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Synthesis, Characterization, and Structures of Palladium(II) and Platinum(II) Complexes Containing *N*,*N*-Bis(diphenylphosphanyl) Naphthylamine

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Abstract. The reaction of 1-naphthylamine with two equivalents of chlorodiphenylphosphine in the presence of triethylamine gave the ligand $C_{10}H_7$-1-$N(PPh_2)_2$ (**1**). Reaction of **1** with $PdCl_2(CH_3CN)_2$ or $PtCl_2$(cod) (1:1 molar ratio) afforded the complexes *cis*-[$PdCl_2${$C_{10}H_7$-1-$N(PPh_2)_2$}] (**2**) and *cis*-[$PtCl_2${$C_{10}H_7$-1-$N(PPh_2)_2$}] (**3**), respectively. Compounds **1**–**3** were identified and characterized by multinuclear NMR (^1H, ^{13}C, ^{31}P NMR) and IR spectroscopy. Crystal structure determinations of complexes **2** and **3** were carried out.

Introduction

The importance of aminophosphines with direct P–N bonds and their derivatives in the fight against cancer[1–4] and also on the subject of catalysis for industrially important reactions,[5–7] as well as herbicidal, neuroactive and antimicrobial agents[8–10] has prompted us to extend our studies on the synthesis and solid-state structures of chelated *N*,*O* and *N*,*N* complexes[11] to synthesize new chelating phosphorus(III) ligands containing P–N linkages for transition metal chemistry and catalytic applications.[12]

As a part of our research program on this subject, we herein report the synthesis and spectroscopic properties of $C_{10}H_7$-1-$N(PPh_2)_2$ (**1**) ligand, the corresponding square planar complexes *cis*-[$PdCl_2${$C_{10}H_7$-1-$N(PPh_2)_2$}] (**2**) and *cis*-[$PtCl_2${$C_{10}H_7$-1-$N(PPh_2)_2$}] (**3**) and the crystal structures of **2** and **3**.

Experimental Section

General Remarks: All experiments were carried out in purified dry nitrogen using standard Schlenk and vacuum line techniques. Solvents were dried and freshly distilled under nitrogen.[13] $PdCl_2(CH_3CN)_2$ was prepared according to the literature.[14,15] The chemicals chlorodiphenylphosphine, 1-naphthylamine and [$PtCl_2$(cod)] (cod = /cycloocta-1,5-diene) were used as purchased. Infrared spectra were recorded with a Perkin–Elmer System 2000 FT-IR spectrometer between 4000 and 400 cm^{-1} using KBr disks. The NMR spectra were recorded at 25 °C with a Bruker AVANAC II 400 MHz NMR spectrometer operating at the appropriate frequencies using tetramethylsilane for ^1H and 85 % H_3PO_4 for ^{31}P as external standards. Melting points were carried out with a Gallenkamp Model apparatus with open capillaries.

***N*,*N*-bis(diphenylphosphanyl)-1-naphthylamine (1):** Chlorodiphenylphosphine (4.89 g, 22.20 mmol) was added dropwise to a solution of 1-naphthylamine (1.95 g, 11.10 mmol) and triethylamine (2.25 g, 22.20 mmol) in THF (100 mL) at room temperature with vigorous stirring. After completion of the addition, the reaction mixture was stirred at room temperature for 12 h. Afterwards, the white precipitate (triethylamine hydrogen chloride) was filtered off through a sintered Schlenk tube. The volume was reduced to 50 mL, the reaction mixture was cooled to 0 °C, and a white solid was obtained that was recrystallized from a 1:4 dichloromethane/*n*-hexane solution (v/v) at 0 °C to give the product as colorless crystals in 85 % yield. M.p. 121–122 °C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 6.60–8.10 (m, 27, $C_{10}H_7$ and $4C_6H_5$) ppm. **^{13}C NMR** (100.63 MHz, $CDCl_3$): δ = 110.60, 120.08, 124.27, 125.45, 126.43, 127.84, 128.33, 129.14, 130.52, 131.16, 132.22, 133.03, 134.50, 135.36 ($C_{10}H_7$ and $4C_6H_5$) ppm. **^{31}P NMR** (161.98 MHz, $CDCl_3$): δ = 63.46 (s, 2P) ppm. **IR** (selected bands, KBr): $\tilde{\nu}$ = 1439 (P–Ph), 910 (P–N) cm^{-1}.

Dichloro{*N*,*N*-bis(diphenylphosphanyl)-1-naphthylamine}palladium(II) (2): To a solution of $PdCl_2(CH_3CN)_2$ (0.24 g, 0.93 mmol) (generated in situ by heating $PdCl_2$ in CH_3CN to reflux for 4 h) in CH_3CN (80 mL) was added dropwise to a solution of **1** (0.47 g, 0.93 mmol) in CH_3CN (50 mL) and the reaction mixture was stirred at room temperature for 4 h. The solution was concentrated to 10 mL, and THF (10 mL) was added. Cooling this solution to 0 °C gave **2** as yellow crystals in 80 % yield. M.p. 194–196 °C. **^{1}H NMR** (400.13 MHz, $CDCl_3$): δ = 6.58–7.89 (m, 27 H, $C_{10}H_7$ and $4C_6H_5$) ppm. **^{13}C NMR** (100.63 MHz, $CDCl_3$): δ = 123.49, 124.80, 125.63, 126.41, 127.34, 127.61, 128.07, 129.06, 129.96, 130.25, 133.23, 134.35, 134.56, 136.06 ($C_{10}H_6$ and $4C_6H_5$) ppm. **^{31}P NMR** (161.98 MHz, $CDCl_3$): δ = 37.78 (s, 2P) ppm. **IR** (selected bands, KBr): $\tilde{\nu}$ = 288 and 310 (Pd–Cl), 1441 (P–Ph), 840 (P–N) cm^{-1}.

