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An imidazole-based P-N bridging ligand and its binuclear copper(I), silver(I) and palladium(I) complexes: synthesis, characterizations and X-ray structures

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Abstract

Reaction of 1-methylimidazole with *n*-BuLi in tetrahydrofuran at -78° C followed by addition of chlorodiphenylphosphine afforded a P-N bridging ligand, 2-(diphenylphosphino)-1-methylimidazole (dpim) in good yield. The structure of the ligand was determined by single crystal X-ray analysis. Reaction of a stoichiometric amount of the ligand with [Cu(MeCN)₄]ClO₄ in acetonitrile led to the binuclear complex $[Cu_2(\mu-dpim)_3(MeCN)](ClO_4)_2 \cdot 2CH_3CN$ (1·2CH₃CN), whose structure was determined by single crystal X-ray analysis. The solid state structure shows that the two copper ions are held by three dpim ligands and the coordination geometry around each metal atom is different, one being three- and the other being four-coordinated. One of the copper ions forms a distorted tetrahedral array with two P and one N atoms from the dpim ligand and an additional N atom from an acetonitrile ligand, whereas the other copper ion is three coordinated with two N and one P atoms from the dpim ligand. The nitrate-bridged polymeric silver(I) complex, $\{[Ag_2(\mu-dpim)_2(NO_3)](NO_3)\}_{\mu}$ (2) was prepared by the reaction of equimolar amounts of the ligand and silver nitrate in methanol and was characterized by IR, NMR and X-ray analysis. The dimeric unit, $[Ag_2(\mu-dpim)_2]$, possesses an eight-membered annular core structure with two ligands bridging the two metal ions in a head-to-tail configuration. Two types of nitrate ions are present in 2: one makes an infinite one-dimensional chain by joining the dimeric units through its two oxygen atoms in an anti-anti bridging mode whereas the other is disordered with a half occupancy and is located at the left and right sides of the chain. The dynamic behavior of 2 in acetone was also studied by variable temperature ³¹P NMR. The binuclear palladium(I) complex $[Pd_2Cl_2(dpim)_2]$ (4) was prepared by a conproportionation reaction between complex [PdCl₂(dpim)₂] (3) and [Pd(dba)₂] (dba = dibenzylideneaceton). Only one geometric isomer, probably head-to-tail (HT), was formed in this reaction. Complex 3 was prepared by treating [PdCl₂(PhCN)₂] with two moles of ligand in dichloromethane solution. In this complex the ligand acts as a P-monodentate. In solution it exists as a mixture of cis and trans isomers. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years there has been great interest in binuclear complexes where two metal ions are held in close proximity [1]. These bimetallic complexes in some cases exhibit unusual and unexpected structures and react with unsaturated and small molecules by a process in

bimetallic systems are interesting for their potential applications in catalysis [4]. The ligands bis-(diphenylphosphino)methane (dppm) and (diphenylphosphino)pyridine (dppy) are frequently used to prepare binuclear complexes. The binuclear transition metal complexes of the latter unsymmetric and rigid dppy ligand have been the focus of much investigation in the last few years because of the novel structural and reactive features of these complexes. In addition to a large number of binuclear complexes [5],

which both metals participate simultaneously to give a new substrate reactivity [2,3]. For these reasons, such

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several mononuclear species [6] as well as clusters [7] and oligomers [8] have also been reported. The ligand can act also as a P-monodentate [9] and PN-chelate [6a,c]. Some catalytic reactions of these complexes including hydrogenation [3], hydroformylation [5,10] and carbonylation [11] have also been investigated.

