11954 *Inorg. Chem.* **2009**, *48*, 11954–11962
DOI: 10.1021/ic9018579

Inorganic Chemistry
Article

Tridentate Assembling Ligands Based on Oxazoline and Phosphorus Donors in Dinuclear Pd(I)−Pd(I) Complexes

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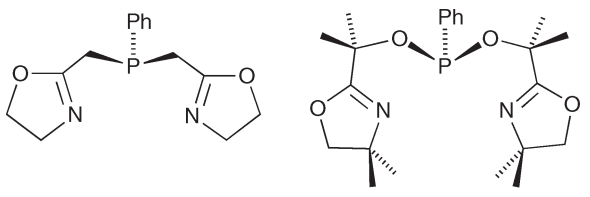
Received September 21, 2009

To examine the bonding preferences of potentially tridentate phosphorus, nitrogen donor ligands on a dinuclear metal core, we have studied the coordination of the oxazoline-based ligands bis(4,5-dihydro-2-oxazolylmethyl)phenylphosphine (NPN) and bis(4,4-dimethyl-2-oxazolyl dimethylmethoxy)phenylphosphine ($NOPON^{Me2}$) toward the dinuclear d^9-d^9 Pd(I) complex $[Pd_2(NCMe)_6][BF_4]_2$. In the dinuclear product $[Pd_2(NPN\text{-}N,P,N)_2](BF_4)_2$ (**1**), in which the Pd−Pd bond length of 2.5489(7) Å is rather short, the two interacting metal centers are P,N bridged by two molecules of the NPN ligand, forming two six-membered rings. The other oxazoline ring of each ligand further chelates a Pd center through its nitrogen atom, forming five-membered chelates, as in the mononuclear complex $[PdCl_2(NPN\text{-}N,P)]$ (**5**). In contrast, the reaction between $[Pd_2(NCMe)_6](BF_4)_2$ and $NOPON^{Me2}$ in the presence of LiCl afforded the mononuclear cationic complex $[Pd(NOPON^{Me2}\text{-}N,P,N)Cl](BF_4)$ (**3**), which is also obtained by halide abstraction from $[Pd(NOPON^{Me2}\text{-}N,P)Cl_2]$ with $NaBF_4$. When this reaction was performed in the presence of 1 equiv of *t*-BuNC, the new dinuclear Pd(I)−Pd(I) complex $[Pd_2Cl_2(CNt\text{-}Bu)(NOPON^{Me2}\text{-}N,P,N)]$ (**4**) was isolated, which can also be obtained from a comproportionation reaction between Pd(II) and Pd(0) complexes. The oxazoline in the P,N bridge is involved in a seven-membered ring moiety, a situation rarely encountered in Pd(I)−Pd(I) chemistry. Its nitrogen atom is coordinated *trans* to the isonitrile ligand whereas that of the P,N chelate at Pd(1) is *trans* to Pd(2). The fluxional processes involving the oxazoline moieties of the NPN and $NOPON^{Me2}$ ligands in **1** and **4**, respectively, were examined by variable-temperature NMR spectroscopy. The crystal structures of **1**, **3**·0.5CH_3CN, and **4** have been determined by X-ray diffraction. Prior to this work, relatively few complexes have been reported in the literature in which a potentially tridentate functional phosphorus ligand is simultaneously chelating and bridging a dinuclear Pd(I)−Pd(I) system.

Introduction

Oxazoline-based ligands continue to be much investigated in transition metal chemistry, largely because of the increasing number of their applications in homogeneous catalysis, in particular for asymmetric synthesis.[1] When an oxazoline moiety is associated with one or more donor atoms, such as phosphorus, nitrogen, or oxygen, a range of bifunctional ligands results which often lead to unique properties for their metal complexes in stoichiometric or catalytic reactions. We have previously reported the synthesis of two new tridentate ligands which associate two oxazoline moieties with a phosphine- or a phosphonite-type donor, NPN[2] and $NOPON^{Me2,3}$ respectively:



NPN **$NOPON^{Me2}$**

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(1) (a) Gómez, M.; Muller, G.; Rocamora, M. *Coord. Chem. Rev.* **1999**, *193−195*, 769–835. (b) Helmchen, G. *J. Organomet. Chem.* **1999**, *576*, 203–214. (c) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336–345. (d) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680–699. (e) Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953–3967. (f) Speiser, F.; Braunstein, P.; Saussine, L. *Acc. Chem. Res.* **2005**, *38*, 784–793. (g) Braunstein, P. *Chem. Rev.* **2005**, *106*, 134–159. (h) Desimoni, G.; Faita, G.; Jorgensen, K. A. *Chem. Rev.* **2006**, *106*, 3561–3651. (i) Agostinho, M.; Braunstein, P. *Chem. Commun.* **2007**, 58–60. (j) Agostinho, M.; Braunstein, P.; Welter, R. *Dalton Trans.* **2007**, 759–770. (k) Agostinho, M.; Braunstein, P. *C. R. Chim.* **2007**, *10*, 666–676. (l) Gade, L. H.; Bellemin-Laponnaz, S. *Coord. Chem. Rev.* **2007**, *251*, 718–725. (m) Kermagoret, A.; Pattacini, R.; Chavez Vasquez, P.; Rogez, G.; Welter; Braunstein, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6438–6441. (n) McManus, H. A.; Cusack, D.; Guiry, P. J. *Phosphorus Ligands Asymmetric Catal.* **2008**, *2*, 549–596. (o) Nishiyama, H.; Ito, J.-i.; Shiomi, T.; Hashimoto, T.; Miyakawa, T.; Kitase, M. *Pure Appl. Chem.* **2008**, *80*, 743–749. (p) Fraile, J. M.; Garcia, J. I.; Mayoral, J. A. *Coord. Chem. Rev.* **2008**, *252*, 624–646. (q) Kermagoret, A.; Braunstein, P. *Organometallics* **2008**, *27*, 88–99. (r) Pattacini, R.; Margraf, G.; Messaoudi, A.; Oberbeckmann-Winter, N.; Braunstein, P. *Inorg. Chem.* **2008**, *47*, 9986–9997. (s) Hargaden, G. C.; Guiry, P. *J. Chem. Rev.* **2009**, *109*, 2505–2550. (t) Maggini, S. *Coord. Chem. Rev.* **2009**, *253*, 1793–1832. (u) Pattacini, R.; Jie, S.; Braunstein, P. *Chem. Commun.* **2009**, 890–892.

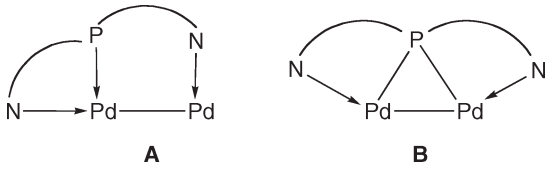
(2) Braunstein, P.; Fryzuk, M. D.; Naud, F.; Rettig, S. J. *J. Chem. Soc., Dalton Trans.* **1999**, 589–594.

(3) Braunstein, P.; Naud, F.; Dedieu, A.; Rohmer, M.-M.; DeCian, A.; Rettig, S. J. *Organometallics* **2001**, *20*, 2966–2981.

 Published on Web 11/18/2009

Whereas it was expected that these ligands would behave either as P,N-bidentate or N,P,N-tridentate donors toward a metal center, the recent finding that a ligand of the NPN family could also act as a N,N-chelate to form an eight-membered chelate, with no participation of the phosphorus group, was surprising.[4,5] Furthermore, these ligands can display hemilabile behavior in their metal complexes[1d] and lead to active catalysts in (asymmetric) transfer hydrogenation of acetone in propan-2-ol,[2,6] cyclopropanation of olefins,[6] and oligomerization of ethylene.[5] Until now, only few studies have been concerned with the reactivity of oxazoline-based heterotopic ligands with metal−metal bonded complexes,[7] the general focus having been placed on mononuclear complexes or on non metal−metal bonded polynuclear systems.[1,8]