Dichloro{*N*,*N*-bis(diphenylphosphanyl)-1-naphthylamine}platinum(II) (3): To a solution of [Pt(cod)Cl_2] (0.29 g, 0.76 mmol) in 50 mL of CH_2Cl_2, a solution of **1** (0.40 g, 0.76 mmol) in CH_2Cl_2 (50 mL) was added dropwise and the reaction mixture was stirred at room temperature for 4 h. The solution was concentrated to 5 mL, and acetone (5 mL) was added. Cooling this solution to 0 °C gave **3** as white crystals in 80 % yield. M.p. 290–

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292 °C. **^{1}H NMR** (400.13 MHz, DMSO): δ = 6.55–7.95 (m, 27 H, $C_{10}H_7$ and $2C_6H_5$) ppm. **^{13}C NMR** (100.63 MHz, DMSO): δ = 121.42, 122.89, 124.85, 125.29, 126.16, 127.13, 127.90, 128.78, 128.94, 129.67, 129.91, 132.33, 133.30, 133.77 ($C_{10}H_6$ and $2C_6H_5$) ppm. **^{31}P NMR** (161.97 MHz, DMSO): δ = 22.34 (s, 2P, $^1J_{Pt–P}$ = 1666.77 Hz) ppm. **IR** (selected bands, KBr): $\tilde{\nu}$ = 290 and 312 (Pt–Cl), 1438 (P–Ph), 810 (P–N) cm^{-1}.

Data Collection and Structure Determination: Crystallographic data are given in Table 1. Data were collected with a Rigaku Mercury375R/M CCD (XtaLAB mini) diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71075 Å), equipped with a Rigaku low temperature gas spray cooler. In these cases, data were processed with the Rigaku CrystalClear software.[16] The data were corrected for Lorentz and polarization effects.[17] All calculations were performed using the Crystal Structure crystallographic software package,[18] except for refinement, which was performed using SHELXL-97.[19] All structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms.

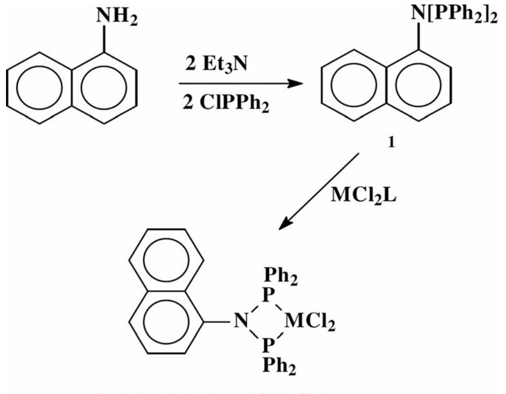
Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-850261 for **2** and CCDC-850262 for **3** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Results and Discussion

Synthesis

Scheme 1 summarizes the synthesis of **1**–**3**. Ligand **1** was previously used in the chromium-catalyzed tri- and tetramerization of ethylene. With the exception of ^{13}P NMR spectroscopy, ligand **1** was not structurally characterized.[6] The reaction of 1-naphthylamine with two equivalents of chlorodiphenylphosphine in the presence of triethylamine, proceeds in tetrahydrofuran at room temperature under nitrogen to give $C_{10}H_7$-1-N(PPh_2)$_2$ (**1**) in good yield (85 %). The compound is an air-stable solid but gradually undergoes decomposition on exposure to moisture. The coordination chemistry of ligand **1** with selected transition metals (Pd and Pt) was explored. The palladium(II) dichloride complex **2** was formed by direct reaction of ligand **1** in THF with $PdCl_2(CH_3CN)_2$ (1:1 molar ratio). Moreover, the reaction of ligand **1** with one equivalent of $PtCl_2$(cod) (cod = 1,5-cyclooctadiene) in dichloromethane gave the corresponding platinum(II) complex **3**. It has been found that the solvent (THF) for the synthesis of ligand **1** has a significant influence on the reaction rate and on the reaction product.

Compounds **1**–**3** were isolated from the reaction solution and fully characterized by IR and multinuclear NMR spectroscopy. Furthermore, the molecular structures of **2** and **3** were elucidated by single-crystal X-ray diffraction.



2 : M = Pd; L = $(CH_3CN)_2$
3 : M = Pt; L = cod

Scheme 1. Preparation of **1**–**3**.

^{1}H, ^{13}C, and ^{31}P NMR Spectra

Due to the presence of naphthyl and phenyl groups and coupling with ^{31}P, the ^{1}H and ^{13}C NMR spectra of **1**–**3** were complex and difficult to fully interpret, especially in the aromatic region.[20] The ^{1}H NMR spectra of **2**–**3** have the expected signals characteristic for the organic ligand **1**. The resonances corresponding to the phenyl and naphthyl protons display overlapped multiplet signals in the region 6.50–8.52 ppm.

