Synthesis of β-P,N Aminophosphines and Coordination Chemistry to Pd^{II}. X-ray Structures of $[PdCl_2(Ph_2PCH_2CH(Ph)NHPh\text{-}\kappa P,\kappa N)]$ and $[PdCl(\eta^3\text{-}C_3H_5)(Ph_2PCH_2CH(Ph)NHPh\text{-}\kappa P)]$

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The reaction of the C═N bond in PhCH═NPh with the carbanionic species $Ph_2PCH_2^-$, leading to the *N*-phenyl β-aminophosphine $Ph_2PCH_2CH(Ph)NHPh$, **L1**, is described. This molecule reacts with different organic electrophiles to afford related compounds $Ph_2PCH_2CH(Ph)NPhX$ (X = $SiMe_3$, **L2**; COPh, **L4**), $[Ph_2MePCH_2CH(Ph)NHPh]^+(I^-)$, **L3**, and $[Ph_2PCH_2CH(Ph)N(Ph)CO]_2$, **L5**, containing two amido and two phosphino functions. The coordination properties of **L1**, **L2**, and **L4** have been studied in palladium chemistry. The X-ray structure of $[PdCl_2(Ph_2PCH_2CH(Ph)NHPh\text{-}\kappa P,\kappa N)]$ shows the bidentate coordination mode for the **L1** ligand with equatorial $C_{Ph}-N_{Ph}$ phenyl groups. $[PdCl_2(Ph_2PCH_2CH(Ph)NHPh\text{-}\kappa P,\kappa N)]$ crystallizes at 298 K in the space group $P2_1/n$ with cell parameters $a = 10.689(2)$ Å, $b = 21.345(3)$ Å, $c = 12.282(2)$ Å, $\beta = 90.294(12)°$, $Z = 4$, $D_{calcd} = 1.526$. The reaction between 2 equiv of **L1** and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ affords the $[PdCl(\eta^3\text{-}C_3H_5)(Ph_2PCH_2CH(Ph)NHPh\text{-}\kappa P)]$ complex in which an unexpected N−H···Cl intramolecular interaction has been observed by an X-ray diffraction analysis. $[PdCl(\eta^3\text{-}C_3H_5)(Ph_2PCH_2CH(Ph)NHPh\text{-}\kappa P)]$ crystallizes at 298 K in the monoclinic space group *Cc* with cell parameters $a = 10.912(1)$ Å, $b = 17.194(2)$ Å, $c = 14.169(2)$ Å, $\beta = 100.651(9)°$, $Z = 4$, $D_{calcd} = 1.435$. Neutral and cationic alkyl or allyl palladium chloride complexes containing **L1** are also reported as well as a neutral allyl palladium chloride complex containing **L4**. Variable-temperature $^{31}P\{^1H\}$ NMR studies on the allyl complexes show that the η^3/η^1 allyl interconversion is enhanced by a positive charge and also by a N−H···Cl intramolecular interaction.

Introduction

The synthesis and the coordination studies of aminophosphines have been the subject of detailed investigations owing to catalytic applications of the corresponding Ru,[1−3] Ni,[4,5] Rh,[6,7] and Pd[8,9] complexes. However, the synthesis of aminophosphines in which the heteroatoms are separated by two carbon atoms (named hereafter β-P,N) requires a multistep reaction or a tedious method.[10−13] Moreover, functional phosphines of this type containing a secondary amine have received little attention.[10,11] In particular, no study of the potential hemilabile character of such ligands has been reported. Therefore, we were interested in elaborating a short synthetic method allowing opening of the access not only to new β-P,N ligands but also to their complexes. A particular interest for such ligands in neutral and cationic palladium complexes is the examination of the consequences of a relatively weak electron-donating −NHPh group on the *κP* versus *κP,κN* coordination mode as well as on hemilability.

We have recently reported that the C═N double bond in free organic or $(CO)_3Cr$-coordinated benzaldimines undergoes the addition of Ph_2PH to afford the first stable chiral α-P,N ligands.[14,15] Then, we wished to extend the reactivity of the *N*-phenylbenzaldimines toward $Ph_2PCH_2^-$ in order to open a one-step access to related β-aminophosphines. In fact, the carbanionic $Ph_2PCH_2^-$ reagent[16−18] has allowed preparation of β-alcohol-phosphines by a similar addition to the C═O double bond of benzophenone or hexafluoroacetone.[16,19]

Experimental Section

All reactions were performed in Schlenk-type flasks under argon. Solvents were purified and dried under argon by conventional methods. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 instrument for both room and higher temperature experiments. The $^1H-^1H$ and $^1H-^{13}C$ COSY, DEPT-135, and the variable- (low-) temperature experiments were recorded on a Bruker 500 DRX

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instrument. Numbering scheme used for the **L¹** ligand: H^a, H^b, and H^c are the nonequivalent PCH_2 and the NCH protons, respectively. Numbering scheme used for the allyl ligand: C^1, C^2, and C^3 are trans to the P atom, the central carbon, and cis to the P atom, respectively. Whenever diastereoisomeric forms are present, the carbon and proton chemical shifts are noted C, H and C′, H′ respectively. The infrared spectra were recorded in Nujol or in CH_2Cl_2 solution with an IFS 66 Perkin-Elmer instrument. The elemental analyses were performed at the LSEO in Dijon. Compounds $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, $[PdCl_2(COD)]$, and $[Pd(CH_3)Cl(COD)]$ were prepared according to the literature.[20,21] The reagents *n*-BuLi (2.5 M in hexanes), PhCH═NPh, and Ph_2PCH_3 were commercial products from Aldrich and were used as received.

Synthesis of $Ph_2PCH_2CH(Ph)NHPh$, L¹. Lithiation of methyldiphenylphosphine was carried out according to Peterson's procedure from TMEDA (2.0 mL, 13.25 mmol) and *n*-BuLi (5.3 mL, 13.25 mmol).[16] After the mixture was stirred for 15 min at room temperature, methyldiphenylphosphine (2.5 mL, 13.25 mmol) was added. The mixture was stirred further, leading to a bright yellow precipitate within 30 min. The precipitate was dissolved by addition of 4 mL of THF. After stirring for an additional 30 min, *N*-benzylideneaniline (1.79 g, 9.88 mmol) was added and the mixture was stirred overnight. The reaction mixture was then transferred into 30 mL of degassed water. The organic phase was separated, and the water phase was separated and extracted twice with 20 mL of Et_2O. After drying over $MgSO_4$, the solvent was removed in vacuo. Addition of 5 mL of cold dry methanol afforded a precipitate, which was isolated by filtration. Recrystallization from cold methanol afforded the ligand **L¹** as a white powder, which was isolated by filtration and dried in vacuo for 3 h. Yield: 1.82 g (48.3% relative to the imine used).^{1}H NMR ($CDCl_3$): 7.70−6.21 (m, 20H aromatics), 4.38 (m, 2H, NCH + NH), 2.59 (m, 2H, PCH_2). ^{1}H NMR (C_6D_6): 7.70−6.21 (m, 20 H aromatics), 4.37 (m, 1H, NCH^c), 4.19 (s, br, 1H, NH, exchange with D_2O), 2.43 part A of ABMX system for the PCH^aH^b−CH^c (ddd, 1H, PCH^a, $^2J(H^a,H^b)$ = 14.0 Hz, $^2J(P,H^a)$ = 4.8 Hz, $^3J(H^a,H^c)$ = 1.3 Hz), 2.28 part B of ABMX system for the PCH^aH^b−CH^c (ddd, 1H, PCH^b, $^2J(H^b,H^a)$ = 14.0 Hz, $^2J(P,H^b)$ = 9.9 Hz, $^3J(H^b,H^c)$ = 3.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −22.02 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 147.4−113.9 (m, 24 C aromatics), 56.6 (d, 1C, NCH, $^2J(P,C)$ = 15.0 Hz) and 39.5 (d, 1C, PCH_2, $J(P,C)$ = 15.9 Hz). IR (Nujol): ν(NH) = 3390 cm^{-1} (w). Anal. Calcd for $C_{26}H_{24}NP$: C, 81.87; H, 6.33; N, 3.67. Found: C, 82.21; H, 6.34; N, 3.37.

Synthesis of $Ph_2PCH_2CH(Ph)N(Ph)(Si(CH_3)_3)$, L². This ligand has been prepared similarly to **L¹**, from PPh_2Me (2.1 mL, 0.011 mol), *n*-BuLi (6.7 mL, 0.011 mol), TMEDA (1.6 mL, 0.011 mol), and PhCH═NPh (1.95 g, 0.011 mol). The mixture was left to stir overnight. Instead of the addition of distilled water, Me_3SiCl (1.4 mL, 0.011 mol) was added dropwise. There was a color change from red to pale yellow, and the mixture was stirred for 3 h. The solvent was removed. The dark brown residue was then dissolved in 20 mL of toluene and filtered through Celite. Due to high solubility in common solvents (i.e., ether or pentane), the product could not be purified by washing. Consequently, the product was purified by removal of Ph_2PCH_3 and TMEDA by vacuum distillation at 110 °C, leading to a sensitive and very viscous white oil. Yield: 2.57 g (48%).^{1}H NMR (C_6D_6): 7.52−6.84 (m, 20H aromatics), 4.55 (m, 1H, NCH), 2.84 part A of ABX system for the PCH^aH^b (dd, 1H, PCH^a, $^2J(P,H^a)$ = 13.7 Hz, $^2J(H^b,H^a)$ = 7.4 Hz), 2.74 part B of ABX system for the PCH^aH^b (dd, 1H, PCH^b, $^2J(P,H^b)$ = 13.7 Hz, $^2J(H^b,H^a)$ = 7.4 Hz), 0.17 (s, br, 9H, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −20.94 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 144.6−124.2 (m, 24 C aromatics), 58.7 (d, 1C, NCH, $^2J(P,C)$ = 17.6 Hz), 34.3 ppm (d, 1C, PCH_2, $J(P,C)$ = 13.9 Hz) and −1.1 (s, 3C, $Si(CH_3)_3$). Elemental analysis of the pure ligand could not be performed due to its air sensitivity and very viscous nature. It was used without further purification.

