Nitrogen-Assisted Ortho Lithiation: One-Pot Synthesis of New Classes of Bidentate and Tetradentate Mixed P∼N Ligands

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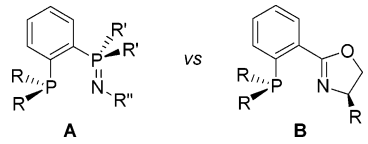
Summary: Metalation of one aryl group of $Ph_3P{=}NR$ (R = methyl, isopropyl) affords an easy access to the corresponding lithium salt, which in turn reacts with chlorophosphines R_2PCl (R = Ph, i-Pr) to yield a new class of bidentate ligand featuring one iminophosphorane and one phosphino group. Reaction of the phenyl derivative with [Pd(COD)Cl$_2$] yielded the expected six-membered palladacycle complex, which was structurally characterized. Extension of this new synthetic methodology toward the elaboration of enantiomerically pure tetradentate ligands has also been achieved.

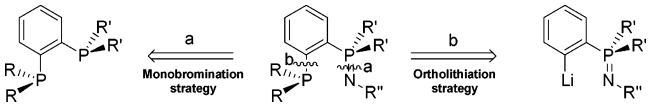
Introduction

The development of straightforward synthetic approaches toward new polydentate heteroatomic ligands is a field of continuing interest. Among various possible combinations of heteroatoms, P∼N systems have attracted a lot of attention due to the significant electronic differentiation induced by these two electronically different binding sites. In particular, bidentate P∼N ligands featuring the combination of a phosphine and an imine ligand (heterocycles or classical imines) have found numerous applications in coordination chemistry and catalysis, and therefore, these systems are by far the most widespread.[1−3] So far, only slight attention has been paid to P∼N ligands featuring a phosphine and a harder donor nitrogen ligand such as an iminophosphorane. These ligands, which are the nitrogen equivalent of phosphorus ylides, have recently found promising applications in homogeneous catalysis.[4,5] Last year, we reported on a very simple synthetic approach that allows the elaboration of mixed bidentate phosphine−iminophosphorane ligands featuring various functional groups at nitrogen (including chiral groups).[6] This procedure, which is derived from the Kirsanov method, relies on the selective bromination of one phosphorus atom of the dppm ligand (bis(diphenylphosphino)methane) followed by trapping of this intermediate by a primary amine.

Chart 1



Scheme 1



The most significant advantage of this procedure, which constitutes a competitive alternative to the Staudinger reaction, is its versatility, since different types of primary amines can be employed (aryl, alkyl, optically pure derivatives, ...).

In our ongoing studies aimed at exploring the use of these new P∼N ligands in coordination chemistry and catalysis, we recently explored the extension of this synthetic procedure to other bidendate phosphine ligands such as 1,2-bis(diphenylphosphino)benzene. We first reasoned that this diphosphine could be a convenient starting precursor for the elaboration of rigid bidentate phosphine−iminophosphorane ligands (**A**; Chart 1) that can form six-membered metallacycles. Indeed, this would lead to the iminophosphorane analogue of the extensively studied ligand developed by Pfaltz and Helmchen (**B**; Chart 1).[2,7]

We present here the results of this new strategy in both the synthesis of the desired bidentate ligand and the extension to a previously unknown tetradentate derivative.

Results and Discussion

In a first series of experiments, we tried to extend our previously reported methodology to 1,2-bis(diphenylphosphino)-benzene. Unfortunately, bromination of this diphosphine led to an unusable mixture of several brominated adducts, no matter what experimental conditions were used (solvent, temperature, amount of Br_2, and chlorinating agent such as C_2Cl_6). Therefore, failure of this approach (path a, Scheme 1) led us to devise a new one which relies on the assisted ortho-metalation process of triphenylphosphine-based iminophosphoranes (path b).

