New Organometallic Palladium(II) Complexes Containing P∩N Ligands – Synthesis, Characterization and X-ray Structure

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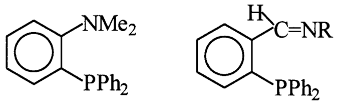
New neutral organometallic palladium(II) complexes, [PdPhI(PNMe$_2$)] (**1**), [PdPhI(PC=NMe)] (**2**), [PdPhI(PC=NEt)] (**3**), and [PdMeCl(PNMe$_2$)] (**4**), {PNMe$_2$ means *N*,*N*-dimethyl-2-(diphenylphosphanyl)aniline; PC=NMe means *N*-[2-(diphenylphosphanyl)benzylidene]-*N*-methylamine; PC=NEt means *N*-[2-(diphenylphosphanyl)benzylidene]-*N*-ethylamine} have been synthesized by oxidative addition of PhI to [Pd(dba)$_2$] in the presence of the P∩N ligand (**1**–**3**), or by substitution reaction on [PdMeCl(COD)] with PNMe$_2$ (**4**). Cationic σ-organometallic species [PdR(PPh$_3$)(P∩N)]$^+$ are obtained upon treating complexes of the type [PdRX(P∩N)] with PPh$_3$ and AgCF$_3$SO$_3$ and consist predominantly of the *trans*-P,P isomer in CDCl$_3$ solution, as shown by NMR spectroscopic studies. The cationic η^3-allyl complex [Pd(η^3-all)(PNMe$_2$)]PF$_6$ has also been prepared and characterized, both in solution and in the solid state. Compounds [PdPhI(PNMe$_2$)] ($P2_1/n$), [PdPhI(PC=NMe)] ($P\bar{1}$), [PdPhI(PC=NEt)] ($P\bar{1}$), and [Pd(η^3-all)(PNMe$_2$)]PF$_6$ ($P\bar{1}$) have been authenticated by X-ray analysis

Introduction

We have recently synthesized a number of nickel(II) complexes featuring mixed *soft-hard* coordination spheres[1][2][3] of the types {P$_2$NCl$_2$} and {P$_2$NCl}. The ultimate aim of this work was the evaluation of these species as potential catalysts in the oligomerization of olefins (Shell Higher Olefin Process, SHOP[4]). Although the catalytic results turned out to be unsatisfactory, P∩N ligands of the type depicted in Scheme 1 are expected to exhibit hemilabile behavior when coordinated to a *soft* metal center such like palladium(II)[5]. This feature, coupled with the known ability of palladium(II) complexes to promote catalytically a series of important C−C bond-forming reactions (such as the oligomerization of olefins[6], copolymerization of CO/ethylene[7], and the telomerization of butadiene[8]), prompted us to extend our investigations to this metal center[*].

Scheme 1



PNMe$_2$ **PC=NR**

The P∩N ligands employed in this work can be expected to exhibit rather different coordinating behavior. While the PNMe$_2$ ligand clearly contains *hard* (N) and *soft* (P) donor atoms and forms five-membered metal chelates[9], the imino nitrogen in PC=NR can be expected to possess appreciable *soft* character (π-acceptor properties) and the ligands clearly afford six-membered rings upon metal coordination. In this context, it is remarkable that the coordinating ability

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[*] Preliminary catalytic results indicate that the new complexes reported in this paper, [PdMe(PPh$_3$)(PNMe$_2$)]CF$_3$SO$_3$·C$_6$H$_6$, and [Pd(η^3-all)(PNMe$_2$)]PF$_6$, are efficient catalysts in the telomerization of butadiene with MeOH.

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of these imino ligands remains largely unexplored, with the exception of their behavior towards rhodium(I)[10].

The importance of ligands based on a P,N set of donor atoms is well illustrated by other results obtained, e.g. by Vrieze with 1-(dimethylamino)-8-(diphenylphosphanyl)-naphthalene and 1-(dimethylamino)-3-(diphenylphosphanyl)propane[11], and by Venanzi with 2-(2-pyridyl)-4,5-dimethylphosphinine[12].

Results and Discussion

The investigated $\mathrm{P^{\cap}N}$ ligands form neutral and cationic η^3-allyl and σ organometallic complexes, characterized as (i) neutral complexes: $[\mathrm{PdPhI(PNMe_2)}]$ (**1**), [PdPhI(PC=NMe)] (**2**), [PdPhI(PC=NEt)] (**3**), $[\mathrm{PdMeCl(PNMe_2)}]\cdot 0.5\ \mathrm{C_6H_6}$ (**4**), and (ii) cationic complexes: $[\mathrm{PdMe(PPh_3)(PNMe_2)}]\mathrm{CF_3SO_3}\cdot\mathrm{C_6H_6}$ (**5**), $[\mathrm{PdPh(PPh_3)(PNMe_2)}]\mathrm{CF_3SO_3}\cdot 0.5\ \mathrm{C_6H_6}$ (**6**), $[\mathrm{PdPh(PPh_3)(PC{=}NMe)}]\mathrm{CF_3SO_3}\cdot 0.5\ \mathrm{C_6H_6}$ (**7**), $[\mathrm{PdPh(PPh_3)(PC{=}NEt)}]\mathrm{CF_3SO_3}\cdot 0.5\ \mathrm{C_6H_6}$ (**8**), $[\mathrm{Pd}(\eta^3\text{-all})(\mathrm{PNMe_2})]\mathrm{PF_6}$ (**9**), where $\mathrm{PNMe_2}$ means *N*,*N*-dimethyl-2-(diphenylphosphanyl)aniline, PC=NMe stands for *N*-[2-(diphenylphosphanyl)benzylidene]-*N*-methylamine, and PC=NEt for *N*-[2-(diphenylphosphanyl)benzylidene]-*N*-ethylamine.

While the phosphanylamine $\mathrm{PNMe_2}$ is well-known as a ligand from the literature[9] and its reactivity with many metal centers[1][2][3][13], including palladium(II)[9], has been widely investigated, only a few rhodium(I)[10], molybdenum(0)[14], and iridium(I)[15] complexes with PC=NR (R = Me, Et) have been produced, and generally speaking, the coordination chemistry of ligands of this type has yet to be fully explored.

Synthesis and Characterization of the Neutral σ Organometallic Complexes [PdRX($\mathrm{P^{\cap}N}$)]

Two routes have been followed for the synthesis of complexes $[\mathrm{PdPhI(PNMe_2)}]$ (**1**), [PdPhI(PC=NMe)] (**2**), [PdPhI(PC=NEt)] (**3**), and $[\mathrm{PdMeCl(PNMe_2)}]\cdot 0.5\ \mathrm{C_6H_6}$ (**4**), depending on the type of organic group. The phenyl complexes [PdPhI($\mathrm{P^{\cap}N}$)] were prepared by oxidative addition of iodobenzene to the palladium(0) complex $[\mathrm{Pd(dba)_2}]$[16] (dba = dibenzylideneacetone) in the presence of the $\mathrm{P^{\cap}N}$ ligand (see Eq. 1)[17].

$$[\mathrm{Pd(dba)_2}] + \mathrm{PhI} + \mathrm{P^{\cap}N} \xrightarrow[\mathrm{N_2,\ THF}]{50\,^{\circ}\mathrm{C,\ 45\ min}} \tag{1}$$

$$[\mathrm{PdPhI(P^{\cap}N)}] + 2\ \mathrm{dba}$$

The complexes [PdPhI($\mathrm{P^{\cap}N}$)] were obtained as colored powders (yellow or pink-yellow) after filtration of the reaction mixture through Celite to eliminate metallic Pd, concentration of the filtrate to dryness, and repeated washing with $\mathrm{Et_2O}$. No further recrystallization was necessary and crystals suitable for X-ray analysis could be grown by slow evaporation of the solvent from $\mathrm{Me_2CO/MeOH}$ solutions.

