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New phosphino-oxazoline and related phosphino-iminolate palladium complexes; structure of an unusual zwitterionic dinuclear Pd(II) complex

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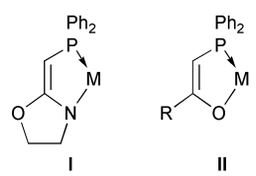
Reaction of the phosphino-oxazoline chiral ligand (4-(*R*)-phenyl-2-oxazoline-2-ylmethyl)diphenylphosphine) (abbreviated (*R*)-PCH$_2$ox^{Ph}) with [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ or [PdCl$_2$(cod)] (cod = 1,5-cyclooctadiene) led to the formation of [Pd(dmba-*C*,*N*){(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}]Cl **1** and [PdCl$_2${(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}] **5**, respectively. Deprotonation of the palladium phosphino-oxazoline complex **1** occurred at the PCH$_2$ group and resulted in the formation of an anionic P,N chelate with a prochiral carbon atom in [Pd(dmba-*C*,*N*){(*R*)-PCHox^{Ph}-κ^2*P*,*N*}] **2**. Reaction of **2** with [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ led to the unexpected and diastereoselective formation of the dinuclear complex [{Pd(dmba-*C*,*N*)Cl}-(*R*)-{CHPPh$_2$-(*R*)-ox^{Ph}}Pd(dmba-*C*,*N*)] **4** in which a Pd(dmba-*C*,*N*)Cl moiety is directly bonded to the carbon α to the P atom of the anionic P,N chelate of **2**. This results in an unsual zwitterionic structure. In the course of this work, crystals of [(dmba-*C*,*N*)Pd(μ-OH)(μ-Cl)Pd(dmba-*C*,*N*)]·1/2[Pd(dmba-*C*,*N*)-(μ-Cl)]$_2$ **7** were obtained and the single crystal X-ray analyses of complexes **2**, **4**·2THF, **5**·CH$_2$Cl$_2$, [PdCl(Me)-{(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}] **6** and **7** are presented.

Introduction

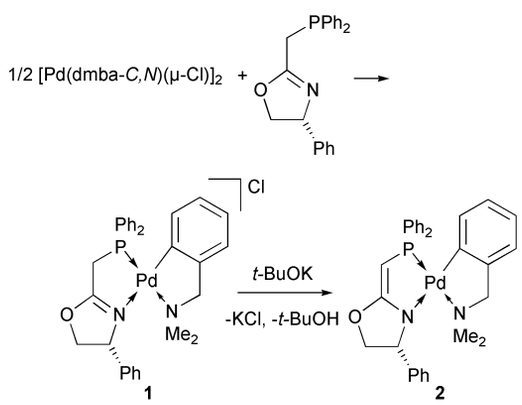
As part of a general research effort in the design of new ligands leading to high reactivity and enantioselectivity in metal-catalysed asymmetric synthesis, oxazoline-based bidentate ligands have proven very valuable, in particular bis(oxazolines) and heterodifunctional ligands like phosphino-oxazolines.[1] Whereas the oxazoline moiety is generally neutral in such ligands, with the nitrogen atom acting as a two-electron donor toward the metal centre, we reported recently the synthesis of Pd(II) and Ru(II) complexes with a new anionic ligand system of type **I**. The corresponding Ru(II) complexes were found to be better catalysts for the transfer hydrogenation of acetophenone in propan-2-ol than related complexes bearing the neutral phosphino-oxazoline ligand.[2] Such a three-electron donor P,N chelate provides an interesting similarity to the P,O phosphino-enolate ligands present in complexes of type **II**. Metal complexes of the latter type were found to be very reactive towards a range of organic[3] or inorganic electrophiles,[4] and display very interesting catalytic properties in ethylene oligomerisation (M = Ni),[5] alkane activation (M = Rh)[6] or in transfer hydrogenation reactions (M = Ru).[7]



We then felt it of interest to explore the behaviour of a chiral, optically pure phosphino-oxazoline ligand, prepare the corresponding phosphino-iminolate palladium complexes and carry out studies on their reactivity towards electrophilic metal complexes.

Results

Starting with D-phenylglycine from the chiral pool, the corresponding new (*R*)-PCH$_2$ox^{Ph} ligand was prepared by following procedures described in the literature for the parent compounds.[8,9] Its reaction with [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ in CH$_2$Cl$_2$ afforded [Pd(dmba-*C*,*N*){(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}]Cl **1** whose deprotonation with *t*-BuOK occurred at the PCH$_2$ carbon (Scheme 1), as expected from previous results with other PCH$_2$-oxazoline or β-ketophosphine ligands chelating a Pd(II) centre.[2,10]



Scheme 1

The resulting complex [Pd(dmba-*C*,*N*){(*R*)-PCHox^{Ph}-κ^2-*P*,*N*}] **2** was characterized (*i*) in the IR by the disappearance of the band around 1635 cm^{-1} assigned to the C=N double bond of the oxazoline moiety in **1**, which is replaced by a new absorption around 1540 cm^{-1} for the *ν*(C⋯C) + *ν*(C⋯N) vibration,[2b] (*ii*) in ^{1}H NMR by a singlet at 3.1 ppm for the PCH proton ($^2J_{PH}$ coupling to phosphorus being accidentally zero) and by diastereotopic OCH$_2$, NMe$_2$ and NCH$_2$ protons, and (*iii*) in ^{31}P{^{1}H} NMR by a singlet at 26.1 ppm. Like in **1**, the chemical shifts of the NMe$_2$ protons are very different ($\Delta\delta$ = 0.9 ppm in **2**). The high field shift experienced by the protons of one of the Me groups corresponds to the group situated above the phenyl group of the oxazoline. This was confirmed by an X-ray diffraction study on **2**. Selected bond distances and angles are given in Table 1 and a view of the structure is shown in Fig. 1.