We envisioned the selective electrophilic trapping of an ortho-lithiated iminophosphorane derivative. Indeed, the iminophosphorane moiety was reported as early as 1976 by Stuckwisch to favor the α-deprotonation of a phenyl group of the PPh_3 in $Ph_3P{=}NPh$.[8] Later in 1995, Steiner and Stalke reported the dimeric X-ray crystal structure of the anionic salt [$(Ph_2(C_6H_4$-Li)P=N-TMS)$_2$(Et_2O)] derived from $Ph_3P{=}NTMS$ iminophos-

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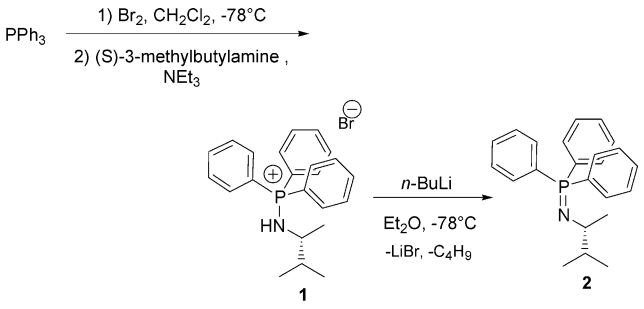
Scheme 2

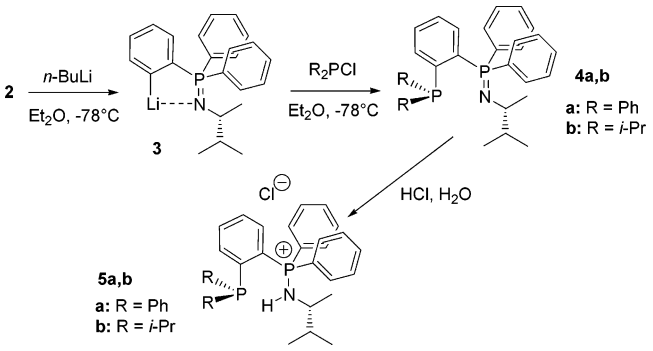


phorane.[9] The coordination ability of this anionic species has been investigated with group 10,[10] copper, zinc,[11] group 13,[10,12] iron, and germanium centers.[12] Much more recently, Stephan et al. reported the coordination of this anionic species to rhodium(I) and iridium(I) centers.[13] However, to the best of our knowledge, the utilization of these anionic species as starting points for the development of novel bidentate P∼N or polydentate ligands has not been explored. In fact, we reasoned that a simple trapping of this reactive species with various electrophiles could provide such compounds.

To test this hypothesis, the synthesis of the enantiomerically pure alkyl-substituted aminophosphonium salt **1** was prepared by following the classical Kirsanov procedure.[14] Reaction of 1 equiv of bromine at −78 °C followed by a subsequent trapping of the triphenylbromophosphonium salt with (*S*)-3-methylbutylamine in the presence of Et_3N as a base afforded the salt **1** as a white powder in 92% yield. This salt was fully characterized using NMR techniques ($^{31}P\{^1H\}$ NMR δ ($CDCl_3$) 36.9 ppm) and elemental data. As previously reported, **1** can be further deprotonated using *n*-butyllithium at low temperature to afford the iminophosphorane **2**, which was characterized by NMR techniques (Scheme 2). As previously observed by us and others, the formation of compound **2** results in a significant upfield shift in ^{31}P NMR spectroscopy (δ (Et_2O) −0.4 ppm). However, **2** proved to be rather sensitive toward moisture to afford satisfactory elemental data. Nevertheless, as will be seen later, the sensitivity of **2** is not a problem, since its isolation can be avoided.

