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Synthesis and Structural Studies of Binuclear Platinum(II) Complexes with a Novel Phosphorus–Nitrogen–Phosphorus Ligand[†]

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The new pyridinediphosphinite ligand PONOP (**1**) was synthesized in one step from 2,6-pyridinedimethanol and diphenylchlorophosphane. Reaction of **1** with $PtCl_2(PhCN)_2$ led to the neutral homobimetallic complex $[Pt_2Cl_4(PONOP)_2]$ (**2**), where the benzonitriles have been substituted by the phosphorus atoms of **1**. The X-ray structure of **2** revealed a metallamacrocycle where the pyridines remained free. Addition of 2 equiv of $[Cu(MeCN)_4](BF_4)$ to **2** led to CuCl and to the binuclear dicationic complex $[Pt_2Cl_2(PONOP)_2](BF_4)_2$ (**3**), where chloro ligands have been substituted by pyridine groups. Conversely, reaction of **3** with chloride anions gave back complex **2**. Solid-state (X-ray) and solution (NMR) studies indicated that after the transformation of **2** into **3**, the platinum centers were brought much closer and the pyridinediphosphinite ligand was stiffened. The methylene NMR protons of **3** were strongly deshielded, and the corresponding proton–phosphorus coupling constants followed a Karplus-type relationship.

Introduction

Polydentate ligands have been widely used in the field of inorganic and organometallic chemistry. They coordinate metallic ions either as chelates, yielding monometallic complexes, or as bridges, yielding polynuclear (especially dinuclear) complexes. With transition metals, the former complexes have encountered great success, e.g. in homogeneous catalysis.[1] The latter have also found extremely diverse applications in the fields of redox chemistry, catalysis, cluster chemistry, self-assembly, encapsulation, or biomimetic chemistry.[2] Several reports have appeared in the literature concerning the structural and electronic factors that govern the formation of monomers or dimers upon coordination of metallic complexes.[3] With diphosphines, it was elucidated that the chain length or the bulkiness of the substituents on phosphorus were of prime importance.[3a−d]

We have recently investigated the coordination chemistry of various achiral trifunctional ligands, such as terpyridines, triphosphines, or pyridinediphosphines, with transition metals such as palladium[4] or ruthenium.[5] In our hands, these ligands have led to mononuclear complexes, coordinating the metal in either a bidentate or a tridentate meridional mode. Chiral, C_2-symmetric tridentate ligands have also been devised and

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applied to asymmetric homogeneous catalysis by transition metal complexes.[6] Their interest lies in the fact that if the ligand is coordinated in a tridentate meridional geometry, the quadrant effect is enhanced in octahedral catalytic intermediates, and the substrate undergoes a close interaction with the chiral substituents of the ligand.

As part of our project on the design and application of trifunctional ligands, we report hereafter the synthesis of the pyridinediphosphinite **1** as a novel mixed-P,N-donor ligand and the study of its complexation behavior toward platinum(II).

Experimental Section

General Procedures. All experiments were carried out under a nitrogen or argon atmosphere, using a vacuum line or Vacuum Atmospheres glovebox equipped with a Dri-Train HE-493 inert gas purifier. Pentane and THF were distilled over sodium and benzophenone, toluene over sodium, and dichloromethane over calcium hydride under nitrogen immediately before use. 2,6-Bis(hydroxymethyl)pyridine (Aldrich) and *n*-butyllithium (Fluka, 1.6 M solution in hexanes) were used as received. Diphenylchlorophosphane (95% min., Strem) was distilled at 170 °C under reduced pressure and stored under argon. $PtCl_2(PhCN)_2$[7] and $[Cu(MeCN)_4](BF_4)$[8] were prepared following reported procedures. The NMR spectra were recorded at room temperature (unless otherwise indicated) on Bruker spectrometers. ^1H NMR spectra were recorded at 300.16 MHz (AC-300 instrument) or 500.13 MHz (ARX-500) and referenced to $SiMe_4$. $^{31}P\{^1H\}$ (broadband decoupled) were recorded at 121.51 MHz (AC-300) or 202.46 MHz (ARX-500) and referenced to 85% aqueous H_3PO_4; for compound **3**, the numbering of the phosphorus atoms refers to the crystallographic structure (Figure 2). The assignments given are supported by 2D NMR analysis performed on the ARX-500 spectrometer (COSY, $^1H-^{31}P$ HMQC). FT-IR spectra were recorded on a Perkin-Elmer 1600 series spectrometer on KBr pellets. FAB MS spectra and elemental analyses were carried out by the corresponding facilities at the Fédération de Recherche de Chimie, Université Louis Pasteur, Strasbourg.

