Stable Palladium(0), Palladium(II), and Platinum(II) Complexes Containing a New, Multifunctional and Hemilabile Phosphino−Imino−Pyridyl Ligand: Synthesis, Characterization, and Reactivity

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Received November 22, 1995[⊗]

The new, multifunctional, hemilabile phosphorus−bis(nitrogen) ligand *N*-(2-(diphenylphosphino)benzylidene)(2-(2-pyridyl)ethyl)amine, PNN, containing phosphine, imine, and pyridyl donor groups and alkyl-, allyl-, and acylpalladium complexes, methylplatinum complexes, and a zerovalent palladium complex containing PNN have been synthesized and characterized with ^{1}H-, ^{13}C-, ^{31}P-, and ^{15}N-NMR. PNN commonly coordinates in a terdentate fashion, resulting in ionic complexes of the type $[(PNN)M^{II}(R)]Y$ (M = Pd, Pt, R = CH_3, Y = Cl, CF_3SO_3; M = Pd, R = $C(O)CH_3$, Y = CF_3SO_3; M = Pd, R = η^1-$CH_2C(H)=CH_2$, Y = Cl, CF_3SO_3). Bidentate coordination of PNN is observed for $[(PNN)Pd^{II}(\eta^3\text{-}(CH_3)_2CC(CH_3)C(CH_3)_2)]Cl$ and surprisingly also for neutral $(PNN)Pd^{II}(C(O)CH_3)(Cl)$. An unprecedented zerovalent palladium complex $(PNN)Pd^0$ has been isolated, which is stabilized by PNN only. Preliminary results show that palladium complexes of PNN are very active in allylic alkylation reactions.

As part of our ongoing research on palladium complexes in stoichiometric[1] and catalytic reactions,[2] it was our goal to design a multifunctional, hemilabile ligand that would stabilize both Pd(0) and Pd(II) under reaction conditions. Such a ligand may facilitate a catalytic reaction involving a Pd(0)−Pd(II) cycle, like the C−C cross-coupling reaction, without the aid of additional stabilizing ligands. This may be achieved by a ligand that is able to act as a bidentate as well as a terdentate ligand and that has variable chelate angles. It has recently been found that P−N ligands in particular are suitable ligands for palladium-catalyzed allylic alkylation[3,4] and cross-coupling reactions,[5a,b] although other mixed-donor ligands, such as ones with a N−S donor set, may also be very active.[6]

We thus designed the multifunctional phosphorus−bis(nitrogen) ligand *N*-(2-(diphenylphosphino)benzyli-

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⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1996.

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S0276-7333(95)00904-6 CCC: $12.00

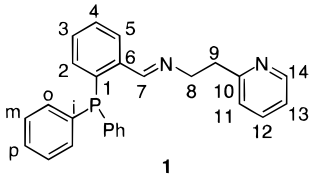

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Figure 1. Structure and adopted numbering scheme of PNN, **1**.

dene)(2-(2-pyridyl)ethyl)amine (PNN, **1**); see Figure 1. The new potentially terdentate ligand **1** contains three donor atoms, a diphenylphosphino, an imino, and a pyridyl group. The latter two were chosen in an effort to enhance the π-accepting capacity of the system. Such π-accepting abilities are a prerequisite for the stabilization of zerovalent palladium complexes. The intrinsic flexibility of the ligand facilitates the adaptation of the bite angles between the metal and the donor atoms, as needed for the different oxidation states of palladium. Because of its flexible structure, **1** can act either as a monodentate P ligand, as a bidentate P−N one, or as a terdentate P−N−N one. Upon coordination both the P−N and the N−N sets will form six-membered chelate rings. Preliminary results of the coordination chemistry of ligand **1** in palladium complexes have been reported recently,[7] and $Mo(CO)_4$ complexes containing related ligands have been reported briefly by Rauchfuss.[8]

Results

The PNN Ligand, 1. The orange, potentially terdentate ligand **1** has been synthesized in 81% yield from the Schiff's base condensation reaction of 2-(diphenylphosphino)benzaldehyde and 2-(2-aminoethyl)pyridine according to the method of Lavery and Nelson.[9] **1** was characterized by ^{1}H-, ^{13}C-, ^{31}P-, and ^{15}N-NMR, IR, and mass spectroscopy (Figure 1). The ligand proved to be fairly insensitive toward oxidation. In the solid state the ligand is stable for months, and in solution, no significant amounts of the oxidation product were observed within 4 weeks.

The ^{1}H-NMR spectrum of **1**, see Table 1, shows a phosphorus coupling constant of 4.7 Hz on H^7, which is absent in the spectra of its palladium and platinum complexes **2**−**11**. Presumably this is a through-space coupling, indicating a conformation of free **1** in which the imino-hydrogen atom points toward the phosphorus lone pair.[10] This feature was also reported by Rauchfuss for the related ligands $(C_5H_6)_2$P-2-C_6H_4C(H)=NR (R = *p*-$C_6H_4OCH_3$, $CH_2C(H)=CH_2$, CH_2-2-C_5H_4N, and CH_2-CH_2SCH_3).[8] Phosphorus couplings of 3.9 and 4.7 Hz are found on H^2 and H^4 of the benzaldimino group, respectively, which are also present in the palladium complexes of **1**. The ^{13}C-NMR spectrum of **1**, see Table 2, shows phosphorus couplings on the resonances of the two phenyl groups and on C^2 and C^7 of the benzaldimino group. The resonances of the ethylpyridyl moiety have no visible phosphorus couplings (J(P−H) < 1 Hz). Table 3 shows the ^{31}P- and ^{15}N-NMR and IR data. The two nitrogen nuclei of **1** shift −45.2 and −68.3 ppm relative to nitromethane, which are expected values for imino and pyridyl nitrogens, respectively.[11,12] The imino nitrogen shows a small 3.0 Hz phosphorus coupling. The phosphorus atom in **1** has a chemical shift of −13.6 ppm, which is in agreement with similar triarylphosphine ligands, e.g. triphenylphosphine. The IR shows the expected resonance of the C=N group at 1635 cm^{-1}.[8]

Methylpalladium Compounds. Methylpalladium compound [(PNN)Pd(CH_3)]Cl, **2**, was synthesized from (η^2,η^2-1,5-cyclooctadiene)Pd(CH_3)(Cl) in chloroform or dichloromethane at room temperature as published recently; see Figure 2.[7] The isostructural complex [(PNN)Pd(CH_3)]CF_3SO_3, **3**, has been synthesized from **2** upon metathesis with silver trifluoromethanesulfonate at room temperature in acetonitrile. The platinum analogues of **2** and **3**, [(PNN)Pt(CH_3)]Cl, **9**, and [(PNN)Pt-(CH_3)]CF_3SO_3, **10**, have been obtained via the same procedures, starting with (COD)Pt(CH_3)(Cl).

Whereas compounds **2** and **3** readily dissolve in solvents such as chloroform, dichloromethane, acetonitrile, and DMSO and are moderately soluble in less polar solvents like benzene and toluene, **9** and **10** are only moderately soluble in dichloromethane and chloroform and poorly soluble in benzene and toluene. In the solid state as well as in solution **2**, **3**, **9**, and **10** are stable in solution at ambient temperature for several months.

In **2**, **3**, **9**, and **10**, PNN coordinates in a static terdentate fashion as can be concluded from (i) the presence of small phosphorus couplings on the ^{13}C-NMR resonances of the pyridyl ring, (ii) a very characteristic set of multiplets for H^8 and H^9, (iii) a 45 Hz phosphorus coupling on the resonance of the pyridyl N in the ^{15}N-NMR in combination with a coordination induced shift (CIS) of *ca.* −50 ppm, and (iv) conductometric experiments, since terdentate coordination of PNN in divalent palladium complexes results in ionic compounds.

Additionally, ^{195}Pt couplings are present in the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra of the platinum compounds **9** and **10** (Tables 1−3); large Pt−P coupling constants of 4101 and 4078 Hz, Pt−H coupling constants of 70 Hz on the methyl ligand and 36 and 32 Hz on H^{14}, and Pt−C coupling constants of 659 and 668 Hz on the methyl ligand of **9** and **10**, respectively, indicate that the methyl resides *cis* with respect to the phosphorus.[13] Unlike the coordination behavior of nonsymmetric terdentate nitrogen ligands,[11,14] of which the flexible ethylpyridyl moiety easily dissociates, PNN coordinates to **2**, **3**, **9**, and **10** in a static terdentate fashion at the NMR time scale, as concluded from the lack of fluxionality in the NMR spectra recorded between 223 and 323 K.