In his original paper, Stuckwisch used PhLi as a metalating agent, whereas Stalke and Stephan employed MeLi. We found that metalation can be easily achieved in diethyl ether at low temperature using 1 equiv of *n*-butyllithium. The corresponding anion **3**, which is formed quantitatively using this procedure, was only characterized by ^{31}P NMR spectroscopy (singlet at 23.1 ppm). Note that this chemical shift is very close to that recorded by Stalke for the [($Ph_2(C_6H_4Li)P$═N-TMS)$_2$(Et_2O)] salt (δ (C_6D_6) 19.8 ppm). Trapping experiments of compound **3** were carried out using Ph_2PCl and (i-Pr)$_2$PCl as examples for both electron-neutral and electron-rich phosphines. Both reactions were conducted on freshly prepared solutions of **3** in ether at −78 °C using 1 equiv of the chlorophosphine. Both reactions proceeded cleanly to afford the corresponding iminophosphoranes **4a**,**b**, which were characterized by ^{31}P NMR spectroscopy

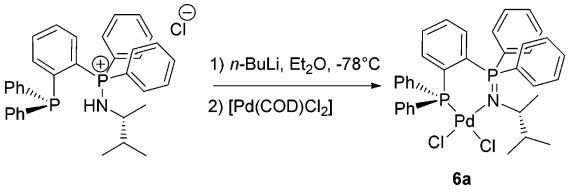
Scheme 3



exclusively. The most significant piece of data that supports the formulation proposed is given by their ^{31}P NMR spectra which both exhibit a characteristic AX spin system pattern. For example, in **4a**, the phosphino group appears at −13.0 ppm (in Et_2O), whereas the pentavalent tetracoordinated phosphorus resonates at −2.3 ppm ($^3J_{PP}$ = 16 Hz). Both iminophosphoranes were converted to the corresponding hydrochloride salts **5a**,**b**, which are the preferred storing forms. Protonation of **4a**,**b** could be achieved by acidification at room temperature in dichloromethane using a HCl/H_2O solution (Scheme 3). Salts **5a**,**b** were characterized by conventional NMR techniques and elemental data.[15]

In refining our synthetic procedures, we found that the full sequence can be carried out in one pot and, thus, the isolation of iminophosphoranes **2** and **4a**,**b** is not needed. Therefore, when salt **1** is used as the starting material along with 2 equiv of *n*-butyllithium, salts **5a**,**b** can be obtained in very satisfactory yields (81 and 85%).

These salts were deprotonated in situ prior to coordination. As an example, the synthesis of a palladium(II) complex is presented here. Thus, reaction of the salt **5a** with 1 equiv of *n*-butyllithium in THF cleanly yielded the corresponding iminophosphorane **4a**, which in turn reacts with [Pd(COD)Cl_2] to afford the corresponding dichloride complex **6a** (eq 1).



(1)

Complex **6a**, which precipitates in THF, was formed in satisfactory yield and obtained as an orange powder after a conventional workup (see the Experimental Section). It was characterized by a combination of NMR techniques and elemental data. Additional evidence for its formulation was given by an X-ray crystal structure analysis. Single crystals of complex **6a** were obtained by slow diffusion of hexanes into a dichloromethane solution of the complex at room temperature. A view of one molecule of complex **6a** is shown in Figure 1, and the most significant metric parameters are listed in the corresponding caption. Crystal data and structural refinement details are given in Table 1.

The quantitative ortho-lithiation and trapping reactions led us to extend the strategy to the synthesis of tetradentate ligands. Indeed, the double deprotonation of a bis(iminophosphorane)

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(15) Iminophosphorane ligands are moisture sensitive and over time afford both the phosphine oxide and aminophosphonium salts. Therefore, they are not a convenient storage form. A brief reaction with acidified water affords cleanly aminophosphonium salts which can be stored indefinitely.

