5)_2(C_9H_8N)$ (**1**; 0.30 g, 0.95 mmol) and NaH (0.028 g, 1.17 mmol) were added to a Schlenk vessel charged with nitrogen. Anhydrous tetrahydrofuran (10 mL) was added via syringe, and the colorless solution was stirred for 1 h at ambient temperature. Iodomethane (0.065 mL, 1.04 mmol) was added, and the resulting solution immediately turned yellow. The solution was stirred for 2 h at ambient temperature. Volatile solvents were removed in vacuo, affording a yellow residue. The product was purified by column chromatography with an eluant of hexanes/dichloromethane (2:1), affording the product as a white powder (0.15 g, 48%).

Diphenyl(1,3-methyl-2-indolyl)phosphine ($P(C_6H_5)_2(C_{10}H_{10}N)$, (*N*-Me)-1). Anal. Calcd for $C_{22}H_{20}NP$ (329.1): C, 80.22; H, 6.12; N, 4.25. Found: C, 80.29; H, 6.22; N, 4.27. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −33.1. ^1H NMR ($CDCl_3$, δ, ppm): 7.18−7.70 (m, 14H), 3.58 (s, 3H, N−CH_3), and 2.32 (s, 3H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 139.4, 135.5, 132.1, 128.9, 128.6, 128.4, 128.1, 123.2, 123.0, 119.4, 118.9, 109.4, 32.0, and 10.6. EI-MS: *m/z* 329 [M^+, 100].

Diphenyl(1-benzyl-3-methyl-2-indolyl)phosphine ($P(C_6H_5)_2(C_{16}H_{14}N)$, (*N*-Bz)-1). The preparation for **(*N*-Me)-1** was followed. **(*N*-Bz)-1** was obtained as a white powder (0.20 g, 52%). Crystals suitable for single-crystal X-ray diffraction were obtained from slow evaporation of the ligand in a hexane−dichloromethane solution. Anal. Calcd for $C_{22}H_{20}NP$ (405.2): C, 82.94; H, 5.97; N, 3.45. Found: C, 83.04; H, 6.04; N, 3.45. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −32.0. ^1H NMR ($CDCl_3$, δ, ppm): 6.83−7.62 (m, 19H), 5.61 (d, 2H, $^4J_{PH}$ = 3 Hz, CH_2−N), and 2.26 (s, 3H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 138.8, 137.8, 134.8, 132.3, 129.1, 129.0, 128.5, 128.4, 128.3, 128.2, 126.3, 126.1, 123.3, 121.9, 119.3, 110.3, 48.4, and 10.7. EI-MS: *m/z* 405 [M^+, 100], 328 [M^+ − Ph, 8], and 314 [$M^+ - CH_2C_6H_5$, 24].

Diphenyl[1-(2,3,4,5,6-pentafluorobenzyl)-3-methyl-2-indolyl]phosphine ($P(C_6H_5)_2(C_{16}H_9F_5N)$, (*N*-$F_5$Bz)-1). The preparation for **(*N*-Me)-1** was followed. **(*N*-F_5Bz)-1** was obtained as a white powder (0.26 g, 56%). HRMS (EI) for $C_{28}H_{19}F_5NP$ (M^+): calcd, 495.1175; found, 495.1182. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −30.8 (t, $^6J_{PFo}$ = 25 Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −141.6 (ddd, $^6J_{PFo}$ = 31 Hz, $^3J_{FoFm(cis)}$ = 23 Hz, $^5J_{FoFm(trans)}$ = 8 Hz, 2F, *o*-F), −154.2 (t, $^3J_{FpFm}$ = 21 Hz, 1F, *p*-F), and −161.1 (ddd, $^3J_{FmFo(cis)}$ = 23 Hz, $^3J_{FmFp}$= 21 Hz, $^5J_{FmFo(trans)}$ = 8 Hz, 2F, *m*-F). ^1H NMR ($CDCl_3$, δ, ppm): 7.13−7.53 (m, 14H), 5.75 (s, 2H, CH_2−N), and 2.80 (s, 3H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 146.6, 143.9, 141.7, 139.2, 138.7, 138.5, 136.0, 134.2, 132.3, 129.2, 129.1, 128.5, 128.4, 123.6, 122.4, 119.5, 111.6, 109.2, 37.6, and 10.4. EI-MS: *m/z* 495 [M^+, 100], 418 [M^+ − Ph, 54], 314 [$M^+ - CH_2C_6F_5$, 20], and 181 [$CH_2C_6F_5^+$, 28].

Diphenyl(1-(*R*)-(−)-myrtenyl-3-methyl-2-indolyl)phosphine ($P(C_6H_5)_2(C_{19}H_{22}N)$, (*N*-(*R*)-(−)-myrtenyl)-1). The preparation for **(*N*-Me)-1** was followed. **(*N*-(*R*)-(−)-myrtenyl)-1** was obtained as a white powder (0.18 g, 42%). HRMS (EI) for $C_{31}H_{32}NP$ (M^+): calcd, 449.2272. found, 449.2278. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −31.9. ^1H NMR ($CDCl_3$, δ, ppm): 6.96−7.58 (m, 14H), 5.01 (d, 1H, $^2J_{HH}$ = 17 Hz, N−CH_2), 4.89 (d, 1H, $^2J_{HH}$ = 17 Hz, N−CH_2), 4.51 (s, 1H, alkene CH on myrtenyl), 2.31 (s, 2H, CH_2 bridge on myrtenyl), 2.26 (s, 1H, CH on myrtenyl), 2.20 (m, 1H, CH on myrtenyl), 1.88 (s, 3H, CH_3 on indole), 1.14 (s, 3H, CH_3 on myrtenyl), 0.96 (d, 2H, $^3J_{HH}$ = 6 Hz, CH_2 on myrtenyl), and 0.70 (s, 3H, CH_3 on myrtenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 144.4, 138.6, 135.3, 132.6, 132.4, 128.8, 128.4, 128.3, 128.1, 122.8, 119.0, 117.0, 110.4, 109.4, 49.0, 43.5, 40.8, 38.2, 31.4, 30.8, 26.1, 21.0, and 10.6. EI-MS: *m/z* 449 [M^+, 100] and 434 [M^+ − Me, 15].

Phenylbis(1,3-dimethyl-2-indolyl)phosphine ($P(C_6H_5)(C_{10}H_{10}N)_2$, (*N*-Me)$_2$-2). The preparation for **(*N*-Me)-1** was followed, with the exception of using $P(C_6H_5)(C_9H_8N)_2$ (**2**; 0.30 g, 0.82 mmol), NaH (0.047 g, 1.96 mmol), and iodomethane (0.11 mL, 1.77 mmol). **(*N*-Me)$_2$-2** was obtained as a white product (0.15 g, 38%). HRMS (EI) for $C_{26}H_{25}N_2P$ (M^+): calcd, 396.1755; found, 396.1752. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −53.3. ^1H NMR ($CDCl_3$, δ, ppm): 7.10−7.56 (m, 13H), 3.65 (s, 6H, CH_3−N), and 2.04 (s, 6H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 139.3, 134.2, 132.5, 130.9, 128.8, 128.7, 128.4, 126.7, 122.9, 120.6, 119.0, 109.1, 123.3, 31.5, and 9.9. EI-MS: *m/z* 396 [M^+, 100], 381 [$M^+ - CH_3$, 6], 252 [M^+ − (1,3-methylindole), 13], and 144 [(1,3-methylindole)$^+$, 17].

Phenylbis(1-benzyl-3-methyl-2-indolyl)phosphine ($P(C_6H_5)(C_{16}H_{14}N)_2$). The preparation for **(*N*-Me)$_2$-2** was followed. **(*N*-Bz)$_2$-2** was obtained as a white powder (0.19 g, 46%). HRMS (EI) for $C_{38}H_{33}N_2P$ (M^+): calcd, 548.2381; found, 548.2370. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −53.6. ^1H NMR ($CDCl_3$, δ, ppm): 6.65−7.46 (m, 23H), 5.37 (d, 2H, $^2J_{HH}$ = 17 Hz, N−CH_2), 5.28 (d, 2H, $^2J_{HH}$ = 17 Hz, N−CH_2), and 1.89 (s, 6H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 138.8, 137.9, 133.0, 132.6, 129.3, 128.6, 128.4, 128.1, 126.7, 126.5, 126.0, 123.0, 121.1, 119.1, 118.9, 109.9, 48.1, and 10.1. EI-MS: *m/z* 548 [M^+, 9], 457 [M^+ − Benz, 7], 220 [1-benzyl-3-methylindole$^+$, 8] and 91 [benzyl$^+$, 100].

