

# Isolation and crystallographic characterization of solvate- and anion-stabilized PCP pincer complexes of palladium(II)

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## Abstract

Pincer PCP-Pd(II) complex [PdCl(PCP)] (**1**) (PCP = <sup>-</sup>CH(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>) reacts with AgNO<sub>3</sub> to give [Pd(NO<sub>3</sub>)(PCP)] (**2**). Similar reaction with AgBF<sub>4</sub> gives the aqua complex [Pd(OH<sub>2</sub>)(PCP)][BF<sub>4</sub>] (**3**) and the dinuclear complex [{Pd(PCP)}<sub>2</sub>(μ-Cl)][BF<sub>4</sub>] (**4**) with singly bridging chloro ligand. All new complexes were characterized by NMR spectroscopy, ESI-MS and single-crystal X-ray diffraction. Complex **1** and the triflate complex [Pd(OTf)(PCP)] (**5**) are active towards Suzuki–Miyaura coupling between aryl bromides and phenyl boronic acid.

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**Keywords:** Pincer; Palladium; Phosphine; Suzuki–Miyaura Coupling

## 1. Introduction

Research in PCP pincer complexes arising from coordination-assisted C–X activation (X = H, C or halogen) continues to advance at a brisk pace [1]. This is driven largely by their catalytic capabilities [2] and their role as precursors to a range of novel bi- and polymetallic systems [3]. We have recently used a Pd(II) pincer *viz.* [PdCl(PCP)] (**1**) as a model to demonstrate the utility of electrospray ionization mass spectrometry (ESI-MS) in guiding chemical syntheses [4]. These complexes contain a metallated sp<sup>3</sup> carbon that has been reported to enhance catalytic activity [5] or to give unique reactivity [6] due to higher electron density at the metal centre. Herein we report the metathesis reactions of **1** with AgX (X = NO<sub>3</sub>, BF<sub>4</sub>) to give complexes [Pd(NO<sub>3</sub>)(PCP)] (**2**) and [Pd(OH<sub>2</sub>)(PCP)][BF<sub>4</sub>] (**3**). The dinuclear complex [{Pd(PCP)}<sub>2</sub>(μ-Cl)][BF<sub>4</sub>] (**4**) with a chloro ligand bridging between the two pincer Pd(II) moi-

eties was isolated during the preparation of **3**. Such unsupported chloro-bridged complexes of palladium and platinum [7] are of interest especially when they are possible intermediates in the catalyst deactivation process involving cationic complexes [8]. Included herein is the catalytic activity of **1** and the earlier reported triflate complex [Pd(OTf)(PCP)] (**5**) [9] towards Suzuki–Miyaura coupling reaction. As unsaturated metal complexes or their precursors are important catalysts [10], their isolation could suggest an easy access to a range of PCP-Pd(II) pincer-based catalytic materials.

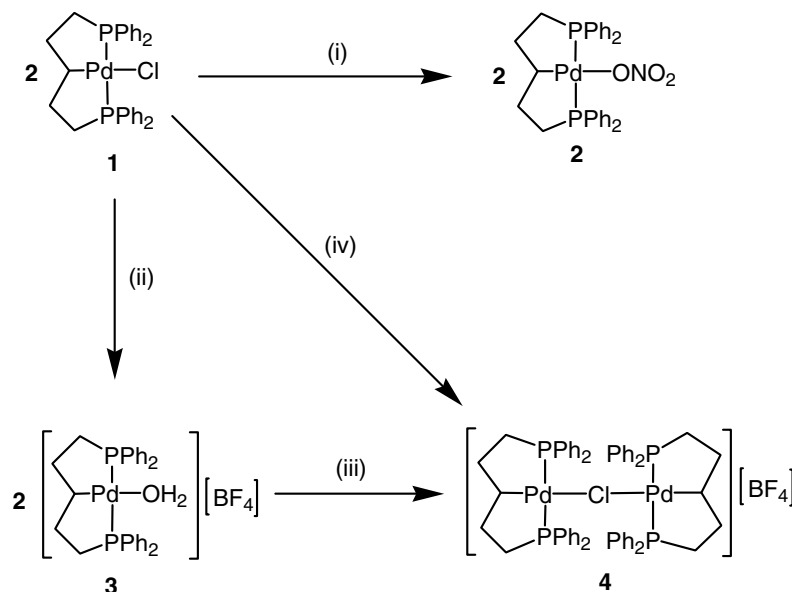
## 2. Results and discussion

*2.1. Synthesis and characterization of mononuclear complexes [Pd(NO<sub>3</sub>)(PCP)] (**2**), [Pd(OH<sub>2</sub>)(PCP)][BF<sub>4</sub>] (**3**) and dinuclear complex [{Pd(PCP)}<sub>2</sub>(μ-Cl)][BF<sub>4</sub>] (**4**)*

We have recently reported the formation of a triflate-coordinated complex **5** (79% yield) from **1** and excess AgOTf in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (Scheme 1) [9]. Similar reaction

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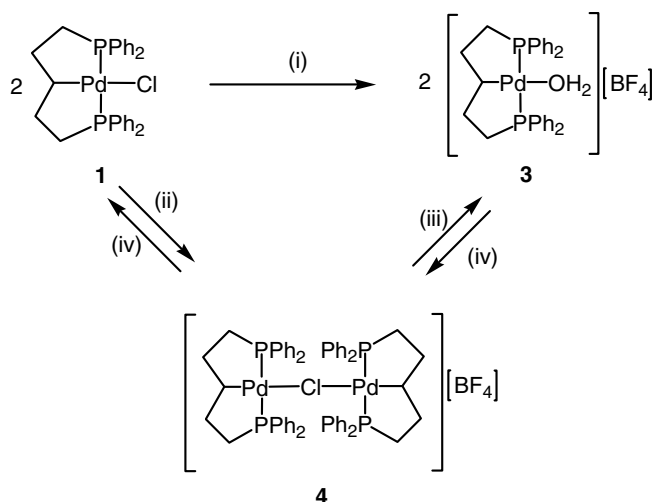
Scheme 1. Preparation of complexes **2**, **3** and **4**. (i) Excess AgNO<sub>3</sub>, acetone/H<sub>2</sub>O 3:1; (ii) excess AgBF<sub>4</sub>, acetone/H<sub>2</sub>O 3:1; (iii) **1**, CH<sub>2</sub>Cl<sub>2</sub>; (iv) AgBF<sub>4</sub>.