The ^{31}P NMR spectrum of **1** shows a singlet resonance at δ = 63.46 ppm, indicating two equivalent phosphorus atoms. The value is in agreement with those reported in the literature.[6] The ^{31}P NMR signals of **2** and **3** appear as singlet signals at δ = 37.78 ppm (**2**) and δ = 22.34 ppm (**3**). The phosphorus resonances of **2** and **3** are shifted downfield by ca. 26 and 41 ppm, respectively, in comparison with the parent organic ligand **1**. The ^{31}P NMR signal in **3** is shifted upfield compared to that of **2**, which reflects the electronic influence of the amino group.

The ^{31}P NMR signal of **3** is flanked by two ^{135}Pt satellites with $^1J_{Pt,P}$ coupling constant of 1666.77 Hz. This latter value is a clear indication of *cis* coordination of the diphosphine to the platinum(II) atom, yielding *cis*-[$PtCl_2$(**1**)] (**3**). The magnitude of the $^1J_{Pt,P}$ = 1666.77 Hz is typical for a bisphosphine ligand *trans* to chloride and thus in agreement with the proposed *cis* coordination of the ligand to Pt^{II}.[21–23]

IR Spectra and Yields

The IR spectra of **1**–**3** show bands in the range of 1438–1441 cm^{-1} and 810–910 cm^{-1} due to ν(P–Ph) and ν(P–N) stretching, respectively.[22] The ν(P–N) frequencies were observed at 840 cm^{-1} for **2** and 810 cm^{-1} for **3**. These ν(P–N) frequencies for the complexes were shifted toward lower frequencies compared to those of the free ligand **1**. In their IR spectra compounds **2** and **3** show bands that can be assigned to ν(Pd–Cl) (288 and 310 cm^{-1}) and ν(Pt–Cl) (290 and 312 cm^{-1}), respectively, which suggest that the ligand coordinates in a *cis* arrangement and therefore the complex has a four-membered *M*PNP (*M* = Pd or Pt) chelate ring.[24,25] This fact may be related to a decrease in the ν(P–N) bond strength upon coordination. Compounds **1**–**3** were obtained in a 80–85 % yield.

Molecular Structures of 2 and 3

Crystals of **2** and **3** were obtained as described in Experimental Section. Complexes **2** and **3** crystallize in the monoclinic space group *Cc* and *C*2/*c*, respectively. Crystallographic data are given in Table 1 and selected interatomic distances and angles are collected in Table 2. The molecular structures are depicted in Figure 1 and Figure 2.

Table 1. Crystal data and structure refinement for **2** and **3**.

	2	**3**
Formula	$C_{34}H_{27}Cl_2NP_2Pd\cdot 1.5C_4H_8O$	$C_{34}H_{27}Cl_2NP_2Pt\cdot 1.134C_3H_6O$
M_r	797.01	843.32
Temp. /K	213	173
Crystal system	monoclinic	monoclinic
Space group	*Cc*	*C*2/*c*
a /Å	37.31(3)	36.881(13)
b /Å	12.144(10)	12.118(4)
c /Å	16.700(14)	16.740(6)
α /°	90	90
β /°	99.572(8)	100.257(4)
γ /°	90	90
V /Å^3	7461(11)	7362(5)
Z	8	8
$\rho_{calcd.}$ /Mg·m^{-3}	1.419	1.522
F(000)	3264	3330
Abs coeff /mm^{-1}	0.760	4.058
No. of rflns coll.	31304	25421
No. of indep. rflns	13087	8454
R_{int}	0.1012	0.0869
No. of params	760	464
R_1 [$I > 2\sigma(I)$]	0.0835	0.0478
wR_2 (all data)	0.2612	0.1195
$(\Delta/\rho)_{max}$ /e·Å^{-3}	2.840	1.260
$(\Delta/\rho)_{min}$ /e·Å^{-3}	–1.430	–2.030

Table 2. Selected bond lengths /Å and bond angles /° for **2a**, **2b**, and **3**.

	M = Pd (**2a**)	*M* = Pd (**2b**)	*M* = Pt (**3**)
M–Cl(1)	2.363(10)	2.357(11)	2.3566(17)
M–Cl(2)	2.338(11)	2.341(10)	2.3566(17)
M–P(1)	2.249(9)	2.216(9)	2.1987(16)
M–P(2)	2.189(9)	2.223(9)	2.2201(16)
P(1)–N	1.72(2)	1.73(2)	1.714(6)
P(2)–N	1.67(2)	1.74(2)	1.710(6)
P–*M*–P	72.4(3)	72.6(3)	72.53(7)
∑ angles at N	360.0	359.9	359.8
Cl–*M*–Cl	94.9(3)	94.2(3)	91.08(6)
P–N–P	101.3(8)	98.4(9)	99.5(3)
M–P(1)–N	91.4(7)	94.7(8)	94.22(18)
M–P(2)–N	94.8(8)	94.2(8)	93.59(18)
P(1)–*M*–Cl(1)	94.2(4)	93.8(4)	95.99(6)
P(1)–*M*–Cl(2)	170.4(4)	171.3(4)	172.27(6)
P(2)–*M*–Cl(1)	98.5(4)	99.5(4)	100.38(6)
P(2)–*M*–Cl(2)	166.6(4)	166.4(4)	168.51(6)

The X-ray structure of **2** contains two crystallographically independent molecules, **2a** and **2b** (Figure 1), in the asymmetric unit, along with three THF molecules. They differ in the orientation of the naphthyl group and are related by a pseudo-inversion center. The asymmetric unit of complex **3** (Figure 2) contains about 1.13 molecules of acetone.

