

# Formation of P,C-chelated palladium complexes by phosphine-assisted oxidative addition of an aliphatic C–Cl bond

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## Abstract

Reactions of the (chloralkyl) phosphine 1-chloro-3-(diisopropylphosphino)propane (**3**) with chelated Pd(0) complexes have been given, leading to P,C-chelated complexes. Reaction of a methyl- $\pi$ -allylpalladium chloride dimer with 1,3-(diisopropylphosphino)propane and a base gives the binuclear complex **2a**. Pd(dippe)<sub>2</sub> (dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with **3** to yield the mononuclear bis-chelated complex **6**. As expected, the intramolecular coordinatively assisted oxidative addition of the aliphatic C–Cl bond in **3** to the metal center is much faster than that of the intermolecular reaction of *n*-butyl chloride. The X-ray structure of **2a** was determined.

**Keywords:** Palladium; Chelate; Oxidative addition; Metallation; Alkyl chloride

## 1. Introduction

Pd(dipp)<sub>2</sub> (**1**) (dipp = 1,3-bis(diisopropylphosphino)propane) is an efficient catalyst for several synthetically useful reactions of aryl chlorides, including carbonylation to give esters, amides and acids [1], formylation to give aldehydes [2], reduction to arenes [3] and vinylation under basic [4a] and neutral [4b] conditions of aryl chlorides to give aromatic olefins. While preparing Pd(dipp)<sub>2</sub> we observed the formation of a side product, which turned out to be a dimeric complex involving a five-membered P,C-chelate. This interesting complex was then intentionally prepared and studied. There are many reports of P,C-chelates, most of them involving aryl or benzyl carbon donors [5]; they were obtained by intramolecular C–H activation following pre-coordination of the phosphorus terminus of the ligand. When aliphatic carbon atoms are involved, this usually requires bulky tert-butyl substituents on phosphorus, which lead to severe steric hindrance around the metal center [5,6].

We describe the formation and crystal structure of a relatively unhindered P,C-chelate involving an alkyl chain prepared by a new route involving intramolecular C–Cl activation following coordination by a phosphine.

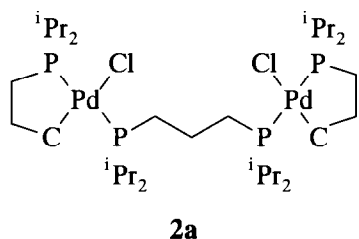
## 2. Results and discussion

During the intended preparation of Pd(dipp)<sub>2</sub> (**1**) from a particular batch of dipp, unexpected results were obtained. White crystals were formed and, in sharp contrast with **1**, were air and moisture stable were insoluble in pentane and did not catalyze any of the reactions catalyzed by **1**. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the product exhibited four sets of two doublets: two large doublets at 30.9 and 83.2 ppm (*J* = 379.7 Hz), and three pairs of small doublets at 32.4 and 82.3 ppm (*J* = 378.7 Hz), at 27.9 and 82.7 ppm (*J* = 380.2 Hz) and at 30.4 and 82.6 ppm (*J* = 380.5 Hz). There were also small signals in the free phosphine region (about 2 ppm) and in the phosphine oxide region (about 51 ppm). The <sup>1</sup>H NMR spectrum exhibited many overlapping multiplets between 0.8 and 2.4 ppm and a small triplet at 3.35 ppm (*J* = 6.2 Hz). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum and elementary analysis did not provide a conclusive indication of the identity of the new compound, probably owing to the presence of four different species in the sample. At this stage the exact nature of the new compounds was not clear; it was obvious that all four of them contained two chemically non-equivalent, mutually *trans* coordinated phosphine moieties (the large P–P coupling constants observed in the spectrum indicated a mutually *trans* disposition of the two phosphorus atoms). It was also clear that a chloride

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ligand was present in the complexes, since the addition of  $\text{AgBF}_4$  to their solution caused immediate precipitation of  $\text{AgCl}$  and a major change in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which indicated that all four species reacted with  $\text{Ag}^+$ .