with AgNO<sub>3</sub> gives the analogous nitrate complex **2** in poor yield. Use of AgBF<sub>4</sub> as the chloride extracting agent in wet solvent gives the cationic aqua complex [Pd(OH<sub>2</sub>)(PCP)]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> (**3**) and the dinuclear complex [{Pd(PCP)}<sub>2</sub>(μ-Cl)]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> (**4**). Pure complex **3** was obtained by changing CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O to acetone/H<sub>2</sub>O mixture. Analytically pure complex **4** can be obtained by fractional crystallization from the reaction mixture of **1** and AgBF<sub>4</sub> (1:2 equiv.) or **1** and **3**. These complexes have been characterized by NMR, ESI-MS and single-crystal X-ray diffraction. All of them contain typical square-planar Pd(II) centers. Complex **4** possibly arises from the addition reaction between **1** and its chloride-extracted form such as **3**. A similar method was used in the preparation of chloro-bridged [{Pt(CH<sub>2</sub>Ph)(PCH<sub>2</sub>-ox)}<sub>2</sub>(μ-Cl)]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> (PCH<sub>2</sub>-ox = κ<sup>2</sup>-P, *N*-(oxazolinylmethyl)-diphenylphosphine) [7b].

The proton at the metallated carbon of complexes **1** (3.18 ppm) [4], **2** (3.35 ppm), **3** (3.53 ppm) and **5** (3.45 ppm) [9] give characteristic signals in their <sup>1</sup>H NMR spectra. The phosphorus chemical shifts of **2** (44.6 ppm) and **3** (46.0 ppm) are comparable to complex **5** (44.8 ppm) [9] but downfield shifted as compared to **1** (41.8 ppm) [4]. This is consistent with successful replacement of chloro ligand by the oxygen-donating NO<sub>3</sub>, aqua and OTf ligands. The metallated carbons give upfield signals in <sup>13</sup>C{<sup>1</sup>H} NMR spectra suggesting shielding upon chloride replacement (**1** = 60.8 ppm [4]; **2** = 56.0 ppm; **3** = 58.6 ppm and **5** = 58.3 ppm [9]). Other NMR features are similar to those of **1**, suggesting that the pincer fragment is intact. The <sup>19</sup>F{<sup>1</sup>H} NMR spectra of **3** (δF = -76.09 ppm and -76.14 ppm) and **4** (δF = -77.38 ppm and -77.43 ppm) show two broad peaks which can be explained by the <sup>10</sup>B-<sup>11</sup>B isotopic shift with the downfield signal corresponding to the fluorine coupled to <sup>10</sup>B nuclei while the upfield signal is due to fluorine cou-

pled to <sup>11</sup>B nuclei [11]. The possibility of an exchange process between the free and coordinated BF<sub>4</sub><sup>-</sup> was ruled out since addition of excess chloride ion (in form of aqueous NaCl solution) did not cause disappearance of any peak. Two peaks at *m/z* = 545 (major) and *m/z* = 586 (minor) were observed in the ESI mass spectra of complexes **2** and **3**. The former is assigned to cationic [Pd(PCP)]<sup>+</sup> ions (calculated *m/z* = 546) while the latter corresponds to the acetonitrile coordinated species [Pd(CH<sub>3</sub>CN)(PCP)]<sup>+</sup> (calculated *m/z* = 586). Trapping of CH<sub>3</sub>CN in the capillary system by cationic pincer Pd(II) fragment is common and has been described previously [4].

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **4** recorded in CDCl<sub>3</sub> gives a broad peak at 44.9 ppm (*v*<sub>1/2</sub> = 10 Hz), different from the mononuclear complexes which give sharper peaks in their <sup>31</sup>P{<sup>1</sup>H} NMR spectra. The broadness arises possibly from the restricted rotation about the Pd-Cl bonds as a result of the close contacts of the two sterically bulky pincer fragments. Addition of aqueous NaCl solution to complex **3** gives rise to two peaks (δP = 42.4 and 45.0 ppm) which can be assigned to complexes **1** and **4**. Further addition of excess of NaCl gives complex **1**, thus suggesting that the bridge cleavage can be promoted by excess Cl<sup>-</sup>. However, addition of excess AgBF<sub>4</sub> to an acetone-*d*<sub>6</sub> solution of complex **4** gives rise to a spectrum that is similar to that of **3** dissolved in acetone-*d*<sub>6</sub> (49.0 ppm), presumably due to the formation of an acetone-coordinated complex. These results lend additional support to the assignment of <sup>31</sup>P chemical shift for complex **4**. They also established the relationship among **1**, **3** and **4** (Scheme 2). The dinuclear molecular ion of **4** is observed in the ESI mass spectrum recorded under mild conditions (calculated *m/z* = 1127, observed *m/z* = 1127).



Scheme 2. Inter-conversion of complexes **1**, **3** and **4**. (i) aq.  $\text{AgBF}_4$ ; (ii) complex **3**; (iii) aq.  $\text{AgBF}_4$ ; (iv) aq.  $\text{NaCl}$ .

