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Mono and dinuclear palladium complexes of *o*-alkyl substituted arylphosphane ligands: Solvent-dependent syntheses, NMR-spectroscopic characterization and X-ray crystallographic studies

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Abstract

Palladium(II) chloride complexes of *o*-alkyl substituted phosphanes were prepared in various solvents with the phosphane ligands *o*-methylphenyldiphenylphosphane, *o*-ethylphenyldiphenylphosphane, *o*-isopropylphenyldiphenylphosphane, *o*-cyclohexylphenyldiphenylphosphane and *o*-phenylphenyldiphenylphosphane. The structures of the complexes were characterized by ^{1}H NMR and ^{31}P NMR spectroscopy and elemental analysis. The X-ray structures of $PdCl_2$(*o*-methylphenyldiphenylphosphane)$_2$, $PdCl_2$(*o*-isopropylphenyldiphenylphosphane)$_2$, $PdCl_2$(*o*-cyclohexylphenyldiphenylphosphane)$_2$, $PdCl_2$(*o*-phenylphenyldiphenylphosphane)$_2$, [$PdCl_2$-(*o*-methylphenyldiphenylphosphane)]$_2$, [$PdCl_2$(*o*-ethylphenyldiphenylphosphane)]$_2$ and [$PdCl_2$(*o*-cyclohexylphenyldiphenylphosphane)]$_2$ were also determined. We report a systematic, solvent-dependent method to prepare palladium(II) complexes of the aryl phosphines *o*-methylphenyldiphenylphosphane, *o*-cyclohexylphenyldiphenylphosphane and *o*-phenylphenyldiphenylphosphane with a desired nuclearity. We demonstrated that chlorinated solvents promote the formation of dinuclear chlorine-bridged palladium complexes for all five ligands. The ligands preferentially form mononuclear palladium complexes in other solvents where the starting materials are only weakly soluble in the solvent.

Keywords: Phosphane ligands; Solvent effects; Substitute effects; Arylphosphane

1. Introduction

Phosphorous containing ligands, such as phosphanes (PR_3) and especially arylphosphanes are one of the most widely used groups of ligands in palladium chemistry. These have been used to prepare catalysts for various reactions for decades [1,2]. The general class of dinuclear *sym*-[$PdCl_2P$]$_2$ complexes has been known since the early studies of Mann et al. [3] and their isomerisation and anion exchange mechanisms have been described in numerous publications. $Pd_2Cl_4(PPh_3)_2$, the dinuclear analogue of $PdCl_2(PPh_3)_2$, and other related dinuclear palladium complexes are used as promoters, catalysts and starting materials [4] in different reactions with promising results. Dinuclear palladium complexes are structurally different from their mononuclear analogues, and therefore could possibly mediate new types of catalytic mechanisms [5].

Since the early nineties, there has been an underlying interest in modifying the well-established $PdCl_2(PPh_3)_2$ catalyst using more efficient and selective phosphane ligands [6]. Palladium and platinum complexes have shown enhanced catalytic activity and selectivity in carbonylation and hydrogenation reactions [6–9] when the well established triphenylphosphane ligand is replaced by new modified arylphosphanes. There are also abundant examples of this in the Suzuki–Miyaura reactions [10]. Replacing the PPh_3 ligand by modified *o*-alkyl substituted ligands give

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promising results in various alkene hydroformylation reactions. We recently observed that the *o*-alkyl substituents have significant effects on the activity and selectivity in the rhodium and ruthenium catalyzed hydroformylation of propene [11,12]. However, the Rh and Ru complexes of these ligands could not be crystallized and sometimes were found to be unstable in solution. In contrast, palladium complexes provide stable square planar surroundings around the metal ion in studies of the steric nature and other properties of the *o*-alkyl substituents (see Figs. 1–5).

In this study we synthesized and characterized new mono- and dinuclear square planar palladium complexes (see Scheme 1) of the *o*-alkyl substituted arylphosphanes *o*-methylphenyldiphenylphosphane **(1)**, *o*-ethylphenyldiphenylphosphane (**2**), *o*-isopropylphenyldiphenylphosphane (**3**),

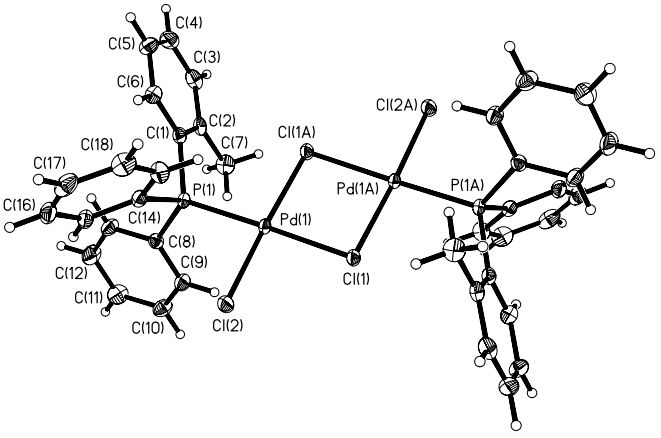


Fig. 1. Crystal structure of complex **6**. The solvent has been omitted for clarity. The thermal ellipsoids are drawn at 50% probability level.

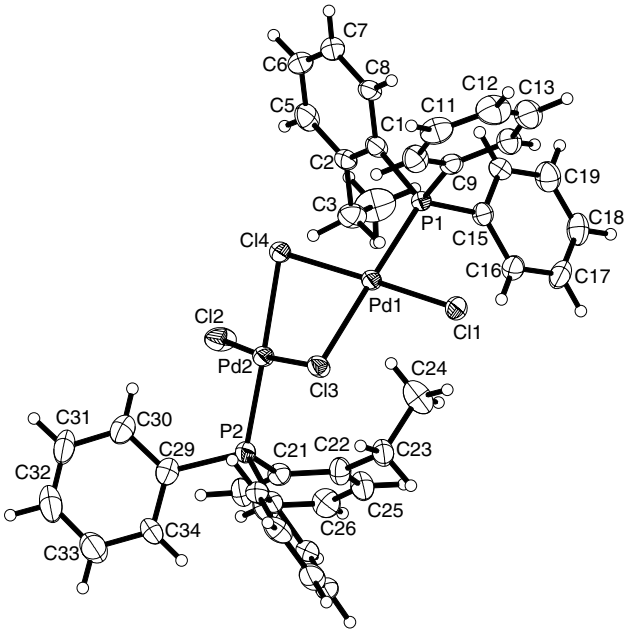


Fig. 2. Crystal structure of complex **7**. Thermal ellipsoids are drawn with 50% probability level.