It is well established that the properties and catalytic activities of complexes of phosphine ligands often vary considerably depending upon the nature of the ligands. Since dppy has proven to be a useful bridging ligand, it is important to develop new such P-N bridging ligands containing other N-heterocycles. In this context 1methylimidazole would be an excellent candidate which has been found to be a better π -donor and poorer π -acceptor ligand compared to pyridine [12]. E and C values for 1-methylimidazole suggest that it is a stronger base than pyridine with 'softer' properties [13]. Furthermore, imidazole has great biological importance. Herein we report a P-N bridging ligand containing an imidazole donor, 2-(diphenylphosphino)-1methylimidazole (dpim) and some binuclear complexes. Because of its similarity to the dppy ligand, it should be capable of substitution for dppy in any of the numerous complexes of this popular ligand.



Scheme 1.



Fig. 1. An ORTEP view of the molecular structure of the ligand dpim.

Table 1 Selected bond distances (Å) and angles (°) for the ligand dpim

Bond distances			
P1–C3	1.822(2)	N1-C3	1.365(3)
P1-C5	1.829(3)	N1-C4	1.461(3)
P1-C11	1.831(3)	N2-C3	1.324(3)
Bond angles			
C3-P1-C5	104.1(1)	C5-P1-C11	101.8(1)
C3-P1-C11	100.3(1)	P1-C3-N2	128.5(2)

2. Results and discussion

2.1. Synthesis of the ligand

The ligand was prepared conveniently using the onepot reaction outlined in Scheme 1. Lithiation of 1methylimidazole at its 2-position by *n*-BuLi followed by addition of an equimolar amount of chlorodiphenylphosphine afforded the ligand in fairly good yield ($\approx 75\%$). Recrystallization from diethylether-hexane afforded analytically pure colorless crystals.

Although, the compound is known, the preparative method is different and needs a long reaction time [14]. Furthermore, the coordination chemistry of the compound is totally unexplored. The present synthetic method is very simple and convenient. In the previous paper complete analytical data were not given and the reported melting point ($80-82^{\circ}$ C) is significantly different from the present value ($58-60^{\circ}$ C). We have characterized the compound fully by elemental analysis, NMR spectroscopies and single crystal X-ray analysis. The ORTEP view of the molecular structure of dpim is depicted in Fig. 1 and selected bond distances and angles are listed in Table 1.

The P–C(Ph) distances (1.829(3) and 1.831(3) Å for C5 and C11 respectively) are very similar to those for dppy [1.824(2) and 1.824(2)] [15]. However, the P–C(im) bond distance [1.822(2) Å] is slightly shorter than the P–C(py) distance [1.837(3) Å] of dppy. The observed bite distance for dpim is about 2.841 Å whereas it is about 2.648 Å for dppy. Although the bite distance of the present ligand is slightly longer than that of dppy, we found the ligand is more effective, in some cases, at holding two metal ions in close proximity compared to dppy (vide infra).

2.2. Synthesis and characterization of complexes

The syntheses of the complexes are shown in Eqs. (1)-(4).





Fig. 2. An ORTEP view of the cation of 1.2MeCN. All phenyl rings and hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) for 1.2CH₃CN

Bond distances			
Cu1-P1	2.272(1)	Cu1–P2	2.278(1)
Cu1-N5	2.041(3)	Cu1–N7	2.101(4)
Cu2–P3	2.197(1)	Cu2-N1	2.006(3)
Cu2–N3	1.974(3)	P1-C3	1.796(4)
P1-C5	1.830(4)	P1-C11	1.836(4)
P2-C19	1.801(4)	P2-C21	1.822(4)
P2-C27	1.826(4)	P3-C35	1.802(4)
P3-C37	1.829(4)	P3-C43	1.817(4)
N7-C49	1.132(5)	C49-C50	1.453(7)
Bond angles			
P1-Cu1-P2	124.31(4)	P1-Cu1-N5	117.54(9)
P1-Cu1-N7	99.79(10)	P2-Cu1-N5	113.14(9)
P2-Cu1-N7	95.40(10)	N5-Cu1-N7	97.1(1)
P3-Cu2-N1	112.75(9)	P3-Cu2-N3	130.22(10)
N1-Cu2-N3	115.7(1)	Cu1-P1-C3	116.2(1)
Cu1-P1-C5	113.7(1)	Cu1-P1-C11	114.8(1)
C3-P1-C5	100.4(2)	C3-P1-C11	104.1(2)
C5-P1-C11	106.1(2)	Cu1-P2-C19	119.3(1)
Cu1-P2-C21	112.3(1)	Cu1-P2-C27	110.3(1)
C19-P2-C21	102.1(2)	C19-P2-C27	104.3(2)
C21-P2-C27	107.8(2)	Cu2-P3-C35	111.5(1)
Cu2-P3-C37	118.8(1)	Cu2-P3-C43	109.8(1)
C35–P3–C37	100.9(2)	C35–P3–C43	106.4(2)
Cu1-N7-C49	164.7(3)	N7-C49-C50	178.6(5)