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Table 1 Selected intramolecular distances (Å) and angles (°) for [Pd(dmba-*C*,*N*){(*R*)-PCHox^{Ph}-κ^2*P*,*N*)}] **2**

Pd–N1	2.135(4)	N1–C16	1.465(5)
Pd–N2	2.167(4)	N2–C29	1.485(5)
Pd–P	2.248(3)	N2–C30	1.493(6)
Pd–C23	2.014(3)	N2–C31	1.491(6)
P–C1	1.833(5)	C13–C14	1.367(5)
P–C7	1.816(4)	C15–C16	1.531(6)
P–C13	1.744(5)	C16–C17	1.522(5)
O–C14	1.378(4)	C23–C28	1.407(6)
O–C15	1.449(6)	C28–C29	1.489(6)
N1–C14	1.336(5)		
N1–Pd–C23	178.6(2)	Pd–N2–C29	104.0(2)
N1–Pd–N2	99.9(2)	C14–O–C15	105.9(3)
N2–Pd–C23	81.3(2)	P–C13–C14	113.1(3)
P–Pd–N1	83.1(1)	N1–C14–C13	126.6(3)
P–Pd–N2	174.1(1)	N1–C14–O	113.7(3)
P–Pd–C23	95.6(2)	N1–C16–C17	114.4(3)
Pd–P–C1	117.0(2)	N1–C16–C15	101.6(3)
Pd–P–C7	116.5(2)	C15–C16–C17	111.6(4)
Pd–P–C13	102.6(2)	O–C15–C16	103.6(3)
C1–P–C7	105.1(2)	Pd–C23–C28	112.1(3)

Estimated standard deviations in the least significant figure are given in parentheses.

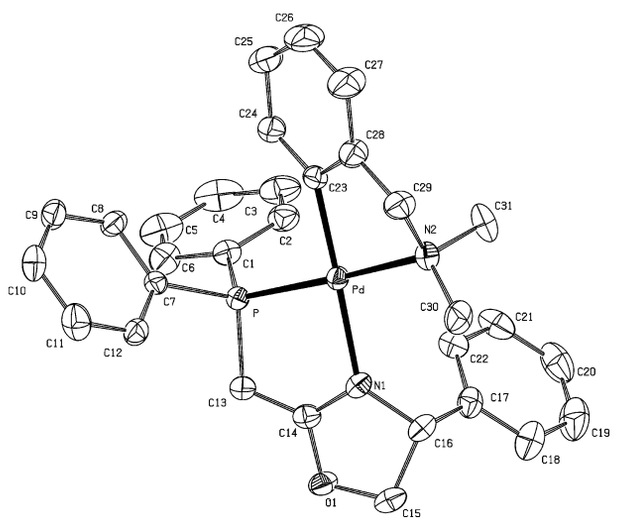
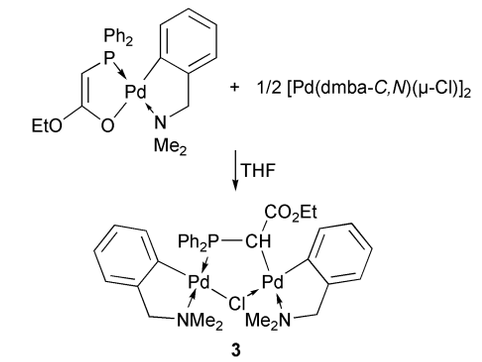


Fig. 1 View of the crystal structure of [Pd(dmba-*C*,*N*){(*R*)-PCHox^{Ph}-κ^2*P*,*N*)}] **2**. Thermal ellipsoids are drawn at the 50% probability level.

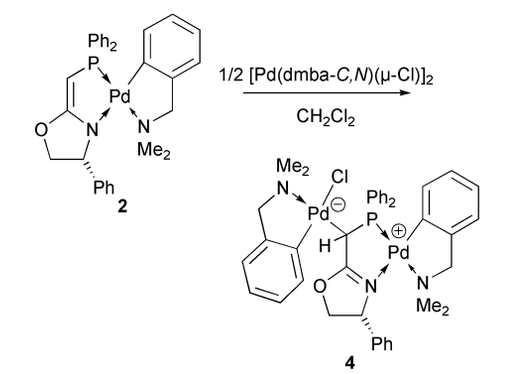
The structure of **2** shows for the P,N chelate a C(13)–C(14) bond distance of 1.367(5) Å, much shorter than the corresponding CH_2–C_{ox} distances of 1.480(4) Å in [$PdCl_2$(PCH_2-ox^{Me2}-κ^2*P*,*N*)][9] or of 1.485(7) Å and 1.493(4) Å in [$PdCl_2$]{(*R*)-PCH_2ox^{Ph}-κ^2*P*,*N*}] **5** and [PdCl(Me){(*R*)-PCH_2ox^{Ph}-κ^2*P*,*N*}] **6**, respectively (see below), thus confirming its partial double bond character. The C(16)–C(17) bond involving the phenyl substituent of the oxazoline moiety makes an angle of 112(1)° with the oxazoline best plane and the dihedral angle between the phenyl ring C(17)–C(22) and the oxazoline planes amounts to 77(1)°.

In order to explore the reactivity of the carbon-carbon formal double bond in the P,N chelate of **2** towards electrophiles, this complex was reacted with [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$. The idea was to compare its reactivity to that of complexes of type **II** (R = OEt) since [Pd(dmba-*C*,*N*){Ph_2PCH=C(=O)OEt-*C*,*N*}] has previously been shown to react with [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ to yield the dinuclear complex **3** which contains a bridging phosphinoenolate ligand (eqn. (1)).[10a,b] Its μ-P,C bonding mode clearly indicated the nucleophilic character of the enolate carbon.

When a mixture of **2** and half an equivalent of [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ was stirred in CH_2Cl_2 for 24 h, a new complex **4** was isolated in high yield (eqn. (2)).



(1)



(2)

Its ^{1}H NMR and ^{31}P NMR data indicated the formation of only one compound, and thus only one diastereoisomer, but these data were not sufficient to conclude about the exact molecular structure of the complex. An X-ray diffraction study was therefore carried out and a view of the structure is shown in Fig. 2 and selected bond distances and angles are given in Table 2.