Synthesis of 2,6-Bis[(diphenylphosphinyl)oxymethyl]pyridine (1). A solution of *n*-BuLi in hexanes (9.44 mL, 15.1 mmol) was added dropwise at −78 °C to 2,6-bis(hydroxymethyl)pyridine (1.00 g, 7.19 mmol) partly dissolved in 200 mL of THF, leading to a purple solution. The solution was stirred at −78 °C for 30 min, and the temperature was raised to 0 °C. PPh_2Cl (2.80 mL, 15.1 mmol) was slowly added to the solution via syringe, after which the solution turned pale yellow. Stirring was maintained at 0 °C for 30 min and then at room temperature for 3 h. The solution was evaporated to dryness, and the resulting thick oil was extracted five times with 25 mL of pentane. Evaporation of the pentane solutions to dryness led to **1** as a colorless oil (1.52 g, 42% yield). It could be further purified by distillation through a short path elbow (bp 150 °C/0.01 mmHg). Anal. Calcd for $C_{31}H_{27}NO_2P_2$: C, 73.37; H, 5.36; N, 2.76. Found: C, 73.25; H, 5.18; N, 2.57. MS (FAB$^+$, NBA matrix): *m*/*z* 508 ($[M + 1]^+$, 10%), 306 ($[M - OPPh_2]^+$, 65%), 230 ($[M + 1 - OPPh_2 - Ph]^+$, 10%), 201 ($OPPh_2^+$, 100%). IR (cm^{-1}): 1576, 1592 (pyridine). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 116.7 (s). ^1H NMR (300 MHz, $CDCl_3$) δ 4.95 (d, 4H, $^3J_{HP} = 9.3$ Hz, CH_2), 7.2−7.7 (m, 23H, H_{ar}).

Synthesis of Compound 2. A solution of **1** (1.00 g, 1.97 mmol) in 30 mL of dichloromethane was slowly added at room temperature to a solution of $PtCl_2(PhCN)_2$ (0.930 g, 1.97 mmol) in 50 mL of dichloromethane. The yellow solution was stirred at room temperature for 1.5 h and filtered. After concentration of the solution to ca. 50 mL and slow addition of pentane, complex **2** precipitated as a white powder (1.04 g, 68% yield). It could be recrystallized from dichloromethane/pentane. Anal. Calcd for $C_{62}H_{54}Cl_4N_2O_4P_4Pt_2$: C, 48.14; H, 3.52; N, 1.81. Found: C, 48.01; H, 3.35; N, 1.84. IR (cm^{-1}): 295, 318 (Pt−Cl), 1576, 1594 (pyridine). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 84.7 (s, $^1J_{PPt} = 4201$ Hz). ^1H NMR (300 MHz, CD_2Cl_2) δ 4.85 (d, 8H, $^3J_{HP} = 6.1$ Hz, CH_2), 6.84 (d, 4H, $^3J_{HH} = 7.8$ Hz, $H_{pyridine\ meta}$), 7.34−7.80 (m, 42H, H_{ar}).

