Journal of Organometallic Chemistry 693 (2008) 3932–3938

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Palladium complexes of 8-(di-*tert*-butylphosphinooxy) quinoline

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ARTICLE INFO

Article history:
Received 21 July 2008
Received in revised form 1 October 2008
Accepted 2 October 2008
Available online 8 October 2008

Keywords:
Palladium organometallic complexes
Phosphinito–quinoline ligands
Solution and solid state structure
Suzuki–Miyaura reaction

ABSTRACT

The preparation of the new ligand 8-(di-*tert*-butylphosphinooxy)quinoline (**1**) and the palladium derivatives $[PdCl_2(\mathbf{1})]$ (**2**), $[Pd(\eta^3\text{-all})(\mathbf{1})]^+$ [all = C_3H_5 (**3a**), 1-PhC_3H_4 (**3b**) and 1,3-$Ph_2C_3H_3$ (**3c**)] and $[Pd(\eta^2\text{-ol})(\mathbf{1})]$ [ol = dimethyl fumarate (**4a**) and fumaronitrile (**4b**)] is reported. The cationic species **3a**–**3c** have been isolated as BF_4^- salts. The complex **3a**(BF_4) is obtained either from the reaction of **1** with $[Pd(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)]_2$ or from the reaction of $ClP(CMe_3)_2$ with $[Pd(\eta^3\text{-}C_3H_5)(8\text{-oxyquinoline})]$, followed in both cases by chloride abstraction with $NaBF_4$. In the complexes, the ligand **1** is P,N chelated to the central metal, as shown by the X-ray structural analysis of **3a**(BF_4). At 25 °C in solution, **3a**(BF_4) and **3b**(BF_4) undergo a fast $\eta^3-\eta^1-\eta^3$ dynamic process which brings about a *syn–anti* exchange only for the allylic protons *cis* to phosphorus, while for **4a** and **4b** a slow rotation of the olefin around its bond axis to palladium takes place. The complexes **2** and **3a**(BF_4) are efficient catalyst precursors in the coupling of the phenylboronic acid with aryl bromides and chlorides.

1. Introduction

As a new generation of exceedingly active catalysts has become available in the last decade, the palladium- or nickel-catalyzed coupling of aryl halides with arylboronic acids (Suzuki–Miyaura reaction) has gained an enormous importance as synthetic tool in organic chemistry [1]. Despite the increasing number of reports dealing with catalytic systems able to promote various couplings such as Heck, Stille, Suzuki–Miyaura and Sonogashira reactions there is a continuing interest in the design of new catalysts for these reactions. In particular, the use of P,O, P,N or P,S chelating ligands is a very attractive approach because during the catalytic cycle the metal centre needs to house in its coordination sphere a certain number of species which differ in their coordination ability. The use of bidentate ligands in Suzuki-Miyaura has been recently reviewed [2]. Accordingly, our work has been focused on the study of the synthetic utility of palladium species containing P,N ligands. We have recently shown that iminophosphine–palladium(0) complexes are very efficient catalysts for the Suzuki–Miyaura reaction between arylboronic acid and aryl bromides [3]. However, they were unable to catalyzed the same reaction with aryl chlorides. On the other hand, the coupling of aryl chlorides with arylboronic acid, was reported to be catalyzed by palladium phosphinite complexes [4] and, more efficiently, by palladium complexes with sterically hindered phosphine [5]. These findings prompted us to synthesize new P,N bidentate ligands which would combined both the presence of bulky substituents on the phosphorus atom and the chelating ability towards palladium through a nitrogen-donor moiety. Herein, we report the preparation of a ligand of this type, namely the 8-(di-*tert*-butylphosphinooxy)quinoline, and of some palladium(II) and palladium(0) complexes as possible candidates for catalytic application in the Suzuki–Miyaura coupling.

2. Results and discussion

2.1. Preparation of the ligand and palladium complexes

The 8-(di-*tert*-butylphosphinooxy)quinoline **1** and the palladium derivatives **2**–**4** have been prepared according to reactions (1)–(5) of Scheme 1.

The ligand **1** contains a phosphinito group and, like other phosphinites [6], is rather unstable as it decomposes quickly even when stored at −20 °C under N_2 atmosphere. This prevented any further purification and characterization by elemental analysis. Nevertheless, as shown by ^1H and $^{31}P\{H^1\}$ NMR spectroscopy, the raw product is sufficiently pure to be used as such in the reactions (2) and (3). On the other hand, **1** is stabilized upon coordination so that the complexes **2, 3** and **4** appear thermally stable and no decomposition was observed after prolonged time at ambient temperature both in the solid state and in solution. P,N ligands with an 8-oxyquinoline group have already been studied [7], but, to the best of