The ability of compound **1** to act as bidentate *P,P'*-chelating ligand to palladium and platinum metal atoms results in the formation of two four-membered metallacycles, i.e., P–N–P–Pd and P–N–P–Pt, respectively, that are nearly planar with torsion angles P–N–P–Pd of 1.8(7)° in **2a** [2.3(7)° in **2b**] and P–N–P–Pt of 3.3(2)° in **3** with smaller P–Pd–P [**2a**: 72.4(3); **2b**: 72.6(3)°] and P–Pt–P [**3**: 72.53(7)°] bite angles and larger P–N–P [**2a**: 101.3(8); **2b**: 98.4(9); **3**: 99.5(3)°] bond angles.

A comparison of the structural data of the P–Pd–P, P–Pt–P, and P–N–P bond angles in **2a**, **2b**, and **3** (Table 2) with those of the four-membered rings in palladium(II) complexes **4–12** and platinum(II) complexes **13–20** (Table 3) shows that the P–Pd–P bite angles in **2a** and **2b** are larger than those in **4–10** and smaller than the one in **11**, whereas the P–Pt–P bite angle in **3** is larger than those in **13** and **14** and smaller than those in **15–20**. The P–N–P bond angle in **3** is larger than those in **13–15** and **20** and smaller than those in **16–19**. Additionally, the P–N–P bond angle in **2a** (Table 2) is larger than those in **4–12**, whereas the P–N–P bond angle in **2b** is larger than those in **4**, **8** and **10** and smaller than those in **5–7**, **9**, **11**, and **12**.

The P–N–P [**2a**: 101.3(8); **2b**: 98.4(9); **3**: 99.5(3)°] bond angles are significantly smaller than those in the free diphosphinoamine ligands.[22,28] due to the formation of a strained four-membered chelate ring.

The C-naphthyl skeletons in **2a**, **2b**, and **3** are almost planar and virtually perpendicular to the P–N–P–Pd and P–N–P–Pt planes. A planar environment would be expected for the three-coordinate nitrogen atoms in **2a**, **2b**, and **3**, and the sums of bond angles in **2a**, **2b**, and **3** are indeed close to 360° (Table 2).

The distorted tetrahedral arrangement at the central phosphorus atoms [**2a**: 91.4(7)–123.8(6); **2b**: 94.2(8)–120.0(6); **3**: 93.59(13)–123.9(3)°] dictates that the phenyl groups are spread above and below the P–N–P–Pd and P–N–P–Pt planes, and ring stacking (face-to-face association) is thus prevented. Apparently, the presence of the naphthyl and phenyl groups decreases the P–Pd–P and P–Pt–P bite angles, presumably as a result of steric reasons, as the relatively bulky naphthyl and phenyl groups occupy much of the lateral space surrounding the P–N–P–Pd and P–N–P–Pt rings, which led to a distorted square-planar arrangement around the palladium and platinum atoms with the aminophosphine moieties coordinated in a mutual *cis* fashion, in agreement with the spectroscopic data.

Despite the difference of the two metal atoms, the P–Pt–P [**3**: 72.53(7)°] and P–Pd–P [**2a**: 72.4(3); **2b**: 72.6(3)°] bite angles are close to each other and significantly lower than the ideal 90° in a regular square-planar arrangement.

The P–Pd–Cl *trans* angles of **2a** [166.6(4) and 170.4(4)°], **2b** [166.4(4) and 171.3(4)°], and the P–Pt–Cl *trans* angles of **3** [168.51(6) and 172.27(6)°] differ significantly from 180°. The variations of the *trans* angles [**2a**: 3.8(4); **2b**: 4.9(4); **3**: 3.76(6)°] are larger than those of **4** [168.87(6)–166.46(6)°], **5** [167.18(10)–165.81(9)°], and **14** [171.69(5)–169.93(4)°].

The Cl–Pt–Cl angle in **3** [91.08(6)°] is smaller than those in similar platinum(II) complexes **13–17**, **19**, and **20** and larger than the one in **18**, whereas the Cl–Pd–Cl angles in **2a** [94.9(3)°] and **2b** [94.2(3)°] are larger than those in the similar Pd^{II} complexes **4–7** and **9–12** and smaller than that found in **8**. The Cl–Pt–Cl angle in **3** is smaller than the Cl–Pd–Cl angles in **2a** and **2b** (Table 2).