2dpim + PdCl₂(PhCN)₂ -----





The copper(I) complex $[Cu_2(\mu-dpim)_3(MeCN)][ClO_4]_2$ (1) was prepared by treating an acetonitrile solution of [Cu(MeCN)₄]ClO₄ with dpim (2:3 molar ratio) at 40-45°C for 3 h. Addition of diethylether to the reaction mixture gives the complex as a white powder. In the complex both nitrogen and phosphorus atoms of the ligand are coordinated, as shown by significant downfield shifts of the H⁴ proton and ³¹P resonances compared to those in the free ligand. The relatively large chemical shift observed for the H⁴ proton in complexes compared to the free ligand probably results from its proximity to the nitrogen donor atom; this proton would be expected to experience the strongest σ -effect. The structure of 1.2CH₃CN was determined by single crystal X-ray analysis. An ORTEP view of the complex cation is depicted in Fig. 2; selected bond distances and angles are listed in Table 2.

The X-ray structure of 1.2CH₃CN comprises two copper ions bridged by three dpim ligands, where the coordination geometry around each metal atom is different, one being three- and the other four-coordinated. This structural type with higher number of bridging ligands is a rare example, probably due to the extensive crowding around the metal centers. The dppy ligand also forms a similar type of complex, [Cu2(µdppy)₃(MeCN)][BF₄]₂, in which trigonal planar coordination of one copper atom and distorted tetrahedral coordination of the other copper atom are observed [16]. In 1·2CH₃CN Cu1 forms a distorted tetrahedral array with two P and one N atoms from the dpim ligand and an additional N atom from an acetonitrile ligand. The other Cu atom, Cu2, is three coordinated with two N and one P atoms from the dpim ligand. The Cu-P and Cu-N bond distances of four coordinated copper are longer than those of the three coordinated copper [Cu1-P1 2.272(1), Cu1-P2 2.278(1) and Cu2-P3 2.197(1); Cu1-N5 2.041(3), Cu2-N1 2.006(3) and Cu2-N3 1.974(3) Å]. All of these bond distances are very similar to those of the dppy complex. The acetonitrile is coordinated to Cu1 in a bent fashion, as indicated by the Cu1-N7-C49 angle of 164.7(3)° with a Cu1-N7 distance of 2.101(4) Å. The Cu-Cu separation (2.875(1) Å) is considerably longer than that of the dppy analog [2.721(3) Å].

The polymeric silver(I) complex $\{[Ag_2(\mu-dpim)_2-(NO_3)](NO_3)\}_n$ (2) was prepared by refluxing an equimolar amount of silver nitrate and the dpim ligand in methanol for 1 h. The complex was precipitated out as colorless crystals when the reaction mixture was



Fig. 3. ORTEP drawing showing the chain structure of 2. All phenyl rings and hydrogen atoms are omitted for clarity.

allowed to cool at ambient temperature. The structure was determined by single crystal X-ray analysis. The X-ray analysis reveals that the complex has a nitrate bridged polymeric chain structure consisting of binuclear $\{Ag_2(\mu-dpim)_2\}$ units having a crystallographic C_i symmetry (Fig. 3). Selected bond distances and angles are listed in Table 3.