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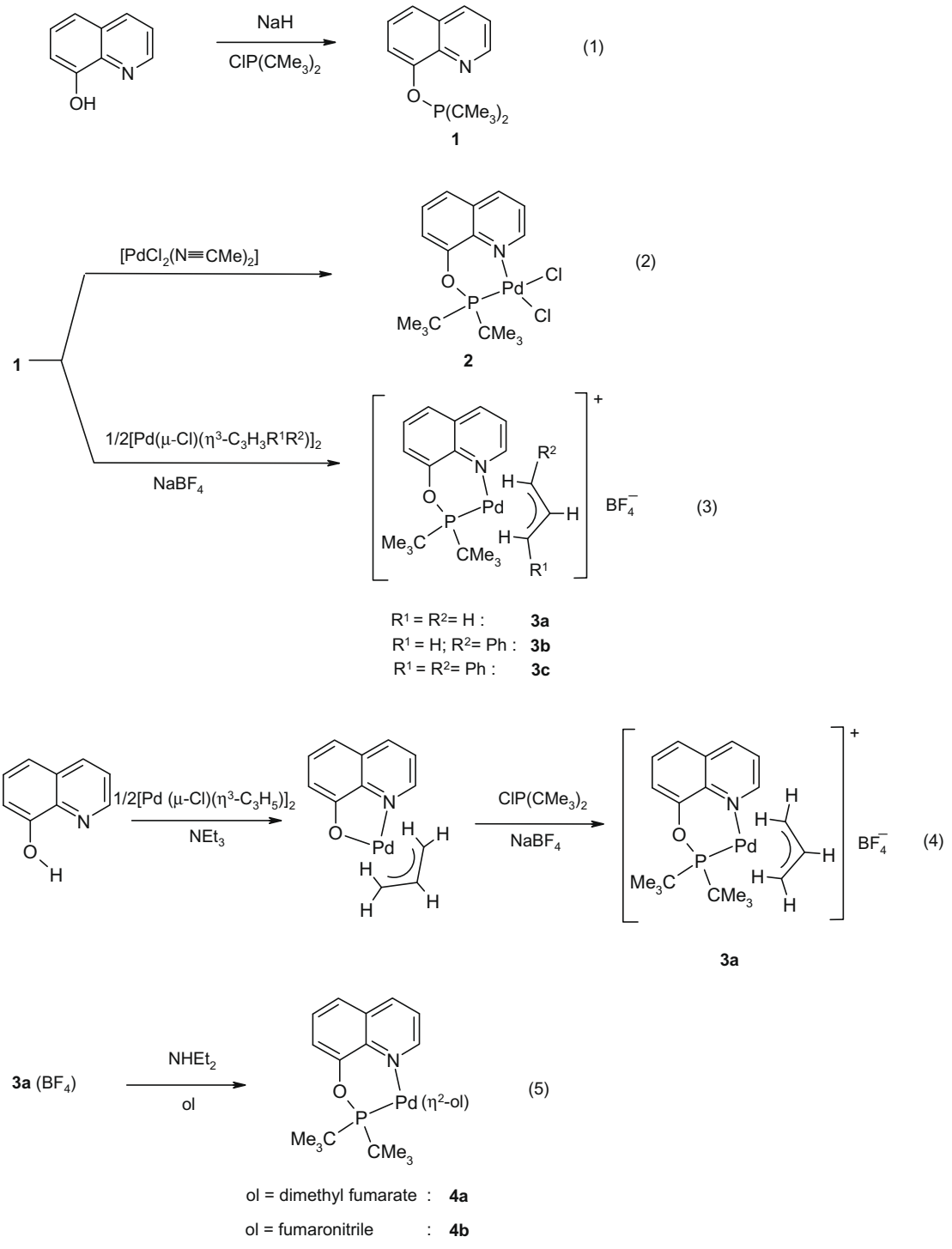
doi:10.1016/j.jorganchem.2008.10.001



Scheme 1.

our knowledge, this is the first example of a phosphinito–quinoline compound.

The cationic complex **3a** may also be prepared according to the reaction sequence (4). In the first step, the reaction of 8-hydroxyquinoline with $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ in the presence of NEt_3 (in the 1:0.5:2 molar ratio) yields the neutral product $[Pd(\eta^3\text{-}C_3H_5)(8\text{-oxyquinoline})]$, isolated and characterized by elemental analysis and ^1H NMR spectroscopy. In the second step, upon addition of $ClP(CMe_3)_2$ (Pd/chlorophosphine 1:1 molar ratio) the complex **3a** is readily formed through a reaction which involves rupture of the P–Cl bond and insertion of the phosphorus atom into the Pd–O bond. The complexes **3a**–**3c** are isolated as BF_4^- salt, and their ionic nature is confirmed by conductivity measurements in CH_2Cl_2 solution. In line with a similar reaction previously reported for cationic η^3-allylpalladium(II) complexes [8], **3a** reacts with $NHEt_2$ in the presence of activated olefins to give the palladium(0) derivatives **4a** and **4b** [reaction (4) of Scheme 1].

The IR spectrum of **2** in the solid state shows two *ν(Pd–Cl)* bands at 339 and 277 cm^{-1}, respectively, in accord with the presence of two *cis* chloride ligands. As suggested by the downfield shifts of

the ^{1}H NMR signal of the H(2) quinoline proton and of the ^{31}P NMR signal upon coordination (Table 1), the 8-(di-*tert*-butylphosphinooxy)quinoline acts as a P,N-bidentate ligand in its complexes. The chelating nature of **1** is clearly indicated by the X-ray structural analysis of **3a**(BF_4) (*vide infra*). For **4a** and **4b** a planar structure is proposed with the olefin carbons lying in the P–Pd–N coordination plane, as found for [Pd(η^2-ol)(P–N)] (ol = fumaronitrile, P–N = iminophosphine) [9].

2.2. Solution behaviour

From the coupling constant values of the allylic protons in the ^{1}H NMR spectra (Table 1) it appears that in solution the allyl ligands of **3b** and **3c** assume a configuration with the phenyl substituents in *syn* position [10]. For the 1-phenylallyl complex **3b**, two geometrical isomers are possible depending on the position of the phenyl group relative to the P,N donor atoms of the ligand **1**. In $CDCl_3$ solution, only the isomer with the phenyl group *trans* to the phosphorus atom is present. The structural assignment is based on the J(PH) value of 10.1 Hz for the allylic *anti* proton *trans* to phosphorus [10] and on the marked shielding of the H(2), H(3) and H(4) quinoline protons (as compared to the resonances of the corresponding protons in **3a**) caused by the aromatic ring currents of the phenyl substituent in close proximity. Consistently, comparable shielding are observed for the 1,3-diphenylallyl complex **3c**, where the *syn* phenyl group (*trans* to phosphorus) is close to the H(2), H(3) and H(4) quinoline protons.

In the ^{1}H NMR spectra of **3a** and **3b** at 25 °C, the H_{syn} and H_{anti} signals of the allylic CH_2 terminus *cis* to phosphorus coalesce into a broad singlet, while the CH_3 signals of the diastereotopic *tert*-butyl groups appear as a doublet. These spectral features can be rationalized by a fast $\eta^3-\eta^1-\eta^3$ rearrangement of the allyl ligand through initial rupture of the Pd–C_{all} bond *trans* to phosphorus [10,11], which brings about the interconversion of the *syn* and *anti* protons of the allylic CH_2 unit and the formation of a time-averaged plane of symmetry on the P–Pd–N coordination plane when the η^3-bound allyl complex is reformed (Scheme 2).