The methyl complex $[\mathrm{PdMeCl(PNMe_2)}]\cdot 0.5\mathrm{C_6H_6}$ (**4**) was prepared by a substitution reaction on the complex [PdMeCl(COD)][18] (see Eq. 2) (COD = 1,5 cyclooctadiene), similar to that employed with related $\mathrm{P^{\cap}N}$ ligands[11].

$$[\mathrm{PdMeCl(COD)}] + \mathrm{PNMe_2} \xrightarrow[\mathrm{N_2,\ C_6H_6,\ 24\ h}]{\mathrm{r.t.}} \tag{2}$$

$$[\mathrm{PdMeCl(PNMe_2)}]\cdot 0.5\ \mathrm{C_6H_4} + \mathrm{COD}$$

Some IR and NMR spectroscopic data of the complexes [PdRX($\mathrm{P^{\cap}N}$)] and of the corresponding free ligands are reported in Table 1.

Direct evidence for the coordination modes of the ligands $\mathrm{PNMe_2}$, PC=NMe, PC=NEt has been obtained from X-ray analyses of complexes **1**, **2**, and **3** (see below). The coordination of the $\mathrm{P^{\cap}N}$ ligands through both the P and N atoms has also been deduced in solution on the basis of NMR data, where the resonances of the $^{31}\mathrm{P}$ nucleus and of the protons of the amino or imino alkyl groups are shifted towards lower fields than the corresponding resonances of the free ligand. NMR data also give useful information about the composition of the reaction product mixtures in $\mathrm{CDCl_3}$ solutions. In fact, both reactions 1 and 2 produce only one isomer of complexes **2−4**, while $[\mathrm{PdPhI(PNMe_2)}]$ (**1**) is obtained as a mixture of *trans* P,I and *cis* P,I isomers in a 3:1 ratio (Table 1). IR data are less helpful in distinguishing the type of coordination; in fact, the typical C=N stretching bands (at 1637 $\mathrm{cm^{-1}}$) of the phosphanyl-imines PC=NMe and PC=NEt in the spectra of **2** and **3** are practically unchanged relative to those of the free ligands. However, at the same time, coordination of the ligand slightly affects the aromatic C=C stretching values.

The available data are not helpful in unambiguously establishing the geometries of [PdPhI(PC=NMe)] and [PdPhI(PC=NEt)], which are present as single isomers in solution. As a matter of fact, upon crystallization, the *trans*-P,I isomer is obtained. In contrast to these cases, the assignment of the molecular structure as *trans*-P,Cl in solution is possible for $[\mathrm{PdMeCl(PNMe_2)}]\cdot 0.5\ \mathrm{C_6H_6}$ by virtue of the $^3J_{\mathrm{PH}}$ coupling constant value[11].

Synthesis and Characterization of the Cationic Palladium(II) Complexes

The cationic complexes of the type $[\mathrm{PdR(PPh_3)(P^{\cap}N)}]^+$ (with $\mathrm{CF_3SO_3}^-$ as the counterion), $[\mathrm{PdMe(PPh_3)(PNMe_2)}]^+\cdot\mathrm{C_6H_6}$ (**5**), $[\mathrm{PdPh(PPh_3)(PNMe_2)}]^+\cdot 0.5\ \mathrm{C_6H_6}$ (**6**), $[\mathrm{PdPh(PPh_3)(PC{=}NMe)}]^+\cdot 0.5\ \mathrm{C_6H_6}$ (**7**), $[\mathrm{PdPh(PPh_3)(PC{=}NEt)}]^+\cdot 0.5\ \mathrm{C_6H_6}$ (**8**), were synthesized by adding an $\mathrm{AgCF_3SO_3/PPh_3}$ solution in $\mathrm{Me_2CO}$ to a $\mathrm{CH_2Cl_2}$ solution of the corresponding neutral precursor [PdRX($\mathrm{P^{\cap}N}$)] at 0°C (see Eq. 3). Removal of the silver salt by filtration and recrystallization of the product from $\mathrm{CH_2Cl_2}$, $\mathrm{C_6H_6}$, and $\mathrm{Et_2O}$ afforded the pure products as white or off-white powders. Complexes **5−8** are stable in the solid state, but they tend to decompose slowly in solution (over a period of days).

Table 1. Selected IR and NMR absorptions of complexes $[PdRX(P^{\cap}N)]$ and of the corresponding free ligands

	$\nu^{[a]}$ (cm^{-1})		$\delta^{[b]}$ (ppm), J (Hz)				
	C=C	C=N	CH_2	CH_3	H$_{arom}$	HC=N	$^{31}P\{^1H\}$
Complex **1**	1574			3.40 (s)[c], 3.66 (s)	6.63–6.72 (m), 6.88–6.99 (m), 7.22–7.89 (m)		24.3(s)[c], 37.3 (s)
$PNMe_2$	1570			2.58 (s)	6.50–7.50 (m)		–16.2 (s)
Complex **2**	1562	1637		4.00 (s)	6.38–6.68 (m), 7.04–7.68 (m)	8.00 (bs)	23.6 (s)
PC=NMe	1582	1640		3.38 (d) $^3J_{HH}$ = 1.8	6.80–6.97 (m), 7.13–7.48 (m), 7.89–8.05 (m)	8.85–8.95 (m) $^4J_{PH}$ = 4.8	–14.0 (s)
Complex **3**	1561	1637	4.42 (q) $^3J_{HH}$ = 7.3	1.22 (t) $^3J_{HH}$ = 7.3	6.40–6.68 (m), 6.99–7.70 (m)	8.00 (bs)	21.6 (s)
PC=NEt	1583	1637	3.49 (qd) $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 4.4	1.10 (t) $^3J_{HH}$ = 4.4	6.75–6.95 (m), 7.13–7.56 (m), 7.91–8.03 (m)	8.84–8.93 (m) $^4J_{PH}$ = 4.8	–13.3 (s)
Complex **4**	1583			0.78 (d, Pd–CH_3) $^3J_{HP}$ = 2.9; 3.15 [s, N(CH_3)$_2$]	7.13–7.81 (m)		35.6 (s)

[a] In KBr: C=C refers to the aromatic C=C stretching, while C=N refers to the C=N stretching. – [b] In $CDCl_3$. – [c] More abundant isomer.

$$[PdRX(P^{\cap}N)] + AgCF_3SO_3 + PPh_3 \xrightarrow[CH_2Cl_2,\ Me_2CO]{0\,°C,\ 45\ min} [PdR(PPh_3)(P^{\cap}N)]CF_3SO_3 + AgX \qquad (3)$$

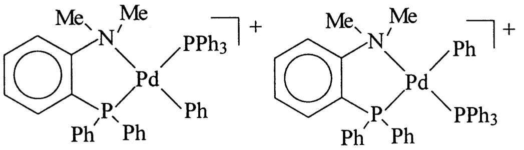
The more stable allyl complex $[Pd(\eta^3\text{-all})(PNMe_2)]PF_6$ (**9**) was obtained as a cream-coloured powder following a different synthetic procedure, employing $[Pd(\eta^3\text{-all})Cl]_2$[19], two equivalents of the ligand $PNMe_2$, and a large excess of KPF_6 (see Eq. 4).

$$[Pd(\eta^3\text{-all})Cl]_2 + PNMe_2 + 2\ KPF_6 \xrightarrow[CH_2Cl_2,\ 3\ h]{r.t.} 2\ [Pd(\eta^3\text{-all})(PNMe_3)]PF_6 + 2\ KCl \qquad (4)$$

All the cationic complexes have been characterized by means of the usual physicochemical techniques. Molar conductivity values of 152 ohm^{-1}cm^{2}mol^{-1} (see Experimental Section) confirm that they are uni-univalent electrolytes[20] and the presence of the anions $CF_3SO_3^-$ and PF_6^- is confirmed by very sharp, intense bands in their solid-state IR spectra at 1265 cm^{-1} [ν(S–O)] and 834 cm^{-1} [ν(P–F)], respectively[21].