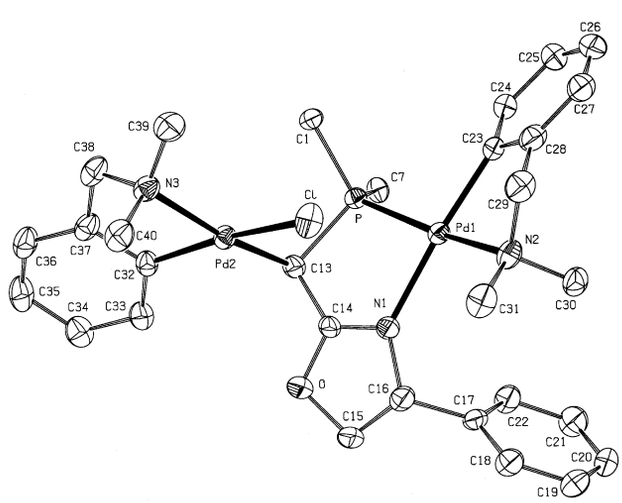


Fig. 2 View of the crystal structure of the dinuclear complex [{Pd(dmba-*C*,*N*)Cl}-(*R*)-{CHPPh_2-(*R*)-ox^{Ph}}Pd(dmba-*C*,*N*)] **4** in **4**·2THF. Thermal ellipsoids are drawn at the 50% probability level. For clarity, only the *ipso* carbons C(1) and C(7) of the phenyl groups at P are shown.

This revealed the formation of a dinuclear complex resulting from a nucleophilic attack of the sp^2 carbon atom C(13), directly bonded to the phosphorus atom of **2**, on the Pd(II) centre of the [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ reagent (eqn. (2)). Although a direct, covalent C(13)–Pd bond is created (2.095(3) Å) from the enolate carbon, as in eqn. (1), the structure of **4** is totally different from that of **3** since the P,N ligand remains a *chelate* instead of becoming a three-electron donor *bridging* ligand. Since the carbon atom C(13) is now covalently bonded to a 14-electron Pd(dmba-*C*,*N*)Cl moiety, a formally zwitterionic structure

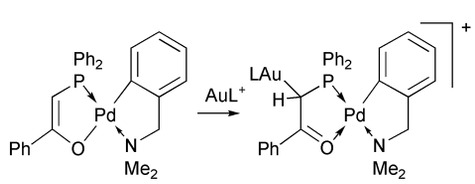
Table 2 Selected intramolecular distances (Å) and angles (°) for [{Pd(dmba-*C*,*N*)Cl}-(*R*)-{CHPPh$_2$-(*R*)-ox^{Ph}}Pd(dmba-*C*,*N*)] **4** in **4**·2THF

Pd1–C23	2.003(4)	N1–C14	1.294(5)
Pd1–N1	2.143(3)	N1–C16	1.472(5)
Pd1–N2	2.176(3)	N3–C38	1.482(5)
Pd1–P	2.2329(9)	O–C14	1.364(4)
Pd2–Cl	2.4342(11)	O–C15	1.446(5)
Pd2–N3	2.153(3)	C13–C14	1.455(5)
Pd2–C13	2.095(3)	C15–C16	1.523(6)
Pd2–C32	1.984(4)	C37–C38	1.486(6)
P–C13	1.827(4)		
C23–Pd1–P	96.10(11)	C32–Pd2–C13	91.43(15)
N1–Pd1–P	82.35(9)	C7–P–C1	103.13(16)
N2–Pd1–P	167.95(9)	C13–P–C1	107.81(16)
N1–Pd1–N2	101.97(13)	C7–P–C13	105.76(16)
C23–Pd1–N1	170.48(14)	C14–N1–Pd1	116.6(2)
C23–Pd1–N2	81.45(15)	C14–N1–C16	107.2(3)
N3–Pd2–Cl	92.46(9)	C38–N3–Pd2	103.8(2)
C32–Pd2–Cl	168.19(11)	C14–C13–Pd2	109.1(2)
C13–Pd2–N3	165.90(13)	P–C13–Pd2	105.28(17)
C32–Pd2–N3	82.91(14)	C14–C13–P	107.6(2)
C13–Pd2–Cl	95.42(10)	N3–C38–C37	110.2(3)

Estimated standard deviations in the least significant figure are given in parentheses.

results. The C(13)–C(14) distance of 1.455(5) Å confirms the single bond character of the C_P–C_{ox} bond (compare with the values of 1.367(5) Å for C_P=C_{Ox} in **2** and 1.480(4) Å for C_P–C_{Ox} in [PdCl$_2$(PCH$_2$ox^{Me2}-κ^2*P*,*N*)][9]). Accordingly, the N_{Ox}=C_{Ox} distance N(1)–C(14) of 1.294(5) Å is significantly shorter than the N_{Ox}–C_{Ox} distance of 1.336(5) Å in **2** and similar to the N_{Ox}=C_{Ox} distance of 1.276(4) Å in [PdCl$_2$(PCH$_2$ox^{Me2}-κ^2*P*,*N*)],[9] thus confirming restoration of its double bond character. The sp^3 character of C(13) is evidenced by the Pd(2)–C(13)–C(14) and P–C(13)–C(14) angles of 109.1(2) and 107.6(2)°, respectively. The C(16)–C(17) bond makes an angle of 123(1)° with the oxazoline best plane and the dihedral angle between the planes containing the phenyl substituent of the oxazoline ring and the oxazoline itself is 80(2)°.

Although one could have envisaged that the C=C double bond of the P,N chelate ligand in **2** would act as a two-electron donor toward the unsatured 14-electron fragment Pd(dmba-*C*,*N*)Cl resulting from splitting of the chloride bridges of [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$, the Pd(2)–C(14) distance is too long (2.935(4) Å) to represent a bonding interaction. The bonding situation in **3** appears unprecedented and contrasts with that observed when related Pd(II) phosphinoenolate complexes were reacted with electrophilic metal complexes. Whereas in these cases metallation of the enolate carbon was also observed, the resulting complexes were either neutral, with a μ-P,C bridge (see eqn. (1)),[10a,b] or cationic, with retention of a P,O chelate (eqn. (3)),[4] but never zwitterionic.