For **3a** in CD_2Cl_2, such a dynamic process cannot be frozen even at –35 °C, the lowest temperature explored. At this temperature, however, the *anti* proton of the allylic CH_2 group *cis* to phosphorus appears as a slightly broad doublet at 2.70 ppm and the *syn* proton as a slightly broad singlet at 3.97 ppm, while the CH_3 protons of the *tert*-butyl groups resonate as two doublets at 1.41 and 1.36 ppm, respectively. For 3c, the $\eta^3-\eta^1-\eta^3$ rearrangement is much slower, if it occurs, and in this case the CH_3 resonances of the *tert*-butyl groups are detected as two distinct doublets in the ^{1}H NMR spectrum at 25 °C.

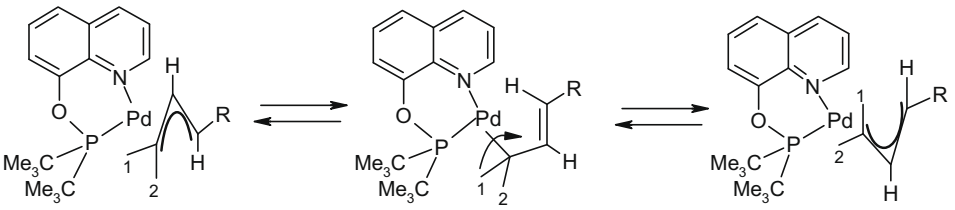
As far as the solution behaviour of the palladium(0) derivatives **4a** and **4b** is concerned, it is well known that the related complexes [Pd(η^2-ol)(P–N)] (ol = activated olefin, P–N = P,N chelating ligand) undergo various dynamic process, such as olefin dissociation–association or olefin rotation or P,N ligand site exchange through initial breaking of the Pd–N bond [8,12]. The ^{1}H NMR spectra of **4a** and **4b** in toluene-d_8 solution show a progressive broadening and loss of fine structure for the olefin protons signals on raising the temperature from 25 to 100 °C. However, no appreciable broadening is observed for the $P(CMe_3)_2$ signals which remain a sharp doublet of doublets throughout the temperature range (Fig. 1).

These spectral changes are clearly due to interconversion of the olefin protons, and can be accounted for only by a rotation

Table 1
Selected ^{1}H and ^{31}P{^{1}H} NMR data.[a]

Compound	Ligand **1** protons				Allyl protons		Olefin protons		^{31}P resonances
	H(2)	H(3)	H(4)	CH_3	H_{syn}	H_{anti}	H[b]	H[c]	
1	8.95 dd	7.5–7.3[d]	8.11 dd	1.30d *J*(PH) = 11.9					161.2 s
2	10.35 dd	7.8–7.6[d]	8.53 dd	1.65 d *J*(PH) = 16.3					169.7 s
3a	9.68 dd	7.7–7.5[d]	8.55 dd	1.40 d *J*(PH) = 15.6	5.24 dd [b] *J*(HH)[e] = 6.5 *J*(PH) = 7.7 3.35 s(br)[c,f]	4.43 dd [b] *J*(HH)[e] = 14.4 *J*(PH) = 9.8 3.35 s(br)[c,f]			191.4 s
3b	8.55 dd	6.85 dd	8.27 dd	1.45 d *J*(PH) = 15.7	3.51 s(br)[c,f]	5.94 dd[b] *J*(HH)[e] = 13.7 *J*(PH) = 10.1 3.51 (br)[c,f]			192.0 s
3c	8.87 dd	6.77 dd	8.11 dd	1.43 d *J*(PH) = 15.5 0.95 d *J*(PH) = 15.5		6.01 dd[b] *J*(HH)[e] = 12.8 *J*(PH) = 9.9 5.05 d[c] *J*(HH)[e] = 11.0			185.4 s
4a	9.50 dd	7.6–7.4[d]	8.30 dd	1.40 d *J*(PH) = 14.2 1.24 d *J*(PH) = 14.1			3.59 dd *J*(HH) = 9.9 *J*(PH) = 9.9	4.31 dd *J*(HH) = 9.9 *J*(PH) = 3.0	196.4 s
4b	9.49 dd	7.7–7.5[d]	8.41 dd	1.40 d *J*(PH) = 14.4 1.38 d *J*(PH) = 14.6			2.54 dd *J*(HH) = 9.6 *J*(PH) = 9.6	3.44 dd *J*(HH) = 9.6 *J*(PH) = 3.4	195.7 s

[a] In $CDCl_3$ at 25 °C; satisfactory integration values were obtained; coupling constants in Hz; the numbering H(2), H(3) and H(4) refers to the hydrogen atoms in position 1, 2 and 3, respectively, on the 8-quinolyl group.
[b] *trans* to phosphorus.
[c] *cis* to phosphorus.
[d] Overlapping multiplets.
[e] Coupling constant with the central allyl proton.
[f] Coalescing signals.



Scheme 2.