In the basic binuclear unit, two silver atoms are doubly bridged by two dpim ligands in a head-to-tail configuration. As shown in Fig. 3, two kinds of nitrate anions are present in 2: one makes an infinite polymeric chain by connecting the binuclear units in an anti-anti bridging mode through its two oxygen atoms [Ag-O =2.64(2) Å], while the other is disordered with a half occupancy and located at the left and right sides of the chain. Each silver atom is tricoordinated in a distorted trigonal fashion. The structural features of 2 are quite different from those of the dppy silver complex $[Ag_2(NO_3)_2(\mu$ -dppy)_2] [17]. The dppy afforded a dinuclear complex in which each silver ion is tetracoordinated in a distorted tetrahedral fashion and both of the nitrate ions are coordinated to a silver ion in a chelating fashion (Ag-O 2.57 and 2.58 Å). In spite of the longer bite distance of dpim compared to dppy, the Ag. Ag separation of 2 [2.918(3) Å] is significantly shorter than that of the dppy complex (3.146 Å). However, the Ag-P and Ag-N bond distances of 2 [2.391(3) and 2.214(9) Å, respectively] are not significantly different from those of the dppy complex [2.378(2) and 2.234(6) Å, respectively]. The Ag. Ag separation of 2 is also significantly shorter than that of $[Ag_{2}(\eta^{1}-dppy)(\mu-dppy)_{2}][ClO_{4}]_{2}$ [3.072(1) A] where the silver ions are held together by two dppy ligands acting as bridges through P and N atoms in a head-to-tail configuration, while the third ligand is coordinated to only one silver ion through its P donor [18].

Variable temperature ³¹P NMR of **2** in acetone indicates a ligand exchange process involving dissociation of Ag–P bonds [19]. Selected ³¹P NMR spectra are presented in Fig. 4. At 296 K no ³¹P resonance of **2** was observed. At 273 K two broad signals were observed at about 2.3 and 6.3 ppm. However, a resolved spectrum centered at 5.28 ppm was obtained at 213 K.

The spectrum arises from the superposition of three different spin systems attributable to the isotopomers $[^{107}Ag_2(\mu\text{-dpim})_2]^{2+}$, $[^{109}Ag_2(\mu\text{-dpim})_2]^{2+}$ and $[^{107}Ag^{-109}Ag(\mu\text{-dpim})_2]^{2+}$. The observed coupling constants for ^{107}Ag -P and ^{109}Ag -P are 623 and 696 Hz, respectively; these values are considerably higher than those usually observed in silver-phosphine complexes. However, the ratio of the ^{31}P -Ag coupling constants (1.146) is very close to the ratio of the nuclear magnetic moments of the two metal isotopes.

The binuclear palladium complex $Pd_2Cl_2(dpim-P)_2$ (4) was prepared by the conproportionation reaction

Table 3 Selected bond distances (Å) and angles (°) for **2**

Bond distances			
Ag1–P1	2.391(3)	Ag1–N1	2.214(9)
Ag1–O2	2.64(1)	P1-C3	1.82(1)
O1–N3	1.23(2)	O2–N3	1.25(1)
Bond angles			
P1-Ag1-N1'	156.1(3)	P1-Ag1-O2	111.2(3)
O2–Ag1–N1′	92.5(4)	Ag1–P1–C3	109.6(4)



Fig. 4. Selected ${}^{31}P$ NMR spectra of 2 in acetone-d₆ at various temperatures.

between Pd(II) and Pd(0) complexes. This method has proven to be useful for the preparation of dimeric Pd(I), Pt(I), and Rh(I) complexes of the dppy ligand. Thus treatment of $PdCl_2(dpim)_2$ (3) with $Pd(dba)_2$ in dichloromethane solution produced 4 in 62% yield. The ³¹P NMR spectrum of this complex consists of a single peak at $\delta = 7.60$ indicating the presence of one isomer either head-to-tail or head-to-head. The spectroscopic data do not distinguish between head-to-tail and headto-head orientations of the dpim ligand. However, the head-to-tail structure is more likely since the Ag(I) complex 2 has been shown to have this orientation. Complex 4 does not give any ring opening product or A-frame complex with small organic molecules such as CO. However, the dppy-bridged palladium complex gives ring opening products with CO [20]. This observation suggests that imidazolyl nitrogen is more strongly bound with the metal ion than pyridine nitrogen.

