Palladium Complexes with a New Hemilabile Bis(oxazoline)phenylphosphonite Ligand. Characterization of an Unprecedented Chloro Palladium(II)−(η^1-Allyl) Complex[||]

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The coordination chemistry of the new, structurally characterized ligand bis(oxazoline)-phenylphosphonite (**I**, abbreviated NOPON^{Me_2}), shows its flexibility which is due to the possible formation of six-membered chelate rings. In the Pd(II) complexes [Pd(NCMe)-(NOPON^{Me_2}-*N*,*P*,*N*)](BF$_4$)$_2$, **1** (characterized by X-ray diffraction in **1**·0.5Et$_2$O·0.33MeCN), and [PdCl(NOPON^{Me_2}-*N*,*P*,*N*)](PF$_6$), **2**, this ligand behaves in a static tridentate manner, whereas in [Pd(Me)Cl(NOPON^{Me_2}-*N*,*P*)], **3**, [PdI$_2$(NOPON^{Me_2}-*N*,*P*)], **4**, [PdCl$_2$(NOPON^{Me_2}-*N*,*P*)], **5**, and the allyl complex [Pd(η^3-C$_3$H$_5$)(NOPON^{Me_2}-*N*,*P*)](PF$_6$), **6**, it displays fluxional bidentate behavior, as shown by variable-temperature NMR studies. In **3**, only the isomer in which the methyl ligand is trans to nitrogen is formed. In the related complex [Pd(η^3-C$_3$H$_5$)-(NOPON^{Me_2}-*N*,*P*)]Cl, **7**, an equilibrium has been evidenced between **7a** and **7b**, which involves coordination of the chloride and isomerization of the allyl ligand from η^3 to η^1. The latter isomer is quantitatively formed in toluene at 259 K and in the solid state. This was established using NMR spectroscopy by combined variable-temperature solution and solid-state studies. Isomer **7b** was also characterized by X-ray diffraction, a rare example of a fully characterized allyl η^1-bonding mode for Pd complexes and the first in transition metal chemistry for a mutual cis arrangement of η^1-allyl and chloride ligands, a situation relevant to intermediates involved in catalytic transformations. The tridentate coordination mode of **I** found in complexes **1** or **2** never occurred in the related alkyl or allyl complexes. This is consistent with the antisymbiotic effect between carbon and phosphorus donors, and this finding was confirmed by theoretical calculations. To understand whether the mutually cis disposition in **3** and **7b** of the chloride ligand (trans to P) and of a σ-donor ligand such as the methyl or the η^1-allyl ligand (trans to N) is intrinsic to the nature of these ligands or related in one way or another to the *P*,*N* heterobidentate nature and resulting asymmetry of the NOPON^{Me_2} ligand, DFT-B3LYP calculations were carried out on a series of isomeric structures of four- and three-coordinate chloro, methyl, and η^1-allyl Pd(II) complexes. The existence of an energetic barrier against the formation of a compound where the phosphorus atom of tridentate NOPON^{Me_2} is trans to an alkyl or η^1-allyl ligand was established.

Introduction

The design of heterotopic ligands bearing phosphorus and nitrogen or oxygen donor atoms is a field of constant ongoing research owing to the often unique properties that such ligands confer to their metal complexes in stoichiometric or catalytic reactions.[1−4] The different (stereo)electronic characteristics of the donor groups often control the reactivity at the metal site. This is nicely illustrated in, for example, the asymmetric allylic alkylation reaction catalyzed by palladium complexes[5,6] where high enantioselectivities are achieved with the *P*,*N* chelating (phosphinoaryl)oxazoline ligand.[7−9] Furthermore, hemilability by reversible decoordination of

[||] Dedicated to Prof. K. Vrieze for his numerous and outstanding contributions to chemistry.

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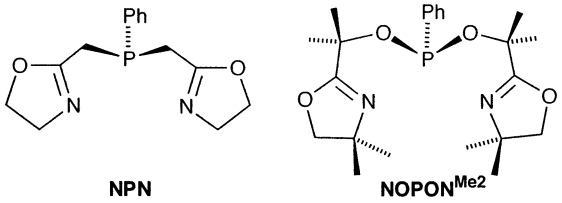
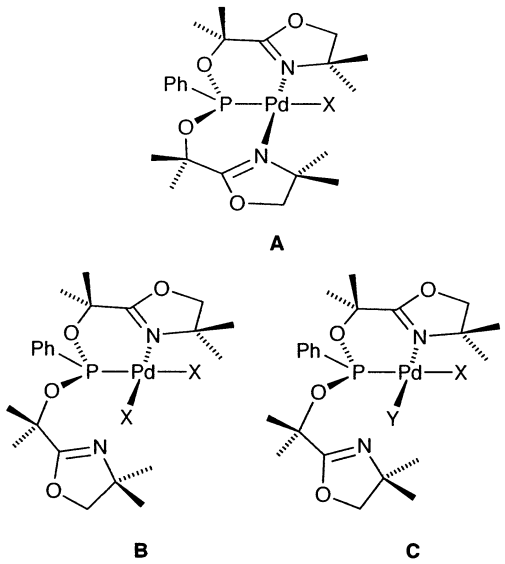
one arm of the ligand has been very successfully applied to the selective activation of small molecules.[3,4,10,11] Among the nitrogen-based ligands, oxazolines have aroused considerable interest owing to the remarkable catalytic properties of their metal complexes.[12,13] In the past decade, several groups have been interested in the study of stoichiometric and catalytic reactions promoted by complexes with *P,O*-type ligands.[1−4,10,14−21] We have recently prepared new ligands bearing phosphine and oxazoline moieties such as (oxazolinylmethyl)diphenylphosphine[22−24] and bis(oxazolinylmethyl)phenylphosphine[25] (the latter is abbreviated NPN in the following), which combine the phosphorus donor atom as a soft Lewis base with the harder nitrogen atom of the oxazoline ring (coordination of an oxazoline through the oxygen has never been observed). (Pseudo)octahedral ruthenium complexes have been characterized where the NPN ligand coordinates either as a static bidentate *N,P* chelate or as a facial (*fac*) *N,P,N* tridentate ligand, and very high catalytic activity in transfer hydrogenation of ketones was observed.[25] We now wish to report the synthesis and properties of the new heterotopic ligand bis[1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-methylethyl]phenyl phosphonite, referred to as bis(oxazoline)phenylphosphonite and abbreviated NOPON^{Me_2} in the following.



The increased flexibility offered by the ligand NOPON^{Me_2} compared to NPN, due to the larger chelate size, has led us to isolate Ru(II) complexes where the tridentate ligand adopts either a *fac* or a *mer* coordination mode.[26] We will see in this paper that NOPON^{Me_2} can exhibit tridentate or fluxional bidentate behavior in Pd(II) complexes (see **A** and **B**, Scheme 1), the latter illustrating its potentially hemilabile character. The coordination behavior of NOPON^{Me_2} will be compared to that of other multifunctional *N,N,N*-, *P,N,N*-, *P,N,P*-, or *P,P,P*-type ligands.[27−30] Differences in bonding mode and reactivity of the complexes were observed especially in structures of type **C**, where chemically different groups X and Y are in trans position to the phosphorus and nitrogen atoms, respectively (Scheme 1).

Scheme 1



Transition metal allyl complexes present a rich chemistry.[5,27] The allyl ligand can coordinate to a transition metal in three limiting ways: as a η^1-bound ligand, as a $\eta^1-\eta^3$ ligand, or as a fully η^3 ligand. The latter bonding mode is the most general, while η^1-allyl complexes have been isolated mainly with platinum,[28−30] very recently with iridium,[31] or with early transition metals.[32−34] The manner in which an allyl fragment coordinates to a transition metal center and the versatility of its coordination geometries will influence the stereochemistry of reactions proceeding via allyl intermediates.[5,27] For instance, it is well known in Pd-allyl chemistry that an $\eta^3-\eta^1-\eta^3$ mechanism may be operative and that it can be either detrimental or obligatory for enantioselection. Therefore it appears important to recognize the bonding mode of the allyl in a system in order to understand or rationalize its reactivity. Whereas numerous Pd complexes with an η^3-allyl ligand have been isolated, only few Pd complexes containing η^1-allyl ligands have been reported despite their considerable interest as either reactive species or proposed intermediates in C−C coupling reactions.[28,35−37] Recent studies have reported the isolation of either static or dynamic η^1-allyl Pd complexes formed upon *mer* coordination of strong

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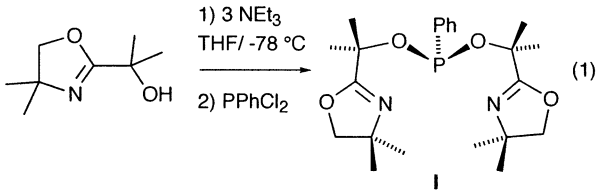
tridentate ligands.[35,36,38,39] Although NOPON^{Me_2} did not display a tridentate coordination in Pd-allyl complexes, we will see that it led to the isolation and full characterization of an unprecedented η^1-allyl chloro Pd complex in which the Pd-bound carbon atom is always trans to nitrogen.

Results

Ligand Synthesis. The synthesis of bis(2-oxazoline-4,4-dimethyl-2-hydroxydimethyl)phenylphosphonite (**I**), abbreviated NOPON^{Me_2} in the following, was performed in THF at −78 °C via a one-pot reaction between $PPhCl_2$ and a mixture of 4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole and triethylamine (3-fold excess) (eq 1). This synthetic route differs slightly from that reported by Pfaltz et al. for the synthesis of a phosphite-oxazoline ligand.[40] It is straightforward and allows ligand synthesis in gram-scale quantities.



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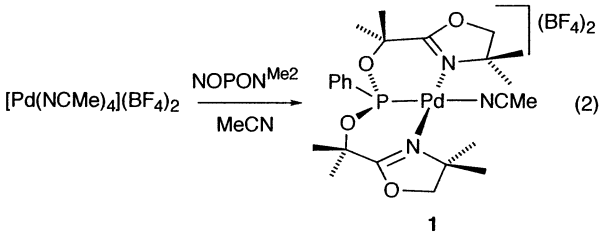
The ^{1}H NMR spectrum of NOPON^{Me_2} in $CDCl_3$ reveals a set of four singlets for the methyl protons and an AB spin system for the methylenic protons of the oxazoline. The only symmetry element in the molecule is a mirror plane which includes the phenyl ring and the phosphorus atom. The NMR spectrum is in agreement with each arm of the ligand holding enantiotopic pairs of diastereotopic methyl protons and methylene protons. The IR spectrum in a KBr pellet exhibits a strong band at 1661 cm^{-1} assigned to the ν(C═N) vibrations of the oxazoline. A single-crystal X-ray diffraction study confirmed the structure of NOPON^{Me_2} (Figure 1).

Selected bond distances and angles are given in Table 1 and will be used below for comparison with values found for this ligand in palladium complexes. The characterization of complexes with bidentate *N,P*- or tridentate *N,P,N*-NOPON^{Me_2} was of particular interest.

Pd Complexes with NOPON^{Me_2} as a Tridentate *N,P,N* Ligand. Reaction of ligand **I** with [Pd(NCMe)$_4$](BF$_4$)$_2$ in acetonitrile yielded [Pd(NCMe)(NOPON^{Me_2}-*N,P,N*)](BF$_4$)$_2$, **1**, in 90% yield (eq 2).



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Its IR spectrum in acetonitrile shows only one ν(C═N) band at 1622 cm^{-1}, consistent with the coordination of both oxazolines to Pd. Phosphorus coordination leads to a ^{31}P{^{1}H} NMR upfield shift of 44 ppm. The ^{1}H NMR spectrum of complex **1** shows an AB spin system for the methylenic protons of the oxazoline rings. This indicates the existence of a mirror plane in the molecule which exchanges both arms of the ligand. Four resonances, three singlets and one doublet, correspond to the eight methyl groups of the molecule. The doublet arises from a $^4J_{PC}$ of 2.0 Hz between the protons of one methyl goup of the OC(CH_3)$_2$ fragment and the phosphorus atom, as shown by ^{1}H{^{31}P} NMR experiments. There are four well-separated ^{13}C{^{1}H} NMR resonances for the methyl groups, two of which correspond to the two nonequivalent OC(CH_3)$_2$ methyls and exhibit a doublet at δ 25.0 and 30.0, with $^3J_{PC}$ = 7.8 and $^3J_{PC}$ = 2.9 Hz, respectively. The C═N carbon appears as a doublet at 174.2 ppm ($^3J_{PC}$ = 8.7 Hz), which is downfield shifted by 8 ppm compared to uncoordinated **I** (see Table 2 for comparative purposes). From these data we conclude that the ligand coordinates in a tridentate fashion.