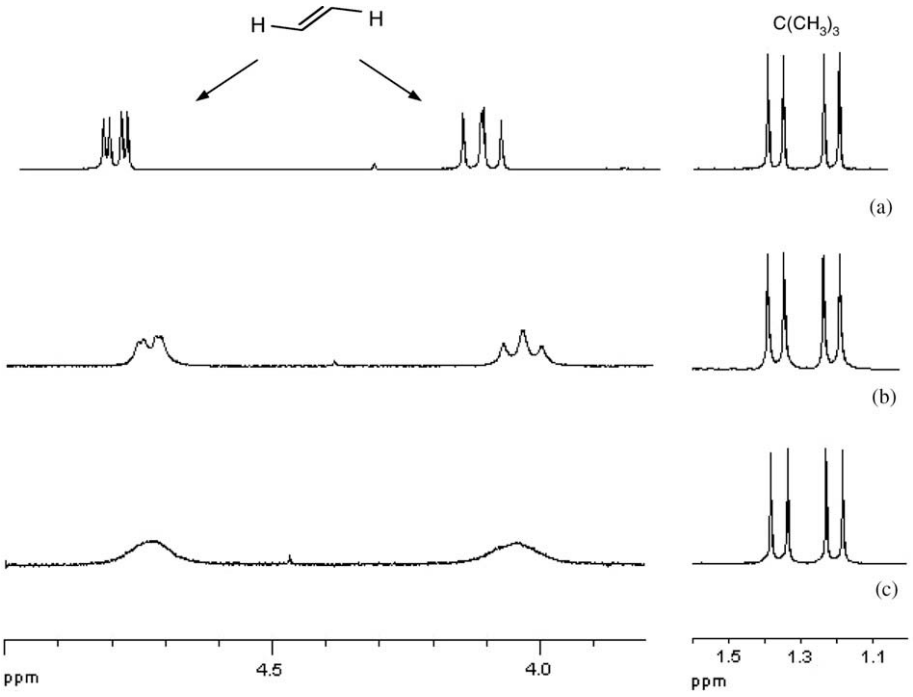


Fig. 1. ^{1}H NMR spectra of complex **4a** in toluene-d_8 at different temperatures: (a) 300 K; (b) 330 K and (c) 350 K.

of the η^2-olefin around its bond axis to the central metal. The other dynamic processes, if they occur, would cause a progressive broadening of the $P(CMe_3)_2$ signals and, eventually, their coalescence into one doublet either by formation of a time-averaged plane of symmetry on the P–Pd–N coordination plane (olefin dissociation–association) or by interconversion of the *tert*-butyl groups (P,N ligand site exchange). The lack of dissociation processes implies the presence of rather strong Pd–N and Pd–olefin bonds in **4a** and **4b.**

2.3. X-ray structure of ***3a***(BF_4)

The solid-state structure of the η^3-allyl complex **3a**(BF_4) has been determined by X-ray diffraction analysis in order to complete the characterization of the labile ligand **1** and to gain a better insight into its coordination properties. On the other hand, there are only a few literature reports on the structure of palladium(II) complexes with similar ligands, such as phosphinito–oxazolines [13] and phosphinito–pyridines [14]. The molecular structure of **3a** and atom labelling scheme are shown in Fig. 2.

Some selected bond lengths and angles are reported in Table 2.

The orientation around the central metal is distorted square-planar with the allylic carbons and the P and N donor atoms comprising the immediate coordination sphere. The bite angle P–Pd–N of 92.8(2)° is close to the idealized value of 90° and in line with the presence of a flexible six-membered chelate ring. The quinoline plane N–C(4)–C(5)–C(6)–C(7)–C(8)–C(9)–C(10)–C(11)–C(12) makes a dihedral angle of 30.2(1)° with the P–Pd–N plane, the oxygen atom being at a distance of 0.152(4) Å from this plane.

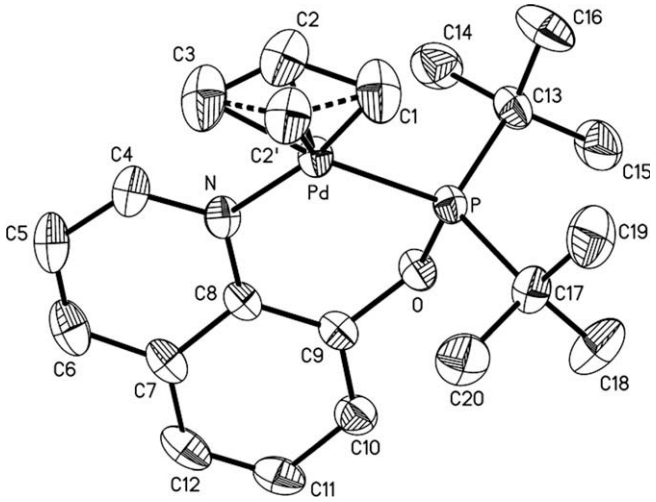


Fig. 2. An ORTEP drawing of complex **3a**(BF_4) showing the atom labelling scheme and thermal ellipsoids at 40% probability level. Hydrogen atoms and the BF_4^- anion are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) of **3a**.

Pd–N	2.137(5)	Pd–P	2.255(1)
Pd–C(1)	2.111(6)	Pd–C(2)	2.188(11)
Pd–C(2)′	2.208(12)	Pd–C(3)	2.288(9)
P–O	1.632(4)	O–C(9)	1.392(6)
C(1)–C(2)	1.39(2)	C(3)–C(2)	1.26(3)
C(1)–C(2)′	1.36(2)	C(3)–C(2)′	1.34(2)
N–Pd–P	92.8(2)	C(1)–Pd–C(3)	66.9(3)
C(1)–Pd–N	167.1(2)	C(1)–Pd–P	100.0(2)
C(2)–Pd–N	130.4(6)	C(2)–Pd–P	135.4(6)
C(3)–Pd–N	100.3(3)	C(3)–Pd–P	166.9(2)
O–P–Pd	108.4(1)	C(9)–O–P	129.5(3)
C(1)–C(2)–C(3)	133(2)	C(1)–C(2)′–C(3)	128(1)

The central carbon of the allyl ligand is disordered in two positions with an occupancy factor of 0.60 for C(2) and 0.40 for C(2)′. Such structural disorder seems to be a common feature for cationic complexes of the type $[Pd(\eta^3\text{-}C_3H_5)(P{-}N)]^+$ (P–N = iminophosphine or phosphino–oxazoline) [9,15], although it was not found for the complex where P–N is a phosphinito–oxazoline [13a]. In both orientations, the three allylic carbon atoms are bonded to palladium. In the C(1)–C(2)′–C(3) unit the C–C bond distances are of comparable values [1.36(2) and 1.34(2) Å], whereas in the C(1)–C(2)–C(3) unit the C–C bond lengths are significantly different [1.39(2) and 1.26(3) Å]. The longer Pd–C(3) bond *trans* to phosphorus [2.208(9) Å], compared to Pd–C(1) *trans* to nitrogen [2.111(6) Å], reflects the greater *trans* influence of the P donor atom. The dihedral angles between the allyl planes C(1)–C(2)–C(3), C(1)–C(2)′–C(3) and the P–Pd–N plane are 128(2)° and 121(2)°, respectively.