The P-bonded mononuclear palladium complex $PdCl_2(dpim)_2$ (3) was prepared by the reaction of $PdCl_2(PhCN)_2$ with two moles of dpim in dichloromethane followed by precipitation with diethyl ether. In solution this compound is a non-electrolyte. Its ³¹P NMR spectrum in CDCl₃ consists of two resonances at 77.52 and 79.50 with relative intensities 1:7 respectively. Thus in solution it exists as a mixture of *cis* and *trans* isomers.

3. Conclusion

A convenient synthesis of an imidazole based P-N bridging ligand has been carried out. The ligand is found to be very effective at bridging two metal ions in close proximity and is able to give stable bimetallic complexes. A rare type of triply bridged binuclear

copper(I) complex and a nitrate-bridged polymeric silver(I) complex have been synthesized and characterized by single crystal X-ray analyses. A binuclear palladium(I) complex has also been prepared. It is found that in some cases the ligand afforded different types of complexes from the dppy ligand under the same reaction conditions. The present ligand may able to provide a very good opportunity to compare its chemistry with that of the widely used dppy ligand. Syntheses of other homo- and heterobinuclear complexes of dpim are in progress.

4. Experimental

4.1. Methods

All reactions were carried out in oven-dried glassware under an atmosphere of N2 gas. Anhydrous solvents used in reactions were either purchased in anhydrous form or distilled prior to use (THF from sodium benzophenone). $[Cu(MeCN)_4]ClO_4$ [21]. PdCl₂(PhCN)₂ [22], and Pd(dba)₂ [23] were prepared according to published procedures. All chemicals were reagent grade and were used as received. The organic phase from all liquid-liquid extraction was dried over anhydrous Na₂SO₄. Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities with appropriate precautions.

4.2. Instruments

All NMR spectra were recorded with a JEOL JMTC 400 MHz spectrometer and are reported in δ units. ¹H spectra were referenced to TMS and ³¹P spectra were referenced to 85% H₃PO₄ as an external standard. Elemental analyses were performed by the Faculty of Pharmaceutical Science, Kanazawa University. X-ray measurements were made on a Rigaku AFC7R diffractometer or Rigaku Raxis IV imaging plate area detector.

4.3. Preparations

4.3.1. 2-(diphenylphosphino)-1-methylimidazole (dpim)

To a stirred solution of 1-methyl imidazole (50 mmol, 4 ml) in THF (100 ml), *n*-butyllithium (1.5 M, 50 mmol, 33.5 ml) was added at -78° C. After 1 h chlorodiphenylphosphine (50 mmol, 9 ml) was added slowly via a syringe and the reaction mixture was stirred for 6 h at ambient temperature. After removing THF, diethylether and water were added and the organic layer was collected. The solvent was removed by evaporation and then hexane was added to afford an oily solid precipitation. Recrystallization of the oily

solid from diethylether-hexane gave the analytically pure ligand as colorless crystals (10.30 g, 75%), m.p. 58-60°C (literature m.p. 80-82°C). *Anal.* Calc. for C₁₆H₁₅N₂P: C, 72.17; H, 5.68; N, 10.52. Found: C, 71.90; H, 5.78; N, 10.29%. ¹H NMR (CDCl₃) δ = 3.73 (s, 3H, N-CH₃), 7.04 (d, 1H, H⁵), 7.24 (d, 1H, H⁴), 7.32-7.44 (m, 10H, Ph). ³¹P NMR (CDCl₃, 296 K) δ = -31.21 (s).