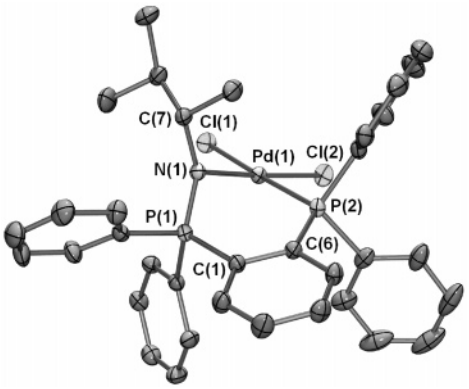


Figure 1. Molecular structure of complex **6a**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Pd(1)−N(1), 2.075(1); Pd(1)−P(2), 2.2323(5); Pd(1)−Cl(2), 2.3132(5); Pd(1)−Cl(1), 2.3719(5); P(1)−N(1), 1.596(2); P(1)−C(1), 1.825(2); P(2)−C(6), 1.832(2); C(1)−C(6), 1.412(2); N(1)−Pd(1)−P(2), 92.68(4); N(1)−Pd(1)−Cl(2), 177.41(4); P(2)−Pd(1)−Cl(2), 87.27(2); N(1)−Pd(1)−Cl(1), 92.14(4); N(1)−P(1)−C(1), 116.23(8); Cl(2)−Pd(1)−Cl(1), 87.89(2); C(7)−N(1)−P(1), 120.4(1).

Table 1. Crystal Data and Structural Refinement Details for the Structure of Complex 6a

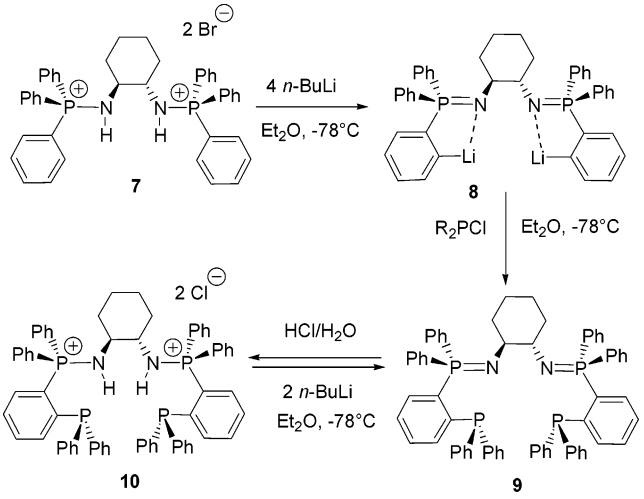
cryst size (mm)	0.20 × 0.20 × 0.12
empirical formula	$C_{35}H_{35}Cl_2NP_2Pd$
mol wt	708.88
cryst syst	monoclinic
space group	$P2_1$
a (Å)	8.495(1)
b (Å)	16.870(1)
c (Å)	11.447(1)
α (deg)	90.00
β (deg)	106.974(1)
γ (deg)	90.00
V (Å^3)	1569.0(2)
Z	2
calcd density (g cm^{-3})	1.500
abs coeff (cm^{-1})	0.890
$2\theta_{max}$ (deg)	30.02
F(000)	724
index ranges	−11 to +11; −18 to +23; −16 to +16
no. of collected/indep rflns	7858
no. of rflns used	7714
R_{int}	0.0000
abs cor	multiscan; 0.8421 min, 0.9007 max
no. of params refined	374
no. of rflns/params	20
final R1[a]/wR2 ($I > 2\sigma(I)$)[b]	0.0191/0.0522
goodness of fit on F^2	1.007
diff peak/hole (e Å^{-3})	0.359(0.050)/−0.672(0.050)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

derivative followed by trapping with an electrophile would lead in one step to "salen like ligands". Moreover, an entry into the optically pure derivative would be readily available via the use of bis(iminophosphorane) derivatives such as those reported by Réau and Reetz in 1998.[16,17] This strategy was tested by starting from the bis salt derivative **7**, obtained from the chiral diaminocyclohexane. Although the multiple possible sites of deprotonation could have led to the formation of inseparable mixtures, the use of analogous reaction conditions (Et_2O at −78 °C) resulted in the formation of a single highly sensitive anionic species (Scheme 4).