A low temperature X-ray crystallographic study was performed on colorless prismatic crystals obtained by vapor diffusion of pentane into a toluene solution and atom coordinates in Table 2, showed that they were of **2a** (Fig. 1). Diffraction data were measured on a Rigaku 4FC5R diffractometer and corrected for absorption using  $\Psi$  scan measurements. Structure solution was by automated Patterson methods using SHELXS-86 and refinement was by the least-squares method using SHELX-76. Hydrogen atoms were located on a difference map and their positions refined with a common isotropic thermal parameter. Further crystallographic details are listed in Table 1, and selected bond lengths and angles in Table 3. A complete list of bond lengths and angles and tables of thermal parameters and H atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.



the P,C-chelate C(1)–Pd(1)–P(4) is  $82.2(2)^\circ$  and is noticeably smaller than the ideal square planar angle. The angles at the metal formed by any other two ligands are slightly greater than  $90^\circ$ . The chelate phosphines are closer to palladium by about  $0.05 \text{ \AA}$  than the phosphines

Table 1

Crystal data and details of the data collection and refinement for **2a**

Molecular weight	877.581
Space group	$P\bar{1}$ (triclinic)
Temperature (K)	90
Cell constants	
$a$ (Å)	18.160(4)
$b$ (Å)	16.296(6)
$c$ (Å)	8.500(4)
$\alpha$ (°)	98.69(2)
$\beta$ (°)	82.33(2)
$\gamma$ (°)	114.44(2)
Cell volume (Å <sup>3</sup> )	2344(2)
Formula	$\text{C}_{33}\text{H}_{73}\text{P}_4\text{Cl}_2\text{Pd}_2\text{C}_7\text{H}_8$
$D(\text{calc.})$ (g cm <sup>-3</sup> )	1.22
$\mu$ (cm <sup>-1</sup> )	6.64
Diffractometer scan	Rigaku AFC5R w-20
Source	rotating anode Rigaku RU-300
Speed of measurement (min <sup>-1</sup> )	8
Radiation, graphite monochromator	( $\lambda \approx 0.7114 \text{ \AA}$ )
Maximum crystal dimensions (mm)	$0.4 \times 0.3 \times 0.2$
Number of reflections measured	11169
Number of reflections with $I > 3.0$	8578
Scan limits (°)	$2.0 \leq 2\theta \leq 54$
Final R; final $R_w$	0.029; 0.0304
Goodness of fit	1.16
Largest residual density (electrons Å <sup>-2</sup> )	0.86 new Pd atoms

of the bridging dipp as a result of the strain in the chelate ring.

On investigating the origin of **2a**, we found by  $^1\text{H}$

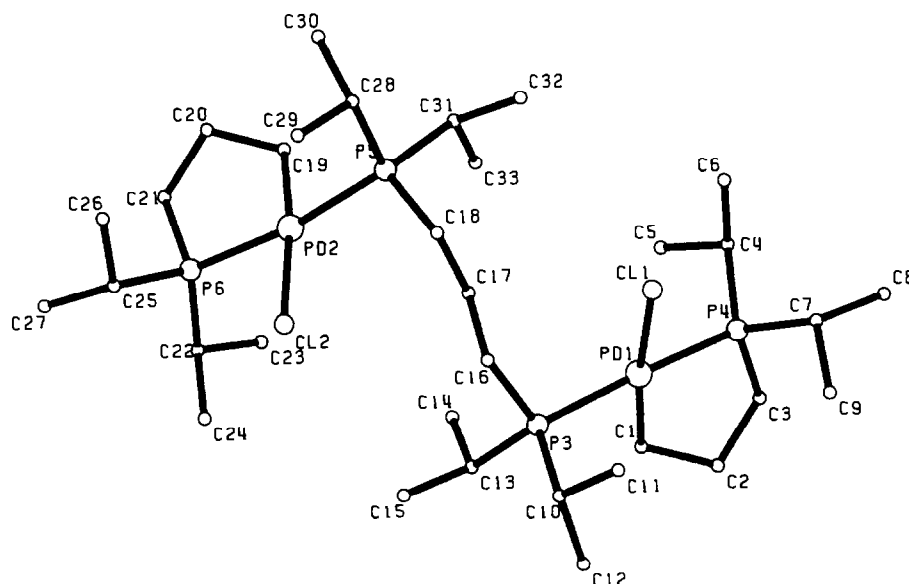
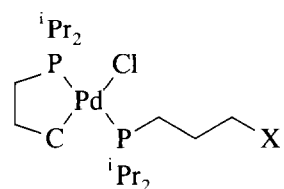
Fig. 1. X-ray structure of **2a**.