An X-ray diffraction study on single crystals of **1**·0.5Et$_2$O·0.33MeCN confirmed the geometry of the molecule (Figure 2, Table 3). There is no symmetry

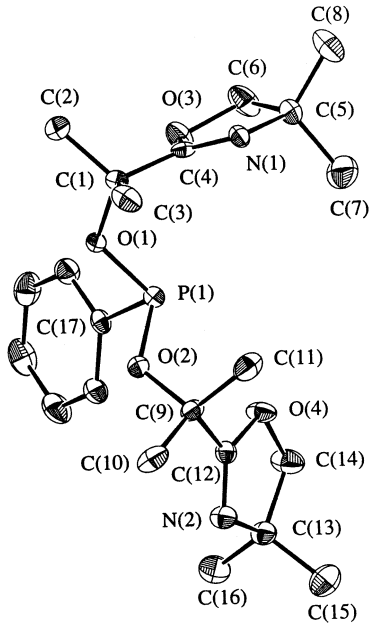

Figure 1. ORTEP view of the structure of the ligand NOPON^{Me_2} (**I**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Ligand NOPON^{Me_2} (I)

P(1)−O(1)	1.650(1)	C(4)−O(3)	1.375(2)
P(1)−O(2)	1.644(2)	C(4)−N(1)	1.260(3)
P(1)−C(17)	1.834(2)	C(4)−C(1)	1.513(3)
		O(1)−C(1)	1.460(2)
O(1)−P(1)−C(17)	94.24(8)	C(4)−C(1)−O(1)	110.0(2)
O(2)−P(1)−C(17)	96.76(9)	P(1)−O(1)−C(1)	121.3(1)
O(1)−P(1)−O(2)	101.26(7)	O(3)−C(4)−N(1)	119.1(2)
C(5)−N(1)−C(4)	106.3(2)	O(3)−C(4)−C(1)	114.1(2)
N(1)−C(4)−C(1)	126.9(2)		

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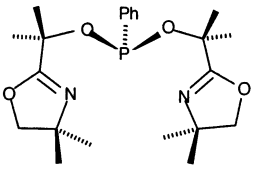
Table 2. Selected $^{13}C\{^1H\}$ and IR Data for Ligand I and Complexes 1−7[a]



I

compound	$OC(CH_3)_2$	$OC(CH_3)_2$	C=N	OCH_2	$NC(CH_3)_2$	$NC(CH_3)_2$	ν(C=N)
$NOPON^{Me_2}$ [b,f] (**I**)	75.6	27.2/28.15	167.2	79.1	67.3	27.2, 28.15	1661
$[Pd(NCMe)(NOPON^{Me_2}\text{-}N,P,N)](BF_4)_2$ [c,g] (**1**)	86.5	25.0/30.0	174.2	83.8	72.7	27.0, 28.5	1622
$[PdCl(NOPON^{Me_2}\text{-}N,P,N)](PF_6)$ [d,f] (**2**)	83.7	25.3/29.6	172.5	84.1	73.0	27.1, 28.5	1618
$[Pd(Me)Cl(NOPON^{Me_2}\text{-}N,P)]$ [b,f] (**3**)	79.8, 77.4	26.7−29.9	169.5, 166.0	82.4, 79.8	71.4, 67.8	26.7−29.9	1660, 1634
$[PdI_2(NOPON^{Me_2}\text{-}N,P)]$ (**4**)							
293 K [d,g]	83.2	29.0−29.8	169.7	83.2	71.2	29.0−29.8	1662, 1631
172 K [d,h]	84.6, 80.9	28.7−30.4	172.6, 166.6	84.9, 81.5	73.3, 69.4	28.7−30.4	
$[PdCl_2(NOPON^{Me_2}\text{-}N,P)]$ [b,f] (**5**)	80.0−84.0	27.4−27.8	168.0−170.0	80.0−84.0	70.0−71.0	27.4−27.8	1662, 1631
$[Pd(C_3H_5)(NOPON^{Me_2}\text{-}N,P)](PF_6)$ (**6**)							
293 K [d,f]	81.15	27.8−28.5	168.5	80.3	68.9	27.8−28.5	1662, 1630
solid state [h]	77.0−82.0	27.5−32.1	171.9, 164.0	77.0−82.0	69.5, 67.8	27.5−32.1	
$[Pd(C_3H_5)Cl(NOPON^{Me_2}\text{-}N,P)]$ (**7**)							
293 K [b,g] (**7a** ⇌ **7b**)	78.7	27.1/27.15	167.0	79.5	67.9	26.6/26.9	1659, 1637
177 K [d,h] (**7a**)	78.4, 78.0	26.5−28.5	170.5, 164.2	80.8, 79.8	69.1, 66.7	26.5−28.5	
259 K [e,h] (**7b**)	77.8	27.0−28.8	167.5	80.2	69.3	27.0−28.8	
solid state [h] (**7b**)	78.2, 74.2	24.3−29.6	169.7, 163.2	81.0, 76.0	69.9, 66.8	24.3−29.6	

[a] Chemical shifts in ppm, and IR absorptions in cm^{-1}. [b] $CDCl_3$. [c] Acetonitrile-d_3. [d] CD_2Cl_2. [e] Toluene-d_8. [f] 50.3 MHz. [g] 75.4 MHz. [h] 125.7 MHz.

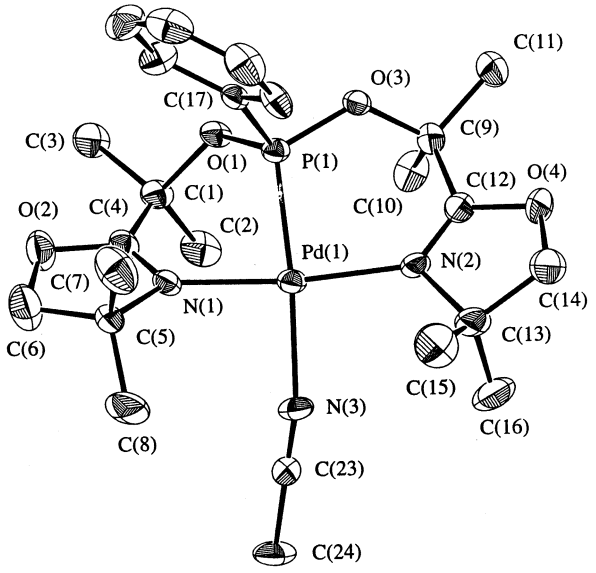


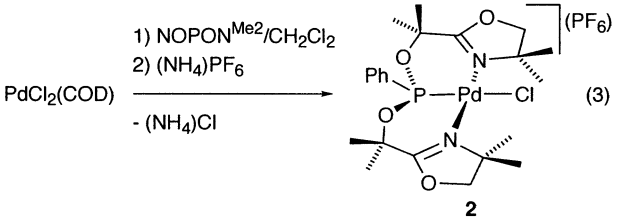
Figure 2. ORTEP view of the structure of $[Pd(NCMe)(NOPON^{Me_2}\text{-}N,P,N)](BF_4)_2$ in **1**·0.5Et_2O·0.33MeCN.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Pd(NCMe)(NOPON^{Me_2}\text{-}N,P,N)](BF_4)_2$ (1)

Pd(1)−N(1)	2.038(3)	C(4)−N(1)	1.278(4)
Pd(1)−N(2)	2.039(3)	C(4)−C(1)	1.496(6)
Pd(1)−N(3)	2.104(3)	C(1)−O(1)	1.484(4)
Pd(1)−P(1)	2.174(1)	O(1)−P(1)	1.579(2)
		C(4)−O(2)	1.345(4)
P(1)−Pd(1)−N(1)	83.28(9)	N(1)−C(4)−O(2)	117.1(4)
P(1)−Pd(1)−N(2)	90.40(9)	O(2)−C(4)−C(1)	116.9(4)
N(1)−Pd(1)−N(3)	91.1(1)	N(1)−C(4)−C(1)	125.9(4)
N(3)−Pd(1)−N(2)	96.0(1)	C(4)−C(1)−O(1)	107.3(3)
N(1)−Pd(1)−N(2)	172.1(1)	C(1)−O(1)−P(1)	126.1(2)
P(1)−Pd(1)−N(3)	167.6(1)	O(1)−P(1)−Pd(1)	109.20(9)
Pd(1)−N(3)−C(23)	159.3(3)	O(3)−P(1)−Pd(1)	114.18(9)

element in the molecule. The coordination around the metal center approximates a square-planar geometry in which $NOPON^{Me_2}$ forms a tridentate ligand. It can be compared to that in other Pd complexes containing a tridentate triphosphine ligand.[41,42] The nonideal geometry is reflected by the different structural features of the two six-membered ring chelates. The N(2)−Pd(1)−P(1) and N(1)−Pd(1)−P(1) bite angles are 90.40(9)° and 83.28(9)°, respectively; this decrease is accompanied by a pinch of the Pd(1)−P(1)−O(1) angle of 5°. The planes Pd, N(1), C(1), C(4), C(5), and O(2) and Pd, N(2), C(9), C(12), C(13), and O(4) form an angle of 23.4°, which causes the methyl substituents of the oxazolines to be eclipsed. This could explain the displacement of the Pd−N(3) vector out of the plane defined by Pd(1), P(1), N(1), and N(2), such that N(3) is ca. 0.40 Å above this plane, as well as the remarkably small Pd(1)−N(3)−C(23) angle of 159.3(3)°, far from the expected 180°.

To further establish the characteristic spectroscopic features associated with a tridentate behavior of **I**, $[PdCl(NOPON^{Me_2}\text{-}N,P,N)](PF_6)$ (**2**) was synthesized, in a one-pot procedure, by reacting **I** with $[PdCl_2(COD)]$ followed by the addition of 1 equiv of $(NH_4)PF_6$ (eq 3).



2

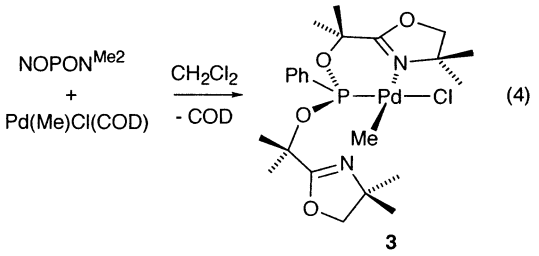
The spectroscopic data are similar to those for **1** (see Table 2). The oxazoline methylenic protons form an enantiotopic pair of diastereotopic protons revealed by the corresponding AB spin system at δ 4.30 and 4.45. The four diastereotopic methyl groups appear in the ^1H NMR spectrum as three singlet peaks and one doublet.

(41) Barbaro, P.; Togni, A. *Organometallics* **1995**, *14*, 3570.
(42) Wander, S. A.; Miedaner, A.; Noll, B. C.; Barkley, R. M.; DuBois, D. L. *Organometallics* **1996**, *15*, 3360.

The latter, at δ 1.80, was shown by $^1H\{^{31}P\}$ NMR experiments to be coupled to the phosphorus atom by a $^4J_{PH}$ of 2.0 Hz.

We then attempted to isolate and characterize complexes exhibiting a somewhat restricted bidentate coordination mode for ligand **I**.

Pd(II) Complexes with Bidentate and Fluxional Bidentate NOPON^{Me_2}. The reaction of [Pd(Me)Cl(COD)] (COD = 1,5-cyclooctadiene) with NOPON^{Me_2} afforded [Pd(Me)Cl(NOPON^{Me_2}-*N*,*P*)], **3** (eq 4), in 57% isolated yield.

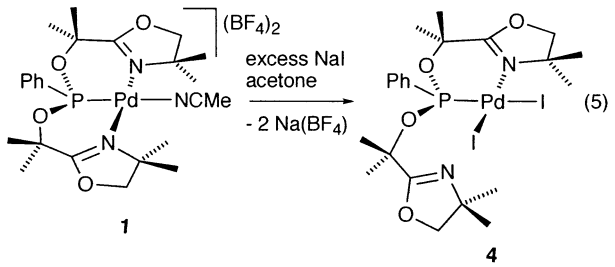


(4)

3

Its two IR bands (KBr pellet) at 1660 and 1634 cm^{-1} are assigned to the C=N vibrations of the uncoordinated and coordinated oxazoline, respectively (Table 2). The Pd−CH_3 protons appear in the ^1H NMR spectrum as a doublet at δ 0.75 ppm with a $^3J_{PH}$ = 2.9 Hz indicative of a cis relationship between the phosphorus atom and the Pd−CH_3 group. As expected for a different behavior of the two oxazoline moieties, their methylenic protons appear at room temperature as two separate AB spin systems integrating for two protons each. Six singlets are observed in the methyl region, four integrate for three protons each and two account for six protons each. The ^1H NMR spectrum of **3** at 223 K shows eight singlets for the methyl protons, integrating for three protons each. The fact that at room temperature only six rather than eight singlets are observed results from accidental coincidence. The $^{13}C\{^1H\}$ NMR spectrum at room temperature shows two resonances for the oxazoline C=N at δ 169.5 and 166.0 ppm, the latter being identical with the chemical shift of the imine carbon in the free ligand. Similarly, the other oxazoline carbon atoms appear as two sets of resonances, with one being identical to those for the free ligand. The methyl carbons give rise to overlapping singlets and doublets from δ 26.7 to 29.9 ppm. These data are consistent with an asymmetric coordination mode of NOPON^{Me_2} and account for the existence of a coordinated and a dangling oxazoline arm.

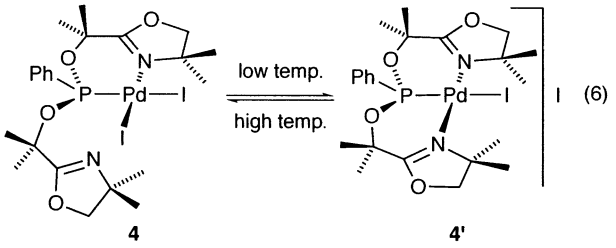
We felt it interesting to compare the behavior of **3** with that of the more symmetrical complex [PdI_2(NOPON^{Me_2}-*N*,*P*)], **4**. The latter was prepared by reaction of **1** with excess NaI in acetone (eq 5).



(5)

1 **4**

There are two bands at 1662 and 1631 cm^{-1} in the IR spectrum of **4** in THF, for the ν(C=N) vibrations of the uncoordinated and coordinated oxazolines, respectively. In contrast to the case of **3**, the ^1H NMR spectrum exhibits only one AB spin system at δ 4.02 and 4.06 ppm, which accounts for the four methylenic protons. Consistently, the methyl protons are observed as four singlets. Each type of carbon atom gives rise to a singlet in the $^{13}C\{^1H\}$ NMR spectrum. These NMR data indicate the equivalence of the two oxazoline arms, although they are not consistent with the static tridentate coordination mode established for **1** and **2**. This led us to envisage a rapid fluxional behavior for the NOPON^{Me_2} ligand, and we therefore performed low-temperature ^1H and $^{13}C\{^1H\}$ NMR experiments. At 172 K two species were indeed found to coexist (eq 6).



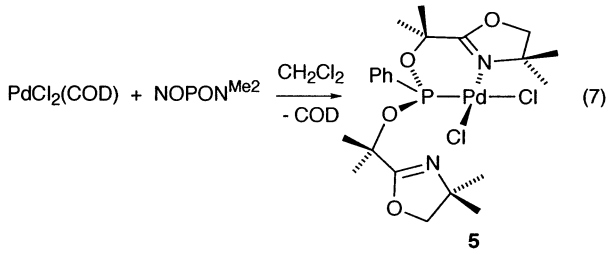
(6)

4 **4'**

The major compound at 172 K shows a ^1H NMR spectrum very similar to that of complex **3** at 223 K, with two AB spin systems integrating for two protons each and eight lines in the methyl region. The $^{13}C\{^1H\}$ NMR spectrum exhibits resonances corresponding to coordinated and uncoordinated oxazolines. When the temperature was raised to 227 K, the two N*C*$(CH_3)_2$ singlets coalesced into one resonance. The same observation was made with all the other carbon atoms and was particularly clear for the C=N resonance. The activation barrier calculated for this oxazoline exchange is $\Delta G^{\ddagger}$ = ca. 42 kJ·mol^{-1}.[43] The minor isomer **4′** in eq 6 (10%) shows ^1H and $^{13}C\{^1H\}$ resonances very similar to those of compounds **1** or **2**. Its $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at δ 102.5 (to be compared with δ 116.0 for **4**), a chemical shift almost identical to that of the complex formed upon addition of 1 equiv of $(NH_4)PF_6$ to a CD_2Cl_2 solution of **4**. Thus, compound **4′** would correspond to the cationic complex [PdI(NOPON^{Me_2}-*N*,*P*,*N*)]I. Upon warming, the intensity of its resonances decreases and eventually vanishes at 273 K. These experiments show that the room-temperature NMR data, eventhough they first seem to correspond to a compound with a certain degree of symmetry, relate in fact to an asymmetric structure in which fast exhange of the coordinated and dangling oxazolines occurs on the NMR time scale. Such a mechanism does not allow the exchange of the methyl and methylenic protons below and above the plane of the molecule; thus the OCH_2 protons appear as an AB spin system at room temperature. The different time scales of the IR and NMR experiments account for the observation of two different oxazoline rings in the IR spectrum.