The dilithium salt **8** exhibits a singlet at 18.8 ppm ($^{31}P\{^1H\}$ NMR) very close to that of anion **3**. Trapping of dianion **8** with 2 equiv of diphenylchlorophosphine in ether at −78 °C cleanly yielded the expected tetradentate ligand **9**, which shows a characteristic AB spin system pattern in ^{31}P NMR spectroscopy.

Scheme 4



As for **5**, addition of an excess of HCl solution led to the quantitative formation of the bis(dihydrochloride) salt **10**. All NMR data and elemental analysis confirm the formulation proposed. Importantly, as is the case for compounds **5**, the salt **10** serves as a convenient precursor of the free ligand **9** upon deprotonation with *n*-butyllithium in Et_2O at −78 °C (Scheme 4).

In conclusion, we have devised a straightforward approach toward new types of bi- and tetradentate ligands featuring iminophosphorane and phosphine functionalities. This approach is sufficiently flexible to allow the elaboration of various structures bearing iminophosphorane−phosphine ligands and probably heteroatoms other than phosphorus (O, S, N). We are currently exploring these possibilities as well as the coordination chemistry and the use in catalysis of these new P∼N ligands and their corresponding protected hydrochloride salts. These developments will be reported in due course.

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and glovebox techniques. Solvents were freshly distilled under argon from Na/benzophenone (THF, diethyl ether, hexanes), from Na (toluene), or from P_2O_5 (dichloromethane, $CDCl_3$, NEt_3). Triphenylphosphine, diisopropylchlorophosphine, diphenylchlorophosphine, (*S*)-(+)-3-methyl-2-butylamine, and (1*R*,2*R*)-(−)-1,2-diaminocyclohexane were obtained from Aldrich and used without further purification. Ligand **7**[16] and $[Pd(COD)Cl_2]$[18] were prepared according to literature procedures. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as the external standard. ^{31}P shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual.

Synthesis of Aminophosphonium Salt 1. Bromine (196 μL, 3.8 mmol) was added slowly to a solution of triphenylphosphine (1.0 g, 3.8 mmol) in dichloromethane cooled to −78 °C. After 30 min, (*S*)-(+)-3-methyl-2-butylamine (445 μL, 3.8 mmol) and triethylamine (530 μL, 3.8 mmol) were added to the cloudy solution of the bromophosphonium salt. The clear solution obtained after cold bath removal was washed twice with water, the organic layer was dried over $MgSO_4$, and the solvent was removed under vacuum. The residue was washed with THF, and **1** was obtained as a white solid. Yield 92% (1.5 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.9. ^1H NMR

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($CDCl_3$): δ 0.78 (d, 3H, $^3J_{HH}$ = 3.7 Hz, *i*-Pr), 0.80 (d, 3H, $^3J_{HH}$ = 3.7 Hz, *i*-Pr), 1.34 (d, 3H, $^3J_{HH}$ = 6.7 Hz, Me), 1.91 (m, 1H, CH), 2.52−2.70 (m, 1H, CHN), 7.48−7.66 (m, 6H, PhP), 7.68−7.76 (m, 3H, PhP), 7.78−7.93 (m, 6H, PhP), NH not seen. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.8 (*i*-Pr), 19.7 (d, $^3J_{CP}$ = 3 Hz, Me), 20.0 (*i*-Pr), 34.6 (d, $^3J_{CP}$ = 6 Hz, CH), 56.4 (d, $^3J_{CP}$ = 3 Hz, CHN), 122.2 (d, $^1J_{CP}$ = 103 Hz, C_{ipso}−P), 129.6 (d, J_{CP} = 13 Hz, *o*,*m*-CH), 133.7 (d, J_{CP} = 11 Hz, *o*,*m*-CH), 134.4 (d, $^4J_{CP}$ = 3 Hz, *p*-CH). Anal. Calcd for $C_{23}H_{27}BrNP$: C, 64.49; H, 6.35. Found: C, 64.33; H, 6.40.