Synthesis of Compound 3. A solution of $[Cu(MeCN)_4](BF_4)$ (45 mg, 0.143 mmol) in 3 mL dichloromethane was added dropwise at room temperature to a white suspension of **2** (0.11 g, 0.071 mmol) in 10 mL dichloromethane. After addition of half of the copper (I) solution, the mixture became clear, and then progressively turned back to a white, cloudy suspension until the end of the addition. After stirring at RT for 3 h, the suspension was filtered on Celite. After concentration of the solution and slow addition of pentane, complex **2** precipitated as a white powder (82 mg, 70% yield). It could be recrystallized from dichloromethane/pentane. Anal. Calcd for $C_{62}H_{54}B_2Cl_2F_8N_2O_4P_4Pt_2$: C, 45.14; H, 3.30; N, 1.70; Cl 4.30; F, 9.21. Found: C, 44.96; H, 3.21; N, 1.83; Cl 4.20; F, 8.78. MS (FAB$^+$, NBA matrix): *m*/*z* 1475.0 ($[M - 2BF_4]^+$, 13%), 738.0 ($[M - 2BF_4]^{2+}$, 100%), 702.0 (Pt(**1**), M$^+$, 21%). IR (cm^{-1}): 307 (Pt−Cl), 1575, 1610 (pyridine). $^{31}P\{^1H\}$ NMR (202.5 MHz, DMSO-d_6): δ 86.3 (d, 2P, $^2J_{PP} = 14$ Hz, $^1J_{PPt} = 3870$ Hz, P2), 90.0 (d, 2P, $^2J_{PP} = 14$ Hz, $^1J_{PPt} = 3760$ Hz, P1). ^1H NMR (500 MHz, DMSO-d_6) δ 5.69 (dd, 2H, $^2J_{HH} = 13.9$ Hz, $^3J_{HP} = 31.5$ Hz, H_4), 6.28 (d, 2H, $^2J_{HH} = 14.1$ Hz, H_2), 6.67 (dd, 2H, $^2J_{HH} = 13.7$ Hz, $^3J_{HP} = 6.7$ Hz, H_3), 7.28 (dd, 2H, $^2J_{HH} = 14.2$ Hz, $^3J_{HP} = 7.5$ Hz, H_1), 6.70−8.30 (m, 46H, H_{ar}).

Collection of the X-ray Data and Structure Determination for 2 and 3. The crystal data of **2** were collected on a CAD4-MACH3 diffractometer and those of **3** on a Kappa CCD diffractometer, using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Details of data collection parameters and refinements results are listed in Table 1. The structures were solved using direct methods. Hydrogen atoms were introduced as fixed contributors at calculated positions (C−H = 0.95 Å, B(H) = 1.3 Beqv)), except for the solvent molecules. Final difference maps revealed no significant maxima. All calculations were done using the Nonius OpenMoleN package.[9] Neutral atom scattering factor coefficients and anomalous dispersion coefficients were taken from a standard source.[10]

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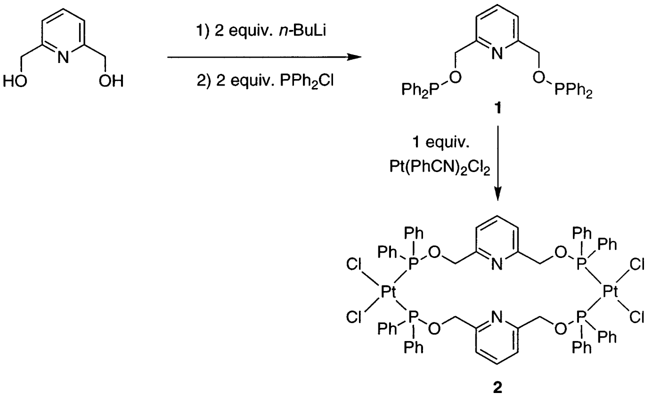
Table 1. Summary of the Crystal and Refinement Data for Compounds **2** and **3**

compound	**2**·2CH$_2$Cl$_2$	**3**·4CH$_3$NO$_2$·C$_6$H$_6$
formula	$C_{64}H_{58}Cl_8N_2O_4P_4Pt_2$	$C_{72}H_{72}B_2Cl_2F_8N_6O_{12}P_4Pt_2$
mol wt	1716.89	1972.00
space group	$P12_1/n1$	$P\bar{1}$
a (Å)	11.311(3)	11.412(1)
b (Å)	15.927(4)	12.815(1)
c (Å)	19.080(5)	13.718(1)
α (deg)		87.01(6)
β (deg)	105.81(2)	82.71(6)
γ (deg)		79.45(6)
V (Å^3)	3307(1)	1955.4(5)
Z	2	1
D_{calc} (g cm^{-3})	1.72	1.67
wavelength (Å)	0.71073	0.71073
μ (mm^{-1})	4.693	3.805
temp (K)	294	173
R^a	0.031	0.026
$R_w{}^b$	0.036	0.045

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$.