Crystal Structure Determination of [*N*-(2-(diphenylphosphino)benzylidene)(-(2-(2-pyridyl)ethyl)amine]methylpalladium(II) Trifluoromethanesulfonate, 3. The precise arrangement of the ligands in complexes **2**[7] and **3** has been determined by X-ray studies of their colorless crystals. The structural data

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Table 1. Selected ^{1}H-NMR Data for the Compounds 1−11

	^{1}H-NMR (ppm)						
compd (solvent	M−R	H^2	H^5	H^7	H^8	H^9	H^{14}
1 ($CDCl_3$)		7.93 [3.9]	7.03	8.85 [4.7]	3.89	2.97	8.49
2 ($CDCl_3$)	0.36 [2.7]	8.15 [4.3]	7.07 [11]	9.47	4.22	3.48	8.41
3 ($CDCl_3$)	0.35 [2.7]	7.90 [4.3]	7.16 [10]	8.80	4.00	3.49	8.42
4 ($CDCl_3$)	2.19 [1]	obscured	7.14[a]	8.51	4.25	3.38	8.45
5 ($CDCl_3$)	2.13	7.91[b]	7.11[a]	8.50	4.24	3.42	8.44
6 ($CDCl_3$)	2.19[c]	8.08 [4.3]	7.11 [10]	9.43	4.03	3.54	8.59
7 (CD_2Cl_2)	2.27[c]	7.91[b]	7.20 [10]	8.63	3.86	3.41	8.63
8 (CD_2Cl_2)		obscured	6.77 [10]	8.14	4.41	3.34	8.36
9 ($CDCl_3$)	0.34 [3] {70}	8.21 [4.2]	7.09 [11]	9.85 {44}	4.35	3.40	8.45 {36}
10 ($CDCl_3$)	0.44 [3] {70}	8.02[b]	7.15 [11]	9.26 {41}	4.23	3.48	8.46 {32}
11 ($CDCl_3$)		8.49[b]	7.09 [11]	10.00	4.11	3.56	8.87

[a] Phosphorus couplings could not be determined since H^5 has coincided with H^4. [b] J(P−H) could not be determined. [c] $H^{1'}$ of the η^1-allyl moiety.

Table 2. Selected ^{13}C-NMR Data for the Compounds 1−11

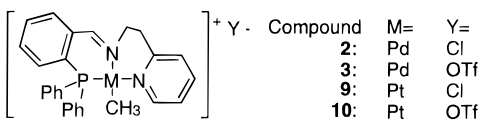
	^{13}C-NMR (ppm)							
compd (solvent)	M−R	C^i	C^1	C^2	C^6	C^7	C^8	C^9
1 ($CDCl_3$)		137.1 [10]	140.1 [17]	128.4 [4.5]	137.2 [20]	160.7 [21]	61.6	40.1
2 ($CDCl_3$)	5.0 [4]	123.8 [45]	128.0 [56]	138.6 [9]	137.5 [14]	168.2 [6.8]	56.2	39.1
3 ($CDCl_3$)	5.2 [3.8]	123.8 [45]	127.9 [56]	138.3 [9]	137.2 [14]	167.4 [6.8]	56.1	38.9
6 ($CDCl_3$)	31.9[a]	124.4 [45]	127.2 [52]	134.6 [12]	137.2 [14]	169.4 [5]	54.4	39.3
8 (CD_2Cl_2)		128.0 [43]	125.8 [34]	ca. 133	136.5 [15]	170.9 [-]	66.0	41.6
9 ($CDCl_3$)	−8.5 [6.2] {659}	122.1 [57]	126.7 [66]	137.6 [9]	137.0 [13]	165.7 [5.3]	54.8	38.3
10 ($CDCl_3$)	−8.1 [6.8] {668}	125.6 [56]	129.2 [78]	139.3 [9]	139.1 [13]	167.0 [5.3]	55.3	38.8
11 ($CDCl_3$)		120.4	125.5 [55]	139.4 [8]	137.3 [16]	159.9 [6]	58.9	37.9

[a] $C^{1'}$ of the η^1-allyl moiety.

Table 3. ^{31}P- and ^{15}N-NMR, and IR Data for the Compounds 1−11

		^{15}N-NMR		
compd (solvent)	^{31}P-NMR: δ (ppm)	δ(imine) (ppm)	δ(pyridyl) (ppm)	IR:[c] ν (cm^{-1})
1 ($CDCl_3$)	−13.6	−45.2 [3]	−68.3	1635 (m), C=N
2 ($CDCl_3$)	37.0	−123 [3]	−122 [45]	
3 ($CDCl_3$)	37.2	−121 [3]	−123 [45]	
4 ($CDCl_3$)	20.9			1686 (m), C=O
5 ($CDCl_3$)	24.9			1680 (m), C=O
6 ($CDCl_3$)	33.1	−119[a]	−119[a]	
6a ($CDCl_3$)	22.9			
7 (CD_2Cl_2)	33.3			
8 (CD_2Cl_2)	24.9			
9 ($CDCl_3$)	12.2 {4101}	−131 [3] {210}	−133 [72][b]	
10 ($CDCl_3$)	12.3 {4078}			
11 ($CDCl_3$)	30.9			

[a] Only one, broad signal has been observed. [b] No platinum satelites have been observed because of a poor S/N ratio. [c] In KBr.



Compound	M=	Y=
2:	Pd	Cl
3:	Pd	OTf
9:	Pt	Cl
10:	Pt	OTf

Figure 2. Structure of the methylpalladium and methylplatinum complexes **2**, **3**, **9**, and **10**.

are listed in Tables 4−6 and 8. The asymmetric unit contains two crystallographically independent molecules **3** and two molecules of chloroform. The molecular structure of {(PNN)Pd(CH_3)}CF_3SO_3, **3**, comprises the expected square planar arrangement of the three donor atoms of PNN and the methyl ligand around the palladium atom (Figure 3), analogous to **2**.[7]

The bond angles between Pd and two neighboring donor atoms are between 87.2(2)° [87.0(2)°] and 91.87(13)° [91.67(17)°]. Values so close to the ideal 90° must be attributed to the flexibility of the ligand even when it acts as a terdentate ligand. The ligand−palladium distances are close to those of the analogous chloride complex **2**[7] and other palladium complexes containing five-membered and six-membered phosphino−imino or

Table 4. Selected Bond Lengths (Å) for the Non-Hydrogen Atoms of the Two Independent Molecules of (PNN)methylpalladium(II) Trifluoromethanesulfonate, 3 (with Esd's between Parentheses)

	$n = 1$	$n = 2$
Pd(n)−N(n01)	2.106(5)	2.107(5)
Pd(n)−N(n02)	2.125(5)	2.120(4)
Pd(n)−C(n27)	2.084(8)	2.066(8)
Pd(n)−P(n)	2.1986(17)	2.1998(15)
P(n)−C(n14)	1.821(5)	1.818(5)
C(n08)−C(n9)	1.475(7)	1.461(7)
N(n02)−C(n08)	1.269(8)	1.276(7)
C(n14)−C(n09)	1.402(7)	1.398(7)
P(n)−C(n15)	1.816(6)	1.806(5)
P(n)−C(n21)	1.814(5)	1.803(5)

phosphino−amino chelates.[5c,13,15] The Pd−C(27) distances of 2.084(8) Å [2.066(8) Å] are relatively short compared to those of known (P−N)Pd(CH_3)(Cl) com-

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Table 5. Selected Bond Angles (deg) for the Non-Hydrogen Atoms of the Two Independent Molecules of (PNN)methylpalladium(II) Trifluoromethanesulfonate, 3 (with Esd's between Parentheses)

	$n = 1$	$n = 2$
P(n)−Pd(n)−N(n02)	91.87(13)	91.49(12)
N(n02)−Pd(n)−N(n01)	91.01(13)	91.67(17)
N(n01)−Pd(n)−C(n27)	89.8(3)	89.6(3)
C(n27)−Pd(n)−P(n)	87.2(2)	87.0(2)
P(n)−Pd(n)−N(n01)	176.51(12)	175.84(13)
N(n02)−Pd(n)−C(n27)	174.4(2)	174.2(2)
Pd(n)−P(n)−C(n14)	111.33(17)	111.63(16)
P(n)−C(n14)−C(n09)	122.0(4)	121.5(4)
C(n10)−C(n09)−C(n08)	114.5(5)	115.1(5)
C(n14)−C(n09)−C(n08)	126.3(5)	126.2(5)
C(n09)−C(n08)−N(n02)	128.5(5)	129.4(5)
C(n08)−N(n02)−Pd(n)	128.9(3)	128.4(3)
C(n07)−N(n02)−Pd(n)	115.2(4)	115.7(3)
C(n07)−N(n02)−C(n08)	115.7(5)	115.6(4)
C(n01)−N(n01)−C(n05)	118.1(5)	118.5(5)
N(n01)−C(n05)−C(n06)	116.8(5)	116.7(5)

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for the Non-Hydrogen Atoms of (*N*-(2-(Diphenylphosphino)benzylidene)-(2-(2-pyridyl)ethyl)amine)chloroacetylpalladium(II), 4 (with Esd's between Parentheses)

Bond Distances			
Pd−C(1)	2.379(4)	C(16)−C(11)	1.39(2)
Pd−P(1)	2.232(3)	C(16)−C(10)	1.48(2)
Pd−N(1)	2.19(1)	C(10)−N(1)	1.29(2)
C(1)−O(1)	1.18(2)	P(1)−C(21)	1.83(1)
C(1)−C(2)	1.51(2)	P(1)−C(31)	1.832(9)

Bond Angles			
P(1)−Pd−N(1)	90.0(3)	Pd−N(1)−C(10)	127.3(8)
P(1)−Pd−C(1)	90.8(4)	P(1)−Pd−Cl(1)	174.8(1)
C(1)−Pd−Cl(1)	84.3(4)	N(1)−Pd−C(1)	178.9(4)
N(1)−Pd−Cl(1)	95.0(3)	C(2)−C(1)−O(1)	122(1)
Pd−P(1)−C(11)	111.1(4)	N(1)−C(10)−C(16)	128(1)
Pd−C(1)−C(2)	117(1)	C(3)−N(1)−C(10)	115(1)
Pd−C(1)−O(1)	121.4(8)	P(1)−C(11)−C(16)	123.6(8)
Pd−N(1)−C(3)	117.3(8)	C(11)−C(16)−C(10)	127(1)

pounds,[5c,13] probably due to the better π-accepting capacity of the *trans*-situated imino nitrogen N(1) in the case of **3**. The double six-membered ring chelate of the PNN ligand causes a twisted conformation of the ligand around the palladium atom. The pyridyl group is rotated 43.7(2)° [42.1(3)°], the imino group C(n07)−N(n02)−C(n08)−C(n09) 22.2(5)° [21.8(5)°] with regard to the palladium coordination plane (P(n), N(n01), N(n02), and C(n27)).