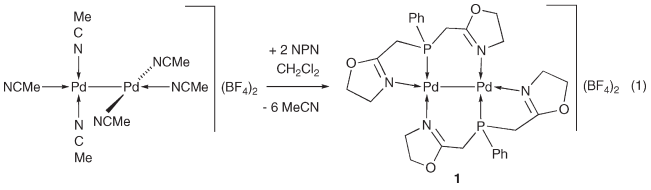
As an extension of our previous work on the NPN and $NOPON^{Me2}$ ligands,[2−5] we were interested in investigating their behavior in metal−metal bonded complexes, and we selected first the dinuclear Pd(I)−Pd(I) system, which has often been used in short-bite ligand chemistry where $Ph_2PCH_2PPh_2$ (dppm) and 2-(diphenylphosphino)pyridine (P-Py) belong to the most frequently used assembling ligands.[9] The ligands NPN and $NOPON^{Me2}$ would then lead to six- and seven-membered ring systems, respectively, in contrast to the five-membered rings commonly observed in dinuclear dppm or P-Py chemistry. Considering that additional stabilization might be required, we have chosen as a dinuclear template the metal−metal bonded d^9-d^9 complex $[Pd_2(NCMe)_6](BF_4)_2$,[10] with six labile acetonitrile ligands, because in addition to the anticipated P-coordination and bridge formation involving one oxazoline group, this dinuclear precursor should allow chelation of the other oxazoline and formation of a favorable five-membered (in the case of NPN) or six-membered ring chelate (in the case of $NOPON^{Me2}$) in an arrangement of type **A**. In addition to the molecular stabilization it provides, combined bridge and chelate formation is attractive in the context of cooperative bimetallic catalysis.[11] A more unusual arrangement of type **B** could not be ruled out.[12] Indeed, examples of tertiary phosphines bridging two metal centers were first reported in 2000 in Rh(I) chemistry,[13] then in Pd(II) and Pt(II) chemistry,[14] and, more recently, also observed in Cu(I)[15,16] and Ag(I)[16,17] complexes. Particularly relevant to our systems are the results by Réau and co-workers with a 2,5-bis(2-pyridyl)phosphole ligand which bridges a dipalladium unit in a symmetrical μ_2-manner via the phosphorus atom,[14] and those by Klausmeyer on phenylbis(pyrid-2-ylmethyl)phosphine and bis(pyrid-2-ylmethyl) phenylphosphonite ligands with symmetrically bridge dicopper and disilver units.[16]



Open questions at the onset of the work include whether on steric grounds one or two of our potentially tridendate ligands can be accommodated by the dinuclear template, and whether the ligand system will be static or display fluxional behavior.

Results and Discussion

The reaction of $[Pd_2(NCMe)_6](BF_4)_2$ with 2 equiv of the NPN ligand in CH_2Cl_2 afforded the yellow complex **1** in 80% yield (eq 1). This compound is poorly soluble in most common organic solvents (CH_2Cl_2, $CHCl_3$, THF, etc.) but can be dissolved in acetonitrile or nitromethane. Since the coordinated phosphorus becomes a stereogenic center, a pair of diastereoisomeric complexes is expected. However, we have no evidence for the presence of the *meso* diastereoisomer, neither in solution nor in the solid-state (see below).



Its $^{31}P\{^1H\}$ NMR spectrum in CD_3NO_2 contains only a singlet at δ 13.3 ppm, a value which is consistent with coordination of the phosphorus atom.[2] Surprisingly, the ^1H NMR of **1** in CD_3NO_2 at room temperature contains only a doublet for the PCH_2 protons and two triplets for the methylene protons of the oxazoline rings (see below). This simplification of the ^1H NMR and $^{31}P\{^1H\}$ NMR spectra of **1** suggests a fluxional behavior at room temperature. Therefore, low temperature NMR measurements have been undertaken, and the results are detailed below. The IR spectrum of **1** in KBr shows a

(4) Kermagoret, A.; Braunstein, P. *Dalton Trans*. **2008**, 585–587.
(5) Kermagoret, A.; Tomicki, F.; Braunstein, P. *Dalton Trans*. **2008**, 2945–2955.
(6) (a) Braunstein, P.; Naud, F.; Pfaltz, A.; Rettig, S. J. *Organometallics* **2000**, *19*, 2676–2683. (b) Braunstein, P.; Naud, F.; Rettig, S. J. *New J. Chem*. **2001**, *25*, 32–39.
(7) (a) Braunstein, P.; Clerc, G.; Morise, X.; Welter, R.; Mantovani, G. *Dalton Trans*. **2003**, 1601–1605. (b) Cabeza, J. A.; Da Silva, I.; Del Rio, I.; Gossage, R. A.; Miguel, D.; Suarez, M. *Dalton Trans*. **2006**, 2450–2455. (c) Braunstein, P.; Clerc, G.; Morise, X. *New J. Chem*. **2003**, *27*, 68–72. (d) Jie, S.; Pattacini, R.; Rogez, G.; Loose, C.; Kortus, J.; Braunstein, P. *Dalton Trans*. **2009**, 97–105.
(8) Jie, S.; Agostinho, M.; Kermagoret, A.; Cazin, C. S. J.; Braunstein, P. *Dalton Trans*. **2007**, 4472–4482.
(9) (a) Murahashi, T; Kurosawa, H. *Coord. Chem. Rev*. **2002**, *231*, 207–228. (b) Newkome, G. R. *Chem. Rev*. **1993**, *93*, 2067–2089. (c) Mague, J. T. *J. Cluster Sci*. **1995**, *6*, 217–269. (d) Zhang, Z.-Z.; Cheng, H. *Coord. Chem. Rev*. **1996**, *147*, 1–39. (e) Espinet, P.; Soulantica, K. *Coord. Chem. Rev*. **1999**, *193−195*, 499–556. (f) Braunstein, P.; Knorr, M.; Stern, C. *Coord. Chem. Rev*. **1998**, *178−180*, 903–965.
(10) Murahashi, T.; Nagai, T.; Okuno, T.; Matsutani, T.; Kurosawa, T. *Chem. Commun*. **2000**, 1689–1690.
(11) Aubry, D. A.; Bridges, N. N.; Ezell, K.; Stanley, G. G. *J. Am. Chem. Soc*. **2003**, *125*, 11180.
(12) Braunstein, P.; Boag, N. *Angew. Chem., Int. Ed*. **2001**, *40*, 2427–2433.
(13) (a) Pechman, T.; Brandt, C. D.; Werner, H. *Angew. Chem., Int. Ed*. **2000**, *39*, 3909–3911. (b) Werner, H. *Angew. Chem., Int. Ed*. **2004**, *43*, 938–954.
(14) (a) Sauthier, M.; Le Guennic, B.; Deborde, V.; Toupet, L.; Halet, J.-F.Réau, R. *Angew. Chem., Int. Ed*. **2001**, *40*, 228–231. (b) Leca, F.; Sauthier, M.; Deborde, V.; Toupet, L.; Réau, R. *Chem.—Eur. J*. **2003**, *9*, 3785–3795.
(15) (a) Leca, F.; Lescop, C.; Rodriguez-Sanz, E.; Costuas, K.; Halet, J.-F.; Réau, R. *Angew. Chem., Int. Ed*. **2005**, *44*, 4362–4365. (b) Nohra, B.; Rodriguez-Sanz, E.; Lescop, C.; Réau, R. *Chem.—Eur. J*. **2008**, *14*, 3391–3403.
(16) Hung-Low, F.; Renz, A.; Klausmeyer, K. K. *Eur. J. Inorg. Chem*. **2009**, 2994–3002.
(17) (a) Welsch, S.; Lescop, C.; Scheer, M.; Réau, R. *Inorg. Chem*. **2008**, *47*, 8592–8594. (b) Welsch, S.; Nohra, B.; Peresypkina, E. V.; Lescop, C.; Scheer, M.; Réau, R. *Chem.—Eur. J*. **2009**, *15*, 4685–4703.

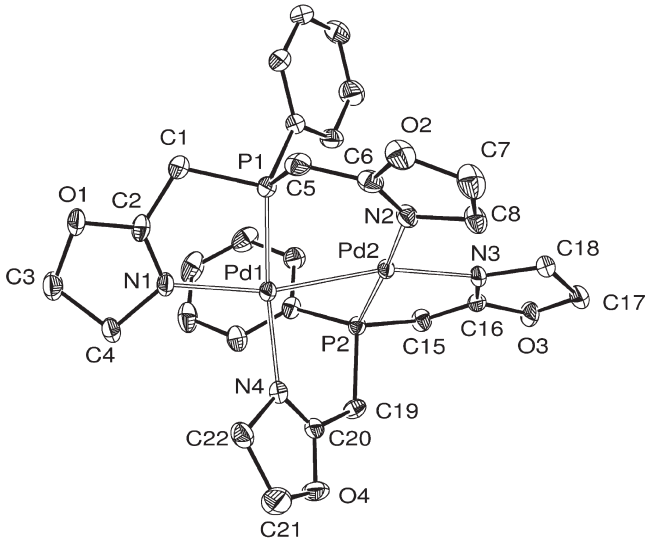


Figure 1. ORTEP of the molecular structure of **1**, hydrogen atoms and anions omitted for clarity. Ellipsoids drawn at 50% probability level. Selected bond distances (Å) and angles (deg): Pd1−Pd2 2.5489(7), Pd1−P1 2.189(1), Pd2−P2 2.189(1), Pd1−N1 2.135(3), Pd1−N4 2.111(3), Pd2−N2 2.114(3), Pd2−N3 2.194(3), N1−C2 1.274(5), N2−C6 1.281(5), N3−C16 1.276(5), N4−C20 1.270(5), P1−Pd1−Pd2 81.42(3), N1−Pd1−P1 84.83(9), N4−Pd1−N1 99.8(1), N4−Pd1−Pd2 94.79(8), P2−Pd2−Pd1 75.95(3), P2−Pd2−N3 83.42(9), N2−Pd2−N3 102.5(1), N2−Pd2−Pd1 97.86(9).

strong absorption at 1640 cm^{-1} consistent with the coordination of each oxazoline to palladium. Unfortunately, it was not possible to measure its IR absorption in solution owing to the low solubility of the complex in usual solvents and the absorptions of nitromethane and acetonitrile in this spectral region. The solid-state structure of **1** was established by single crystal X-ray diffraction (see Figure 1).