Phenylbis[1-(2,3,4,5,6-pentafluorobenzyl)-3-methyl-2-indolyl]phosphine ($P(C_6H_5)(C_{16}H_9F_5N)_2$, (*N*-$F_5$Bz)$_2$-2). The preparation for **(*N*-Me)$_2$-2** was followed. **(*N*-F_5Bz)$_2$-2** was obtained as a white powder (0.19 g, 32%). HRMS (EI) for $C_{38}H_{23}F_{10}N_2P$ (M^+): calcd, 728.1439; found, 728.1428. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −52.3 (quintet, $^6J_{PFo}$ = 20 Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −142.3 (ddd, $^6J_{PFo}$ = 28 Hz, $^3J_{FoFm(cis)}$ = 22 Hz, $^5J_{FoFm(trans)}$ = 8 Hz, 4F, *o*-F), −154.6 (t, $^3J_{FpFm}$ = 21 Hz, 2F, *p*-F), and −162.3 (ddd, $^3J_{FmFo(cis)}$ = 22 Hz, $^3J_{FmFp}$= 21 Hz, $^5J_{FmFo(trans)}$ = 8 Hz, 4F, *m*-F). ^1H NMR ($CDCl_3$, δ, ppm): 7.17−7.54 (m, 13H), 5.75 (d, 2H, $^2J_{HH}$ = 17 Hz, N−CH_2), 5.65 (d, 2H, $^2J_{HH}$ = 17 Hz, N−CH_2), and 1.82 (s, 6H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 146.2, 143.8, 141.4, 139.5, 138.2, 135.8, 132.6, 131.4, 128.9, 128.8, 128.5, 125.1, 123.7, 122.3, 119.7, 118.9, 111.0, 109.0, 37.1, and 9.3. EI-MS: *m/z* 728 [M^+, 100], 547 [$M^+ - CH_2C_6F_5$, 8], and 181 [$CH_2C_6F_5^+$, 21].

Phenylbis(1-(*R*)-(−)-myrtenyl-3-methyl-2-indolyl)phosphine ($P(C_6H_5)(C_{19}H_{22}N)_2$, (*N*-(*R*)−(−)myrtenyl)$_2$-2). The preparation for **(*N*-Me)$_2$-2** was followed. **(*N*-(*R*)-(−)myrtenyl)$_2$-2** was obtained as a white powder (0.21 g, 40%). HRMS (EI) for $C_{44}H_{29}N_2P$ (M^+): calcd, 636.3633; found, 636.3641. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −55.2. ^1H NMR ($CDCl_3$, δ, ppm): 6.89−7.47 (m, 13H), 4.87 (d, 2H, $^2J_{HH}$ = 17 Hz, N−CH_2), 4.75 (d, 2H, $^2J_{HH}$ = 17 Hz, N−CH_2), 4.66 (s, 2H, alkene CH on myrtenyl), 2.37 (m, 2H, CH on myrtenyl), 2.24 (s, 4H, CH_2 bridge on myrtenyl), 2.19 (s, 2H, CH on myrtenyl), 1.84 (s, 6H, CH_3 on indole), 0.99 (s, 6H, CH_3 on myrtenyl), 0.90 (d, 4H, $^3J_{HH}$ = 7 Hz, CH_2 on myrtenyl), and 0.59 (s, 6H, CH_3 on myrtenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 144.3, 138.9, 135.8, 132.9, 130.0, 129.0, 128.6, 128.3, 123.3, 122.7, 118.9, 118.8, 117.8, 110.3, 49.1, 43.4, 40.4, 38.1, 31.4, 30.8, 26.1, 20.9, and 10.1. EI-MS: *m/z* 636 [M^+, 44], 621 [M^+ − Me, 18], 559 [M^+ − Ph, 6], 501 [M^+ − myrtenyl, 23], and 264 [1-myrtenyl-3-methylindole, 25].

Bis(1-methyl-3-indolyl)methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{19}H_{16}N_2)$, (*N*-Me)$_2$-3). The preparation for **(*N*-Me)-1** was followed, with the exception of using $P(C_6H_5)(C_{17}H_{12}N_2)$ (**3**; 0.30 g, 0.85 mmol), NaH (0.049 g, 1.18 mmol), and iodomethane (0.12 mL, 1.93 mmol). **(*N*-Me)$_2$-3** was obtained as a white powder (0.27 g, 82%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of the ligand from a hexane−dichloromethane solution. HRMS (EI) for $C_{25}H_{21}N_2P$ (M^+): calcd, 380.1442; found, 380.1437. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −64.4. ^1H NMR ($CDCl_3$, δ, ppm): 7.17−7.79 (m, 13H), 4.64 (dd, 1H, $^2J_{HH}$ = 21 Hz, $^4J_{PH}$ = 4 Hz, CH_2 bridge), 4.48 (dd, 1H, $^2J_{HH}$ = 21 Hz, $^4J_{PH}$ = 4 Hz, CH_2 bridge), and 3.72 (s, 6H, CH_3 on indole). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 139.6, 136.1, 134.3, 130.0, 129.8, 128.8, 127.1, 122.4, 119.1, 118.8, 115.7, 109.0, 31.0, and 21.5. EI-MS: *m/z* 380 [M^+, 100], 365 [M^+ − Me, 8], 303 [M^+ − Ph, 31].

Bis(1-benzyl-3-indolyl)methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{31}H_{24}N_2)$, (*N*-Bz)$_2$-3). The preparation for **(*N*-Me)$_2$-3** was followed. **(*N*-Bz)$_2$-3** was obtained as a white powder (0.38 g, 84%). HRMS (EI) for $C_{37}H_{29}N_2P$ (M^+): calcd, 532.2068; found, 532.2070. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −66.3. ^1H NMR ($CDCl_3$, δ, ppm): 6.78−7.84 (m, 23H), 5.50 (d, 2H, $^2J_{HH}$ = 17 Hz, N−CH_2), 5.35 (d, 2H, $^2J_{HH}$ = 17 Hz, N−CH_2), 4.74 (dd, 1H, $^2J_{HH}$ = 21 Hz, $^4J_{PH}$ = 3 Hz, CH_2 bridge), and 4.60 (dd, 1H, $^2J_{HH}$ = 21 Hz, $^4J_{PH}$ = 3 Hz, CH_2 bridge). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 142.7, 139.3, 137.4, 134.3, 130.3, 128.5, 128.4, 127.7, 127.0, 126.2, 122.7, 119.5, 118.9, 116.3, 110.0, 48.4, and 22.7. EI-MS: *m/z* 532 [M^+, 89], 455 [M^+ − Ph, 8], 441 [$M^+ - CH_2C_6H_5$, 81], and 91 [$CH_2C_6H_5^+$, 100].

Bis[1-(2,3,4,5,6-pentafluorobenzyl)-3-indolyl]methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{31}H_{14}F_{10}N_2)$, (*N*-$F_5$Bz)$_2$-3). The preparation for **(*N*-Me)$_2$-3** was followed. **(*N*-F_5Bz)$_2$-3** was obtained as a white powder (0.56 g, 92%). Crystals suitable for single-crystal X-ray diffraction were obtained from slow evaporation of the ligand in a $CDCl_3$ solution. HRMS (EI) for

Table 2. Crystallographic Data of Ligands 1 and 2 and of the N-Functionalized Ligands (*N*-Bz)-1, (*N*-CH_2NMe_2)$_2$-3, and (*N*-F_5Bz)$_2$-3

