Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 1895–1902
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Imidazolium salicylaldimine frameworks for the preparation of tridentate *N*-heterocyclic carbene ligands

Mahmut Ulusoy [a], Onur Şahin [b], Orhan Büyükgüngör [b], Bekir Çetinkaya [a,*]

[a] *Department of Chemistry, Ege University, 35100 Bornova, Izmir, Turkey*
[b] *Department of Physics, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey*

Received 19 January 2008; received in revised form 16 February 2008; accepted 16 February 2008
Available online 10 March 2008

Abstract

Sterically hindered salicylaldimine functionalized imidazolium salts **2** have been prepared. The structures of the synthesized compounds were determined by spectroscopic techniques. The reaction of these salts containing arylmethyl-*N* chain (aryl: phenyl (**2a**), 2,4,6-trimethylphenyl (**2b**), 2,3,4,5,6-pentamethylphenyl (**2c**)) with $Pd(OAc)_2$ in boiling toluene afforded Pd(II) complexes **3** in high yields. The X-ray structure of 1-[3-(3,5-di-*tert*-butyl-2-oxophenyl)propyliminato]-3-(2,4,6-trimethylbenzyl)imidazol-2-ylidenebromopalladium(II) (**3b**) has been determined. The Suzuki–Miyaura reaction was used to investigate their activity as catalysts either prepared in situ or from well-defined complexes. They are efficient when activated arylbromides are used as substrates.

Keywords: Bulky salicylaldimine; *N*-heterocyclic carbene; Tridentate ligands; Carbene-imine ligands; Salicylaldiminato–NHC; Suzuki–Miyaura

1. Introduction

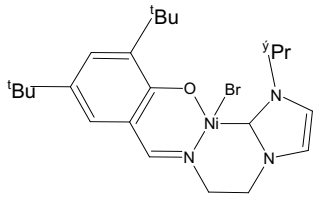
Over the past decades *N*-heterocyclic carbene (NHC) ligands have received intense attention because of their ease of preparation, high stability and wide applications in the field of catalysis such as C–C coupling, olefin metathesis, hydrogenation and hydroformylation [1]. The recent search for NHCs for transition metal ions has focused on chelating ligands which might control the stability of the active species and improve the catalytic activity. In this context, NHCs have been synthesized that contain pendant heteroatom functionalized groups such as NHC–pyridyl [2], NHC–amino [2d,3] and NHC–amido [4]. Several researchers have reported Pd(II) complexes with chelating iminocarbene ligands in 5- and 6-membered ring systems [4a,4c–6].

The coordination of iminocarbene ligand systems has been found to be drastically affected by the number and substitution pattern of methylene linkers between the *N* atoms of the imine and imidazole ring [5–7]. For example, sterically bulky systems form non-chelating κ^1-*C* imino-NHC–Pd(II) complexes [5], whereas 1-mesitylimidazol-2-ylidene-3-[$CH_2(Bu^t)=NPr^i$] is enolizable to afford an enamine [6]. Structural and hapticity changes were observed to be solvent-dependent.

On the other hand, salicylaldiminato complexes of late transition metal ions were reported to be highly active and stable precatalysts, and they can control the performance of metals in a number of catalytic transformations. Furthermore, NHC–imine complexes of second generation Grubbs catalysts are proposed to enter the olefin metathesis catalytic cycle with decoordination of the imine rather than the phosphine dissociation [7]. Salicylaldimines generally act as deprotonated bidentate ligands with the κ^2-*N*,*O* donor atoms, and are synthesized via Schiff base condensation, where salicyaldehyde is reacted with a primary amine, to produce an imine.