In the molecular structure of the dinuclear cation in **1**, the two interacting metal centers are P,N bridged by two molecules of the NPN ligand, forming two six-membered rings. The other oxazoline ring of each ligand further chelates a Pd center through its nitrogen atom, forming five-membered chelates. Overall, the tridentate ligand adopts a type **A** configuration. The geometry around the metal centers can be described as distorted square-planar, when the Pd−Pd bond is considered. The cation has an approximate C_2 symmetry, the axis passing through the middle of the Pd−Pd bond (see Figure 2).

The Pd−Pd bond length of 2.5489(7) Å is in the lower part of the normal bond length range[18] observed in metal−metal bonded dinuclear palladium complexes and is shorter than that in $[Pd\{PhP(CH_2CH_2PPh_2)_2\}]_2[BF_4]_2$ (2.617(1) Å).[19] This relatively short Pd−Pd bond length can be related to the weaker *trans* influence of the oxazoline nitrogen compared to that of phosphorus in $[Pd\{PhP(CH_2CH_2PPh_2)_2\}]_2[BF_4]_2$.[19] The Pd−N bond *trans* to the metal−metal bond are longer than those in *trans* position with respect to phosphorus (Pd1−N1 2.135(3) and Pd1−N4 2.111(3) Å; Pd2−N3 2.194(3) and Pd2−N2 2.114(3) Å, respectively),

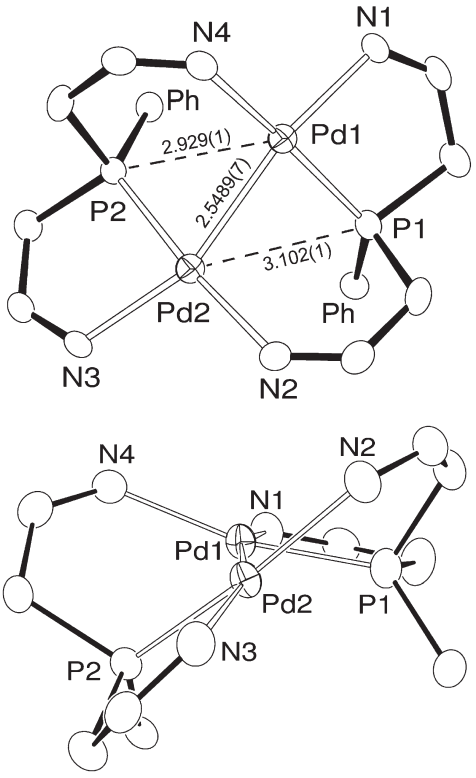
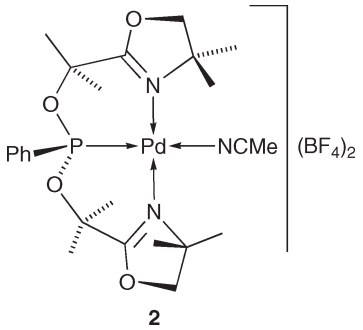


Figure 2. Approximately orthogonal views of the crystal structure of the cation in **1**. Oxazoline rings and phenyls omitted for clarity. Distances are in Å.

indicating that the Pd atoms exert a higher *trans* influence.[19] The Pd−P distances of 2.189(1) Å are in the expected range. The non-bonding P2···Pd1 distance of 2.929(1) Å is significantly shorter than the P1···Pd2 distance of 3.102(1) Å, which suggests a slight distortion toward a **B**-type structure for the P2 ligand, when compared to P1. The angle between the two mean planes defined by the atoms P1, Pd1, N1, N4 and P2, Pd2, N2, N3 is 49.60(5)°.

When $[Pd_2(NCMe)_6](BF_4)_2$ was reacted with 1 or 2 equiv of $NOPON^{Me2}$, a rapid color change occurred, but the only palladium complex that could be isolated was the known $[Pd(NOPON^{Me2})(NCMe)](BF_4)_2$ (**2**)[3] and formation of palladium metal was observed.



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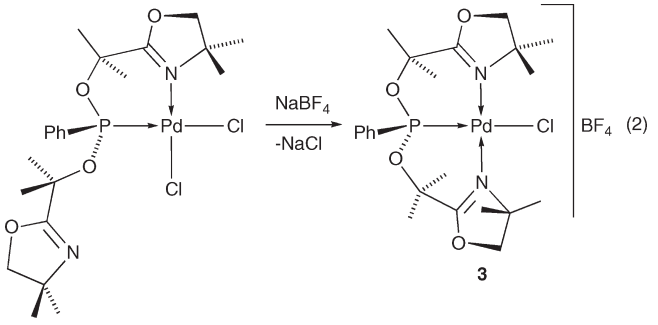
Obviously, a redox reaction has occurred which corresponds to the disproportionation of the precursor complex: Pd(I)−Pd(I) → Pd(0) + Pd(II). Other approaches to obtain Pd(I) complexes with this ligand have been explored, such as comproportionation reactions

(18) CCDC database, November 2008 update. Median of the Pd−Pd bond lengths on 77 tetracoordinate dinuclear complexes: 2.594 Å, mean: 2.583 Å (σ = 0.055).

(19) DuBois, D. L.; Miedaner, A.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 8753–8764.

where Pd(0) species ([Pd(dba)$_2$] or [Pd$_2$(dba)$_3$]) and NOPON^{Me2} were added to a solution of **2**, unfortunately without success. The lack of formation of the NOPON^{Me2} analogue of **1** could be related to the lower stability of a seven-membered ring bridge compared to the six-membered ring found in **1** and to a possible steric hindrance generated by the oxazoline methyl groups.

When the reaction between [Pd$_2$(NCMe)$_6$](BF$_4$)$_2$ and NOPON^{Me2} was performed in the presence of LiCl, the complex [Pd(NOPON^{Me2}-*N,P,N*)Cl](BF$_4$) (**3**) was isolated and some decomposition to Pd(0) was also observed. A better synthesis of this complex was achieved by halide abstraction from [Pd(NOPON^{Me2}-*N,P*)Cl$_2$] with NaBF$_4$ (eq 2) (see Experimental Section).



The IR spectrum of **3** in CH_2Cl_2 shows only one ν(C=N) band, at 1623 cm^{-1}, consistent with the coordination of both oxazolines to Pd. Phosphorus coordination leads to a $^{31}P\{^1H\}$ NMR signal at 114.5 ppm which corresponds to an upfield shift of 36 ppm with respect to the free ligand, and of 8 ppm compared to [Pd(NOPON^{Me2})(NCMe)](BF$_4$)$_2$ (**2**), which reflects the coordination of the chloride in place of acetonitrile. The ^{1}H NMR spectrum of **3** contains only one AB spin system for the methylene protons of the oxazoline rings, consistent with the expected C_v symmetry of the complex. Three singlets and a doublet correspond to the eight methyl groups of the molecule. The doublet arises from a $^4J_{PH}$ coupling of 2.0 Hz between the protons of one methyl group of the OC(CH_3)$_2$ fragment and the P atom, as observed in the complex [Pd(NOPON^{Me2})(NCMe)](BF$_4$)$_2$ (**2**).[3] The detailed assignment of the resonances (see Experimental Section) was made from COSY ^{1}H/^{1}H experiments. To examine whether the charge difference between **2** and **3** had any influence on the bonding parameters, the crystal structure of **3**·1/2MeCN was determined by single crystal X-ray diffraction (Figure 3). There are two independent but almost identical molecules in the unit cell.

In the molecular structure of **3**, the tridentate NOPON^{Me2} ligand acts as *pincer* through the phosphorus and the nitrogen atoms. The metal center adopts a slightly distorted square-planar geometry, similar to that found in **2**.[3] Slight elongations of the donor-Pd bonds are observed in **3** when compared with **2**, in agreement with the lower charge of the cation, and the longer Pd−P distance is also consistent with a higher *trans* influence of the chloride with respect to the acetonitrile ligand [Pd−P distance: 2.1889(1) Å in **3** vs 2.174(1) Å in **2**; Pd−N bonds: 2.044(2) and 2.055(2) Å in **3** vs 2.038(2) and 2.030(2) Å in **2**]. The length of the Pd1−Cl1 bond is consistent with the high *trans* influence of the P donor.[20] The NOPON^{Me2} ligand coordinates in a slightly asymmetrical manner, with a distortion from the ideal C_v symmetry. The N1−Pd1−P1−C17 dihedral angle [69.4(1)°] is smaller than the N2−Pd1−P1−C17 one [75.2(1)°], resulting, for example, in mutually non-equivalent orientations of the methyl groups with respect to the metal coordination plane. The oxazoline rings are not coplanar; the angle between the mean planes formed by their atoms is 33.3(1)°.