Carbonylation Reactions with Methylpalladium Complexes of PNN. Carbonylation of **2** and **3** at room temperature under atmospheric CO pressure proceeds very slowly.[5d,13] However, under 25 bar of CO at 50 °C quantitative carbonylation was achieved within 2 days. When the reaction was followed with ^{31}P-NMR, using a single-crystal sapphire high-pressure NMR tube, CO insertion half-lives of 20 h have been determined for **2** and **3**.[16] Unfortunately, the methylplatinum compounds **9** and **10** failed to react with CO, even under these reaction conditions.

(15) (a) Sacco, A.; Vasopollo, G.; Nobile, C. F.; Piergiovanni, A.; Pellinghelli, M.; A.; Lanfranchi, M. *J. Organomet. Chem.* **1988**, *356*, 397 (with Pd−P = 2.290(3) Å, Pd−N = 2.073(8) Å, Pd−C = 1.991(10) Å, and P−Pd−N = 83.6(2)° (five-membered ring)). (b) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Monetti, S.; Orlandini, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1989**, *211* (with Pd−P = 2.357(4) Å, Pd−N = 2.23(2) Å, and P−Pd−N = 84.6(1)° (five-membered ring)). (c) Clark, G. R.; Palenik, G. J. *Inorg. Chem.* **1970**, *9*, 274 (with Pd−P = 2.243 Å, Pd−N = 2.148 Å, and P−Pd−N = 92.4° (six-membered ring)).

(16) (a) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. (b) For applications in palladium chemistry, see: Elsevier, C. J. *J. Mol. Catal.* **1994**, *92*, 285.

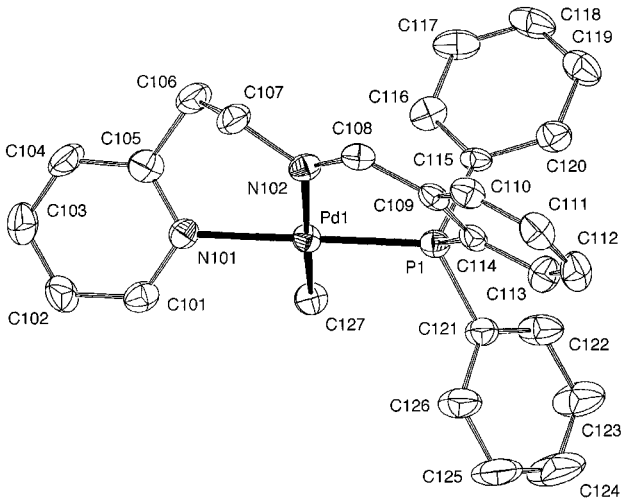
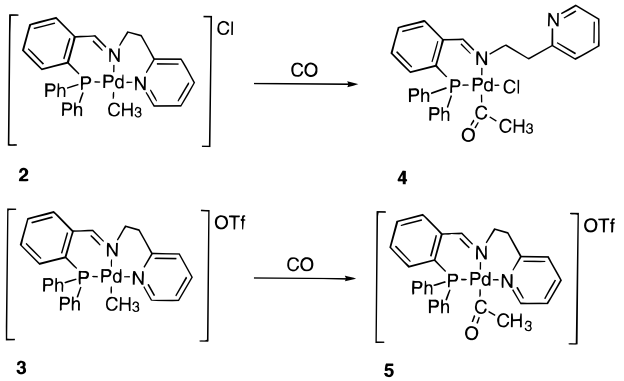


Figure 3. ORTEP (drawn at the 50% probability level) of **3**. Only one of the crystallographically independent cations is shown.

Scheme 1. Structures of Neutral (PNN)Pd(C(O)CH$_3$)(Cl), 4, and Ionic [(PNN)Pd(C(O)CH$_3$)]OTf, 5



For the carbonylation of **2**, a vanishing Pd−CH_3 resonance of **2** at 0.36 ppm and a growing Pd−C(O)-CH_3 resonance of **4** at 2.19 ppm are observed in the ^{1}H-NMR, while in the ^{31}P-NMR the resonance of **2** at 37.0 ppm vanished with simultaneous formation of the resonance of **4** at 20.9 ppm. In the IR the carbonyl resonance at 1661 cm^{-1} typical for the acetyl group has been observed for **4**. Similar results have been obtained for the carbonylation of **3** (Tables 1 and 3).

The isostructural compounds **2** and **3** and also **9** and **10** have almost identical NMR spectra. However, **4** and **5** have quite different NMR and IR spectra, most prominently in the ^{31}P-NMR spectra, suggesting that **4** and **5** have different structures. Whereas in **5** PNN coordinates in the terdentate fashion, and hence is isostructural with ionic **2** and **3**, in 4 PNN coordinates in a bidentate fashion as a phosphino−imino chelate with the chloride ligand coordinating; see Scheme 1. For example, in the ^{1}H-NMR spectra of **4** the resonances of the bridging region (−CH_2CH_2−) have two sharp triplets which are also present in the free ligand and in analogous palladium complexes with a free ethylpyridyl group[11,14] but not in **2**, **3**, **5**, **9**, and **10**. Crystals of **4** suitable for X-ray analysis were obtained, and a crystal structure determination has been carried out, *vide infra*, which confirms the proposed structure of **4**.

During the formation of **4**, weak signals belonging to the acetyl(carbonyl)palladium intermediate [(PNN)Pd-(C(O)CH$_3$)(CO)]Cl, **4a**, have been observed with reso-

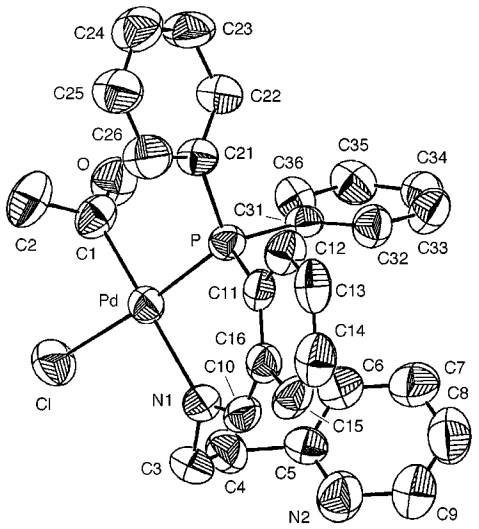


Figure 4. ORTEP (drawn at the 50% probability level) of (PNN)Pd(C(O)CH_3)(Cl), **4**.

nances at 2.15 ppm (C(O)CH_3) in the ^{1}H- and at 31.7 ppm in the ^{31}P-NMR, beside the growing signals of the acylpalladium compound **4**. Experiments performed under 7 bar of ^{13}CO failed to show the carbonyl resonance in the ^{13}C-NMR because of the low concentration of **4a**, although in the IR a carbonyl ^{13}C=O vibration at 2099 cm^{-1} and an acetyl ^{13}C=O vibration at 1686 cm^{-1} were observed. A similar intermediate [(PAN)Pd(C(O)CH_3)(CO)]Cl (PAN = 1-(diphenylphosphino)-8-(dimethylamino)naphthyl) was observed by us in the past.[13]

Acetylpalladium compounds **4** and **5** are stable as solids for weeks but dissolved in $CDCl_3$ only for a few hours. In $CDCl_3$, resonances in the ^{31}P-NMR belonging to the degradation products [(PNN)Pd(Cl)]Y (Y = Cl, OTf)[7] at 31.1 ppm become visible. For example, after the formation of the acetylpalladium compounds **4** was completed, *ca.* 15% of the dichloropalladium compound was already formed and upon standing **4** is completely converted into [(PNN)PdCl]Cl *without* the formation of Pd-black.

Crystal Structure Determination of [*N*-(2-(diphenylphosphino)benzylidene)(2-(2-pyridyl)ethyl)amine]chloroacetylpalladium(II), 4. A small crop of white crystals of **4** could be isolated after release of the CO pressure, filtration of the solution, and slow diffusion of diethyl ether into the solution. The molecular structure of (PNN)Pd(C(O)CH_3)(Cl), **4**, is presented in Figure 4. The positional data are listed in the Supporting Information, selected bond distances and bond angles are in Table 6, and the crystal and refinement data are in Table 8.