Lithiation of 1 and Trapping by Chlorophosphine. *n*-Butyllithium (290 μL, 1.6 M in hexane, 0.46 mmol) was added dropwise to a suspension of ligand **1** (100 mg, 0.23 mmol) in Et_2O (10 mL) cooled to −78 °C. After 15 min of stirring at room temperature, a yellow solution was obtained and the lithiated adduct **3** was characterized by NMR ($^{31}P\{^1H\}$ (Et_2O) δ 23.1 ppm).

5a,b. To a freshly prepared solution of **3** (0.23 mmol) in Et_2O (10 mL) cooled to −78 °C was added the chlorophosphine (0.23 mmol). The solution turned immediately from yellow to colorless and became cloudy. Crude **4a** was characterized by $^{31}P\{^1H\}$ NMR (δ (Et_2O) −13.0 (d, $^3J_{PP}$ = 16 Hz, P^{III}), −2.3 (d, $^3J_{PP}$ = 16 Hz, P^V)). After 1 h of stirring the solvent was removed under vacuum and the residue dissolved in dichloromethane. The crude mixture was washed once with a HCl solution and twice with a saturated aqueous solution of NaCl, the organic layer was dried over $MgSO_4$, and solvent was removed under vacuum. The residue was washed with diethyl ether to give the expected product as a white solid.

5a. Yield: 85% (110 mg). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −15.3 (d, $^3J_{PP}$ = 24 Hz, P^{III}), 36.8 (d, $^3J_{PP}$ = 24 Hz, P^V). ^1H NMR ($CDCl_3$): δ 0.73 (d, 3H, $^3J_{HH}$ = 6.7 Hz, *i*-Pr), 0.78 (d, 3H, $^3J_{HH}$ = 6.7 Hz, *i*-Pr), 1.28 (d, 3H, $^3J_{HH}$ = 6.6 Hz, Me), 1.81−1.98 (m, 1H, CH), 2.52−2.67 (m, 1H, CHN), 6.68−6.81 (m, 4H, PhP), 7.81−8.11 (m, 20H, PhP), 8.68−8.80 (m, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.5 (*i*-Pr), 19.4 (d, $^3J_{CP}$ = 2 Hz, Me), 20.1 (*i*-Pr), 34.7 (d, $^3J_{CP}$ = 6 Hz, CH), 56.8 (CHN), 123.2 (dd, $^1J_{CP}$ = 102 Hz, $^4J_{CP}$ = 3 Hz, C_{ipso}−P), 123.5 (dd, $^1J_{CP}$ = 105 Hz, $^4J_{CP}$ = 3 Hz, C_{ipso}−P), 128.4 (dd, J_{CP} = 7 Hz, J_{CP} = 3 Hz), 128.9 (d, J_{CP} = 3 Hz), 129.1 (d, J_{CP} = 13 Hz), 130.9 (d, J_{CP} = 4 Hz), 132.7 (dd, J_{CP} = 19 Hz, J_{CP} = 6 Hz), CH), 133.4 (dd, J_{CP} = 4 Hz, J_{CP} = 11 Hz), 133.6 (d, J_{CP} = 4 Hz), 134.1 (d, J_{CP} = 4 Hz), 134.5 (dd, J_{CP} = 44 Hz, J_{CP} = 9 Hz, C_{ipso}−P), 137.2 (dd, J_{CP} = J_{CP}' = 10 Hz), 138.5 (d, J_{CP} = 13 Hz), 140.8 (dd, J_{CP} = 14 Hz, J_{CP} = 19 Hz, C_{ipso}−P). Anal. Calcd for $C_{35}H_{36}ClNP_2$: C, 74.00; H, 6.39. Found: C, 73.76; H, 6.42.