Table 2  
Selected bond lengths (Å) and angles (°) for **2a**

Bond lengths			
Cl(1)–Pd(1)	2.405(3)	P(3)–Pd(1)	2.328(3)
P(4)–Pd(1)	2.274(3)	C(1)–Pd(1)	2.071(5)
Cl(2)–Pd(2)	2.432(3)	P(5)–Pd(2)	2.329(3)
P(6)–Pd(2)	2.282(3)	C(19)–Pd(2)	2.071(5)
C(16)–P(3)	1.832(4)	C(3)–P(4)	1.838(5)
C(18)–P(5)	1.832(5)	C(21)–P(6)	1.834(5)
C(2)–C(1)	1.525(6)	C(3)–C(2)	1.532(7)
C(17)–C(16)	1.523(6)	C(18)–C(17)	1.532(5)
C(20)–C(19)	1.522(7)	C(21)–C(20)	1.532(7)
Bond angles			
P(3)–Pd(1)–Cl(1)	92.4(1)	P(4)–Pd(1)–Cl(1)	91.7(1)
P(4)–Pd(1)–P(3)	175.9(1)	C(1)–Pd(1)–Cl(1)	172.6(1)
C(1)–Pd(1)–P(3)	93.7(2)	C(1)–Pd(1)–P(4)	82.2(2)
P(5)–Pd(2)–Cl(2)	94.0(1)	P(6)–Pd(2)–Cl(2)	91.4(1)
P(6)–Pd(2)–P(5)	172.1(1)	C(19)–Pd(2)–Cl(2)	173.4(1)
C(19)–Pd(2)–P(5)	92.3(2)	C(19)–Pd(2)–P(6)	82.1(2)
C(16)–P(3)–Pd(1)	112.1(2)	C(3)–P(4)–Pd(1)	105.2(2)
C(18)–P(5)–Pd(2)	110.9(2)	C(21)–P(6)–Pd(2)	105.0(2)
C(2)–C(1)–Pd(1)	111.7(3)	C(3)–C(2)–C(1)	110.6(3)
C(2)–C(3)–P(4)	106.4(3)	C(17)–C(16)–P(3)	112.3(3)
C(18)–C(17)–C(16)	113.5(3)	C(17)–C(18)–P(5)	110.0(3)
C(20)–C(19)–Pd(2)	111.3(3)	C(21)–C(20)–C(19)	110.9(3)
C(20)–C(21)–P(6)	106.4(3)		

NMR spectroscopy that the batch of dipp<sub>2</sub> used in the preparation contained a significant amount of <sup>i</sup>Pr<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl (**3**). Oxidative addition of the C–Cl and in **3** to the Pd(0) center would produce the five-membered P,C-chelate ring observed in **2a**. The high downfield shift observed for the chelate phosphorus in <sup>31</sup>P{<sup>1</sup>H} NMR (around 83 ppm) is characteristic of a five-membered chelate ring [7].

The complexes accompanying **2a** seem likely to be species **2b–2d**.