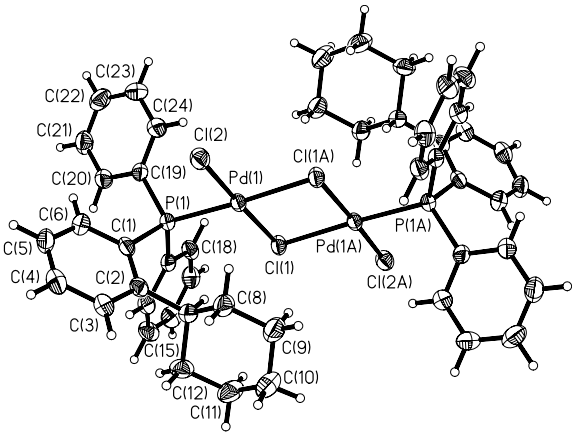


Fig. 3. Crystal structure of complex **9**. The thermal ellipsoids are drawn at 50% probability level.

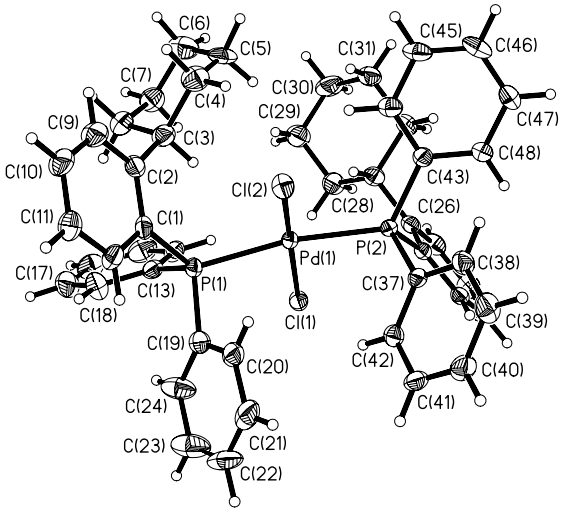


Fig. 4. Crystal structure of complex **14**. Thermal ellipsoids are drawn with 50% probability. The solvent has been omitted for clarity.

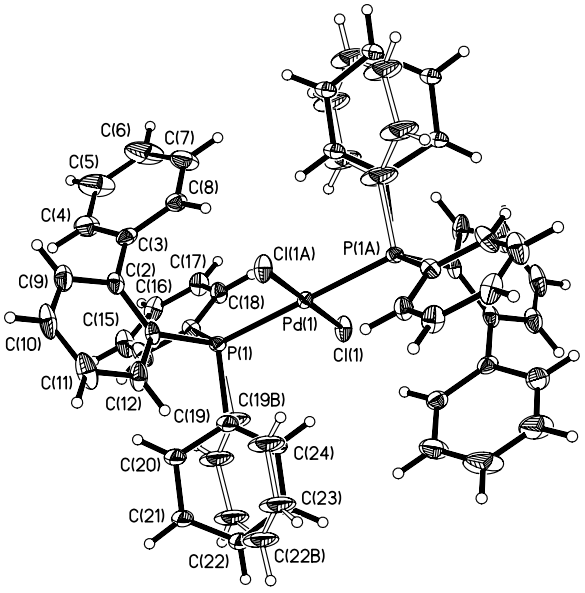
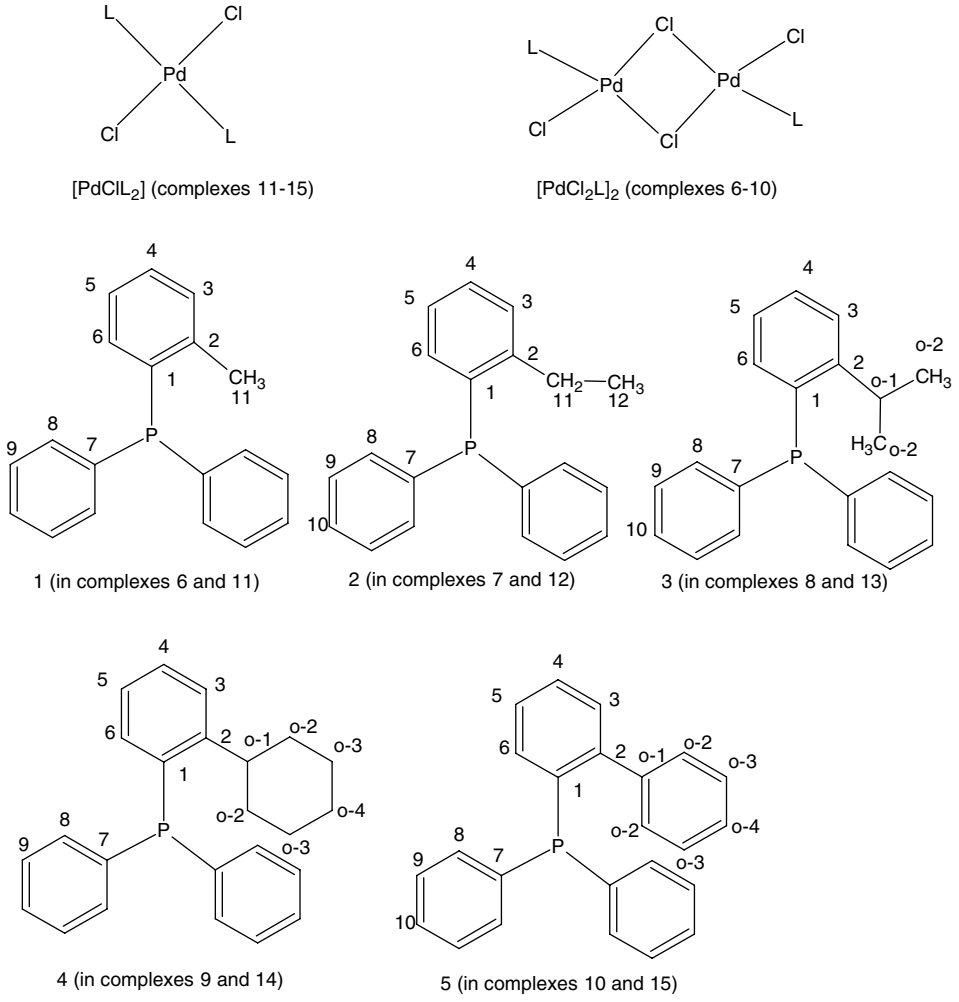