Scheme 1



Results and Discussion

The ligand 2,6-bis[(diphenylphosphinyl)oxymethyl]pyridine (**1**) (abbreviated PONOP) has been easily synthesized in one step with 42% yield from 2,6-bis(hydroxymethyl)pyridine. The alcohol functions were first deprotonated with *n*-butyllithium, and the resulting bis-alkoxide reacted with 2 equiv diphenylchlorophosphane, yielding **1** and lithium chloride (Scheme 1). Both phosphorus atoms are equivalent; the chemical shift of their ^{31}P NMR signal (116.7 ppm) lies in the normal range for a phosphinite.[11] The methylene signal on the ^{1}H NMR spectrum is a doublet at 4.99 ppm with a proton−phosphorus coupling constant that also falls in the expected range (9.4 Hz).[12]

PONOP (**1**) was converted into the dimeric macrocyclic complex [Pt$_2$Cl$_4$(μ-PONOP)$_2$] (**2**) in 68% yield, by reaction with 1 equiv of Pt(PhCN)$_2$Cl$_2$ in methylene chloride at room temperature, resulting from the substitution of the labile benzonitrile ligands by the phosphinites (Scheme 1). The reaction proceeded cleanly without formation of any monomeric or polymeric material; although Lindner et al. had to use high-dilution conditions to synthesize similar diplatinamacrocycles,[2e] this precaution was not necessary in our case.

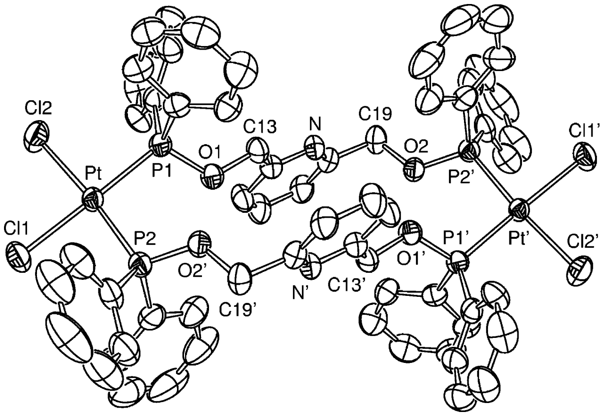


Figure 1. Ortep drawing of [Pt$_2$Cl$_4$(PONOP)$_2$] (**2**) showing 50% probability thermal ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**

Pt−Cl1	2.348(2)	Pt−P1	2.219(2)
Pt−Cl2	2.346(2)	Pt−P2	2.226(2)
P1−O1	1.615(4)	P2−O2′	1.602(4)
Cl1−Pt−Cl2	88.24(7)	P1−Pt−P2	95.62(6)
Cl1−Pt−P1	177.67(7)	Pt−P1−O1	111.18(6)
Cl1−Pt−P2	86.31(6)	Pt−P2−O2′	111.68(6)
Cl2−Pt−P1	89.89(6)	P1−O1−C13	121.7(4)
Cl2−Pt−P2	173.96(6)	P2−O2′−C19′	123.2(4)

Single crystals of complex **2** were obtained by cooling a saturated CH$_2$Cl$_2$ solution to −20 °C. The X-ray structure of **2** is shown in Figure 1, and the corresponding bond lengths and angles are given in Table 2. Complex **2** consists of a neutral bimetallic molecule where PONOP acts as a bridging ligand between both platinum centers, forming a large 20-membered diplatinamacrocycle. Each platinum is coordinated by two chloro ligands, which point outside the macrocycle, and two phosphorus atoms in a cis geometry. It seems highly probable that the *cis,cis* isomer is the thermodynamic product, by comparison with analogous platinum complexes.[3c,13] Interestingly, the reaction product **2** had the same configuration whether the reagent was *cis*- or *trans*-Pt(PhCN)$_2$Cl$_2$.