Synthesis of $[Ph_2CH_3PCH_2CH(Ph)NHPh]$(I), L³. To a solution of **L¹** (0.165 g, 0.433 mmol) in 4 mL of toluene was added MeI (27 μL, 0.433 mmol). A white precipitate formed, and the mixture was stirred for 60 h. The solid was isolated by filtration, washed 3 times with 4 mL of toluene and 3 times with 5 mL of pentane, and dried in vacuo. Yield: 0.186 g (82%). ^{1}H NMR (C_6D_6): 7.90−6.35 (m, 20H aromatics), 5.05 (m, 1H, NCH), 4.56 (s, br, 1H, NH), 3.05 (d, 3H, CH_3P, $^2J(P,H)$ = 14.3 Hz), 2.85 (m, 2H, PCH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.41 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 146.1−114.6 (m, 24C aromatics), 54.1 (d, 1C, NCH, $^2J(P,C)$ = 3.8 Hz), 31.6 (d, 1C, PCH_2, $J(P,C)$ = 48.0 Hz), and 11.3 (d, 1C, PCH_3, $J(P,C)$ = 54.6 Hz). Anal. Calcd for $C_{27}H_{27}NPI$: C, 61.96; H, 5.20; N, 2.68. Found: C 61.83; H, 5.437; N, 2.55.

Synthesis of $Ph_2PCH_2CH(Ph)N(Ph)C(O)Ph$, L⁴. To a suspension of **L¹** (0.200 g, 0.525 mmol) in 20 mL of Et_2O was added Et_3N (0.18 mL, 1.29 mmol). The mixture was cooled to 0 °C, and benzoyl chloride (70 μL, 0.545 mmol) was then introduced. After stirring for 2.5 h, the suspension was hydrolyzed by addition of 13 mL of 0.1 M NaOH. The colorless organic phase was separated, and the aqueous phase was extracted with 10 mL of Et_2O. After filtration of the combined organic layers, the solvent was removed in vacuo yielding yellow oil. The product was obtained as a colorless oil following removal of the volatile impurities by heating at 120 °C under vacuum for 2 h. Yield: 0.235 g (92%).^{1}H NMR (C_6D_6): 7.14−6.65 (m, 25H aromatics), 6.49 (m, 1H, NCH^c), 3.09 part A of ABMX system for the PCH^aH^b−CH^c (ddd, 1H, PCH^a, $^2J(H^a,H^b)$ = 14.0 Hz, $^2J(P,H^a)$ = 11.0 Hz, $^3J(H^a,H^c)$ = 3.0 Hz), 2.76 part B of ABMX system for the PCH^aH^b−CH^c (ddd, 1H, PCH^b, $^2J(H^b,H^a)$ = 14.0 Hz, $^2J(P,H^b)$ = 5.0 Hz, $^3J(H^b,H^c)$ = 2.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −22.25 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 171.6 (s, 1C, NC(O)Ph), 140.7−127.9 (m, 30C aromatics), 57.4 (d, 1C, NCH, $^2J(P,C)$ = 16.2 Hz) and 32.2 (d, 1C, PCH_2, $J(P,C)$ = 14.3 Hz). IR (Nujol): ν(C═O) = 1642 cm^{-1} (s). Elemental analysis of the pure ligand could not be performed due to its sensitive and very viscous nature. It was used without further purification.

Synthesis of $[Ph_2PCH_2CH(Ph)N(Ph)C(O)]_2$, L⁵. To a suspension of **L¹** (0.500 g, 1.313 mmol) in 15 mL of Et_2O was added Et_3N (0.5 mL, 3.58 mmol). The mixture was cooled to 0 °C, and oxalyl chloride (57 μL, 0.653 mmol) was then introduced. After stirring for 3 h at room temperature, the suspension was hydrolyzed by 33 mL of degassed 0.1 M NaOH. The colorless organic phase was separated, and the aqueous phase was extracted with 3 × 10 mL of Et_2O. After drying of the combined organic layers over $MgSO_4$ and filtering, the solvent was removed in vacuo and a yellow residue was obtained. The pure ligand was obtained as a white powder by crystallization from cold methanol. Yield: 0.330 g (61%).^{1}H NMR ($CDCl_3$): 7.29−6.64 (m, 40H aromatics), 5.71 (m, 2H, NCH), 2.40 (m, 4H, PCH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −23.93 (s) and −24.01 (s) (two diastereoisomers in ca. 1:1 ratio). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 164.5 (s, 1C, NC(O)Ph) and 164.4 (s, 1C, NC′(O)Ph), 139.3−127.9 (m, 48C aromatics), 55.3 (d, 1C, NCH, $^2J(P,C)$ = 18.7 Hz), 54.9 (d, 1C, NC′H, $^2J(P,C')$ = 18.7 Hz), 31.2 ppm (d, 1 C, PCH_2, $J(P,C)$ = 14.7 Hz) and 30.5 ppm (d, 1C, $PC'H_2$, $J(P,C')$ = 14.8 Hz). IR (Nujol): ν(C═O) = 1664 (vs) and 1643 (vs) cm^{-1}. Anal. Calcd for $C_{54}H_{46}N_2O_2P_2$: C, 79.40; H, 5.67; N, 3.43. Found: C, 79.41; H, 5.73; N, 3.73.

Synthesis of $[PdCl_2(Ph_2PCH_2CH(Ph)NHPh\text{-}\kappa P,\kappa N)]$, 1. To a mixture of $[PdCl_2(COD)]$ (0.600 g, 2.10 mmol) and **L¹** (0.804 g, 2.10 mmol) was added 10 mL of toluene. The resulting solution was refluxed for 2 h. The mixture was then cooled to room temperature. A green-yellow solid was separated by filtration and washed with pentane, followed by extraction in CH_2Cl_2 and filtration through Celite (in order to eliminate some traces of palladium metal). After evaporation of the solvent, a yellow powder was obtained, which was washed with pentane and dried in vacuo. Yellow single crystals of **1** were obtained by slow diffusion from CH_2Cl_2/pentane. Yield: 0.680 g (58%). ^{1}H NMR ($CDCl_3$): 7.74−6.99 (m, 20H aromatics), 8.10 (s, br, 1H, NH exchange with D_2O), 3.79 (m, 2H, NCH + PCH^a), 2.48 (m, 1H, PCH^b). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 38.77 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 40.88 (s). No $^{13}C\{^1H\}$ NMR spectra were recorded due to the low solubility of **1** in $CDCl_3$ or in CD_2Cl_2. Anal. Calcd for $C_{26}H_{24}NPPdCl_2$: C, 55.89; H, 4.33; N, 2.51. Found: C, 55.59; H, 4.67; N, 2.81.

Synthesis of $[PdCl_2\{Ph_2PCH_2CH(Ph)N(Ph)(Si(CH_3)_3)\text{-}\kappa P,\kappa N\}]$, 2. To a mixture of $[PdCl_2(COD)]$ (0.119 g, 0.42 mmol) and **L²** (0.208 g, 0.45 mmol) was added 10 mL of toluene. The orange solution was refluxed for a few minutes and then stirred for 2 days at room temperature. After filtration, the solvent was removed in vacuo, yielding an orange powder, which was washed with pentane and dried in vacuo. The product was purified by slow diffusion from CH_2Cl_2/pentane (ratio 1:3) at − 30 °C. Yield: 0.202 g (71%). ^{1}H NMR ($CDCl_3$): 7.48−6.57

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(m, 20H aromatics), 4.77 (m, br, 1H, NCH), 3.22 (d, 1H, PCH^a, $^2J(P,H^a)$ = 11.6 Hz), 3.18 (d, 1H, PCH^b, $^2J(P,H^b)$ = 12.5 Hz), − 0.07 (s, 9H, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR($CDCl_3$): 28.42 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 143.9−124.9 (m, 24C aromatics), 58.4 (s, 1C, NCH), 33.0 (d, 1C, PCH_2, $J(P,C)$ = 27.5 Hz) and −1.0 (s, 3C, $Si(CH_3)_3$). Anal. Calcd for $C_{29}H_{32}NPCl_2SiPd$: C, 55.21; H, 5.07; N, 2.21. Found: C, 54.92; H, 4.86; N, 2.47.