Fig. 5. Crystal structure of complex **15**. Thermal ellipsoids are drawn with 50% probability. The solvent has been omitted for clarity.



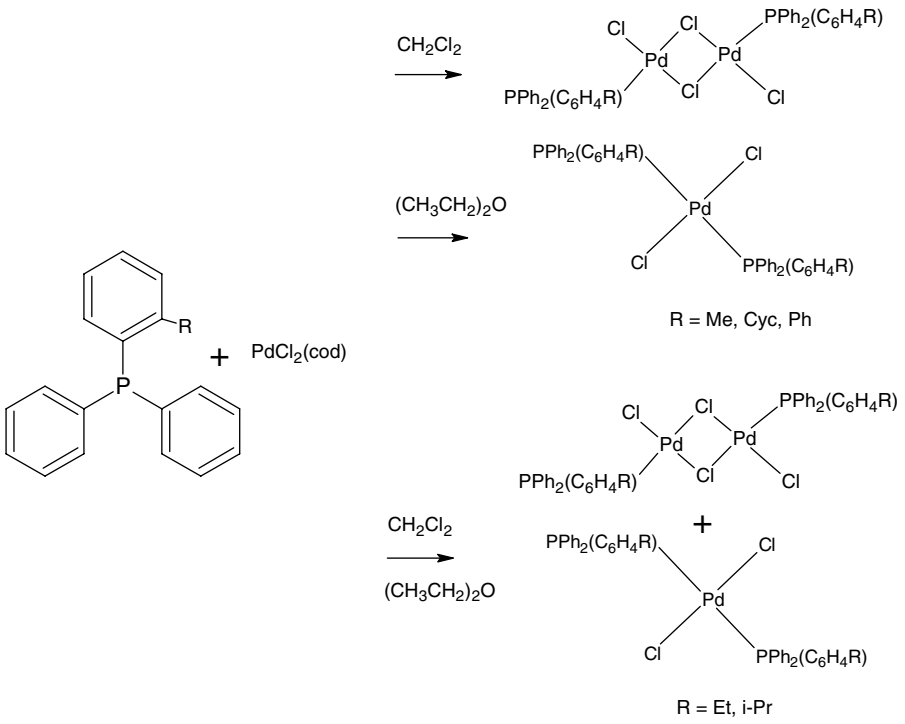
Scheme 1. Structures of the phosphane ligands **1**–**5** and palladium complexes **6**–**15**.

o-cyclohexylphenyldiphenylphosphane (**4**) and *o*-phenylphenyldiphenylphosphane (**5**). The following dinuclear palladium complexes were prepared: di-μ-chlorodichlorobis(*o*-methylphenyldiphenylphosphane)di- palladium (**6**), di-μ-chlorodichlorobis(*o*-ethylphenyldiphenylphosphane)di-palladium (**7**), di-μ-chlorodichlorobis(*o*-isopropylphenyldiphenylphosphane)di- palladium (**8**), di-μ-chlorodichlorobis-(*o*-cyclohexylphenyldiphenylphosphane)di- palladium (**9**) and di-μ-chlorodichlorobis(*o*-phenylphenyldiphenylphosphane)di- palladium (**10**). We also prepared the following mononuclear complexes: dichlorobis(*o*-methylphenyldiphenylphosphane) palladium (**11**), dichlorobis(*o*-ethylphenyldiphenylphosphane) palladium (**12**), dichlorobis(*o*-isopropylphenyldiphenylphosphane) palladium (**13**), dichlorobis(*o*-cyclohexylphenyldiphenylphosphane) palladium (**14**) and dichlorobis(*o*-phenylphenyldiphenylphosphane) palladium (**15**). The X-ray structures of **6**, **8**–**12** and **14** were also obtained. The lack of control for the formation of complexes with the desired nuclearity has been recognized as a problem in various papers [9,10,12–15]. We tested a variety of solvents in order to clarify the role of solvents and to develop a method to produce palladium complexes of *o*-alkyl substituted arylphosphanes with the desired nuclearity. Reactions between the *o*-alkyl substituted phosphane ligands and $PdCl_2(cod)$ (cod = C_8H_{12}) were also carried out using different Pd:P ratios in order to test the influence of the absolute concentration of the reaction mixture on the formation of the complexes.

2. Results and discussion

2.1. Syntheses

A 2:1 reaction of the *o*-alkyl substituted phosphane ligands **1**, **4** and **5** with $PdCl_2(cod)$ in dichloromethane produced the chlorine-bridged dinuclear palladium complexes **6**, **9** and **10** with the general formula $[PdCl_2L]_2$ (see Scheme 2). Interestingly, a similar reaction of the *o*-alkyl substituted phosphane ligands **1**, **4** and **5** with $PdCl_2(cod)$ in diethyl ether produced the mononuclear palladium complexes **11**, **14** and **15** with the general formula $[PdCl_2L_2]$ (see Scheme 2). For ligands **2** and **3**, the reaction in dichloromethane produced the mononuclear complexes **12** and **13** as the main products, and the dinuclear complexes **7** and **8** surprisingly as only side-products. A similar reaction was obtained when ligands **2** and **3** in diethyl ether pro-



Scheme 2. A general reaction scheme for the preparation of the palladium complexes **6**–**15**.

duced the mononuclear complexes as the main products correspondingly as the other ligands, but a minor amount of the dinuclear complexes was once again formed.