## 2.2. Crystal structures of complexes **2**, **3** · $(\text{C}_2\text{H}_5)_2\text{O}$ , and **4**

The ORTEP plots of complexes **2** and **3** ·  $(\text{C}_2\text{H}_5)_2\text{O}$  ·  $\text{CH}_2\text{Cl}_2$  are shown in Figs. 1 and 2, respectively. Selected bond lengths and bond angles are listed in Table 1. Complexes **2** and **3** show that the incoming oxygen-donors ( $\text{NO}_3$  and  $\text{H}_2\text{O}$ ) are coordinated to the Pd(II) center in a monodentate fashion. The Pd–O bond lengths of **2** [2.190(4) Å] and **3** [2.200(4) Å] are slightly shorter than the bulky *tert*-butyl analogue  $[\text{Pd}(\text{OH}_2)(\text{PCP-}^t\text{Bu})][\text{BPh}_4]$  (PCP- $^t\text{Bu} = ^-\text{CH}(\text{CH}_2\text{CH}_2\text{P}^t\text{Bu}_2)_2$ ) [2.301(6) Å] [12] but longer than those in the Pd(II) complexes that are not influenced by the labilising Pd–C bonds at *trans*-position like  $[(\text{dppp})\text{Pd}(\text{OH}_2)(\text{OTf})][\text{OTf}]$  (dppp = 1,3-

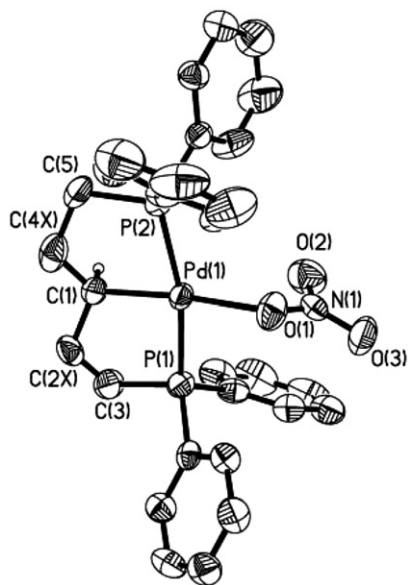


Fig. 1. ORTEP plot of complex **2** with 50% thermal ellipsoids. (The methylene carbons C(2X) and C(4X) are disordered into two positions with 50:50 occupancy.)

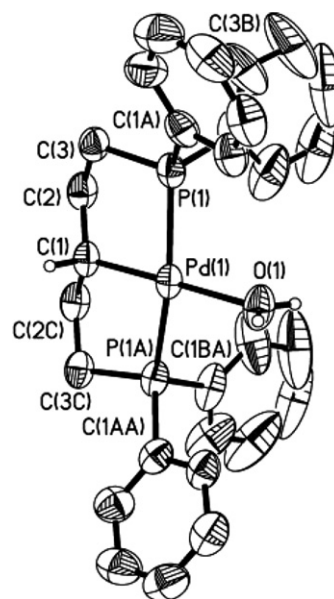


Fig. 2. ORTEP plot of complex **3** ·  $(\text{C}_2\text{H}_5)_2\text{O}$  ·  $\text{CH}_2\text{Cl}_2$  with 50% thermal ellipsoids. (The  $\text{BF}_4^-$  anion, diethyl ether and  $\text{CH}_2\text{Cl}_2$  molecules are omitted for clarity.)

bis(diphenylphosphino)propane)  $[\text{Pd}-\text{O}_{\text{H}_2\text{O}} = 2.106(4)$  Å,  $\text{Pd}-\text{O}_{\text{OTf}} = 2.159(3)$  Å] [13], (dppe) $\text{Pd}(\text{NO}_3)_2$  (dppe = 1,2-bis(diphenylphosphino)ethane)  $[\text{Pd}-\text{O} = 2.103(2)$  Å and  $2.114(2)$  Å] [14] and  $[\text{Pd}(\text{PPh}_3)_2(\text{OH}_2)_2][\text{OTf}]_2$ ,  $[\text{Pd}-\text{O} = 2.130(2)$  Å and  $2.119(2)$  Å] [15]. Nevertheless, the Pd–O bond length is comparable to the Pd–O bond length in complex **5** [2.211(2) Å] [9].

The steric bulk of the pincer substituent also forces the C–Pd–O angles of complex **2** to deviate significantly from linearity  $[\text{C}(1)-\text{Pd}(1)-\text{O}(1) = 172.2(2)^\circ]$ . Such deviation was also observed in the analogous complex **5** [171.66(9)°] [9],  $[\text{Pd}(\text{CH}_3)(\text{PCP-}^t\text{Bu})]$  [171.9(2)°] and  $[\text{Pd}(\text{OH}_2)(\text{PCP-}^t\text{Bu})][\text{BPh}_4]$  [171.1(3)°] [12]. The distortion is less apparent in **1** [177.3(2)°] [4] and **3** [177.6(2)°] in which the anion is less sterically demanding. The P–Pd–P angles of **2** [166.8(4)°] and **3** [162.9(5)°] are comparable to that of **1** [165.9(7)°] [4] and **5** [166.2(2)°] [9] as well as the *tert*-butyl complexes  $[\text{PdCH}_3(\text{PCP-}^t\text{Bu})][\text{BPh}_4]$  [166.2(1)°] and  $[\text{Pd}(\text{OH}_2)(\text{PCP-}^t\text{Bu})][\text{BPh}_4]$  [167.2(1)°] [12].