In the case of complexes $[PdR(PPh_3)(P^{\cap}N)]^+$, the presence of two nonequivalent ^{31}P nuclei and the value of their coupling constants[22] (Table 2) permits the assignment of their molecular structures in $CDCl_3$ solution. This is fortunate, since no crystal structure could be determined. Thus, the $^{31}P\{^1H\}$ spectrum of $[PdPh(PPh_3)(PNMe_2)]^+$ is very informative and the complex is found to consist of a mixture of isomers (Figure 1), the *trans* isomer being prevalent (82%) (the terms *cis* and *trans* refer here to the mutual P positions).

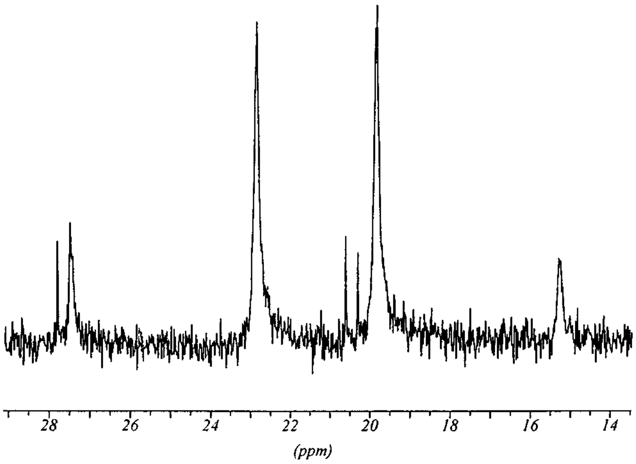
Figure 1. The *trans* and *cis* isomers of complex **6**



6 ***trans*** **6** ***cis***

In the $^{31}P\{^1H\}$ spectrum of complex **6** (Figure 2), the AB system ($^2J_{PP}$ = 372 Hz) is associated with the *trans* species, while the AX system ($^2J_{PP}$ = 24 Hz) is associated with the *cis* species.

Figure 2. $^{31}P\{^1H\}$-NMR spectrum of the mixture of isomers of complex **6**



On the basis of these findings, and the values reported in Table 2, it can be stated that the phosphanyl-imino complexes **7** and **8** exhibit only the *trans* configuration.

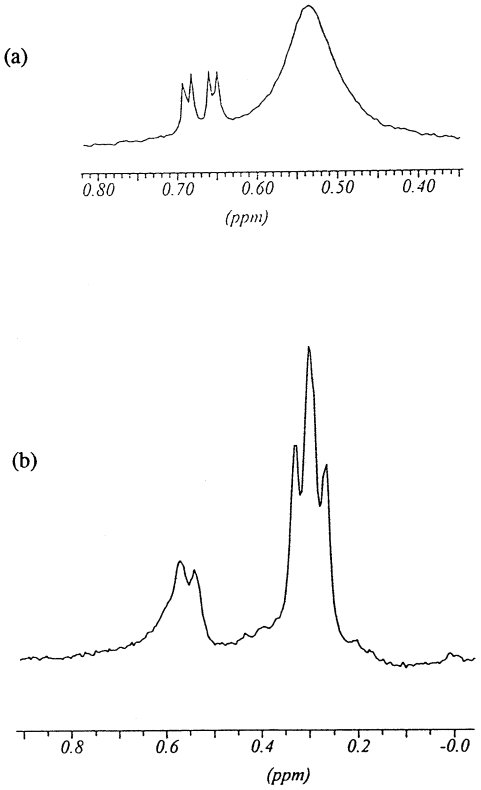
The methyl σ organometallic cationic complex $[PdMe(PPh_3)(PNMe_2)]^+$ (**5**) gives rise to an interesting ^1H-NMR spectrum, which indicates the presence of the two expected isomers; while the *cis* species is stereochemically rigid at room temperature [the signal of the methyl group bound to palladium(II) of this isomer appears as a doublet of doublets at δ = 0.67 with $^3J_{HP}$ = 2.2 and 6.6 Hz] (Figure 3a), the *trans* species is stereochemically nonrigid. Broad signals at δ = 0.53 (Figure 3a) and δ = 2.87 can be attributed to the protons of the methyl group bound to palladium(II) and of the methyl groups of the dimethylamino ligand, respectively. This isomer is the prevalent species, as deduced from integration of the signals. In the $^{31}P\{^1H\}$ spectrum,

Table 2. NMR absorptions of the palladium(II) cationic complexes

			δ (ppm)[a], J (Hz)		
Complex	CH_2	CH_3	H_{arom}	CH	$^{31}P\{^{1}H\}$
5		0.53 (bs, Pd–CH_3 *trans*), 0.67 (dd, Pd–CH_3 *cis*) $^{3}J_{HP}$ = 2.2, 6.6; 2.87 [bs, N(CH_3)$_2$ *trans*]; 3.25 [s, N(CH_3)$_2$ *cis*]	6.90–7.97 (m)		23.8 (d, *cis*) $^{2}J_{PP}$ = 26, 40.1 (d, *cis*) $^{2}J_{PP}$ = 26
6		2.76 (bs), 2.94 (s)	6.16–6.67 (m), 6.91–7.97 (m)		18.4 (d, *trans*) $^{2}J_{PP}$ = 372, 24.4 (d, *trans*) $^{2}J_{PP}$ = 372; 20.5 (d, *cis*) $^{2}J_{PP}$ = 24, 27.7 (d, *cis*) $^{2}J_{PP}$ = 24
7		2.87 (s)	6.30–6.49 (m), 6.65–6.79 (m), 6.88–8.05 (m)	8.21 (bs)	20.1 (d, *trans*) $^{2}J_{PP}$ = 376, 21.6 (d, *trans*) $^{2}J_{PP}$ = 376
8	3.03 (q) $^{3}J_{HH}$ = 7.3	0.54 (t) $^{3}J_{HH}$ = 7.3	6.32–6.53 (m), 6.69–6.80 (m), 7.00–7.92 (m)	8.33 (bs)	17.8 (d, *trans*) $^{2}J_{PP}$ = 389, 22.2 (d, *trans*) $^{2}J_{PP}$ = 389
9		3.45 (s)	6.40–6.68 (m), 6.99–7.70 (m)	2.90–3.80 (m, H^{3},$H^{3'}$)[b], 4.17 (dd, H^{1}) $^{3}J_{HP}$ = 9.5, $^{3}J_{HH}$ = 13.9, 4.95 (dd, $H^{1'}$) $^{3}J_{HP}$ = 5.3, $^{3}J_{HH}$ = 7.7, 5.80–6.15 (m, H^{2})	–141[c] (sept, J_{PF} = 708) 33.6 (s)

[a] In $CDCl_3$. – [b] $H^{1'}H^{1}C^{1}C^{2}H^{2}C^{3}H^{3'}H^{3}$, where C^{1} is *trans* to P. – [c] In CD_3CN.