Synthesis of [PdCl(CH_3)(Ph_2PCH_2CH(Ph)NHPh-$\kappa P,\kappa N$)], 3. To a solution of [PdCl(CH_3)(COD)] (0.094 g, 0.355 mmol) in 5 mL of CH_2Cl_2 was added a solution of **L[1]** (0.135 g, 0.355 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred for 4 h and then filtered through Celite. The solution was concentrated to 2 mL, and then 15 mL of Et_2O was added with stirring, leading to a white powder, which was washed with 20 mL of Et_2O. After filtration, the product was crystallized by slow diffusion from CH_2Cl_2/pentane and obtained as pale yellow crystals. Yield: 0.123 g (56%). ^1H NMR ($CDCl_3$): 8.02−6.94 (m, 20H aromatics), 6.27 (d, 1H, NH, $^3J(P,H)$ = 11.5 Hz, exchange with D_2O), 3.87 (m, 1H, NCH), 3.45 (m, 1H, PCH^a), 2.66 (m, 1H, PCH^b) and 0.75 (d, 3 H, CH_3, $^2J(P,H)$ = 3.5 Hz). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 40.15 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 145.9−124.0 (m, 24C aromatics), 66.2 (d, 1C, NCH, $^2J(P,C)$ = 28.2 Hz), 39.2 (d, 1C, PCH_2, $J(P,C)$ = 27.5 Hz) and −4.2 (s, 1C, CH_3). Anal. Calcd for $C_{27}H_{27}NPPdCl.CH_2Cl_2$: C, 53.96; H, 4.69; N, 2.25. Found: C, 54.38; H, 4.59; N, 2.59.

Synthesis of [PdCl(η^3-C_3H_5)(Ph_2PCH_2CH(Ph)NHPh-κP)], 4. To a solution of [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (0.150 g, 0.821 mmol) in 5 mL of CH_2Cl_2 was slowly added a solution of **L[1]** (0.313 g, 0.821 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred for 4 h. Yellow crystals of **4** suitable for an X-ray structure analysis were obtained by slow diffusion of pentane into a CH_2Cl_2 solution. Yield: 0.329 g (71%). ^1H NMR ($CDCl_3$, 298 K): 7.38−6.37 (m, 20H aromatics), 4.52 (m, 1H, NCH), 4.00 (s, br, 1H, NH exchange with D_2O), 3.50 (m, 1H, PCH^a) and 2.50 (m, 1H, PCH^b). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 16.65 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 146.8−113.2 (m, 24C aromatics), 53.9 (s, 1C, NCH), 35.8 (d, 1C, PCH_2, $J(P,C)$ = 22.1 Hz). ^1H NMR ($CDCl_3$, 233 K): 7.83−6.58 (m, 20H + 20H′ aromatics), 5.55 (m, 1H, CH^2(allyl)), 5.50 (m, 1H, $CH^{2\prime}$(allyl)), 4.85 (s, br, 1H, NCH), 4.77 (s, br, 1H, NCH′), 4.11 (s, b, 2H, NH + NH′), 3.66 (m, 8H, CH^{1a}, CH^{3s}, $CH^{1a\prime}$, $CH^{3s\prime}$ of allyl fragment plus PCH_2 and PCH_2') and 2.59 (m, 8H, CH^{1s}, CH^{3a} and $CH^{1s\prime}$, $CH^{3a\prime}$ of allyl fragment). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K): 17.12 (s) and 16.23 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 233 K): 146.4−126.3 (m, 24C + 24C′ aromatics), 117.8 (d, 1C, C^2(allyl), $^3J(P,C)$ = 17 Hz), 116.6 (d, 1C′, $C^{2\prime}$(allyl), $^3J(P,C')$ = 17 Hz), 80.5 (d, 1C, C^1(allyl), $^2J(P,C)$ = 31.4 Hz), 80.3 (d, 1C′, $C^{1\prime}$(allyl), $^2J(P,C')$ = 31.6 Hz), 59.4 (s, 1C, NCH), 57.3 (s, 1C′, NC′H), 54.0 (s, 1C, C^3(allyl)), 53.2 (s, 1C, C^3(allyl)), 34.9 (d, 1C, PCH_2, $J(P,C)$ = 23.9 Hz), 34.6 ppm (d, 1C′, PC′H_2, $J(P,C')$ = 24.4 Hz). IR (Nujol): ν(NH) = 3300 cm^{-1} (w). Anal. Calcd for $C_{29}H_{29}NPPdCl$: C, 61.71; H, 5.18; N, 2.48. Found: C, 61.60; H, 5.30; N, 2.85.

Synthesis of [Pd(CH_3)(Ph_2PCH_2CH(Ph)NHPh-$\kappa P,\kappa N$)(NCMe)]-(BF_4), 5. The solid [PdCl(CH_3)(COD)] (0.070 g, 0.26 mmol) and the ligand **L[1]** (0.100 g, 0.26 mmol) were stirred overnight in 10 mL of CH_2Cl_2 at room temperature. The solvent was removed, leaving a white solid, which was washed twice with 20 mL of ether and dried in vacuo. The crude product was dissolved in 5 mL of CH_2Cl_2 and was then added to $AgBF_4$ (0.048 g, 0.26 mmol) in the presence ca. 0.5 mL of acetonitrile. After stirring for 30 min, the mixture was filtered through Celite. The filtrate was concentrated to ca. 2 mL. Addition of 20 mL of ether yielded a white precipitate, which was isolated by filtration and dried in vacuo. Yield: 0.080 g (49%). ^1H NMR ($CDCl_3$): 8.02−6.97 (m, 20H aromatics), 6.39 (d, 1H, NH, exchange with D_2O, $^3J(P,H)$ = 11.7 Hz), 3.94 (ddd, 1H, NCH^c, $^3J(H^c,P)$ = 25 Hz, $^3J(H^c,H^a)$ = 7 Hz, $^3J(H^c,H^b)$ = 3 Hz), 3.40 (dt, 1H, PCH^a, $^3J(H^a,H^c)$ = 7 Hz, $^2J(P,H^a)$ = $^2J(H^a,H^b)$ = 14 Hz), 2.70 (dt, 1H, PCH^b, $^3J(H^b,H^c)$ = 3 Hz, $^2J(P,H^b)$ = $^2J(H^b,H^a)$ = 14 Hz), 1.93 (s, 3H, CH_3CN) and 0.48 (d, 3H, CH_3, $^3J(P,H)$ = 1.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.7 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 122.3−145.3 (m, 24C aromatics), 118.5 (s, 1C, $NCCH_3$), 65.4 (d, 1C, NCH, $^2J(P,C)$ = 5.5 Hz), 39.0 (d, 1C, PCH_2, $J(P,C)$ = 28.9 Hz), 2.2 (s, $NCCH_3$), −4.6 (s, Pd−CH_3). Anal. Calcd for $C_{29}H_{30}BF_4N_2PPd$: C, 55.20; H, 4.79; N, 4.44. Found: C, 54.91; H, 4.91; N, 4.68.

Synthesis of [Pd(η^3-allyl)(Ph_2PCH_2CH(Ph)NHPh-$\kappa P,\kappa N$)](PF_6), 6. The complex [PdCl(η^3-C_3H_5)]$_2$ (0.097 g, 0.26 mmol) and the ligand **L[1]** (0.202 g, 0.53 mmol) were stirred in 10 mL of CH_2Cl_2 at room temperature for 30 min. The solution was added to $NaPF_6$ (0.223 g, 1.30 mmol). After stirring for 3 h, the mixture was filtered through Celite. The filtrate was concentrated in vacuo to ca. 2 mL, and the addition of 15 mL of pentane yielded a white powder. The solid was isolated by filtration and dried in vacuo. Yield: 0.315 g (89%). ^1H NMR ($CDCl_3$, 298 K): 7.83−6.60 (m, 20H + 20H′ aromatics), 6.53 (d, 1H, NH exchange with D_2O, $^3J(H,P)$ = 11 Hz), 6.33 (d, 1H′, NH′ exchange with D_2O, $^3J(H',P)$ = 12 Hz), 5.85 (apparent tt, 1H′, $CH^{2\prime}$(allyl), $^3J(H^{2\prime},H^{1a\prime})$ = $^3J(H^{2\prime},H^{3a\prime})$ = 14 Hz, $^3J(H^{2\prime},H^{1s\prime})$ = $^3J(H^{2\prime},H^{3s\prime})$ = 7 Hz), 5.61 (apparent tt, 1H, CH^2(allyl), $^3J(H^2,H^{1a})$ = $^3J(H^2,H^{3a})$ = 14 Hz, $^3J(H^2,H^{1s})$ = $^3J(H^2,H^{3s})$ = 7 Hz), 4.37 (d, 1H, CH^{1a}(allyl), $^3J(H^{1a},H^2)$ = 14 Hz), 4.35 (d, 1H′, $CH^{1a\prime}$(allyl), $^3J(H^{1a\prime},H^{2\prime})$ = 14 Hz), 4.19 (m, 1H′, $NCH^{c\prime}$), 4.09 (m, 1H, NCH^c), 4.00 (d, 1H, CH^{3s}(allyl), $^3J(H^{3s},H^2)$ = 7 Hz), 3.74 (d, 1H, $CH^{3s\prime}$(allyl), $^3J(H^{3s\prime},H^{2\prime})$ = 7 Hz), 3.66 (t, 1H, CH^{1s}(allyl), $^3J(H^{1s},H^2)$ = $^3J(H^{1a},P)$ = 7 Hz), 3.37 (dt, 1H, PCH^a, $^2J(H^a,P)$ = $^2J(H^a,H^b)$ = 15 Hz, $^3J(H^a,H^c)$ = 2.5 Hz), 3.18 (dt, 1H′, $PCH^{a\prime}$, $^2J(H^{a\prime},P)$ = $^2J(H^{a\prime},H^{b\prime})$ = 15 Hz, $^3J(H^{a\prime},H^{c\prime})$ = 2.5 Hz), 3.07−2.94 (m, 4 H, $CH^{3a\prime}$ (allyl) + $CH^{1s\prime}$ (allyl) + PCH^b + $PCH^{b\prime}$), 2.75 (d, 1H, CH^{3a}(allyl), $^3J(H^{3a},H^2)$ = 14 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 31.64 (s) (both diastereoisomers) and −143.34 (hept, PF_6^-, $J(P,F)$ = 716 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): 31.24 (s) (both diastereoisomers) and −143.24 (hept, PF_6^-, $J(P,F)$ = 708 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 148.4−121.3 (m, 24C + 24C′ aromatics), 123.0 (s, 1C, C^2(allyl)), 120.6 (s, 1C′, $C^{2\prime}$(allyl)), 87.1 (d, 1C, C^1(allyl), $^2J(P,C)$ = 26.9 Hz), 84.6 (d, 1C′, $C^{1\prime}$(allyl), $^2J(P,C')$ = 28.3 Hz), 68.8 (s, 1C, NCH), 68.5 (s, 1C′, NC′H), 52.1 (s, 1C, C^3(allyl)), 51.4 (s, 1C′, $C^{3\prime}$(allyl)), 37.9 (d, 1C, PCH_2, $J(P,C)$ = 22.6 Hz), 37.7 (d, 1C′, PC′H_2, $J(P,C)$ = 21.4 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K): 31.70 (s), 31.63 (s) and 143.30 (hept, PF_6^-, $J(P,F)$ = 711 Hz). Anal. Calcd for $C_{29}H_{29}F_6NP_2Pd$: C, 51.69; H, 4.34; N, 2.08. Found: C, 51.70; H, 4.56; N, 2.29.