* Corresponding author. Tel./fax: +90 232 3888264.
E-mail address: bekir.cetinkaya@ege.edu.tr (B. Çetinkaya).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.02.017



A

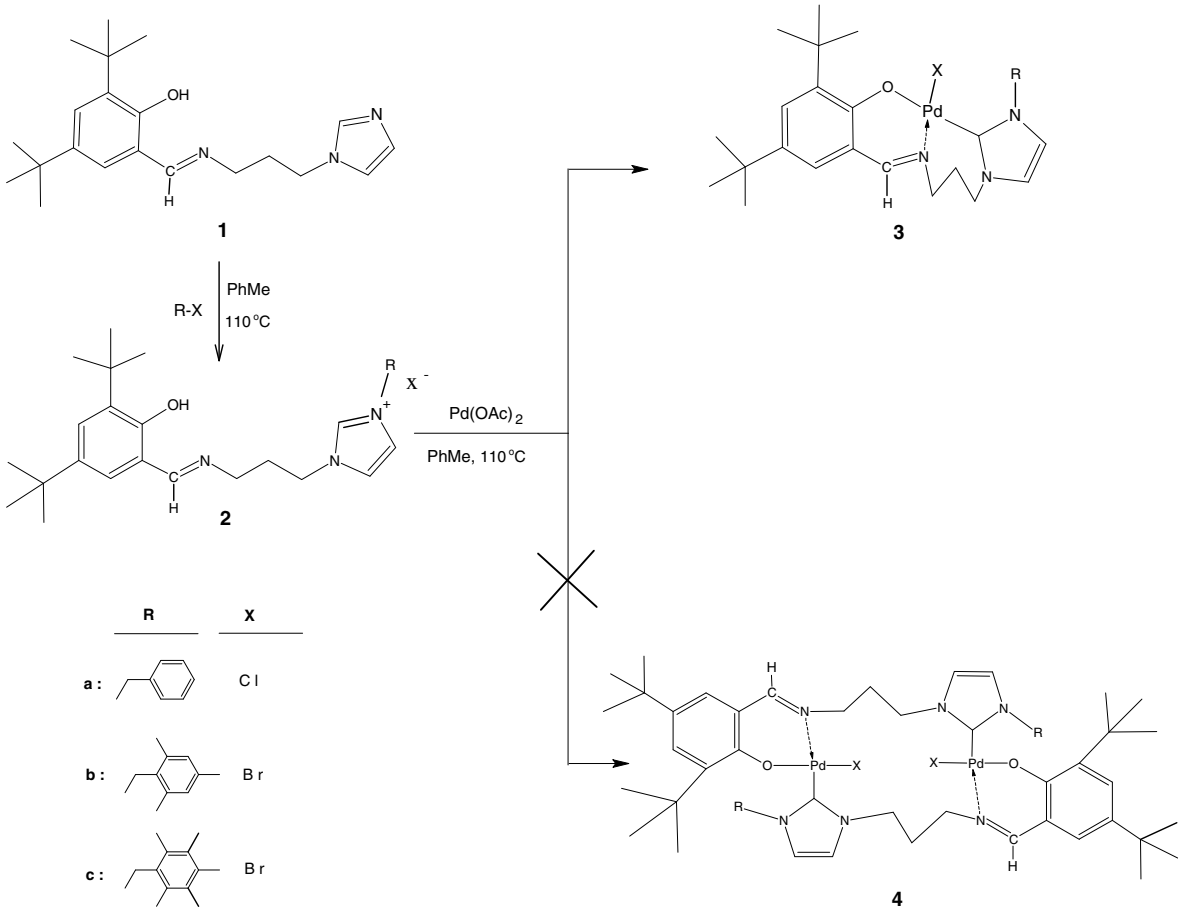
To our surprise, here is only one example of an imidazole moiety (**A**) being connected to the imine N of 3,5-di-*t*-butylsalicylaldimines [8]. Herein, we report the synthesis of the new tridentate Pd(II) complexes **3** from the salicylaldimine side-armed imidazolium salts **2** which can be regarded as homologues of ligand precursor of **A**. Thus, we will be able to determine whether the length of the linker on the wing of the complexes has an effect on the catalytic activity of the complexes. The Suzuki–Miyaura reaction was used to study their activity as catalysts/precatalysts which were prepared either in situ or from well-defined complexes.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic route used for the preparation of the novel salicylaldimine-functionalized imidazolium bromides (**2**) is shown in Scheme 1. The Schiff base **1** was prepared by condensation of 3,5-di-*t*-butylsalicylaldehyde [9] with commercially available *N*-(3-aminopropyl)imidazole by the method reported [10]. Subsequently, *N*-salicylaldimine armed imidazolium salts **2** were prepared in good yields by quarternization of the imidazole moiety of the salicylaldimine using benzyl halides (benzyl **a**, 2,4,6-trimethylbenzyl **b**, 2,3,4,5,6-pentamethylbenzyl **c**) as the reactant in toluene at reflux in high yields (*ca.* 92–96%). The imidazolium salts **2** were isolated and washed with diethyl ether to remove traces of reactants.