Figure 3. (a) ^{1}H-NMR signals of the methyl groups bound to palladium(II) of the mixture of isomers of complex **5** at 25°C; (b) ^{1}H-NMR signals of the methyl groups bound to palladium(II) of the mixture of isomers of complex **5** at –20°C

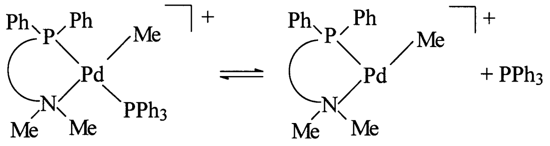


only the *cis* isomer gives rise to well-defined, sharp signals ($^{2}J_{PP}$ = 26 Hz).

Lowering of the temperature blocks the stereochemical nonrigidity of the *trans* species and at –20°C the AB system of the stereoisomer eventually appears (δ = 27.0 and δ = 31.7 with $^{2}J_{PP}$ = 375 Hz). The signal of the methyl group bound to palladium(II) (Figure 3b) becomes a triplet at δ = 0.30 with $^{3}J_{HP}$ = 6.5 Hz, this value being of the same order as the corresponding value of 5 Hz observed in the ^{1}H-NMR spectrum of *trans*-[PdMeI(PPh$_3$)$_2$][23].

We speculate that at low temperature (–20°C) the *trans* species is undissociated. When the temperature is increased, a fast dissociation process takes place so that the triplet, arising from the coupling of the protons of the methyl bound to palladium(II) with the two ^{31}P nuclei, merges into one very broad singlet. Considering the high *trans* effect of the phosphane group and the stabilization of the P$^\frown$N ligand due to the chelate effect, we postulate that this dissociation process involves the PPh$_3$ ligand, leading to a T-shaped intermediate (Figure 4).

Figure 4. Dissociation of the PPh$_3$ group and formation of a T-shaped intermediate in the case of *trans*-[PdMe(PPh$_3$)(PNMe$_2$)]$^+$

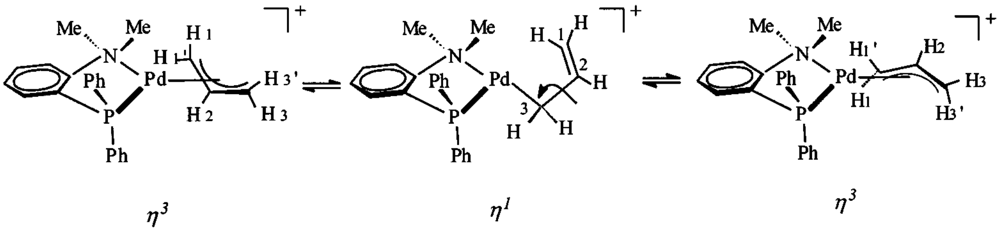


The complex [Pd(η^3-all)(PNMe$_2$)]PF$_6$ is also stereochemically nonrigid in CDCl$_3$ as a consequence of a selective *syn-anti* interchange of the allyl protons *trans* to the NMe$_2$ group through the usual η^3–η^1–η^3 interconversion process (Scheme 2).

This fluxional phenomenon has been observed previously[24]. The PPh$_2$ group weakens the *trans* Pd–CH$_2$ bond, thus promoting the opening of the allyl ring and, by rotation about the σ bonds, the interchange of the *syn-anti* H^3 and H$^{3'}$ protons.

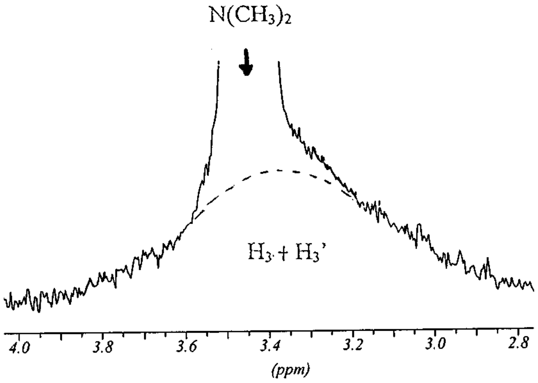
The relevant signal is not discernible in the ^{1}H-NMR spectrum owing to its partial overlap with that of the N(CH$_3$)$_2$ group (Figure 5) and only a broad absorption can be observed. On the contrary, the signals of the other three

Scheme 2



protons (Figure 6) are well defined: the multiplet between $\delta = 5.80$ and $\delta = 6.15$ is due to the central allyl proton H^2, while the two doublets of doublets at $\delta = 4.95$ ($^3J_{HH} = 7.7$ Hz and $^3J_{HP} = 5.3$ Hz) and at $\delta = 4.17$ ($^3J_{HH} = 13.9$ Hz and $^3J_{HP} = 9.5$ Hz) can be assigned to H^1 (*anti* in relation to H^2) and $H^{1'}$ (*syn* in relation to H^2), respectively, on the basis of the magnitudes of the coupling constants[25].

Figure 5. Overlapping of the signals of the protons of the $N(CH_3)_2$ group and of the protons H^3 and $H^{3'}$ in the ^{1}H-NMR spectrum of complex **9** in $CDCl_3$



X-ray Structure

The unique portion of the unit cells is different in compounds **1**, **2**, **3**·3/2 H_2O, and **9**. In **1**, the asymmetric unit consists of a single molecule of the neutral complex [PdPhI(PNMe$_2$)] (Figure 7), while two molecules of [PdPhI(PC=NMe)] are present in **2** (Figure 8). In **3**·3/2 H_2O, the unique portion comprises two molecules of [PdPhI(PC=NEt)], along with three molecules of water (Figure 9), and in **9** two molecules of the salt [Pd(η^3-C_3H_5)(PNMe$_2$)]PF_6 are likewise present (Figure 10). In **2**, **3**·3/2 H_2O, and **9**, the geometries shown by the two such independent and chemically well-separated molecules are practically superimposable (Figure 11), the differences being restricted to minor features only. This is also confirmed by the fact that no bond distance differs by more than two standard deviations in any of these molecule pairs. Hence, in the present discussion, all geometrical parameters refer to the mean values.