In **4** PNN is coordinating in a bidentate fashion as a P−N chelate with a pendant ethylpyridyl group. As expected, the acetyl group and the phosphorus atom, being the strongest donors,[17] are situated in a *cis* position. The palladium ligand distances Pd−P = 2.232(3) Å, Pd−N(1) = 2.19(1) Å, Pd−Cl = 2.379(4) Å, and Pd−C(1) = 2.00(1) Å of **4** are in agreement with those of similar structures found in the literature.[5c,13,15]

The short Pd−C(1) distance of 2.00(1) Å, although *ca.* 0.10 Å shorter than in analogous methylpalladium compounds, is normal for an acetylpalladium bond.[18,19] The Pd−N(1) distance of 2.19(1) Å is longer than in **2**[7] and **3**, which can be attributed to the higher *trans*-influence of the acetyl group *trans* to N(1), when compared to the lower *trans*-influence of the methyl group in **2** and **3**.[17] However, we have recently observed shorter Pd−N distances of the *trans* nitrogen for acetyl groups than for methyl groups in the case of palladium complexes with α-diimine ligands, which is in contrast with the trend observed here. For these compounds, the shorter Pd−N(*trans*) bond has been attributed to an electronic push−pull effect, in which the higher *trans* influence of the acetyl increases the back-donation of charge from the palladium to the nitrogen. In **4**, both the imino group C(3)−N(1)−C(10) and the acetyl group C(2)−C(1)−O are rotated (63.9(6) and 77.2(8)°, respectively) with respect to their ideal coplanar and perpendicular positions, while these groups make an angle of 104.9(7)° with each other. Such deformations from the ideal values may prevent suitable overlap of the relevant orbitals and diminish the push−pull effect, resulting in a longer Pd−N(1) distance for **4** than for **2** and **3**.

The bite angle of the P−N(1) chelate has the ideal value of 90.0(3)°, which must be attributed to the flexibility of the six-membered chelate ring. However, the Cl−Pd−C(1) angle of 84.3° is small whereas the Cl−Pd−N(1) angle is large. Such deviations from the ideal values are not commonly observed for palladium compounds with very flexible ligands. Its origin may be the pendant ethylpyridyl group, forcing the chloride ligand toward the acetyl group.

Allylpalladium Complexes of PNN. In order to prepare a precursor for the zerovalent PNN palladium compound **11**, we have synthesized allylpalladium complexes of PNN, since allylpalladium complexes can be reduced to zerovalent palladium complexes by soft carbanions or amines.[3,4] When PNN is reacted with 0.5 equiv of $[(C_3H_5)Pd(\mu\text{-}Cl)]_2$[20] in chloroform at room temperature, a 1:1 mixture of ionic [(PNN)Pd(η^1-C_3H_5)]Cl, **6**, and neutral (PNN)Pd(η^3-C_3H_5)(Cl), **6a**, are initially formed, as concluded from the two sets of resonances present in the ^{1}H- and ^{31}P-NMR spectra. Heating the mixture of **6** and **6a** in chloroform at 65 °C for 2 h resulted in **6** exclusively.

The terdentate coordination fashion of the PNN ligand in **6** was easily determined, via a procedure analogous to the one used for the methylpalladium compounds **2** and **3**; *vide supra*. In addition, the η^1-allyl moiety shows the characteristic resonances of 2.19 (d, 2H, H$^{1'}$), 4.50 (d, H$^{3'}$), 4.62 (d, H$^{3'}$), and 5.52 ppm (m, H$^{2'}$) in the ^{1}H-NMR and of 31.9 (C$^{1'}$) and 110.7 ppm (C$^{3'}$) in the ^{13}C-NMR.[4,21] The ^{13}C-NMR resonances are slightly broadened, while C$^{2'}$ is concealed by resonances of **1**. In the ^{31}P-NMR a sharp resonance at 33.1 ppm is observed, a value typical for compounds of the type (P−N)Pd(alkyl)(Y) and close to **2** and **3**.

(17) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

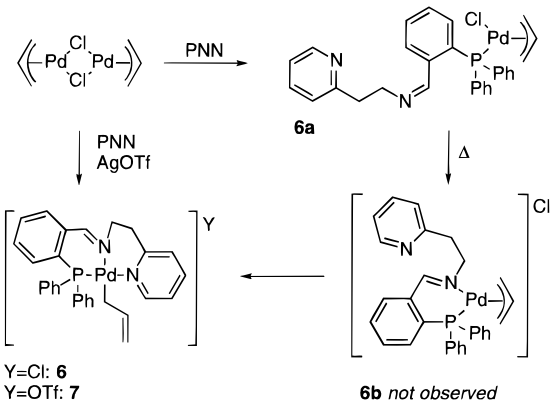
(18) Rülke, R. E.; Delis, J. G. P.; Groot, A. M.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K.; Goubitz, K.; Schenk, H. *J. Organomet. Chem.* **1996**, *508*, 109.

(19) (a) Bardi, R.; del Pra, A.; Piazzesi, A. M.; Toniolo, L. *Inorg. Chim. Acta* **1979**, *35*, L345. (b) Bardi, R.; Piazzesi, A. M.; Cavinato, G.; Cavoli, P.; Toniolo, L. *J. Organomet. Chem.* **1982**, *224*, 407. (c) Bardi, R.; Piazzesi, A. M.; del Pra, A.; Cavinato, G.; Toniolo, L. *Inorg. Chim. Acta* **1985**, *102*, 99. (d) Markies, B. A.; Wijkens, P.; Boersma, J.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 133.

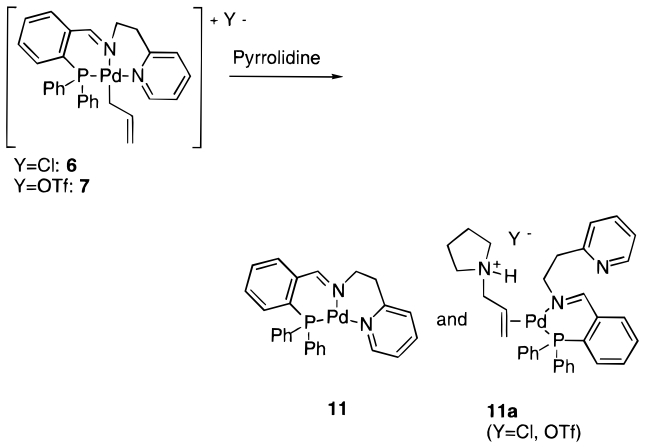
(20) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

(21) Numata, S.; Okawara, R.; Kurosawa, H. *Inorg. Chem.* **1977**, *16*, 1737.

Scheme 2. Formation of (η^1-Allyl)palladium Compounds 6 and 7 from the Allylchloropalladium Dimer



Scheme 3. Formation of Zerovalent 11 and 11a by Reaction of 6 with Pyrrolidine



6a shows strongly broadened resonances in both ^{1}H- and ^{31}P-NMR at room temperature. When the mixture of **6** and **6a** is cooled to 223 K, these signals sharpen up. Although in the ^{1}H-NMR some resonances of **6a** are concealed by signals belonging to **6**, the presence of an η^3-allyl group in **6a** was easily determined. The proposed structure is confirmed by the resonance at 22.9 ppm in the ^{31}P-NMR spectrum, a typical value for complexes of the type $(PR_3)Pd(\eta^3\text{-allyl})(Cl)$ (R═aryl).[22] In **6a**, PPN is coordinating in a monodentate fashion and not as a P−N chelate (**6b** in Scheme 2), since **6a** is not observed when the reaction is carried out in the presence of AgOTf. In this experiment, [(PNN)Pd(η^1-allyl)]OTf, **7**, is formed instantaneously, without a sign of other isomeric compounds (Scheme 2).

When PNN is added to *in situ* formed (pentamethylallyl)palladium chloro dimer[1a,23] in dichloromethane in the presence of silver triflate, [(PNN)Pd(η^3-C_8H_{15})]OTf, **8**, is readily formed as concluded from the ^{1}H-, ^{13}C-, and ^{31}P-NMR data. The allylic carbons and the five methyl substituents have the chemical shifts and the phosphorus couplings characteristic of complexes of the type [(P−N)Pd(allyl)]Y.[24] Unfortunately, additional characterization of **8** by elemental analysis was not possible since it is not very well possible to synthesize [(η^3-C_8H_{15})Pd(Cl)]$_2$ quantitatively from (COD)Pd(CH_3)(Cl): due to the very slow insertion of TMA,[1a,23] the reaction cannot be completed in order to prevent degradation reactions. A small amount of the starting material therefore cannot be avoided. Thus, after reaction with PNN, **8** always contains a certain amount of simultaneously generated **2**, which, however, does not seem to affect the structural integrety of **8** nor complicates its NMR characterization.

Zerovalent Palladium Complexes of PNN. Synthesis of the zerovalent compound (PNN)Pd, **11**, which is stabilized only by PNN without the aid of additional stabilizing ligands such as alkenes, was achieved by *in situ* reduction of the allylpalladium complexes **6** or **7** with pyrrolidine, as outlined in Scheme 3.

In doing so, a mixture of (PNN)Pd^0, **11**, was obtained as concluded from the spectroscopic data (see Scheme 3), along with a small amount of a second product, **11a**, which we tentatively formulate as the η^2-*N*-allylpyrrolidinium chloride stabilized zerovalent palladium compound {(PNN)Pd^0[η^2-H_2C═C(H)CH_2N(H)C_4H_8]}Cl. Dissolved in chloroform, this mixture of **11** and **11a** proved to be stable only for a few hours. Yet, we were able to characterize **11** by ^{1}H-, ^{31}P-, and ^{13}C-NMR spectroscopy, but due to the small amount present, **11a** could not be characterized. In the ^{31}P-NMR spectrum, resonances at 30.9 ppm for **11** and at 35.1 ppm for **11a** have been found. The first resonance was found before when synthesizing **11** from $Pd_2(DBA)_4$ (DBA = bis(benzylidene)acetone), although we were not able to isolate the zerovalent compound from this reaction mixture. Column chromatography of the mixture of **11** and **11a** resulted in almost pure **11** with traces of **6**. Zerovalent **11** is soluble in dichloromethane and chloroform and only moderately soluble in toluene and benzene. As a solid, **11** is stable for a few weeks.