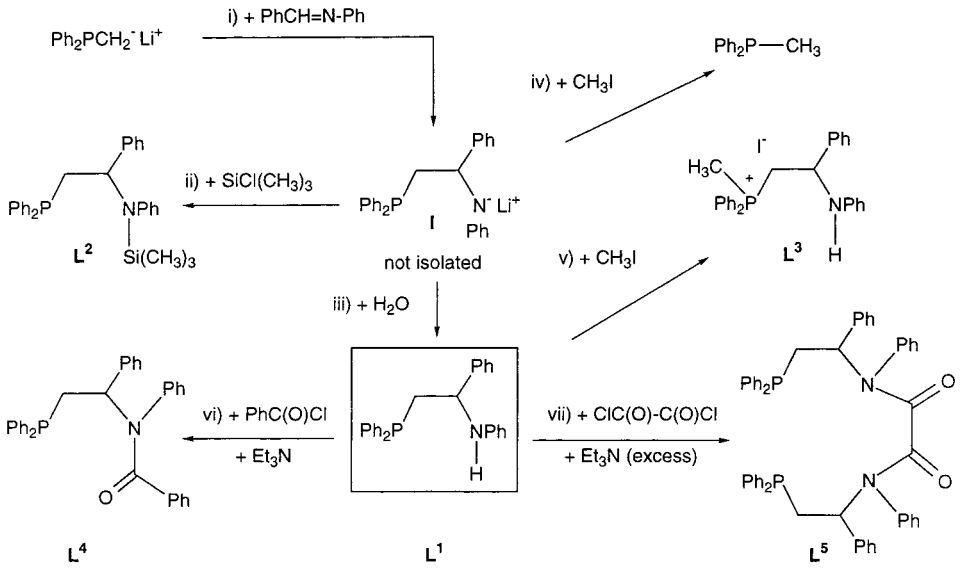
$^{31}P\{^1H\}$ NMR Experiments of the Phosphine Exchange Leading to 7a−c. (a) With 1 equiv of L[1]. To a mixture of **6** (12 mg, 0.018 mmol) and **L[1]** (7 mg, 0.018 mmol) was added 5 mL of CH_2Cl_2. The solution was stirred for 15 min, and the solvent was removed in vacuo. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 24.90 (s) and −143.34 (hept, PF_6^-, $J(P,F)$ = 716 Hz) for **7a**.

(b) With 1 equiv of PMe_3. To a solution of **6** (17 mg, 0.025 mmol) in THF (4 mL) was added PMe_3 (25 μL, 0.025 mmol, 1 M in THF). The solution was stirred for 15 min, and the solvent was removed in vacuo. The variable-temperature experiments were carried out in CD_3CN solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 24.90 (s) for **7a**, −18.49 (s) for **7b**, 13.61 (d, $^2J(P,P)$ = 40 Hz) and −18.46 (d, $^2J(P,P)$ = 40 Hz) for **7c**, and −143.34 (hept, PF_6^-, $J(P,F)$ = 716 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): 24.90 (s) for **7a**, −18.49 (s) for **7b**, 14.72 (d, $^2J(P,P)$ = 42 Hz) and −17.20 (d, $^2J(P,P)$ = 42 Hz) for **7c**, and −143.23 (hept, PF_6^-, $J(P,F)$ = 705 Hz).

(c) With 2 equiv of PMe_3. To the above $CDCl_3$ solution containing **7a−c** was added a second equivalent of PMe_3 (25 μL, 0.025 mmol, 1 M in THF). The mixture was then stirred for 10 min. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): −18.49 (s, br) for **7b**, −21.79 (s) for free **L[1]** and −143.34 (hept, PF_6^-, $J(P,F)$ = 716 Hz) for **7b**.

Synthesis of [PdCl(η^3-C_3H_5)(Ph_2PCH_2CH(Ph)N(Ph)C(O)Ph-κP)], 8. To a mixture of [PdCl(η^3-C_3H_5)]$_2$ (0.074 g, 0.200 mmol) in 5 mL of CH_2Cl_2 was slowly added a solution of **L[4]** (0.196 g, 0.400 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred for 3 h. The solvent was removed in vacuo. The addition of 10 mL of Et_2O afforded a white powder, which was isolated by filtration and washed with pentane and dried under vacuum. Yield: 0.150 g (56%). ^1H NMR ($CDCl_3$, 298 K): 7.46−7.08 (m, 25H + 25H′ aromatics), 6.41 (m, 2H, NCH + NCH′), 5.32 (apparent tt, 1H, CH^2(allyl), $^3J(H^2,H^{1a})$ = $^3J(H^2,H^{3a})$ = 12 Hz, $^3J(H^2,H^{1s})$ = $^3J(H^2,H^{3s})$ = 6 Hz), 5.11 (apparent tt, 1H′, $CH^{2\prime}$(allyl), $^3J(H^{2\prime},H^{1a\prime})$ = $^3J(H^{2\prime},H^{3a\prime})$ = 12 Hz, $^3J(H^{2\prime},H^{1s\prime})$ = $^3J(H^{2\prime},H^{3s\prime})$ = 6 Hz), 4.56 (t, 1H, CH^{1s}(allyl), $^3J(H^{1s},H^2)$ = $^3J(H^{1a},P)$ = 6 Hz), 3.70−3.42 (m, 6H, PCH_2 + PCH_2' + CH^{1a}(allyl) + $CH^{1a\prime}$(allyl)), 3.28−3.20 (m, 3H, CH^{3s}(allyl) + $CH^{3s\prime}$(allyl)), 2.67 (d, 1H, CH^3(allyl), $^3J(H^{3a},H^2)$ = 12 Hz), 2.18 (d, 1H, $CH^{3a\prime}$(allyl), $^3J(H^{3a\prime},H^2)$ = 12 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 15.69 (s) and 14.73 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 171.4 (s, 1C, NC(O)Ph), 171.3 (s, 1C, NC′(O)Ph), 140.7−127.8 (m, 30C + 30C′ aromatics), 118.1 (s, 1C, C^2(allyl)), 117.6 (s,

Scheme 1



1C′, $C^{2\prime}$(allyl)), 79.7 (d, 1C, C^1 (allyl), ^2J(P,C) = 32.7 Hz), 79.4 (d, 1C′, $C^{1\prime}$(allyl), ^2J(P,C′) = 32.7 Hz), 59.9 (s, 1C, C^3(allyl)), 59.8 (s, 1C′, $C^{3\prime}$(allyl)), 58.7 (s, NCH), 57.9 (s, 1C′, NC′H), 31.2 (d, 1C, PCH_2, J(P,C) = 21.4 Hz), 30.8 (d, 1C′, PC′H_2, J(P,C′) = 20.1 Hz). IR (CH_2Cl_2): ν(C=O) = 1641 cm^{-1} (vs). Anal. Calcd for $C_{36}H_{33}ClNOPPd$: C, 64.68; H, 4.98; N, 2.10. Found: C, 64.43; H, 5.09; N, 2.55.

Crystal Structure Analysis of 1 and 4. Pale yellow crystals of **1** and **4** suitable for X-ray analysis were obtained by layering *n*-pentane onto a saturated methylene chloride solution of **1** or **4** at room temperature. Data for both compounds were collected on an Enraf-Nonius diffractometer at 293 K using Mo Kα radiation. A 6% decay found for **1** was linearly corrected.[22]

Both structures were solved via a Patterson search program[23] and refined with full-matrix least-squares methods[23,24] based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **1**, except for the disordered solvate molecule, the hydrogen atoms of the complex were included in their calculated positions and refined with a riding model. One chlorine atom of the methylene chloride solvate molecule is disordered and occupies two positions with occupation factors imposed as x and $(1 - x)$ with x refined to 0.56. In **4**, except for the allyl ligand hydrogen atoms and those bonded to the nitrogen atom which were found by a Fourier difference synthesis, the hydrogen atoms of the complex were included in their calculated positions and refined with a riding model. After refinement of **4**, the Flack absolute structure parameter[25] converged to 0.00(6) (1.04(6) for the inverted structure). Experimental details and final agreement indices are reported in Table 3.