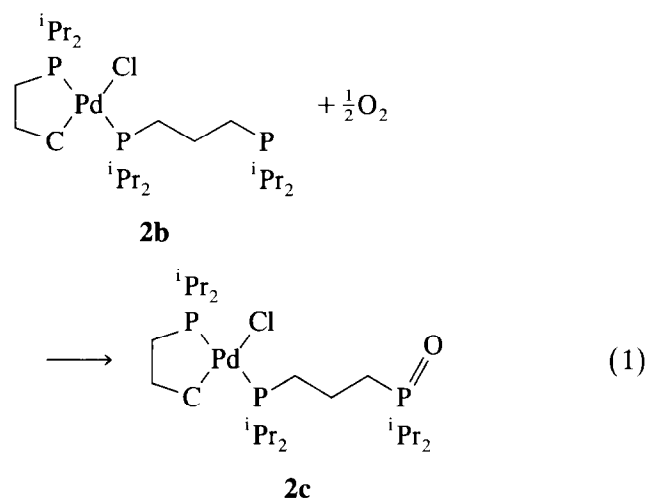
**2b**: X = P<sup>i</sup>Pr<sub>2</sub>

**2c**: X = P(O)<sup>i</sup>Pr<sub>2</sub>

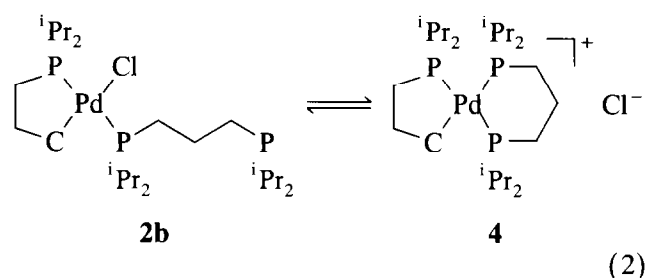
**2d**: X = Cl

The existence of an equilibrium between **1**, [(dipp<sub>2</sub>)Pd]<sub>2</sub>(μ-dipp<sub>2</sub>) and (dipp<sub>2</sub>)Pd[P(<sup>i</sup>Pr)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(<sup>i</sup>Pr)<sub>2</sub>PO] was described previously [8,9]; these three complexes are Pd(0) “analogues” of **2b**, **2a** and **2c** respectively. The following facts support the identification of **2b–2d**. First, when the solution of the four complexes is exposed to air, one of the small pairs of doublets and the small peak at 2 ppm disappear, while

the other pair of small doublets and the small peak at 51 ppm increase in intensity. Oxidative addition of the free phosphine moiety of **2b** and formation of **2c**, i.e.



is the only likely explanation of these observations. Another finding provides additional proof of the nature of **2c**. This is that, when the white crystals of the mixture are dissolved in methanol, three of the four pairs of doublets are retained (although *J* is reduced to about 362 Hz) while the fourth pair and a small signal at 2 ppm disappear. In addition, a new set of signals, identified as **4**, appears: 12.5 (dd, *J* = 50.9 and 34.9 Hz), 25.7 (dd, *J* = 296.0 and 50.9 Hz) and 80.2 (dd, *J* = 296.0 and 34.9 Hz) ppm. The only way in which this could be formed is through the equilibrium of Eq. (2)

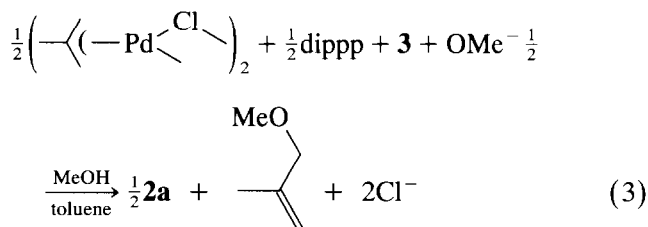


In toluene, neutral **2b** is preferred, whereas in the polar methanol the equilibrium is shifted to the ionic **4**. Similar behavior of Rh(dipp<sub>2</sub>)<sub>2</sub>Cl in solvents of various polarities was previously reported [8].

The triplet at 3.35 ppm in the <sup>1</sup>H NMR spectrum is assigned to the CH<sub>2</sub>Cl group in **2d**. Although this is fairly poor evidence for the presence of this complex, the formation of **2d** from a reaction mixture which contains both Pd(0) and **3** seems logical.