We also carried out the reactions between $PdCl_2$(cod) and the phosphane ligands **1–5** with P:Pd ratios 4:1, 1:1, 1:2 and 1:4 both in diethyl ether and dichloromethane, in order to test the effect of the absolute concentration of the reaction mixture on the nuclearity of the formed complexes. The reactions still produced only mononuclear complexes with the ligands **1**, **4** and **5** in diethyl ether in each case. For ligands **2** and **3**, all reactions performed in diethyl ether also seemed to proceed as before. However, this time the Pd:P 1:4 reactions did not produce any dinuclear complexes even as trace side products. In the reactions which occurred in dichloromethane, the ligands **1**, **4** and **5** still produced only dinuclear complexes despite the varied ratios between the ligand and $PdCl_2$(cod). Where an excess of the $PdCl_2$(cod) was used, the unreacted $PdCl_2$(cod) could be recovered from the reaction mixture. For ligands **2** and **3**, the results were similar as before, combinations of mono and dinuclear complexes were formed regardless of the Pd:P ratio. Similar results were reported previously [15,16].

We also carried out the 2:1 and 1:2 Pd:P reactions in toluene, THF, acetone, DMF and methanol for comparison. For all ligands, the results were similar as for the reactions in diethyl ether. Correspondingly, using chlorobenzene or chloroform as a solvent produced similar results as to those reactions where dichloromethane was used. The nuclearity of the main product seemed to depend on the used solvent for ligands **1**, **4** and **5**, whereas in the case of ligands **2** and **3**, a mononuclear complex was always the main product.

The stability of the mononuclear complexes were tested by an equimolar reaction between the isolated complexes and $PdCl_2$(cod) at room temperature in dichloromethane. The reactions produced the dinuclear complex products as expected. Moreover, it is well known that the dinuclear complexes [$PdCl_2$L]2 easily undergo bridge-splitting reactions with a variety of neutral ligands to yield mononuclear derivatives. Therefore the stability of the isolated dinuclear complexes was studied by a 1:2 reaction between the dinuclear complexes and the corresponding ligands at ambient temperature in dichloromethane and at 135 °C in chlorobenzene. However, no bridge-splitting reactions could be observed and the dinuclear complexes remained unreactive.

With all chlorinated solvents (dichloromethane, chloroform, chlorobenzene), the only products in the case of the ligands **1**, **4** and **5** were the dinuclear complexes. Even though the mononuclear complexes were the main products for reactions involving ligands **2** and **3**, there was also a reasonable amount of the dinuclear complex formed. In order to get further insight into the role of the halogenated solvents in the reactions, we also carried out the reactions with ligands **1** and **5** in bromoform and diiodomethane. The dinuclear complexes **6** and **10** were the only products formed, which indicates that other halogen containing solvents also promote the formation of dinuclear palladium complexes. However, we did not observe any introduction of bromine or iodine in the crystal structures of the dinuclear complexes, which suggests that the solvent itself does not react.

An interesting observation was that the starting material $PdCl_2$(cod) is only slightly soluble in diethyl ether, and the reaction between it and the phosphanes results in mononu-

clear palladium complexes, which are also only slightly soluble in all solvents. In contrast, the starting material $PdCl_2$(cod) is readily soluble in dichloromethane and other halogenated solvents. The reaction between $PdCl_2$(cod) and the phosphanes results in dinuclear palladium complexes which are also readily soluble in halogenated solvents. The implication is that the formation of $PdCl_2L_2$ is essentially due to the low solubility of $PdCl_2$(cod) resulting in a P:Pd ratio >2 in solution, and that the low solubility of the product [$PdCl_2L_2$] prevents the reaction with $PdCl_2$(cod) to form dinuclear complexes. However, this does not explain the formation of both mononuclear and dinuclear complexes in dichloromethane observed in the reactions involving ligands **2** and **3**. Conversely, we observed that the mononuclear complexes **12** and **13** were notably more insoluble even in halogenated solvents than the other mononuclear complexes. Therefore a possible explanation might be that the low solubility prevents a complete reaction between the mononuclear species and $PdCl_2$(cod) to form dinuclear complexes.

2.2. Structural characteristics

In all the obtained crystal structures the palladium atoms had slightly distorted square planar environments. All bond lengths and angles were typical for related species. The metal-metal distances in the dinuclear compounds **6**, **7**, and **9** varied between 3.2345(7) and 3.4713(5) Å (see Table 1). The Pd–Pd distances were somewhat shorter than those of the corresponding PPh_3 compounds (3.528 or 3.492 Å) [17,18] but still well in the range of Pd–Pd distances found in these types of dimers. In **6** and **9** the bridging chlorides, terminal chlorides and phosphorus atoms were found to be coplanar. In **7** a bridging chloride, terminal chloride and P(1) were coplanar. Likewise, a bridging chloride, terminal chloride and P(2) were coplanar. Two square planes were formed around Pd(1) and Pd(2). The angle between the two planes was 48.63(5)°. Such bending shortened the Pd–Pd distance in **7** compared to that of **6** and **9**. In the dinuclear complexes the Pd–Cl bonds *trans* to phosphorus (2.4300(5) (**6**), 2.422(2), 2.427(2) (**7**) and 2.3205(8) Å (**9**)) were slightly elongated compared to the corresponding Pd–Cl bonds *trans* to Cl (2.3165(5) (**6**), 2.280(2) (**7**), 2.274(2) (**7**), and 2.2847(8) Å (**9**)) or compared to the Pd–Cl in the mononuclear complexes (see Table 1). A similar effect has been observed with other [$PdCl_2L$]2 compounds, including $Pd_2Cl_4[PPh_3]_2$ [18], $Pd_2Cl_4[PBu_3]_2$ [19] and $Pd_2Cl_4[PCy_3]_2$ [20].