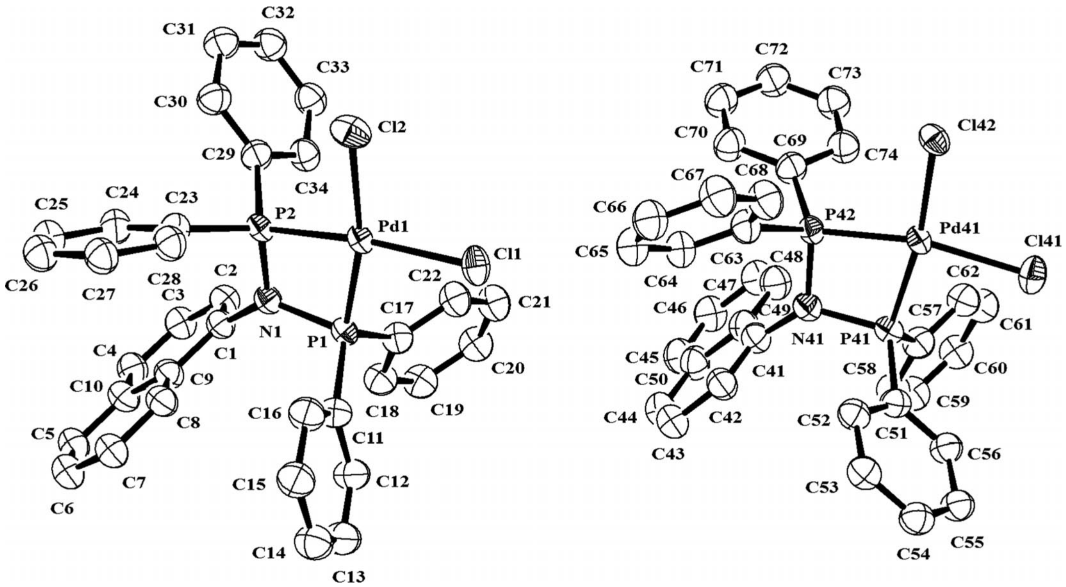


Figure 1. Molecular structure of the two independent molecules **2a** (left) and **2b** (right) (hydrogen atoms and solvent molecules are omitted for clarity).

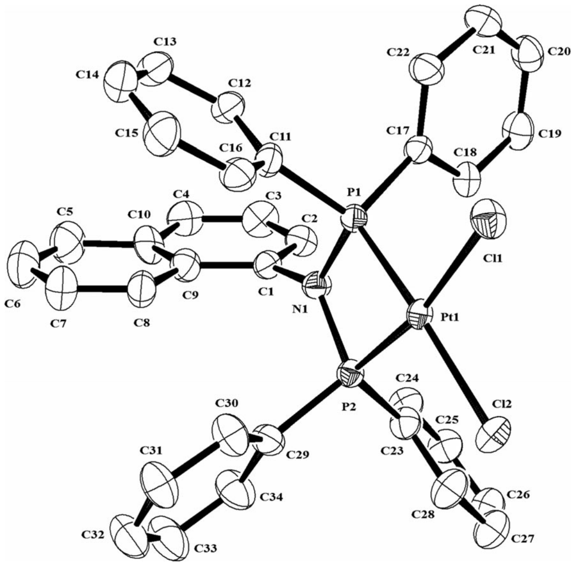


Figure 2. Molecular structure of **3** (hydrogen atoms and solvent molecules are omitted for clarity).

The P–N bond lengths in **2a** [1.72(2) and 1.67(2) Å] and **2b** [1.73(2) and 1.74(2) Å] are essentially similar, but they are longer than that of the platinum complex **3** [1.714(6) and 1.710(6) Å], although they are within the expected value range on comparison to similar palladium(II) complexes **4**–**12** and platinum(II) complexes **13**–**20** (Table 3) and smaller than the sum of Pauling covalent radii (1.77 Å) as expected due to P–N π-bonding. in agreement with this, the nitrogen atom is nearly planar as evidenced by the sum of angles about nitrogen being 360.0° for **2a**, 359.9° for **2b**, and 359.8° for **3**. Also, the average P–N bond lengths in **2a**, **2b**, and **3** are slightly shorter than those in the free diphosphinoamine ligands,[22,28] which clearly indicate an enhancement of π-bonding in the P–N unit.

The Pd–P bond lengths are 2.189(9)–2.249(9) in **2a** and 2.216(9)–2.223(9) Å in **2b**, whereas in **3** the Pt–P bond lengths are 2.1987(16)–2.2201(16) Å. The two Pd–P bond lengths in **2a** or **2b** are relatively different. The shorter Pd–P or Pt–P distance involves the phosphorus atom, which is closer to the $PdC1_2$ or $PtCl_2$ plane. Apparently, the large steric constraints in the ligand prevent appropriate orbital overlap when the two Pd–P or Pt–P bonds are equal and coplanar with the $PdC1_2$ or $PtCl_2$ unit.

The Pd–Cl bond lengths are 2.338(11)–2.363(10) Å for **2a** and 2.341(10)–2.357(11) Å for **2b**. The longer Pd–Cl bond is *trans* to the shorter Pd–P bond, which is in agreement with a *trans* effect of the phosphine. The two Pd–P bond lengths in **3** are similar [2.3566(17) Å], apparently, the bi(phosphanyl) amine ligand in **3** has the best steric fit and equal donor properties of $–Ph_2P$ groups.