The pyridines remain uncoordinated, which is consistent with the stronger affinity of late transition metals toward phosphorus rather than nitrogen.[3g,4b] The molecule is centrosymmetric, an inversion center being present between the pyridines. The planes of the pyridine moieties are parallel and separated by 3.58(1) Å; their dipolar moments are antiparallel. No π-stacking is involved, as long as the pyridines are not positioned one above the other. The platinum-donor atom bond distances are in good agreement with the crystallographic data of *cis*-[(phosphinite)PtCl$_2$] complexes reported in the literature.[11] The Pt−Cl bond lengths [2.348(2) and 2.346(2) Å] are long, in connection with the strong *trans* influence of the P donor atom.[14] On the contrary, the moderate *trans* influence of the chloro ligand

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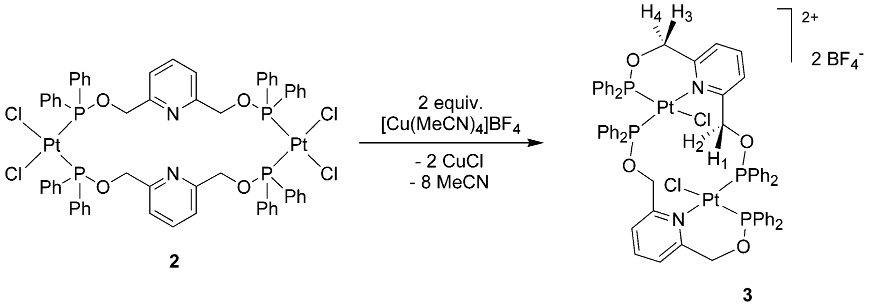
Scheme 2



is at the origin of the rather short Pt−P bond lengths [2.219(2) and 2.226(2) Å]. The P1−Pt−P2 angle is larger [95.62(6)°] and the Cl1−Pt−Cl2 smaller [88.24(7)°] than the ideal 90°, probably because of mutual steric repulsions of the phenyl rings borne by each phosphorus atom. The size of the 20-membered metallacycle is such that the platinum atoms are located far one from the other, with an intermetallic distance of 11.543(1) Å.

IR spectroscopy provides confirmation of the structural features provided by the X-ray diffraction analysis. The presence of two ν_{Pt-Cl} signals at 295 and 318 cm^{-1} in the IR spectrum of **2** is characteristic of a *cis*,*cis* complex.[15] The pyridine ring vibrations[16] at 1576 and 1592 cm^{-1} are unchanged in comparison with the spectrum of the free ligand **1**, which confirms that the pyridines are uncoordinated.

Upon coordination of the phosphorus atoms of **1** to platinum, the ^{31}P NMR signal is shifted to lower frequency at 84.7 ppm, as shown on the spectrum of **2**. This upfield shift, as well as the large value of $^1J_{PPt}$ (4201 Hz), is indicative of a *cis* coordination,[11] in agreement with our X-ray data. Further confirmation is provided by the ^1H NMR spectrum, because in a *trans* coordination mode a virtual triplet would have been expected for the methylene signal.[17] Instead, it appears as a doublet; we note that the value of $^3J_{HP}$ (6.1 Hz) is reduced in comparison with that of the free ligand **1**. The 20-membered metallamacrocycle is flexible enough so that all methylene protons are chemically equivalent at 298 K.

The coordination behavior of PONOP toward Pt^{II} sharply contrasts with that of the closely related ligand 2,6-(diphenylphosphinomethyl)pyridine (PNP):[18] the reaction of Pt$(PhCN)_2Cl_2$ with PNP leads to the mononuclear species [Pt(PNP)Cl]Cl, where the ligand is tridentate. The chelate effect of PNP may explain this, as long as two five-membered metallacycles exist in this latter complex. By contrast with PNP, ligand PONOP has longer “arms”, which reduces the chelate effect and favors a bridging coordination as in **2**.