The *o*-alkyl groups were pointed outside the cone of the ligand in all structures **6**, **7**, **8**, **9**, **11**, **13**, **14**, and **15**. This orientation is also favored in the free ligand [21,22]. The *o*-alkyl groups were oriented reasonably close to the Pd center (shortest intramolecular Pd–H distances were 2.89 for **9** and 3.29 Å for **6**). This orientation is expected to be favored mostly due to the packing effects in solid state. It is also expected that in solution, rotation about the P–C bond is relatively free and not strongly restricted by the other ligands. However, the correlation found between the solid state orientation and catalytic behavior of the complexes suggests that the orientation of the *o*-substituent

Table 1
Selected bond lengths and angles for **6** · 2(CH_2Cl_2), **7**, **9**, **14** · (CH_2Cl_2), and **15** · (CH_2Cl_2)

	6 · 2(CH_2Cl_2)	**7**	**9**	**14** · (CH_2Cl_2) (A)	**14** · (CH_2Cl_2) (B)	**15** · (CH_2Cl_2)
Pd(1)–Cl(1)	2.4300(3)	2.280(2)	2.3205(8)	2.3078(10)	2.3085(10)	2.2958(13)
Pd(1)–Cl(1A)	2.3165(6)		2.4111(8)			
Pd(1)–Cl(2)	2.2822(5)		2.2847(8)	2.2999(10)	2.3039(10)	2.2958(13)
Pd(1)–Cl(3)		2.422(2)				
Pd(1)–Cl(4)		2.319(2)				
Pd(2)–Cl(2)		2.274(2)				
Pd(2)–Cl(3)		2.324(2)				
Pd(2)–Cl(4)		2.427(2)				
Pd(1)–Pd(2)		3.2345(7)				
Pd(1)–Pd(1A)	3.4482(2)		3.4713(5)			
Pd(1)–P(1)	2.2332(5)	2.2433(18)	2.2356(9)	2.3203(10)	2.3455(10)	2.3370(14)
Pd(1)–P(2)				2.3260(11)	2.3150(10)	2.3370(14)
Cl(1)–Pd(1)–Cl(2)	89.96(2)		175.36	171.19(4)	177.98(3)	180
Cl(1)–Pd(1)–Cl(1A)						
P(1)–Pd(1)–P(2)				169.16(4)	172.30(4)	180
P(1)–Pd(1)–P(1A)						
Pd(1)–Cl(3)–Pd(2)		85.89(5)				
Pd(1)–Cl(4)–Pd(2)		85.88(5)				
Pd(1)–Cl(1)–Pd(1A)	93.15(2)		94.37			
Cl(1)–Pd(1)–Cl(4)		173.03(7)				
P(1)–Pd(1)–Cl(3)		178.52(7)				
Cl(3)–Pd(2)–Cl(4)		83.27(6)				
Cl(2)–Pd(2)–Cl(3)		171.79(7)				
P(2)–Pd(2)–Cl(4)		178.57(7)				
P(1)–Pd(1)–Cl(1)	176.71(2)		90.72(3)			
Cl(2)–Pd(1)–Cl(1A)	176.56(2)		95.93(3)			

Table 2
Spectroscopic data for the free and coordinated ligands

Ligand (L)	Free phosphane ^{31}P NMR δ (ppm)	[$PdCl_2L_2$] ^{31}P NMR δ (ppm)	[$PdCl_2L$]2 ^{31}P NMR δ (ppm)	$\Delta = \delta_{complex} - \delta_L$ [$PdCl_2L_2$]	$\Delta = \delta_{complex} - \delta_L$ [$PdCl_2L$]2
1	−10.7	19.6	29.8	30.3	40.5
2	−14.2	20.1	30.0	34.3	44.2
3	−13.8	20.3	31.2	34.1	45.0
4	−13.6	21.0	29.4	34.6	43.0
5	−11.9	22.3	28.4	34.2	40.3

can have an effect on the catalytic reactivity of the metal centre even in solution. We observed such effects on activity and selectivity in hydroformylation, even though the specific mechanism remained unclear [22].

Some of the complexes crystallize with a dichloromethane molecule as a part of the crystal structure. However, we were not able to detect the signal of the dichloromethane molecule from the ^{1}H NMR spectra of the purified, isolated complexes, nor did it appear to be a part of the structure based on the elemental analysis data. Therefore we do not believe that the dichloromethane molecule is chemically bonded to the metal complexes in solution, rather it is introduced into the structure in the crystallization process.

2.3. Spectroscopic data

The ^{1}H NMR spectra of the complexes are consistent with the crystal structures and can be assigned on the basis of the spectra of the free ligands and decoupling experiments. The ^{1}H NMR signals were almost identical to those of the free phosphane ligands, the chemical shifts had shifted downfield only slightly [11,21].

The ^{31}P–{^{1}H} NMR data is summarized in Table 2. As previous results have shown, the individual signals of the phosphanes in the ^{31}P–{^{1}H} NMR spectra tend to move to a lower field when a phosphane is coordinated to a metal center [11,21,22]. As expected, complexes **6**, **9**, **10**, **11**, **14** and **15** showed one sharp signal initially. The reaction mixtures in the preparation of the complexes **7**, **12**, **8** and **13** initially showed the two respective signals of the mononuclear and the dinuclear complex. However, the complexes can be separated using column chromatography. The coordination chemical shifts were quite similar for complexes **6**–**10** and for **11**–**15**. In addition to the ^{1}H NMR and elemental analysis data, this further supports the assumed similar structures for the complexes **8**, **10**, and **12**, which could not be crystallized.

3. Conclusion

The formation of palladium complexes with unwanted nuclearity had previously been described as a problem in various reports. Moreover, the suggested reasons for the nuclearity of the formed palladium complexes varied in each case. In this study we report a convenient method to prepare palladium(II) complexes of *o*-alkyl substituted arylphosphanes with the desired nuclearity in good yields for ligands **1**, **4** and **5**. Diethyl ether was found to be an ideal solvent for preparing mononuclear palladium complexes with all five *o*-alkyl substituted aryl phosphane ligands **1**–**5** due to the low solubility of the starting materials and the reaction products. In contrast, chlorine-bridged dinuclear palladium complexes of ligands **1**, **4** and **5** can be prepared using halogenated solvents. Dinuclear complexes of ligands **2** and **3** were only acquired as side-products regardless of the solvent used. It is also possible to prepare dinuclear palladium complexes by a reaction between a mononuclear complex and $PdCl_2$(cod).