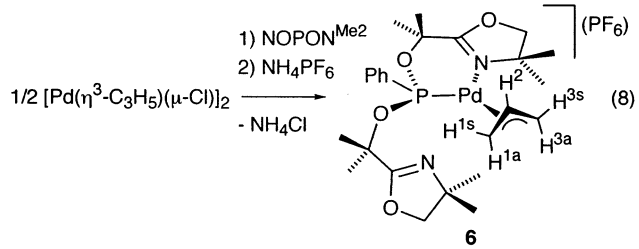
(43) Sandström, J. In *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

For comparative purposes, we prepared [$PdCl_2$-($NOPON^{Me_2}$)] (**5**) according to (eq 7).



Its spectroscopic data are very similar to those of **4**. Thus, the ^{1}H NMR spectrum at room temperature shows only one AB spin system assigned to the four methylenic protons of the oxazolines. The methyl region exhibits four lines including a broad singlet for the diastereotopic $NC(CH_3)_2$ methyls. This is due to the fact that the two methyls each coalesce at a different temperature and thus appear with a different line shape at a given temperature. This ^{1}H NMR spectrum at room temperature is comparable to that of **4** at 249 K. In the room-temperature $^{13}C\{^1H\}$ NMR spectrum, all resonances except the aryl carbons are broad, being close to coalescence, and slightly downfield shifted when compared to the free ligand. Again, this spectrum is similar to that of **4** at 249 K. The IR and NMR data of **5** indicate that the ligand behaves as a fluxional *N*,*P* chelate, as in **4**. Upon cooling to 177 K two species were found to coexist, the minor one corresponds to a static [$PdCl_2$($NOPON^{Me_2}$-*N*,*P*)], while the major exhibits ^{1}H NMR features identical to those of [PdCl($NOPON^{Me_2}$-*N*,*P*,*N*)](PF_6), **2**.

We then felt it interesting to investigate the behavior of $NOPON^{Me_2}$ complexes in which an *additional* ligand could also display changes in hapticity and examine their mutual influence. The allyl ligand was a candidate of choice. Complex [Pd(η^3-C_3H_5)($NOPON^{Me_2}$-*N*,*P*)](PF_6), **6**, was isolated in 71% yield in two steps from the reaction of 2 equiv of $NOPON^{Me_2}$ with 1 equiv of [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ followed by the addition of 2 equiv of NH_4PF_6 (eq 8).



The two IR bands at 1662 and 1630 cm^{-1} correspond to the C=N vibrations of the uncoordinated and coordinated oxazoline, respectively. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **6** exhibit sharp resonances for the $NOPON^{Me_2}$ ligand with features similar to those in **4**. The three allyl carbons appear at three different chemical shifts (Table 4).

The terminal CH_2 carbons show doublets at δ 54.7 ($^2J_{PC}$ = 6.4 Hz) and 78.8 ppm ($^2J_{PC}$ = 40.1 Hz) for the carbon cis and trans to phosphorus, respectively. This assignment is consistent with the larger trans influence

Table 4. $^{13}C\{^1H\}$ NMR Data (*J* in Hz in parentheses) for the Allyl Protons in 6 and 7a/b[a]

compound	C^1	C^2	C^3
[Pd(C_3H_5)($NOPON^{Me_2}$-*N*,*P*)](PF_6) (**6**)			
solid state (η^3-allyl)	50−60	123.0	75−85
298 K, CD_2Cl_2[b]	54.7 (6.4)	121.5 (8.8)	78.8 (40.1)
[Pd(C_3H_5)Cl($NOPON^{Me_2}$-*N*,*P*)] (**7**)			
solid state (η^1-allyl) (7**b**)	22.0	143.4	110.3
298 K, CD_2Cl_2[b] (**7a** ⇌ **7b**)	37.5 (br)	132.2 (6.7)	96.0 (br)
177 K, CD_2Cl_2[b] (**7a**)	52.5	121.9 (br)	78.2
259 K, toluene-d_8[b] (**7b**)	27.8	143.0	108.5

[a] Chemical shifts given in ppm. [b] At 125.7 MHz.

of the P donor compared to N[44] and with literature data for complexes of the type [Pd(η^3-C_3H_5)(*P*,*N*)]$^+$.[45,46] The five protons of the allyl ligand appear as four resonances in the ^{1}H NMR spectrum. Two protons exhibit two dd (with appearance of triplet) at δ 4.95 and 3.75 due to $^3J_{HH}$ with the central allylic proton of 7.5 and 13.8 Hz, respectively, and to a $^3J_{PH}$ coupling of 8.0 and 14.0 Hz, respectively, as shown by homonuclear decoupling and $^1H\{^{31}P\}$ NMR experiments. While the ^{1}H COSY NMR spectrum shows that these two protons are not coupled to each other, the $^1H-^{13}C$ HMQC experiments indicate they are held by the same carbon that is trans to phosphorus and resonates at δ 78.8. These data allow us to assign them to the allylic protons H^{3s} and H^{3a} respectively (see **6** for labeling). The H^{1s} and H^{1a} protons appear as a broad single resonance integrating for two protons in the 500.13 MHz ^{1}H NMR spectrum at room temperature but exhibit a broad doublet with a $^3J_{H^1H^2}$ of 6.8 Hz in the 300.16 MHz spectrum. This coupling to the central allylic proton H^2 was determined by homonuclear decoupling ^{1}H experiments. That the syn and anti protons appear as a broad resonance is consistent with an $\eta^3-\eta^1$ allyl isomerization through selective opening of the Pd−C(3) bond trans to the phosphorus atom, followed by rotation about the C(1)−C(2) bond.[5,47]

We next examined the situation where the chloride ligand has not been replaced by PF_6^- and could therefore influence the dynamic behavior of the ligands by coordination to the palladium. Mixing [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ with 2 equiv of $NOPON^{Me_2}$ yielded complex **7** in 93% yield (eq 9, Scheme 2). The IR spectrum in CH_2Cl_2 exhibits two bands at 1659 and 1637 cm^{-1} assigned to the C=N vibrations of uncoordinated and coordinated oxazolines, respectively. We will first examine ^{1}H and $^{13}C\{^1H\}$ NMR experiments performed at low temperature in order to slow any fluxional process additional to that of $NOPON^{Me_2}$ itself (see **4** above). At 177 K, the ^{1}H NMR resonances of the $NOPON^{Me_2}$ ligand in **7** correspond to two broad AB spin systems for two inequivalent sets of OCH_2 protons and eight singlets in the methyl region. This is similar to the low-temperature NMR data for **3** or **4** except that, in contrast with the latter, no additional species exhibiting a tridentate coordination mode of $NOPON^{Me_2}$ could be detected in

(44) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.
(45) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620.
(46) Park, J.; Quan, Z.; Lee, S.; Ahn, H.; Cho, C.-W. *J. Organomet. Chem.* **1999**, *584*, 140.
(47) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067.

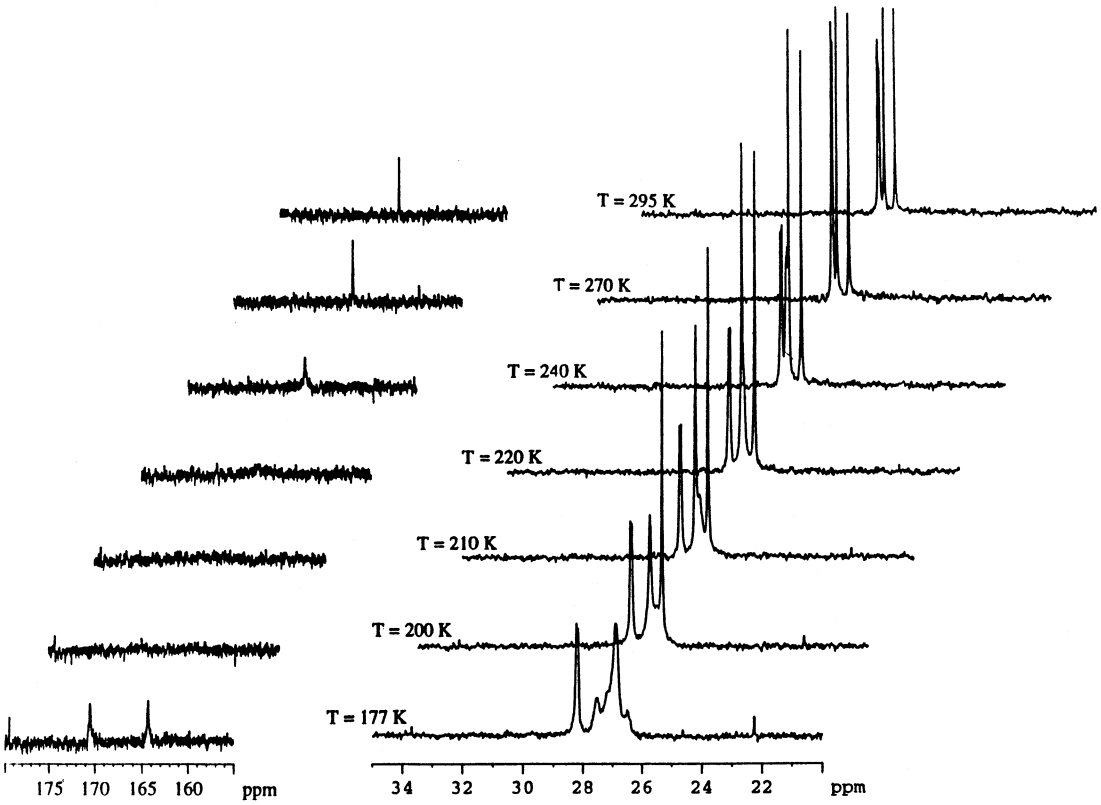
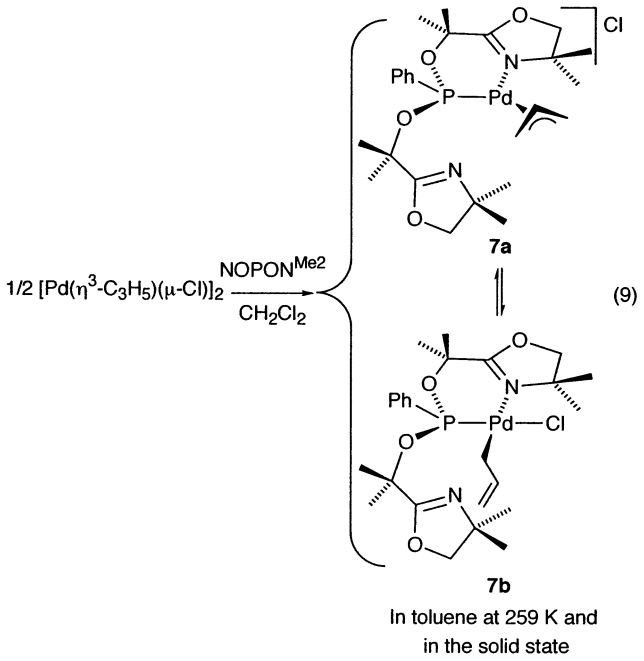


Figure 3. Variable-temperature $^{13}C\{^1H\}$ NMR spectrum of **7** in the oxazoline region.

Scheme 2



7. At 177 K the allyl protons and carbons of **7** exhibit the same pattern and chemical shifts as those of **6** at room temperature (see Table 4).

Therefore, at low temperature the allyl fragment adopts an η^3 bonding mode, while NOPON^{Me_2} behaves as a bidentate *N*,*P* chelate as depicted in **7a**. For clarity, we shall describe first the fluxional behavior of NOPON^{Me_2} and then that of the allyl ligand. The ^1H and $^{13}C\{^1H\}$ NMR spectra of NOPON^{Me_2} in **7a** change on raising the solution temperature (see Figures 3−5). In the variable-temperature $^{13}C\{^1H\}$ NMR spectra the two singlets at δ 69.1 and 66.7 ppm for the two OCH_2 carbons from coordinated and uncoordinated oxazoline, respectively, coalesce at 205 K to give an averaged broad singlet, which sharpens upon further increase of the temperature (see Figure 5). A similar feature is observed for the two singlets of the C═N carbons from coordinated and uncoordinated oxazolines (see Figure 3).

The eight methyl singlets in the variable-temperature ^1H NMR spectra at 177 K give rise to four singlets above 220 K. Two coalescence temperatures can be observed: at 200 K for the $NC(CH_3)_2$ protons at δ 1.35 and 0.92 ppm and 195 K for the $OC(CH_3)_2$ protons at δ 1.50 and 1.80 ppm. The four singlets observed at 220 K sharpen upon further increase of the temperature (see Figure 4). These variable-temperature ^1H NMR and $^{13}C\{^1H\}$ NMR data establish the fast exchange between coordinated and dangling oxazolines and provide an estimate of the activation barrier $\Delta G^{\ddagger}$ for the oxazoline exchange of ca. 38 kJ·mol^{-1}.[43] This situation is similar to that described with **4**. Looking now at the allyl ligand, we also find that the ^1H and $^{13}C\{^1H\}$ NMR spectra are temperature dependent. Upon raising the temperature from 177 to 295 K, the resonances of the terminal carbons shift in opposite direction from 52.5 to 37.5 ppm for the carbon cis to P and from 78.2 to 96 ppm for the C trans to P, and they are broad at room temperature (see Figure 5).