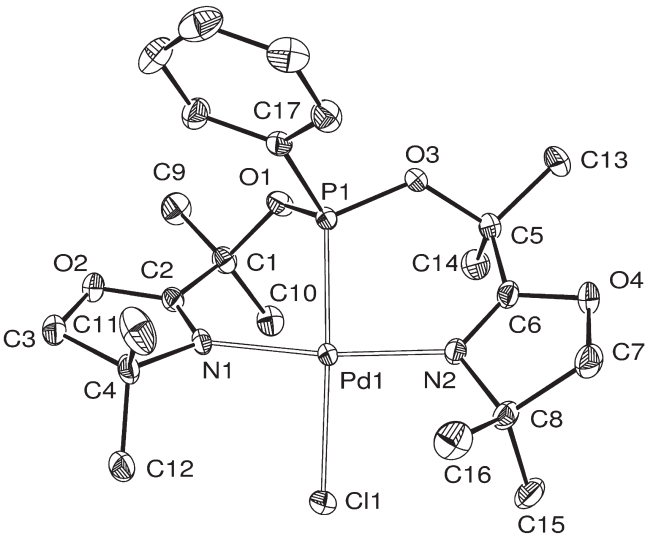


Figure 3. ORTEP of the molecular structure of the cation in **3**·1/2MeCN, hydrogen atoms, solvent and anions omitted for clarity. Only one of the two similar independent molecules is shown. Ellipsoids drawn at 50% probability level. Selected distances (Å) and angles (deg): Molecule A: Pd1−N1 2.044(2), Pd1−N2 2.055(2), Pd1−P1 2.1889(7), Pd1−Cl1 2.3734(7), N1−Pd1−P1 82.68(6), N2−Pd1−P1 91.02(6), N1−Pd1−Cl1 92.79(6), N2−Pd1−Cl1 94.73(6); Molecule B: Pd2−N3 2.043(2), Pd2−N4 2.051(2), Pd2−P2 2.1876(7), Pd2−Cl2 2.3729(7), N3−Pd2−P2 83.01(6), N4−Pd2−P2 89.96(6), N3−Pd2−Cl2 92.42(6), N4−Pd2−Cl2 95.87(6).

When the reaction between [Pd$_2$(NCMe)$_6$](BF$_4$)$_2$ and NOPON^{Me2} was performed in the presence of 2 equiv of LiCl and 1 equiv of *t*-BuNC, the new dinuclear complex **4** was isolated in about 20% yield (eq 3). It has been identified by single crystal X-ray diffraction (Figure 4, see below). Its ^{1}H NMR spectrum at room temperature shows only one AB spin system for the four methylene protons of the oxazoline rings and four singlet resonances corresponding to the eight methyl group protons of the oxazoline rings. This is consistent with the existence of a fluxional process between the two oxazolines of the NOPON^{Me2} ligand which render them equivalent on the ^{1}H NMR time scale. Thus low temperature NMR measurements have been undertaken, and their results are detailed below. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 contains a singlet at δ 127.8 ppm which is consistent with coordination of the phosphorus atom.[3] The IR spectrum of **4** in KBr shows a strong, broad band at 1641 cm^{-1}, corresponding to the coordination of both oxazolines to Pd, but in CH_2Cl_2, the IR spectrum shows two absorptions at 1642 cm^{-1} and 1654 cm^{-1}, supporting the presence of coordinated and uncoordinated oxazoline rings.[3]

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

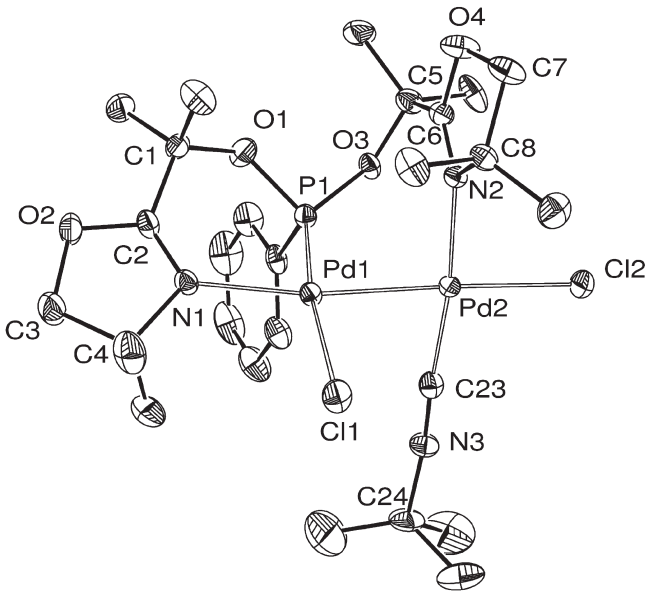
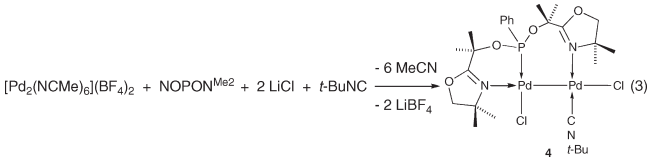
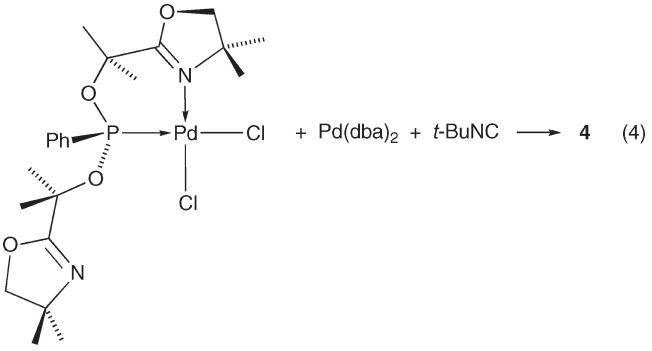


Figure 4. ORTEP of the molecular structure of the cation in **4**, hydrogen atoms omitted for clarity. Ellipsoids drawn at 50% probability level. Selected bond distances (Å) and angles (deg): Pd1−Pd2 2.5230(4), Pd1−P1 2.1553(9), Pd1−N1 2.175(3), Pd1−Cl1 2.395(1), Pd2−Cl2 2.429(1), Pd2−C23 1.909(4), Pd2−N2 2.087(3); P1−Pd1−N1 89.04(8), N1−Pd1−Cl1 99.74(8), P1−Pd1−Pd2 79.72(3), Cl1−Pd1−Pd2 91.60(3), C23−Pd2−Cl2 95.3(1), N2−Pd2−Cl2 92.54(8), C23−Pd2−Pd1 83.6(1), N2−Pd2−Pd1 88.44(8).



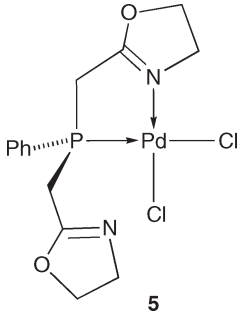
In the molecular structure of the dinuclear complex **4**, the two metal−metal bonded palladium atoms are P,N-bridged by a NOPON^{Me2} ligand to form a seven-membered ring, a situation rarely encountered in Pd(I)−Pd(I) chemistry (Figure 4). The nitrogen atom of the second oxazoline is bound to Pd1, which leads to a six-membered chelate. Overall, the NOPON^{Me2} ligand gives rise to a chelating-bridging coordination mode of type **A**, similar to that observed for the PNP ligand in **1**. Both metals are further coordinated by a terminal chloride and show a distorted square planar coordination geometry. The coordination sphere around Pd2 is completed by a *t*-BuNC ligand. The Pd−Pd bond length of 2.5230(4) Å is shorter than that in **1** (2.549(1) Å) and in $[Pd_2X_2(\mu\text{-dppm})_2]$ (X = anionic ligand),[21] but longer than in $[Pd_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3\text{-}2\text{-}C_5H_4N\}_2][BF_4]_2\cdot 4H_2O$ (2.500(1) Å).[22] This relatively short Pd−Pd bond distance in complex **4** may be due to the moderate *trans* influences of the oxazoline nitrogen and of the chloride donors. The terminal chlorides Cl1 and Cl2 are in *cis* and *trans* positions with respect to the Pd−Pd bond, respectively. The isonitrile ligand is *trans* to the nitrogen donor, which is consistent with the relative *trans* influences of these ligands and the antisymbiotic effect.[23] The angle between the two coordination planes defined by the atoms P1, Pd1, N1, Cl1 and Pd2, N2, Cl2, C23 is relatively large [70.77(6)°] compared to that in complex **1** [49.60(5)°], in $[Pd_2\{PhP(CH_2CH_2PPh_2)_2\}][BF_4]_2$ (67°),[19] or in $[Pd_2\{o\text{-}Ph_2PC_6H_4CH_2O(CH_2)_3\text{-}2\text{-}C_5H_4N\}_2][BF_4]_2\cdot 4H_2O$ (58°).[22] This difference can be related to the fact that **4** contains only one tridentate ligand, which results in less steric strain in the complex.