	1	2	(*N*-Bz)-1	(*N*-CH_2NMe_2)$_2$-3	(*N*-F_5Bz)$_2$-3
formula	$C_{21}H_{18}NP$	$C_{24}H_{21}N_2P$	$C_{28}H_{24}NP$	$C_{29}H_{31}N_4P$	$C_{37}H_{19}F_{10}N_2P\cdot CHCl_3$
formula wt	315.33	368.40	405.45	466.55	831.88
cryst color, shape	colorless, block	colorless, block	colorless, block	colorless, plate	colorless, block
cryst size, mm	0.35 × 0.30 × 0.30	0.20 × 0.18 × 0.18	0.46 × 0.30 × 0.22	0.30 × 0.25 × 0.12	0.32 × 0.30 × 0.22
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	9.9678(2)	10.3563(3)	13.7780(5)	12.8780(3)	16.5993(5)
b, Å	10.3453(2)	10.3027(6)	8.7875(4)	18.6590(6)	12.00343(3)
c, Å	17.4704(4)	19.0016(8)	18.6350(7)	11.6680(3)	17.1393(4)
α, deg	79.973(8)	90	90	90	90
β, deg	75.992(7)	104.383(3)	105.301(2)	116.2791(18)	98.811(2)
γ, deg	74.133(9)	90	90	90	90
V, Å^3	1670.09(6)	1963.9(2)	2176.2(2)	2513.94(12)	3374.7(2)
Z	4	4	4	4	4
D_{calcd}, g cm^{-3}	1.254	1.246	1.237	1.233	1.637
F(000)	664	776	856	992	1672
μ, mm^{-1}	0.163	0.150	0.141	0.134	0.409
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
limiting indices	$0 \le h \le 12$	$-13 \le h \le 13$	$-17 \le h \le 17$	$-15 \le h \le 13$	$-21 \le h \le 21$
	$-12 \le k \le 13$	$-13 \le k \le 13$	$-10 \le k \le 11$	$-22 \le k \le 22$	$-15 \le k \le 15$
	$-21 \le l \le 22$	$-24 \le l \le 24$	$-23 \le l \le 24$	$-13 \le l \le 13$	$-22 \le l \le 22$
2θ range, deg	2.55−27.48	2.27−27.50	2.38−27.50	2.93−25.04	1.59−27.53
max and min transmission	0.9526 and 0.9450	0.993 and 0.602	0.971 and 0.909	0.9841 and 0.9609	0.964 and 0.852
no. of rflens collected	22 759	16 135	19 191	17 602	32 929
no. of indep rflns/R_{int}	7596/0.046	4736/0.0904	5299/0.0466	4431/0.065	8134/0.0528
extinction coeff	0.0014(16)	0.0111(16)	0.0073(17)	0.0064(12)	0.0013(4)
no. of refined params	426	255	273	312	488
final R1, wR2	0.0449, 0.1140	0.0546, 0.1221	0.0520, 0.1298	0.0473, 0.1095	0.0438, 0.1071
final R1, wR2 (all data)	0.0767, 0.1320	0.1017, 0.1442	0.0866, 0.1529	0.0725, 0.1237	0.0721, 0.1221
goodness of fit	1.029	1.020	1.029	1.019	1.027
$\Delta\rho_{min}$, $\Delta\rho_{max}$, e Å^{-3}	−0.258, 0.257	−0.318, 0.359	−0.391, 0.346	−0.229, 0.580	−0.494, 0.367

$C_{37}H_{19}F_{10}N_2P$ (M^+): calcd, 712.1126; found, 712.1124. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −67.3 (quintet, $^6J_{PFo} = 27$ Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −141.4 (ddd, $^6J_{PFo} = 27$ Hz, $^3J_{FoFm(cis)} = 22$ Hz, $^5J_{FoFm(trans)} = 8$ Hz, 4F, *o*-F), −154.4 (t, $^3J_{FpFm} = 21$ Hz, 2F, *p*-F), and −161.8 (ddd, $^3J_{FmFo(cis)} = 22$ Hz, $^3J_{FmFp} = 21$ Hz, $^5J_{FmFo(trans)} = 8$ Hz, 4F, *m*-F). ^1H NMR ($CDCl_3$, δ, ppm): 6.96−7.78 (m, 14H), 5.50 (d, 2H, $^2J_{HH} = 18$ Hz, CH_2−N), 5.45 (d, 2H, $^2J_{HH} = 18$ Hz, CH_2−N), 4.59 (dd, 1H, $^2J_{HH} = 20$ Hz, $^4J_{PH} = 4$ Hz, CH_2 bridge), and 4.50 (dd, 1H, $^1J_{HH} = 20$ Hz, $^4J_{PH} = 4$ Hz, CH_2 bridge). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 146.6, 144.0, 142.0, 139.6, 139.3, 138.7, 136.0, 133.2, 129.7, 129.6, 128.7, 127.4, 123.3, 119.9, 119.2, 118.0, 110.7, 109.2, 37.3, and 21.6. EI-MS: *m/z* 712 [M^+, 89], 635 [M^+ − Ph, 6], 531 [M^+ − $CH_2C_6F_5$, 100], 453 [M^+ − $CH_2C_6F_5$ − Ph], 350 [M^+ − 2($CH_2C_6F_5$), 40], 273 [M^+ − 2($CH_2C_6F_5$) − Ph, 33], and 181 [$CH_2C_6F_5^+$, 16].

Bis(1-(*R*)-(−)-myrtenyl-3-indolyl)methane-(2,12)-phenylphosphine ($P(C_6H_5)(C_{37}H_{40}N_2)$, (*N*-(*R*)-(−)-myrtenyl)$_2$-3). The preparation for **(*N*-Me)$_2$-3** was followed. **(*N*-(*R*)-(−)-myrtenyl)$_2$-3** was obtained as a yellow powder (0.43 g, 81%). HRMS (EI) for $C_{43}H_{45}N_2P$ (M^+): calcd, 620.3320; found, 660.3332. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −66.8. ^1H NMR ($CDCl_3$, δ, ppm): 7.07−7.80 (m, 13H), 4.96 (s, 2H, alkene CH on myrtenyl), 4.69 (d, 2H, $^2J_{HH} = 18$ Hz, N−CH_2), 4.66 (dd, 1H, $^2J_{HH} = 21$ Hz, $^4J_{PH} = 3$ Hz, CH_2 bridge), 4.55 (d, 2H, $^2J_{HH} = 18$ Hz, N−CH_2), 4.53 (dd, 1H, $^2J_{HH} = 21$ Hz, $^4J_{PH} = 3$ Hz, CH_2 bridge), 2.32 (s, 4H, CH_2 bridge on myrtenyl), 2.27 (s, 2H, CH on myrtenyl), 2.18 (m, 2H, CH on myrtenyl), 1.15 (d, 4H, $^3J_{HH} = 5$ Hz, CH_2 on myrtenyl), 0.81 (s, 6H, CH_3 on myrtenyl), and 0.72 (s, 6H, CH_3 on myrtenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 142.9, 139.5, 137.2, 134.7, 130.8, 129.7, 128.6, 127.5, 122.4, 119.1, 118.7, 118.1, 116.0, 110.4, 49.4, 43.3, 40.9, 38.3, 31.6, 31.0, 26.2, 21.7, and 21.1. EI-MS: *m/z* 620 [M^+, 81], 486 [M^+ − myrtenyl, 12], and 351 [M^+ − 2(myrtenyl), 9].

[$PdP(C_6H_5)_2(C_9H_8N)Cl(\mu$-Cl)]$_2$, (4). A solution of **1** (0.022 g, 0.070 mmol) in acetonitrile (5 mL) was added dropwise to a solution of $Pd(COD)Cl_2$ (0.022 g, 0.070 mmol) in acetonitrile. The resulting orange mixture was stirred at room temperature for 15 min. The solvent was removed in vacuo, affording a red powder. The powder was recrystallized from a dichloromethane−hexanes mixture (3:1 v/v) at ambient temperature to give red plates suitable for single-crystal X-ray diffraction (0.0303 g, 88%). Anal. Calcd for $C_{42}H_{36}Cl_4N_2P_2Pd_2$ (985.35): C, 51.20; H, 3.68; N, 2.84. Found: C, 50.91; H, 4.01; N, 2.67. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 14.6. ^1H NMR ($CDCl_3$, δ, ppm): 10.2 (s, 2H, NH), 7.14−7.66 (m, 28H), 1.68 (s, 6H, CH_3 on indole).

[$PdP(C_6H_5)(C_9H_8N)_2Cl(\mu$-Cl)]$_2$ (5). The preparation for **4** was followed with the exceptions of using **2** (0.022 g, 0.070 mmol) and $Pd(COD)Cl_2$ (0.024 g, 0.065 mmol). The resultant powder after filtration was recrystallized from a dichloromethane−diethyl ether mixture (3:1 v/v) at ambient temperature to afford red blocks suitable for single-crystal X-ray diffraction (0.0338 g, 95%). Anal. Calcd for $C_{48}H_{42}Cl_4N_4P_2Pd_2\cdot 4H_2O$ (1163.53): C, 49.62; H, 4.21; N, 4.83. Found: C, 49.70; H, 4.07; N, 4.42. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −5.7. ^1H NMR ($CDCl_3$, δ, ppm): 9.06 (s, 2H, NH), 7.16−7.62 (m, 26H), 2.00 (s, 12H, CH_3 on indole).

[$PdP(C_6H_5)(C_{17}H_{12}N_2)Cl(\mu$-Cl)]$_2$ (6). The preparation for **4** was followed with the exceptions of using **3** (0.028 mg, 0.089 mmol) and $Pd(COD)Cl_2$ (26.0 mg, 0.074 mmol). The resultant powder after filtration was recrystallized from dichloromethane−hexanes (3:1 v/v) at ambient temperature to give red blocks suitable for single-crystal X-ray diffraction (0.0352 g, 90%). Anal. Calcd for $C_{46}H_{34}Cl_4N_4P_2Pd_2\cdot 2H_2O$ (1095.42): C, 50.41; H, 3.23; N, 5.29. Found: C, 50.28; H, 3.26; N, 5.04. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −14.9. ^1H NMR ($CDCl_3$, δ, ppm): 9.76 (s, 2H, NH, br), 7.16−7.62 (m, 26H), 4.42 (dd, 1H, $^2J_{HH} = 21$ Hz, $^4J_{PH} = 4$ Hz, CH_2 bridge), and 4.34 (dd, 1H, $^2J_{HH} = 21$ Hz, $^4J_{PH} = 4$ Hz, CH_2 bridge).