Similarly, the central carbon resonance is downfield shifted from 121.9 to 132.2 ppm, but in contrast to C^1 and C^3 it sharpens upon warming (d, $^3J_{PC}$ = 6.7 Hz). The chemical shifts of the η^3-allyl carbons progressively move with increasing temperature toward those of a static η^1-allyl structure (see below for characterizing data of the η^1-allyl form). In the variable-temperature ^1H NMR spectra the broad signal for the syn and anti

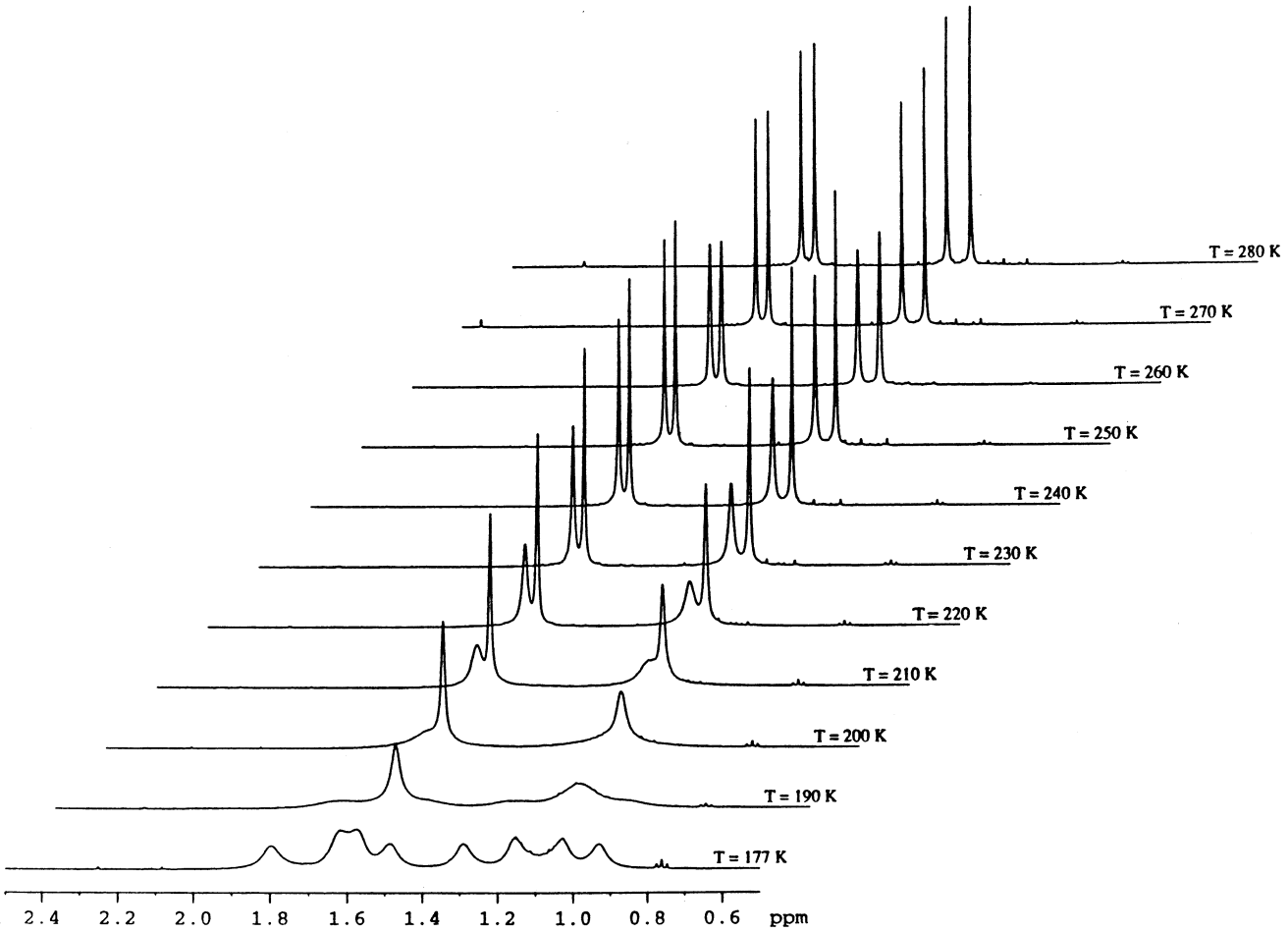


Figure 4. Variable-temperature ^{1}H NMR spectrum of **7** in the oxazoline region.

H^1 protons sharpens upon warming to form at 230 K a well-resolved doublet integrating for two protons. At higher temperature, the doublet broadens to become very broad at room temperature. The well-resolved apparent triplets for the allylic H^3 protons at 177 K broaden above 250 K. The central allylic proton, which exhibits a complex multiplet due to couplings to the H^{1s}, H^{1a}, H^3, and P atoms, appears above 270 K as a doublet of quintuplets with a $^3J_{HH}$ of 10.6 Hz and a $^3J_{PC}$ of 1.7 Hz. This pattern is consistent with an AB_4X (A = B = H, X = P) spin system where the four terminal protons have become equivalent. Fast equilibrium between η^3- and η^1-allyl is known to occur in Pd-allyl complexes and could account for the equivalence of the allyl protons in compound **7** at room temperature. Due to decomposition of the complex in CD_2Cl_4 solution above 333 K, we could not observe the end of the coalescence phenomenon for the terminal allylic protons and carbons.

Replacing the NMR solvent CD_2Cl_2 with toluene-d_8 allowed the observation at 259 K of the allyl fragment in a static η^1-bonding mode, as shown by the characteristic $^{13}C\{^1H\}$ NMR chemical shifts at 27.8, 108.5, and 143.0 for the Pd−CH_2, =CH_2, and HC= carbons, respectively (see for example, Mo−CH_2−CH=CH_2, 32.8, 144.9, 106.1 ppm; Pt−CH_2−CH=CH_2, 12.8, 143.0, 111.0 ppm).[30,36,48] The allyl protons were assigned unambiguously by HETCOR $^1H/^{13}C$ NMR experiments and correspond to a static η^1-allyl ligand. At room temperature the ^{1}H NMR spectrum exhibit broad resonances for the allylic resonances. Again raising the temperature in order to observe the end of the coalescence phenomena resulted in the decomposition of the complex at temperatures above 333 K.

Variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy did not provide additional information about the coordination mode of the allyl ligand since the chemical shifts of **7** in toluene at 203 K (δ 137.7) and at 258 K (δ 136.7) are not very different from the values at room temperature (δ 135.7) or in CH_2Cl_2, either at 203 K (δ 135.8), 258 K (δ 134.7), or room temperature (δ 133.0).

An X-ray diffraction study showed the complex to adopt structure **7b** in the solid state, a rare example of a fully characterized allyl η^1-bonding mode for Pd complexes[39] and the first in transition metal chemistry for a mutual cis arrangement of η^1-allyl and chloride ligands (see below).

The far-IR spectrum of crystals of [Pd(η^1-C_3H_5)Cl-(NOPON^{Me_2}-*N*,*P*)] is identical to that of the powder obtained after workup, confirming that the complex isolated in the solid has the same structure as in the single crystals. By comparison with the far-IR spectra of [Pd(η^3-C_3H_5)(NOPON^{Me_2}-*N*,*P*)](PF_6) and [Pd(Me)Cl-(NOPON^{Me_2}-*N*,*P*)], the strong band at 287 cm^{-1} in **7b** is assigned to the ν(Pd−Cl) vibration.[44] Furthermore, we recorded a solid state $^{13}C\{^1H\}$ NMR CP-MAS spectrum of [Pd(η^1-C_3H_5)Cl(NOPON^{Me_2}-*N*,*P*)]. The allyl ligand exhibits three resonances at δ 143.4, 110.3, and 21.0

(48) Bailey, N. A.; Kita, W. G.; McCleverty, J. A.; Murray, A. J.; Mann, B. E.; Walker, N. W. J. *J. Chem. Soc., Chem. Commun.* **1974**, 592.

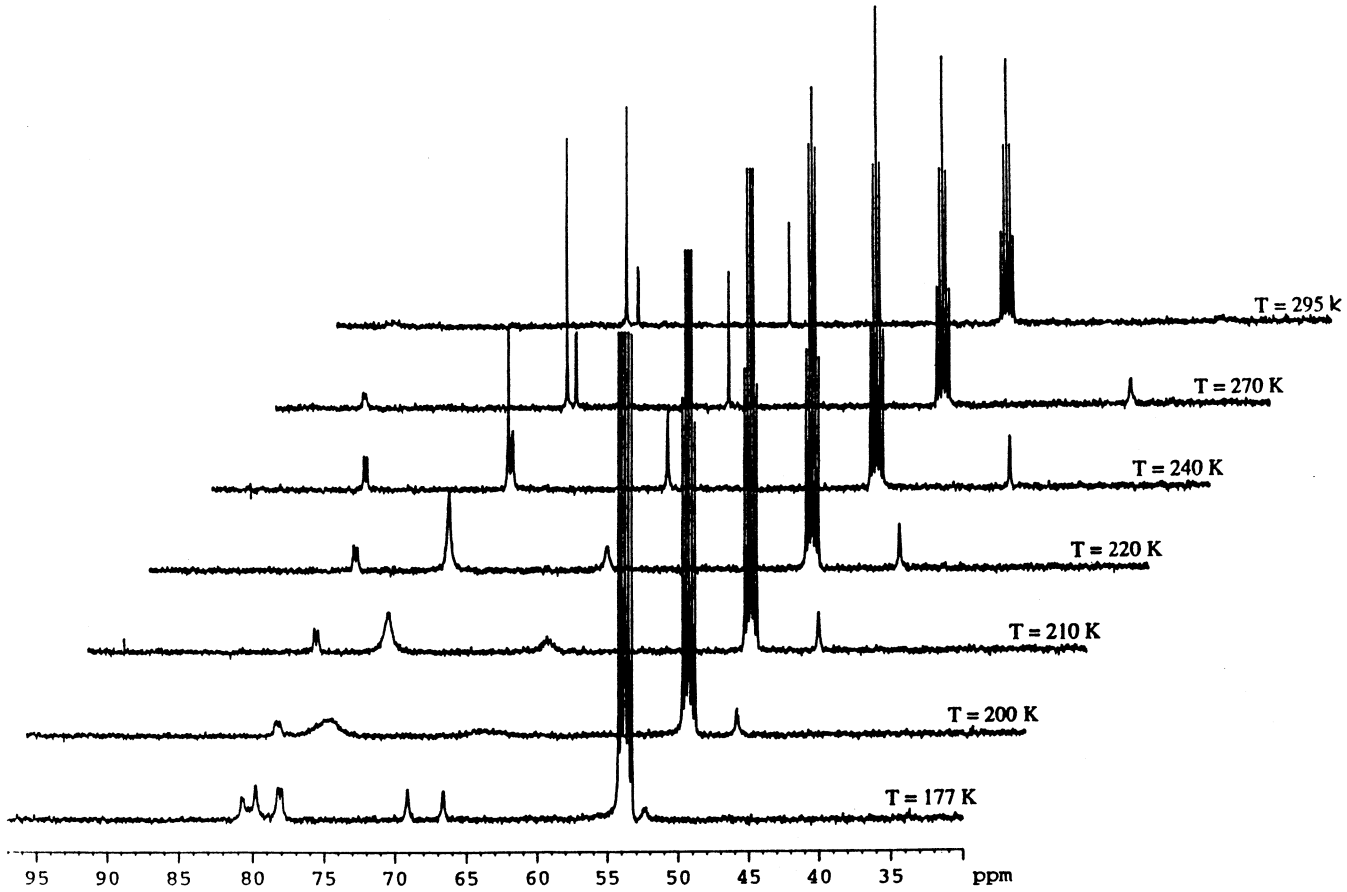


Figure 5. Variable-temperature $^{13}C\{^1H\}$ NMR spectrum of **7** in the allyl region.

ppm assigned to the CH, olefinic CH_2, and Pd−CH_2 carbons, respectively. These data are in agreement with the solution $^{13}C\{^1H\}$ NMR data on toluene-d_8 at 259 K for complexes that show a static η^1-C_3H_5 ligand. For comparison, we performed a solid state ^{13}C CP-MAS NMR study of [Pd(η^3-C_3H_5)(NOPON^{Me_2}-*N*,*P*)](PF_6) and found that the allylic carbons appear indeed in the expected range for an η^3-bonding mode at chemical shifts similar to those found in the solution NMR spectrum. Furthermore, the carbon chemical shifts of the NOPON^{Me_2} ligand in **7b** in the solid state NMR spectra are similar to those observed at 177 K in solution, thus confirming the occurrence of a frozen bidentate behavior for the NOPON ligand.

The structure of complex **7b** was determined by X-ray diffraction. It approximates square-planar geometry, the distortion arising from the angles P−Pd−C(23) and N(1)−Pd−Cl of 85.99(6)° and 95.83(4)°, respectively (Figure 6, Table 5).

It confirms the cis arrangement of the η^1-allyl fragment and the phosphorus atom. The N(1)−Pd−P angle in the six-membered ring of 91.95(4)° is similar to the larger of the two P−Pd−N angles of NOPON^{Me_2} in compound **1**. The Pd−C(23) and Pd−Cl bond distances and P−Pd−N(1) angle are similar to those in [Pd(Me)Cl(*P*,*N*)], where *P*,*N* is a six-membered ring phosphinoamine ligand.[49] The C−C bond distances and angles within the allyl ligand are consistent with other examples of transition metal η^1-allyl complexes described in the literature.[29−32,35,39,50]

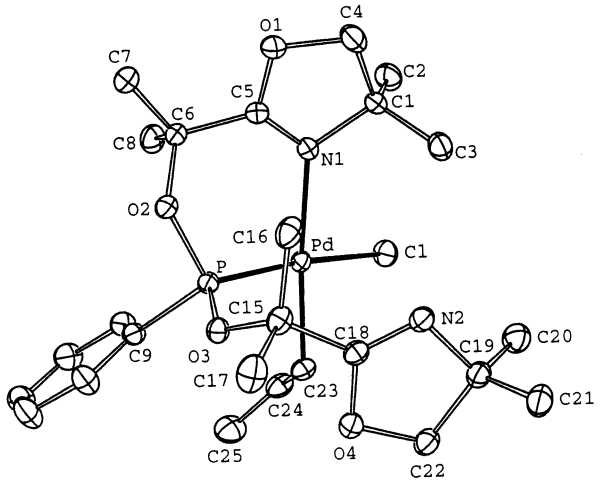


Figure 6. ORTEP view of the structure of [Pd(η^1-C_3H_5)Cl(NOPON^{Me_2}-*N*,*P*)], **7b**.