Results and Discussion

Synthesis of the β-Aminophosphine L^1 and Some Related Ligands. The $Ph_2PCH_2^-Li^+$ salt was prepared according to Peterson's procedure.[16] As the deprotonation reaction of the Ph_2PCH_3 precursor does not proceed beyond 85% (due to a secondary reaction as documented in the literature[17,18]), a substoichiometric amount of imine was used to afford the desired ligand $\mathbf{L^1}$ as shown in Scheme 1. After hydrolysis, the composition of the crude product was analyzed by NMR spectrocopy. In the $^{31}P\{^1H\}$ NMR spectrum, the excess of Ph_2PCH_3 was detected at −26.4 ppm in the presence of a new peak at −22.0 ppm corresponding to $\mathbf{L^1}$. The ligand was purified by crystallization in cold methanol and did not decompose by P−C bond cleavage in contrast to analogous α-P,N ligands.[14,15] The ^1H, ^{13}C, ^{31}P chemical shifts found for the ligand $\mathbf{L^1}$ were consistent with the β-P,N ($Ph_2PCH_2CH(Ph)NHPh$) ligand which has been previously obtained by a tedious multistep reaction.[13] An attempt to use the same procedure with $(Ph)_2C{=}NPh$ led unfortunately to a mixture of unidentified phosphorus-containing products.

In order to explore whether the β-P,N ligand could open the access to related N,N-disubstituted ligands, we have investigated the reactivity of the deprotonated form **I**. The reaction with CH_3I afforded Ph_2PCH_3 instead of the expected ligand, see Scheme 1. In the same manner, the addition of H_2O led to diphenylphosphine, although only as a minor byproduct. A reasonable explanation for the formation of these products is that the anionic nitrogen atom could exhibit a lower reactivity (or nucleophilicity) than expected due to the negative charge being delocalized on the *N*-phenyl fragment. Consequently, the phosphorus atom competes effectively as a nucleophile toward the electrophic reagents H^+ or CH_3^+. This assumption is in agreement with the easy phosphorus alkylation of $\mathbf{L^1}$ with 1 equiv of CH_3I (see experimental part), which affords the stable phosphonium salt $\mathbf{L^3}$ [$Ph_2MeP^+CH_2CH(Ph)NH(Ph)$]($I^-$). The expected byproduct of the methylation of **I** is an aziridine which was not further characterized. Further confirmation of this course of action comes from the following observations. The ligand $\mathbf{L^3}$ is stable, but the addition of a strong base such as *t*-BuOK led to the formation of Ph_2PCH_3, which was detected by $^{31}P\{^1H\}$ NMR. An analogous phosphonium ligand containing an oxygen instead of a nitrogen function, namely, [$Ph_2MeP^+CH_2C(Ph)_2OH$](I^-), led to a similar P−C bond cleavage upon deprotonation with formation of $Ph_2MeP{=}O$ and $(Ph)_2C{=}CH_2$.[16]

In regards to these observations, we wished to find an alternative synthetic method to alkylate the nitrogen anion. This method is based on the use of an electrophilic reagent which is more reactive toward the attack by harder bases relative to softer ones, such as TMSCl (chlorotrimethylsilane) or an acyl chloride. In the latter case, the acyl group in the expected product could lead to the corresponding alkyl fragment by a further reduction reaction.[11] Both related ligands $\mathbf{L^2}$ and $\mathbf{L^4}$ (see Scheme 1) have

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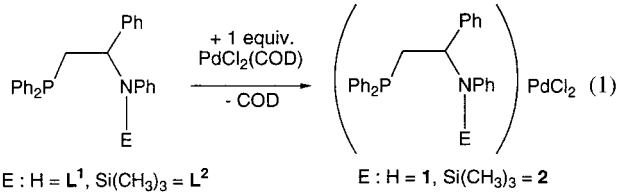
Table 1. $^{13}C\{^1H\}$ NMR Data for the Ligands $\mathbf{L^1}-\mathbf{L^5}$ (Chemical Shifts in ppm; $^2J_{PC}$ or $^3J_{PC}$ in Hz in Parentheses)

	$\mathbf{L^1}$	$\mathbf{L^2}$	$\mathbf{L^3}$	$\mathbf{L^4}$	$\mathbf{L^5}$ dia1, dia2
P*C*	39.5 (16)	34.3 (14)	31.6 (48)	32.2 (14)	30.8 (15), 31.2 (15)
N*C*	56.6 (15)	58.7 (18)	54.1 (4)	57.4 (16)	54.9 (19), 55.3 (19)
P-*Ph*					
C_{ipso}	138.1 (12)	138.6 (14)	118.3 (15)	138.6 (12)	138.3 (15), 138.4 (15)
	138.7 (13)	139.4 (15)	121.6 (14)	138.9 (12)	138.4 (16), 138.5 (16)
C_{ortho}	133.3 (19)	133.0 (20)	132.5 (10)	133.1 (19)	132.9 (19), 133.0 (19)
		133.2 (20)	132.8 (9)	133.9 (20)	133.7 (20), 133.8 (20)
C_{meta}	129.1	128.0	130.7 (12)	128.7	128.8, 128.9
	129.3	128.2	131.1 (11)	128.9	128.9, 129.0
C_{para}	129.0	128.5	135.1	129.5	129.0, 129.1
	129.1	128.7	135.7	129.6	129.2, 129.2
C-*Ph*					
C_{ipso}	144.9 (5)	143.4 (5)	141.5 (14)	140.7 (6)	139.1 (4), 139.3 (4)
C_{ortho}	126.5	128.7	127.2	128.8	128.7, 128.8
C_{meta}	129.2	131.2	129.4	131.2	131.7, 131.8
C_{para}	127.6	127.0	128.4	127.9	127.9, 128.0
N-*Ph*					
C_{ipso}	147.4	144.6	146.1	137.5	136.2, 136.5
C_{ortho}	113.9	128.4	114.6	128.1	128.4, 128.5
C_{meta}	129.4	128.8	129.4	129.3	128.9, 128.9
C_{para}	117.8	124.2	118.9	128.3	128.6, 128.8
other signal assignments		1.1 Si*Me*$_3$	11.3 (54) *Me*	171.6 *C*=O 140.6 CO*Ph*$_{ipso}$ 129.0 CO*Ph*$_{ortho}$ 129.1 CO*Ph*$_{meta}$ 129.1 CO*Ph*$_{para}$	164.4, 164.5 *C*=O

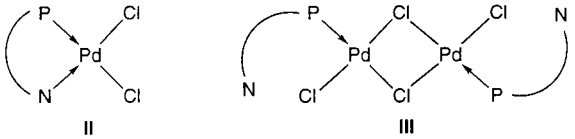
been successfully obtained in good yields. By extension of this procedure, ligand $\mathbf{L^5}$ was prepared by using oxalyl chloride (see Scheme 1). According to Nagel's reduction procedure, we have attempted to convert the amide function in the ligand $\mathbf{L^4}$ to a tertiary amine group. Unfortunately, even after 7 days of reflux in THF in the presence of an excess of $LiAlH_4$ and after hydrolysis, the reaction did not lead to the expected ligand but rather to $\mathbf{L^1}$. This observation shows that the reduction stops after the formation of the iminium salt, which then hydrolyzes to $\mathbf{L^1}$.[26] We might expect that the replacement of the *N*-phenyl substituent with an unconjugated fragment such as an alkyl or benzyl group will eventually increase the nucleophilic character of the amine function. The preparation of new imines and their use as starting materials for the synthesis of other β-P,N are currently in progress. The ^{13}C NMR data of ligands $\mathbf{L^{1-5}}$ are given in Table 1.

Coordination Properties of $\mathbf{L^1}$ and $\mathbf{L^2}$ toward Palladium(II) Complexes. It is well-known that N,N-disubstitued aminophosphines act as mono- or bidentate ligands in palladium(II) and platinum(II) complexes, with a hemilabile character.[27] Moreover, Sadler and Habtemariam have shown by $^{31}P\{^1H\}$ and ^{195}Pt NMR spectroscopy in aqueous solution that the equilibrium between the dangling and chelating forms in bis(β-P,N) (with β-P,N = $Ph_2P(CH_2)_2NMe_2$) platinum(II) complexes is pH dependent and can be controlled by the N-substituents. Indeed, when the tertiary amine in the $Ph_2P(CH_2)_2NMe_2$ ligand is replaced by a primary amine, the hemilabile character is lost.[28] In regard to these coordination properties, our ligand contains a secondary amine substituted by a phenyl group, which is not a particularly strong electron-donating group. Thus, we wished to examine the consequences of the weak donor character of the amine function in the κP versus $\kappa P,\kappa N$ coordination mode of $\mathbf{L^1}$ and $\mathbf{L^2}$.