The Pd–C lengths of **2** [2.072(5) Å] and **3** [2.076(4) Å] are comparable. They are intermediate between that of  $[\text{Pd}(\text{OH}_2)(\text{PCP-}^t\text{Bu})][\text{BPh}_4]$  [2.056(6) Å] [12], **5** [2.071(2) Å] [9], **1** [2.111(7) Å] [4] and  $[\text{Pd}(\text{CH}_3)(\text{PCP-}^t\text{Bu})]$  [2.129(4) Å] [12], reflecting the *trans* influence of the ligands that are *trans* to the metallated carbon. The aqua ligand in **3** is hydrogen bonded to the disordered  $\text{BF}_4^-$  [ $\text{H}\cdots\text{F} = 1.903$  Å] and the  $\text{Et}_2\text{O}$  solvate [ $\text{H}\cdots\text{O} = 1.895$  Å]. Such hydrogen bonding was also observed for  $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}^t\text{Bu})_2\}_2(\text{OH}_2)][\text{BF}_4] \cdot \text{THF}$  [16] and  $[\text{Pd}(5, 8, 11, 14, 17\text{-pentaoxa-2,20-dithia[21]-}m\text{-cyclophane})(\text{OH}_2)][\text{BF}_4]$  [17]. Such bonding supplements and strengthens the cation–anion interaction and contributes towards the formation and stability of the aqua complex **3** [18].

Table 1  
Selected bond lengths (Å) and bond angles (°) of complexes **2**, **3** · (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O · CH<sub>2</sub>Cl<sub>2</sub> and **4** · CH<sub>2</sub>Cl<sub>2</sub>

Complex	<b>2</b> <sup>a</sup>	<b>3</b> · (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O · CH <sub>2</sub> Cl <sub>2</sub>	<b>4</b> · CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>
<i>Bond lengths</i> (Å)			
Pd(1)–P(1)	2.304(1)	2.309(1)	2.302(9)
Pd(1)–P(2)	2.300(1)	–	2.289(9)
Pd(2)–P(3)	–	–	2.292(8)
Pd(2)–P(4)	–	–	2.297(1)
Pd(1)–O(1)	2.190(4)	2.200(4)	–
Pd(1)–Cl(1)	–	–	2.453(8)
Pd(2)–Cl(1)	–	–	2.466(9)
Pd(1)–C(1)	2.072(5)	2.076(4)	2.097(3)
Pd(2)–C(6)	–	–	2.086(3)
C(1)–C(2)	1.497(7)	C(1)–C(2X)	1.552(5)
C(1)–C(4)	1.469(7)	C(1)–C(4X)	1.518(5)
C(6)–C(7)	–	–	1.518(5)
C(6)–C(9)	–	–	1.531(5)
<i>Bond angles</i> (°)			
Pd(1)–Cl(1)–Pd(2)	–	–	123.8(4)
P(1)–Pd(1)–P(2)	166.8(4)	162.9(5)	P(1)–Pd(1)–P(1)#1
P(3)–Pd(2)–P(4)	–	–	156.4(3)
P(1)–Pd(1)–O(1)	95.5(1)	97.2(3)	–
P(2)–Pd(1)–O(1)	97.6(1)	–	–
P(1)–Pd(1)–Cl(1)	–	–	100.1(3)
P(2)–Pd(1)–Cl(1)	–	–	95.9(3)
P(3)–Pd(2)–Cl(1)	–	–	98.6(3)
P(4)–Pd(2)–Cl(1)	–	–	96.4(4)
P(1)–Pd(1)–C(1)	82.9(1)	83.0(3)	82.9(1)
P(2)–Pd(1)–C(1)	83.8(1)	–	82.9(1)
P(3)–Pd(2)–C(6)	–	–	82.3(1)
P(4)–Pd(2)–C(6)	–	–	83.1(1)
O(1)–Pd(1)–C(1)	172.2(2)	177.6(2)	–
Cl(1)–Pd(1)–C(1)	–	–	174.1(1)
Cl(1)–Pd(2)–C(6)	–	–	178.5(1)
Pd(1)–C(1)–C(2)	112.8(4)	Pd(1)–C(1)–C(2X)	114.8(3)
Pd(1)–C(1)–C(4)	113.1(5)	Pd(1)–C(1)–C(4X)	114.7(2)
Pd(2)–C(6)–C(7)	–	–	115.0(2)
Pd(2)–C(6)–C(9)	–	–	113.9(3)
C(2)–C(1)–C(4)	115.9(7)	C(2X)–C(1)–C(4X)	110.8(3)
C(7)–C(6)–C(9)	–	–	111.7(3)

<sup>a</sup> X refers to the carbon of the methylene backbone that is disordered into two positions with 50:50 occupancy.

<sup>b</sup> Angle between P(1)–Pd(1)–P(2)–C(1)–Cl(1) and P(3)–Pd(2)–P(4)–C(6)–Cl(1) planes = 72.6°.

The crystal structure of **4** · CH<sub>2</sub>Cl<sub>2</sub> shows that the cation contains two pincer Pd(II) fragments solely bridged by a chloro ligand at a bent geometry, with a Pd(1)–Cl(1)–Pd(2) angle of 123.8(4)° (Fig. 3 and Table 1). This angle is within the range of the M–Cl–M angles in [Pt(CH<sub>2</sub>Ph)(PCH<sub>2</sub>-ox)]<sub>2</sub>(μ-Cl)]BF<sub>4</sub> [Pt–Cl–Pt = 119.1(3)°] [7b] and the related NCN-pincer palladium complex [{(C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-O, O')Pd]<sub>2</sub>(μ-Cl)]BF<sub>4</sub> [Pd–Cl–Pd = 134.8(1)°] [7g]. The metal separation distance [Pd···Pd = 3.910(6) Å] suggests that there is no direct metal–metal bonding. To avoid conflict and minimize contacts between the two PPh<sub>2</sub> moieties, the two coordination planes are twisted away from each other (interplanar angle made by P(1)–Pd(1)–P(2)–C(1)–Cl(1) and P(3)–Pd(2)–P(4)–C(6)–Cl(1) = 72.6°) (Fig. 4). Similar twists are observed in [Pt(CH<sub>2</sub>Ph)(PCH<sub>2</sub>-ox)]<sub>2</sub>(μ-Cl)]BF<sub>4</sub> [87(1)°] [7b] and [{(C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-O, O')Pd]<sub>2</sub>(μ-Cl)]BF<sub>4</sub> [88.5(2)°] [7g]. The two Pd–C bonds are slightly different