2.4. Preliminary catalytic studies

As stated in the introduction, our studies are focused on the design of new well defined palladium species to be valuably employed as precatalysts in reactions leading to C–C bond formation such as the Suzuki–Miyaura reaction. For a preliminary assessment, we have tested the catalytic activity of complexes **2** and **3a**(BF_4) in the coupling of phenylboronic acid with aryl bromides and chlorides (Scheme 3).

The initial experiments were carried out with complex **2** in toluene using an aryl bromide/palladium ratio of 100000:1 in the presence of K_2CO_3 as the base (Table 3).

While at temperatures lower than 90 °C the reaction with *p*-bromoacetophenone proceeds at modest rates, above 100 °C the catalyst activity becomes impressive (entry 1 of Table 3) so that a complete substrate conversion is achieved in two hours. Very favourably, such high reaction rates are observed even in the coupling of phenylboronic acid with bromobenzene which is a substrate lacking an activating EWG (entry 2 of Table 3). Encouraged by these results, we extended our investigations to the more challenging coupling of phenylboronic acid with aryl chlorides. Under the same reaction conditions and with a substrate/catalyst ratio of 200:1, the coupling of *p*-chlorocetophenone with phenylboronic acid proceeds to completion in two hours (entry 3 of Table 3) and also the less activated chlorobenzene is coupled with phenylboronic in high yield. Further experiments showed that also the cationic allyl complex **3a** is active in promoting the Suzuki coupling of phenylboronic acid with the same aryl halides (entries 5–8 of Table 3); not surprisingly the catalytic activity of **2** and **3a** turned out to be almost identical.

Table 3
Suzuki–Miyaura couplings using complexes **2** and **3a**(BF_4) as the precatalysts.[a]

Entry	Complex	ArX	ArX/Cat.	Conv.[b] (%)	TON[c]	TOF[d]
1	**2**	4-$CH_3COC_6H_4Br$	100000	100	100000	50000
2	**2**	C_6H_5Br	100000	100	100000	50000
3	**2**	4-$CH_3COC_6H_4Cl$	200	100	200	100
4	**2**	C_6H_4Cl	200	85	170	85
5	**3a**(BF_4)	4-$CH_3COC_6H_4Br$	100000	90	90000	45000
6	**3a**(BF_4)	C_6H_5Br	100000	100	100000	50000
7	**3a**(BF_4)	4-$CH_3COC_6H_4Cl$	200	100	200	100
8	**3a**(BF_4)	C_6H_4Cl	200	100	200	100

[a] Reaction conditions. Solvent: toluene (12 mL); *t* = 2 h; *T*: 110 °C; aryl halide: 4.0 mmol; phenylboronic acid: 6.0 mmol; base: K_2CO_3 (8.0 mmol).
[b] By GLC with *n*-undecane as internal standard.
[c] TON: mol of substrate converted/mol of catalyst.
[d] TOF: mol of substrate converted/mol of catalyst per hour.

Considering that the reaction conditions were not optimized, the catalytic potential of complexes **2** and **3a** appears of particular interest. As a matter of fact, the coupling of aryl chlorides with boronic acids is usually carried out using 1–3 mol% of catalyst [2,16,17] and only a small number of catalysts [16,18] are able to activate aryl chloride substrates at loading lower than 1 mol% in short reaction time. More detailed studies on catalytic activity of **2**, **3a**(BF_4), **4a** and **4b** are currently in progress.

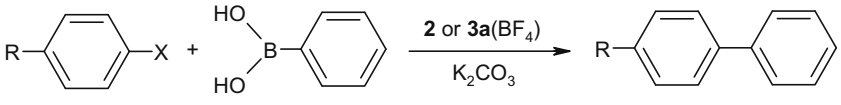
3. Conclusion

The labile 8-(di-*tert*-butylphosphinooxy)quinoline **1** can be stabilized by coordination to a palladium centre. This allows the preparation of a series of palladium complexes and the study of their solution behaviour also at high temperatures. The P,N chelating mode of **1** in the complexes is confirmed by an X-ray diffraction analysis of the cationic derivative $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{1})]^+$ (**3a**). Preliminary data show that the $PdCl_2$ adduct **2** and the allyl complex **3a** are efficient catalysts (or catalyst precursors) in the coupling of the arylboronic acid with aryl bromides and chlorides.

4. Experimental

4.1. General procedures

The preparations were carried out under N_2 atmosphere using standard Schlenk techniques, unless otherwise stated. The solvents, tetrahydrofuran, diethyl ether and toluene, were distilled over sodium/benzophenone, dichloromethane over calcium hydride, under N_2 and immediately used [19]. Chlorobenzene and



R = H, $COCH_3$
X = Cl, Br

Scheme 3.

bromobenzene wer distilled before the use. 8-Hydroxyquinoline, di-*tert*-butylchlorophosphine, NaH, diethylamine, dimethyl fumarate, fumaronitrile, bromobenzene, 4-bromoacetophenone, 4-chloroacetophenone, phenylboronic acid and anhydrous potassium carbonate were obtained commercially and used without further purification. The complexes $[PdCl_2(N{\equiv}CMe)_2]$, $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$, $[Pd(\mu\text{-}Cl)(\eta^3\text{-}1\text{-}PhC_3H_4)_2]$ and $[Pd(\mu\text{-}Cl)(\eta^3\text{-}1,3\text{-}Ph_2C_3H_3)_2]$ were prepared by literature methods [3c,20–22]. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.13, 121.49 and 65.47 MHz and, respectively. Chemical shifts are reported in ppm downfield from $SiMe_4$ for ^1H and ^{13}C, and from H_3PO_4 as external standard for ^{31}P. The spectra were run at 25 °C except when noted. IR spectra were recorded on a Perkin–Elmer 983G spectrophotometer. Mass spectra were recorded on a HP 5890 series II gas chromatograph interfaced to a HP 5971 quadrupole mass detector. The catalytic reactions were monitored by GLC on a 6850 Agilent Technologies gas chromatograph.