X-ray Crystallography. Details about data collection and solution refinement are given in Tables 2 and 3. X-ray data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A combination of 1° ϕ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package. The structures were solved and refined with the SHELXTL-PC v5.1 software

Table 3. Crystallographic Data of Complexes 4−6

	4	5	6
formula	$C_{42}H_{36}Cl_4N_2P_2Pd$	$C_{24}H_{21}Cl_2N_2PPd$	$C_{46}H_{34}N_4O_2P_2Pd_2Cl_4{\cdot}H_2O{\cdot}CH_2Cl_2$
formula wt	985.27	545.70	1265.20
cryst color, shape	red-orange, plate	red-orange, needle	red-orange, plate
cryst size, mm	0.56 × 0.30 × 0.02	0.08 × 0.05 × 0.04	0.32 × 0.18 × 0.02
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	15.6092(5)	8.2002(4)	8.7188(2)
b, Å	8.0167(2)	19.310(1)	11.8646(4)
c, Å	15.9823(4)	14.4641(9)	12.2122(3)
α, deg	90	90	79.43(1)
β, deg	96.823(1)	100.594(2)	79.39(1)
γ, deg	90	90	87.59(1)
V, Å^3	1985.77(9)	2251.2(2)	1220.56(6)
Z	2	4	1
D_{calcd}, g cm^{-3}	1.648	1.610	1.721
F(000)	984	1096	632
μ, mm^{-1}	1.289	1.147	1.285
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
limiting indices	$-20 \le h \le 20$	$-10 \le h \le 10$	$-11 \le h \le 11$
	$-8 \le k \le 10$	$-25 \le k \le 25$	$-15 \le k \le 15$
	$-19 \le l \le 20$	$-18 \le l \le 18$	$-15 \le l \le 15$
2*θ* range, deg	1.02− 27.48	1.02−27.48	1.02−27.48
max and min transmission	0.9747 and 0.5322	0.9556 and 0.9138	0.9748 and 0.6839
no. of rflens collected	14 479	19 038	19 119
no. of indep rflns/R_{int}	4839/0.0501	5317/0.1572	5618/0.0635
extinction coeff	0.0021(5)	0.0138(9)	0.0043(9)
no. of refined params	241	274	315
final R1, wR2	0.0320, 0.825	0.0625, 0.1260	0.0387, 0.0943
final R1, wR2 (all data)	0.0407, 0.0878	0.1546, 0.1721	0.0510, 0.1019
goodness of fit	1.035	0.985	1.050
$\Delta\rho_{min}$, $\Delta\rho_{max}$, e Å^{-3}	−1.066, 0.676	−1.056, 1.167	−1.367, 0.887

package. Refinement was by full-matrix least squares on F^2 using data (including negative intensities). Absorption corrections were made for every structure. Hydrogen atoms were introduced at calculated positions and treated as riding atoms, included in structure factor calculations, and not refined. All the heavy atoms were refined anisotropically.

Results and Discussion

Syntheses and Characterizations of Ligands 1−3. Ligands **1**−**3** were synthesized by modifying the method of Katritzky and co-workers,[11] in which substitution at the phosphorus atom proceeds via a C2-lithiated indole intermediate. Lithiation of indole occurs preferentially at the nitrogen and subsequently at the C3 position of the ring.[11] By introducing a methyl group at the C3 position and an ortho metal-directing aminal protecting group on the nitrogen, lithiation of 1-[(dimethylamino)methyl]-3-methylindole occurs was achieved at the C2 position. The addition of the appropriate chlorophenylphosphine leads to chloride substitution by the indolyl groups to provide **1** and **2**. While removal of the aminal protecting group took place during the acidic aqueous workup of phosphine **1**, reaction with $NaBH_4$ in a refluxing 1:1 ethanol−tetrahydrofuran mixture was required to displace the aminal protecting group from **2**. Subsequent recrystallization from methanol afforded **1** and **2** in good yields. The preparation of ligand **3** was achieved in a similar manner. Lithiation at the C2 position of 1,1′-bis[(dimethylamino)methyl]bis(1*H*-3-indolyl)methane followed by the addition of dichlorophenylphosphine at −78 °C replaced the chlorides of the phosphine ligand with the coupled indolyl substituent. As observed in the synthesis of **2**, displacement of the aminal-protected groups from the product required the use of $NaBH_4$ in a refluxing 1:1 ethanol−tetrahydrofuran mixture over 5 h. Removal of the volatile solvents, followed by acidic aqueous workup and subsequent recrystallization from methanol, afforded **3** in good yields.

The ^{31}P NMR spectra of **1** and **2** both indicated the presence of a single phosphorus environment; the additional indolyl substituent of **2** results in the upfield shift of its ^{31}P NMR signal (δ −59.3 ppm) relative to the monoindolyl substituted **1** (δ −33.1 ppm). The ^{1}H and ^{13}C NMR spectra of **1** and **2** confirmed the presence of one and two methylindolyl substituents respectively bound to phosphorus, as well as the removal of the aminal protecting groups from the indolyl nitrogen atoms. The small difference in ^{31}P NMR chemical shift of **3** (δ −56.0 ppm) in comparison to that of **2** (δ −59.3 ppm) suggests that the coupling of the two indolyl substituents induces little strain in the resulting unconjugated six-membered phosphacycle.

While ^{31}P coupling to the ^{13}C resonances of **1** and **2** indicated that indole substitution had occurred,[9] the position of phosphorus substitution about the indole ring awaited confirmation by X-ray crystallography. Single crystals of **1** were grown by slow evaporation from toluene. Figure 2 shows the molecular structure and numbering scheme of the ligand, and Table 4 lists selected bond distances and angles. Phosphine **1** crystallizes in the space group $P\bar{1}$, with two crystallographically independent molecules in the asymmetric unit. The independent molecules are adequately similar in structure, such that discussion is confined to one of them.[12] The geometry about the phosphorus atoms is best

(11) Katritzky, A. R.; Lue, P.; Chen, Y.-X. *J. Org. Chem.* **1990**, *55*, 3688.

(12) The most significant difference between the two molecules is the C(2)−P(1)−C(17) bond angles of 99.94(8) and 101.94(9)°.

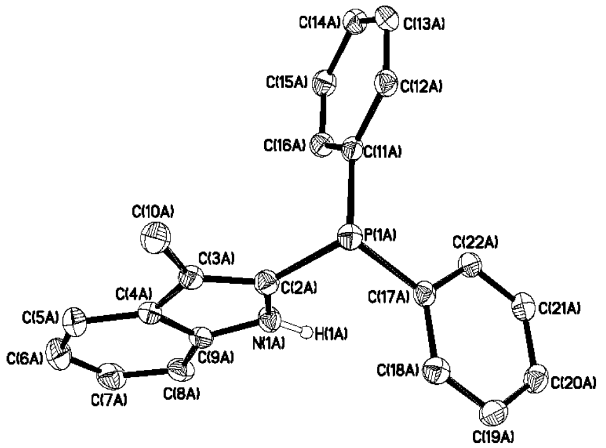


Figure 2. ORTEP diagram of **1** showing the numbering scheme. Ellipsoids are at the 35% probability level. All hydrogen atoms except for the amine proton have been omitted for clarity.

described as trigonal pyramidal with the aromatic substituents adopting a twisted propeller-blade-like orientation. The P(1)−indolyl C(2) bond distance of 1.813(2) Å is significantly shorter than the bond distances from phosphorus to the α-C atoms of the phenyl rings (average 1.838(2) Å). No chemical significance is associated with the bond angle between the indolyl and one of the phenyl substituents, C(2A)−P(1A)−C(17A) (99.9(8)°), being significantly smaller than the other bond angles of C(2A)−P(1A)−C(11A) (101.6(8)°) and C(11A)−P(1A)−C(17A) (103.0(8)°). Bonding of phosphorus at the C2 position induces no important changes in the structural features of the methylindolyl substituent.