At this stage, our purpose was to take advantage of the pyridines in the cavity of the macrocycle to encapsulate a metallic guest in **2**. Precedents exist in the literature of similar strategies involving metallamacrocycles, which lead to trinuclear complexes.[2a,e,19] We first tried to coordinate a third dichloroplatinum(II) fragment by the pyridines by allowing 2 equiv of ligand **1** to react with 3 equiv of $Pt(PhCN)_2Cl_2$; yet we were not successful, as this led only to complex **2**. We then chose copper(I) as guest, as bis-coordinate complexes of this metal ion have been reported with *ortho*-substituted pyridines.[20]

However, treatment of complex **2** with excess (2 equiv) $[Cu(MeCN)_4](BF_4)$ in CH_2Cl_2 did not lead to inclusion of the Cu^I atom. Instead, Cu^I removed one chloride atom from the coordination sphere of each platinum center, the vacant coordination site being occupied by a pyridine (vide infra). This led to the dicationic platinum dimer $[Pt_2Cl_2(PONOP)_2](BF_4)_2$ (**3**) in 70% yield and to CuCl (Scheme 2). We observed by ^1H NMR that **2** was completely converted into the dication $[Pt_2Cl_2(PONOP)_2]^{2+}$ even if only 1.2 equiv of $[Cu(MeCN)_4]^+$ was used. A possible explanation is that CuCl can remove a second chloro ligand to yield the $[CuCl_2]^-$ anion.[21] This hypothesis also allows us to understand why the reaction mixture, which was at the beginning a white suspension of **2**, became a clear colorless solution after 1 equiv of Cu^I was added to **2** (see Experimental Section): the intermediate species was probably the soluble compound $[Pt_2Cl_2(PONOP)_2](CuCl_2)(BF_4)$. The addition of the second equivalent of Cu^I then led to **3** and precipitation of CuCl, which resulted from the comproportionation reaction 1.

$$CuCl_2^- + Cu^+ \rightarrow 2CuCl\downarrow \qquad (1)$$

We also observed that zinc(II) triflate could abstract some chloro ligands from **2** and convert it into $[Pt_2Cl_2(PONOP)_2]^{2+}$ like copper(I) did; a white precipitate formed, which was very probably $ZnCl_2$.

The interconversion of **2** into **3** is reversible: addition of 2 equiv of PPh_4Cl to compound **3** in DMSO at room temperature gave back compound **2**. This can be interpreted in terms of competition between Cl^- and the pyridine moiety for coordination of platinum, which is in favor of Cl^- in our case. On the contrary, **3** is stable in DMSO, as shown by

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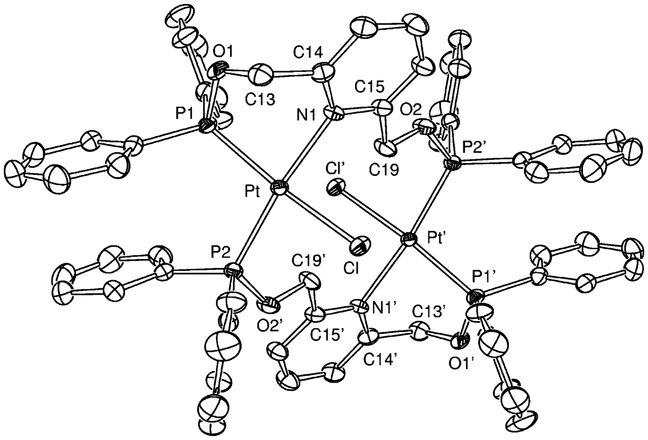

Figure 2. Ortep drawing of $[Pt_2Cl_2(PONOP)_2](BF_4)_2$ (**3**) showing 50% probability thermal ellipsoids. Hydrogen atoms, BF_4^- anions, and solvent molecules are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **3**