5b. Yield: 81% (93 mg). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −3.8 (d, $^3J_{PP}$ = 20 Hz, P^{III}), 38.7 (d, $^3J_{PP}$ = 20 Hz, P^V). ^1H NMR ($CDCl_3$): δ 0.24−0.38 (m, 6H, *i*-PrP), 0.63 (d, 3H, $^3J_{HH}$ = 6.7 Hz, *i*-Pr), 0.70 (d, 3H, $^3J_{HH}$ = 6.7 Hz, *i*-Pr), 0.74−0.89 (m, 6H, *i*-PrP), 1.05 (d, 3H, $^3J_{HH}$ = 6.6 Hz, Me), 1.24−1.36 (m, 1H, CHP), 1.60−1.83 (m, 2H, CHP and CH-*i*-Pr), 2.36−2.51 (m, 1H, CHN), 7.48−7.68 (m, 10H, PhP), 7.72−7.94 (m, 4H, PhP), 8.20−8.37 (m, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.9 (*i*-Pr), 19.1 (d, J_{CP} = 5 Hz, Me), 19.3 (CHP), 19.5 (*i*-Pr), 20.2 (CHP), 25.5 (d, $^2J_{CP}$ = 11 Hz, *i*-PrP), 25.7 (d, $^2J_{CP}$ = 11 Hz, *i*-PrP), 34.3 (d, $^3J_{CP}$ = 6 Hz, CHP), 56.6 (b, CHN), 123.0 (dd, $^1J_{CP}$ = 107 Hz, $^4J_{CP}$ = 2 Hz, C_{ipso}−P), 123.5 (dd, $^1J_{CP}$ = 101 Hz, $^4J_{CP}$ = 2 Hz, C_{ipso}−P), 129.2 (d, J_{CP} = 13 Hz), 129.4 (d, J_{CP} = 13 Hz), 130.2 (d, J_{CP} = 13 Hz), 133.6 (m), 134.1 (m), 134.6 (m), 135.6 (dd, J_{CP} = 12 Hz, J_{CP} = 10 Hz), 142.3 (dd, J_{CP} = 15 Hz, J_{CP} = 20 Hz, C_{ipso}−P). Anal. Calcd for $C_{29}H_{40}ClNP_2$: C, 69.66; H, 8.06. Found: C, 69.42; H, 8.11.

Lithiation of 7 and Trapping by Chlorodiphenylphosphine. *n*-Butyllithium (970 μL, 1.6 M in hexane, 1.55 mmol) was added dropwise to a suspension of ligand **7** (310 mg, 0.39 mmol) in Et_2O (30 mL) cooled to −78 °C. After 15 min of stirring at room temperature, a yellow solution was obtained and the lithiated adduct **8** was characterized by NMR ($^{31}P\{^1H\}$ NMR (Et_2O) δ 18.8 ppm).