It is evident from the crystal structure of **1** that the C2-bound methylindolyl group constitutes a markedly larger phosphorus substituent than the phenyl ring. An average separation of 2.40(6) Å between the two phenyl carbon atoms positioned ortho to phosphorus on each ring serves as an effective measure of the width of the phosphine's two phenyl groups. In comparison, measured from its nitrogen atom to the methyl carbon atom C(10A), the equivalent width of 3.713(4) Å for the methylindolyl group of **1** suggests that the indolylphosphines **1** and **2** possess cone angles larger than that of PPh_3,[13,14] perhaps bearing a closer similarity in size to P(*o*-tolyl)$_3$.[15]

Crystals of ligand **2** were grown from slow evaporation of a saturated solution in dichloromethane. Figure 3 shows the molecular structure and numbering scheme of the ligand, and Table 4 lists selected bond distances and angles. Ligand **2** crystallizes in the space group $P2_1/c$. The phosphorus atom adopts a trigonal-pyramidal geometry with the aromatic substituents situated in a twisted propeller-blade-like fashion, similar to the solid-state structure of **1**. Likely due to steric influences, the indolyl substituents are oriented such that the methyl moieties at the C(3) and C(13) positions point away from the pyramid formed by the substituents around P(1). In addition, the P(1)−indolyl C(2) and P(1)−indolyl C(12) bond distances of 1.812(2) and 1.809(2) Å, respectively, are shorter than the P(1)−phenyl C(21) bond distance of 1.841(2) Å. As with **1**, the bonding of the phosphorus atom at the C2 positions on indolyl do not impose chemically significant changes in the structural features of its methylindolyl substituent.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Ligands 1 and 2 and N-Functionalized Ligands (*N*-Bz)-1, (*N*-CH_2NMe_2)$_2$-3, and (*N*-F_5Bz)$_2$-3

Compound 1			
P(1A)−C(2A)	1.813(2)	N(1A)−C(9A)	1.378(2)
P(1A)−C(11A)	1.838(2)	N(1A)−C(2A)	1.399(2)
P(1A)−C(17A)	1.837(2)		
C(2A)−P(1A)−C(11A)	101.64(8)	C(9A)−N(1A)−C(2A)	109.3(6)
C(2A)−P(1A)−C(17A)	99.94(8)	C(3A)−C(2A)−N(1A)	109.0(2)
C(11A)−P(1A)−C(17A)	102.97(8)		
Compound 2			
P(1)−C(2)	1.812(2)	N(1)−C(2)	1.398(3)
P(1)−C(12)	1.809(2)	N(11)−C(19)	1.382(3)
P(1)−C(21)	1.841(2)	N(11)−C(12)	1.395(3)
N(1)−C(9)	1.373(3)		
C(2)−P(1)−C(12)	100.3(1)	N(1)−C(9)−C(4)	107.5(2)
C(2)−P(1)−C(21)	101.3(1)	C(19)−N(11)−C(12)	109.3(2)
C(1)−P(1)−C(21)	102.2(1)	C(13)−C(12)−N(11)	108.8(2)
C(9)−N(1)−C(2)	109.1(2)	N(11)−C(19)−C(14)	107.3(2)
C(3)−C(2)−N(1)	109.2(1)		
Compound (*N*-Bz)-1			
P(1)−C(2)	1.819(2)	N(1)−C(9)	1.377(3)
P(1)−C(11)	1.836(2)	N(1)−C(2)	1.400(3)
P(1)−C(17)	1.831(2)	N(1)−C(23)	1.454(4)
C(2)−P(1)−C(11)	103.60(9)	C(9)−N(1)−C(2)	108.8(2)
C(2)−P(1)−C(17)	101.0(1)	C(3)−C(2)−N(1)	108.4(2)
C(11)−P(1)−C(17)	103.24(9)	N(1)−C(23)−C(24)	113.6(2)
Compound (*N*-CH_2NMe_2)$_2$-3			
P(1)−C(2)	1.811(2)	N(1)−C(26)	1.453(3)
P(1)−C(12)	1.814(2)	N(11)−C(19)	1.379(3)
P(1)−C(20)	1.845(2)	N(11)−C(12)	1.397(3)
N(1)−C(9)	1.383(3)	C(13)−C(10)	1.503(3)
N(1)−C(2)	1.404(3)	N(11)−C(30)	1.453(3)
C(3)−C(10)	1.492(3)		
C(2)−P(1)−C(12)	94.72(10)	N(1)−C(26)−N(27)	112.9(2)
C(2)−P(1)−C(20)	101.3(1)	C(19)−N(11)−C(12)	108.6(2)
C(12)−P(1)−C(20)	101.7(1)	C(13)−C(12)−N(11)	109.2(2)
C(9)−N(1)−C(2)	108.0(2)	N(11)−C(19)−C(14)	107.8(2)
C(3)−C(2)−N(1)	109.4(2)	N(11)−C(30)−N(31)	111.4(2)
N(1)−C(9)−C(4)	108.3(2)	C(3)−C(10)−C(13)	113.0(2)
(*N*-F_5Bz)$_2$-3			
P(1)−C(2)	1.802(2)	N(1)−C(26)	1.452(3)
P(1)−C(12)	1.813(2)	N(11)−C(19)	1.378(3)
P(1)−C(20)	1.844(2)	N(11)−C(12)	1.396(3)
N(1)−C(9)	1.383(3)	C(13)−C(10)	1.497(3)
N(1)−C(2)	1.399(3)	N(11)−C(33)	1.442(3)
C(3)−C(10)	1.494(3)	N(1)−C(26)−C(27)	115.3(2)
C(2)−P(1)−C(12)	94.36(9)	C(19)−N(11)−C(12)	108.9(2)
C(2)−P(1)−C(20)	103.20(9)	C(13)−C(12)−N(11)	109.4(2)
C(12)−P(1)−C(20)	101.63(9)	N(11)−C(19)−C(14)	107.8(2)
C(9)−N(1)−C(2)	108.5(2)	N(11)−C(33)−C(34)	116.2(2)
C(3)−C(2)−N(1)	109.3(2)	C(3)−C(10)−C(13)	112.9(2)
N(1)−C(9)−C(4)	108.0(2)		

Synthesis and Characterization of N-Substituted Ligands. The steric and electronic properties of ligands **1**−**3** were modified with a variety of substituents introduced at the indole nitrogen positions. Functionalization proceeded by initial NaH deprotonation of the indolylphosphine's nitrogen atoms followed by the addition of the appropriate alkyl halide to afford the target ligand in moderate yields. Table 1 lists the N-functionalized derivatives of ligands **1**−**3** that have been synthesized, their corresponding ^{31}P NMR chemical shifts,

(13) Bunten, K. A.; Chen, L.; Fernandez, A. L.; Poe, A. J. *Coord. Chem. Rev.* **2002**, *233*−*234*, 41.
(14) Mueller, T. E.; Mingos, D. M. P. *Transition Met. Chem.* **1995**, *20*, 533.
(15) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

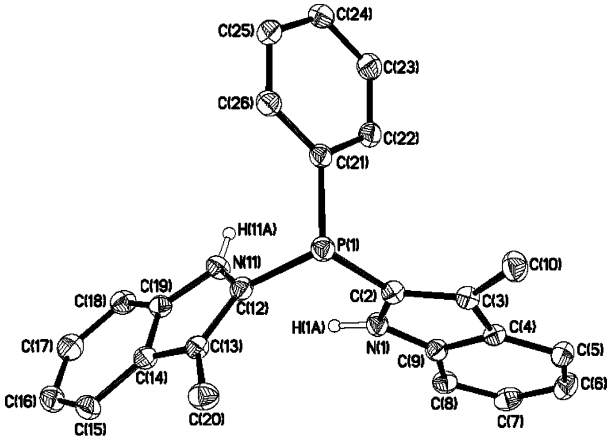


Figure 3. ORTEP diagram of **2** showing the numbering scheme. Ellipsoids are at the 35% probability level. All hydrogen atoms except for the amine protons have been omitted for clarity.

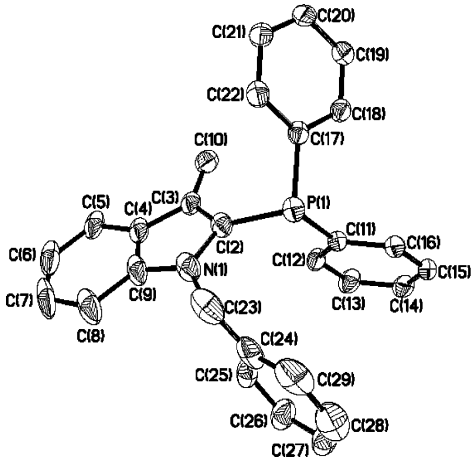


Figure 4. ORTEP diagram of **(*N*-Bz)-1** showing the numbering scheme. Ellipsoids are at the 35% probability level. All hydrogen atoms have been omitted for clarity.

and their yields. The introduction of these diverse substituents β to the phosphorus center demonstrates a facile and general route to systematically adjust the steric environment and electronic character of the phosphorus center in these ligands. This modular approach to creating new phosphines through substituent modification following P-substituent bond formation lies in contrast to the more customary methods of phosphine synthesis. Therein, the challenging and often substituent-specific intricacies and vagaries of P−C bond formation must be overcome each time that a different structural element of interest is incorporated into the phosphine.