The coordination bond lengths of the platinum and palladium atoms (Table 2) are essentially the same and are well within the range reported for similar palladium(II) **4**–**12** and platinum(II) complexes **13**–**20** (Table 3). It is interesting to note that the Pd–P and Pt–P bond lengths are smaller than those in four-membered ring phosphine complex *cis*-$[PdCl_2\{Ph_2PCH_2PPh_2\}]$ [Pd–P = 2.234(1), 2.250(1); Pd–Cl = 2.362(1), 2.365(1) Å][37] and *cis*-$[PtCl_2(PMe_3)_2]$ [Pt–P = 2.315(10) Å],[38] but the Pd–Cl and Pt–Cl are slightly smaller than those in these examples. These results suggest that the basic nitrogen lone pair make the phosphorus atom better donor on the coplanar to the phosphorus atom and the formation of π bond by back bonding from the metal. We could say that the ligand **1** exerts a stronger *trans* effect than the phosphine ligands and that the platinum and palladium complexes may be used as catalyst in various organic synthesis such as the copolymerization of olefin and CO.[39]

The P–Pd–P and P–Pt–P bite angles are smaller than those of the strained five-membered rings in **21**–**24** and much

Table 3. Selected bis(phosphanyl)amine palladium and platinum dichloride complexes.

Complex	No.	Ring syst.	P–*M*–P /°	Cl–*M*–Cl /°	P–N–P /°	Ref.
cis-[Pd{(Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$}Cl$_2$]·(C$_2$H$_5$)$_2$O	**4**	4	71.93(4)	96.96(5)	98.02(16)	[26]
cis-[PdCl$_2$ {Ph$_2$PN(*o*-C$_6$H$_4$OMe)PPh$_2$}]	**5**	4	71.99(5)	96.36(6)	99.3(2)	[27]
cis-[Pd{(Ph$_2$P)$_2$N-C$_6$H$_3$-3,5-OMe}Cl$_2$]	**6**	4	71.99(5)	95.46(5)	99.4(2)	[28]
cis-[Pd{(Ph$_2$P)$_2$N-C$_6$H$_3$-2,4-OMe}Cl$_2$]	**7**	4	72.20(6)	96.20(4)	98.8(3)	[28]
cis-[Pd{C$_6$H$_4$(*o*-Ph)N(PPh$_2$)$_2$}Cl$_2$]	**8**	4	72.23(3)	92.39(3)	97.70(13)	[29]
cis-[Pd{C$_6$H$_4$(*m*-CN)N(PPh$_2$)$_2$}Cl$_2$]	**9**	4	72.29(5)	95.31(5)	100.2(2)	[29]
cis-[PdCl$_2${(Ph$_2$P)$_2$N-C$_6$H$_4$-(C$_2$H$_5$)}]	**10**	4	72.30(9)	98.41(9)	97.6(4)	[30]
cis-[Pd{(Ph$_2$P)$_2$N-C$_6$H$_3$-3,4-OMe}Cl$_2$]	**11**	4	72.55(5)	96.57(4)	99.32(16)	[28]
cis-[Pd{C$_6$H$_4$(*p*-CN)N(PPh$_2$)$_2$}Cl$_2$]	**12**	4	72.62(4)	95.18(4)	100.1(2)	[29]
cis-[PtCl$_2${(C$_3$H$_5$)N(PPh$_2$)$_2$}]	**13**	4	72.10(8)	91.78(9)	99.2(4)	[31]
cis-[Pt{(Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$}Cl$_2$]·(C$_2$H$_5$)$_2$O	**14**	4	72.52(4)	92.92(5)	97.82(17)	[26]
cis-[Pt{(Ph$_2$P)$_2$N-C$_6$H$_3$-2,4-OMe}Cl$_2$]	**15**	4	72.54(8)	92.26(8)	98.7(3)	[28]
cis-[Pt{(Ph$_2$P)$_2$N-C$_6$H$_3$-3,5-OMe}Cl$_2$]	**16**	4	72.59(3)	91.91(3)	99.63(2)	[28]
cis-[Pt{C$_6$H$_4$(*m*-CN)N(PPh$_2$)$_2$}Cl$_2$]	**17**	4	72.77(3)	92.03(3)	99.99(13)	[29]
cis-[PtCl$_2${(Ph$_2$P)$_2$N-C$_6$H$_4$-(C$_2$H$_5$)}]	**18**	4	72.80(4)	90.74(4)	99.72(18)	[30]
cis-[Pt{C$_6$H$_4$(*o*-Ph)N(PPh$_2$)$_2$}Cl$_2$]	**19**	4	72.95(7)	91.84(7)	99.9(3)	[29]
cis-[Pt{C$_6$H$_4$(*p*-CN)N(PPh2)2}Cl2]	**20**	4	73.38(4)	91.23(2)	98.7(7)	[29]
cis-[PdCl$_2${(PhO)$_2$PN(Et)N(Et)P(OPh)$_2$}]	**21**	5	82.24(6)	93.20(6)	–	[32]
cis-[PtCl$_2${(PhO)$_2$PN(Et)N(Et)P(OPh)$_2$}]	**22**	5	82.55(6)	91.55(6)	–	[32]
cis-[PtCl$_2${(*o*-C$_6$H$_4$OCH$_3$)$_2$PN(Me)N(Me)P(*o*-C$_6$H$_4$OCH$_3$)$_2$}]	**23**	5	85.1(2)	91.0(2)	–	[32]
cis-[PtCl$_2${(*o*-C$_6$H$_4$OCH$_3$)$_2$PN(Et)N(Et)P(*o*-C$_6$H$_4$OCH$_3$)$_2$}]	**24**	5	84.9(2)	91.1(2)	–	[32]
cis-[PdCl$_2${Ph$_2$PN(C$_2$H$_4$)$_2$NPPh$_2$}]	**25**	7	93.9(2)	92.1(2)	–	[33]
cis-[PdCl$_2${Ph$_2$PN(*R*)(CH$_2$)$_2$N(R)PPh$_2$}][*R* = CH(CH$_3$)(Ph)]	**26**	7	96.74(2)	90.19(2)	–	[34]
cis-[PdCl$_2${MeC$_6$H$_3$(NHPPh$_2$)$_2$-3,4}]	**27**	7	91.31(8)	–	–	[35]
cis-[PtCl$_2${*i*Pr$_2$PN(CH$_2$Ph)CH$_2$CH$_2$N(CH$_2$Ph)P*i*Pr$_2$}]	**28**	7	100.64(3)	86.01(3)	–	[36]
cis-[PtCl$_2${Ph$_2$PN(C$_5$H$_{10}$)NPPh$_2$}]	**29**	7	97.3(1)	89.1(1)	–	[33]