Compound **11** was further characterized by mass spectroscopy using the Europium plasma desorption ionization technique. Besides small impurities at *m/z* 536.3 and *m/z* 541 belonging to [(PNN)Pd(Cl)]$^+$ and [(PNN)Pd(C_3H_5)]$^+$, **6**, respectively, a signal at *m/z* 500.7 is present which is clearly due to **11**. Europium plasma desorption is a very soft ionization technique, and the presence of a stabilizing molecule (solvent, alkene) should have been detected.

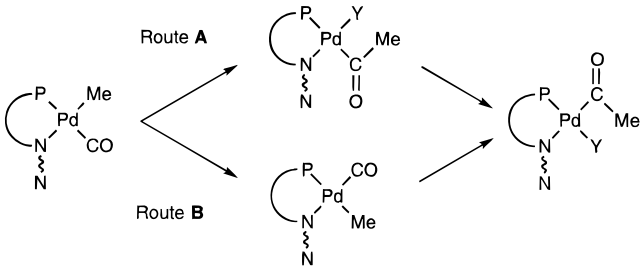
C−C Bond Formations Catalyzed by Palladium Complexes of PNN. In order to test the catalytic activity of palladium complexes of PNN, some allylic alkylation reactions have been performed starting with **6** as the precursor.[3,4] The results are listed in Table 7. The catalytic reactions were carried out on a 1 mmol (allylic substrate) scale in THF at room temperature with 1 mol % of **6** (entries 1−3). In the case of 3-acetoxy-1,3-diphenylpropene (entry 4 in Table 7), a typical substrate for studies on enantioselective allylic alkylation reactions, 3 mol % of the catalyst precursor **6** and 3 mmol of sodium diethylmalonate were used in order to compare the performance of PNN with ligands in the literature.[4] Samples were taken at 0.5, 1, 4, and 24 h of reaction time, although most reactions were completed within 0.5 h. These rates are much higher than those reported for enantioselective allylic alkylations catalyzed by palladium complexes with amino−phosphine, sulfido−phosphine, and amino−sulfide ligands.[4,6] Furthermore, no significant formation of Pd-black was

(22) (a) Cotton, F. A.; Faller, J. W.; Musco, A. *Inorg. Chem.* **1967**, *6*, 179. (b) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839. (c) Kurosawa, H.; Kajimaru, H.; Ogoshi, S.; Yoneda, H.; Miki, K.; Kasai, N.; Murai, S.; Ikeda, I. *J. Am. Chem. Soc.* **1992**, *114*, 8417.

(23) Ankersmit, H. A.; Veldman, N.; Spek, A. L.; Eriksen, K.; Goubitz, K.; Vrieze, K.; van Koten, G. *Inorg. Chim. Acta*, in press.

(24) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620.

Scheme 4. CO Insertion into Methylpalladium Complexes of PNN



observed during and after the catalytic reaction, and no change in the product distribution in the case of 3-chlorobutene (entry 2 in Table 7) due to palladium-catalyzed isomerization reactions was observed within 24 h.

Discussion

The structural characterization of the complexes **2**, **3**, **5**, **6**, **9**, and **10** and also of [(PNN)Pd(Cl)]Cl and of [(PNN)Pd(solvent)[OTf_2, which were published recently,[7] shows that **1** has a very strong tendency to coordinate in a terdentate fashion. Such a strong tendency has not been observed for ligands with a P−N−N donor set unless steric constraints are imposing terdentate coordination, such as palladium complexes of terpyridine.[1e,11,14,25]

The strong tendency of **1** to maintain coordination in the terdentate fashion is particularly remarkable in allylpalladium compound **6**. Whereas the isomer in which PNN coordinates in a monodentate fashion **6a** has been observed for a few hours, no sign of the expected P−N-coordinating isomer **6b** has been observed; see Scheme 2. Only when η^1-coordination of the allyl moiety is unfavorable, as in (pentamethylallyl)-palladium compound **8**, is a P−N chelate observed.

The reason for the surprising bidentate coordination fashion in the acetylpalladium complex **4** is not well understood, although a similar behavior was observed recently for palladium complexes containing the trinitrogen ligand 2-((2-(2′-methylidene-6′-methylpyridyl)-imino)ethyl)pyridine.[14] Apparently, the Pd−Cl bond is stronger in **4** than the one in **2**. Perhaps the Coulombic interaction Pd^+Cl^- is relatively strong in **4** (and in acetylpalladium complexes in general) due to a higher positive charge on Pd^+, caused by the more electronegative acetyl group.

The low reactivity of the methylpalladium compounds **2**, **3**, **9**, and **10** toward insertion of CO is not unexpected. CO insertion half-lives between 0.5 and 3 h at 25 bar of CO and at room temperature have been found for complexes of the type (P−N)Pd(CH_3)(Y) (P−N = 1-(dimethylamino)-8-(diphenylphosphino)naphthalene,[13] 1-(dimethylamino)-3-(diphenylphophino)propane, and[13] cyclopentadienyl(7-(dimethylamino)-1-(diphenylphosphino)-4,5,6,7-tetrahydroindenyl)iron;[5d] Y = Cl, OTf). In order to insert CO into the Pd−C bond of a methylpalladium compound containing a P−N ligand, the reaction has to pass either via a large kinetic barrier in the migration step (route A in Scheme 4) or via a prearrangement equilibrium reaction with an unfavorable equilibrium constant (route B in Scheme 4). This is not the case for complexes containing symmetric bidentate ligands for which much shorter CO insertion half-lives (minutes) have been found.[1c,14,18]

The observation that **2** and **3** have CO insertion half-lives even longer ($t_{1/2}$ = 20 h) than methylpalladium complexes of the above mentioned bidentate P−N ligands may have two origins. First, the Pd−N(pyridyl) bond in **2** and **3** may be stronger than the Pd−Cl bond in complexes (P−N)Pd(CH_3)(Cl), due to π-back-donation. Second, the methyl group in **2** and **3** is stabilized by the π-accepting imino nitrogen in the *trans* position. This stabilizing push−pull effect is not present in the three above mentioned compounds, since these have amine nitrogens, which have no relevant π-accepting properties.

Although the allylic alkylation reactions catalyzed by **6** have not been studied in full detail, the results show that catalytic system performs very well and with very high rates compared with other palladium complexes containing P−N [4] and N−S [6] ligands used in (enantioselective) allylic alkylation reactions. It is not very probable that this remarkable performance can be attributed to the interaction of the pendant ethylpyridyl group with sodium diethyl malonate, similar to P−P−N−OH ligands reported by Hayashi. Palladium complexes with such bifunctional ligand systems did not show a significant accelerating effect and only enhance the stereoselectivity of the reaction.[4a−f] Alternatively, the observed high rates might be cause by the presence of the imino nitrogen in the P−N chelate of PNN. In this scenario, the electrophilicity of the η^3-allyl ligand—providing the reactive species contains a η^3-allyl group—is increased by the π-accepting properties of the imino group, thus increasing its succeptibility for nucleophilic attack. Indeed, Helmchen and co-workers also observed a very fast reaction for the similar ligand 2-[2-(diphenylphosphino)phenyl)]-4-(2-propyl)-4,5-dihydrooxazole, but surprisingly, this rate enhancing effect was not observed for analogous phosphino−oxazole ligands.[4k] As yet, the exact mechanistic implications of both the ethylpyridyl group and the presence of an imino nitrogen remain unclear.

Conclusions

We have shown that the potentially terdentate ligand **1** can coordinate to palladium in mono-, bi-, and terdentate coordination fashions. **1** stabilizes a series of organopalladium(II) and -platinum(II) complexes, with a strong tendency to terdentate coordination. Bidentate coordination is preferred in the acetylchloropalladium complex **4** and in (pentamethylallyl)palladium compound **8**. Interestingly, the Pd(0) compound **11** meets the stability we aimed for. It is stable in the solid state for weeks as well as in solution in benzene or toluene for hours. The stability of both the zerovalent and divalent palladium complexes and the proven multifunctional coordination behavior of **1** now open a way to catalytic applications through a Pd(0)−Pd(II) cycle without additional stabilizing ligands. Indeed, our preliminary results of allylic alkylation reactions show that palladium complexes of PNN are very active.

Experimental Section

Materials and Apparatus. All manipulations were carried out in an atmosphere of purified, dry nitrogen by using

(25) Rülke, R. E.; Han, I. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F.; Zoutberg, M. C.; Wang, Y.-F.; Stam, C. H. *Inorg. Chim. Acta* **1990**, *169*, 5.

standard Schlenk techniques. Solvents were dried and stored under nitrogen, with acetonitrile also stored over 3 Å molecular sieves. Starting compounds (COD)Pd(CH_3)(Cl),[11] (COD)Pt(CH_3)(Cl),[13,26] and [(C_3H_5)Pd(Cl)]$_2$[20] have been synthesized according to the literature. [(η^3-C_8H_{15})Pd(Cl)]$_2$ was synthesized from (COD)Pd(CH_3)(Cl) by insertion of tetramethylallene into the Pd−C bond.[23] Other starting chemicals are commercially available and were used without further purification except where mentioned explicitly. Carbon monoxide (2.5 grade) was obtained from HoekLoos and ^{13}CO from Campro. Silver trifluoromethanesulfonate was stored under nitrogen and in the dark.