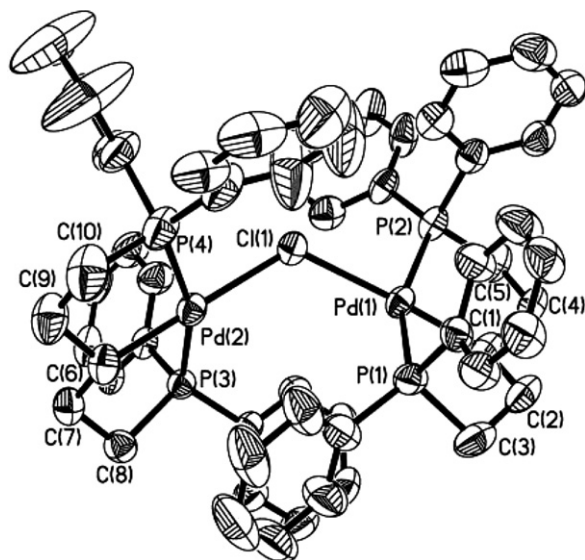


Fig. 3. ORTEP plot of complex **4** · CH<sub>2</sub>Cl<sub>2</sub> with 50% thermal ellipsoids (BF<sub>4</sub><sup>−</sup> anion and solvent molecule are omitted for clarity).

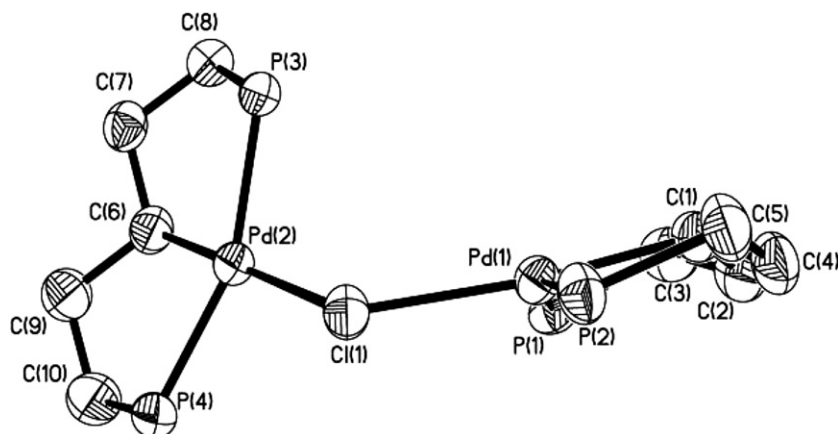


Fig. 4. ORTEP plot of complex **4** · CH<sub>2</sub>Cl<sub>2</sub> with 50% thermal ellipsoids showing the Pd coordination planes twisted away from each other. (The phenyl rings, BF<sub>4</sub><sup>−</sup> anion and solvent molecule are omitted for clarity.)

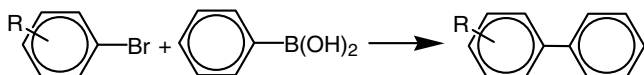
[Pd(1)–C(1) = 2.097(3) Å; Pd(2)–C(6) = 2.086(3) Å] and are shorter than that of complex **1** [Pd(1)–C(1) = 2.111(7) Å] [4]. As expected, the terminal Pd–Cl bond in **1** [Pd(1)–Cl(1) = 2.431(1) Å] [4] is shorter than that of the bridging chloride in **4** [Pd(1)–Cl(1) = 2.453(8) Å; Pd(2)–Cl(1) = 2.466(9) Å]. Such M–Cl (M = Pd, Pt) bond lengthening is commonly observed for this type of complexes [7].

### 2.3. Preliminary catalytic study of complexes **1** and **5** in Suzuki–Miyaura reaction

As complexes **1** and **5** represent a saturated and a potentially unsaturated pincer in this series, and that they can be conveniently prepared in high yields, they were chosen as models to examine the catalytic performance of this series of PCP pincers towards Suzuki–Miyaura reactions (Scheme 3). Preliminary results suggested that substrates with an electron withdrawing group in the *para* position tend to give higher yields (entries 1, 2, 5, and 6) (Table 2).

Further investigations using 4-bromoacetophenone as substrate with catalysts **1** and **5** revealed that inorganic bases (K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and NaOH) are bases of choice for both catalysts (Table 3). Both complexes shows good catalytic activity when the coupling reactions are performed in commonly-used solvents for this type of reaction, being either polar solvent (1,4-dioxane and DMF) or non-polar (toluene). The conversion remains quantitative for catalysts **5** even when the catalyst load is reduced to as low as 0.1 mol% (Entry 19).

Full conversion can be achieved within 4 h for both catalysts albeit at a high temperature. The catalysts are active at r.t. but the yields are generally lower compared to other



Scheme 3. Cross coupling reaction between aryl bromides and phenyl boronic acid.

Table 2

Selected catalytic data of **1** and **5** towards Suzuki–Miyaura cross coupling reaction of phenyl boronic acid and aryl bromides<sup>a,b</sup>

Entry	Aryl bromide	Time (h)	Cat	Isolated yield (%)
1	4-Bromoacetophenone	16	<b>1</b>	90
2	4-Bromobenzonitrile	15	<b>1</b>	65
3	Bromobenzene	16	<b>1</b>	52
4	4-Bromoanisole	20	<b>1</b>	19
5	4-Bromoacetophenone	17	<b>5</b>	78
6	4-Bromobenzonitrile	19	<b>5</b>	80
7	Bromobenzene	15	<b>5</b>	72
8	4-Bromoanisole	15	<b>5</b>	32

<sup>a</sup> Reaction conditions are generally not optimized.