smaller than those of the seven-membered rings in **25–29** (Table 3). We see that the P–Pd–P or P–Pt–P bite angle is dependent only on the ligand and the angles are virtually identical in the appropriate pair. The aromatic rings in **3** and **4** as expected have usual bond lengths and angles.

Conclusions

We have shown the successful synthesis of P–N–P ligand **1**. The coordination behavior of ligand **1** towards platinum and palladium is described. The new compounds were characterized by IR and multinuclear NMR spectroscopy. The ligand shows clear tendency to coordinate in a *cis* fashion to these palladium and platinum, as indicated by ^{31}P NMR spectroscopy. The molecular structures of the complexes *cis*-[PdCl$_2$(**1**)] (**2**) and *cis*-[PtCl$_2$(**1**)] (**3**) are determined. It was found out that ligand **1** exerts a stronger *trans* effect than the phosphine ligands and that the platinum and palladium complexes may be used as catalysts in various organic synthesis such as the co-polymerization of olefins and CO. We are currently probing the insertion of CO, alkene, etc., into the P–N bond of this ligand and its reactions with a variety of transition metals, main group halides, and chalcogens.

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References

[1] a) S. J. Berners-Price, P. J. Sadler, *Struct. Bonding (Berlin)* **1988**, *70*, 27–102; b) R. Meijboom, R. J. Bowen, S. J. Berners-Price, *Coord. Chem. Rev.* **2009**, *253*, 325–342.

[2] a) F. R. Hartley, *The Chemistry of Organophosphorus Compounds*, Vol. 1, John Wiley and Sons, England, Manchester, **1990**, pp. 255–294; b) F. Agbossou, F. Carpentier, J. F. Hapiot, I. Suisse, A. Mortreux, *Coord. Chem. Rev.* **1998**, *178–180*, 1615–1645; c) Z. Fei, P. J. Dyson, *Coord. Chem. Rev.* **2005**, *249*, 2056–2074.

[3] J. Reedijk, *Chem. Commun.* **1996**, 801–806.

[4] J. Y. Zhang, J. J. Vittal, Keat, W. Henderson, J. R. Wheaton, I. H. Hall, T. S. Andy Hor, Y. K. Yan, *J. Organomet. Chem.* **2002**, *650*, 123–132.

[5] M. Aydemir, A. Baysal, B. Gümgüm, *J. Organomet. Chem.* **2008**, *693*, 3810–3814 and references cited therein.

[6] E. Killian, K. Blann, A. Bollmann, J. T. Dixon, S. Kuhlmann, M. C. Maumela, H. Maumela, D. H. Morgan, P. Nongodlwana, M. J. Overett, M. Pretorius, K. Höfener, P. Wasserscheid, *J. Mol. Catal. A* **2007**, *270*, 214–218.

[7] I. Bachert, I. Bartusseck, P. Braunstein, E. Guillon, J. Rose, G. Kickelbick, *J. Organomet. Chem.* **1999**, *580*, 257–264.

[8] P. Bhattacharyya, T. Q. Ly, A. M. Z. Slawin, J. D. Woollins, *Polyhedron* **2001**, *20*, 1803–1808.

[9] P. Kafarski, P. Mastalerz, *Aminophosphonates: Natural Occurrence, Biochemistry and Biological Properties, Beiträge zur Wirkstoffforschung, Berlin,* **1984**.

[10] S. Priya, M. S. Balakrishna, J. T. Mague, *Inorg. Chem. Commun.* **2001**, *4*, 437–440.