Knowing the structure of the Pd(I)−Pd(I) complex **4**, we were able to devise an alternative, higher yield synthesis (80%) for this complex which consisted in the comproportionation reaction shown in eq 4:



However, when [Pd(NOPON^{Me2}-*N,P,N*)Cl](BF$_4$) (**3**) was reacted with 1 equiv each of [Pd(dba)$_2$], *t*-BuNC, and LiCl in CH_2Cl_2, **4** was obtained in only 65% yield and 22% of **3** was recovered. This slightly lower yield may be due to the relatively poor solubility of the added LiCl. It also appears that [Pd(NOPON^{Me2}-*P,N*)Cl$_2$] reacts faster with the Pd(0) precursor than **3**. It is therefore possible that when the latter is used, it first reacts with LiCl to give [Pd(NOPON^{Me2}-*P,N*)Cl$_2$] and then **4**, rather than directly with the Pd(0) complex to give a cationic dinuclear Pd(I) complex which would then react with LiCl.

To examine whether an NPN analogue of **4** could be obtained, we first synthesized [Pd(NPN-*P,N*)Cl$_2$] (**5**) by reaction of [PdCl$_2$(COD)] with 1 equiv of the NPN ligand. Its $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 contains only a singlet at 21.4 ppm which is consistent with coordination of the phosphorus atom. Its ^1H NMR spectrum is quite intricate as there is no symmetry element in the molecule. Therefore a detailed peak assignment has been made using $^1H/^1H$ COSY and $^1H/^{13}C$ HMBC experiments at room temperature (see Experimental Section). Complex **5** was then reacted with [Pd$_2$(dba)$_3$] (or [Pd(dba)$_2$]) in the presence of 1 equiv of *t*-BuNC under the same conditions as **4**. The solution turned dark orange within a few hours, and its ^{31}P NMR spectrum revealed the formation of several products but none of them has been successfully isolated.



Dynamic Behavior of Complexes 1 and 4. As mentioned above, NMR and IR data of **4** indicate the existence of a

(21) Besenyei, G.; Párkányi, L.; Gács-Baitz, E.; James, B. R. *Inorg. Chim. Acta* **2002**, *327*, 179–187.
(22) Tani, K.; Nakamura, S.; Yamagata, T; Kataoka, Y. *Inorg. Chem.* **1993**, *32*, 5398–5401.
(23) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712–713.

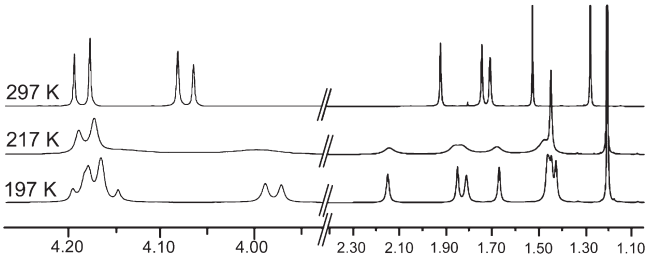


Figure 5. Variable temperature ^{1}H NMR spectra of **4** in CD_2Cl_2.

fluxional process involving the oxazoline moieties of the NOPON^{Me2} ligand which make them become equivalent on the ^{1}H NMR time-scale. We thus examined the low temperature behavior of **4**. At 197 K, the ^{1}H and ^{13}C{^{1}H} NMR spectra show two sets of signals for the two chemically non-equivalent oxazoline moieties. The detailed assignments resulted from ^{1}H/^{1}H and ^{1}H/ ^{13}C COSY and HMQC experiments. Seven ^{1}H NMR singlets correspond to the eight methyl groups because 2 methyl groups accidentally resonate at δ 1.47 ppm (see Figure 5).

In the ^{13}C{^{1}H} spectrum, eight resonances are indeed observed for the methyl groups. The OCH_2 protons give rise to two AB spin systems which partly overlap and two singlets are observed in the ^{13}C{^{1}H} spectrum for the OCH_2 carbons. The *C*OP carbons gives rise to a singlet and a doublet (with $^2J_{PC}$ = 9.8 Hz). When the temperature is increased to 207 K, the resonances of the O*C*H_2 protons broaden, and the methyl resonances at 1.44 and 1.46 coalesce. Upon further warming, general broadening occurs around 217 K, and the resonances progressively sharpen until both oxazoline arms have become equivalent. The dynamic behavior of the molecule may be explained by an opening/closing movement of the 6-membered ring followed by that of the 7-membered ring, or vice versa, and complete exchange of the oxazolines by ligand rotation about the P−Pd bond. Opening of the N(1)−Pd(1) bond *trans* to the metal−metal bond could be easier than that *trans* to the RNC ligand, owing to the *trans* effect of the former. Given a coalescence temperature of 225(5) K for the OCH_2 protons, the estimated $\Delta G^{\ddagger}$ of the overall process is 45(1) KJ/mol.

The ^{1}H NMR spectrum of **1** in CD_3NO_2 at room temperature contains only one AA′X spin system for the PCH_2 protons (which appears as a deceptively simple A_2X system) and two AA′MM′ spin systems (which appear in the form of two triplets as deceptively simple A_2M_2 systems) for the methylene groups of the oxazoline rings, unlike the ^{1}H NMR pattern of the free ligand where one ABX spin system and two ABMN spin systems have been observed.[2] These data indicate intricate fluxional behavior for complex **1**. An opening/closing mechanism of the chelate arm of the ligand and the decoordination/rotation process described for **4** are not sufficient to explain the oversimplification of the NMR pattern. At variance with the case described above, the protons of each CH_2 group appear magnetically equivalent in the spectrum of **1** recorded at 298 K. This can be only explained by an inversion of the configuration at P. Consequently, low temperature NMR experiments have been undertaken in CD_3NO_2/CD_2Cl_2 (2:1). At 218 K, the ^{1}H NMR spectrum shows the presence of two chemically inequivalent oxazoline arms. ^{1}H/^{1}H COSY and ^{1}H/^{13}C

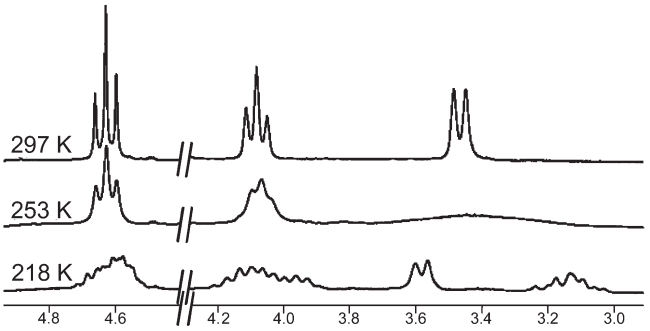


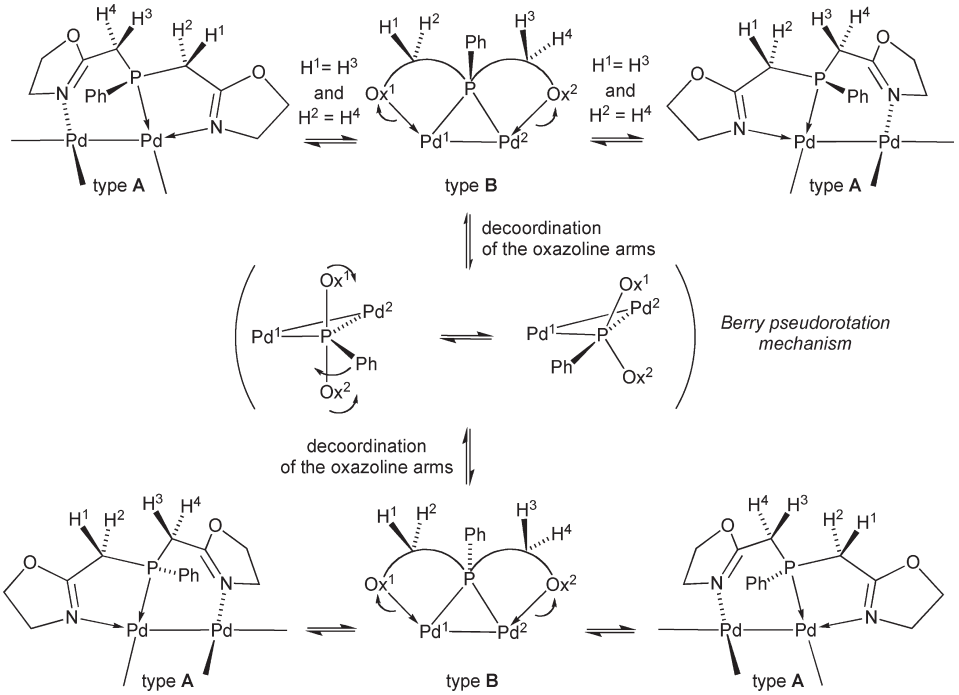
Figure 6. Variable temperature ^{1}H NMR spectra of **1** in CD_3NO_2/CD_2Cl_2 (2:1).