The salts **2** have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR ($CDCl_3$) spectra of the salts all show proton signals for the proton attached to the imine group and the protons from the aryl rings and proton signals at *ca.* 1 ppm indicating the presence of the



Scheme 1. Synthetic route to the imino–NHC complexes.

Table 1
Characteristic IR bands (cm^{-1}) of the synthesized compounds as KBr pellets

Compound	IR spectra (cm^{-1})	
	υO–H	υC=N
1	3410	1626
2a	3400	1630
2b	3408	1630
2c	3430	1631
3a		1618
3b		1603
3c		1612

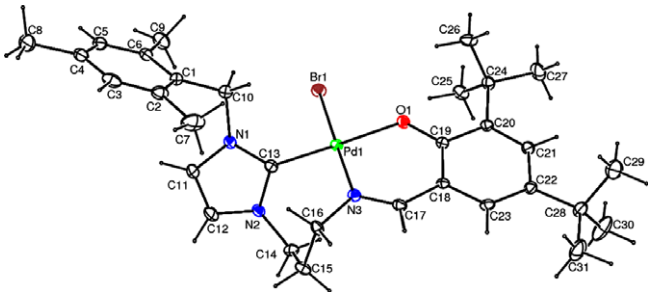


Fig. 1. The molecular structure of **3b**. Displacement ellipsoids are drawn at the 30% probability. Selected bond distances and angles are listed in Table 3.

Table 2
Summary of crystallographic data for compound **3b**

Empirical formula	$C_{31}H_{42}BrN_3OPd$
Formula weight	658.99
Temperature (K)	296
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	25.0912(13)
b (Å)	9.5897(7)
c (Å)	13.1721(7)
α(°)	90.00
β(°)	102.793(4)
γ(°)	90.00
Volume ($Å^3$)	3090.8(3)
Z	4
Calculated density ($Mg\,m^{-3}$)	1.416
Absorption coefficient (mm^{-1})	1.92
F(000)	1352
Crystal size (mm)	$0.02 \times 0.33 \times 0.76$
θ Range for data collection (°)	1.6–26.1
Independent reflection	6018
Collected reflection	30085
Absorption correction	Integration
T_{min}	0.448
T_{max}	0.939
R_{int}	0.112
θ_{max} (°)	26.0
h	−28 to 30
k	−11 to 11
l	−16 to 16
Refinement method	Full-matrix least-squares on F^2
$wR(F^2)$	0.092
Goodness-of-fit on F^2	0.91
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.048$
R indices (all data)	$R_1 = 0.106$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$ (e $Å^{-3}$)	0.43
$\Delta\rho_{min}$ (e $Å^{-3}$)	−0.62

^{t}Bu substituents on the aryl rings of the salt at positions 3 and 5. The characteristic signals of imidazolium C2–*H* at 10.95 ppm for **2a**, 10.53 ppm for **2b** and 10.19 ppm for **2c** were also observed. The ^{13}C NMR data for **2** are consistent with the proposed structures. In the ^{13}C NMR ($CDCl_3$) the central (–N*C*HN–)imidazolium carbon resonances in the region of 167.90–167.96 ppm. Details of the synthesis and product characterization are given in Section 5. The IR spectra of imidazolium salts **2** showed peaks in the υC=N stretching frequency region at 1630 cm^{-1}. The bands at 3430–3400 cm^{-1} are due to the O–H of the salicylaldimine units as given in Table 1.