In **1** and **9**, the bidentate P⁀N ligand coordinates to palladium(II) forming a five-membered chelate ring, which adopts a somewhat envelope-like (C_s) conformation (pertinent torsion angles in the range from −16.1° to +16.1°). The

Figure 6. Signals of protons H^1, $H^{1'}$, and H^2 in the ^{1}H-NMR spectrum of complex **9** in $CDCl_3$

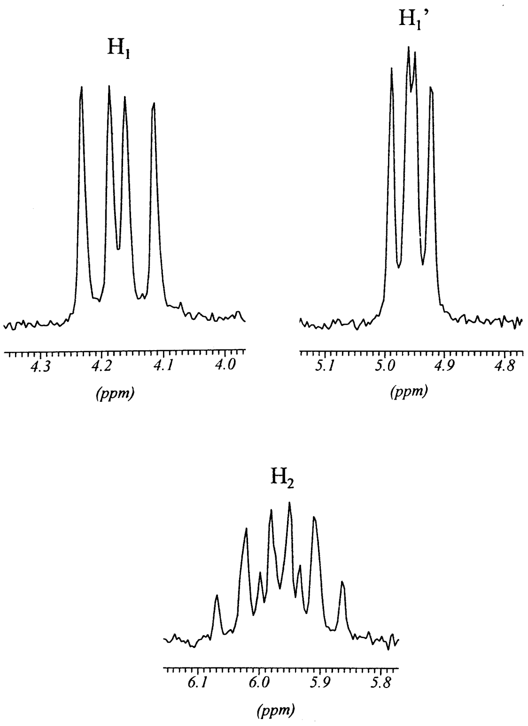


Figure 7. Molecular structure of **1**. H atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level

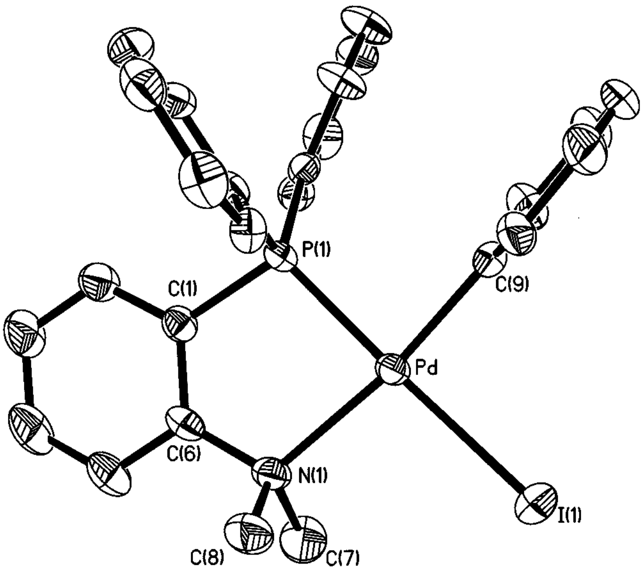


Figure 8. The asymmetric unit of **2**. H atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level

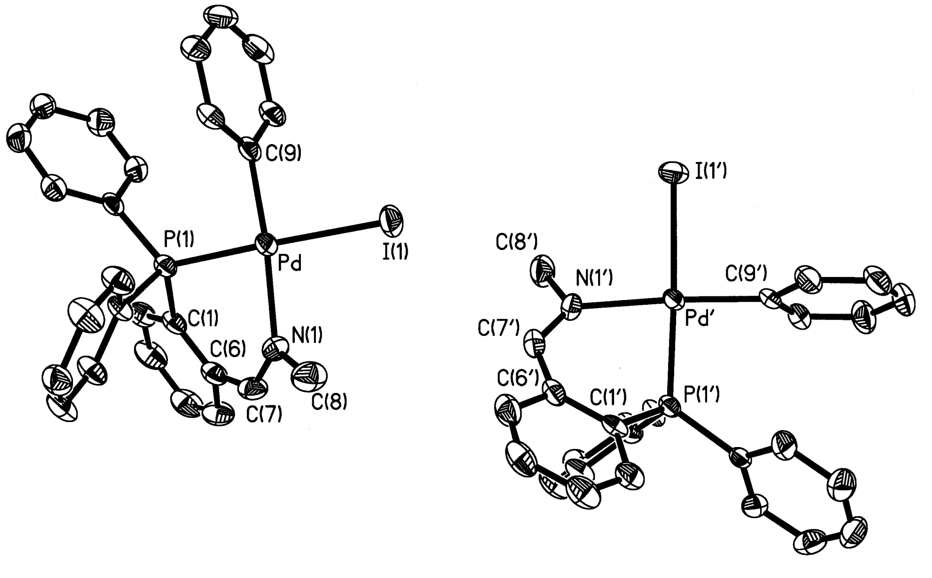


Figure 9. The asymmetric unit of **3**·3/2 H_2O. H atoms have been omitted for clarity. The C(9′) atom obscures N(1′).

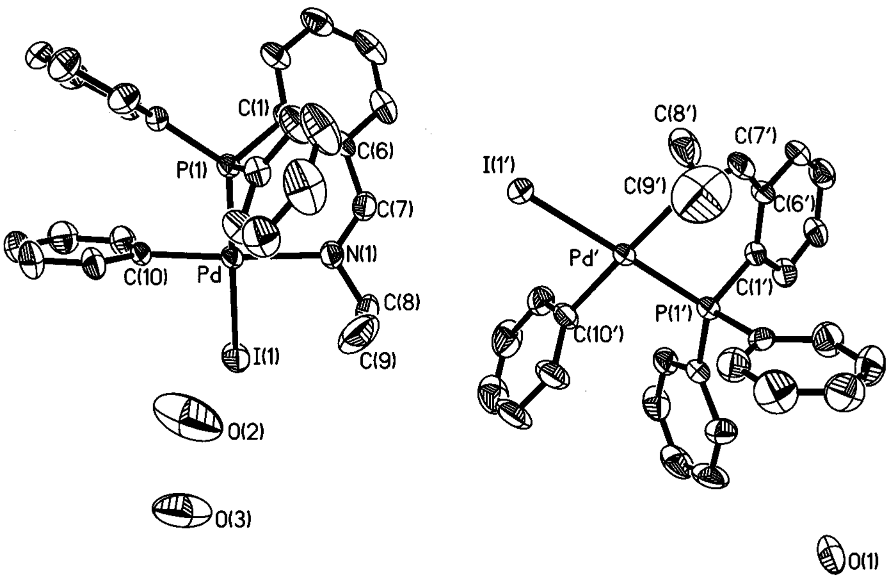


Figure 10. The asymmetric unit of **9**. H atoms have been omitted for clarity

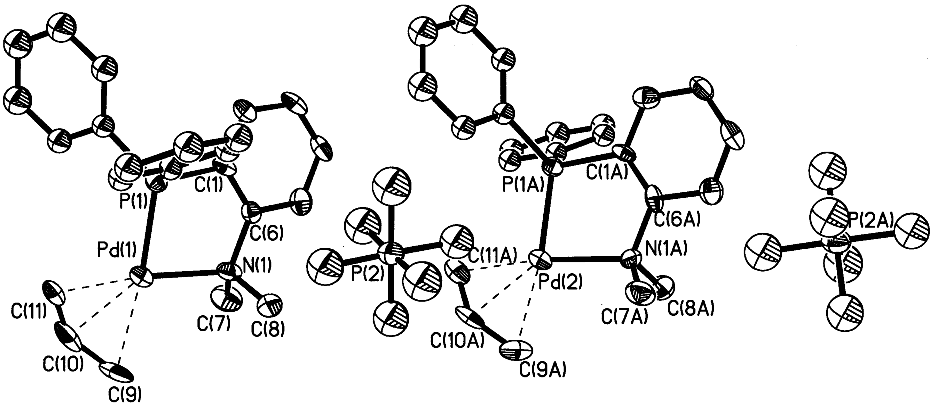
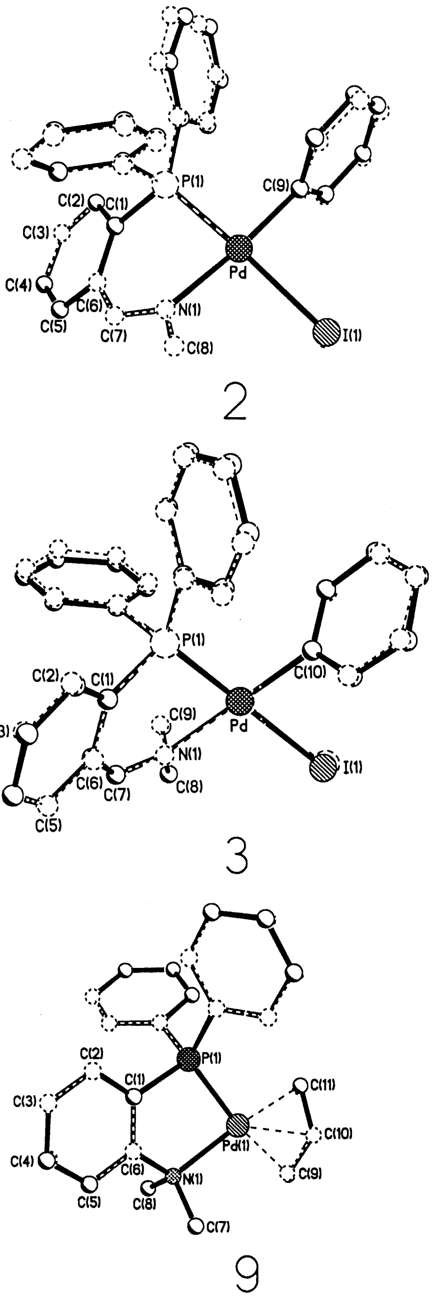