HMQC experiments, at 500.13 and 125.7 MHz, respectively, have allowed here a detailed assignment. At this temperature, a ^{31}P{^{1}H} NMR singlet at 9.6 ppm indicates the presence of only one diastereoisomer. The P*C*H_2 groups give rise to two different ^{1}H spin systems: a doublet at 3.58 and a multiplet at 3.13 ppm which has an important upfield shift of 0.32 ppm with respect to the room temperature PCH_2 signal. The multiplet has been identified as an ABX spin system and coupling constants have been obtained by simulation. The ^{13}C{^{1}H} NMR spectrum showed also the appearance of two broad singlets which can each be assigned to a different PCH_2 group (J_{PC} in both cases has not been resolved). The ^{1}H/^{1}H COSY experiment also revealed a ^5J coupling between the P*C*H_2 and N*C*H_2 protons. The ^{1}H/^{13}C HMQC and ^{1}H/^{1}H COSY experiments revealed the presence of two different but overlapping N*C*H_2 multiplets at 4.09 and 3.98 ppm. The O*C*H_2 peaks overlapped and appeared as an intricate multiplet at 4.61 ppm. Upon further warming, the peaks broaden, the P*C*H_2 resonances coalesce at 253 K and sharpen at room temperature (see Figure 6).

To know whether the NMR signals at low temperature are those of the diastereoisomer identified by single crystal X-ray diffraction, NMR spectra of a solution prepared by dissolution of the crystals below 218 K were recorded. These ^{1}H, ^{1}H/^{1}H, and ^{31}P{^{1}H} experiments afforded the same spectra as the solution prepared at room temperature from a powder sample. Overall, the spectrum observed at 218 K is consistent with the solid state structure, in which the two oxazoline arms within one ligand are not equivalent while the two ligands can be related by the aforementioned C_2 pseudosymmetry. As expected, all the CH_2 groups appear diastereotopic, with the exception of a PCH_2 group, whose ABX spin system is not fully resolved. To explain the oversimplification of the spectrum at room temperature, inversion of the P configuration is required, and this may occur via an intermediate structure of type **B** (Scheme 1), which would be related to situations described with the 2,5-bis(2-pyridyl)phosphole *N,P,N* ligand.[14] From structural and strain considerations, it should be also easier to envisage first the uncoordination of the oxazoline arms to enable the Berry pseudorotation mechanism.[24] Given the coalescence temperature of 253(5) K for the PCH_2 system and a $\Delta\nu$ = 129 Hz at low temperatures for these two signals, the estimated global $\Delta G^{\ddagger}$ of the process is 49(1) KJ/mol.

(24) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933–938.

Scheme 1. Proposed Dynamic Behavior Based on Variable-Temperature NMR Experiments[a]



[a] For symmetry reasons, we consider only one of the two N,P,N ligands bound to the dinuclear unit.

Conclusion

It appears clearly from this study that coordination of the trifunctional NPN and NOPON^{Me2} ligands to a d^9-d^9 dipalladium unit requires specific conditions. Whereas NPN was better suited than NOPON^{Me2} for the synthesis of complexes of type **1** in which two ligands simultaneously bridge and chelate the dinuclear unit, and this may be due to steric reasons, the reverse is true for complex **4** which contains only one trifunctional bridging-chelating ligand and has no counterpart with the NPN ligand. This may have electronic origins since NPN is perfectly suited from a steric point of view to bridge-chelate the Pd_2 unit. Furthermore, the presence of the methyl groups in NOPON^{Me2} may stabilize the structure of **4** through multiple non-classical H-bonding interactions between methyl protons and proximal chlorides. We have also demonstrated that both complexes display fluxional behavior at room temperature and, for each of them, low temperature NMR measurements have been carried out and a mechanism has been proposed to account for their dynamic behavior. Whereas an uncoordination/rotation process has been suggested for **4**, a Berry pseudorotation mechanism has been proposed for **1**, involving a pentacoordinated phosphorus in a type **B** structure.

To the best of our knowledge, relatively few complexes have been reported in the literature in which a potentially tridentate functional phosphine ligand is simultaneously chelating and bridging a dinuclear Pd(I)−Pd(I) system.[1t,19,22,25] Multidentate ligands displaying different types of donor functions, such as phosphorus and nitrogen in this study, and able to simultaneously bridge and chelate a dinuclear metal core in a chemoselective manner,[1t] offer the possibility of undergoing hemilabile[1d] or more complex dynamic behavior which may in turn facilitate the fixation and activation of small organic molecules.[26]

Experimental Section

All reactions were performed under nitrogen; solvents were purified and dried under nitrogen by conventional methods. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at room temperature at 300.13, 121.5, and 75.4 MHz, respectively, unless otherwise stated. IR spectra in the 4000−400 cm^{-1} range were recorded on a Bruker IFS66 FT Spectrometer. The ligands NPN[2] and NOPON^{Me2},[3] and the complexes $[Pd_2(NCMe)_6][BF_4]_2$,[10] $[Pd_2(dba)_3]\cdot CHCl_3$,[27] and $[Pd(dba)_2]$[28] were prepared according to the literature.

$[Pd_2$(NPN-*N,P,N*)$_2](BF_4)_2$ (1). In a 100 mL Schlenk tube were placed NPN (0.315 g, 1.14 mmol) and $[Pd_2(NCMe)_6][BF_4]_2$ (0.360 g, 0.57 mmol) in CH_2Cl_2 (30 mL) at −78 °C. The solution turned yellow orange within 1 h, and a yellow precipitate formed. The precipitation was completed by addition of Et_2O (50 mL), the solid was collected by filtration and washed twice with Et_2O (2 × 50 mL). Yield: 0.430 g (80%). This yellow solid can be recrystallized from CH_3CN/Et_2O (1:3) or CH_3NO_2/Et_2O (1:3) affording yellow orange parallepipedic crystals. Selected IR data (KBr): 1640 (s, ν(C=N) cm^{-1}. ^1H NMR (CD_3NO_2, 298 K) δ: 3.45 (d, $^2J_{PH}$ = 10.8 Hz, 8H, PCH_2), 4.07 (t, $^3J_{HH}$ = 9.6 Hz, 8H, NCH_2), 4.71 (t, $^3J_{HH}$ = 9.6 Hz, 8H, OCH_2), 7.34−7.58 (m, 10H, aromatic). $^{13}C\{^1H\}$ (CD_3NO_2, 298 K) δ: 32.8 (d, $^1J_{PC}$ = 34 Hz, PCH_2), 55.7 (s, NCH_2), 72.8 (s, OCH_2), 130.7 (d, J_{PC} = 11.9 Hz, aryl), 131.4 (d, J_{PC} = 12.5 Hz, aryl), 132.6 (s, *p*-aryl), 132.7 (d, $^1J_{PC}$ = 24.1 Hz, *ipso*-aryl), 174.7 (d, $^2J_{PC}$ = 12.5 Hz, C=N). $^{31}P\{^1H\}$ (CD_3NO_2, 298 K)

(25) Wachtler, H.; Schuh, W.; Ongania, K.-H.; Kopacka, H.; Wurst, K.; Peringer, P. *J. Chem. Soc., Dalton Trans.* **2002**, 2532–2535. Song, H.-B.; Zhang, Z.-Z.; Mak, T. C. W. *Inorg. Chem. Commun.* **2002**, *5*, 442–445. Nuricumbo Escobar, J. J.; Campos-Alvarado, C.; Rios-Moreno, G.; Morales-Morales, D.; Walsh, P. J.; Parra-Hake, M. *Inorg. Chem.* **2007**, *46*, 6182–6189.

(26) See, for example, Jones, N. D.; Foo, S. J. L.; Patrick, B. O.; James, B. R. *Inorg. Chem.* **2004**, *43*, 4056–4063.

(27) Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanta, A.; Zangrando, E.; Silvano, G.; Meastroni, G. *Organometallics* **1997**, *16*, 5064.

(28) Ukai, T.; Kawazura, H.; Ishii, H.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253–266.