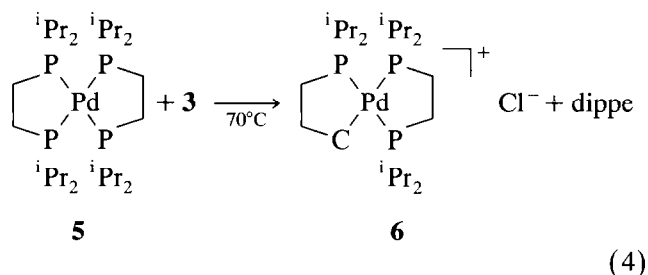
With the aim of establishing the mode of formation of **2a**, we repeated the procedure for preparation of Pd(0) complexes [9] using a mixture of two equivalents of the phosphine 1-chloro-3-(diisopropylphosphino)propane (**3**) and one equivalent of dipp<sub>2</sub> per equivalent of

the methylallylpalladium dimer. The formation of **2a** according to



and the three accompanying species (three pairs of similar doublets in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum) was detected (51% of the total Pd amount). The mixture of the four species was precipitated by pentane.

Moreover, when pre-formed  $\text{Pd}(\text{dippe})_2$  (**5**) (which, being saturated, is less prone to oxidative addition than **1** (**9**)) was reacted with one equivalent of **3**, complex **6** (analogous to **4**) was formed as a single product:



In contrast with **4**, **6** retains its ionic structure even in the non-polar benzene, demonstrating again the greater stability of five- vs. six-membered chelates [10].

Formation of the P,C-chelate is an excellent example of an oxidative addition reaction assisted by pre-coordination. Binding of the  $-\text{P}^i\text{Pr}_2$  group of **3** to the Pd(0) center enhances the reactivity in the oxidative addition of the C–Cl functionality of **3** by several orders of magnitude. By comparison, oxidative addition of  $^n\text{BuCl}$  to **1** is very slow even with a tenfold excess of substrate at  $100^\circ\text{C}$  (9.5% conversion after 3 h).

The alkyl ligand in **2a–2d** and **6** is expected to be thermally stable. Heating solutions of the compound at  $80^\circ\text{C}$  for prolonged periods has only a marginal effect, and no  $\beta$ -H elimination is observed. This indicates that the P,C-chelate is very stable and essentially does not open, i.e. the equilibrium concentration of the species obtained by dissociation of the P,C-chelate, if any at all is present, is very low.

To the best of our knowledge, this is a rare case of chelate formation involving oxidative addition of an aliphatic C–Cl bond. Examples of chelate formation by oxidative addition of the C–H bond are more common and were surveyed in a number of reviews by Omae [5]. Usually aryl–H or benzyl–H bonds are involved, and samples involving aliphatic C–H bonds are less common.

### 3. Experimental details

All procedures with air- and moisture-sensitive compounds were performed in a nitrogen-filled glove-box (Vacuum Atmospheres, equipped with an MO-40 purification system) or on a high vacuum line by use of Schlenk techniques. All solvents were reagent grade or better. Toluene and pentane (Frutarom, Merck) were distilled over sodium–benzophenone ketyl. Methanol (Biolab) was distilled over magnesium. All solvents were degassed and stored under high purity nitrogen after distillation. All deuterated solvents were purchased from Aldrich and dried over 3 Å molecular sieves. The purest-available NaOH pellets (Frutarom), silver tetrafluoroborate (Aldrich) and  $^n\text{BuCl}$  (Fluka) were used as received. Dipp [11],  $[(2\text{-methylallyl})\text{PdCl}]_2$  [12],  $\text{Pd}(\text{dipp})_2$  and  $\text{Pd}(\text{dippe})_2$  [9] were prepared by published methods.