Elemental analyses have been carried out by Dornis and Kolbe Mikroanalytisches Laboratorium, Mühlheim a.d. Ruhr, Germany, and by Mikroanalytisches Laboratorium (J. Theiner), Universität Wien, Wien, Austria. ^{1}H-, ^{13}C-{^{1}H}-, ^{31}P-{^{1}H}-, and ^{15}N-INEPT-NMR spectra were recorded on a Bruker AMX 300 spectrometer, and the HP-NMR experiments, on a Bruker AC 100 spectrometer. Mass spectra were acquired using a Bio-Ion desorption time-of-flight mass spectrometer with a 15 cm flight tube (ABI Sweden, Uppsala, Sweden). The acceleration voltage was 18 kV. Samples were deposited from an acetonitrile solution of the complex on a nitrocellulose-coated target. GC-FID spectra were recorded on a Hewlett-Packard HP5790 gas chromatograph, the GC-MS spectra on a Hewlett-Packard HP5790 gas chromatograph equipped with a HP 5971A mass selective detector in the EI mode, and infrared spectra on a BioRad FTS-7 spectrophotometer.

NMR spectra have been obtained from $CDCl_3$ solutions, unless noted otherwise. Chemical shifts are relative to TMS (^{1}H- and ^{13}C-{^{1}H}-NMR), H_3PO_4 (^{31}P-{^{1}H}-NMR) and CH_3NO_2 (^{15}N-{^{1}H}-NMR).[27] Coupling constants J(H−H) are listed between J(P−H) and J(P−C) between parentheses, and J(Pt−H) and J(Pt−C) between braces. INEPT measurements were performed using the standard INEPT pulse sequence[27] with an evolution time τ set at 22.7 ms.

In order to save space, the homonuclear coupling constants of the ligand are not listed individually. The values for compounds **1**−**11** are as follows: H^2 dd (7.7, 1.3), H^3 t (7.7), H^4 dd (7.7, 1.0), H^5 d (7.7), H^7 s, H^8 t (7.4), H^9 t (7.4), H^{11} d (7.7), H^{12} dt (7.7, 1.2), H^{13} dd (7.7, 5.5), and H^{14} d (5.5). H^o, H^m, and H^p generally coincide and often conceal the resonances of H^3, H^5, H^{11}, and H^{13}. Numbering of the allyl moiety in **6** and **7**: PdC$^{1'}$C$^{2'}$=C$^{3'}$; in **6a** and **8**: $^{1'}$ = *trans* P, $^{2'}$ = central, $^{3'}$ = *cis* P, ^{a} = *anti*, ^{s} = *syn*.

Synthesis of (N-(2-(Diphenylphosphino)benzylidene)-(2-(2-pyridyl)ethyl)amine), 1. To a solution of 1.58 g (5.45 mmol) of 2-(diphenylphosphino)benzaldehyde[28] in 50 mL of benzene was added 699.2 mg (5.72 mmol) of 2-(2-aminoethyl)-pyridine, and the solution was refluxed for 1 h. The solution was dried on $MgSO_4$ and the solvent removed in vacuo to yield a pale yellow oil. The oil was dissolved in hot hexane and subsequently cooled in an ice bath. An orange precipitate is formed slowly. After decanting of the hexane and removal of the volatiles in vacuo, **1** was obtained purely.

1: Orange microcrystals; yield 81%, mp 75 °C (from hexane). Anal. Found: C, 78.9; H, 6.0; N, 7.2; P, 7.7. Calcd: C, 79.2; H, 5.9; N, 7.1; P, 7.9. ^{1}H-NMR ($CDCl_3$): 2.97 (H^9), 3.89 (H^8), 6.86 ([4.7], H^4), 7.03 (H^5), 7.05 (H^{13}), 7.30 (11H: H^o + H^m + H^p + H^{11}), 7.38 (H^3), 7.50 (H^{12}), 7.93 ([3.9], H^2), 8.49 (H^{14}), 8.85 ([4.7], H^7). ^{13}C-NMR ($CDCl_3$): 40.1 (C^9), 61.6 (C^8), 121.7 (C^{13}), 124.1 (C^5), 128.4 ([4.5], C^2), 129.1 ([7.5], C^m), 129.3 (C^p), 129.4 (C^{11}), 130.8 (C^3), 134.0 (C^4), 134.7 ([20], C^o), 136.7 (C^{12}), 137.1 ([10], C^i), 137.2 ([20], C^6), 140.1 ([17], C^1), 149.81 (C^{14}), 160.3 (C^{10}), 160.7 ([21], C^7). ^{31}P-NMR ($CDCl_3$): −13.6. ^{15}N-NMR ($CDCl_3$): −45 ([3], imine N), −68 (pyridyl N).

Synthesis of Methylpalladium and Methylplatinum Compounds of PNN. The syntheses of the methylpalladium complexes **2**, **3**, **9**, and **10** have been carried out according to published methods, starting with (COD)Pd(CH_3)(Cl)[11] or (COD)-Pt(CH_3)(Cl).[13,26]

2: Colorless crystals; yield 78%. ^{1}H-NMR ($CDCl_3$): 0.36 ([2.7], CH_3), 3.48 (H^9), 4.22 (H^8), 7.07 ([11], H^5), 7.48 (13H, H^o, H^m, H^p, H^4, H^{11}, and H^{13}), 7.66 (H^3), 7.88 (H^{12}), 8.15 ([4.3], H^2), 8.41 (H^{14}), 9.47 (H^7). ^{13}C-NMR ($CDCl_3$): 5.0 [4.0], Pd−Me, 39.1 (C^9), 56.2 (C^8), 123.8 ([45], C^i), 124.3 ([<1], C^{13}), 125.6 ([2.3], C^5), 128.0 ([56], C^1), 129.8 ([12], C^m), 132.4 ([2.3], C^p), 133.1 ([<1], C^{11}), 133.3 ([7.5], C^3), 134.4 ([12], C^o), 134.4 (C^4), 137.5 ([14], C^6), 138.6 ([9], C^2), 140.4 (C^{12}), 150.4 (C^{14}), 160.9 (C^{10}), 168.2 ([6.8], C^7). ^{31}P-NMR ($CDCl_3$): 37.0. ^{15}N-NMR ($CDCl_3$): −122 ([45], pyridyl N), −123 ([3], imine N). Anal. Found for [(PNN)Pd(CH_3)]Cl·H_2O: C, 57.06; H, 5.23; N, 4.99. Calcd: C, 56.96; H, 4.96; N, 4.92.

3: Colorless crystals; yield 70%. ^{1}H-NMR ($CDCl_3$): 0.35 ([2.7], CH_3), 3.49 (H^9), 4.00 (H^8), 7.16 ([10], H^5), 7.50 (13H, H^o, H^m, H^p, H^4, H^{11}, and H^{13}), 7.68 (H^3), 7.90 ([4.3], H^2), 7.96 (H^{12}), 8.42 (H^{14}), 8.80 (H^7). ^{13}C-NMR ($CDCl_3$): 5.2 ([3.8], Pd−Me), 38.9 (C^9), 56.1 (C^8), 123.8 ([45], C^i), 124.6 ([<1], C^{13}), 125.7 ([2.3], C^5), 127.9 ([56], C^1), 129.8 ([11], C^m), 132.5 ([2.3], C^p), 133.2 ([<1], C^{11}), 133.5 ([7.5], C^3), 134.4 ([12], C^o), 134.5 (C^4), 137.2 ([14], C^6), 138.3 ([9.0], C^2), 140.7 (C^{12}), 150.5 (C^{14}), 160.9 (C^{10}), 167.4 ([6.8], C^7). ^{31}P-NMR ($CDCl_3$): 37.2. ^{15}N-NMR ($CDCl_3$): −121 ([3], imine N), −123 ([45], pyridyl N).

9: Pale yellow microcrystals; yield 73%. ^{1}H-NMR ($CDCl_3$): 0.34 ([3.0], {70}, CH_3), 3.40 (H^9), 4.35 (H^8), 7.09 ([11], H^5), 7.46 (13H: H^o, H^p, H^m, H^{11}, H^{13}, H^4), 7.66 (H^3), 8.00 (H^{12}), 8.21 ([4.2], H^2), 8.45 ({36}, H^{14}), 9.85 ({44}, H^7). ^{13}C-NMR ($CDCl_3$): −8.5 ([6.2], {659}, Pt−Me), 38.3 (C^9), 54.8 (C^8), 122.1 ([57], C^i), 124.2 ({36}, C^{13}), 125.1 ([<1], C5), 126.7 ([66], {43}, C^1), 128.8 ([11], C^m), 131.8 ([2.3], C^p), 132.5 ([<1], C^4), 132.7 ([8.0], C^3), 132.9 ([<1], C^{11}), 133.7 ([11], {45}, C^o), 137.0 ([13], C^6), 137.6 ([9.1], C^2), 141.0 (C^{12}), 149.9 (C^{14}), 160.0 (C^{10}), 165.7 ([5.3], C^7). ^{31}P-NMR ($CDCl_3$): 12.2 {4101}. ^{15}N-NMR ($CDCl_3$): −131.5 ([3], {210}, imine N), −132.6 ([72], pyridyl N, platinum satellites not visible due to the low signal to noise ratio). Anal. Found for [(PNN)Pt(CH_3)[Cl·H_2O: C, 52.16; H, 4.65; N, 4.24. Calcd: C, 54.40; H, 4.57; N, 4.23.