Pt−Cl	2.3561(9)	Pt−P1	2.2260(9)
Pt−N1	2.139(3)	Pt−P2	2.2520(9)
P1−O1	1.609(2)	P2−O2′	1.611(3)
Cl−Pt−P1	168.63(7)	Pt−P1−O1	106.46(3)
Cl−Pt−N1	87.93(8)	Pt−P2−O2′	110.24(3)
Cl−Pt−P2	86.10(7)	Pt−N1−C14	119.54(8)
N1−Pt−P1	85.78(8)	Pt−N1−C15	120.52(7)
N1−Pt−P2	172.75(8)	P1−O1−C13	120.7(2)
P1−Pt−P2	100.77(7)	P2−O2′−C19′	123.94(7)

our NMR analyses; therefore, DMSO does not compete with the pyridine moiety of **1** as a ligand.

Compound **3** is colorless, air-stable, soluble in nitromethane or DMSO, and moderately soluble in dichloromethane or acetone. In comparison with **2**, modifications in the region of the pyridine vibrations (1550−1650 cm^{-1}) are observed on the IR spectrum of **3**. In particular, a new high-frequency band characteristic of a coordinated pyridine appears at 1610 cm^{-1}.[16]

Single crystals of compound **3** were obtained by slow diffusion of toluene into a saturated CD_3NO_2 solution, and its molecular structure was established by an X-ray diffraction study (Figure 2). Selected bond distances and angles are listed in Table 3. The structure of **3** consists of a dinuclear dicationic complex with unbound tetrafluoroborate anions. Like **2**, **3** displays a crystallographic symmetry center. The X-ray analysis of **3** reveals a drastic change of the tridimensional structure in comparison with that of **2**. Coordination of the pyridines onto the platinum centers has induced a double folding of the dimer, with a sharp decrease of the Pt···Pt nonbonding distance to 5.3087(1) Å. Each platinum is also coordinated by one chloro ligand, which now points inside the cavity, and two phosphorus atoms in a classical distorted square-planar geometry. The phosphorus atoms remain in the *cis* position as they were in complex **2**; the coordination of pyridine induces therefore no *cis*−*trans* isomerization.

The Pt−P1 and Pt−Cl bond lengths [respectively 2.2268(9) and 2.3555(9) Å] are almost unchanged in comparison with **2**, but Pt−P2 (in *trans* position with regard to the pyridine) is slightly longer [2.2529(9) Å] than Pt−P1. In connection with the strong *trans* influence of the phosphinite, the Pt−N bond distance is rather long [2.142(3) Å]. The P1−Pt−P2 bond angle has increased from 95.62(6)° (in complex **2**) to 100.77(3)°, which is probably related to steric interactions between phenyl groups. Figure 2 indicates clearly that these phenyls are π-stacked, with their planes nearly parallel and about 3.3 Å apart.

One "arm" of ligand PONOP is bridging between the platinum atoms, whereas the other one makes a six-membered chelate ring in a boat conformation. The Pt−P1−O1 bond angle, which belongs to this constrained ring, is smaller than the Pt−P2−O2′ angle [106.46(3)° vs 110.24(3)°]. The pyridine ring is tilted with respect to the coordination plane, with a C14−N1−Pt−P1 torsion angle of 57.95(7)°. The Cl atom lies 0.4620(3) Å out of the mean plane defined by Pt, N1, P1, and P2, 4.8434(3) Å away from Pt′ and roughly on its *z* axis. Both platinum−chloride vectors of complex **3** are antiparallel. The 12-membered diplatinamacrocycle appears almost planar; its atoms display maximal deviations of 0.2 Å from its mean plane. Espinet et al. have reported a palladium binuclear complex, the solid-state structure of which shows a very similar, highly puckered macrocycle.[3f]

The ^{31}P NMR spectrum of **3** exhibits two doublets at 86.3 and 90.0 ppm, representative of an AB system; the small P−P coupling constant (14 Hz) is characteristic of phosphorus donor atoms located in a *cis* position. Both values of J_{PtP} are significantly smaller than in complex **2** (3870 and 3760 Hz).