All of the ligand derivatives have been fully characterized using high-resolution mass spectrometry and ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. Single crystals of **(*N*-Bz)-1** were obtained from slow evaporation of a saturated solution of the ligand in dichloromethane. Figure 4 shows the molecular structure and numbering scheme of the ligand, and Table 4 lists selected bond distances and angles. The ligand **(*N*-Bz)-1** crystallizes in the monoclinic space group $P2_1/c$. The geometry about P(1) is trigonal pyramidal, and the aromatic substituents are oriented in a similar fashion as **1** and **2**. The benzyl group adopts an orientation in which it forms a slipped pseudo-eclipsed π-stacking interaction with one

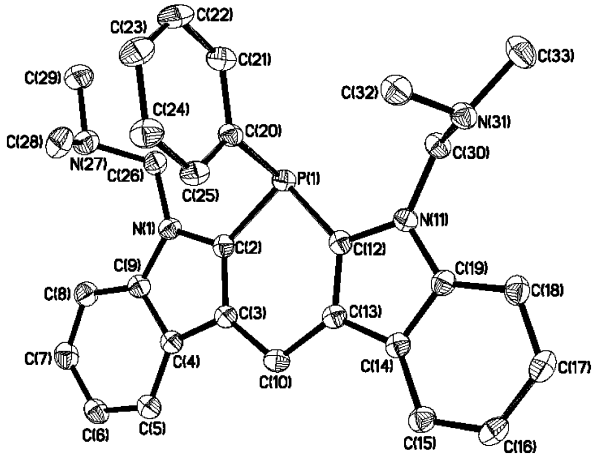


Figure 5. ORTEP diagram of **(*N*-CH$_2$NMe$_2$)$_2$-3** showing the numbering scheme. Ellipsoids are at the 35% probability level. All hydrogen atoms have been omitted for clarity.

of the phenyl moieties on P(1) with a ring-to-ring distance of 4.413 Å. The benzylated methylindolyl substituent represents a significantly larger phosphorus substituent than the phenyl moieties. The analogous width of the benzylated methylindolyl, measured from indolyl's methyl carbon atom C(10) to the N-substituted methylene carbon C(23), was determined to be 5.061(4) Å, suggesting that the introduction of any group on the indolyl nitrogen renders that phosphine substituent a cone angle markedly greater than that of a phenyl group.

Crystals of aminal-protected **3**, **(*N*-CH$_2$NMe$_2$)$_2$-3**, were grown by solvent vapor diffusion of pentane into a solution of the phosphine in dichloromethane. The protected ligand crystallized in the monoclinic space group $P2_1/c$. Figure 5 shows the molecular structure and numbering scheme of the ligand, and Table 4 lists selected bond distances and angles. The X-ray structure determination of **(*N*-CH$_2$NMe$_2$)$_2$-3** confirmed the incorporation of the phosphorus atom P(1) into the six-membered ring through bonding to the coupled indolyl substituent at its two C2 positions, C(2) and C(12).

The formation of the phosphacycle was also evident in the structure determination of **(*N*-F$_5$Bz)$_2$-3**, single crystals of which were obtained by slow solvent evaporation from a $CDCl_3$ solution of the phosphine. **(*N*-F$_5$Bz)$_2$-3** crystallizes in the monoclinic space group $P2_1/n$ with one deuteriochloroform solvent molecule present. Figure 6 shows the molecular structure and numbering scheme of **(*N*-F$_5$Bz)$_2$-3**, and Table 4 lists selected bond distances and angles. A comparison of its solid-state structure with that of **(*N*-CH$_2$NMe$_2$)$_2$-3** reveals that the replacement of the electron-rich aminal groups with the electron-withdrawing pentafluorobenzyl substituents imparts little structural change upon the rest of the molecule. For example, the P(1)−C(2) and P(1)−C(12) bond lengths of 1.802(2) and 1.813(2) Å, respectively, in **(*N*-F$_5$Bz)$_2$-3** are effectively the same as the analogous bond lengths of 1.811(2) and 1.814(2) Å in **(*N*-CH$_2$NMe$_2$)$_2$-3** and are not significantly different from the P(1)−indolyl C(2) separation of 1.813(2) Å observed in **1**. Consistent with the ^{31}P NMR behavior of **3**, the structural data for both derivatives of **3** suggest that their six-membered rings do not experience sub-

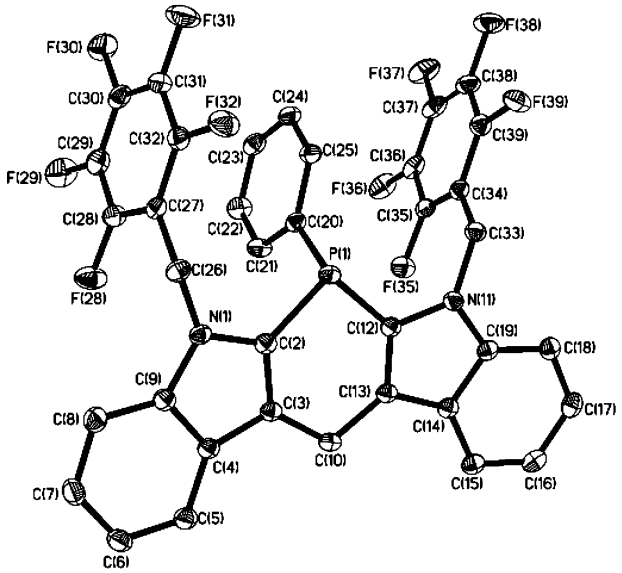


Figure 6. ORTEP diagram of **(*N*-F_5Bz)$_2$-3** showing the numbering scheme. Ellipsoids are at the 35% probability level. All hydrogen atoms and the $CHCl_3$ solvent molecule have been omitted for clarity.

stantial ring strain. The respective C(3)−C(10)−C(13) bond angles of 113.0(2) and 112.9(2)° about the methylene carbon of the phosphacycles of **(*N*-CH_2NMe_2)$_2$-3** and **(*N*-F_5Bz)$_2$-3** are only slightly smaller than the corresponding bond angle of 115.4(2)° measured in 3,3′-diindolylmethane.[16] Interestingly, coupling of the indolyl substituents does produce a compression of almost 6° upon the C(2)−P(1)−C(12) bond angle from comparison of the values of 94.72(10) and 94.36(9)° in **(*N*-CH_2NMe_2)$_2$-3** and **(*N*-F_5Bz)$_2$-3**, respectively, with that of 100.3(1)° measured between the uncoupled indolyl substituents of **2**. This is not considered to impart significant ring strain to the phosphacycle, because of the facility with which phosphorus subtlely changes hybridization in order to accommodate substituents of differing electronic or steric requirements. The six-membered rings are essentially planar in both structures with a root-mean-square deviation of less than 0.02Å.

In the solid state, the aminal-protecting groups of **(*N*-CH_2NMe_2)$_2$-3** and the pentafluorobenzyl groups of **(*N*-F_5Bz)$_2$-3** both adopt conformations in which they are oriented in the same direction as the phenyl substituent on the phosphorus atom. The fluorinated benzyl groups additionally exhibit a slipped pseudo-eclipsed π-stacking conformation with the lone phenyl substituent of P(1). Distances between ring centroids of 3.547 and 3.805 Å and an angle of 146° described by them suggest the near-planar π-stacking of the three rings.

Synthesis and Characterization of the Complexes [Pd(1)Cl(μ-Cl)]$_2$ (4), [Pd(2)Cl(μ-Cl)]$_2$ (5), and [Pd(3)Cl(μ-Cl)]$_2$ (6). Phosphines **1**−**3** were reacted with Pd(II) in order to demonstrate P-coordination of the ligands exclusively. In reaction with $Pd(COD)Cl_2$, displacement of COD provides two sites of coordination with which an indolylphenylphosphine such as **1** may act as either a monodentate P-donor or as a chelating or bridging bidentate P,N-Lewis base.

(16) Rampersad, N. C.; Farrar, D. H. Unpublished results.

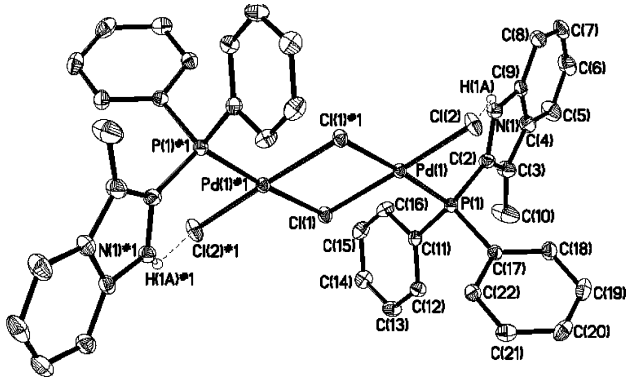


Figure 7. ORTEP diagram of complex **4** showing the numbering scheme. Ellipsoids are at the 35% probability level. All hydrogen atoms except for the amine protons have been omitted for clarity. Intramolecular hydrogen bonding is also exhibited.