(3)

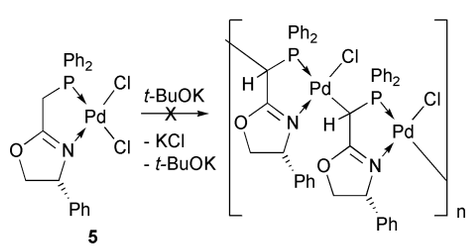
The fact that the metallation reaction of the prochiral carbon atom C(13) in **2** (eqn. (2)) by the bulky Pd(dmba-*C*,*N*)Cl moiety only led to one diastereomer is most likely due to the steric shielding exerted by the phenyl substituent of the oxazoline. The ^{1}H NMR patterns of the CH$_2$ groups in **4** reflect their diastereotopic nature. A detailed assignment of the ^{1}H NMR resonances was made possible through ^{1}H-COSY experiments (see Experimental).

Table 3 Selected intramolecular distances (Å) and angles (°) for [PdCl$_2${(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*)}] **5** in **5**·CH$_2$Cl$_2$

Pd–P	2.210(5)	O–C15	1.464(6)
Pd–N	2.034(7)	O–C14	1.336(6)
Pd–Cl1	2.362(6)	N–C14	1.282(6)
Pd–Cl2	2.292(7)	N–C16	1.481(6)
P–C1	1.794(3)	C13–C14	1.485(7)
P–C7	1.807(6)	C15–C16	1.545(7)
P–C13	1.838(6)	C16–C17	1.519(6)
Cl1–Pd–Cl2	92.84(4)	C14–O–C15	105.4(3)
P–Pd–Cl1	176.25(4)	C14–N–Pd	120.3(3)
P–Pd–Cl2	89.97(4)	C14–N–C16	108.5(4)
N–Pd–Cl1	94.0(2)	C16–N–Pd	130.8(3)
N–Pd–Cl2	173.2(1)	P–C13–C14	106.2(3)
N–Pd–P	83.3(2)	O–C14–C13	118.9(3)
Pd–P–C1	116.0(2)	N–C14–O	117.6(4)
Pd–P–C7	116.1(2)	N–C14–C13	123.5(4)
Pd–P–C13	102.8(2)	N–C16–C15	101.4(3)
C1–P–C7	109.2(2)	N–C16–C17	111.7(3)
C1–P–C13	106.8(2)	C15–C16–C17	114.6(3)
C7–P–C13	104.5(2)		

Estimated standard deviations in the least significant figure are given in parentheses.

The reaction of eqn. (2) triggered an attempt to generate a polymeric structure by deprotonation of the PCH$_2$ group of the neutral complex [PdCl$_2${(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}] **5**, according to eqn. (4).



5 (4)

Whereas the latter complex was readily obtained by reaction of [PdCl$_2$(cod)] with (*R*)-PCH$_2$ox^{Ph}, no product could be characterized by NMR or IR spectroscopy upon reaction with *t*-BuOK.

We then examined a similar reaction with the alkyl complex [PdCl(Me){(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}] **6** with the hope that the 14-electron fragment PdMe{(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*} generated *in situ* by deprotonation would behave differently to PdCl{(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}. Unfortunately, this reaction only yielded a mixture of products which could not be characterized.

For comparative purposes, the structures of **5** and **6** have been determined by X-ray diffraction and selected bond distances and angles are given in Tables 3 and 4 and a view of the structures is shown in Figs. 3 and 4, respectively.

The five-membered ring containing the P,N chelate is almost planar in **5** and **6**. The C(16)–C(17) bond in **5** makes an angle of 115(2)° with the oxazoline moiety and the phenyl substituent makes an angle of 78.7(1)° with the metal coordination plane. Similarly, in complex **6**, the C(16)–C(17) bond makes an angle of 117(2)°. The Pd–Cl(1) distance *trans* to the P atom (2.362(6) Å) in **5** is longer than that *trans* to N (Pd–Cl(2) 2.292(7) Å). These values are similar to those found in [PdCl$_2$(PCH$_2$ox^{Me2}-κ^2*P*,*N*)][9] and are consistent with the higher *trans* influence of the phosphorus donor. Although the spectroscopic data of **5** and **6** are comparable, the PCH$_2$ protons of **6** are accidentally equivalent and appear as a doublet of doublets owing to $^2J_{PH}$ and $^5J_{HH}$ couplings. In general, the assignments of the ^{1}H NMR resonances resulted from ^{1}H-COSY experiments.

In the course of attempts to convert **4** into a complex with both a P,N and a new C_P,O chelate by chloride abstraction with TlPF$_6$, which failed, we isolated a few crystals of a complex, **7**, that did no longer contain phosphorus but was not identical to

Table 4 Selected intramolecular distances (Å) and angles (°) for [PdMe(Cl){(*R*)-PCH_2ox^{Ph}-κ^2P,N)}] **6**

Pd–P	2.199(2)	O–C14	1.340(4)
Pd–N	2.147(3)	O–C15	1.461(4)
Pd–Cl1	2.375(2)	N–C14	1.285(4)
Pd–C23	2.046(3)	N–C16	1.490(4)
P–C1	1.817(3)	C13–C14	1.493(4)
P–C7	1.820(3)	C15–C16	1.553(5)
P–C13	1.849(4)	C16–C17	1.507(5)
Cl1–Pd–C23	93.3(2)	C14–O–C15	105.1(3)
P–Pd–Cl1	173.5(1)	C14–N–Pd	117.0(2)
P–Pd–C23	92.4(2)	C14–N–C16	107.7(3)
N–Pd–Cl1	93.4(1)	C16–N–Pd	135.2(2)
N–Pd–C23	172.8(2)	P–C13–C14	105.5(2)
N–Pd–P	81.1(1)	O–C14–C13	118.0(3)
Pd–P–C1	125.7(2)	N–C14–O	118.6(3)
Pd–P–C7	113.1(2)	N–C14–C13	123.4(3)
Pd–P–C13	102.1(2)	N–C16–C15	101.5(3)
C1–P–C7	103.7(2)	N–C16–C17	111.4(3)
C1–P–C13	106.4(2)	C15–C16–C17	113.9(3)
C7–P–C13	103.6(2)		

Estimated standard deviations in the least significant figure are given in parentheses.