4. Experimental

4.1. General comments

The phosphanes used in this study are air- and moisture-sensitive, both as pure solid compounds or in solution. Furthermore, without protection the phosphanes showed observable oxidation within one day. Therefore all reactions were carried out using standard Schlenk techniques under either a nitrogen or an argon atmosphere. The metal complexes were stable both as solid compounds and in solution. Therefore they were isolated and characterized in air. Diethyl ether, benzene and THF were distilled over sodium-benzophenone ketyl before use. Nitrogen was bubbled through all chlorinated solvents before use. Other commercial reagents were used as received. The *o*-substituted bromobenzenes were obtained from Lancaster and Aldrich. The diphenylchlorophosphane, *n*-butyl lithium (2.5 M solution in hexane), and dichloro(1,5-cyclooctadiene)-palladium (99%) were obtained from Aldrich.

Spectroscopy: The characterization of the complexes was based on ^{1}H- and ^{31}P–{^{1}H} NMR spectroscopy. NMR spectra were recorded on a Bruker DPX400 spectrometer at room temperature in $CDCl_3$ (99.8% D, 0.03% TMS). 85% H_3PO_4 was used as an external standard for ^{31}P–{^{1}H} NMR.

Elemental analyses: C and H analyses were performed using a Perkin–Elmer 2400 CHNS analyzer from the purified, solid metal complex powders.

X-ray crystal structure determinations: The crystals were immersed in perfluoropolyether, mounted in a cryo-loop and measured at 100–120 K. The X-ray diffraction data were collected by a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The DENZO-SCALEPACK program package [23] was used for cell refinements and data reductions. Structures were solved by direct meth-

ods using the SHELXS-97 [24] or SIR2002 program [25] with the WINGX graphical user interface. [26] An empirical absorption correction was applied to all data using XPREP in SHELXTL or SADABS programs [27,28] (T_{min}/T_{max} were: 0.3908/0.4379, 0.8686/0.9448, 0.1992/0.2391, 0.7362/0.8069, 0.7378/0.9176 for **6** · 2(CH_2Cl_2), **7**, **9**, **14** · (CH_2Cl_2) and **15** · (CH_2Cl_2), respectively). Structural refinements were carried out with SHELXL-97 [24]. Compounds **6**, **7** and **9** are dimers, which crystallize in centrosymmetric space groups. The asymmetric unit of **14** · (CH_2Cl_2) consists of two palladium molecules whereas the asymmetric unit of **15** · (CH_2Cl_2) contains only half a palladium molecule. In **15** · (CH_2Cl_2) one of the phenyl rings was disordered over two sites with occupancies of ca. 0.6/0.4. A rigid group fitting with constant C–C distances was applied to these rings. All hydrogens were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 3. The selected bond lengths and angles are shown in Table 1.

4.2. Preparation of the ligands

The previously characterized *o*-alkyl substituted phosphane ligands **1**–**5** were prepared according to a modified literature method [11,21] at 0 °C from brominated organic reagents by lithiation with *n*-butyl lithium and an overnight reaction with halogenated arylphosphanes. The ligands were recrystallized from ethanol or a 1:1 mixture of ethanol and hexane, and if necessary, purified by column chromatography using silica gel and hexane–dichloromethane 2:1 mixture.

4.3. Preparation of the palladium complexes

The dinuclear palladium complexes **6**, **9** and **10** were prepared by a substitution of cyclooctadiene (cod) in $PdCl_2$(cod) with the preferred phosphane ligand in dichloromethane. $PdCl_2$(cod) reacts relatively easily with one mol equiv. of phosphane ligands in dichloromethane at room temperature overnight, and produces a chlorine bridged dinuclear complex of the type $[PdCl_2L]_2$. The complexes **11**–**15** were prepared by a similar reaction of cyclooctadiene (cod) in $PdCl_2$(cod) with 2 mol equiv. of a preferred phosphane ligand in diethyl ether at room temperature overnight. The reaction produces mononuclear complexes of the type $[PdCl_2L_2]$. The dinuclear palladium complexes **7** and **8** were acquired only as side-products in reactions in both diethyl ether and dichloromethane. The yellow (mononuclear) or orange (dinuclear) precipitates obtained were filtered and washed with a small amount of hexane and diethyl ether and dried in vacuo. If necessary, the complexes were further purified by column chromatography using silica gel and dichloromethane–hexane 2:1 or THF–hexane 2:1 mixture. The separation of the mono- and dinuclear complexes in the synthesis of complexes **7**, **8**, **12** and **13** was done by column chromatography using silica gel and a 5:1 dichloromethane–hexane mixture. Single crystals for X-ray crystallographic analysis were obtained by slow evaporation of the dichloromethane–hexane or chlorobenzene–hexane solvent mixture at room temperature.

4.3.1. Pd_2Cl_4(*o*-methylphenyldiphenylphosphane)$_2$ (**6**)

o-Methylphenyldiphenylphosphane (0.103 g, 0.37 mmol) and $PdCl_2$(cod) (0.096 g, 0.34 mmol) were dissolved in dichloromethane (15 ml). The mixture was stirred at room temperature for 24 h. After filtration of the solution and purification by column chromatography, the product isolated was as a dark orange solid. The yield of the product was 0.265 g (0.29 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 2.38$ (3H, s, H^{11}), 6.90 (1H, dd, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-P} = 4.5$ Hz, H^6), 7.18–7.50 (13H, m, H^{3-5}, H^{8-10}). The ^{31}P–{^{1}H}

Table 3
Crystal Data for **6** · 2(CH_2Cl_2), **7**, **9**, **14** · (CH_2Cl_2), and **15** · (CH_2Cl_2)