4.2. Synthesis of ligand **1**

8-Hydroxyquinoline (0.726 g, 5 mmol) was added to a suspension of NaH (0.18 g, 6 mmol, 80% in mineral oil) in THF (40 ml) and the mixture was refluxed for 1 h. After cooling at room temperature, di-*tert*-butylchlorophosphine (0.10 g, 5.5 mmol) was added dropwise under stirring. The suspension was refluxed for 18 h and filtered over neutral aluminium oxide. The resulting solution was evaporated to dryness to give **1** as white solid (0.75 g, 52% yield, based on 8-hydroxyquinoline). The product was used immediately without further purification.

4.3. Preparation of complex **2**

The freshly prepared ligand **1** (1.146 g, 3.96 mmol), dissolved in CH_2Cl_2 (20 ml), was added to a solution of $[PdCl_2(N{\equiv}CMe)_2]$ (0.934 g, 3.6 mmol) in 20 ml of CH_2Cl_2. After stirring for 0.5 h, the resulting solution was concentrated to small volume and diluted with diethyl ether to precipitate, the product as an orange powder (1.38 g, 82% yield). The complex was purified by crystallization from hot acetonitrile. Anal. Calc. for $C_{17}H_{24}Cl_2NOPPd$: C, 43.75; H, 5.18; N, 3.00. Found: C, 43.86; H, 5.16; N, 2.96%. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): 8-oxyquinoline carbons, δ = 159.5 s, 149.2 s, 141.3 s, 133.1 s, 130.9 s, 128.1 s, 124.9 s, 122.4 s, 120.8 s; *tert*-butyl carbons, δ = 44.5 d [*J*(PC) = 22 Hz], 28.8 s.

4.4. Preparation of complexes **3a**(BF_4), **3b**(BF_4) and **3c**(BF_4)

The complexes were prepared from the reaction of $[Pd(\mu\text{-}Cl)(\eta^3\text{-all})]_2$ (1.5 mmol, all = C_3H_5, 1-PhC_3H_4, 1,3-$Ph_2C_3H_3$) with the ligand **1** (0.897 g, 3.1 mmol) in CH_2Cl_2 (25 ml) followed by addition of $NaBF_4$ (0.66 g, 6 mmol) dissolved in 15 ml of MeOH. After stirring for 1 h, the solvents were evaporated to dryness at reduced pressure. The solid residue was extracted with CH_2Cl_2 (20 ml) in the presence of activated charcoal. After filtration on celite, the solution was concentrated to small volume (*ca.* 3 ml) and diluted with diethyl ether to precipitate the products as yellow-orange solids. The complexes were purified by a further precipitation from a CH_2Cl_2/Et_2O solvent mixture.

3a(BF_4) (1.32 g, 84%). Anal. Calc. for $C_{20}H_{29}BF_4NOPPd$: C, 45.87; H, 5.58; N, 2.67. Found: C, 46.09; H, 5.40; N, 2.67%. IR (Nujol): ν(B–F) at 1054 cm^{-1}. Molar conductivity: 61.5 ohm^{-1} cm^2 mol^{-1} for a 1.0×10^{-3} mol/l CH_2Cl_2 solution at 25 °C.

3b(BF_4) (1.29 g, 72%). Anal. Calc. for $C_{26}H_{33}BF_4NOPPd$: C, 52.07; H, 5.55; N, 2.34%. Found: C, 52.06; H 5.45; N, 2.36%. IR (Nujol): ν(B–F) at 1053 cm^{-1}. Molar conductivity: 69.2 ohm^{-1} cm^2 mol^{-1} for a 1.0×10^{-3}mol/l CH_2Cl_2 solution.

3c(BF_4) (1.83 g, 90%). Anal. Calc. for $C_{32}H_{37}BF_4NOPPd$: C, 56.87; H, 5.52; N, 2.07. Found: C, 56.45; H, 5.30; N, 1.98%. IR (Nujol): ν(B–F) at 1052 cm^{-1}. Molar conductivity: 66.0 ohm^{-1} cm^2 mol^{-1} for a 1.0×10^{-3}mol/l CH_2Cl_2 solution.

4.5. Preparation of [Pd(η^3-C_3H_5)(8-oxyquinoline)]

8-Hydroxyquinoline (0.290 g, 2 mmol) was added to a solution of $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ (0.366 g, 1 mmol) and NEt_3 (0.405 g, 4 mmol) in $CHCl_3$ (20 ml). After stirring for 1 h, the solvent was evaporated to dryness. The solid residue was washed with water (3×10 ml) and dried *in vacuo*. Precipitation from a $CHCl_3/Et_2O$ solvent mixture afforded the product as a yellow microcrystalline solid (0.52 g, 89%). Anal. Calc. for $C_{12}H_{11}NOPd$: C, 49.42; H, 3.80; N, 4.80. Found: C, 49.10; H, 3.63; N, 4.65%. ^1H NMR ($CDCl_3$, 25 °C): 8-oxyquinoline ligand, δ = 8.57 [dd, *J*(HH) = 4.6 Hz, *J*(HH) = 1.3 Hz, 1H, H(2)], 8.24 [dd, *J*(HH) = 8.3 Hz, *J*(HH) = 1.3 Hz, 1H, H(4)], 7.48 [t, *J*(HH) = 7.9 Hz, 1H, H(6)], 7.34 [dd, *J*(HH) = 8.3 Hz, *J*(HH) = 4.6 Hz, 1H, H(3)], 7.10 [d, *J*(HH) = 7.9 Hz, 1H, H(5)], 6.97 [d, *J*(HH) = 7.9 Hz, 1H, H(7)]; allyl ligand, δ = 5.63 [m, 1H, central proton], 4.20 [d, *J*(HH) = 6.2 Hz, 1H, *syn* proton], 3.82 [d, *J*(HH) = 6.7 Hz, 1H, *syn* proton], 3.16 [d, *J*(HH) = 11.1 Hz, 1H, *anti* proton], 3.12 [d, *J*(HH) = 11.0 Hz, 1H, *anti* proton].