<sup>b</sup> Conditions: aryl bromide (1 mmol), phenyl boronic acid (1.5 mmol), catalyst (0.01 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), 1,4-dioxane 110 °C (10 ml), the reactions were conducted at atmospheric pressure.

active systems [19]. Room-temperature yields can be improved by conducting the reaction in the presence of water (Entries 10 vs. 9, and 21 vs. 20) [20], but some catalyst decomposition (formation of black solid which is presumably palladium metal) was also observed. The activity profile of **1** and **5** under similar conditions are generally comparable.

### 3. Conclusion

The chloro PCP-Pd(II) pincer complex **1** exchanges with labile ligands to give Lewis acidic pincers that could capture a coordinatively saturated pincer to give a dinuclear complex. Ongoing work is directed to the use of these complexes as precursors to other homo- and hetero-metallic systems.

### 4. Experimental

#### 4.1. General procedures

Complexes **1** [4] and **5** [9] were prepared according to the reported procedures. All solvents were freshly dried using

Table 3

Selected catalytic data of **1** and **5** towards Suzuki–Miyaura cross coupling reaction of phenyl boronic acid and 4-bromoacetophenone under different conditions<sup>a</sup>

Entry	Catalyst	Base	Solvent	Temperature <sup>b</sup>	Catalyst loading <sup>c</sup> (mol%)	Conversion (%) <sup>d</sup>
1	<b>1</b>	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	110 °C	1	100
2	<b>1</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	110 °C	1	100
3	<b>1</b>	NaOH	1,4-Dioxane	110 °C	1	100
4	<b>1</b>	NEt <sub>3</sub>	1,4-Dioxane	110 °C	1	46
5	<b>1</b>	K <sub>2</sub> CO <sub>3</sub>	Toluene	110 °C	1	100
6	<b>1</b>	K <sub>2</sub> CO <sub>3</sub>	DMF	110 °C	1	81
7	<b>1</b>	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	110 °C	0.5	100
8	<b>1</b>	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	110 °C	0.1	88
9	<b>1</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	RT	1	45
10	<b>1</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane/H <sub>2</sub> O (2:1 v/v)	RT	1	92 <sup>e</sup>
11	<b>1</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	70 °C	1	86
12	<b>5</b>	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	110 °C	1	100
13	<b>5</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	110 °C	1	100
14	<b>5</b>	NaOH	1,4-Dioxane	110 °C	1	93
15	<b>5</b>	NEt <sub>3</sub>	1,4-Dioxane	110 °C	1	48
16	<b>5</b>	K <sub>2</sub> CO <sub>3</sub>	Toluene	110 °C	1	100
17	<b>5</b>	K <sub>2</sub> CO <sub>3</sub>	DMF	110 °C	1	99
18	<b>5</b>	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	110 °C	0.5	100
19	<b>5</b>	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	110 °C	0.1	100
20	<b>5</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	RT	1	22
21	<b>5</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane/H <sub>2</sub> O (2:1 v/v)	RT	1	72 <sup>e</sup>
22	<b>5</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	70 °C	1	94

<sup>a</sup> Conditions: 4-Bromoacetophenone (1 mmol), phenyl boronic acid (1.5 mmol), base (2 mmol), solvent (10 ml), reaction time (16 h).

<sup>b</sup> The reactions were conducted at atmospheric pressure.

<sup>c</sup> Relative to 4-Bromoacetophenone used in the reaction.

<sup>d</sup> Determined using GC–MS based on aryl halide with *n*-dodecane as internal standard.

<sup>e</sup> Catalyst decomposition observed.

molecular sieves. All reagents were commercial products and were used as received. Elemental analyses were performed by the Chemical, Molecular and Materials Analysis Center (CMMAC) of NUS.

#### 4.2. NMR spectroscopy

The NMR spectra were measured at 25 °C using a Bruker ACF 300 NMR spectrometer. Chemical shifts are reported relative to TMS where  $\delta$  CHCl<sub>3</sub> = 7.26 ppm (<sup>1</sup>H) or  $\delta$  CDCl<sub>3</sub> = 77.1 ppm (<sup>13</sup>C{<sup>1</sup>H}). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra were externally referenced to 85% H<sub>3</sub>PO<sub>4</sub> at 121.39 MHz while <sup>19</sup>F{<sup>1</sup>H} NMR spectra were referenced to CF<sub>3</sub>COOH at 282.38 MHz.

#### 4.3. Electrospray ionisation mass spectrometry (ESI-MS)

Mass spectra were recorded in positive ion mode using a Thermo Finnigan LCQ spectrometer. MeOH or MeOH/H<sub>2</sub>O mixture (80:20 v/v) were used as the mobile phase. The compounds were dissolved in minimal quantities of CH<sub>2</sub>Cl<sub>2</sub> or acetone and diluted using the mobile phase. The solution of complex **4** was introduced *via* a syringe pump. Only the molecular ions or their related fragment peaks are reported here. Assignment of ions was aided by comparison with the predicted isotope distribution patterns. The predicted isotope patterns were calculated using the MS/MS ISOPRO [21] computer program.

#### 4.4. Synthesis of [Pd(NO<sub>3</sub>)(PCP)] (**2**)

Complex **1** (0.10 g, 0.17 mmol) was dissolved in degassed acetone (30 ml). To this solution was added a solution of AgNO<sub>3</sub> (0.15 g, 0.86 mmol) in deionised H<sub>2</sub>O (10 ml). The mixture was stirred for 4 h shielded from light, giving a colourless solution with a brown residual solid. It was filtered through a celite column to remove AgCl. The filtrate was evaporated under reduced pressure. The milky white solid obtained was washed with deionised H<sub>2</sub>O (2 × 5 ml) followed by Et<sub>2</sub>O (2 × 5 ml). The solid was then dissolved in acetone (5 ml) and dried with anhydrous MgSO<sub>4</sub>. The solution was then filtered and dried under vacuum. The milky white powder was washed with Et<sub>2</sub>O (2 × 3 ml) to give complex **2** (0.02 g, 20%).