The transformation of **2** into **3** is followed by a general splitting of the ^1H NMR signals, in connection with a loss of symmetry. In particular, the methylene doublet is split into four distinct signals, three of them being observable at low frequency as one doublet (6.28 ppm) and two doublets of doublets (5.69 and 6.67 ppm). A 2D COSY spectrum of **3** allowed us to detect the fourth one at 7.28 ppm among the aromatic signals, and to identify the methylene protons as two pairs of geminally coupled diastereotopic protons. The measured *gem* $^2J_{HH}$ coupling constants are normal (ca. 14 Hz), whereas $^3J_{HP}$ ranges between extreme values (from 0 up to 31.5 Hz). Applying the extension of the Karplus relationship to H−C−O−P systems,[22] we found a good correlation between the values of $^3J_{HP}$ and the H−C−O−P dihedral angles estimated from calculated positions of the protons in the X-ray structure of **3**. This allowed us to assign the four methylene signals as indicated in Scheme 2. Indeed, (1) the coupling of H_2 with phosphorus is not detectable, in agreement with a dihedral angle close to 90° (exactly −83°); (2) a large value of J_{HP} (31.5 Hz) is associated with a nearly straight angle (−167°) for H_4; and (3) intermediate and close values of both J_{HP} and H−C−O−P angles are found for H_1 and H_3 (respectively 7.5 Hz/41° and 6.7 Hz/−43°).

In comparison with **2**, the methylene protons of PONOP in **3** are strongly deshielded (0.84 ppm < $\Delta\delta$ < 2.43 ppm).

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This probably results from their position relative to the anisotropic cones of the aromatic groups in the molecule. Furthermore, the most deshielded methylene protons, viz. H_1 and H_2, lie inside the cavity created by the diplatinacycle and are therefore in a pseudoaxial position with respect to the platinum centers. The shortest interatomic H•••Pt distances estimated from crystallographic data are 3.00 Å (H_1) and 2.88 Å (H_2). Such downfield NMR shifts of protons associated with close H•••M contacts in d^8 metal complexes have been reported[23] and interpreted in terms of paramagnetic anisotropy of the metal, hydrogen bonding, weakly agostic interaction, or repulsive interaction.[23a,24]

The ^{1}H NMR spectrum of **3** in DMSO-d_6 undergoes no modification up to 386 K; thus, the molecule is not fluxional in this temperature range. The close agreement between the NMR and X-ray data suggests that the tridimensional structure of **3** is roughly the same in solution and in the solid state. In particular, no conformational equilibrium involving the methylene groups is taking place. Consequently, the transformation of **2** into **3** is followed by a marked rigidification of ligand **1** within the binuclear complex.

Concluding Remarks

The work presented here provides a new insight into the coordination chemistry of P−N−P-type ligands. We found that by contrast with 2,6-(diphenylphosphinomethyl)pyridine, the coordination reaction of the pyridinediphosphinite PONOP on platinum(II) leads cleanly to a binuclear metallamacrocyclic complex. The central pyridine behaves as a hemilabile ligand that competes reversibly with chloride; this hemilabile behavior of PONOP is reminiscent of similar systems reported by Mirkin et al.[2f] Copper(I) can play the role of a chloride-abstracting agent; Braunstein et al. have reported the similar behavior of $[Cu(MeCN)_4]^+$, which could break a Pd−Cl bond.[25] We note that, on the contrary, a tetranuclear Ru_2–Cu_2 complex has been prepared from $[Cu(MeCN)_4]^+$ and a ruthenium carbonyl chloro complex without any abstraction of the chloro ligands.[26]

The reversible interconversion of **2** into **3** is accompanied by a folding of the complex. This folding results in a marked shortening of the intermetallic distance and a significant stiffening of PONOP, as shown by NMR and X-ray studies. We plan to take advantage of this rigidity in asymmetric catalysis using chiral derivatives of this ligand,[6a] with platinum or other platinum metals.

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Supporting Information Available: NMR data of **3**, and X-ray crystallographic files in CIF format for the crystal structures of **2** and **3**. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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