10: Pale yellow microcrystals; yield 86%. ^{1}H-NMR ($CDCl_3$): 0.44 ([3.0] {70}, Pt−Me), 3.48 (H^9), 4.23 (H^8), 7.15 ([11], H^5), 7.47 (13H, H^o, H^p, H^m, H^111, H^{13}, and H^5), 7.65 (H^3), 8.02 (m, H^2 and H^{12}), 8.46 ({32}, H^{14}), 9.26 ({41}, H^7). ^{13}C-NMR ($CDCl_3$): −8.1 ([6.8], {668}, Pt−Me), 38.8 (C^9), 55.3 (C^8), 125.6 ([56], C^i), 127.2 [<1], C^{13}), 127.7 ([4.0], C^5), 129.2 ([78], {43}, C^1), 131.4 ([11], C^m), 134.4 ([2.3], C^p), 135.1 (C^4), 136.0 ([8.0], C^3), 136.2 (C^{11}), 136.4 ([12], C^o), 139.1 ([13], C^6), 139.3 ([9.0], C^2), 143.0 C^{12}), 152.7 (C^{14}), 162.2 (C^{10}), 167.0 ([5.3], C^7). ^{31}P-NMR ($CDCl_3$): 12.3 {4078}.

Synthesis of (PNN)Pd(C_3H_5)]Cl, 6. To a stirred solution of 9.8 mg (0.054 mmol of "Pd") of [(C_3H_5)Pd(μ-Cl)]$_2$[20] in 5 mL of chloroform was added 21.1 mg (0.054 mmol, 1.0 equiv) of **1**. In order to obtain **6** purely, the solution was refluxed for 2 h and the solvent removed *in vacuo* to give pure **6**. Similarly, **6** can also be prepared in dichloromethane.

6: Yellow microcrystals. ^{1}H-NMR ($CDCl_3$, 223 K): 2.19 (dd, $H^{1'}$), 3.54 (H^9), 4.03 (H^8), 4.50 ($H^{3'}$), 4.62 (d, $H^{3'}$), 5.52 (ddt, $H^{2'}$), 7.11 ([10], H^5), 7.40 (m, 14H, H^o, H^m, H^p, H^3, H^4, H^{11}, H^{13}), 7.94 (H^{12}), 8.08 ([4.3], H^2), 8.59 (H^{14}), 9.43 (H^7). ^{13}C-NMR ($CDCl_3$): 31.9 ($C^{1'}$), 39.3 (C^9), 54.4 (C^8), 110.7 ($C^{3'}$), 124.4 ([45], C^i), 124.8 (C^{13}), 126.1 ([2], C^5), 127.2 ([52], C^1), 130.1 ([11], C^m), 132.7 ([2], C^p), 133.1 ([2], C^{11}), 133.4 ([8], C^3), 133.6 ([2], C^4), 134.6 ([12], C^o), 137.2 ([14], C^6), 138.5 ([9], C^2), 140.8 (C^{12}), 149.9 (C^{14}), 159.8 (C^{10}), 169.4 ([5], C^7). ^{31}P-NMR ($CDCl_3$, 223K): 33.1. ^{15}N-NMR ($CDCl_3$, 223 K): −119 (broad, imine

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(27) Nitromethane is preferred by us as internal standard instead of the recommended standard liquid, anhydrous ammonia, because of the relative temperature independence of the first and its widespread use in articles about organic and organometallic compounds. Conversion to the recommended ammonia standard by adding 380 ppm to the nitromethane standard, for this reason, only gives a rough indication. For theoretical aspects of ^{15}N-INEPT-NMR spectroscopy, see: Benn, R.; Günther, H. *Angew. Chem.* **1983**, *95*, 381.

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Table 7. Results from Selected Allylic Alkylation Reactions Catalyzed by 6

entry	electrophile	time (h)	yield (%)	product (ratio)
1	$ClCH_2CH{=}CH_2$	0.5	>99[a]	$H_2C{=}CHCH_2CH(COOEt)_2$
2	$ClCH(CH_3)CH{=}CH_2$	0.5	50[a]	
		1	86[a]	
		24	>99[a]	$H_2C{=}CHCH(CH_3)CH(COOEt)_2$ (38%) *E*-$H_3CCH{=}CHCH_2CH(COOEt)_2$ (54%) *Z*-$H_3CCH{=}CHCH_2CH(COOEt)_2$ (8%)
3	$BrCH_2CH{=}CHPh$	0.5	>99[a]	*E*-$PhCH{=}CHCH_2CH(COOEt)_2$
4	$AcOCH(Ph)CH{=}CH(Ph)$	1	>99[b]	*E*-$PhCH{=}CHCH(Ph)CH(COOEt)_2$

[a] According to GC. [b] According to ^{1}H-NMR.

N and pyridyl N). Anal. Found for $[(PNN)Pd(C_3H_5)]Cl{\cdot}CH_2Cl_2$: C, 48.52; H, 4.22; N, 4.18. Calcd: C, 49.28; H, 4.29; N, 4.26.

6a: ^{1}H-NMR ($CDCl_3$, 223 K): 2.73 (d, (11.7), $H^{3'a}$), 2.89 (t, [12.9], $H^{1'a}$), 3.17 (H^8), 3.94 (dd, [7], [15], $H^{3's}$), 4.18 (dd, [9], [12], $H^{1's}$), 4.87 (H^9), 6.06 (m, $H^{2'}$), 8.76 (H^{14}), 8.90 (H^7), other signals concealed by signals of **6**. ^{31}P-NMR ($CDCl_3$, 223 K): 22.9.

Synthesis of $[(PNN)Pd(C_3H_5)]OTf$, 7, and $(PNN)Pd(C_8H_{15})]OTf$, 8. To a stirred solution of 15.3 mg (0.084 mmol of "Pd") of $[(C_3H_5)Pd(\mu\text{-}Cl)]_2$[20] in 3.0 mL of dichloromethane were added 33.0 mg (0.084 mmol, 1.0 equiv) of **1** and 16.3 mg (0.084 mmol, 1.0 equiv) AgOTf. The instantaneously formed white precipitate was filtered off and the solvent removed *in vacuo*, yielding pure **7**. The pentamethylallyl analogue **8** was obtained via the same procedure, starting from $[(C_8H_{15})Pd(\mu\text{-}Cl)]_2$,[23] and was used for NMR characterization without isolation.

7: Yellow microcrystals. ^{1}H-NMR (CD_2Cl_2, 223 K): 2.27 (t, $H^{1'}$), 3.41 (t, H^9), 3.86 (H^8), 4.52 (d, $H^{3'}$), 4.65 (d, $H^{3'}$), 5.57 (dd, $H^{2'}$), 7.20 (H^5), 7.40−7.65 (14H, H^o, H^m, H^p, H^3, H^4, H^{11}, H^{13}), 7.91 (H^{12}), 7.91 (H^2), 8.37 (H^7), 8.63 (H^{14}). ^{31}P-NMR (CD_2Cl_2, 223 K): 33.3.

8: Yellow microcrystals. ^{1}H-NMR (CD_2Cl_2, 293 K): 0.99 ([10], $H^{1'a}$), 1.23 ([6], $H^{3'a}$), 1.91 ([5], $H^{3's}$), 1.94 ([9], $H^{1's}$), 2.06 ($H^{2'}$), 3.34 (H^9), 4.41 (H^8), 6.11 (H^{11}), 6.77 ([10], H^5), 7.50 (15H, H^o, H^m, H^p, H^2, H^3, H^4, H^{12} and H^{13}), 8.14 (H^7), 8.36 (H^{14}). ^{13}C-NMR ($CDCl_3$): 20.2 ($Me^{3'a}$), 26.7 ($Me^{2'}$), 27.0 ([5] $Me^{1's}$), 28.3 ([2] $Me^{1'a}$), 29.1 ($Me^{3's}$), 41.6 (C^9), 66.0 (C^8), 76.4 ([7] $C^{3'}$), 109.1 ([26]), 121.6 ([5] $C^{2'}$), 125.8 (C^{13}), 125.8 ([34] C^1), 126.1 (C^5), 128.0 ([43] C^i), 128.4 ([43] $C^{1'}$), 129.9 ([9] C^m), 130.6 ([10] C^o), 132−135 (complex pattern of C^{11}, C^2, C^3, C^4, and C^p signals), 136.5 ([15] C^6), 139.6 (C^{12}), 153.7 (C^{14}), 157.0 (C^{10}), 170.9 (C^7). ^{31}P-NMR ($CDCl_3$, 223 K): 24.9.

Synthesis of (PNN)Pd, 11. To an NMR tube containing a solution of 14.2 mg (0.025 mmol) of **6**, or an equimolar amount of **7**, in 0.5 mL of $CDCl_3$ at room temperature was added 2.0 mL (1.7 mg, 1.0 equiv of pyrrolidine, and the reaction was monitored with ^{1}H- and ^{31}P-NMR. After 30 min, the formed mixture of **11** and **11a** was separated on a small column of activated silica with ethyl acetate as the eluent.