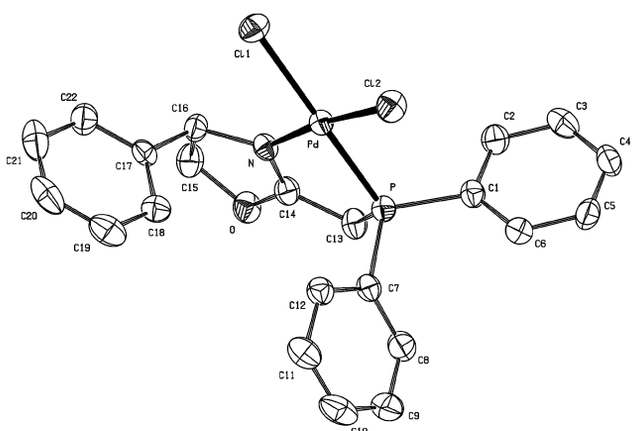


Fig. 3 View of the crystal structure of [$PdCl_2$\{(*R*)-PCH_2ox^{Ph}-κ^2P,N)}] **5** in **5**·CH_2Cl_2. Thermal ellipsoids are drawn at the 50% probability level.

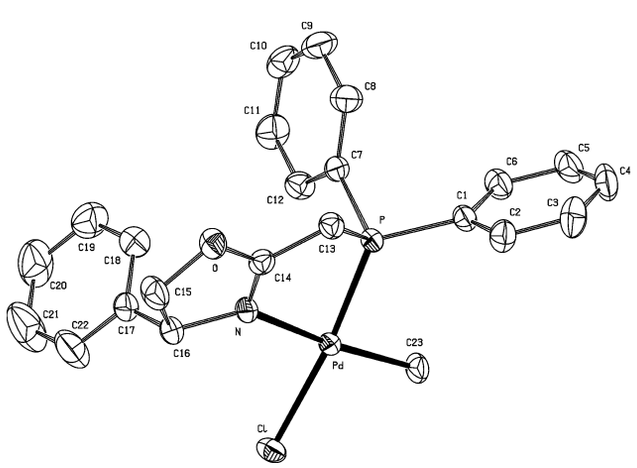


Fig. 4 View of the crystal structure of [PdMe(Cl){(*R*)-PCH_2ox^{Ph}-κ^2P,N)}] **6**. Thermal ellipsoids are drawn at the 50% probability level.

[Pd(dmba-*C*,*N*)(μ-Cl)]$_2$. Unfortunately, we did not obtain enough material to perform complete NMR characterization and elemental analysis on **7**. The structure of this compound could however be determined by X-ray diffraction and revealed the presence of two different dinuclear complexes. Selected bond distances and angles are given in Table 5 and a view of the structure is shown in Fig. 5.

Table 5 Selected intramolecular distances (Å) and angles (°) for [(dmba-*C*,*N*)Pd(μ-OH)(μ-Cl) Pd(dmba-*C*,*N*)]·½[Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ **7**

Pd1–C1	1.965(4)	Pd3–N3	2.068(4)
Pd1–N1	2.076(4)	Pd3–Cl2	2.321(2)
Pd1–Cl1	2.478(2)	Pd3–Cl2a	2.466(2)
Pd1–O	2.041(3)	N1–C7	1.494(6)
Pd2–C10	1.967(5)	N1–C8	1.481(6)
Pd2–N2	2.095(3)	N1–C9	1.485(6)
Pd2–Cl1	2.471(2)	C1–C6	1.403(6)
Pd2–O	2.041(3)	C6–C7	1.498(6)
Pd1–Pd2	3.234(1)	C15–C16	1.510(6)
Pd3–C19	1.972(4)	C24–C25	1.502(7)
C1–Pd1–O	94.9(2)	Pd1–O–Pd2	104.8(2)
C1–Pd1–N1	82.3(2)	Pd1–Cl1–Pd2	81.6(1)
C1–Pd1–Cl1	178.0(2)	C19–Pd3–N3	82.6(2)
N1–Pd1–Cl1	97.6(2)	C19–Pd3–Cl2	95.5(2)
O–Pd1–N1	174.4(2)	C19–Pd3–Cl2a	176.4(2)
O–Pd1–Cl1	85.4(1)	N3–Pd3–Cl2	178.0(2)
C10–Pd2–O	93.9(2)	N3–Pd3–Cl2a	95.8(2)
C10–Pd2–N2	82.9(2)	Cl2–Pd3–Cl2a	86.2(1)
C10–Pd2–Cl1	177.0(2)	Pd3–Cl2–Pd3a	93.8(1)
N2–Pd2–Cl1	97.2(2)	C7–N1–Pd1	106.5(2)
O–Pd2–N2	172.5(2)	C16–N2–Pd2	107.5(3)
O–Pd2–Cl1	85.6(1)	C27–N3–Pd3	112.2(3)

Estimated standard deviations in the least significant figure are given in parentheses.