Figure 11. Superimposition of the two independent moieties of **2**, **3**·3/2 H_2O, and **9**. Weighted root mean square deviation of 0.02, 0.05, and 0.03 Å, respectively, when fitting is performed on the labelled atoms



2

3

9

coordination sphere of **1** is completed by an iodide and a phenyl ligand, whereas the remaining coordination positions in **9** are occupied by the η^3-allyl ligand. In the latter compound, the coordination plane can be defined by the P,N donor atoms and by the terminal carbon atoms of the allyl group, the central carbon atom residing 0.50 Å above this plane. The mean plane defined by the eight atoms P(1), C(1)−(6), N(1) forms dihedral angles of 5.4° and 5.1° with the mean coordination plane in **1** and **9**, respectively. The P−N "bite" distance and the P−Pd−N angle are 3.00(1) Å and 85.1(3)° in both complexes. The Ph ligand in **1** is roughly orthogonal to the mean coordination plane (dihedral angle of 82.1°).

In **2** and **3**·3/2 H_2O, the P∩N ligand forms a six-membered chelate ring with the palladium(II) center. In this arrangement, the Pd and N(1) atoms in **2** deviate by +1.56 Å and +0.49 Å from the mean plane defined by the eight atoms P(1), C(1)−(7). The corresponding values in **3**·3/2 H_2O are +1.41 and +0.32 Å. The latter plane forms dihedral angles ("elbow angles") of 55.8° and 53.9° with the coordination plane in **2** and **3**·3/2 H_2O, respectively. In turn, the Ph ligand forms a dihedral angle with the coordination plane of 72.0° (in **2**) and of 75.3° (in **3**·3/2 H_2O). The "bite" distances and angles match those found in **1** and **9** [2.95(1) Å, 84.0(2)° in **2** and 3.00(1) Å, 85.8(2)° in **3**·3/2 H_2O].

The donor atoms deviate from the mean coordination plane by ±0.04 Å in **1**, ±0.07 Å in **2**, ±0.04 Å in **3**·3/2 H_2O, and ±0.06 Å in **9**, with the palladium(II) correspondingly out by 0.02, 0.02, 0.04, and 0.09 Å. In all the complexes, the major departure from the ideal square-planar geometry is manifested in the "bite" angle. From comparison of the distances with reference values obtained from the Cambridge Structural Database[26], the following comments can be made: (i) The $Pd^{II}-I$ distance (mean 2.654 Å) is consistent with both the reference value (2.639 Å) derived from 164 observations and the sum of the covalent radii (1.33 + 1.31 Å)[27]; (ii) the $Pd^{II}-P$ distance in the three neutral complexes (mean 2.228 Å), which is slightly shorter than that in the allyl cationic complex (2.260 Å), is remarkably shorter than the $Pd^{II}-PPh_3$ bond reference value (2.302 Å) encountered in 248 entries, and falls at the short end of a wide range (2.21−2.46 Å); (iii) the $Pd^{II}-C_{Ph}$ distance (mean 2.015 Å) matches the reference value (2.013 Å) derived from 34 observations, and (iv) the $Pd^{II}-N$ distance in **1** (2.252 Å) is considerably longer than the corresponding distances in **2** and **3**·3/2 H_2O (mean 2.17 Å), which may be ascribed to the different environment of the nitrogen. Accordingly, on going from a five- to a six-membered chelate ring, the Pd−N(sp^3)−C angle (113.6°) widens to the mean value of 125.5° observed for Pd−N(sp^2)=C.

The packing observed for the four complexes does not show intermolecular contacts shorter than the sum of the van der Waals' radii, the shortest I−H approach being 3.1 Å. The opportunity for hydrogen bonding seems to be restricted to that between the water molecules of **3**·3/2 H_2O, which show O−O separations of 2.8 Å.

Conclusions

The phosphanyl-amine $PNMe_2$ and the phosphanyl-imines PC=NMe and PC=NEt are able to stabilize organometallic neutral and cationic palladium(II) complexes, acting as chelating bidentate ligands via their P and N donor atoms, forming five- or six-membered rings with the metal center in the expected manner.

The neutral complexes [PdRX(P∩N)] are stable species, both in solution and in the solid state. The phenyl complexes [PdPhI($P{\cap}N$)] and [PdMeCl($PNMe_2$)] exist as the *trans*-P,I isomer in the solid state, as indicated by X-ray analysis, as well as *trans*-P,Cl isomer in solution, as deduced from the ^1H-NMR spectrum in $CDCl_3$.

The σ organometallic cationic complexes [PdR(PPh_3)($P{\cap}N$)]$^+$ can be obtained by the reaction of the neutral precursor with PPh_3 and $AgCF_3SO_3$ and exist in solution mainly as *trans*-P,P species. In particular, a fluxional behavior is observed for *trans*-[PdMe(PPh_3)($PNMe_2$)]$^+$, probably due to the dissociation of a PPh_3 molecule. The η^3-allyl complex [Pd(η^3-all)($PNMe_2$)]PF_6, obtained from the dimer [Pd(η^3-all)Cl]$_2$ and a stoichiometric amount of $PNMe_2$ in the presence of excess KPF_6, also exhibits fluxional behavior in $CDCl_3$ solution, owing to the selective interchange of the protons of the CH_2 group *trans* to the phosphorus of the diphenylphosphanyl group.

Comparison of the crystal structure of [Pd(η^3-all)($PNMe_2$)]PF_6 with those of the neutral complexes containing the phosphanyl-imines PC=NMe and PC=NEt reveals moderate differences relating to the size of the chelate ring in terms of bond lengths and the "bite" angle P−Pd−N.