Discussion

While the preparation of palladium complexes with the new NOPON^{Me_2} ligand **I** is straightforward and can be performed in good to high yields, their characterization requires special attention, owing to the possible occurrence of a fluxional bidentate coordination mode.

(49) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937.

(50) Huffman, J. C.; Laurent, M. P.; Kochi, J. K. *Inorg. Chem.* **1977**, *16*, 2639.

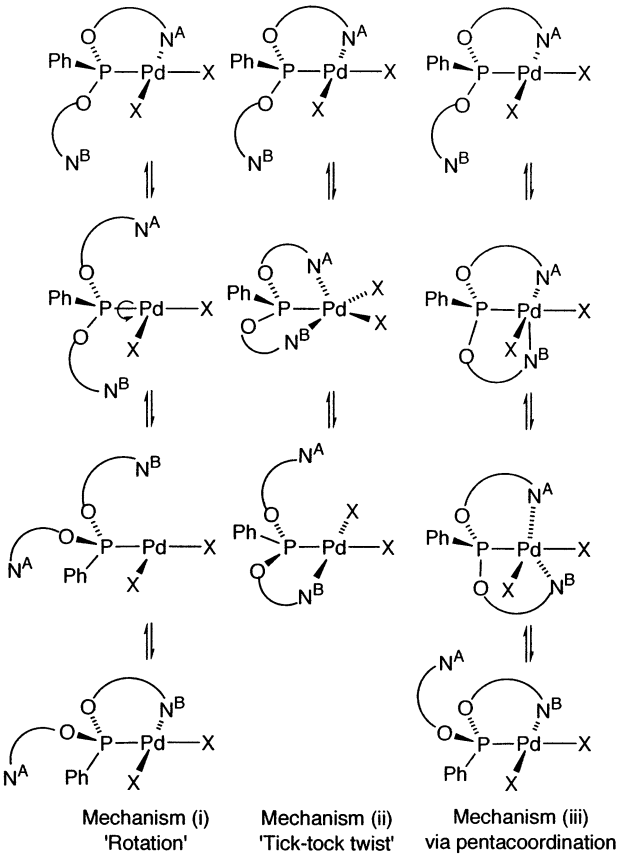
Table 5. Selected Bond Distances (Å) and Angles (deg) for [Pd(η^1-C_3H_5)Cl(NOPON^{Me_2}-*N*,*P*)], 7b

Pd−Cl	2.3944(5)	C(6)−C(5)	1.518(3)
Pd−C(23)	2.071(2)	C(5)−N(1)	1.279(3)
Pd−P	2.1782(5)	C(5)−O(1)	1.334(2)
Pd−N(1)	2.183(2)	P−O(3)	1.606(1)
C(23)−C(24)	1.469(3)	O(3)−C(15)	1.459(2)
C(24)−C(25)	1.341(1)	C(15)−C(18)	1.516(3)
P−O(2)	1.621(1)	C(18)−N(2)	1.264(3)
O(2)−C(6)	1.467(2)	C(18)−O(4)	1.316(2)
Cl−Pd−N(1)	95.83(4)	Pd−P−O(2)	113.62(2)
N(1)−Pd−P	91.95(4)	P−O(2)−C(6)	125.8(1)
P−Pd−C(23)	85.99(6)	O(2)−C(6)−C(5)	108.9(1)
C(23)−Pd−Cl	87.08(6)	C(6)−C(5)−N(1)	125.8(2)
P−Pd−Cl	170.88(2)	C(5)−N(1)−Pd	123.93(7)
N(1)−Pd−C(23)	170.67(7)	C(6)−C(5)−O(1)	115.7(2)
		N(1)−C(5)−O(1)	118.5(2)

Tridentate vs Bidentate Behavior. One of the key tools to distinguish between bi- and tridentate coordination of the NOPON^{Me_2} ligand is IR spectroscopy in solution. Complexes of the type **A** in Scheme 1 exhibit two ν(C═N) bands, one in the range 1662−1659 cm^{-1} for the uncoordinated oxazoline and the other in the range (1637−1630 cm^{-1}) for the coordinated oxazoline. In contrast, compounds with a tridentate NOPON^{Me_2} (structure type **B**) show only one band in the region 1622−1618 cm^{-1}. A clear differentiation between rigid structures **A** and **B** is also provided by NMR spectroscopy with resonances for both coordinated and uncoordinated oxazolines, as in complex **3**. When NOPON^{Me_2} adopts a fluxional bidentate *N*,*P* coordination mode, the fast exchange between the coordinated and dangling arms of the ligand renders the two oxazolines equivalent. Since in complexes bearing tridentate NOPON^{Me_2} both oxazolines are equivalent owing to the presence of a mirror plane in the molecule, a dynamic structure of type **A** or a structure **B** gives rise to four resonances for the four diastereotopic methyls and one AB spin system for the four OCH_2 protons. The OCH_2 protons in fluxional **A** appear at values (4.00−4.15 ppm) that correspond to the average between their chemical shift when ligand **I** is tridentate (4.30−4.60 ppm) and uncoordinated (3.80−3.85 ppm). An additional difference between a fluxional structure **A** and **B** is the existence in the latter case of a small $^4J_{PH}$ coupling of 2 Hz between one of the two diastereotopic $OC(CH_3)_2$ methyl protons and the phosphorus atom.

This hemilabile behavior of the ligand with reversible opening and closing of the *P*,*N* chelate allows intramolecular exchange of the two oxazoline moieties.[1,3,4] Such a fluxional process with a potentially tridentate ligand has been encountered when the ligand is placed in a somewhat restricted bidentate coordination mode, as recently investigated with terpyridine or bis(oxazolinyl)-pyridine (Pybox) ligands.[53−55] On the basis of these findings, we can consider at least three possible mechanisms for the dynamic process: a "rotation" mechanism (Scheme 3 (*i*)) that does not lead to an exchange of the equatorial environment, a "tick-tock twist" that requires

Scheme 3. Possible Mechanisms for the Dynamic Behavior of the NOPON^{Me_2} Ligand



that the ligand adopts a pseudo-tridentate bonding mode in a planar transition state (Scheme 3 (*ii*)), and a mechanism through pentacoordination with a trigonal bipyramidal transition state (Scheme 3 (*iii*)).

In the case of a "rotation" mechanism the fluxional process should be favored in **3** compared to **5** since the higher trans effect of CH_3^- compared to Cl^- in square-planar complexes should facilitate dissociation of the trans-coordinated oxazoline.[44,51] This is not the case since **3** is the only complex that clearly exhibits a static bidentate coordination mode of NOPON^{Me_2} at room temperature. Furthermore, the isolation of square-planar complexes containing a tridentate NOPON^{Me_2} and the observation in the case of **4** and **5** of a species with a tridentate NOPON at low temperature are more in favor of a "tick-tock twist" mechanism. We have no experimental data to support mechanism (*iii*), although it has been invoked in the case of a tridentate *N*,*N*,*N*-type ligand.[52] Further studies would be needed to confirm this, and the use of a chiral version of NOPON^{Me_2} would be of interest since a chiral center usually provides an excellent spectroscopic handle for the elucidation of fluxional mechanistic pathways, although this is accentuated in octahedral complexes.[53]

Competition for Coordination of Tridentate NOPON^{Me_2} vs η^1-Allyl/Cl$^-$ vs η^3-Allyl. Having established the bonding behavior of the NOPON^{Me_2} ligand as a static or dynamic chelate, it became possible to study complexes containing an additional, potentially dynamic ligand. This would allow the investigation of their mutual influence, which in the case of the allyl ligand would be of relevance to key intermediates in

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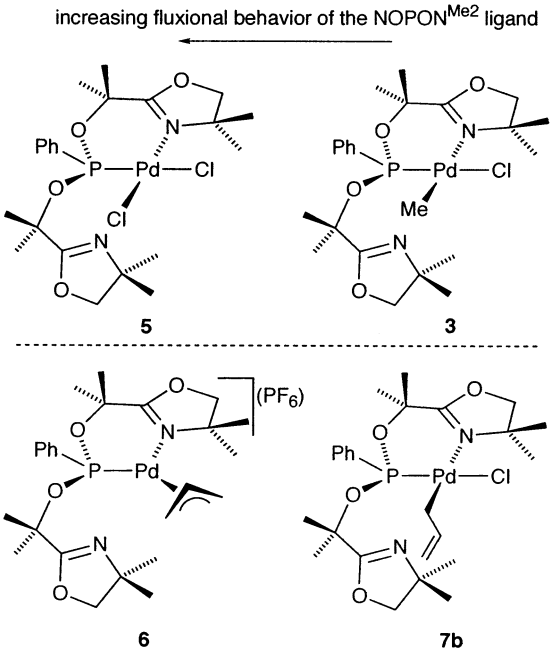
Scheme 4



catalytic reactions. In the solid state the compounds [Pd(η^3-C_3H_5)(NOPON^{Me_2}-*N*,*P*)](PF_6), **6**, and [Pd(η^1-C_3H_5)-Cl(NOPON^{Me_2}-*N*,*P*)], **7b**, show two different ^{13}C−CP/MAS spectra for the allylic carbons, while they show identical patterns for the carbons of ligand **I**, characteristic of a bidentate mode of coordination (see Table 2). As expected, the CH_2 carbons of **6** appear broader in the ^{13}C−CP/MAS solid state spectrum than in solution. The chemical shifts of the allylic carbons are similar in the solid state and in solution, thus confirming the η^3 coordination mode of the allyl ligand of [[Pd(η^3-C_3H_5)-(NOPON^{Me_2}-*N*,*P*)](PF_6) in both phases. We established by ^{13}C NMR that the allyl and NOPON ligands of **7a** are respectively locked in an η^3 and a static bidentate coordination mode and that upon warming to room temperature, **I** remains a bidentate *N*,*P* chelate but exhibits hemilabile behavior. The allylic CH_2 resonances appear broader and move toward the chemical shifts of an η^1-allyl. A similar behavior is observed for the central allylic carbon except that it is broad at low temperature and sharpens upon warming.

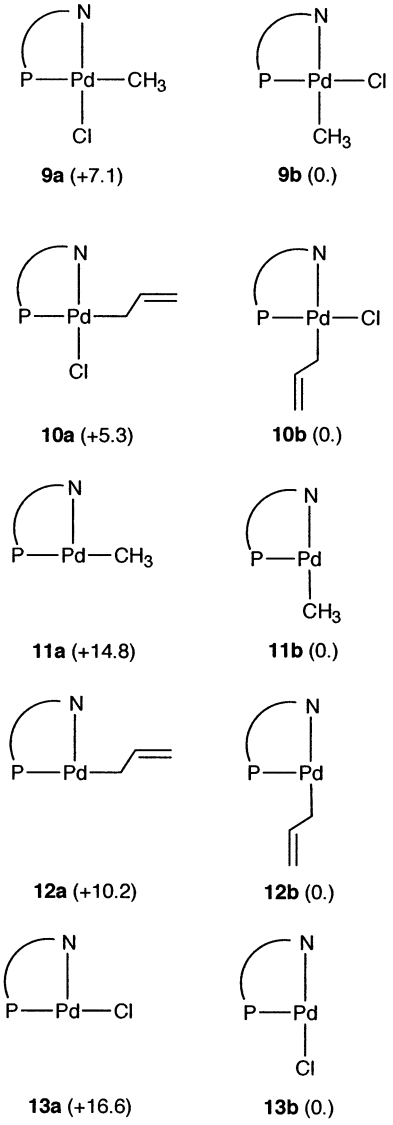
The complexes **5**/**6** and **3**/**7b** depicted in Scheme 4 share structural similarities. The former pair exhibits a more symmetrical environment for the *P*,*N* chelate than the latter since the phosphorus and the nitrogen atoms are trans to two identical atoms.

This is not the case for **3**/**7b**, which contain a σ-bonded carbon cis to phosphorus and a chloride atom cis to nitrogen. This change in the ligand environment of the *P*,*N* chelate manifests itself in a more fluxional behavior of NOPON^{Me_2} in **6** compared to **7b** and in **5** compared to **3**. This was established by ^{1}H NMR spectroscopy since the spectrum of [Pd(η^3-C_3H_5)(NOPON^{Me_2}-*N*,*P*)]PF_6 at 177 K does not indicate a static bidentate bonding of NOPON^{Me_2}, as in the case of [Pd(η^3-C_3H_5)(NOPON^{Me_2}-*N*,*P*)]Cl. Similarly, while NOPON in **5** exhibits fluxional behavior at room temperature, it behaves as a static *N*,*P* bidentate chelate in **3**. These observations are best explained if one considers that the oxazoline exchange follows a "tick-tock twist" mechanism. During this process, complexes **3** and **7b** have to go through an intermediate where the phosphorus and the Pd−CH_3 group are in mutually trans position. Such an arrangement of these two ligands of high trans influence has a destabilizing effect and leads to isomerization into a more stable situation where the σ-carbon and the nitrogen atom are mutually trans. This isomerization is not needed in the case of **5** and **6** and therefore facilitates the fluxional process. Similar observations have been made with Pd complexes in which a symmetrical *P*,*P* or *N*,*N* chelate enhances the dynamic process in trans position, in contrast to *P*,*N* chelates.[49]

A third ligand to be considered in the coordination sphere of **7** is the chloride. Introducing this anion into the coordination sphere of **7** induces a change of the allyl bonding mode from η^3 to η^1, and this, in turn, has an effect on the fluxional process of the NOPON^{Me_2} ligand. This clearly shows the mutual influence of the three ligands on their bonding behavior.