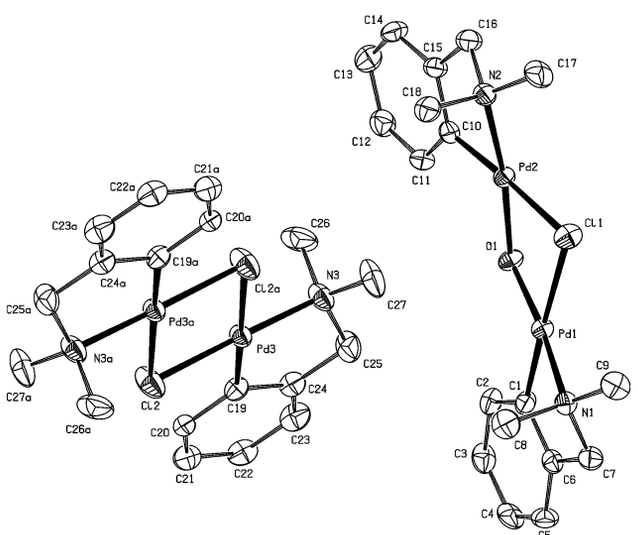


Fig. 5 View of the crystal structure of the two dinuclear palladium complexes present in [(dmba-*C*,*N*)Pd(μ-OH)(μ-Cl)Pd(dmba-*C*,*N*)]·½[Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ **7**. Thermal ellipsoids are drawn at the 50% probability level.

The crystal contains a 2 : 1 mixture of [(dmba-*C*,*N*)Pd-(μ-OH)(μ-Cl)Pd(dmba-*C*,*N*)] and *trans*-[Pd(dmba-*C*,*N*)(μ-Cl)]$_2$, with the latter complex surrounded centrosymmetrically by two [(dmba-*C*,*N*)Pd(μ-OH)(μ-Cl)Pd(dmba-*C*,*N*)] molecules. The unexpected presence of the latter complex in [(dmba-*C*,*N*)Pd(μ-OH)(μ-Cl)Pd(dmba-*C*,*N*)]·½[Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ **7**, most likely results from traces of adventitious water. During work-up, the phosphino-oxazoline moiety which was present in **4** has been eliminated as the pentane soluble fraction. Despite the unsatisfactory mode of obtention of **7**, we believe that this structure is of interest since (*i*) the complex [(dmba-*C*,*N*)Pd)-(μ-OH)(μ-Cl)Pd(dmba-*C*,*N*)] does not seem to have been reported before (it was not found in the CCDC data base), although the bromine analog is known,[11] (*ii*) the roof-like structure of [(dmba-*C*,*N*)Pd)(μ-OH)(μ-Cl)Pd(dmba-*C*,*N*)] (dihedral angle between the Pd coordination planes = 21.47(1)°) contrasts with the *trans*, centrosymmetric structure of the [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ molecule, and (*iii*) the cocrystallisation of the two different dinuclear molecules generates an original packing in

the solid state. The Pd–Cl bond distances are significantly different in [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$, the longer being *trans* to the carbon atom C(19) of larger *trans* influence than nitrogen, whereas the Pd(3)–Cl(2′) and Pd(3′)–Cl(2) distances, both *trans* to a σ-bonded carbon atom, are almost identical and similar to the Pd(1)–Cl(1) or Pd(2)–Cl(1) distances.

In conclusion, we have shown that Pd(II) complexes with the three-electron donor anionic P,N chelate derived from the ligand (*R*)-PCH$_2$ox^{Ph} are readily available. Despite their similarity with complexes of type **II** which contain a three-electron donor P,O phosphinoenolate chelate, their nucleophilic reactivity can lead to novel structures not encountered previously, as exemplified in the case of the dinuclear zwitterionic complex **4**.

Experimental

General

All experiments were conducted under an atmosphere of dry nitrogen using Schlenk techniques. Solvents were freshly distilled under nitrogen from appropriate drying agents before use. NMR-measurements: ^{1}H at 300 MHz and ^{31}P at 121.5 MHz referenced to external H_3PO_4 using a Bruker ARX 300 or Avance 500 instrument (chemical shifts in ppm downfield from $SiMe_4$, coupling constants in Hz).

Syntheses

D-Phenylglycinol, the corresponding oxazoline and the phosphino-oxazoline ligand (*R*)-PCH$_2$ox^{Ph} were prepared by adapting procedures described for the parent ligand,[8,9] and [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ was synthesized according to the literature.[12]

[Pd(dmba-*C*,*N*){(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}]Cl 1. In a 100 ml Schlenk flask were placed together the phosphino-oxazoline ligand (*R*)-PCH$_2$ox^{Ph} (3.50 g, 10.5 mmol) and [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ (2.80 g, 5.07 mmol) in 50 mL CH_2Cl_2. The pale yellow solution was stirred for 1 h and the volume was reduced under vacuum to about 5 mL. Addition of hexane led to the precipitation of a light yellow oil which was triturated with diethyl ether, affording a solid that was washed with hexane and dried *in vacuo*. The product was obtained as a light yellow powder (4.40 g, yield 70%). Calc. for $C_{31}H_{32}ClN_2OPPd$: C, 59.92; H, 5.19; N, 4.51. Found: C, 59.99; H, 5.21; N, 4.38%. ^{1}H NMR (500.13 MHz, $CDCl_3$, 263 K): δ 1.90 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3), 3.36 (dd, B part of an ABX spin system (X = P), 1 H, NC*H*H, $^2J_{HH}$ = 13.5 Hz, $^4J_{PH}$ = 3.5 Hz), 3.71 (dd, B part of an ABX spin system (X = P), 1 H, PC*H*H, $^2J_{HH}$ = 16.5 Hz, $^2J_{PH}$ = 13.8 Hz), 4.03 (dd, A part of an ABX spin system, 1 H, PCH*H*, $^2J_{HH}$ = 16.5 Hz, $^2J_{PH}$ = 8 Hz), 4.10 (t, 1 H, OC*H*H, $^2J_{HH}$ = $^3J_{HH}$ = 9 Hz), 4.52 (d, A part of an ABX spin system, 1 H, NC*H*H, $^2J_{HH}$ = 13.5 Hz, $^4J_{PH}$ = 0 Hz), 5.18 (t, 1 H, OCH*H*, $^2J_{HH}$ = $^3J_{HH}$ = 9 Hz), 5.83 (t, 1 H, NC*H*Ph, $^3J_{HH}$ = 9 Hz), 6.41–8.18 (m, 19 H, aromatic H). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 35.3 (s).