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Experimental Section

General: All chemicals and solvents were of analytical grade and were used as received unless otherwise stated. Anhydrous Et_2O and C_6H_6 were distilled from potassium/benzophenone under N_2; anhydrous THF was freshly distilled from potassium/benzophenone under N_2. The complexes [Pd(dba)$_2$][16], [PdMeCl(COD)][18], [Pd(η^3-all)Cl]$_2$[19] and the ligands $PNMe_2$[9], PC=NR (R = Me, Et)[10] were synthesized according to literature procedures. − IR: Mattson 3030 Fourier transform spectrometer. − ^1H and $^{31}P\{^1H\}$ NMR: Bruker AC-200 (200 MHz for ^1H and 80.9 MHz for ^{31}P). Typical NMR samples were prepared by dissolving the complexes (20 mg) in 0.4 ml of the deuterated solvent. For ^1H NMR, $CDCl_3$ as solvent, TMS as internal standard; for $^{31}P\{^1H\}$ NMR, $CDCl_3$ as solvent, 85% aqueous H_3PO_4 as external standard. − Conductivity measurements: Amel conductimeter Model 131, ca. 10^{-3} M solutions in MeCN at 25°C. − Elemental analyses (C, H, N): Fisons EA 1108 elemental analyzer.

Synthesis of **1**−**3** − *General Procedure:* To a blood-red solution of 0.633 g of [Pd(dba)$_2$] (1.1 mmol) in 90 ml of dry THF at 50°C under N_2, a stoichiometric amount of the $P{\cap}N$ ligand and 520 µl of PhI (4.4 mmol, d = 1.73 g/ml) were added, and the mixture was stirred under N_2 at the same temperature. After 45 min, the yellow-green mixture was concentrated under a flow of N_2 and filtered through Celite. The solvent was removed from the filtrate under reduced pressure and the residue was washed several times with Et_2O until the washings were colorless. The residual solid was then dried in vacuo. Crystals suitable for X-ray analysis were grown by slow evaporation of the solvent from Me_2CO/MeOH solutions (Crystals of complex **3** from Me_2CO/MeOH/H_2O solutions).

Synthesis of **4**: To a solution of 0.508 g of [PdMeCl(COD)] (0.19 mmol) in 60 ml of dry C_6H_6 under N_2, was added 0.058 g of the phosphanyl-amine $PNMe_2$ (0.19 mmol) and the mixture was stirred under N_2. After 15 min, a white solid began to precipitate. After 24 h, the pale-yellow mixture was filtered and the white solid was collected, washed with C_6H_6 and Et_2O, and dried in vacuo. The filtrate was concentrated under a flow of N_2 and upon addition of Et_2O a precipitate was formed. This was filtered off, washed with Et_2O and a small volume of THF, and dried in vacuo.

Synthesis of **5**−**8** − *General Procedure:* To a solution of the neutral complex [PdRX($P{\cap}N$)] (0.41 mmol) in 5 ml of CH_2Cl_2 at 0°C under N_2, a solution containing 0.108 g of PPh_3 (0.41 mmol) and 0.106 g of $AgCF_3SO_3$ (0.41 mmol) in 3 ml of Me_2CO was added dropwise, resulting in immediate silver halide precipitation. After 45 min., the mixture was concentrated under a flow of N_2 and filtered, and the solvent was removed from the filtrate in vacuo. The residue was redissolved in CH_2Cl_2 and upon addition of Et_2O a precipitate was deposited, which was separated from the solution by decantation of the supernatant and redissolved in a small amount of CH_2Cl_2. Addition of C_6H_6 and Et_2O under vigorous stirring caused the formation of a solid, which was filtered off, washed with C_6H_6 and Et_2O, and dried in vacuo.

Synthesis of **9**: To a solution of 0.130 g of [Pd(η^3-all)Cl]$_2$ (0.36 mmol) in 10 ml of CH_2Cl_2 was added 0.265 g of KPF_6 (1.44 mmol) followed by 0.282 g of the ligand $PNMe_2$ (0.40 mmol), and the yellow mixture was stirred at room temperature. After 3 h, the colorless mixture was filtered and the filtrate was concentrated under reduced pressure. Addition of Et_2O caused the formation of a white precipitate, which was filtered off, washed with Et_2O, and dried in vacuo. The solid was recrystallized from MeCN and Et_2O and dried in vacuo. Crystals suitable for X-ray analysis were grown by slow evaporation of the solvent from CH_2Cl_2/EtOH/Et_2O solutions.

[PdPhI($PNMe_2$)] (**1**): Yield 0.574 g (85%). − IR (KBr): $\tilde{\nu}$ = 3055 m cm^{-1}, 1574 m, 1469 s, 1433 s, 743 vs, 691 s, 500 vs. − $C_{26}H_{25}INPPd$ (615.79): calcd. C 50.71, H 4.10, N 2.28; found C 49.03, H 4.03, N 2.02.

[PdPhI(PC=NMe)] (**2**): Yield: 0.637 g (94%). − IR (KBr): $\tilde{\nu}$ = 3050 m cm^{-1}, 1637 m (C=N), 1562 m, 1478 m, 1434 s, 739 s, 688 s. − $C_{26}H_{23}INPPd$ (613.79): calcd. C 50.88, H 3.78, N 2.28; found C 50.73, H 4.01, N 2.13.

[PdPhI(PC=NEt)] (**3**): Yield: 0.421 g (61%). − IR (KBr): $\tilde{\nu}$ = 3043 m cm^{-1}, 1637 m (C=N), 1561 m, 1467 m, 1434 s, 727 vs, 691 vs. − $C_{27}H_{25}INPPd$ (627.82): calcd. C 51.65, H 4.02, N 2.23; found C 51.00, H 3.99, N 2.03.

[PdMeCl($PNMe_2$)]·0.5 C_6H_6 (**4**): Yield: 0.074 g (78%). − IR (KBr): $\tilde{\nu}$ = 3049 w cm^{-1}, 1583 w, 1480 s, 1436 s, 748 s, 694 s, 502 s. − $C_{21}H_{23}ClNPPd\cdot0.5\ C_6H_6$ (501.33): calcd. C 57.50, H 5.24, N 2.79; found C 55.32, H 5.15, N 2.69.

[PdMe(PPh_3)($PNMe_2$)]$CF_3SO_3\cdot C_6H_6$ (**5**): Yield: 0.252 g (67%). − IR (KBr): $\tilde{\nu}$ = 3053 w cm^{-1}, 1593 w, 1502 m, 1435 m, 1273 vs (S−O), 693 s, 636 s. − Λ_M (MeCN): 150 ohm^{-1}cm^{2}mol^{-1}. − $C_{40}H_{38}F_3NO_3P_2PdS\cdot C_6H_6$ (916.31): calcd. C 60.29, H 4.85, N 1.53, S 3.50; found C 60.93, H 5.56, N 1.63, S, 3.36.

[PdPh(PPh_3)($PNMe_2$)]$CF_3SO_3\cdot0.5\ C_6H_6$ (**6**): Yield: 0.362 g (94%). − IR (KBr): $\tilde{\nu}$ = 3056 m cm^{-1}, 1564 m, 1473 m, 1437 s, 1263 vs (S−O), 691 s, 637 s. − Λ_M (MeCN): 152 ohm^{-1}cm^{2}mol^{-1}. − $C_{45}H_{40}F_3NO_3P_2PdS\cdot0.5\ C_6H_6$ (939.32): calcd. C 61.37, H 4.62, N 1.48, S 3.41; found C 61.70, H 5.25, N 1.60, S 3.38.