In contrast to the numerous examples of palladium allyl complexes with bidentate ligands, only few palladium complexes have been described that possess a potentially tridentate ligand.[30,35−38,54] In the latter group, complexes obtained with terpy (terpy = 2,2′:6′,2″-terpyridine) or PNN (PNN = *N*-(2-(diphenylphosphino)-benzylidene)-(2-(2-pyridyl)ethyl)amine)) are of particular relevance. The compound [Pd(C_3H_5)(terpy)]$^+$ is fluxional and the terpy bidentate coordination mode is associated with an η^3-allyl bonding [Pd(η^3-C_3H_5)(terpy-*N*,*N*)]$^+$, while the terpy tridentate coordination mode induces a dynamic η^1-allyl bonding mode [Pd(η^1-C_3H_5)-(terpy-*N*,*N*,*N*)]$^+$ at room temperature.[35] The complex [Pd(η^1-C_3H_5)(PNN-*P*,*N*,*N*)]Cl is easily prepared upon heating a solution of 0.5 equiv of PNN with [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ at 338 K or can be obtained as a triflate salt in the presence of [Ag(O_3SCF_3)] at room temperature. In these latter experiments, no intermediates containing a bidentate PNN and an η^3-allyl were observed.[36,55] These two examples contrast with ours since we never observed a tridentate coordination mode of NOPON^{Me_2} in Pd-allyl complexes. It is interesting to compare the palladium complexes of PNN and NOPON^{Me_2} since both ligands can form two six-membered chelates. The reactivity of NOPON^{Me_2} compared to PNN toward Pd-allyl and Pd-alkyl complexes is different. The strong tendency of the PNN ligand to coordinate in a tridentate fashion is exemplified by its reaction with [Pd(Me)Cl(COD)], which leads at room temperature to the complex [Pd(Me)(PNN-*P*,*N*,*N*)]Cl, or to [Pd(Me)-(PNN-*P*,*N*,*N*)](O_3SCF_3) when an equivalent of [Ag(O_3-SCF_3)] is added. With NOPON^{Me_2} we isolated at room temperature the complex [Pd(Me)Cl(NOPON-*N*,*P*)] (**3**), where the chloride ligand is not labile, since attempts to exchange the counteranion by addition of $(NH_4)PF_6$ led to no reaction. Note that in the case of [$PdCl_2$-(NOPON^{Me_2}-*N*,*P*)] a similar procedure led to the formation of [PdCl(NOPON^{Me_2}-*N*,*P*,*N*)](PF_6) in 84% yield (eq 3). Nevertheless we succeeded in abstracting the chloride of **3** by reaction with [Ag(O_3SCF_3)] in CH_2Cl_2 and obtained a complex of formula [Pd(Me)(NOPON^{Me_2})]-(O_3SCF_3). This complex is highly fluxional, as shown by the ^{1}H NMR spectrum in the range 298−177 K. The chemical shift of the singlet in the ^{31}P{^{1}H} NMR spectrum at δ 132.8 is almost identical to that of its

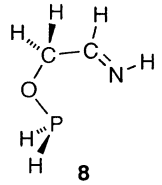
Scheme 5. Schematic Drawing and Relative Energy, in kcal mol^{-1}, of the Two Possible Isomers for Each of the Systems [PdCl(CH_3)(HN−$CHCH_2OPH_2$)] 9a/9b, [PdCl(η^1-C_3H_5)(HN−$CHCH_2OPH_2$)] 10a/10b, [Pd(CH_3)(HN−$CHCH_2OPH_2$)] 11a/11b, [Pd(η^1-C_3H_5)(HN−$CHCH_2OPH_2$)] 12a/12b, and [PdCl(HN−$CHCH_2OPH_2$)] 13a/13b



precursor **3** (133.5 ppm). The IR spectrum indicates the existence of both coordinated and uncoordinated oxazolines. Further studies are needed to determine the exact geometry of the complex, although we can already conclude at this stage that this reaction does not lead to the formation of a mononuclear complex containing a tridentate $NOPON^{Me_2}$.

At this stage one may ask whether the mutually cis disposition in **3** and **7b** of the chloride ligand trans to P, and of a σ-donor ligand such as the methyl or the η^1-allyl ligand trans to N, is intrinsic to the nature of these ligands or whether it is related in one way or another to the *P*,*N* heterobidentate nature and resulting asymmetry of the $NOPON^{Me_2}$ ligand.

Theoretical Studies. To unravel this problem, DFT-B3LYP calculations were carried out on a series of isomeric structures of four- and three-coordinate chloro, methyl, and η^1-allyl Pd(II) complexes bearing the (HN−$CHCH_2OPH_2$) model ligand **8**.



8

These structures, sketched in Scheme 5, comprise the four-coordinate systems [PdCl(CH_3)(HN−$CHCH_2OPH_2$)] **9a**,**b**, [PdCl(η^1-C_3H_5)(HN−$CHCH_2OPH_2$)] **10a**,**b**, and their three-coordinate derivatives obtained by dissociation of either Cl, CH_3, or C_3H_5; see **11a**,**b**, **12a**,**b**, and **13a**,**b**. The fully optimized geometries can be found in the Supporting Information. The relative energies for each **a/b** pair are given in Scheme 5.

In the four-coordinate systems, and in agreement with the above experimental results, the structures with Cl trans to P and either η^1-C_3H_5 or CH_3 trans to N are the most stable ones. For the three-coordinate, T-shaped fragment the most stable structure corresponds to having the nonchelating ligand—either CH_3, η^1-C_3H_5, or Cl—trans to nitrogen, *whatever its nature is*. Thus the structural preference in the four-coordinate systems for Cl trans to P, and CH_3 or η^1-C_3H_5 trans to N, does not result from the dissymmetry of the P−N ligand only. As will now be explained, it also results from the association in the coordination sphere of the P−N ligand with the Cl ligand.

That in the three-coordinate system the third ligand sits always trans to N can be related to the fact that in [(η^3-allyl)Pd(phosphine)(imine)] complexes the Pd−C bond trans to N is stronger (or has a greater covalent character) than the Pd−C bond trans to the phosphorus.[56] In addition to valence-bond type arguments,[56] MO theory arguments have been provided to rationalize this feature:[57] the LUMO of the Pd(phosphine)(imine) fragment is polarized away from the imine ligand; that is, its lobe trans to the imine is greater than the lobe trans to the phosphorus atom.[58] The orbital plot of the LUMO of the Pd(HN−$CHCH_2OPH_2$), Figure 7, shows clearly this polarization. Hence the interaction of palladium with either CH_3, η^1-C_3H_5, or Cl in the three-coordinate system, which takes place via this orbital, will be stronger when these entities are trans to N. This is best exemplified by the relative energies of **11a** vs **11b**, **12a** vs **12b**, and **13a** vs **13b** (see Scheme 5), which are 10−16 kcal mol^{-1} in favor of the trans-N structure.

As a consequence of this stronger Pd−Cl interaction in **13b** compared to **13a**, the LUMO of **13b** is more destabilized than the LUMO of **13a**; see the schematic drawing in the middle of the Figure 8. In turn, it will interact more weakly with the σ orbital of an R ligand (R = CH_3 or η^1-C_3H_5) when R is trans to P, as in **9a** or **10a**, than when R is trans to N as in **9b** or **10b**; see Figure 8. Since this interaction is a two-electron stabilizing one, this results in having **9a** and **10a** less stable than **9b** and **10b**, respectively.

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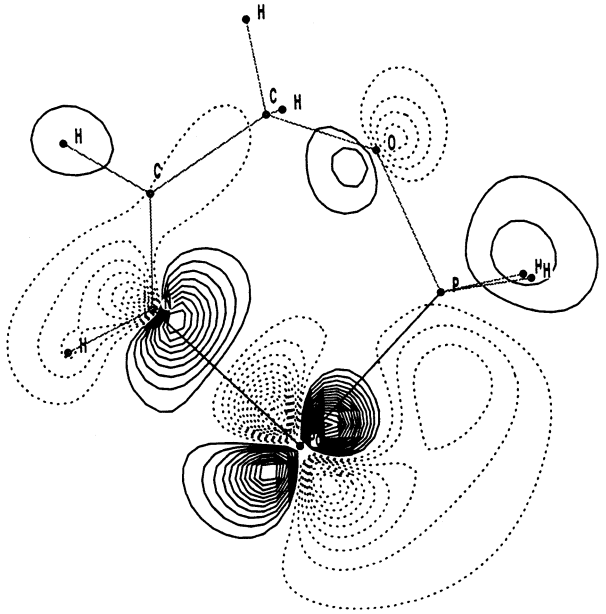

Figure 7. Orbital plot of the LUMO of the $[Pd(HN{-}CHCH_2OPH_2)]^+$ fragment showing the polarization away from the imine ligand. Full lines correspond to positive contours and dotted lines to negative contours. The zero contour has been omitted for the sake of clarity.

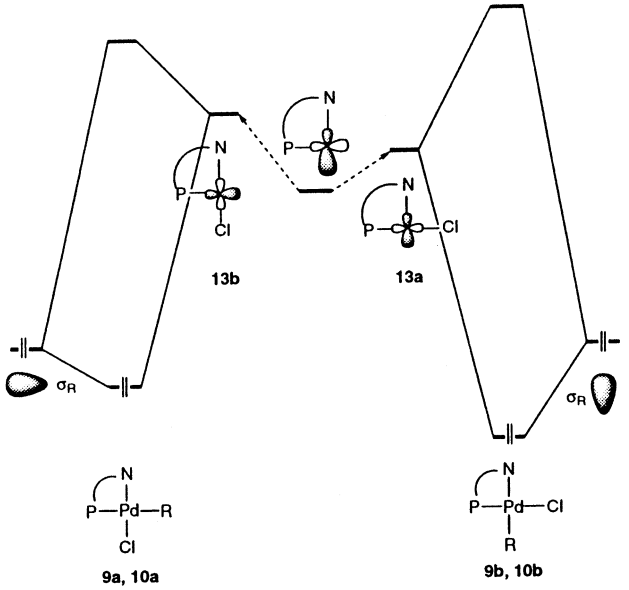

Figure 8. Relative destabilization of the lowest unoccupied molecular orbital in the d^8 $[PdCl(HN{-}CHCH_2OPH_2)]^+$ system upon addition of Cl to $[Pd(HN{-}CHCH_2OPH_2)]^+$, either trans to the phosphorus (see **13a**) or trans to the imine (see **13b**) and its subsequent interaction with the σ orbital of an alkyl or allyl anion to yield **9b**, **10b** or **9a**, **10a**, respectively.

Conclusion

These studies with allyl- and alkyl-palladium complexes indicate the existence of an energetic barrier against the formation of a compound where the phosphorus atom of a tridentate $NOPON^{Me_2}$ is trans to an alkyl or η^1-allyl ligand. This does not happen with the P,N,N ligand since when it adopts a tridentate coordination mode, the phosphorus atom is always cis to the alkyl or η^1-allyl. The X-ray structure of **7b** is the first one for a transition metal complex where an η^1-allyl ligand and a chloride are in mutually cis position. It is interesting to note first that in a recent study Åkermark and Vitagliano have proposed a mechanism for dynamic processes of η^3-allyl palladium complexes accelerated by the addition of chloride.[59] Second, a four-coordinated Pd complex containing a bidentate *N,N* chelate, an η^1-allyl, and a chloride ligand in mutually cis position was postulated as an intermediate. Our results support the possible existence of such compounds, which are also of relevance to species involved in the transition metal-catalyzed allylic alkylation.[5]

We have observed and characterized the changes in the coordination sphere of the palladium allyl complex when varying the solvent or the nature of the counteranion. Surprisingly, while we would have expected the $NOPON^{Me_2}$ to be affected in its coordination mode by the nucleophilic chloride anion, this is actually the allyl ligand which was perturbed. These findings are relevant to the various steps known to occur in, for example, the enantioselective Pd allylic alkylation, and we therefore believe that our basic understanding of the behavior of both $NOPON^{Me_2}$ and the $C_3H_5^-$ ligands should find useful extensions when moving on to more complex systems containing chiral analogues of the new bis(oxazoline)phenylphosphonite ligands reported here.

Experimental Section

All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^1H NMR spectra were recorded at 300.13 MHz, $^{31}P\{^1H\}$ NMR spectra at 81.0 or 121.5 MHz, $^{13}C\{^1H\}$ NMR spectra at 75.4 MHz on a FT Bruker AC200 or AC300 instrument, IR spectra in the 4000−400 cm^{-1} range on a Bruker IFS66 FT spectrometer, and far-IR spectra in the 500−90 cm^{-1} range on a Bruker ATS 83 spectrometer. The compounds 4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole,[60] $[Pd(NCMe)_4](BF_4)_2$,[61] $[PdCl_2(COD)]$,[62] [PdMe(Cl)(COD)],[62] and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$[63] were prepared according to the literature.

Syntheses. $NOPON^{Me_2}$ (I). In a 100 mL Schlenk tube containing 4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole (3.000 g, 19.1 mmol) in THF (40 mL) was added triethylamine (7.99 mL, 57.3 mmol). To the colorless solution cooled to −78 °C was added quickly dichlorophenylphosphine (0.615 mL, 9.55 mmol). This afforded immediately a white precipitate. The reaction mixture was allowed to slowly reach room temperature and was stirred for 16 h. The THF was evaporated under vacuum, and toluene (80 mL) was added to the white solid thus obtained. The white suspension was filtered over Celite, and the filtrate solution was evaporated. The white powder was washed using 3 × 10 mL of pentane and dried in vacuo for 1 night. Yield: 2.750 g (69%). Mp: 99 °C Selected IR data (KBr): ν_{CN} 1661 s cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 1.24 (s, 6 H, $NC(CH_3)(CH_3)$), 1.25 (s, 6 H, $NC(CH_3)(CH_3)$), 1.60 (s, 6 H, $OC(CH_3)(CH_3)$), 1.70 (s, 6 H, $OC(CH_3)(CH_3)$), AB spin system δ_A 3.85 (d, 2 H, $^2J_{HH}$ = 8.0 Hz, OCHH), δ_B 3.90 (d, 2 H, OCHH), 7.30−7.40 (m, 3 H, *m* and *p* aryl), 7.60−7.70 ppm (m, 2 H, *o* aryl). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 27.2−28.15 (overlapping s and d, $OC(CH_3)_2$ and $NC(CH_3)_2$), 67.3 (s, $NC(CH_3)_2$), 75.6 (d, $^2J_{PC}$ = 12.7 Hz, $OC(CH_3)_2$), 79.1 (s, OCH_2), 127.8 (d, $^2J_{PC}$ = 5.0 Hz, *m*-aryl), 129.4 (d, $^3J_{PC}$

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= 6.0 Hz, *o*-aryl), 129.9 (s, *p*-aryl), 144.1 (d, $^1J_{PC}$ = 10.0 Hz, *ipso*-aryl), 167.2 ppm (s, C=N). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 150.5 ppm (s). Anal. Calcd for $C_{22}H_{33}N_2O_4P$: C, 62.84; H, 7.91; N, 6.66. Found: C, 63.14; H, 8.26; N, 6.85.