Analytical data for **2**: (Found: C, 57.12; H, 4.55; N, 2.01. Anal. Calc. for C<sub>29</sub>H<sub>29</sub>P<sub>2</sub>PdNO<sub>3</sub>: C, 57.29; H, 4.82; N, 2.30%) <sup>1</sup>H NMR (CDCl<sub>3</sub>) ( $\delta$ ): 1.52–1.79 (m, 4H, PCH<sub>2</sub>CH<sub>2</sub>, overlapped with H<sub>2</sub>O peak), 2.09 (t, br, 2H, PCH<sub>2</sub>CH<sub>2</sub>), 2.58 (m, 2H, PCH<sub>2</sub>CH<sub>2</sub>), 3.35 (t, br, 1H, PdCH), 7.39–7.90 (m, 20H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) ( $\delta$ ): 29.5 (t, 2C, PCH<sub>2</sub>CH<sub>2</sub>, *J*(C,P) = 13.2 Hz), 36.7 (t, 2C, PCH<sub>2</sub>CH<sub>2</sub>, *J*(C,P) = 6.9 Hz), 56.0 (t, 1C, PdC, *J*(C,P) = 3.1 Hz), 128.9 (t, 8C, Ph, *J*(C,P) = 5.0 Hz), 130.6 (s, 2C, Ph, overlapped with phenyl ring C1 signal), 130.7 (t, 2C, Ph, *J*(C,P) = 18.9 Hz, overlapped with phenyl ring C4 signal), 130.9 (s, 2C, Ph, overlapped with phenyl ring C1 signal), 132.1 (t, 4C, Ph, *J*(C,P) = 6.9 Hz), 132.5

(t, 2C, Ph,  $J(\text{C,P}) = 20.1$  Hz), 133.6 (t, 4C, Ph,  $J(\text{C,P}) = 7.6$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 44.6 (s, 2P,  $\text{PPh}_2$ ). ESI-MS ( $m/z$ , %):  $[\text{2-NO}_3^-]^\dagger$  (545, 100),  $[\text{2-NO}_3^- + \text{CH}_3\text{CN}]^\dagger$  (586, 23).

#### 4.5. Synthesis of $[\text{Pd}(\text{OH}_2)(\text{PCP})][\text{BF}_4] \cdot \text{H}_2\text{O} \cdot (\text{CH}_3\text{CH}_2)_2\text{O}$ (**3** · $\text{H}_2\text{O} \cdot (\text{CH}_3\text{CH}_2)_2\text{O}$ )

Complex **3** was prepared similarly to complex **2** using complex **1** (0.05 g, 0.09 mmol) and  $\text{AgBF}_4$  (0.08 g, 0.43 mmol). The final product was obtained by adding  $\text{Et}_2\text{O}$  into  $\text{CH}_2\text{Cl}_2$  solution of **3** giving yellow crystals (0.03 g, 50%). The presence of  $\text{H}_2\text{O}$  and diethyl ether solvent was confirmed by elemental analysis and NMR spectroscopy.

Analytical data for  $[\text{3} \cdot \text{H}_2\text{O} \cdot (\text{CH}_3\text{CH}_2)_2\text{O}]$ : (Found: C, 53.17; H, 5.35. Anal Calc. for  $\text{C}_{33}\text{H}_{43}\text{P}_2\text{PdO}_3\text{BF}_4$ : C, 53.35; H, 5.85)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 1.19 (t, 6H,  $\text{CH}_3$ , diethyl ether), 1.38–1.78 (m, 4H,  $\text{PCH}_2\text{CH}_2$ ), 2.12 (t, br, 2H,  $\text{PCH}_2\text{CH}_2$ ), 2.62 (m, br, 4H,  $\text{PCH}_2\text{CH}_2 + \text{H}_2\text{O}$ ), 3.53 (q, br, 5H,  $\text{PdCH} + \text{diethyl ether}$ ), 7.45–7.83 (m, 20H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 15.3 (s, 2C,  $\text{CH}_3$ , diethyl ether), 29.1 (t, 2C,  $\text{PCH}_2\text{CH}_2$ ,  $J(\text{C,P}) = 13.2$  Hz), 36.7 (t, 2C,  $\text{PCH}_2\text{CH}_2$ ,  $J(\text{C,P}) = 6.3$  Hz), 58.6 (s, br, 1C, PdC), 65.9 (s, 2C,  $\text{CH}_2$ , diethyl ether), 129.1 (t, 2C, Ph,  $J(\text{C,P}) = 20.1$  Hz), 129.4 (t, 4C, Ph,  $J(\text{C,P}) = 5.0$  Hz), 129.5 (t, 4C, Ph,  $J(\text{C,P}) = 5.0$  Hz), 131.2 (s, 2C, Ph), 131.4 (t, 2C, Ph,  $J(\text{C,P}) = 20.1$  Hz), 131.6 (s, 2C, Ph), 132.2 (t, 4C, Ph,  $J(\text{C,P}) = 6.9$  Hz), 133.5 (t, 4C, Ph,  $J(\text{C,P}) = 6.9$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 46.0 (s, 2P,  $\text{PPh}_2$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ):  $-76.09$  (s, br, 4F, fluorine coupled to  $^{10}\text{B}$  nuclei),  $-76.14$  (s, br, 4F, fluorine coupled to  $^{11}\text{B}$  nuclei). ESI-MS ( $m/z$ , %):  $[\text{3-H}_2\text{O-BF}_4^-]^\dagger$  (545, 100),  $[\text{3-H}_2\text{O-BF}_4^- + \text{CH}_3\text{CN}]^\dagger$  (586, 35).