To a freshly prepared solution of **8** (0.39 mmol) in Et_2O (30 mL) cooled to −78 °C was added the chlorodiphenylphosphine (140 μL, 0.78 mmol). The solution turned immediately from yellow to colorless and became cloudy. The crude mixture of **9** was characterized by NMR ($^{31}P\{^1H\}$ (Et_2O) δ −14.1 (d, $^3J_{PP}$ = 15 Hz, P^{III}), −4.1 (d, $^3J_{PP}$= 15 Hz, P^V)). After 1 h of stirring the solvent was removed under vacuum and the residue dissolved in dichloromethane. The resulting mixture was washed once with a HCl solution and twice with a saturated aqueous solution of NaCl, the organic layer was dried over $MgSO_4$, and the solvent was removed under vacuum. The residue was washed with diethyl ether to give the expected product **10** as a white solid. Yield: 70% (294 mg). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.3 (d, $^3J_{PP}$ = 29 Hz, P^{III}), 37.6 (d, $^3J_{PP}$ = 29 Hz, P^V). ^1H NMR ($CDCl_3$): δ 0.64−0.93 (m, 2H, CH_2), 1.23−1.37 (m, 2H, CH_2), 1.42−1.69 (m, 4H, CH_2), 3.25−3.40 (m, 2H, CHN), 6.46−6.77 (m, 8H, PhP), 6.99−8.20 (m, 40H, PhP), 8.70−8.91 (m, 2H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.4 (CH_2), 35.6 (CH_2), 58.6 (d, $^2J_{CP}$ = 11 Hz, CHN), 120.3 (dd, $^1J_{CP}$ = 104 Hz, $^2J_{CP}$ = 4 Hz, C_{ipso}−P), 124.0 (dd, $^1J_{CP}$ = 108 Hz, $^2J_{CP}$ = 3 Hz, C_{ipso}−P), 128.3 (dd, J_{CP} = 6 Hz, J_{CP} = 4 Hz), 128.8 (d, J_{CP} = 7 Hz), 129.1 (d, J_{CP} = 14 Hz), 129.4 (d, J_{CP} = 13 Hz), 131.1 (d, J_{CP} = 12 Hz), 132.8 (dd, J_{CP} = 19 Hz, J_{CP} = 7 Hz), 133.8 (d, J_{CP} = 3 Hz), 134.0 (d, J_{CP} = 3 Hz), 134.7 (d, J_{CP} = 10 Hz, C_{ipso}−P^{III}), 137.6 (dd, J_{CP} = J_{CP}' = 10 Hz), 138.3 (d, J_{CP} = 12 Hz), 140.6 (dd, J_{CP} = 19 Hz, J_{CP} = 14 Hz, C_{ipso}−P). Anal. Calcd for $C_{66}H_{60}Cl_2N_2P_4$: C, 73.67; H, 5.62. Found: C, 73.52; H, 5.69.

Synthesis of Palladium Complex 6a. To a suspension of **4a** (100 mg, 0.18 mmol) in 5 mL of THF cooled to −78 °C was added dropwise *n*-butyllithium (110 μL, 1.6 M in hexane, 0.18 mmol). The cold bath was removed, and the solution was warmed to room temperature. [Pd(COD)Cl_2] (50 mg, 0.18 mmol) was added, and the solution turned immediately from colorless to orange. After 10 min of stirring, the product precipitated as an orange solid. The latter was isolated by filtration, washed with THF and then hexanes, and dried under vacuum. Yield: 76% (97 mg). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexanes into a solution of **6a** in dichloromethane at room temperature. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 15.5 (d, $^3J_{PP}$ = 40 Hz, P^{III}), 30.1 (d, $^3J_{PP}$ = 40 Hz, P^V). ^1H NMR (CD_2Cl_2): δ 0.31−0.52 (m, 3H, *i*-Pr), 0.54−0.75 (m, 3H, *i*-Pr), 1.32−1.55 (m, 3H, Me), 1.59−1.73 (m, 1H, CH), 2.41−2.71 (m, 1H, CHN), 6.88−7.94 (m, 24H, PhP). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 22.0 (*i*-Pr), 25.2, 34.4 (CH), 60.2 (CHN), 128.5 (d, J_{CP} = 11 Hz), 128.9 (d, J_{CP} = 10 Hz), 129.4 (d, J_{CP} = 12 Hz), 129.8(d, J_{CP} = 14 Hz), 130.9 (d, J_{CP} = 11 Hz), 133.4, 133.8, 134.6 (d, J_{CP} = 10 Hz), 134.9, 135.1, 135.3, 137.3 (d, J_{CP} = 9 Hz), C^{IV} not seen. Anal. Calcd for $C_{35}H_{35}Cl_2NP_2Pd$: C, 59.30; H, 4.98. Found: C, 59.55; H, 5.05.

Crystallography. Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.710 73 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structure was solved using SIR 97 and Shelxl-97. Molecular drawings were made using ORTEP III for Windows and then POV-Ray.

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Supporting Information Available: CIF files and tables giving crystallographic data for **6a** (including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference number 299293 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving-.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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