The reaction between $PdCl_2(COD)$ (COD = 1,5-cyclooctadiene) and $\mathbf{L^1}$ or $\mathbf{L^2}$ in a 1:1 ratio leads to the formation of the complexes **1** and **2**, see eq 1. The presence of the NH or $NSi(CH_3)_3$ protons in the ^1H NMR confirms that HCl or $ClSi(CH_3)_3$ elimination has not occurred.



However, a structural ambiguity persists. The NMR properties are consistent with either a mononuclear structure of type **II** (with a P,N chelate)[18,27] or a chloride-bridged dinuclear one of type **III** (well-known with other bifunctional ligands such as ketophosphines).[29,30]



The $^{31}P\{^1H\}$ NMR spectrum shows a signal at δ 38.8 for **1** and 28.4 ppm for **2** which may be consistent with both coordination modes. The NH proton resonance for complex **1** is found at 8.10 ppm, in constrast to 4.19 ppm for the free ligand, but this does not unambiguously prove structure **II**. Consequently, a structure analysis by X-ray diffraction was carried out for complex **1** (see below). This shows that, indeed, the mononuclear structure-type **II** is adopted. Compound **2** has spectroscopic properties similar to those of **1**, and a mononuclear formulation is also assigned to this compound.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1** and **4**

compound **1**		compound **4**	
Pd−N	2.106(4)	Pd−C(27)	2.176(7)
Pd−P	2.1969(15)	Pd−C(28)	2.135(7)
Pd−Cl(1)	2.3776(14)	Pd−C(29)	2.135(7)
Pd−Cl(2)	2.2846(16)	Pd−P	2.280(2)
N−H	0.874	Pd−Cl	2.371(2)
(N)H···Cl	2.605	C(27)−C(28)	1.29(2)
		C(28)−C(29)	1.33(1)
		N···Cl	3.304(4)
		N−H	0.75
		(N)H···Cl	2.55
N−Pd−P	85.64(11)	C(27)−Pd−Cl	99.7(4)
N−Pd−Cl(1)	91.94(11)	C(27)−Pd−P	163.3(18)
N−Pd−Cl(2)	174.93(12)	C(28)−Pd−Cl	131.6(9)
P−Pd−Cl(1)	172.54(6)	C(28)−Pd−P	128.6(7)
P−Pd−Cl(2)	90.36(6)	C(29)−Pd−Cl	165.9(22)
Cl(1)−Pd−Cl(2)	92.41(6)	C(29)−Pd−P	97.3(4)
N−H···Cl	144	P−Pd−Cl	96.7(1)
		C(27)−C(28)−C(29)	129(2)
		N−H···Cl	175

Table 3. Crystallographic Data for Compounds **1** and **4**

	compound **1**	compound **4**
chemical formula	$C_{26}H_{24}Cl_2NPPd\cdot CH_2Cl_2$	$C_{29}H_{29}ClNPPd$
fw	643.66	564.35
space group	$P2_1/n$	Cc
a, Å	10.689(2)	10.912(1)
b, Å	21.345(3)	17.194(2)
c, Å	12.282(2)	14.169(2)
β, deg	90.294(12)	100.651(9)
V, Å^3	2802.2(8)	2612.6(5)
Z	4	4
T, K	293(2)	293(2)
D_{calcd}, g/cm^3	1.526	1.435
λ, Å	0.71073	0.71073
μ, mm^{-1}	1.117	0.89
$R(F_o)^a$	0.039	0.024
$R_w(F_o^2)^b$	0.099	0.060
GOF^c	1.063	1.073

^{a} $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2 + (0.0523P)^2 + 2.70P]$ for **1** and $w = 1/[\sigma^2(F_o^2 + (0.037P)^2 + 0.58P]$ for **4** where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. ^{c} $\mathrm{GOF} = [\sum w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

X-ray Structure Analysis of Complex 1. The structure of complex **1** shows that the ligand $\mathbf{L^1}$ adopts a $\kappa P,\kappa N$ coordination mode in a square planar coordination geometry for the palladium center. The selected bond lengths and bond angles (see Table 2) of complex **1** compare with those of the only other examples of $PdCl_2$ complexes containing similar saturated aminophosphine ligands, namely, $PdCl_2[\{Ph_2PCH_2CH((CH_2)_nSMe)NMe_2\}$-$\kappa P,\kappa N]$ (with $n = 2$ or 3).[31] The Pd−P, Pd−N, Pd−Cl(1), and Pd−Cl(2) distances are very close to those found in the above-mentioned complexes. The Pd−Cl bond length trans to the P atom [2.3776(14) Å] is longer than that trans to the N atom [2.2846(16) Å] owing to the stronger trans influence of a tertiary phosphine with respect to an amine. The Cl(1)−Pd−Cl(2), N−Pd−Cl(2), Cl(1)−Pd−N, and P−Pd−Cl(2) angles reveal only minor distortions from the ideal value. The P−Pd−N angle of 85.64(11)° is normal for this type of five-membered-ring complex.[31]

It is interesting to observe that there are no N−H···Cl intramolecular interactions. The H−N−Pd−Cl dihedral angle of 87.5° in **1** certainly does not favor the establishment of this interaction, whereas one is observed in the related allyl palladium chloride complex (see below). However, we found that the distance between the N atom of one complex and the Cl from another one (3.33 Å) (N−H = 0.874 Å; H···Cl = 2.605 Å; N−H···Cl = 144°) is significantly smaller than the sum of the N−H bond length and the van der Waals radii of the H and Cl atoms.[32] Consequently, compound **1** is in fact an H-bonded dimer in the solid state with two N−H···Cl intermolecular bridges in the $Pd_2N_2H_2Cl_2$ eight-membered ring. However, it is possible that this dimeric structure is not maintained in solution, especially in solvents capable of establishing H-bonding interactions.

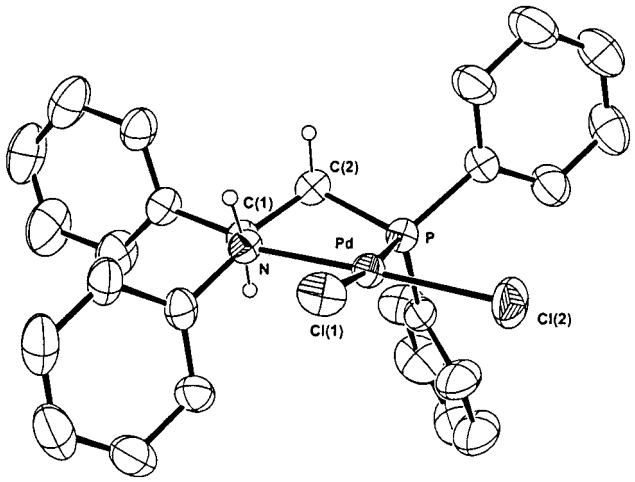
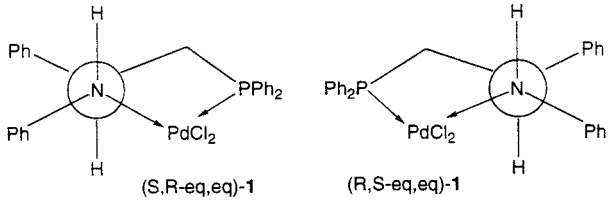


Figure 1. An ORTEP view of complex **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms of phenyl groups are omitted for clarity.

The centrosymmetric unit cell of **1** contains the enantiomeric pair of one diastereoisomer (see ORTEP view in Figure 1). It is interesting to examine the arrangement of the phenyl substituents on the carbon and on the nitrogen atoms. In fact, as the $\mathbf{L^1}$ ligand used is a racemate and as coordination generates a second chiral center at the N atom in addition to that already present at the C atom, four stereoisomers should be expected. However, only two are observed in this structure, which are the (*S*,*R*, eq, eq) and (*R*,*S*, eq, eq), see below.



The hydrogen substituents on adjacent carbon and nitrogen atoms in the five-membered ring are almost completely staggered ($H_{ax}-H_{ax}$) as it has also been observed, in the solid state, for other complexes containing either a diamine or a diphosphine ligand.[33,34] This arrangement tends to minimize the energy of the cyclic structure by analogy with cyclopentane or cyclohexane.[33] However, a ($H_{eq}-H_{eq}$) arrangement has been observed in solution by NMR coupling constant analysis for a similar palladium-coordinated β-P,N ligand (β-P,N = $\{(p\text{-}CH_3C_6H_4)_2$-$PCH_2CH(i\text{-}Pr)NHCH_2(p\text{-}C_6H_4OCH_3)\}$) and confirmed by calculations. The energy difference between the two possible

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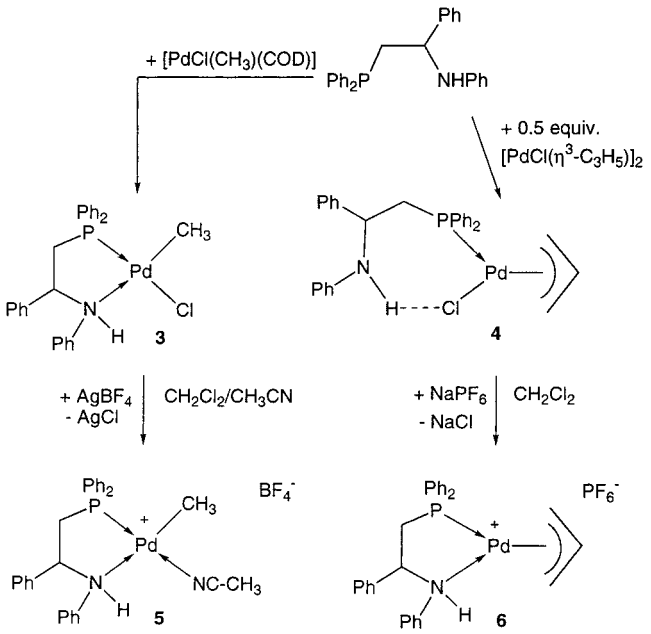
Scheme 2



conformations was found to be about 1 kcal/mol.[18] We wished to examine whether the observed solid state conformation of **1** is retained in solution. On the basis of the H−C−C−H dihedral angles of the P−CH^{a}H^b−CH^c(Ph)N fragment experimentally found to be 60° and 180° in solid state, the corresponding coupling constants ^3J(H,H) are predicted to be ca. 4 Hz (for the (H$^a_{eq}$−H$^c_{ax}$) conformation) and 15 Hz (for the (H$^b_{ax}$−H$^c_{ax}$) conformation).[35] However, the solution structure for **1** could not be elucidated by ^{1}H NMR spectroscopy owing to an overlap of multiplet signals related to the PCH^a−CHN protons.