4.6. Reaction of [Pd(η^3-C_3H_5)(8-oxyquinoline)] with $ClP(CMe_3)_2$

The di-*tert*-butylchlorophosphine (0.092 g, 0.51 mmol) was added to a solution of $[Pd(\eta^3\text{-}C_3H_5)$(8-oxyquinoline)] (0.146 g, 0.5 mmol) in 20 ml of THF. After 4 h at room temperature, a sample (*ca.* 1 ml) of the solution was evaporated to dryness and the residue was dissolved in $CDCl_3$. The ^{31}P NMR spectrum showed the presence of a strong singlet at 186.8 ppm and the disappearance of the singlet of free $ClP(CMe_3)_2$ at 146.6 ppm. Upon addition of solid $NaBF_4$ (0.11 g, 1 mmol), the mixture was stirred overnight and then worked up as described above for the preparation of the cationic η^3-allyl complexes, yielding **3a**(BF_4) (0.17 g, 65%).

4.7. Preparation of complexes **4a** and **4b**

A moderate excess of $NHEt_2$ (0.183 g, 2.5 mmol) was added to a solution of **3a**(BF_4) (0.262 g, 0.5 mmol) and the appropriate olefin (0.6 mmol) in CH_2Cl_2 (50 ml). After standing for 1 h at room temperature, the solvent was evaporated to dryness. The solid residue was repeatedly washed with water and dried *in vacuo*. The products were crystallized from a CH_2Cl_2 solution upon slow addition of a *n*-hexane/Et_2O mixture (1:1 v/v).

4a (0.19 g, 70%). Anal. Calc. for $C_{23}H_{32}NO_5PPd$: C, 51.17; H, 5.97; N, 2.60. Found: C, 51.16, H, 6.10; N, 2.50%. IR (Nujol): ν(C=O) at 1691 and 1678 cm^{-1}.

4b (018 g, 76%). Anal. Calc. for $C_{21}H_{26}N_3OPPd$: C, 53.23; H, 5.53; N, 8.87. Found: C, 53.05, H, 5.41; N, 8.57%; IR (Nujol): ν(C≡N) at 2201 cm^{-1}.

4.8. X-ray measurements and structure determination of **3a**(BF_4)

Crystal data for **3a**(BF_4), $C_{20}H_{29}PNOBF_4Pd$: M = 523.62, monoclinic, space group $P2_1/c$, a = 11.308(2) Å, b = 18.493(3) Å, c = 12.149(3) Å, β = 114.21(4)°, V = 2317.1(8) Å^3, Z = 4, D_{calc} = 1.501 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.912 mm^{-1}, F(000) = 1064.

A yellow crystal was lodged in Lindemann glass capillary and centered on a four circle Philips PW1100 diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å), following the standard procedures at room temperature. All intensities were corrected for Lorentz polarization and absorption [23]. The structures were solved by standard direct methods [24]. Refinement

was carried out by full-matrix least-squares procedures (based on F_o^2) using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in their described geometries and during refinement were allowed to ride on the attached carbon atoms with fixed isotropic thermal parameters ($1.2\boldsymbol{U}_{equiv}$) of the parent carbon atom. For a total of 278 parameters, $wR' = [\Sigma w(F^2_o - F^2_c)^2/\Sigma w(F^2_o)^2]^{1/2} = 0.163$, $S = 1.152$, and conventional $R = 0.055$, based on the F values of 4093 reflections having $I \geqslant 2\sigma(I)$. Structure refinement and final geometrical calculations were carried out with SHELXL-97 [25] program, implemented in the WinGX package [26].

4.9. General procedure for catalysis

The reactions were carried out under an inert atmosphere (argon). The coupling products were identified by their GC–MS and ^{1}H NMR spectra. In a typical experiment (entry 1 of Table 3), a 50 ml glass reactor was charged with 4-bromoacetophenone (0.80 g, 4.0 mmol), phenylboronic acid (0.73 g, 6.0 mmol), K_2CO_3 (1.10 g, 8.0 mmol), *n*-undecane (0.16 g, 1.0 mmol, as the gas chromatographic internal standard) and 12 ml of freshly distilled toluene. To the resulting suspension 100 μl of a 4.0×10^{-4} mol/l solution of complex **2**, in toluene were added, and the mixture was heated under magnetic stirring at 110 °C for 2 h. After cooling to room temperature and filtration on celite, the raw reaction mixture was analyzed by GLC.

5. Supplementary material

CCDC 688238 contains the supplementary crystallographic data for compound **3a**(BF_4). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] N. Miyaura, in: F. Diederich, A. de Mejere (Eds.), Metal-Catalyzed Cross-Coupling Reactions, second ed., Wiley-VCH, Weinheim, 2004 (Chapter 2);
A. Suzuki, in: E. Negishi, A. de Mejere (Eds.), Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley Interscience, New York, 2002 (Chapter III);
J.-P. Corbet, G. Mignani, Chem. Rev. 107 (2007) 874;
L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133.

[2] Z. Weng, S. Teo, T.S.A. Hor, Acc. Chem. Res. (2007) 676.

[3] (a) A. Scrivanti, V. Beghetto, U. Matteoli, S. Antonaroli, A. Marini, F. Mandoj, R. Paolesse, B. Crociani, Tetrahedron Lett. 45 (2004) 5861;
(b) A. Scrivanti, V. Beghetto, U. Matteoli, S. Antonaroli, A. Marini, B. Crociani, Tetrahedron 61 (2005) 9752;
(c) B. Crociani, S. Antonaroli, A. Marini, A. Scrivanti, U. Matteoli, Dalton Trans. (2006) 2698.

[4] R.B. Bedford, S.L. Hazelwood (née Welch), P.N. Horton, M.B. Hursthouse, Chem. Commun. (2003) 4164.