4.3.2. [*Cu*₂(*dpim*)₃(*MeCN*)][*ClO*₄]₂·*H*₂*O*·0.5*MeCN* (1·*H*₂*O*·0.5*MeCN*)

A mixture of [Cu(NCMe)₄]ClO₄ (0.33 g, 1 mmol) and dpim ligand (0.40 g, 1.5 mmol,) was stirred in acetonitrile (50 ml) under mild heating (40–45°C) for 3 h. The resultant solution was concentrated under vacuum and diethylether was added to give a solid which was collected and washed with methanol and dried under vacuum (0.5 g, 83%). *Anal.* Calc. for Cu₂C₅₀H₄₈N₇-P₃Cl₂O₈·H₂O·0.5MeCN: C, 50.85; H, 4.30; N, 8.72. Found: C, 50.54; H, 4.30; N, 9.08%. ¹H NMR (CDCl₃, 273 K) $\delta = 2.92$ (s, 3H, MeCN), 3.14 (s, 9H, N–CH₃), 6.65–7.69 (m, 36H, Ph and Im). ³¹P NMR (CDCl₃, 273 K) $\delta = -18.65$ (s, 1P), -13.71 (s, 2P).

4.3.3. $\{[Ag_2(dpim)_2(NO_3)](NO_3)\}_n$

The ligand dpim (0.27 g, 1 mmol) and $AgNO_3$ (0.17 g, 1 mmol) in methanol (80 ml) were refluxed in the dark for 1 h. Upon concentrating the resultant solution under vacuum an off-white product was precipitated

Table 4

Crystallographic data of the ligand and complexes $1{\cdot}2\text{CH}_3\text{CN}$ and 2

	dpim	$1 \cdot 2 CH_3 CN$	2
Formula	$C_{16}H_{15}N_2P$	Cu ₂ C ₅₄ H ₅₄ N ₉ - P ₃ Cl ₂ O ₈	$Ag_2C_{32}H_{30}N_6-P_2O_6$
Formula weight	266.28	1248.00	872.31
Crystal	0.20×0.20	0.60×0.15	0.30×0.10
dimension (mm)	× 0.50	× 0.10	× 0.50
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	<i>P</i> 2/ <i>c</i> (no. 13)
Unit cell dimen	sions		
a (Å)	13.283(2)	14.215(2)	13.814(4)
b (Å)	9.917(2)	24.872(6)	9.338(2)
c (Å)	10.864(3)	16.093(3)	14.974(4)
β (°)	93.59(2)	91.610(9)	116.21(2)
$U(Å^3)$	1428.3(4)	5687(1)	1733.0(7)
Ζ	4	4	2
$\mu(Mo K_{\alpha})$ (cm ⁻¹)	1.80	9.87	12.71
T (°C)	23.0	-120.0	23
Reflections (total)	3651	8467	4382
Reflections (unique)	3476		4224
$R_{\rm int}$	0.017		0.053
$R; R_w$	0.038; 0.059	0.039; 0.054	0.079; 0.123

out. Recrystallization of this precipitation from hot methanol yielded pure colorless crystals (0.35 g, 80%). *Anal.* Calc. for Ag₂C₃₂H₃₀N₆P₂O₆: C, 44.06; H, 3.46; N, 9.63. Found: C, 43.62; H, 3.77; N, 9.34%. ¹H NMR (acetone-d₆) $\delta = 3.18$ (s, 6H, N–CH₃), 7.15 (d, 2H, H⁵), 7.59 (d, 2H, H⁴) 7.45–7.52 (m, 20H, Ph). ³¹P NMR (acetone-d₆, 213 K) $\delta = 5.28$ (m).