11: Orange microcrystals. ^{1}H-NMR ($CDCl_3$): 3.56 (H^9), 4.11 (H^8), 7.09 ([11], H^5), 7.50 (H, H^o, H^m, H^3, H^4, H^{11}, H^{12} and H^{13}), 7.90 (H^{12}), 8.49 ([3.9], H^2), 8.87 (H^{14}), 10.00 (H^7). ^{13}C-NMR ($CDCl_3$): 37.9 (C^9), 58.9 (C^8), 120.4 (weak, probably C^i), 124.2 (C^{13}), 125.5 ([55], C^1), 125.6 (C^5), 129.8 ([12], C^m), 133.3 (C^p), 133.6−134.1 (coinciding signals from C^3, C^4 and C^{11}), 134.5 ([11], C^o), 137.3 [16], C^6), 139.4 ([8], C^2), 140.9 (C^{12}), 151.8 (C^{14}), 158.8 (C^{10}), 159.9 ([6], C^7). ^{31}P-NMR ($CDCl_3$): 30.9. MS (plasma desorption): *m*/*z* 500.7.

Carbonylation Reactions. A 10 mm o.d. single-crystal sapphire high-pressure NMR tube[16] was filled with 30 mg of **2** or **3** in 1.5 mL of $CDCl_3$ and pressurized with CO to 25 bar. The carbonylation was then followed with ^{1}H- and ^{31}P-NMR at 323 K for 72 h. Experiments with ^{13}CO have been performed in the same fashion, except that the HP-NMR tuve was pressurized to 7 bar of ^{13}CO.

Note: Although the above described high-pressure tubes have been used safely in our institute for years in the pressure range 1−50 bar, it is absolutely recommended to avoid direct exposure to a charged high-pressure tube while preparing, transporting, or immersing it into the NMR probe. To this end we have conveniently employed an explosion-proof tube holder. Details may be obtained from one of the authors (C.J.E.).[16b]

4: White crystals. ^{1}H-NMR ($CDCl_3$): 2.19 ([1], $C(O)CH_3$), 3.38 (H^9), 4.25 (H^8), 7.14 (m, 2H, H^4 and H^5), 7.50 (15H, H^o, H^m, H^p, H^2, H^3, H^{11}, H^{12}, and H^{13}), 8.45 (H^{14}), 8.51 (H^7). ^{31}P-NMR ($CDCl_3$, 223 K): 20.9.

5: Off-white microcrystals. ^{1}H-NMR ($CDCl_3$): 2.13 ($C(O)CH_3$), 3.42 (H^9), 4.24 (H^8), 7.11 (m, 2H, H^4 and H^5), 7.50 (m, 14H, H^o, H^m, H^p, H^3, H^{11}, H^{12}, and H^{13}), 7.91 (H^2), 8.44 (H^{14}), 8.50 (H^7). ^{31}P-NMR ($CDCl_3$, 223 K): 24.9.

Palladium-Catalyzed Allylic Alkylation Reaction. To a stirred solution of 100 mg (1.0 mmol) of sodium diethyl malonate in 3.9 mL of THF at room temperature were subsequently added a solution of 5.8 mg (0.01 mmol) of **6** in 0.9 mL of THF, 10 mL of THF, and 1 mmol of allyl electrophile. Samples (1 mL) of the reaction mixture were taken at 0.5, 1, and 4 h reaction times and the remaining reaction mixture after 24 h. The samples were worked up by quenching with aqueous ammonium chloride, extracting the organic compounds with diethyl ether and drying with magnesium sulfate. Qualitative analysis of the products was carried out by GC-MS, and quantitative analysis, by GC.

In the case of 3-acetoxy-1,3-diphenylpropene, 300 mg (3.0 mmol) of sodium diethylmalonate in 4.0 mL of THF and 0.03 mmol of **6** were used. The workup was done in the same fashion, except that the reaction mixture was purified over silica with 95:5 hexane/ethyl acetate. The product was analyzed with ^{1}H-NMR.

X-ray Data Collection and Structure Refinement of (*N*-(2-(Diphenylphosphino)benzylidene)(2-(2-pyridyl)-ethyl)amine)methylpalladium Trifluoromethanesulfonate, 3. X-ray data were collected on an Enraf Nonius CAD4T/ rotating anode diffractometer (Mo Kα, graphite monochromator) for a colorless crystal cut to size in oil and glued on top of a glass fiber. Accurate unit-cell parameters were derived from the SET4 setting angles of 25 reflections in the range $11° < \theta < 14°$. Reflection data were corrected for *Lp* and absorption (DIFABS)[29] and averaged into a unique dataset ($R_{av} = 0.021$). The structure was solved with DIRDIF92[30] and refined on *F* with SHELX-76.[31] Hydrogen atoms were located from a difference density map. Their positions were refined with individual isotropic atomic displacement parameters. A final difference map showed no residual features (apart from residual absorption artifacts near Pd). Neutral scattering factors and anomalous dispersion corrections were taken from Cromer and Mann and Cromer and Liberman, respectively.[32] Geometrical calculations including the ORTEP illustration were done with PLATON.[33] All calculations were done on a DEC5000 cluster. Numerical data have been collected in Table 8.

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Table 8. Crystal and Refinement Data for 3 and 4

	3	4
	Unit Cell Data	
chem formula	$C_{28}H_{26}F_3N_2O_3PPdS{\cdot}CHCl_3$	$C_{28}H_{26}ClN_2OPPd$
fw	784.36	579.4
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	25.945(2)	13.1382(9)
b, Å	10.5396(3)	10.977(3)
c, Å	27.825(2)	18.776(2)
β, deg	120.66(1)	109.018(8)
V, Å^3	6545.1(10)	2560.0
d_x, g·cm^{-3}	1.592	1.50
Z	8	4
F(000)	3152	1176
μ, cm^{-}11	9.6	77.51
cryst size, mm	0.25 × 0.25 × 0.10	0.05 × 0.30 × 0.70
	Data Collection	
T, K	150	252
θ_{min}, θ_{max}, deg	0.85, 27.5	3.5, 65
λ, Å	0.710 73	1.5418
$\Delta\omega$	0.59 + 0.35 tan θ	1.2 + 0.15 tan θ
scan mode	$\omega/2\theta$	$\omega/2\theta$
ref reflns	$\bar{2}33$, $\bar{2}25$, $\bar{2}34$	$\bar{1}02$, 302
dataset (hkl)	−30:33, 0:13, 0:36	−15:14, 0:12, 0:22
tot. no. of data	16 177	4330
tot. no. of unique reflns	15 010	4330
no. of obsd data	8887	2604
DIFABS corr range	0.84:1.07	0.73:1.42
	Refinement	
no. of params	991	412
R	0.045	0.056
R_w	0.034	0.084
S	1.48	0.40
w^{-1}	$\sigma^2(F)$	$(7.3 + F_o + 0.0139F_o^2)^{-1}$
$\langle\Delta/\sigma\rangle$	0.04	0.51
Δl (min, max)	−0.44, 1.24	−1.2, 0.6

Table 9. Conductometric Data Obtained from 2 and 3

compd (solvent)	specific conductivity, μS·M^{-1} (T, K)
2 ($CHCl_3$)	264 (233), 328 (293), 330 (319)
2 (CH_3CN)	34 900 (233), 74 000 (293), 84 800 (318)
3 ($CHCl_3$)	300 (233), 526 (293), 548 (318)
3 (CH_3CN)	34 500 (233), 71 700 (293), 83 700 (318)

X-ray Data Collection and Structure Refinement of *CN*-(2-(Diphenylphosphino)benzylidene)(2-(2-pyridyl)-ethyl)amine)chloroacetylpalladium, 4. The crystal data were collected (3.5° < θ < 65°, Cu Kα radiation, graphite monochromator) on an Enraf Nonius CAD-4 diffractometer. A total of 4330 unique reflections with 2604 significant [$F_o > 2.5\sigma(F)$] have been obtained (Table 8). Data were corrected for Lp and for a linear decay of 9% of the reference reflections during 53 h of X-ray exposure time. An empirical absorption correction was applied (DIFABS).[29] The structure was solved by direct methods. The hydrogens were calculated. Full-matrix least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to $R = 0.056$, $R_w = 0.084$, $(\Delta/\sigma)_{max} = 0.51$. A weighting scheme $w = (7.3 + F_o + 0.0139F_o^2)^{-1}$ was used. Scattering factors were taken from the literature.[32a,34] The anomalous scattering of Pd, Cl, and P was taken into account. All calculations were performed with XTAL 3.0, unless stated otherwise.[35]

Conductometry. The conductometric experiments were carried out with a Consort K720 conductometer equipped with a Philips PW 9512/00 conductometric cell in a closed glass vessel. For the experiments, *ca.* 20 mg of the complex was dissolved in 5.0 mL of chloroform or acetonitrile. The conductivities were not corrected for the temperature. The results are presented in Table 9.

Acknowledgment. The Innovation Oriented Research Programme (IOP-catalysis) is acknowledged (P.W.) for their financial support. This work was also supported in part (A.L.S) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Foundation for Scientific Research (NWO). Thanks are due to Dr. W. M. A. Niessen of the Rijks Universiteit Leiden for the mass spectroscopy measurements and to Dr. M. Widhalm of the University of Vienna for very fruitful discussions.

Supporting Information Available: Listings of atomic coordinates and U values, anisotropic thermal parameters, and complete bond distances and bond angles of **3** and **4** (26 pages). Ordering information is given on any current masthead page.

OM9509047

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