[Pd(NCMe)(NOPON^{Me_2}-*N,P,N*)](BF$_4$)$_2$ (1). In a 50 mL Schlenk tube $[Pd(NCMe)_4](BF_4)_2$ (0.202 g, 0.45 mmol) was dissolved in acetonitrile (15 mL), and the NOPON^{Me_2} ligand (0.192 g, 0.45 mmol) was added. The yellow solution was stirred for 30 min, and the solvent was removed under vacuum. The pale yellow solid was washed with 2 × 10 mL of diethyl ether and dried in vacuo overnight to afford a pale yellow powder. Yield: 0.305 g (90%). X-ray quality crystals were obtained by slow diffusion in 1:3 acetonitrile/diethyl ether. Selected IR data (MeCN): ν_{CN} 1622 cm^{-1}. ^1H NMR (300.13 MHz, acetonitrile-d_3): δ 1.25 (s, 6 H, NC(C*H*$_3$)(CH$_3$)), 1.55 (s, 6 H, NC(CH$_3$)(C*H*$_3$)), 1.80 (d, 6 H, $^4J_{PH}$ = 2.0 Hz, OC(C*H*$_3$)(CH$_3$)), 2.35 (s, 6 H, OC(CH$_3$)(C*H*$_3$)), AB spin system δ_A 4.50 (d, 2 H, $^2J_{HH}$ = 9.1 Hz, OC*H*H), 4.60 δ_B (d, 2 H, OCH*H*), 7.55−7.75 (m, 4 H, aryl), 7.80−7.90 ppm (m, 1 H, aryl). $^{13}C\{^1H\}$ NMR (75.5 MHz, acetonitrile-d_3): δ 25.0 (d, $^3J_{PC}$ = 7.8 Hz, OC(*C*H$_3$)(CH$_3$)), 27.0 (s, NC(CH$_3$)(*C*H$_3$)), 28.5 (s, NC(*C*H$_3$)(CH$_3$)), 30.0 (d, $^3J_{PC}$ = 2.9 Hz, OC(CH$_3$)(*C*H$_3$)), 72.7 (s, N*C*(CH$_3$)$_2$), 83.8 (s, OCH$_2$), 86.5 (d, $^2J_{PC}$ = 7.4 Hz, O*C*(CH$_3$)$_2$), 128.0−138.2 (m, aryl), 174.2 (d, $^3J_{PC}$ = 8.7 Hz, C=N). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetonitrile-d_3): δ 106.5 (s). Anal. Calcd for $C_{24}H_{36}B_2F_8N_3O_4PPd$: C, 38.87; H, 4.89; N, 5.67. Found: C, 38.78; H, 4.95; N, 5.80.

[PdCl(NOPON^{Me_2}-*N,P,N*)](PF$_6$) (2). In a Schlenk tube were placed together $[PdCl_2(NOPON^{Me_2})]$ (0.105 g, 0.175 mmol) and NH_4PF_6 (0.028 g, 0.175 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 2 h, and the deep yellow solution turned pale yellow. The white precipitate formed was filtered off through Celite, and the filtrate was taken to dryness under reduced pressure. The pale yellow solid was washed with a mixture of 1:4 toluene/pentane (2 × 20 mL). The solid was dried under vacuum overnight; yield 0.104 g (84%). Selected IR data (CH_2Cl_2): ν_{CN} 1618 cm^{-1}; (polyethylene): 471 s, 426 s, 408 m, 378 w, 326 vs, 295 vs. ^1H NMR (300.13 MHz, CD_2Cl_2): δ 1.50 (s, 6 H, NC(C*H*$_3$)(CH$_3$)), 1.75 (s, 6 H, NC(CH$_3$)(C*H*$_3$)), 1.80 (d, 6 H, $^4J_{PH}$ = 2.0 Hz, OC(C*H*$_3$)(CH$_3$)), 2.35 (s, 6 H, OC(CH$_3$)(C*H*$_3$)), AB spin system δ_A 4.30 (d, 2, $^2J_{HH}$ = 9.0 Hz, OC*H*H), δ_B 4.45 (d, 2, OCH*H*), 7.40−7.80 (m, 5 H, aryl). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2): δ 25.3 (d, $^3J_{PC}$ = 7.3 Hz, OC(*C*H$_3$)(CH$_3$)), 27.1 (s, NC(*C*H$_3$)(CH$_3$)), 28.5 (s, NC(CH$_3$)(*C*H$_3$)$_2$), 29.6 (d, $^3J_{PC}$ = 2.0 Hz, OC(CH$_3$)(*C*H$_3$)), 73.0 (s, N*C*(CH$_3$)$_2$), 83.7 (d, $^2J_{PC}$ = 5.1 Hz, O*C*(CH$_3$)$_2$), 84.1 (s, OCH$_2$), 128.0−135.5 (m, aryl), 172.5 (d, $^3J_{PC}$ = 10.0 Hz, C=N). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): δ 115.7 (s). Anal. Calcd for $C_{22}H_{33}ClF_6N_2O_4P_2Pd\cdot 0.5\ CH_2Cl_2$: C, 36.01; H, 4.53; N, 3.73. Found: C, 36.04; H, 4.93; N, 3.83.

[Pd(Me)Cl(NOPON^{Me_2}-*N,P*)] (3). In a Schlenk tube were placed together the NOPON^{Me_2} ligand (0.320 g, 0.76 mmol) and [PdMe(Cl)(COD)] (0.202 g, 0.76 mmol) in 20 mL of CH_2Cl_2. The pale yellow solution was stirred overnight, and the solvent was removed under vacuum. The pale yellow oil thus obtained was washed with 2 × 15 mL of Et_2O to afford a white powder. The solid was dried in vacuo overnight; yield 0.250 g (57%). Selected IR data (KBr): ν_{CN} 1660 cm^{-1} (uncoordinated oxazoline), ν_{CN} 1634 cm^{-1} (coordinated oxazoline); (polyethylene): 479 vs, 406 s, 375 s, 287 vs, 239 s. ^1H NMR (300.13 MHz, $CDCl_3$): δ 0.75 (d, 3 H, $^3J_{PH}$ = 2.9 Hz, Pd−CH$_3$), 1.25 (s, 3 H, NC(C*H*$_3$)(CH$_3$)$_2$ from coordinated oxazoline), 1.35 (s, 3 H, NC(CH$_3$)(C*H*$_3$) from coordinated oxazoline), 1.55 (s, 6, NC(C*H*$_3$)(CH$_3$) from uncoordinated oxazoline), 1.65 (s, 3 H, OC(C*H*$_3$)(CH$_3$) from coordinated oxazoline), 1.80 (s, 6 H, OC(CH$_3$)$_2$ from uncoordinated oxazoline), 1.90 (s, 3 H, OC(CH$_3$)(C*H*$_3$) from coordinated oxazoline), AB spin system δ_A 3.95 (d, 1 H, $^2J_{HH}$ = 8.0 Hz, OC*H*H from uncoordinated oxazoline), 4.02 (br, 2 H overlapping signal for δ_B part of the AB for OCH*H* from uncooordinated oxazoline and δ_A part for the AB for OC*H*H from coordinated oxazoline), δ_B 4.15 (d, 1, $^2J_{HH}$ = 8.2 Hz, OCH*H* from coordinated oxazoline), 7.40−7.50 (m, 3 H, aryl), 7.80−7.90 ppm (m, 2 H, aryl). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ 2.8 (s, PdCH$_3$), 26.7−29.9 (overlapping s and m, OC(*C*H$_3$)$_2$ and NC(*C*H$_3$)$_2$), 67.8 (s, N*C*(CH$_3$)$_2$ from uncoordinated oxazoline), 71.4 (s, N*C*(CH$_3$)$_2$ from coordinated oxazoline), 77.4 (s, O*C*(CH$_3$)$_2$ from uncoordinated oxazoline), 79.8 (overlapping s, O*C*(CH$_3$)$_2$ from coordinated oxazoline and OCH$_2$ from uncoordinated oxazoline), 82.4 (s, OCH$_2$ from coordinated oxazoline), 128.5 (d, $^3J_{PC}$ = 13.5 Hz, *m*-aryl), 131.5 (d, $^2J_{PC}$ = 17.5 Hz, *o*-aryl), 132.1 (s, *p*-aryl), 137.1 (d, $^1J_{PC}$ = 81.5 Hz, *ipso*-aryl), 166.0 ppm (s, C=N from uncoordinated oxazoline), 169.5 (s, C=N from coordinated oxazoline). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 133.5 ppm (s). Anal. Calcd for $C_{23}H_{36}ClN_2O_4PPd$: C, 47.85; H, 6.28; N, 4.85. Found: C, 47.75; H, 6.21; N, 4.79.

[PdI$_2$(NOPON^{Me_2}-*N,P*)] (4). Compound **1** (0.155 g, 0.209 mmol) was dissolved in acetone (20 mL), and solid NaI (0.125 g, 0.840 mmol) was added to the pale yellow solution. It immediatly turned deep red and was stirred for 20 min. The solvent was removed under reduced pressure, and the red solid thus obtained was extracted with toluene (5 × 20 mL). Evaporation of the solvent under vacuum afforded a brown-red powder, which was further washed with pentane (2 × 10 mL) and dried in vacuo; yield 0.075 g (45%). Selected IR data (THF): ν_{CN} 1662 s cm^{-1} (uncoordinated oxazoline), ν_{CN} 1631 s cm^{-1} (coordinated oxazoline); (polyethylene): 490 s, 471 vs, 414 m, 399 w, 378 sh, 372 m, 337 w, 322 m, 232 m, 220 w. ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 1.25 (s, 6 H, NC(C*H*$_3$)(CH$_3$)), 1.45 (s, 6 H, NC(CH$_3$)(C*H*$_3$)), 1.80 (s, 6 H, OC(C*H*$_3$)(CH$_3$)), 1.90 (s, 6 H, OC(CH$_3$)(C*H*$_3$)), AB spin system δ_A 4.02 (d, 2 H, $^2J_{HH}$ = 8.3 Hz, OC*H*H), δ_B 4.06 (d, 2 H, OCH*H*), 7.40−7.60 (m, 3 H, aryl), 7.90−8.00 (m, 2 H, aryl). ^1H NMR (300.13 MHz, CD_2Cl_2, 172 K): major species [PdI$_2$(NOPON-*N,P*)] δ 1.05 (s, 3 H, NC(C*H*$_3$)(CH$_3$) from uncoordinated oxazoline), 1.15 (s, 3 H, NC(CH$_3$)(C*H*$_3$) from uncoordinated oxazoline), 1.25 (s, 3 H, NC(C*H*$_3$)(CH$_3$) from coordinated oxazoline), 1.55 (s, 3 H, NC(CH$_3$)(C*H*$_3$) from coordinated oxazoline), 1.67 (s, 3 H, OC(C*H*$_3$)(CH$_3$) from uncoordinated oxazoline), 1.70 (s, 3 H, OC(CH$_3$)(C*H*$_3$) from uncoordinated oxazoline), 1.85 (s, 3 H, OC(C*H*$_3$)(CH$_3$) from coordinated oxazoline), 1.90 (s, 3 H, OC(CH$_3$)(C*H*$_3$) from coordinated oxazoline), AB spin system δ_A 3.75 (d, 2 H, $^2J_{HH}$ = 7.5 Hz, OC*H*H from uncoordinated oxazoline), δ_B 4.00 (d, 2 H, OCH*H* from uncoordinated oxazoline), AB spin system δ_A 4.10 (d, 2 H, $^2J_{HH}$ = 8.0 Hz, OC*H*H from coordinated oxazoline), δ_B 4.20 (d, 2 H, OCH*H* from coordinated oxazoline), 7.40−7.60 (m, 3 H, aryl), 7.75−7.85 (m, 2 H, aryl); minor species δ 1.20 (s, 3 H, NC(*C*H$_3$)(CH$_3$)), 1.70 (s, 3 H, NC(CH$_3$)(*C*H$_3$)), 1.77 (s, 3 H, OC(*C*H$_3$)(CH$_3$)), 2.35 (s, 3 H, OC(CH$_3$)(*C*H$_3$)), AB spin system δ_A 4.35 (d, 2 H, $^2J_{HH}$ = 8.5 Hz, OC*H*H), δ_B 4.65 (d, 2 H, OCH*H*), 7.40−7.60 (m, aryl), 7.70−7.80 (m, aryl). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 29.0−29.8 (m, OC(*C*H$_3$)$_2$ and NC(*C*H$_3$)$_2$), 71.2 (s, N*C*(CH$_3$)$_2$), 83.2 (two overlapping s, O*C*(CH$_3$)$_2$ and OCH$_2$), 130.0−138.9 (m, aryl), 169.7 (s, C=N). For the low-temperature $^{13}C\{^1H\}$ NMR spectrum of [PdI$_2$(NOPON-*N,P*)] at 293 K see Table 2. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2,172 K): minor species δ 26.8 (d, $^3J_{PC}$ = 5.6 Hz, OC(*C*H$_3$)(CH$_3$)), 28.8−32.5 (m, OC(*C*H$_3$)$_2$ and NC(*C*H$_3$)$_2$), 73.3 (s, N*C*(CH$_3$)$_2$), 83.4 (s, OCH$_2$), 86.7 (d, $^2J_{PC}$ = 5.3 Hz, O*C*(CH$_3$)$_2$), 130.2−138.5 (m, aryl), 172.3 (d, $^3J_{PC}$ = 8.6 Hz, C=N). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 116.0 ppm (s). Anal. Calcd for $C_{22}H_{33}I_2N_2O_4PPd$: C, 33.85; H, 4.26; N, 3.59. Found: C, 34.46; H, 4.20; N, 3.49.