δ: 13.3 (s). In the low temperature spectra, the two different oxazoline arms of the ligands are identified by primed and unprimed labels as a result of 2D ^{1}H−^{1}H and ^{1}H−^{13}C experiments. ^{1}H NMR (300 MHz, CD_3NO_2/CD_2Cl_2 (2:1), 218 K) δ: ABX spin system simulated by *g*-NMR (X = P), δ_A = 3.16 (q, $^2J_{AB}$ = 18.6 Hz, $^2J_{PA}$ = 5.2 Hz, 2H, PC$H'_AH'_B$), δ_B = 3.08 (q, $^2J_{AB}$ = 18.6 Hz, $^2J_{PB}$ = 10.2 Hz, 2H, PC$H'_AH'_B$), 3.58 (d, $^2J_{PH}$ = 11.5 Hz, 4H, PCH_2), 3.94 (m, part of a ABMN spin system, partly masked by the following signal), 4.09 (center of m, 6H, NC$H'_AH'_B$ and NCH_2), 4.6 (overlapping m, 8H, OCH_2 and OCH'_2), 7.14−7.18 (m, 4H, aromatic), 7.45−7.57 (m, 6H, aromatic). ^{31}P{^{1}H} (CD_3NO_2/CD_2Cl_2 (2:1), 218 K) δ: 9.6 (s). ^{13}C{^{1}H} (125.7 MHz, CD_3NO_2/CD_2Cl_2 (2:1), 218 K) δ: 31.2 (br s, PCH_2), 32.8 (br s, PC$'H_2$), 54.1 (masked by CH_2Cl_2 but determined from ^{1}H−^{13}C COSY NMR, s, NC$'H_2$), 55.3 (masked by CH_2Cl_2 but determined from ^{1}H−^{13}C COSY NMR, s, NCH_2), 71.2 (s, OC$'H_2$), 73.2 (s, OCH_2), 129.9 (d, J_{PC} = 11.2 Hz, aryl), 131.4 (d, J_{PC} = 12.8 Hz, aryl), 132.6 (s, *p*-C of aryl), 132.7 (d, $^1J_{PC}$ = 24.1 Hz, *ipso*-C of aryl), 174.7 (br s, C=N and C$'$=N). Anal. Calcd. for $C_{28}H_{34}B_2F_8N_4O_4P_2Pd_2$: C, 35.82; H, 3.65; N, 5.97. Found C, 35.64; H, 3.43; N, 6.03.

[Pd(NOPON^{Me2}-*N,P,N*)Cl](BF$_4$) (3). In a 100 mL Schlenk tube were placed together NOPON^{Me2} (0.63 g, 1.50 mmol) and [$PdCl_2$(COD)] (0.44 g, 1.50 mmol) in CH_2Cl_2 (30 mL). The yellow solution was stirred at room temperature for 1 h, then $NaBF_4$ (0.16 g, 1.50 mmol) was added, and the mixture solution was stirred for another 24 h at room temperature and filtered. The filtrate was taken to dryness under vacuum, the yellow solid thus obtained was washed with a mixture of diethyl ether/pentane (1/3) (3× 20 mL), then pentane (2 × 20 mL), dried under vacuum to obtain **3** as a yellow solid: 0.83 g (87%). Selected IR data (KBr): 1620 (s, ν(C=N)) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ: 1.50 (s, 6H, NC(CH_3)(CH_3)), 1.78 (s, 6H, NC(CH_3)(CH_3)), 1.84 (d, 6H, $^4J_{PH}$ = 2.0 Hz, OC(CH_3)(CH_3)), 2.39 (s, 6H, OC(CH_3)(CH_3)), AB spin system: δ_B 4.38 (d, $^2J_{HH}$ = 9.0 Hz, OCHH), δ_A 4.50 (d, $^2J_{HH}$ = 9.0 Hz, OCHH), 7.55−8.07 (m, 5H, aromatic H). ^{31}C{^{1}H} (CD_2Cl_2) δ: 24.9 (d, $^3J_{PC}$ = 7.4 Hz, OC(CH_3)(CH_3)), 26.6 (s, NC(CH_3)(CH_3)), 28.1 (s, NC(CH_3)(CH_3)), 29.2 (d, $^3J_{PC}$ = 3.4 Hz, OC(CH_3)(CH_3)), 72.5 (s, NC(CH_3)$_2$), 83.4 (d, $^2J_{PC}$ = 5.1 Hz, OC(CH_3)$_2$), 83.7 (s, OCH_2), 128.1−135.2 (m, aryl), 172.1 (d, $^3J_{PC}$ = 10.2 Hz, C=N). ^{31}P{^{1}H} δ: 114.5 (s). Anal. Calcd for $C_{22}H_{33}BClF_4N_2O_4PPd$: C, 40.70; H, 5.12; N, 4.32. Found C, 40.95; H, 5.20; 4.60.

[Pd$_2$Cl$_2$(CN*t*-Bu)(NOPON^{Me2}-*N,P,N*)] (4). Method (a). In a 100 mL Schlenk tube were placed together NOPON^{Me2} (0.116 g, 0.28 mmol) and [Pd_2(NCMe)$_6$][BF_4]$_2$ (0.175 g, 0.28 mmol) in a mixture of MeCN (30 mL) and CH_2Cl_2 (15 mL). The orange-brown solution was immediately cooled to −30 °C, then *t*-BuNC (0.023 g, 0.28 mmol) and LiCl (0.024 g, 0.56 mmol) were added sequentially. The solution was stirred at −30 °C for 24 h and then filtered, the filtrate was taken to dryness under vacuum, and the residue (brown oil) was dissolved in a mixture of diethyl ether (20 mL) and MeCN (3 mL). The solution was kept at −30 °C for several days, which yielded yellow parallel-epipedic crystals. Yield: 0.044 g (20%).

Method (b). In a 100 mL Schlenk tube were placed together [$PdCl_2$NOPON^{Me2}-*P,N*) (0.116 g, 0.45 mmol) and [Pd(dba)$_2$] (0.258 g, 0.45 mmol) in CH_2Cl_2 (30 mL). The red-brown solution was cooled to 0 °C, then *t*-BuNC (0.037 g, 0.45 mmol) in CH_2Cl_2 (3 mL) was added dropwise to the solution. The solution was stirred at 0 °C for 3 h, the yellow solution was filtered, and the filtrate was taken to dryness, the residue solid was washed with a mixture of 1:1 diethyl ether and pentane (3 × 20 mL), and dried overnight under vacuum. Yield: 0.283 g (80%). Selected IR data (KBr): 2174 (s, ν(C≡N)), 1641 (s, ν(C=N)) cm^{-1}; (CH_2Cl_2): 2185 (s, ν(C≡N)), 1654 (m, ν(C=N)), 1642 (s, ν(C=N)) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) δ: 1.30 (s, 9H, C(CH_3)$_3$), 1.55 (s, 6H, NC(CH_3)(CH_3)), 1.73 (s, 6H, OC(CH_3)(CH_3)), 1.76 (s, 6H, NC(CH_3)(CH_3), 1.94 (s, 6H, OC(CH_3)(CH_3)), AB spin system: δ_A 4.09 (d, 2H, $^2J_{HH}$ = 8.5 Hz, OCHH), δ_B 4.20 (d, $^2J_{HH}$ = 8.5 Hz, OCHH), 7.46−7.51 (m, 3H, aromatic H), 7.86−7.90 (m, 2H, aromatic H). ^{31}C{^{1}H} (125.7 MHz, CD_2Cl_2) δ: 27.8 (s, NC(CH_3)(CH_3)), 28.2 (br, OC(CH_3)(CH_3)), 29.0 (overlapping s and br, NC(CH_3)(CH_3) and OC(CH_3)(CH_3)), 30.1 (s, CNC(CH_3)$_3$), 57.7 (s, CNC(CH_3)$_3$), 70.3 (s, NC(CH_3)$_2$), 78.1 (d, $^2J_{PC}$ = 6.0 Hz, OC(CH_3)$_2$), 81.9 (s, OCH_2), 127.0 (br, CNC(CH_3)$_3$)), 128.5 (d, $^3J_{PC}$ = 12.5 Hz, *m*-aryl), 130.3 (d, $^2J_{PC}$ = 16.9 Hz, *o*-aryl), 131.5 (d, $^4J_{PC}$ = 1.9 Hz, *p*-aryl), 140.8 (d, $^1J_{PC}$ = 81.9 Hz, *ipso*-aryl), 167.4 (br s, C=N). ^{31}P{^{1}H} (CD_2Cl_2) δ: 127.8(s). ^{1}H NMR (300 MHz, CD_2Cl_2, 197 K) δ: 1.22 (s, 9H, C(CH_3)$_3$), 1.44 (s, 3H, NC(CH_3)(CH_3)), 1.46 (s, 3H, NC(CH_3)(CH_3)), 1.47 (s, 6H, OC(CH_3)(CH_3) and NC(CH_3)(CH_3)), 1.68 (s, 3H, OC(CH_3)-(CH_3)), 1.83 (s, 3H, OC(CH_3)(CH_3)), 1.86 (s, 3H, NC(CH_3)-(CH_3), 2.16 (s, 3H, OC(CH_3)(CH_3)), 3.99 (d, 1H, $^2J_{HH}$ = 8.5 Hz, OCHH), 4.16−4.21 (overlapping quart. and d, 3H, $^2J_{HH}$ = 8.5 Hz, 2 × OCHH and OCHH), 7.44−7.51 (m, 3H, aromatic H), 7.79−7.83 (m, 2H, aromatic H). ^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2, 197 K) δ: 25.3 (s, OC(CH_3)(CH_3)), 25.4 (s, OC(CH_3)(CH_3)), 26.4 (s, NC(CH_3)(CH_3)), 27.2 (s, OC(CH_3)(CH_3)), 28.0 (s, NC(CH_3)(CH_3)), 29.1 (s, CNC(CH_3)$_3$ and OC(CH_3)(CH_3)), 29.3 (s, NC(CH_3)(CH_3)), 30.5 (s, OC(CH_3)(CH_3)), 57.0 (s, CNC-(CH_3)$_3$), 69.0 (s, NC(CH_3)$_2$), 69.2 (s, NC(CH_3)$_2$), 76.9 (s, OC-(CH_3)$_2$), 77.6 (d, $^2J_{PC}$ = 9.8 Hz, OC(CH_3)$_2$), 80.4 (s, OCH_2), 81.1 (s, OCH_2), 124.6 (s, CNC(CH_3)$_3$)), 127.9 (d, $^3J_{PC}$ = 12.6 Hz, *m*-aryl), 129.5 (d, $^2J_{PC}$ = 17.5 Hz, *o*-aryl), 131.3 (s, *p*-aryl), 138.5 (d, $^1J_{PC}$ = 84.8 Hz, *ipso*-aryl), 163.6 (s, C=N), 168.9 (s, C=N). Anal. Calcd for $C_{28}H_{44}Cl_4N_3O_4PPd_2$ (**4**·CH_2Cl_2) (sample recrystallized from CH_2Cl_2/pentane): C, 38.55; H, 5.08; N, 4.82. Found C, 38.62; H, 5.04; N, 4.70.