Coordination Properties of L^1 in Neutral and Cationic Methyl and Allyl Palladium Complexes. The reaction between the ligand **L^1** and [PdCl(CH$_3$)(COD)] leads to the formation of **3**, see Scheme 2. In this complex, **L^1** behaves as a chelating ligand, $\kappa P,\kappa N$, on the basis of its chemical shift in the ^{31}P{^{1}H} NMR spectrum at 40.1 ppm which is close to the value observed for complex **1**. This P,N coordination mode is also in agreement with the NH proton chemical shift (doublet at 6.27 ppm in **3** with ^3J(P,H) = 11.5 Hz, versus broad singlet at 4.40 ppm in **L^1**). The CH$_3$ group is found at 0.75 ppm in the ^{1}H NMR spectrum with a typical small cis phosphorus coupling constant of ^3J(P,H) = 3.5 Hz.[27] This configuration is certainly due to the larger trans influence of the tertiary phosphine relative to the amine, as is well-known for other methyl palladium chloride complexes containing neutral P,N ligands.[27] When a palladium monochloride complex containing an allyl instead of a methyl group is used in the reaction with ligand **L^1**, a new complex **4** is formed, see Scheme 2. Its ^{1}H NMR spectrum does not show the presence of the allyl fragment at room temperature, and a single peak is observed at 16.6 ppm in the ^{31}P{^{1}H} NMR spectrum. This value is very different from those found for complexes **1**−**3** and seems to indicate a κP coordination mode. At lower temperatures, the ^{1}H and ^{31}P{^{1}H} NMR spectra show all the allyl protons and the presence of two diastereiosomers in an approximate 1:1 ratio. The coalescence temperature for the ^{31}P signals is found at ca. 280 K, see Figure 2.

In order to fully characterize **4**, we have carried out an X-ray structure analysis (see below) which confirms a neutral allyl palladium structure with a β-aminophosphine in the κP coordination mode. It is interesting to note that the free secondary amine function does not transfer the proton to the allyl ligand to lead to propene (a key step suggested for nickel-based butadiene dimerization catalysts[36,37]) nor to reductive elimination to lead to Pd(0) and an allyl phosphinoammonium salt (a key step suggested for palladium-based allyl amination catalysts[37−40]).

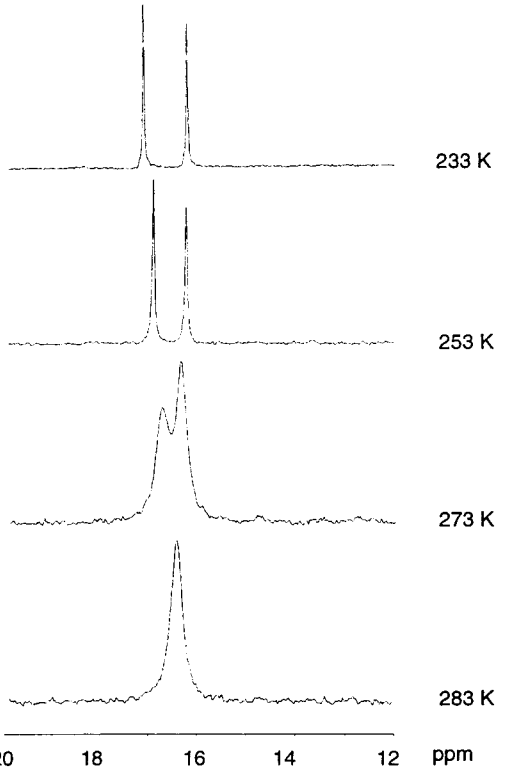


Figure 2. ^{31}P{^{1}H} NMR spectra at variable temperature for complex **4** in $CDCl_3$.

The reaction of the neutral complexes **3** and **4** with chloride-abstracting reagents leads to the corresponding stable cationic complexes **5** and **6**, see Scheme 2. Like for complex **4**, the allyl protons of **6** are invisible in the room temperature ^{1}H NMR spectrum due to the dynamic η^3/η^1 allyl rearrangement. At lower temperatures, the decoalescence allows the detection of the allyl protons for two distinct diastereoisomers. The ^{31}P{^{1}H} resonances are found at 31.70 and 31.63 ppm at lower temperature, and the ^{31}P{^{1}H} coalescence is found at 233 K for **6** versus 285 K for **4**.

X-ray Structure Analysis of Complex 4. The geometry of **4** is shown in Figure 3, and selected bond distances and angles are collected in Table 2. The unit cell contains the enantiomeric pair of one diastereoisomer. The structure confirms the typical geometry of an η^3-allyl group and the typical stereochemistry of d^8 palladium(II). The allyl group is oriented with the central C atom pointing away from the amine function of the κP-coordinated **L^1** ligand. The different Pd−C bond lengths are in agreement with the larger trans influence of the phosphine ligand with respect to the chloro ligand, see Table 2.[41−43]

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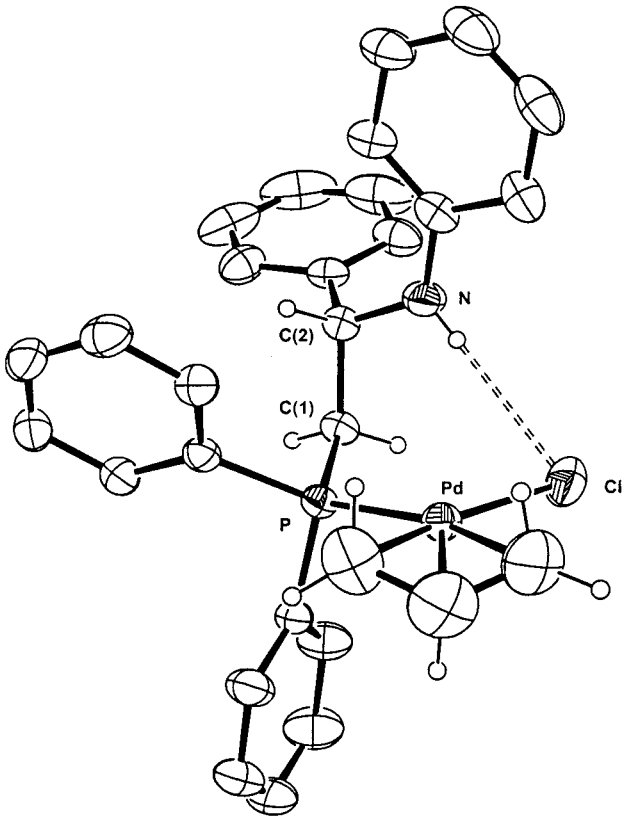
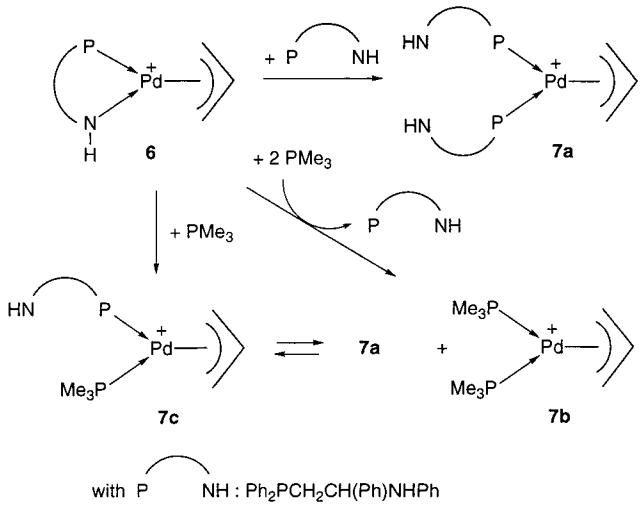


Figure 3. An ORTEP view of complex **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms of phenyl groups are omitted for clarity.

In contrast to **1**, compound **4** exhibits an intramolecular H-bonding interaction, N−H···Cl. The N···Cl distance of 3.303 Å (N−H = 0.75 Å; H···Cl = 2.55 Å) is significantly shorter than the sum of the N−H bond length and the van der Waals radii of H and Cl atoms, 3.80 Å,[32] and the N−H···Cl arrangement is close to linear (175°). Other examples of this type of interaction in seven-membered rings have been recently reported for a copper(I) chloride complex containing the ligand [NH{Si(Me)$_2$CH$_2$PPh$_2$}$_2$]-$\kappa P,\kappa P$[44] and for [PtBr(C$_6$H$_4$CH(Me)-NMe$_2$-(*R*)-2-C,N)(C$_6$H$_4$CH(Me)NHMe$_2$-(*R*)-2-C)].[45] This intramolecular H-bonding interaction is also confirmed by infrared spectroscopy. The ν(N−H) for **4** is shifted at 3300 cm^{-1} whereas it was found at 3390 cm^{-1} for the free ligand **L^1**.