[11] a) H. T. Al-Masri, J. Sieler, E. Hey-Hawkins, *Appl. Organomet. Chem.* **2003**, *17*, 63–67; b) H. T. Al-Masri, J. Sieler, E. Hey-Hawkins, *Appl. Organomet. Chem.* **2003**, *17*, 641–646; c) H. T. Al-Masri, J. Sieler, P. Lönnecke, S. Blaurock, K. Domasevitch, E. Hey-Hawkins, *Tetrahedron* **2004**, *60*, 333–339; d) H. T. Al-Masri, J. Sieler, P. Lönnecke, P. C. Junk, E. Hey-Hawkins, *Inorg. Chem.* **2004**, *43*, 7162–7169; e) H. T. Al-Masri, J. Sieler, P. C. Junk, K.

Domasevitch, E. Hey-Hawkins, *J. Organomet. Chem.* **2005**, *690*, 469–476; f) H. T. Al-Masri, J. Sieler, S. Blaurock, P. Lönnecke, P. Junk, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **2005**, *631*, 518–523; g) H. T. Al-Masri, J. Baldamus, E. Hey-Hawkins, *Polyhedron* **2009**, *28*, 3515–3518.

[12] H. T. Al-Masri, Emwas A. H. Emwas, Z. A. Al-Talla, M. H. Alkordi, *Phosphorus, Sulfur, Silicon Relat. Elem.* **2012**, submitted.

[13] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, New York, **1988**.

[14] G. K. Anderson, M. Lin, *Inorg. Synth.* **1990**, *28*, 60.

[15] J. R. Doyle, P. E. Slade, H. B. Jonassen, *Inorg. Synth.* **1960**, *20*, 60.

[16] *CrystalClear*, Rigaku Corporation, Tokyo, Japan, **2010**.

[17] M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, D. Viterbo, *J. Appl. Crystallogr.* **1989**, *22*, 389.

[18] *CrystalStructure 4*: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (**2000–2009**), 9009 New Trails Dr. The Woodlands, TX 77381, USA.

[19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[20] A. Karacar, M. Freytag, H. Thönnessen, J. Ömelanczuk, P. G. Jones, R. Bartsch, R. Schmeltzer, *Heteroatom. Chem.* **2001**, *12*, 102–113.

[21] M. Aydemir, A. Baysal, G. Oztürk, B. Gümgüm, *Appl. Organomet. Chem.* **2009**, *23*, 108–113.

[22] M. S. Balakrishna, P. P. George, J. T. Mague, *J. Organomet. Chem.* **2004**, *689*, 3388–3394.

[23] M. Aydemir, A. Baysal, B. Gümgüm, *J. Organomet. Chem.* **2008**, *693*, 3810–3814.

[24] A. M. Z. Salwin, J. Wheatley, M. V. Wheatly, J. D. Woolins, *Polyhedron* **2003**, *22*, 1397–1405.

[25] T. Appleby, S. M. Aucott, M. L. Clarke, A. M. Z. Slawin, J. D. Woollins, *Polyhedron* **2002**, *21*, 2639–2645.

[26] M. Aydemir, F. Durap, A. Baysal, O. Akba, B. Gümgüm, S. Özkar, L. T. Yıldırım, *Polyhedron* **2009**, *28*, 2313–2320.

[27] K. G. Gaw, M. B. Smith, A. M. Z. Slawin, *New J. Chem.* **2000**, *24*, 429–435.

[28] N. Biricik, C. Kayan, B. Gümgüm, Z. Fei, R. Scopelliti, P. J. Dyson, N. Gurbuz, I. Özdemir, *Inorg. Chim. Acta* **2010**, *363*, 1039–1047.

[29] Z. Fei, W. H. Ang, D. Zhao, R. Scopelliti, P. J. Dyson, *Inorg. Chim. Acta* **2006**, *359*, 2635–2643.

[30] F. Durap, N. Biricik, B. Gümgüm, S. Özkar, W. H. Ang, Z. Fei, R. Scopelliti, *Polyhedron* **2008**, *27*, 196–202.

[31] A. M. Z. Slawin, H. L. Milton, J. Wheatley, J. D. Woollins, *Polyhedron* **2004**, *23*, 3125–3132.

[32] A. M. Z. Slawin, M. Wainwright, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **2002**, 513–519.

[33] M. R. I. Zubiri, A. M. Z. Slawin, M. Wainwright, J. D. Woollins, *Polyhedron* **2002**, *21*, 1729–1736.

[34] E. J. Zijp, J. I. Vlugt, D. M. Tooke, A. L. Spek, D. Vogt, *Dalton Trans.* **2005**, 512–517.

[35] T. Q. Ly, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1997**, 1611–1616.

[36] M. R. I. Zubiri, H. L. Milton, D. J. Cole-Hamilton, A. M. Z. Slawin, J. D. Woollins, *Polyhedron* **2004**, *23*, 693–699.

[37] W. L. Steffen, G. J. Palenik, *Inorg. Chem.* **1976**, *15*, 2432–2439.

[38] G. G. Messmer, E. L. Amma, J. A. Ibers, *Inorg. Chem.* **1967**, *6*, 725–730.

[39] B. Kim, K. Yang, M. Jung, B. Lee, M. Doh, *Bull. Korean Chem. Soc.* **1997**, *18*, 1162–1166.

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Synthesis, Characterization, and Structures of Palladium(II) and Platinum(II) Complexes Containing *N*,*N*-Bis(diphenylphosphanyl)naphthylamine