The NMR spectra were recorded on a Bruker WH270 spectrometer at 270 MHz ( $^1\text{H}$ ) or 109 MHz ( $^{31}\text{P}$ ). The  $^1\text{H}$  chemical shifts are reported downfield from  $\text{SiMe}_4$  and referenced to the residual solvent- $h_1$  peaks. The  $^{31}\text{P}$  chemical shifts are reported downfield from phosphoric acid and were with the acid as external reference.

#### 3.1. Synthesis of $^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (**3**)

The ligand was prepared by a route analogous to that used for the dipp [11]. In the final coupling step, one equivalent of  $\text{LiP}^i\text{Pr}_2$  (instead of two) was used per equivalent of 1,3-dichloropropane. The ligand was purified by distillation under reduced pressure ( $10^{-3}$  Torr,  $65\text{--}70^\circ\text{C}$ ) [13].  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.1 (s) ppm.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.90 (dd,  $J_{\text{P-H}} = 10.7$  Hz,  $J_{\text{H-H}} = 7.0$  Hz, 6H,  $\text{CH}_3$ ), 0.96 (dd,  $J_{\text{P-H}} = 13.8$  Hz,  $J_{\text{H-H}} = 7.1$  Hz, 6H,  $\text{CH}_3$ ), 1.22 (dt,  $J_{\text{P-H}} = 2.3$  Hz,  $J_{\text{H-H}} = 8.0$  Hz, 2H,  $\text{PCH}_2$ ), 1.47 (dhept,  $J_{\text{P-H}} = 2.0$  Hz,  $J_{\text{H-H}} = 7.1$  Hz, 2H, CH), 1.68 (m(dtt),  $J_{\text{H-H}} = 6.5$  Hz,  $J_{\text{H-H}} = 8.0$  Hz,  $J_{\text{P-H}} = 7$  Hz, 2H,  $\text{CH}_2$ ), 3.21 (t,  $J_{\text{H-H}} = 6.5$  Hz, 2H,  $\text{CH}_2\text{Cl}$ ) ppm.

#### 3.2. Synthesis of **2**

A procedure analogous to that used for **1** [9] was employed, but two equivalents of  $^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{Cl}$  (**3**) and one equivalent of dipp per equivalent of  $[(\eta^3\text{-methylallyl})\text{PdCl}]_2$  were used. The solvents were evaporated in vacuum and the pentane extract of the brown residue (about 5 ml pentane (yellow solution) obtained) was analyzed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.

#### 3.3. Reaction of a mixture of P,C-chelated complexes (**2a–2d**) with $\text{AgBF}_4$

White crystals of the P,C-chelated complexes (**30** mg) were dissolved in 2 ml of methanol, and a solution

of an excess of  $\text{AgBF}_4$  (30 mg) in 1 ml of methanol added. The grayish precipitate that was separated immediately was filtered off and the filtrate was analyzed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.  $^{31}\text{P}\{^1\text{H}\}$  NMR (methanol, room temperature)  $\delta$  104.1 (s), 38.8 (very broad peak) ppm, integration ratio, 1:1.  $^{31}\text{P}\{^1\text{H}\}$  NMR (methanol,  $-80^\circ\text{C}$ )  $\delta$  103.5 (s), 40.5 (broad peak), 33.9 (broad peak) ppm, integration ratio, 2:1:1.

### 3.4. Synthesis of **6**

A mixture of 40 mg of  $\text{Pd}(\text{dippe})_2$  (**5**) and an equivalent amount of **3** in 2 ml of dimethylformamide in a closed vessel for 16 h. The volatiles were evaporated off in vacuum, the residue was dissolved in  $\text{C}_6\text{D}_6$ , and the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum recorded.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  68.1 (dd,  $J = 22.0$  Hz,  $J = 27.8$  Hz, 1P), 76.7 (dd,  $J = 307.6$  Hz,  $J = 22.0$  Hz, 1P), 83.1 (dd,  $J = 307.6$  Hz,  $J = 27.8$  Hz, 1P) ppm. Traces of dippe were also detected ( $\delta$  8.91 (s) ppm). The  $^1\text{H}$  NMR signals were not sufficiently resolved to allow definite assignment.

### Acknowledgments

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