Phosphine Redistribution in the Cationic Allyl Palladium Chloride Complex 6. In order to evaluate the donor and/or the labile character of the amine function in the cationic complex **6**, we have recorded its phosphorus NMR spectra in $CDCl_3$ and CD_3CN. As no significant shift is observed as a function of the solvent, we conclude that the acetonitrile is not sufficiently strong to open the P,N chelate. However, a phosphorus NMR monitoring of the reaction of **6** with 1 equiv of β-P,N ligand in $CDCl_3$ showed the absence of the resonances corresponding to the free ligand and to complex **6** and the presence of a new peak at 24.9 ppm. The latter is attributed to complex **7a**, which has not been further characterized, see Scheme 3. In this case the phosphorus atom of ligand **L^1** is sufficiently strong to open the P,N chelate. By analogy with this experiment, when 1 equiv of the PMe_3 is added to complex **6**, the $^{31}P\{^1H\}$ NMR peaks of **6** and free PMe_3 disappear and are replaced by two new singlets and by one AB pattern. These are consistent with the presence of the three complexes **7a**−**c**. Moreover, when a second equivalent of PMe_3 was added to this solution, the $^{31}P\{^1H\}$ NMR peaks of **7a** and **7c** disappeared whereas a singlet corresponding to free **L^1** ligand appeared and the intensity of the signal of **7b** increased. This P-coordination of the additional ligand could be preceded by the formation of a complex containing a free coordination site generated by the known η^3/η^1 allyl rearrangement. This view would seem consistent with the observation of only one signal in the $^{31}P\{^1H\}$ NMR spectra of complexes **6**, **7a**−**c**, because of the very rapid allyl interconversion at room temperature. When the mixture of complexes **7a**−**c** is heated in CD_3CN at different temperatures, the intensities of all signals decrease at the same time until they disappear at 323 K, see Figure 4, indicating a rapid equilibration for the mixture of the three complexes (see Scheme 3). This equilibrium is similar to one reported for methyl palladium chloride complexes containing mixed functional P,O ligands.[29,30]

Scheme 3



It is interesting to mention the recent van Leeuwen's work on the allylic alkylation catalyzed by [(C$_4$H$_7$)Pd(P,N)]$^+$ or [(C$_9$H$_9$)Pd(P,N)]$^+$ (P,N = aminophosphinite), in which he reports that the presence of an additional equivalent of P,N ligand decreases the regioselectivity of the branched product in the catalytic allylic alkylation from 22% to 8%. To explain this observation, it was proposed that a bis(aminophosphinite-κP) coordinated complex is reversibly formed in equilibrium with the mono $\kappa P,\kappa N$ coordinated complex.[46] Our results above provide evidence in support of this assumption. Indeed, variable-temperature $^{31}P\{^1H\}$ NMR experiments show clearly the easy P,N opening in cationic allyl palladium complex **6** by addition of PMe_3 or **L^1** as well as a partial phosphine decoordination leading to ligand redistribution.

Coordination Properties of L^4 in the Neutral Allyl Palladium Chloride Complex 8. As the ligand **L^4** contains a good oxygen atom donor in the amide function, we have carried out

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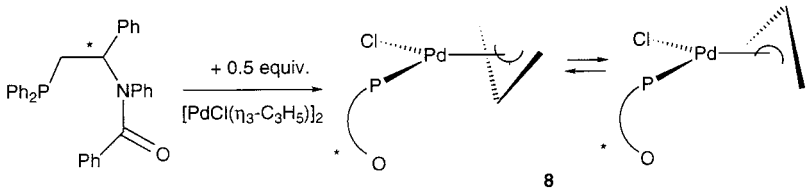
Scheme 4



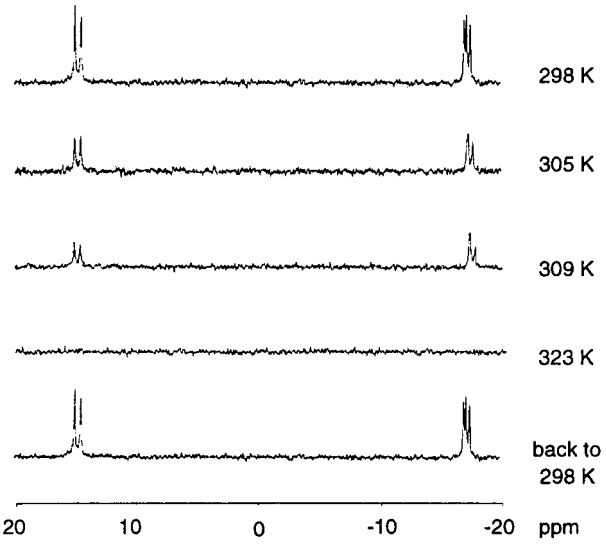


Figure 4. $^{31}P\{^1H\}$ NMR spectra at variable temperature for phosphine exchange on complexes **7a**, **7b**, and **7c** in CD_3CN.

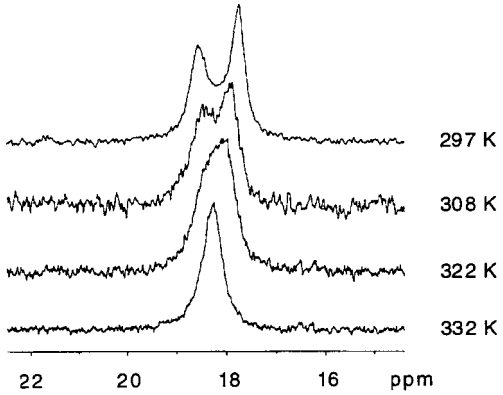


Figure 5. $^{31}P\{^1H\}$ NMR spectra at variable temperature for complex **8** in CD_3CN.

preliminary investigations of its coordination properties to the neutral allyl palladium system. The reaction with $^1/_2$ equiv of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in $CDCl_3$ solution leads to the formation of complex **8**, see Scheme 4. The IR spectrum exhibits an absorption band at 1641 cm^{-1} identical to that found for the free ligand at 1642 cm^{-1}, excluding the O-coordination mode of the functional ligand and suggesting a κP coordination mode analogous to that shown for complex **4**. A similar κP coordination has also been reported for a related palladium complex containing a phosphino−ester ligand.[47,48] However, in contrast to complexes **6** and **7a**−**c** which exhibit only one set of resonances by NMR, the ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra of the reaction product show the presence of two complexes in the same ratio (ca. 1:1) in $CDCl_3$ or in CD_3CN solutions at room temperature, see Scheme 4. The presence of two complexes is consistent with the slow interconversion of two diastereoisomers. The variable-temperature $^{31}P\{^1H\}$ NMR investigation (see Figure 5) shows a coalescence temperature for **8** at ca. 322 K.

Under the assumption that the allyl rearrangement rate can be qualitatively correlated with the coalescence temperatures, the rate decreases in the order **6** > **4** > **8**. A steric effect of the amine or amide function in $\mathbf{L^1}$ or $\mathbf{L^4}$ could reasonably be excluded as the factor determining this rate difference, because these functions are relatively far from the allylic carbon atoms. Rather, the data suggest an electronic control, since the formal charge on the metal center decreases in the order **6** (cationic) > **4** (neutral with H-bond) > **8** (neutral without H-bond). A greater effective positive charge may render the η^3/η^1 allyl rearrangement more facile by reducing the M-allyl back-bonding component.

Conclusion

A β-aminophosphine $\mathbf{L^1}$ has been prepared in only one step by the reaction of the C═N bond in *N*-phenylbenzaldimine toward the carbanionic species $Ph_2PCH_2^-$. When this ligand adopts a $\kappa P,\kappa N$ coordination mode, a new chiral nitrogen center is generated. Its absolute configuration is fixed by that of the adjacent carbon atom, with the C- and N-bonded phenyl groups occupying equatorial positions. In cationic palladium complexes, we have also shown that the N atom chirality may be lost by its hemilabile character in the presence of strong donors (i.e., tertiary phosphines). The synthesis of optically pure ligand $\mathbf{L^1}$ and related ligands is currently in progress.

On the other hand, when $\mathbf{L^1}$ behaves as a monodentate ligand, an unexpected N−H···Cl intramolecular interaction has been observed in the solid state. The variable-temperature $^{31}P\{^1H\}$ NMR experiments have shown that the allyl interconversion rate is strongly affected by the electronic effects in these related palladium complexes. Indeed, this rate is higher for a cationic complex than for a related neutral one owing to the increase of the metal electrophilic character. Surprisingly, different allyl interconversion rates have also been observed for neutral complexes containing either $\mathbf{L^1}$ with a secondary amine function or $\mathbf{L^4}$ ligand with an amide function. This latter observation is rationalized for the first time on the basis of an electron-withdrawing effect generated by the N−H···Cl intramolecular interaction. The effects of this type of weak interaction on the organometallic reactivity and in homogeneous catalysis are also currently examined.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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