[5] R.B. Bedford, C.S.J. Cazin, S.L. Hazelwood (née Welch), Angew. Chem., Int. Ed. 41 (2002) 4120. and references therein.

[6] K.K. Klausmeyer, R.P. Feazell, J.H. Reibenspies, Inorg. Chem. 43 (2004) 1130.

[7] G. Delapierre, J.M. Brunel, T. Constantieux, G. Buono, Tetrahedron: Asymmetr. 12 (2001) 1345.

[8] S. Antonaroli, B. Crociani, J. Organomet. Chem. 560 (1998) 137.

[9] G. Bandoli, A. Dolmella, L. Crociani, S. Antonaroli, B. Crociani, Transition Met. Chem. 25 (2000) 17.

[10] B. Crociani, S. Antonaroli, L. Canovese, F. Visentin, P. Uguagliati, Inorg. Chim. Acta 315 (2001) 172.

[11] B. Crociani, S. Antonaroli, G. Bandoli, L. Canovese, F. Visentin, P. Uguagliati, Organometallics 18 (1999) 1137. and references therein.

[12] B. Jedlicka, R.E. Rülke, W. Weissensteiner, R. Fernández-Galán, F.A. Jalón, B.R. Manzano, J. Rodríguez-de la Fuente, N. Valdman, H. Kooijman, A.L. Spek, J. Organomet. Chem. 516 (1996) 97;
R. Fernández-Galán, F.A. Jalón, B.R. Manzano, J. Rodríguez-de la Fuente, M. Vrahani, B. Jedlicka, W. Weissensteiner, Organometallics 16 (1997) 3758;
K. Selvakumar, M. Valentini, M. Wörle, P.S. Pregosin, A. Albinati, Organometallics 18 (1999) 1207;
F.A. Jalón, B.R. Manzano, F. Gómez-de la Torre, A.M. López-Agenjo, A.M. Rodríguez, W. Weissensteiner, T. Sturm, J. Mahía, M. Maestro, J. Chem. Soc., Dalton Trans. (2001) 2417;
M. Zehnder, M. Neuburger, S. Schaffner, M. Jufer, D.A. Plattner, Eur. J. Inorg. Chem. (2002) 1511;
B. Crociani, S. Antonaroli, L. Canovese, P. Uguagliati, F. Visentin, Eur. J. Inorg. Chem. (2004) 732.

[13] (a) P. Braunstein, J. Zhang, R. Welter, Dalton Trans. (2003) 507;
(b) M. Agostinho, P. Braunstein, R. Welter, Dalton Trans. (2007) 759.

[14] M. Agostinho, A. Banu, P. Braunstein, R. Welter, X. Morise, Acta Crystallogr. C62 (2006) m81.

[15] J. Sprinz, M. Kiefer, G. Helmchem, M. Reggelin, G. Huttner, O. Walter, L. Zsolnai, Tetrahedron Lett. 35 (1994) 1523;
N. Baltzer, L. Macko, S. Schaffner, M. Zehnder, Helv. Chim. Acta 79 (1996) 803;
S. Schaffner, L. Macko, M. Neuburger, M. Zehnder, Helv. Chim. Acta 80 (1997) 463.

[16] R.B. Bedford, C.S.J. Cazin, D. Holder, Coord. Chem. Rev. 248 (2004) 2283. and references therein.

[17] (a) M.-T. Chen, C.-A. Huang, C.-T. Chen, Eur. J. Inorg. Chem. (2008) 3142;
(b) J.V. Kingston, J.G. Verkade, J. Org. Chem. 72 (2007) 2816;
(c) S.K. Schneider, P. Roembke, G.R. Julius, H.G. Raubenheimer, W.A. Herrmann, Adv. Synth. Catal. 348 (2006) 1862;
(d) C.J. O'Brien, E.A.B. Kantchev, C. Valente, N. Hadei, G.A. Chass, A. Lough, A.C. Hopkinson, M.G. Organ, Chem. Eur. J. 12 (2006) 4743;
(e) G.R. Rosa, C.H. Rosa, F. Rominger, J. Dupont, A.L. Monteiro, Inorg. Chim. Acta 359 (2006) 1947;
(f) C. Song, Y. Ma, Q. Chai, C. Ma, W. Jang, M.B. Andrus, Tetrahedron 61 (2005) 7438.

[18] (a) M. Cui, J. Li, A. Yu, J. Zhang, Y. Wu, J. Mol. Catal. A: Chem. 290 (2008) 67;
(b) S.-B. Yu, X.-P. Hu, J. Deng, J.-D. Huang, D.-Y. Wang, Z.-C. Duan, Z. Zheng, Tetrahedron Lett. 49 (2008) 1253;
(c) C. Xu, J.-F. Gong, T. Guo, Y.-H. Zhang, Y.-J. Wu, J. Mol. Catal. A: Chem. 279 (2008) 69;
(d) C.A. Fleckestein, H. Plenio, Organometallics 26 (2007) 2758;
(e) T.E. Barder, J. Am. Chem. Soc. 128 (2006) 898;
(f) N. Marion, O. Navarro, J. Mei, E.D. Stevens, N.M. Scott, S.P. Nolan, J. Am. Chem. Soc. 128 (2006) 4101.

[19] D.D. Perrin, W.L. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon, Oxford, 1988.

[20] R. Hartley, S.R. Jones, J. Orgamomet. Chem. 66 (1974) 465.

[21] M.C. Ashraf, T.G. Burrowes, W.R. Jackson, Aust. J. Chem. 29 (1976) 2643.

[22] P. Barbaro, P.S. Pregosin, R. Salzmann, A. Albinati, R.W. Kunz, Organometallics 14 (1995) 5160.

[23] A.T.C. North, D.C. Philips, F.S. Mathews, Acta Crystallogr. A24 (1968) 351.

[24] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, "SIR–97" J. Appl. Crystallogr. 32 (1999) 115.

[25] G.M. Sheldrick, "SHELXL-97" Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[26] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.