[Pd(dmba-*C*,*N*){(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}]PF$_6$. This complex was prepared in order to facilitate the assignment of the ^{1}H NMR resonances of **1** by preventing dynamic recoordination of the Cl ligand. Solid $TlPF_6$ (0.130 g, 1.15 equiv.) was added to a CH_2Cl_2 solution (10 mL) of **1** (0.200 g, 0.32 mmol) and the reaction mixture was stirred for 0.5 h and then filtered. The filtrate was evaporated under reduce pressure and afforded a pale orange powder that was washed with pentane (2 × 5 mL) and dried under vacuum (0.215 g, yield 91%). Calc. for $C_{31}H_{32}F_6N_2OP_2Pd$: C, 50.94; H, 4.41; N, 3.83. Found: C, 50.86; H, 4.30; N, 3.83%. ^{1}H NMR (500.13 MHz, $CDCl_3$, 292 K): δ 1.88 (d, 3H, NCH_3, $^4J_{PH}$ = 2 Hz), 2.94 (d, 3H, NCH_3, $^4J_{PH}$ = 4 Hz), 3.35 (dd, B part of an ABX spin system (X = P), 1 H, NC*H*H, $^2J_{HH}$ = 13.5 Hz, $^4J_{PH}$ = 4 Hz), 3.56 (dd, B part of an ABX spin system (X = P), 1 H, PC*H*H, $^2J_{HH}$ = 17.5 Hz, $^2J_{PH}$ = 14 Hz), 3.85 (dd, A part of an ABX spin system, 1H, PCH*H*, $^2J_{HH}$ = 17.5 Hz, $^2J_{PH}$ = 8 Hz), 4.20 (t, 1 H, OC*H*H, $^2J_{HH}$ = $^3J_{HH}$ = 8 Hz), 4.59 (d, A part of an ABX spin system, 1H, NCH*H*, $^2J_{HH}$ = 13.5 Hz, $^4J_{PH}$ = 0 Hz), 5.17 (dd, 1 H, OCH*H*, $^2J_{HH}$ = 8 Hz, $^3J_{HH}$ = 10.5 Hz), 5.63 (dd, 1 H, NCHPh, $^3J_{HH}$ = 10.5 and 8 Hz), 6.49–8.25 (m, 19 H, aromatic H). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 37.0 (s), 157.4 (sept., PF_6).

[Pd(dmba-*C*,*N*){(*R*)-PCHox^{Ph}-κ^2*P*,*N*}] 2. To [Pd(dmba-*C*,*N*)-{(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*)}Cl **1** (1.20 g, 1.93 mmol) in THF (50 mL) was added *t*-BuOK (0.220 g, 1.95 mmol) and the mixture was stirred overnight. The deep orange solution was evaporated and the remaining solid was dissolved in 10 mL of CH_2Cl_2 and filtered over Celite. Hexane was added to precipitate an orange powder (0.680 g, yield 60%). X-Ray quality crystals were obtained by slow diffusion of pentane into a CH_2Cl_2 solution. Calc. for $C_{31}H_{31}N_2OPPd$: C, 63.65; H, 5.34; N, 4.79. Found: C, 64.09; H, 5.39; N, 4.71%. ^{1}H NMR (300 MHz, CD_3Cl): δ 1.8 (s, 3H, NCH_3), 2.7 (s, 3H, NCH_3), 3.1 (1H, s, PCH), 3.2 (d, 1H, B part of an AB spin system, NC*H*H, $^2J_{HH}$ = 16 Hz), 4.1 (d, 1H, OC*H*H, $^2J_{HH}$ = 8 Hz), 4.4 (d, 1H, A part of an AB spin system, NCH*H*, $^2J_{HH}$ = 16 Hz), 4.6 (t, 1H, OCH*H*, $^2J_{HH}$ = $^3J_{HH}$ = 8 Hz), 5.0 (d, 1H, C*H*Ph, $^3J_{HH}$ = 8 Hz), 6.4–7.9 (m, 19H, aryl H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 26.1 (s).

[{Pd(dmba-*C*,*N*)Cl}-(*R*)-{CHPPh$_2$-(*R*)-ox^{Ph}}Pd(dmba-*C*,*N*)] 4. To a solution of **2** (0.250 g, 0.426 mmol) in CH_2Cl_2 (10 mL) was added [Pd(dmba-*C*,*N*)(μ-Cl)]$_2$ (0.117 g, 0.213 mmol) and the mixture was stirred overnight. The orange solution turned yellow and after concentration under vacuum, hexane was added to precipitate a light yellow powder. X-Ray quality crystals were obtained by slow diffusion of pentane into the CH_2Cl_2 solution. The NMR spectra showed the formation of only one diastereomer (0.311 g, yield 85%). Calc. for $C_{40}H_{43}ClN_3OPPd_2$: C, 55.80; H, 5.03; N, 4.88. Found: C, 55.70; H, 5.12; N, 4.75%. IR (CH_2Cl_2): 1585 sh, 1572 vs, 1446 m, 1435 m cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) (see numbering of the Pd atoms on Fig. 2): δ 1.67 [s, 3H, NCH_3 (Pd(1))], 2.37 [s, 3H, NCH_3 (Pd(2))], 2.53 [s, 3H, NCH_3 (Pd(2))], 2.92 [s, 3H, NCH_3 (Pd(1))], 3.15 [dd, B part of an ABX spin system (X = P), 1H, NC*H*H (Pd(1)), $^2J_{HH}$ = 14 Hz, $^4J_{PH}$ = 3 Hz], 3.46 [d, B part of an AB spin system, 1H, NC*H*H (Pd(2)), $^2J_{HH}$ = 10 Hz], 3.49 [d, A part of an AB spin system, 1H, NCH*H* (Pd(2)), $^2J_{HH}$ = 10 Hz], 3.65 (d, 1H, PCH, $^2J_{PH}$ = 13 Hz), 3.95 (t, 1H, OC*H*H, $^2J_{HH}$ = $^3J_{HH}$ = 9 Hz), 4.80 (d, A part of an ABX spin system, 1H, NCH*H* (Pd(1)), $^2J_{HH}$ = 14 Hz, $^4J_{PH}$ = 0 Hz), 4.89 (t, 1H, OCH*H*, $^2J_{HH}$ = $^3J_{HH}$ = 9 Hz), 5.26 (t, 1H, NC*H*Ph, $^3J_{HH}$ = 9 Hz), 6.5–8.2 (m, 28H, aryl H). ^{31}P{^{1}H} NMR (121.5 MHz, $CHCl_3$): δ 44.2 (s).