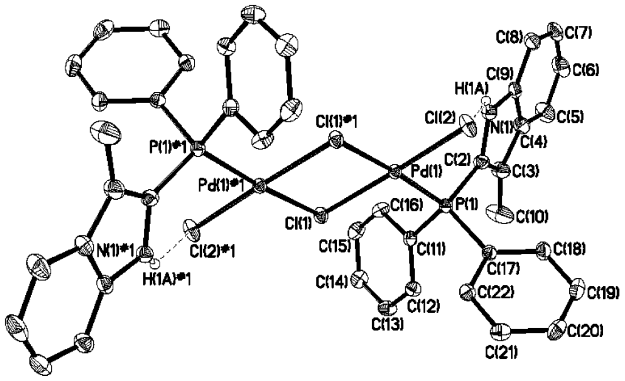


Figure 8. ORTEP diagram of complex **5** showing the numbering scheme. Ellipsoids are at the 35% probability level. All hydrogen atoms except for the amine protons have been omitted for clarity. Intramolecular hydrogen bonding is also exhibited.

Complexes **4**−**6** were obtained by the addition of acetonitrile solutions of 1 equiv of **1**−**3**, respectively, to a solution of $Pd(COD)Cl_2$ in acetonitrile. After the mixture was stirred for 15 min at ambient temperature, dark orange-red solids were obtained upon removal of the solvent under reduced pressure. The Pd(II) complexes were recrystallized in good yields from dichloromethane−hexanes or dichloromethane−diethyl ether mixtures. Complexation of **1**−**3** to Pd(II) resulted in the downfield displacement of their ^{31}P NMR chemical shifts from −33.1, −59.3, and −56.0 ppm, respectively, to 14.6 ppm for [PdP(C_6H_5)$_2$(C_9H_8N)Cl(μ-Cl)]$_2$ (**4**), −5.7 ppm for [PdP(C_6H_5)(C_9H_8N)$_2$Cl(μ-Cl)]$_2$ (**5**), and −14.9 ppm [PdP(C_6H_5)($C_{17}H_{12}N_2$)Cl(μ-Cl)]$_2$ (**6**).

The structures of **4** and **5** were confirmed by X-ray crystallography. Single crystals of sufficient quality were obtained for **4** and **5** from solvent vapor diffusion of hexanes and diethyl ether, respectively, into a solution of each complex in dichloromethane. Figures 7 and 8 show the molecular structures and numbering schemes for complexes **4** and **5**, respectively, while Table 5 lists selected bond distances and angles. Complexes **4** and **5** are isostructural in the solid state, consisting of discrete molecules of dimeric [Pd(**1**)Cl(μ-Cl)]$_2$ and [Pd(**2**)Cl(μ-Cl)]$_2$, respectively, sitting about crystallographic inversion centers in the monoclinic space group $P2_1/c$. Both structures exhibit the expected square-planar coordination geometry about the Pd center and share a number

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complexes 4−6

	Compound **4**		
Pd(1)−Cl(1)	2.3209(6)	P(1)−C(11)	1.810(3)
Pd(1)−Cl(2)	2.2796(7)	P(1)−C(17)	1.808(3)
Pd(1)−P(1)	2.2332(7)	N(1)−C(9)	1.366(4)
P(1)−C(2)	1.797(3)	N(1)−C(2)	1.379(4)
Pd(1)−P(1)−C(2)	116.5(1)	C(11)−P(1)−C(17)	107.2(1)
Pd(1)−P(1)−C(11)	112.9(9)	C(9)−N(1)−C(2)	109.1(3)
Pd(1)−P(1)−C(17)	107.2(9)	C(3)−C(2)−N(1)	109.5(3)
C(2)−P(1)−C(11)	102.9(1)	N(1)−C(9)−C(4)	107.7(3)
C(2)−P(1)−C(17)	109.9(1)		
	Compound **5**		
Pd(1)−Cl(1)	2.319(2)	P(1)−C(21)	1.805(7)
Pd(1)−Cl(2)	2.269(2)	N(1)−C(9)	1.370(10)
Pd(1)−P(1)	2.220(2)	N(1)−C(2)	1.388(9)
P(1)−C(2)	1.795(8)	N(11)−C(19)	1.380(9)
P(1)−C(12)	1.790(8)	N(11)−C(12)	1.403(9)
Pd(1)−P(1)−C(2)	112.6(2)	C(9)−N(1)−C(2)	108.8(6)
Pd(1)−P(1)−C(12)	113.5(3)	C(3)−C(2)−N(1)	109.7(6)
Pd(1)−P(1)−C(21)	110.3(3)	N(1)−C(9)−C(4)	107.5(6)
C(2)−P(1)−C(12)	104.6(3)	C(19)−N(11)−C(12)	107.2(6)
C(2)−P(1)−C(21)	109.3(4)	C(13)−C(12)−N(11)	110.0(6)
C(12)−P(1)−C(21)	106.2(3)	N(11)−C(19)−C(14)	108.7(6)
	Compound **6**		
Pd(1)−Cl(1)	2.3163(7)	P(1)−C(20)	1.807(3)
Pd(1)−Cl(2)	2.2901(8)	N(1)−C(9)	1.365(4)
Pd(1)−P(1)	2.2162(8)	N(1)−C(2)	1.384(4)
P(1)−C(2)	1.772(3)	N(11)−C(19)	1.377(4)
P(1)−C(12)	1.778(3)	N(11)−C(12)	1.388(4)
Pd(1)−P(1)−C(2)	117.4(1)	C(9)−N(1)−C(2)	108.6(2)
Pd(1)−P(1)−C(12)	110.1(1)	C(3)−C(2)−N(1)	109.9(3)
Pd(1)−P(1)−C(20)	111.3(1)	N(1)−C(9)−C(4)	108.0(3)
C(2)−P(1)−C(12)	99.1(1)	C(19)−N(11)−C(12)	108.2(2)
C(2)−P(1)−C(20)	107.9(1)	C(13)−C(12)−N(11)	110.1(2)
C(12)−P(1)−C(20)	110.4(1)		

of structural similarities with previously characterized [Pd(**L**)Cl(μ-Cl)]$_2$ dimers. Most notably, the Pd−P bond lengths of 2.233(7) and 2.220(2) Å for **4** and **5**, respectively, are consistent with Pd−P bond lengths reported for other palladium−phosphine complexes.[21,22] Comparisons of the bond angles between phosphine substituents of **1** with those of **4** as well as comparisons of those of **2** with those of **5** show that the increase in bond angles of approximately 4−5° commonly seen upon metal coordination[21] is also observed upon the bonding of **1** and **2** to Pd(II). The structures confirm that monodentate P-coordination of **1** and **2** to Pd(II) does not sufficiently increase the acidity of the ligand's nitrogen center to result in the indolyl substituent serving as an additional site for metal coordination in the absence of base.

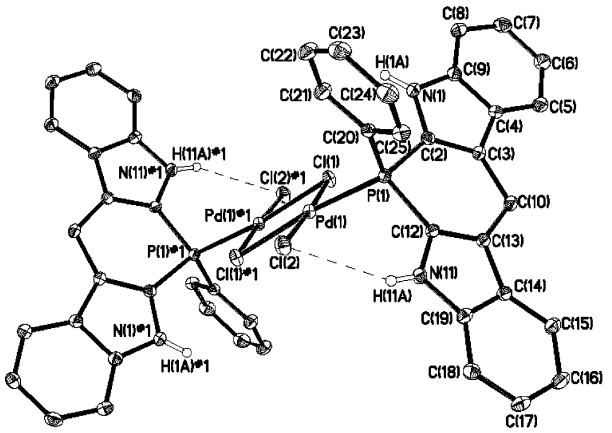


Figure 9. ORTEP diagram of complex **6** showing the numbering scheme. Ellipsoids are at the 35% probability level. All hydrogen atoms except for the amine protons have been omitted for clarity. Intramolecular hydrogen bonding is also exhibited.

Consistent with their characteristic resonances at δ ~10 ppm which were observed in the ^{1}H NMR of **4** and **5**, the difference electron density map confirmed the presence of a proton about each indolyl nitrogen center. The NH moieties of the coordinated indolylphosphines demonstrate a degree of acidic character in their hydrogen bonding in the palladium complexes. Intramolecular hydrogen-bonding contacts are evident between N(1)−H(1A) and the terminally bound Cl(2) in **4** (Figure 7). Similar intramolecular hydrogen-bonding interactions exist between the terminal Cl(2) in **5** and the N(11)−H(11A) group of the suitably orientated indolyl substituent.