#### 4.6. Synthesis of $[\{\text{Pd}(\text{PCP})\}_2(\mu\text{-Cl})][\text{BF}_4]$ (**4**)

Complex **1** (0.05 g, 0.09 mmol) was dissolved in degassed  $\text{CH}_2\text{Cl}_2$  (30 ml). To this solution was added **3** (0.05 g, 0.08 mmol). The pale orange solution was stirred overnight and filtered. The filtrate was concentrated under reduced pressure. Addition of  $\text{Et}_2\text{O}$  (10 ml) gave pale orange powder, which was crystallized twice from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give complex **4** as pale yellow crystals (0.02 g, 22%).

Analytical data for **4**: (Found: C, 57.16; H, 4.71. Anal Calc. for  $\text{C}_{58}\text{H}_{58}\text{P}_4\text{Pd}_2\text{ClBF}_4$ : C, 57.35 H, 4.82%)  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 44.9 (s, br, 2P,  $\text{PPh}_2$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR( $\text{CDCl}_3$ ) ( $\delta$ ):  $-77.38$  (s, br, 4F, fluorine coupled to  $^{10}\text{B}$  nuclei),  $-77.43$  (s, br, 4F, fluorine coupled to  $^{11}\text{B}$  nuclei). ESI-MS ( $m/z$ , %):  $[\text{1-Cl}^-]^\dagger$  (547, 25),  $[\text{1-Cl}^- + \text{CH}_3\text{CN}]^\dagger$  (585, 60),  $[\text{4-BF}_4^-]^\dagger$  (1127, 100).

#### 4.7. General procedure for Suzuki–Miyaura reaction

Aryl bromide (1 mmol) and phenyl boronic acid (1.5 mmol) was added into degassed 1,4-dioxane (10 ml).  $\text{K}_2\text{CO}_3$  (2 mmol) and the palladium complex (0.01 mmol) were introduced. The reaction mixture was refluxed under  $\text{N}_2$  flow. Upon cooling, the solvent was removed under vacuum. Water was added to the residue, followed by  $\text{Et}_2\text{O}$  (2 × 10 ml) and the product extracted. The organic fractions were combined, dried with anhydrous  $\text{MgSO}_4$ , filtered, and the solvent removed under vacuum. The crude product was purified by column chromatography using hexane and ethyl acetate (95:5 v/v) as eluent. The final product was weighed before GC–MS analysis. The conversion was determined by GC–MS based on 4-bromoacetophenone in the crude product with *n*-dodecane as internal standard.

Table 4

Parameters for data collection and structure refinement of **2**, **3** ·  $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{CH}_2\text{Cl}_2$  and **4** ·  $\text{CH}_2\text{Cl}_2$ 

	<b>2</b>	<b>3</b> · $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{CH}_2\text{Cl}_2$	<b>4</b> · $\text{CH}_2\text{Cl}_2$
Chemical formula	$\text{C}_{29}\text{H}_{29}\text{NO}_3\text{P}_2\text{Pd}$	$\text{C}_{33.50}\text{H}_{42}\text{B ClF}_4\text{O}_2\text{P}_2\text{Pd}$	$\text{C}_{59}\text{H}_{60}\text{BCl}_3\text{F}_4\text{P}_4\text{Pd}_2$
Fw, $\text{g mol}^{-1}$	607.87	767.27	1298.91
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$Pnma$	$P2(1)/c$
<i>a</i> , Å	8.6508(5)	10.1550(5)	12.5514(5)
<i>b</i> , Å	15.5988(9)	16.3068(8)	23.5043(10)
<i>c</i> , Å	19.6264(12)	21.9878(11)	20.0366(9)
$\alpha$ , °	90	90	90
$\beta$ , °	90	90	105.4860(10)
$\gamma$ , °	90	90	90
Volume, Å <sup>3</sup>	2648.4(3)	3641.1(3)	5696.4(4)
<i>Z</i>	4	4	4
$\rho_{\text{calc}}$ , $\text{Mg m}^{-3}$	1.525	1.400	1.515
$\mu$ , $\text{mm}^{-1}$	0.853	0.719	0.936
Temperature (K)	223(2)	293(2)	223(2)
No. of reflections collected	18,705	24,811	74,579
No. of independent reflections $R_{\text{int}}$	6067 (0.0472)	4317 (0.0428)	13,085 (0.0294)
No. of parameters	343	240	675
Goodness-of-fit	1.045	1.084	1.054
$R_1$ and $wR_2$ ( $I > 2$ sigma( <i>I</i> ))	$R_1 = 0.0488$ , $wR_2 = 0.1120$	$R_1 = 0.0512$ , $wR_2 = 0.1353$	$R_1 = 0.0420$ , $wR_2 = 0.1074$
$R_1$ and $wR_2$ (all data)	$R_1 = 0.0563$ , $wR_2 = 0.1158$	$R_1 = 0.0620$ , $wR_2 = 0.1416$	$R_1 = 0.0420$ , $wR_2 = 0.1133$

#### 4.8. X-ray crystallography

The X-ray quality crystals of complexes **2** and **4** · CH<sub>2</sub>Cl<sub>2</sub> were grown by layering Et<sub>2</sub>O onto a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of **2** and **4** while yellow crystals of **3** · (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O · CH<sub>2</sub>Cl<sub>2</sub> was obtained by diffusing Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of **3**. Data were collected on a Bruker AXS CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The software SMART [22] was used for data frame collection, indexing reflections and determining lattice parameters. The integration of intensity of reflections and scaling was done by using SAINT [22]; SADABS [23] was used for empirical absorption correction and SHELXL [24] for space group determination, refinements, graphics and structure reporting. Data of complex **2** shows that the methylene carbons of the aliphatic backbone are disorder into two positions at 50:50 occupancy. The parameters for crystal structure determination of complexes **2**, **3** · (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O · CH<sub>2</sub>Cl<sub>2</sub> and **4** · CH<sub>2</sub>Cl<sub>2</sub> are listed in Table 4.

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#### Appendix A. Supplementary material

CCDC 660631, 660632 and 660633 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.031](https://doi.org/10.1016/j.jorganchem.2007.11.031).

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