[PdCl$_2${(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}] 5. To a solution of (*R*)-PCH$_2$ox^{Ph} (0.100 g, 0.30 mmol) in CH_2Cl_2 (10 mL) was added [$PdCl_2$(COD)] (0.082 g, 0.30 mmol) in CH_2Cl_2 (10 mL) and the orange mixture was stirred for 1 h. The solvent was removed under reduced pressure, the residue was washed twice with Et_2O, redissolved in CH_2Cl_2 (10 mL) and the solution was carefully layered with Et_2O. This afforded a yellow powder, which was dried *in vacuo* (0.127 g, yield 83%). X-Ray quality crystals were obtained by slow diffusion of pentane into a CH_2Cl_2 solution. Calc. for $C_{22}H_{20}Cl_2NOPPd$: C, 50.55; H, 3.86; N, 2.68. Found: C, 50.9; H, 3.79; N, 2.51%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.45 (dd, B part of an ABX spin system (X = P), 1H, PC*H*H, $^2J_{HH}$ = 18.7 Hz, $^2J_{PH}$ = 13.5 Hz), 3.97 (dd, A part of an ABX spin system, 1H, PCH*H*, $^2J_{HH}$ = 18.7 Hz, $^2J_{PH}$ = 8 Hz), 4.63 (dd, 1H, OC*H*H, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 4.5 Hz), 5.08 (t, 1 H, OCH*H*, $^2J_{HH}$ = $^3J_{HH}$ = 9 Hz), 5.60 (m, 1H, NCHPh, $^3J_{HH}$ = 9 Hz), 7.00–7.95 (m, 15 H, aryl H). ^{31}P{^{1}H} NMR ($CHCl_3$): δ 24.9 (s).

[PdCl(Me){(*R*)-PCH$_2$ox^{Ph}-κ^2*P*,*N*}] 6. To a solution of [PdCl(Me)(cod)] (0.400 g, 1.51 mmol) in CH_2Cl_2 was added a

Table 6 Crystallographic data

	2	**4**·2THF	**5**·CH_2Cl_2	**6**	**7**
Formula	$C_{31}H_{31}N_2OPPd$·$2CH_2Cl_2$	$C_{40}H_{43}ClN_3OPPd_2$·(C_4H_8O)	$C_{22}H_{20}Cl_2NOPPd$·CH_2Cl_2	$C_{23}H_{23}ClNOPPd$	$C_{27}H_{37}Cl_2N_3OPd_3$
M_w	751.78	1005.20	607.59	502.24	809.70
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P\bar{1}$
T/K	173	193	173	173	173
a/Å	9.011(3)	10.545(1)	8.541(5)	10.998(5)	9.540(5)
b/Å	15.511(3)	17.361(1)	13.825(5)	8.647(5)	12.370(5)
c/Å	23.932(3)	24.6940(10)	20.676(5)	12.017(5)	13.327(5)
α/°					84.288(5)
β/°				107.690(5)	82.088(5)
γ/°					70.423(5)
V/Å^3	3344.9(14)	4520.8(5)	2441.4(18)	1088.8(9)	1465.3(11)
Z	4	4	4	2	2
D_c/g cm^{-3}	1.493	1.477	1.653	1.532	1.835
Radiation, λ(Mo-Kα)/Å	0.71073	0.71070	0.71073	0.71073	0.71073
μ/mm^{-1}	0.951	0.934	1.280	1.062	2.028
No. reflections measured	14455	34396	5580	5518	6670
No. reflections [$I > 2\sigma(I)$]	10434	10932	4479	5076	5146
Residuals R, R_w	0.0639, 0.1277	0.0413, 0.1107	0.0307, 0.0635	0.0277, 0.0737	0.0360, 0.0917
GOF	1.006	1.03	0.754	0.807	0.947
Flack parameter	0.00(3)	−0.01(2)	−0.03(3)	−0.02(2)	—
$\rho_{max,\ min}$/e Å^{-3}	1.038, −1.355	1.25, −0.74	0.641, −0.677	0.421, −0.845	0.766, −1.197

solution of (*R*)-PCH_2ox^{Ph} (0.575 g, 1.1 equiv.) and the mixture was stirred for 2 h. The solvent was evaporated under reduced pressure to yield a yellow–orange solid which was washed with 10 mL of Et_2O and 2 × 10 mL of pentane (0.652 g, yield 86%). X-Ray quality crystals were obtained by slow evaporation of a CH_2Cl_2 solution of the complex in hexane. Calc. for $C_{23}H_{23}ClNOPPd$: C, 55.00; H, 4.62; N, 2.79%. Found: C, 55.20; H, 4.59; N, 2.60%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.55 (d, 3H, $PdCH_3$, $^3J_{PH}$ = 3 Hz), 3.39 (dd, 2H, PCH_2, $^2J_{PH}$ = 10 Hz, $^5J_{HH}$ = 1 Hz), 4.48 (dd, 1H, OC*H*H, $^2J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 5 Hz), 4.78 (dd, 1H, OCH*H*, $^2J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 10 Hz), 5.47 (m, 1H, C*H*Ph), 7.11–7.80 (m, 15H, aryl H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.80 (s).

X-Ray data collection

Single crystals were selected and mounted on a Kappa CCD diffractometer. The relevant data are summarized in Table 6. Data were collected using phi-scans and the structure was solved using direct methods and refined against F^2 using the SHELX 97 software.[13,14] No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C–H}$ = 0.95 Å, U_{11} = 0.04).

CCDC reference numbers 200357–200361.

See http://www.rsc.org/suppdata/dt/b3/b300321n/ for crystallographic files in CIF or other electronic format.

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