	6 · 2(CH_2Cl_2)	**7**	**9**	**14** · (CH_2Cl_2)	**15** · (CH_2Cl_2)
Empirical formula	$C_{40}H_{38}Cl_8P_2Pd_2$	$C_{40}H_{38}Cl_4P_2Pd_2$	$C_{48}H_{50}Cl_4P_2Pd_2$	$C_{49}H_{52}Cl_4P_2Pd$	$C_{50}H_{42}Cl_6P_2Pd$
Formula weight	1077.04	935.24	1043.42	951.05	1023.88
Temperature (K)	120(2)	120(2)	120(2)	100(2)	100(2) K
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073 Å
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$Pn2_1a$	$P\bar{1}$
a (Å)	9.2435(2)	19.0114(7)	9.6950(3)	19.8140(4) Å	9.6986(3)
b (Å)	9.8186(2)	10.5966(3)	17.3842(6)	33.9300(7) Å	9.9748(3)
c (Å)	12.5982(10)	20.5370(7)	14.1760(9)	13.5630(2) Å	13.3530(4)
α (°)	107.213(1)	90	90	90	104.921(1)
β (°)	102.265(1)	115.746(2)	109.316(2)	90	96.314(1)
γ (°)	95.410(1)	90	90	90	112.421(1)
V (Å^3)	1052.02(9)	3726.6(2)	2254.7(2)	9118.3(3)	1122.10(6)
Z	1	4	2	8	1
ρ_{calc} (Mg/m^3)	1.700	1.667	1.537	1.386	1.515
μ (Mo Kα) (mmol^{-1})	1.468	1.367	1.139	0.745	0.878
R_1^a ($I \geqslant 2\sigma$)	0.0265	65386	0.0364	0.0416	0.0696
wR_2^b ($I \geqslant 2\sigma$)	0.0601	7293	0.0795	0.0929	0.1634

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]$.

NMR-data are presented in Table 2. Anal. Calc. for $Pd_2Cl_4P_2C_{38}H_{34}$ (800.81): C, 51.96; H, 3.9. Found: C, 51.62; H, 4.30%.

4.3.2. $PdCl_2$(*o*-methylphenyldiphenylphosphane)$_2$ (**11**)

o-Methylphenyldiphenylphosphane (0.3933 g, 1.42 mmol) and $PdCl_2$(cod) (0.208 g, 0.73 mmol) were added in diethyl ether (30 ml). The mixture was stirred at room temperature for 24 h. After filtration of the solution, the isolated product was a yellow solid. The yield of the product was 0.485 g (91%, 0.66 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 2.39$ (3H, s, H^{11}), 6.93 (1H, dd, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-P} = 4.5$ Hz, H^6), 7.08 (1H, td, $^3J_{H-H} = 7.0$ Hz, $^4J_{H-P} = 2.1$ Hz, H^5), 7.20–7.35 (12H, m, H^{3-4}, H^{8-10}). The ^{31}P–{^{1}H} NMR-data are presented in Table 2. Anal. Calc. for $PdCl_2P_2C_{38}H_{34}$ (788.07): C, 62.5; H, 4.69. Found: C, 62.13; H, 4.62%.

4.3.3. Preparation of Pd_2Cl_4(*o*-Cyclohexylphenyldiphenylphosphane)$_2$ (**9**)

o-Cyclohexylphenyldiphenylphosphane (0.1305 g, 0.38 mmol) and $PdCl_2$(cod) (0.1512 g, 0.53 mmol) were dissolved in dichloromethane (15 ml). The mixture was stirred at room temperature for 24 h. After filtration of the solution and purification by column chromatography, the product isolated was obtained as a dark orange solid. The yield of the product was 0.310 g, (78%, 0.30 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 1.15$–1.25 (2H, m, H^{0-4}), 1.40–1.50 (4H, m, H^{0-2}), 1.70–1.83 (4H, m, H^{0-3}), 3.60 (1H, m, H^{0-1}), 6.85–6.98 (1H, m, H^6), 7.0 (1H, m, H^5), 7.32–7.53 (12H, m, H^{3-4}, H^{8-10}). The ^{31}P–{^{1}H} NMR-data are presented in Table 2. Anal. Calc. for $Pd_2Cl_4P_2C_{48}H_{50}$ (1043.46): C, 55.25; H, 4.8. Found: C, 54.95; H, 4.54%.

4.3.4. Preparation of $PdCl_2$(*o*-cyclohexylphenyldiphenylphosphane)$_2$ (**14**)

o-Cyclohexylphenyldiphenylphosphane (0.4837 g, 1.40 mmol) and $PdCl_2$(cod) (0.2001 g, 0.70 mmol) were added in diethyl ether (30 ml). The mixture was stirred at room temperature for 24 h. After filtration of the solution, the isolated product was obtainedas a yellow solid. The yield of the product was 0.515 g (85%, 0.60 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 1.15$–1.24 (2H, m, H^{0-4}), 1.25–1.40 (4H, m, H^{0-2}), 1.45–1.64 (4H, m, H^{0-3}), 3.30 (1H, m, H^{0-1}), 6.98–7.09 (2H, m, H^{5-6}), 7.30–7.46 (12H, m, H^{3-4}, H^{8-10}). The ^{31}P–{^{1}H} NMR-data are presented in Table 2. Anal. Calc. for $PdCl_2P_2C_{48}H_{50}$ (866.14): C, 66.4; H, 5.8. Found: C, 66.04; H, 5.44%.

4.3.5. Preparation of Pd_2Cl_4(*o*-phenylphenyldiphenylphosphane)$_2$ (**10**)

o-Phenylphenyldiphenylphosphane (0.0504 g, 0.15 mmol) and $PdCl_2$(cod) (0.0932 g, 0.33 mmol) were dissolved in dichloromethane (15 ml). The mixture was stirred at room temperature for 24 h. After filtration of the solution and purification by column chromatography, the isolated product was found to be a dark orange solid. The yield of the product was 0.120 g (77%, 0.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 7.0$–7.5 (19H, m, H^{3-6}, H^{8-10}, H^9, H^{0-2}, H^{0-3}, H^{0-4}). The ^{31}P-{^{1}H} NMR-data was presented in Table 2. Anal. Calc. for $Pd_2Cl_4P_2C_{48}H_{38}$ (924.94): C, 55.25; H, 4.8. Found: C, 55.15; H, 4.64%.