[PdCl$_2$(NOPON^{Me_2}-*N,P*)] (5). In a Schlenk tube were placed together the *NOPON* ligand (0.277 g, 0.66 mmol) and $[PdCl_2(COD)]$ (0.188 g, 0.66 mmol) in 20 mL of CH_2Cl_2. The yellow solution was stirred overnight, and the solvent was removed under vacuum. The yellow powder thus obtained was washed (2 × 20 mL) with a mixture 1:3 Et_2O/pentane. The solid was dried in vacuo overnight; yield 0.350 g (89%). Selected IR data (CH_2Cl_2): ν_{CN} 1662 s cm^{-1} (uncoordinated oxazoline), ν_{CN} 1631 s cm^{-1} (coordinated oxazoline); (polyeth-

ylene): 490 vs, 485 s, 403 m, 379 s, 340 vs, 325 s, 316 m, 289 vs. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.50 (br s, 6 H, NC(CH_3)(CH_3)), 1.60 (br s, 6 H, NC(CH_3)(CH_3)), 1.80 (s, 6 H, OC(CH_3)(CH_3)) 1.85 (s, 6 H, OC(CH_3)(CH_3)), AB spin system δ_A 4.15 (d, 2 H, $^2J_{HH}$ = 7.5 Hz, OC*H*H), δ_B 4.20 (d, 2 H, OCH*H*), 7.40−7.60 (m, 3 H, aryl), 8.00−8.10 (m, 2 H, aryl). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 27.4−27.8 (m, OC(CH_3)$_2$ and NC(CH_3)$_2$), 70.0−71.0 (br, N*C*(CH_3)$_2$), 80.0−84.0 (br, O*C*(CH_3)$_2$ and OCH_2), 128.0−134.0 (m, aryl), 168.0−170.0 (br, C=N). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 106.5 ppm (s). Anal. Calcd for $C_{22}H_{33}Cl_2N_2O_4PPd\cdot0.25CH_2Cl_2$: C, 43.13; H, 5.60; N, 4.68. Found: C, 43.19; H, 5.52; N, 4.54.

[Pd(η^3-C_3H_5)(NOPON^{Me_2}-*N*,*P*)](PF$_6$) (6). The NOPON^{Me_2} ligand (0.155 g, 0.37 mmol) and [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (0.067 g, 0.18 mmol) were dissolved in CH_2Cl_2 (20 mL). The pale yellow solution was stirred for 20 min, and solid NH_4PF_6 (0.66 g, 0.41 mmol) was added. The reaction mixture was stirred for 3 h, and the fine white precipitate formed was filtered off by means of a cannula fitted with a glass fiber filter paper. The filtrate was taken to dryness to give a pale yellow oil. Trituration with pentane afforded an off-white solid, which was further washed with 2 × 10 mL of pentane. The solid was dried under vacuum overnight; yield 0.185 g (71%). Selected IR data: (CH_2Cl_2), ν_{CN} 1662 s cm^{-1} (uncoordinated oxazoline), ν_{CN} 1630 s cm^{-1} (coordinated oxazoline); (polyethylene): 490 s, 476 vs, 419 s, 344 m, 313 w, 294 m. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 293 K): δ 1.20 (s, 6 H, NC(CH_3)(CH_3)), 1.25 (s, 6 H, NC(CH_3)(CH_3)), 1.65 (s, 6 H, OC(CH_3)(CH_3)), 1.75 (s, 6 H, OC(CH_3)(CH_3)), 3.45 (br s, 2 H, allylic CH_2 cis to P), 3.75 (dd, 1 H, $^3J_{HH}$ = 13.8, $^3J_{PH}$ = 14.0 Hz, allylic CH_2 trans to P), AB spin system δ_A 4.10 (d, 2 H, $^2J_{HH}$ = 8.5 Hz, OC*H*H), δ_B 4.15 (d, 2 H, OCH*H*), 4.95 (dd, 1 H, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 8.0 Hz, allylic CH_2 trans to P), 5.75 (m, 1 H, $^3J_{HH}$ = 13.8, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 0.9 Hz, allylic CH), 7.50−7.60 (m, 3H, aryl), 7.65−7.70 (m, 2H, aryl). ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 298 K): δ 27.8 (s, NC(*C*H_3)(CH_3)), 28.0 (s, NC(CH_3)(*C*H_3)), 28.1 (d, $^3J_{PC}$ = 4.3 Hz, OC(*C*H_3)(CH_3)), 28.5 (d, $^3J_{PC}$ = 6.4 Hz, OC(CH_3)(*C*H_3)), 54.7 (d, $^3J_{PC}$ = 6.4 Hz, allylic CH_2 cis to P), 68.9 (s, N*C*(CH_3)$_2$), 78.8 (d, $^3J_{PC}$ = 40.1 Hz, allylic CH_2 trans to P), 80.3 (s, OCH_2), 81.15 (d, $^3J_{PC}$ = 8.8 Hz, O*C*(CH_3)$_2$), 121.5 (d, $^3J_{PC}$ = 8.8 Hz, allylic CH), 129.4 (d, $^3J_{PC}$ = 12.5 Hz, *m*-aryl), 130.5 (d, $^2J_{PC}$ = 18.1 Hz, *o*-aryl), 133.1 (s, *p*-aryl), 136.4 (d, $^1J_{PC}$ = 57.3 Hz, *ipso*-aryl), 168.5 (s, C=N). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): 136.5 (s), −144.0 (sept, J_{PF} = 710 Hz, PF_6^-). Anal. Calcd for $C_{25}H_{38}F_6N_2O_4P_2Pd$: C, 42.42; H, 4.70; N, 3.96. Found: C, 42.35; H, 4.92; N, 3.95.

[Pd(η^3-C_3H_5)Cl(NOPON^{Me_2}-*N*,*P*)] (7). The NOPON ligand (0.164 g, 0.39 mmol) and [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (0.071 g, 0.19 mmol) were dissolved in CH_2Cl_2 (20 mL). The pale yellow solution was stirred for 20 min, and the solvent was removed under vacuum. To the pale yellow oil thus obtained were added 2 mL of CH_2Cl_2 and 20 mL of pentane to allow precipitation of a yellow impurity. The suspension was filtered through a cannula fitted with glass fiber filter paper. The filtrate was taken to dryness, and the off-white powder thus obtained washed with 2 × 5 mL of pentane. The solid was dried overnight under vacuum; yield 0.079 g (93%). Single crystals of **7b** were obtained by slow evaporation of a 1:4 CH_2Cl_2/pentane solution. Selected IR data: (CH_2Cl_2), ν_{CN} 1659 s cm^{-1} (uncoordinated oxazoline), ν_{CN} 1637 s cm^{-1} (coordinated oxazoline); (polyethylene): 495 m, 476 vs, 439 m, 407 s, 371 vs, 342 m, 287 s. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 298 K): δ 1.30 (s, 6 H, NC(CH_3)(CH_3)), 1.35 (s, 6 H, NC(CH_3)(CH_3)), 1.70 (s, 6 H, OC(CH_3)(CH_3)), 1.75 (s, 6 H, OC(CH_3)(CH_3)), 3.00 (very br, 2 H, allylic CH_2), AB spin system δ_A 4.00 (d, 2 H, $^2J_{HH}$ = 8.5 Hz, OC*H*H), δ_B 4.05 (d, 2 H, OCH*H*), 4.30 (very br, 1 H, allylic CH_2), 4.70 (very br, 1 H, allylic CH_2), 6.00 (d quint, 1 H, $^3J_{HH}$ = 10.6, $^4J_{PH}$ = 1.7 Hz, allylic CH), 7.40−7.60 (m, 3 H, aryl), 7.75−7.85 (m, 2 H, aryl). ^{1}H NMR (500.13 MHz, CD_2Cl_2, 177 K): δ 0.90 (s, 3 H, NC(CH_3)(CH_3) from uncoordinated oxazoline), 1.05 (s, 3 H, NC(CH_3)(CH_3) from uncoordinated oxazoline), 1.15 (s, 3 H, NC(CH_3)(CH_3) from coordinated oxazoline), 1.30 (s, 3 H, NC(CH_3)(CH_3) from coordinated oxazoline), 1.45 (s, 3 H, OC(CH_3)(CH_3) from uncoordinated oxazoline), 1.58 (s, 3 H, OC(CH_3)(CH_3) from uncoordinated oxazoline), 1.62 (s, 3 H, OC(CH_3)(CH_3) from coordinated oxazoline), 1.80 (s, 3 H, OC(CH_3)(CH_3) from coordinated oxazoline), 3.40 (br s, 2 H, allylic CH_2 cis to P), AB spin system δ_A 3.70 (br, 2 H, OC*H*H from uncoordinated oxazoline), 3.75 (dd, $^3J_{HH}$ = 9.5, $^3J_{PH}$ = 9.7 Hz, allylic CH_2 trans to P), δ_B 3.90 (br, 2 H, OCH*H* from uncoordinated oxazoline), AB spin system δ_A 4.25 (br, 2 H, OC*H*H from coordinated oxazoline), δ_B 4.35 (d, 2 H, OCH*H* from coordinated oxazoline), 4.80 (dd, $^3J_{HH}$ = 4.0, $^3J_{PH}$ = 4.0 Hz, allylic CH_2 trans to P), 5.75 (m, 1 H, allylic CH), 7.50−7.75 (m, 5 H, aryl). ^{1}H NMR (500.13 MHz, toluene-d_8, 298 K): δ 1.40 (s, 12 H, NC(CH_3)$_2$), 1.50 (s, 6 H, OC(CH_3)$_2$), 1.60 (s, 6 H, OC(CH_3)$_2$), 3.05 (2 H, $^2J_{HH}$ = 6.0, $^3J_{PH}$ = 6.5 Hz, Pd−CH_2), AB spin system δ_A 3.45 (2 H, $^2J_{HH}$ = 8.1 Hz, OC*H*H), δ_B 3.60 (2 H, $^2J_{HH}$ = 8.1 Hz, OC*H*H), 4.65 (1 H, $^3J_{HH}$ = 17.0 Hz, C=C*H*H), 4.85 (1 H, $^3J_{HH}$ = 9.8 Hz, C=CH*H*), 6.80−7.20 (overlapping m for toluene-d_8, C*H*=CH_2 and aryl), 7.90−8.00 (2 H, m, aryl). For the ^{13}C{^{1}H} NMR spectra in CD_2Cl_2 and toluene-d_8 see Tables 2 and 4. ^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2, 298 K): δ 26.6 (s, NC(*C*H_3)(CH_3)), 26.9 (s, NC(*C*H_3)(CH_3)), 27.1 (d, $^3J_{PC}$ = 2.3 Hz, OC(*C*H_3)(CH_3)), 27.15 (s, OC(*C*H_3)(CH_3)), 37.5 (br, allylic CH_2 cis to P), 67.9 (s, N*C*(CH_3)$_2$), 78.7 (d, $^3J_{PC}$ = 7.4 Hz, O*C*(CH_3)$_2$), 79.5 (s, OCH_2), 96.0 (br, allylic CH_2 trans to P), 127.7 (d, $^3J_{PC}$ = 11.5 Hz, *m*-aryl), 130.2 (d, $^2J_{PC}$ = 17.2 Hz, *o*-aryl), 131.1 (s, *p*-aryl), 132.2 (d, $^3J_{PC}$ = 6.7 Hz, allylic CH), 136.0 (d, J_{PC} = 63.2 Hz, *ipso*-aryl), 167.0 (d, $^4J_{PC}$ = 3.0 Hz, C=N). For the low-temperature spectrum, see Tables 2 and 4. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 138.1 (s). Anal. Calcd for $C_{25}H_{38}ClN_2O_4PPd$: C, 49.75; H, 6.35; N, 4.65. Found: C, 50.15; H, 6.50; N, 4.60.

Computational Details. The calculations were carried out at the DFT-B3LYP level with the Gaussian 98 program package.[64] The B3LYP exchange−correlation functional is made of the Becke's three-parameter hybrid exchange functional[65] and the Lee, Yang, and Parr correlation functional.[66] The geometries were fully optimized at that level by the gradient technique, using the standard LANL2DZ basis set to which d polarization functions were added to the carbon, nitrogen, oxygen, phosphorus, and chlorine atoms. In this basis the innermost core electrons of the palladium atom (up to 3d) are described by the relativistic pseudo potential of Hay and Wadt[67] and the remaining outer core and valence electrons by a (341/541/31) basis set where the two outermost 5p functions of the standard LANL2DZ basis set have been replaced by a (41) split of the optimized 5p function from Couty and Hall.[68] The exponents of the d polarization functions are 0.75, 0.80, 0.85, 0.34, and 0.514 for carbon, nitrogen oxygen, phosphorus,[69] and chlorine,[69] respectively. The Cartesian coordinates of the optimized geometries of the systems **9a**−**13b** are given in the Supporting Information together with the corresponding total energies.

X-ray Structural Analyses. The diffraction intensities were collected using Mo Kα graphite-monochromated radiation

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Table 6. Selected Crystallographic Data for Ligand I and Complexes 1·0.5Et$_2$O·0.33MeCN and 7b

	I	**1**·0.5Et$_2$O·0.33MeCN	**7b**
formula	$C_{22}H_{33}N_2O_4P$	$C_{24}H_{36}B_2F_8N_3O_4PPd$·0.5Et$_2$O·0.33MeCN	$C_{25}H_{38}ClN_2O_4PPd$
fw (g mol^{-1})	420.49	790.64	603.42
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1/c$
a (Å)	8.3531(13)	10.7713(8)	15.6689(5)
b (Å)	10.006(3)	18.049(3)	10.0997(4)
c (Å)	15.030(3)	17.5134(6)	17.5458(3)
α (deg)	74.452(7)		
β (deg)	76.372(3)	91.9285(6)	100.359(2)
γ (deg)	73.973(3)		
V (Å^3)	1145.3(4)	1407.6(3)	2731.4(3)
Z	2	4	4
D(calcd) (g·cm^{-3})	1.219	1.543	1.47
μ (cm^{-1})	1.49	6.75	8.68
temperature (K)	180	180	173
diffractometer	Rigaku/ADSC CCD	Rigaku/ADSC CCD	Kappa CCD
no. of reflns total	10 754	31 430	14 307
no. of obsd reflns ($I>3\sigma(I)$)	2251	3730	6187
no. of variables	262	424	307
residuals (R; R_w)[a]	0.090; 0.072	0.041; 0.035	0.037; 0.057
GOF[a]	1.07	1.03	1.16
max. peak in final diff map (e/Å^3)	0.48	1.91	0.66

[a] $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

(λ = 0.71069 Å). The structures were solved by heavy-atom Patterson methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions with C−H = 0.98 Å. Details of the data collection and refinement procedures are given in Table 6.

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Supporting Information Available: Computational details and tables containing X-ray crystal data, atomic coordinates, bond lengths and angles, and thermal displacement parameters for compounds **I**, **1**·0.5Et$_2$O·0.33MeCN, and **7b**. This material has been deposited with the Cambridge Crystallographic Data Centre as Supplementary publication no. CCDC-157514, CCDC-157515, and CCDC-157516. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) and via the Internet at http://pubs.acs.org.

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