Single crystals of **6** were obtained from solvent vapor diffusion of hexanes into a solution of the complex in dichloromethane. Figure 9 shows the molecular structure and numbering scheme of the complex, and Table 5 lists selected bond distances and angles. The dimeric complex **6** crystallizes in the space group $P\bar{1}$, with each half of the dimer sitting about a crystallographic inversion center. Per asymmetric unit, there is one molecule of water and one molecule of dichloromethane also present in the lattice.

As exhibited in **4** and **5**, the Pd center in **6** adopts the expected square-planar coordination geometry, and monodentate P-coordination of the ligand is obtained. Structural consequences derived from coordination of the phosphine **3** in complex **6** can be acquired from a comparison of its solid-state structure with those of the free N-substituted derivatives of **3**. This reveals that the C(3)−C(10)−C(13) bond angle of 113.9(2)° in the phosphacycle of **6** remains essentially unchanged from the values observed in **(*N*-CH$_2$NMe$_2$)$_2$-3** and **(*N*-F$_5$Bz)$_2$-3**. Nevertheless, the 4−5° increase in bond angle between indolyl substituents observed upon P-coordination to Pd(II) in **5** is still seen in **6** and implies that coupling of

(17) Gaw, K. G.; Slawin, A. M. Z.; Simth, M. B. *Organometallics* **1999**, *18*, 3255.
(18) Barkley, J.; Ellis, M.; Higgins, S. J.; McCart, M. K. *Organometallics* **1998**, *17*, 1725.
(19) Hassan, F. S. M.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1501.
(20) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1979**, *169*, 107.
(21) (a) Coles, S. J.; Faulds, P.; Hursthouse, M. B.; Kelly, D. G.; Ranger, D. C.; Toner, A. J.; Walker, N. M. *J. Organomet. Chem.* **1999**, *586*, 234. (b) Slawin, A. M. Z.; Woollins, J. D.; Zhang, Q. *Inorg. Chem. Commun.* **1999**, *2*, 386. (c) Vinogradova, N. M.; Odinets, I. L.; Lyssenko, K. A.; Pasachnik, M. P.; Petrovskii, P. V.; Mastryukova, T. A. *Mendeleev Commun.* **2001**, 219. (d) Cobley, C. J.; Ellis, D. D.; Orpen, A. G.; Pringle, P. G. *Dalton* **2000**, 1101. (e) Brodie, N.; Goubard, F.; Tabuteau, A.; Halut, S. *Mater. Res. Bull.* **1998**, *33*, 1739. (f) Fenske, D.; Prokscha, H.; Becher, H. J. *Z. Naturforsch., B* **1980**, *35*, 1075. (g) Li, G. Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1513. (h) Dyson, P. J.; Steed, J. W.; Sunman, P. *CrystEngComm* **1999**, 2.
(22) (a) Dinger, M. B.; Scott, M. J. *Inorg. Chem.* **2001**, *40*, 856. (b) Vincente, J.; Lagunas, M. C.; Bleuet, E.; Ramirez de Arellano, M. C. Private communication, 1997. (c) Dyer, P. W.; Dyson, P. J.; James, S. L.; Sunman, P.; Davies, J. E.; Martin, C. M. *Chem. Commun.* **1998**, 1375. (d) Grisby, W. J.; Nicholson, B. K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 362. (e) Hydrio, J.; Gouygou, M.; Dallemar, F.; Balavoine, G. G. A.; Daran, J.-C. *J. Organomet. Chem.* **2002**, *643*, 19. (f) Liu, X.; Ong, T. K. W.; Selvaratnam, S.; Vittal, J. J.; White, A. J. P.; Williams, D. J.; Leung, P.-H. *J. Organomet. Chem.* **2002**, *643*, 4. (g) Chaloner, P. A.; Dewa, S. Z.; Hitchcock, P. B. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *51*, 232.

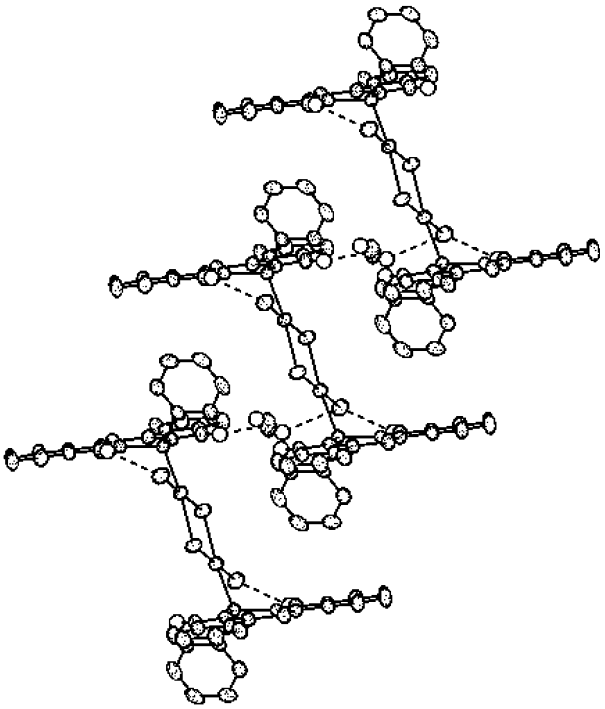


Figure 10. Extended hydrogen-bonding network of complex **6**. The dichloromethane solvent molecules have been omitted for clarity.

the indolyl substituents does not inhibit their "fanning out" upon P-coordination. The introduction of ring strain in the phosphacycle of **6** that may ensue from this fanning out is consistent with the upfield shift in ^{31}P NMR resonance of **6** relative to that of **5**, which is suggestive of a phosphorus center in a strained bonding environment.[18−21] A deviation from coplanarity of 5.6(1)° between the two indolyl groups indicates that the coupled indole remains effectively planar upon P-coordination.

Symmetry-related dimers of **6** pack in a laddered head-to-tail fashion that extends up the *a* axis of the unit cell. Both crystallographically independent indolyl NH groups of each dimer are involved in hydrogen bonding either within or between the dimeric units of the ladder, as shown in Figure 10. One NH group intramolecularly hydrogen bonds to its neighboring terminal chloride, as observed in **4** and **5**. The other NH group hydrogen bonds to the oxygen atom of solvate water, which completes a cyclic network by hydrogen bonding in turn to the terminal chloride of a symmetry-related dimer. The dichloromethane solvate has no significant intermolecular contacts.

Conclusion

This report describes the synthetic methods for the preparation of a series of novel C2-bound indolylphenylphosphines. The solid-state structures of ligands **1**−**3** have established the bonding of the phosphorus center to the C2 position of their respective indolyl substituents. The N-functionalization of these indolylphosphines, confirmed in the solid-state structure of **(*N*-F$_5$Bz)$_2$-3**, affords a variety of electron-withdrawing, electron-donating, and chiral indolyl substituents that may be easily introduced β to the phosphorus center. This ability to systematically alter the steric environment and electronic character of the phosphorus center with such facility has been a frequently cited but rarely achieved goal in phosphine synthesis and offers the opportunity to confer a spectrum of interesting characteristics upon the resulting ligands. Studies are currently underway examining the effectiveness of these and related ligands in catalysis and other important applications as a function of their steric and electronic properties.

In their subsequent coordination to Pd(II), the ability of these potentially P,N-bidentate ligands to act as monodentate P-donor ligands was confirmed by the X-ray crystallographic characterization of the products **4**−**6** as dimeric palladium complexes of the type [Pd(**L**)Cl(μ-Cl)]$_2$. While facile deprotonation of the indolyl nitrogen atoms of the complexed ligands does not occur, the prevalence of extensive intra- and intermolecular hydrogen-bonding interactions in the structure of each palladium complex **4**−**6** suggests that the NH groups of these ligands may indeed serve as centers of further reactivity. To this end, we have recently shown that the deprotonation of an indolylphosphine ligand of **4** leads to clean aggregation of the palladium dimer, in which the ligand serves as a bridging bidentate P,N-donor. We also have demonstrated the stepwise and controlled coordination of each of the phosphines **1**−**3**, initially as a P-donor and subsequently as an N-donor, in their reaction with $Ru_3(CO)_{12}$. These results will be reported elsewhere.

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Supporting Information Available: Tables giving X-ray crystallographic data for ligands **1** and **2**, the N-functionalized ligands **(*N*-Bz)-1**, **(*N*-CH$_2$NMe$_2$)$_2$-3**, and **(*N*-F$_5$Bz)$_2$-3**, and complexes **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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