4.3.6. Preparation of $PdCl_2$(*o*-phenylphenyldiphenylphosphane)$_2$ (**15**)

o-Phenylphenyldiphenylphosphane (0.4740 g, 1.4 mmol) and $PdCl_2$(cod) (0.2014 g, 0.71 mmol) were added in diethyl ether (30 ml). The mixture was stirred at room temperature for 24 h. After filtration of the solution, the product was isolated as a yellow solid. The yield of the product was 0.521 g (86%, 0.61 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 7.0$–7.11 (1H, H^6), 7.12–7.5 (18H, m, H^{3-5}, H^{8-10}, H^{0-2}, H^{0-3}, H^{0-4}). The ^{31}P–{^{1}H} NMR-data are presented in Table 2. Anal. Calc. for $PdCl_2P_2C_{48}H_{50}$ (747.62): C, 67.5; H, 4.49. Found: C, 67.08; H, 4.37%.

4.3.7. Preparation of $PdCl_2$(*o*-ethylphenyldiphenylphosphane)$_2$ (**7**) and Pd_2Cl_4(*o*-ethylphenyldiphenylphosphane)$_2$ (**12**) in Et_2O and CH_2Cl_2

o-Ethylphenyldiphenylphosphane (0.4210 g, 1.45 mmol) and $PdCl_2$(cod) (0.1977 g, 0.69 mmol) were added in diethyl ether (30 ml). The mixture was stirred at room temperature for 24 h. After filtration of the solution and separation by column chromatography, the isolated complex (**12**) was a yellow solid. The yield of the product was 0.380 g (74%, 0.51 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 1.16$ (3H, t, $^3J_{H-H} = 7.6$ Hz, H^{12}), 2.93 (2H, qd, $^3J_{H-H} = 7.5$ Hz, $^3J_{H-P} = 1.6$ Hz, H^{11}), 6.91 (1H, dd, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-P} = 4.2$ Hz, H^6), 7.08 (1H, td, $^3J_{H-H} = 7.0$ Hz, $^4J_{H-P} = 2.5$ Hz, H^5), 7.35–7.56 (12H, m, H^{3-4}, H^{8-10}). The ^{31}P–{^{1}H} NMR-data are presented in Table 2. Anal. Calc. for $PdCl_2P_2C_{40}H_{38}$ (743.40): C, 63.4; H, 5.05. Found: C, 63.21; H, 4.98%.

After separation, the isolated complex (**7**) was isolated as a dark orange solid. The yield of the product was 0.021 g (6.6%, 0.02 mmol).^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 1.17$ (3H, t, $^3J_{H-H} = 7.6$ Hz, H^{12}), 2.98 (2H, qd, $^4J_{H-H} = 7.5$ Hz, $^3J_{H-P} = 1.6$ Hz, H^{11}), 6.88 (1H, dd, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-P} = 4.2$ Hz, H^6), 7.03 (1H, td, $^3J_{H-H} = 7.0$ Hz, $^4J_{H-P} = 2.5$ Hz, H^5), 7.30 –7.54 (12H, m, H^{3-4}, H^{8-10}). The ^{31}P–{^{1}H} NMR-data are presented in Table 2. Anal. Calc. for $Pd_2Cl_4P_2C_{40}H_{38}$ (991.40): C, 51.36; H, 4.0. Found: C, 51.11; H, 4.1%.

A similar reaction of *o*-ethylphenyldiphenylphosphane (0.2046 g, 0.71 mmol) and $PdCl_2$(cod) (0.1983 g, 0.69 mmol) in dichloromethane (15 ml) produced a 58% yield for **12** and 23% for **7**.

*4.3.8. Preparation of Pd_2Cl_4(o-isopropylphenyldiphenylphosphane)$_2$ (**8**) and $PdCl_2$(o-isopropylphenyldiphenylphosphane)$_2$ (**13**) in Et_2O and CH_2Cl_2*

o-Isopropylphenyldiphenylphosphane (0.2969 g, 0.98 mmol) and $PdCl_2$(cod) (0.1388 g, 0.49 mmol) were added in diethyl ether (30 ml). The mixture was stirred at room temperature for 24 h. After filtration of the solution and separation by column chromatography, complex **13** was isolated as a yellow solid. The yield of the product was 0.293 g (76%, 0.37 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 1.13$ (6H, d, $^3J_{H-H} = 6.8$ Hz, H^{0-2}), 3.48 (1H, sep, $^3J_{H-H} = 6.8$ Hz, H^{0-1}), 6.98 (1H, m, H^6), 7.11–7.16 (1H, m, H^5), 7.30–7.44 (12H, m, H^{3-4}, H^{8-10}). The ^{31}P–{^{1}H} NMR-data are presented in Table 2. Anal. Calc. for $PdCl_2P_2C_{42}H_{42}$ (786.16): C, 64.1; H, 5.38. Found: C, 64.5; H, 5.57%.

After separation, complex **8** was isolated as a dark orange solid. The yield of the product was 0.023 g (9.7%, 0.02 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering): $\delta = 1.13$ (6H, d, $^3J_{H-H} = 6.8$ Hz, H^{0-2}), 3.48 (1H, sep,$^3J_{H-H} = 6.8$ Hz, H^{0-1}), 6.94 (1H, m, H^6), 7.01–7.11 (1H, m, H^5), 7.30–7.42 (12H, m, H^{3-4}, H^{8-10}). The ^{31}P–{^{1}H} NMR-data are presented in Table 2. Anal. Calc. for $Pd_2Cl_4P_2C_{42}H_{42}$ (963.48): C, 52.36; H, 4.4. Found: C, 52.42; H, 4.30%.

A similar reaction of *o*-isopropylphenyldiphenylphosphane (0.115 g, 0.38 mmol) and $PdCl_2$(cod) (0.1198 g, 0.42 mmol) in dichloromethane (15 ml) produced a 60% yield for **13**and 22% for **8**.

5. Supplementary material

CCDC 618821, 618822, 618823, 618824, 618825, 618826, and 618827 contain the supplementary crystallographic data for **6**, **7**, **9**, **11**, **13**, **14**, and **15**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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