[PdPh(PPh_3)(PC=NMe)]$CF_3SO_3\cdot0.5\ C_6H_6$ (**7**): Yield: 0.361 g (94%). − IR (KBr): $\tilde{\nu}$ = 3052 m cm^{-1}, 1641 m (C=N), 1564 m, 1482 m, 1435 s, 1261 vs (S−O), 693 s. − Λ_M (MeCN): 152 ohm^{-1}cm^{2}mol^{-1}. − $C_{45}H_{38}F_3NO_3P_2PdS\cdot0.5\ C_6H_6$ (937.3): calcd.

Table 3. Crystal data and summary of data collection and refinement for [PdPhI(PNMe$_2$)] (**1**), [PdPhI(PC=NMe)] (**2**), [PdPhI(PC=NEt)]·3/2 H_2O (**3**·3/2 H_2O), and [Pd(η^3-C_3H_5)(PNMe$_2$)]PF_6 (**9**)

	1	**2**	**3**·3/2 H_2O	**9**
Empirical formula	$C_{26}H_{25}INPPd$	$C_{26}H_{23}INPPd$	$C_{27}H_{28}INO_{1.5}PPd$	$C_{23}H_{25}F_6NP_2Pd$
Form. weight	615.74	613.72	654.77	597.78
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.283(2)	9.200(6)	11.972(4)	9.042(2)
b [Å]	16.645(4)	16.067(10)	15.356(5)	10.980(3)
c [Å]	15.542(4)	16.147(9)	15.874(6)	14.408(3)
α [°]	90	92.86(5)	105.03(3)	72.11(2)
β [°]	94.06(2)	90.95(5)	90.03(3)	71.86(2)
γ [°]	90	96.27(5)	96.63(3)	65.75(2)
V [Å^3]	2395.5(10)	2369(3)	2798(2)	1212.6(5)
Z	4	4	4	2
D_{calcd} [Mg/m^3]	1.707	1.721	1.554	1.637
μ [mm^{-1}]	2.143	2.167	1.843	0.955
λ [Å]	0.71073	0.71073	0.71073	0.71073
obsd. refl.	2512	5059	6798	2672
$R1$, $Rw2$[a]	0.0404, 0.1016	0.0469, 0.1211	0.0727, 0.2012	0.0398, 0.0997
GooF[b]	1.063	1.059	1.105	1.058

[a] $R1 = \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$; $Rw2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. – [b] GooF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{par})]^{1/2}$.

Table 4. Selected bond lengths [Å] and angles [°] for **1**, **2**[a], **3**·3/2 H_2O[a], and **9**[a]

	1	**2**		**3**·3/2H_2O		**9**	
Pd–I(1)	2.655(1)	2.664(2)	2.671(2)	2.628(1)	2.651(1)		
Pd–P(1)	2.208(2)	2.232(2)	2.239(2)	2.228(2)	2.235(3)	2.257(4)	2.263(5)
Pd–N(1)	2.252(5)	2.169(6)	2.172(6)	2.176(8)	2.166(8)	2.17(1)	2.17(1)
Pd–C(9)	2.029(6)	2.007(8)	2.026(7)			2.26(2)	2.19(2)
Pd–C(10)				2.007(8)	2.026(7)	2.15(2)	2.14(2)
P(1)–C(1)	1.819(6)	1.835(7)	1.828(7)	1.826(9)	1.830(9)	1.84(2)	1.85(2)
N(1)–C(6)	1.464(9)	1.26(1)	1.28(1)			1.47(2)	1.50(2)
N(1)–C(7)		175.6(1)	175.4(1)	1.29(1)	1.25(1)		
I(1)–Pd–P(1)	177.7(1)	175.6(1)	175.4(1)	178.3(1)	178.9(1)		
I(1)–Pd–N(1)	97.3(1)	94.6(2)	94.1(2)	94.0(2)	95.6(2)		
I(1)–Pd–C(9)	90.2(2)	89.8(2)	89.6(2)	88.0(2)	87.3(3)		
P(1)–Pd–N(1)	84.9(1)	84.2(2)	83.8(2)	86.2(2)	85.5(2)	85.2(3)	85.1(3)
P(1)–Pd–C(9)	87.7(2)	91.6(2)	92.7(2)			167.4(6)	167.4(6)
P(1)–Pd–C(10)				91.8(3)	91.6(3)	137.1(9)	137.0(8)
P(1)–Pd–C(11)						101.6(6)	102.0(6)
N(1)–Pd–C(9)	171.7(2)	174.9(3)	175.2(3)				
N(1)–Pd–C(10)				175.9(3)	174.7(4)	136.5(9)	136.7(9)
N(1)–Pd–C(11)						173.0(7)	172.4(7)
Pd–P(1)–C(1)	103.4(2)	105.7(3)	105.7(2)	106.4(3)	107.3(3)	100.8(5)	100.8(5)
Pd–N(1)–C(6)	112.6(4)					113.0(9)	112.6(9)
Pd–N(1)–C(7)		127.7(6)	126.7(5)	123.3(7)	124.7(7)		

[a] Since the asymmetric unit contains two independent molecules, two values are reported for each entry.

C 61.50, H 4.42, N 1.50, S 3.42; found C 60.74, H 4.59, N 1.32, S 3.31.

[PdPh(PPh$_3$)(PC=NEt)]CF$_3$SO$_3$ · 0.5 C$_6$H$_6$ (**8**): Yield: 0.316 g (81%). – IR (KBr): $\tilde{\nu}$ = 3056 m cm^{-1}, 1640 m (C=N), 1563 m, 1501 m, 1436 s, 1263 vs (S–O), 694 s, 636 s. – Λ_M (MeCN): 156 ohm^{-1}cm^{2}mol^{-1}. – $C_{46}H_{40}F_3NO_3P_2PdS \cdot 0.5\ C_6H_6$ (951.33): calcd. C 61.86, H 4.57, N 1.47, S 3.37; found C 61.25, H 4.86, N 1.37, S 3.19.

[Pd(η^3-all)(PNMe$_2$)]PF$_6$ (**9**): Yield: 0.200 g {93% based on [Pd(η^3-all)Cl]$_2$}. – IR (KBr): $\tilde{\nu}$ = 3061 w cm^{-1}, 1583 w, 1474 m, 1439 m, 834 vs (P–F), 556 s. – Λ_M (MeCN): 183 ohm^{-1}cm^{2}mol^{-1}. – $C_{23}H_{25}F_6NP_2Pd$ (597.83): calcd. C 46.20, H 4.22, N 2.34; found C 46.35, H 4.30, N 2.38.

X-ray Crystal Structure Determinations: The crystals were mounted on glass fibres, coated with epoxy resin, and were transferred to a Siemens Nicolet R3m/V four-circle automated diffractometer. Using graphite-monochromated Mo-K_α radiation, accurate cell parameters were determined and diffraction intensities (up to Θ 23°) were measured. Two standard reflections were measured after every 150 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz, polarization and absorption (using ψ scans) effects.

The crystals of **3**·3/2 H_2O were found to be slightly sensitive to X-rays (decay of up to 19% during data collection) and decomposed after prolonged irradiation. Consequently, the empirical absorption correction was not applied. No unusually high correlation values were noted between any of the variables in the last cycle of full-matrix least-squares refinements on F^2 and the final difference maps were essentially featureless. Programs used and the sources of scattering factors are contained in the SHELXTL (PC version

4.20 or 5.03) software package provided by Siemens Analytical X-ray Instruments[28][29]. Some details of the data collection and refinements are given in Table 3. Selected bond distances and angles are presented in Table 4.

Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD 408513 (**1**), 408514 (**2**), 408515 (**3**·3/2 H_2O), and 408516 (**9**).

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