[PdCl$_2$(NPN-*N,P*)] (5). In a 100 mL Schlenk tube were placed together NPN (0.215 g, 0.78 mmol) and [$PdCl_2$(COD)] (0.220 g, 0.78 mmol) in CH_2Cl_2 (50 mL) at room temperature. The solution turned light yellow within 1 h, it was concentrated, and the product was precipitated and washed twice by addition of Et_2O (3 × 50 mL). Yield: 0.430 g (80%). Selected IR data (KBr): 1660 (s, ν(C=N)), 1640 (s, ν(C=N)) cm^{-1}. The resonances for the bound and pendant oxazoline arms are identified by primed and unprimed labels, respectively, as a result of 2D ^{1}H−^{1}H and ^{1}H−^{13}C NMR experiments. ^{1}H NMR (CD_2Cl_2) δ: 3.31 (part of an ABX spin system (X = P), q, $^2J_{AB}$ = 18.3 Hz, $^2J_{AX}$ = 13.2 Hz, 1H, PC$H'_BH'_A$), 3.49 (part of an ABX spin system (X = P), apparent t, $^2J_{AB} \approx {}^2J_{AX}$ = 14.5 Hz, 1H, PCH_BH_A), 3.73−3.84 (overlapping q and m, 3H, PCH_BH_A and NCH_2), 3.95−4.31 (overlapping, 5H, NC$H'B$H$'_A$, PCH'_AH$'_B$, NCH$'_B$H$'_A$ and OCH_2), ABMN spin system simulated using *g*-NMR: δ_B = 4.66 ($^2J_{AB}$ = 8.6, $^3J_{BM}$ = 10.6, $^3J_{BN}$ = 8.7 Hz), δ_A = 4.76 ($^2J_{AB}$ = 8.6, $^3J_{AN}$ = 10.6, $^3J_{AM}$ = 8.7 Hz), 7.51−7.65 (m, 3H, aromatic), 7.97−8.04 (m, 2H, aromatic). ^{13}C{^{1}H} (CD_2Cl_2) δ: 25.7 (d, $^1J_{PC}$ = 33 Hz, PCH_2), 28.3 (d, $^1J_{PC}$ = 36 Hz, PC$'H_2$), 52.9 (masked by CH_2Cl_2 but determined from ^{1}H/^{13}C NMR correlations, s, NC$'H_2$), 54.8 (masked by CH_2Cl_2 but determined from ^{1}H/^{13}C NMR, s, NCH_2), 68.1 (s, OCH_2), 72.9 (s, OC$'H_2$), 129.3 (d, J_{PC} = 10 Hz, aryl), 132.3 (s, *p*-C of aryl), 132.6 (d, J_{PC} = 14.3 Hz, aryl), 133.5 (d, $^1J_{PC}$ = 26.1 Hz, *ipso*-C of aryl), 165.1 (d, $^2J_{PC}$ = 6.8 Hz, C=N), 168.0 (d, $^2J_{PC}$ = 6.5 Hz, C$'$=N). ^{31}P{^{1}H} (CD_2Cl_2) δ: 21.4 (s). Anal. Calcd for $C_{14}H_{17}Cl_2N_2O_2PPd$: C, 37.07; H, 3.78; N, 6.18. Found C, 37.24; H, 3.90; N, 6.25.

X-ray Crystallography. Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[29] (graphite monochromated Mo Kα radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in Table 1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares

(29) Bruker-Nonius *Kappa CCD Reference Manual*; Nonius BV: The Netherlands, 1998.

Table 1. Crystallographic data for **1**, **3**·0.5CH_3CN, and **4**

	1	**3**·0.5CH_3CN	**4**
chemical formula	$C_{28}H_{34}N_4O_4P_2Pd_2\cdot 2(BF_4)$	$C_{22}H_{33}ClN_2O_4PPd\cdot 0.5(C_2H_3N)\cdot BF_4$	$C_{27}H_{42}Cl_2N_3O_4PPd_2$
M_r	938.95	669.66	787.31
cell setting, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	orthorhombic, *Pbca*
temperature (K)	173(2)	173(2)	173(2)
a (Å)	17.672(4)	11.580(1)	11.330(1)
b (Å)	11.911(3)	16.228(2)	17.826(2)
c (Å)	17.193(4)	16.892(2)	31.961(3)
α (deg)	90.00	97.809(4)	90.00
β (deg)	110.980(10)	109.390(4)	90.00
γ (deg)	90.00	97.814(6)	90.00
V (Å^3)	3379.1(14)	2910.3(6)	6455.1(11)
Z	4	4	8
D_x (g cm^{-3})	1.846	1.528	1.620
radiation type	Mo-*K*α	Mo-*K*α	Mo-*K*α
μ (mm^{-1})	1.25	0.84	1.37
crystal size (mm)	0.20 × 0.15 × 0.15	0.22 × 0.17 × 0.10	0.17 × 0.15 × 0.13
no. of measd, indep. and obsvd. refl.	16689, 7350, 5766	34106, 12691, 10988	42849, 7040, 5406
R_{int}	0.038	0.039	0.069
θ_{max} (deg)	27.0	27.0	27.0
$R[F^2 > 2\sigma(F^2)]$	0.038	0.031	0.034
$wR(F^2)$, S	0.090, 1.06	0.097, 1.14	0.100, 1.14
no. of parameters	451	723	394
$(\Delta/\sigma)_{max}$	0.001	0.002	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.12, −0.91	1.24, −0.96	0.71, −0.86

procedures (based on F^2, SHELXL-97)[30] with anisotropic thermal parameters for all the non-hydrogen atoms, except those mentioned below. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined *riding* on the corresponding parent atoms.

For **3**·0.5CH_3CN, one of the two BF_4 anions was disordered in two positions, sharing the B atom, with equal occupancy factors. The fluorine atoms were refined with restrained anisotropic parameters. The acetonitrile molecule was found disordered in two positions with unequal occupancy factors and with no atom in common. These atoms were refined with constrained isotropic parameters and restrained C−C and C−N distances.

For **4**, the *t*-Bu group was found disordered in two positions, with equal occupancy factors and having the quaternary carbon in common. The methyl carbon atoms were refined with restrained anisotropic thermal parameters and C−C bond distances.

CCDC 746987 (**1**), 746988 (**3**·0.5CH_3CN), 746989 (**4**) contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. We are grateful to the Ministère de la Recherche for a postdoctoral grant to J.Z., the Centre National de la Recherche Scientifique for financial support, and to N. Auvray for experimental help, Dr. A. DeCian and Prof. R. Welter for the X-ray diffraction analyses, and R. Graff and J. D. Sauer for NMR measurements.

Supporting Information Available: Crystallographic data in CIF file format. This material is available free of charge via the Internet at http://pubs.acs.org.

(30) Sheldrick, M.; *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.