4.3.4. $PdCl_2(dpim)_2 \cdot CH_2Cl_2$ (3 · CH_2Cl_2)

A dichloromethane solution (10 ml) of PdCl₂(PhCN)₂ (0.38 g, 1 mmol) was added dropwise to a solution of dpim (0.53 g, 2 mmol) in dichloromethane (20 ml) and stirred for 2 h. Very faint yellow crystals were precipitated by the dropwise addition of diethylether. The crystals were collected, washed with diethylether and vacuum dried (0.62 g, 78%). *Anal.* Calc. for PdC₃₂H₃₀N₄P₂Cl₂·CH₂Cl₂: C, 49.87; H, 4.06; N, 7.05. Found: C, 50.07; H, 4.45; N, 7.30%. ¹H NMR (CDCl₃) $\delta = 3.70$ (s, 6H, N–CH₃), 6.73–7.96 (m, 24H, Ph, H⁴ and H⁵). ³¹P NMR (CDCl₃) $\delta = 77.52$ and 79.50 (s).

4.3.5. $Pd_2Cl_2(dpim)_2 \cdot 2H_2O$ (4 · 2H₂O)

A blood red solution of Pd(dba)₂ (0.28 g, 0.5 mmol) in dichloromethane (20 ml) was added to a solution of PdCl₂(dpim)₂ (0.35 g, 0.5 mmol) in dichloromethane (20 ml) and the mixture was refluxed for 2 h. The resultant solution was then filtered while hot and the filtrate was evaporated to approximately 5 ml under reduced pressure. The resultant precipitate was collected by filtration, washed with ethanol and dried in vacuo (0.26 g, 62%). *Anal.* Calc. for Pd₂C₃₂H₃₀N₄P₂Cl₂·2H₂O: C, 45.09; H, 4.02; N, 6.57. Found: C, 45.55; H, 3.59; N, 6.53%. ¹H NMR (CDCl₃) δ = 3.01 (s, 6H, N–CH₃), 6.90 (d, 2H, H⁵), 7.35–7.72 (m, 20H, Ph), 8.04 (d, 2H, H⁴). ³¹P NMR (CDCl₃) δ = 7.60 (s).

4.4. X-ray crystallographic studies

All crystallographic data for the ligand and complexes are listed in Table 4. Crystals of the ligand dpim for X-ray diffraction study were grown from etherhexane solution during recrystallization, while crystals of the complex 1.2CH₃CN were grown by slow diffusion of diethylether in acetonitrile solution of complex 1 at -5° C. Crystals of the complex 2 for X-ray diffraction study were obtained by keeping hot methanol-acetone solution at room temperature (r.t.). All measurements of the ligand dpim and 2 were performed on a Rigaku AFC7R diffractometer using graphitemonochromated Mo K_{α} radiation ($\lambda = 0.71070$ Å) at 23°C. The data were collected using an ω -2 θ scan technique to a maximum 2θ value of 55° at a scan speed of 8.0° min⁻¹ and 12.0° min⁻¹ (in ω) for the ligand and 2 respectively. The weak reflections (I < $10.0\sigma(I)$) were rescanned (maximum of five scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection.

Since the crystals of 1.2CH₃CN were efflorescent, an appropriate crystal was picked up on a cold copper plate cooled by liquid nitrogen (approximately -80° C) and mounted on a glass rod. The measurement was carried out by a Rigaku RAXIS-IV imaging plate area detector using graphite monochromated Mo K_{α} radiation ($\lambda = 0.71070$ Å) at -120° C. The crystal-detector distance was 120 mm. In order to determine the cell constants and the orientation matrix, three oscillation photographs were taken with oscillation angle 2° and exposure time 7 min for each frame. Intensity data were collected by taking oscillation photographs (total oscillation range 100°; 50 frames; oscillation angle 2°; exposure time 10 min).

The structure of the ligand was solved by Patterson methods whereas structures of 1.2CH₃CN and **2** were solved by SHELX 86 and SIR 92 respectively and expanded using Fourier technique. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation but not refined. All calculations were performed using the TEXAN crystallographic software package of Molecular Structure Corporation.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC-149992 (ligand dpim), CCDC-149993 (1·2CH₃CN) and CCDC-149994 (2). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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