Since, we have developed a method to synthesize imino-imidazolium salts, it was also of interest to prepare the corresponding imino–NHC complexes. Imino–NHC complexes could be synthesized either from the corresponding silver complex or from the free carbene obtained by treatment of the imidazolium salt with an appropriate base. Most of these complexes were obtained from iminoylimidazolium salts. Direct reactions of imidazolium salts with basic transition metal salts were also used to generate NHC complexes [1b,1c,1d,1e,1f]. Roland et al. reported [11] a direct reaction of an imino–imidazolium salt in various ways with $Pd(OAc)_2$ but could not obtain the desired chelated complexes. In contrast to this study, we report a simple synthetic route to tridentate imino–NHC precursors in high yields.

One-pot synthesis via the direct reaction with one equivalent of palladium acetate as the metal precursor and 1 equiv. of imidazolium salt in refluxing toluene gave the corresponding Pd(II) complexes **3**. All complexes were isolated as yellow-orange solids with yields ranging from *ca.* 71% to 92%. The main advantage of the one-pot synthetic approach is that the free and unstable NHC ligand does not need to be isolated and purified, and that without the formation of salt the target complex is easy to purify. All complexes are inert to air and moisture.

Imino–NHC complexes **3** were fully characterized by ^1H and ^{13}C NMR spectroscopy. In addition, the complex **3a** was characterized by HMQC, COSY and HMBC techniques. In the ^1H NMR ($CDCl_3$) spectra of the complexes, characteristic signals of imidazolium C2–*H* and phenolic O*H* disappeared via cyclometallation to palladium. The ^{13}C NMR ($CDCl_3$) spectra of these complexes were well defined. Pd–*C* resonances were shifted to higher frequency with decreasing electron donating groups in the region of 154.8–157.7 ppm. It is worth noting that the HMBC spectrum of **3a** showed a long range correlation from the

Table 3
Selected bond lengths (Å) and angles (°) for compound **3b**

Pd(1)–N(3)	2.011(4)	Pd(1)–Br(1)	2.4470(7)
Pd(1)–C(13)	1.959(6)	Pd(1)–O(1)	2.002(3)
O(1)–C(19)	1.303(6)	C(13)–N(2)	1.360(6)
C(13)–N(1)	1.356(7)	C(16)–N(3)	1.481(6)
C(13)–Pd(1)–O(1)	175.68(18)	C(13)–Pd(1)–N(3)	92.4(2)
O(1)–Pd(1)–N(3)	91.41(16)	C(13)–Pd(1)–Br(1)	88.39(15)
N(3)–Pd(1)–Br(1)	176.00(13)	O(1)–Pd(1)–Br(1)	87.71(10)

carbene C (157.7 ppm) to benzylic CH_2(6.17; 5.35 ppm), im-N–CH_2-(5.61; 4.11 ppm) and N–CH=CH–N (6.88; 6.84 ppm). The IR spectra of the palladium complexes **3** showed that the C=N stretching band shifted *ca.* 12–27 cm^{-1} to lower frequency compared to the salts (Table 1). This is due to the effect of the metal on the ligand system [12].

In the ^{13}C NMR the imine carbon resonance is found at 164.4, 164.2 and 163.9 for complexes **3a**, **3b** and **3c**, respectively, and are shifted to higher frequency when compared with the imidazolium salts. This shift is indicative of coordination (chelating), with the transfer of electron density from the imine to the metal center [6b].

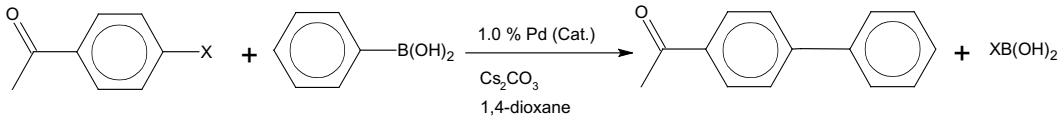
Theoretically, it is possible that NHC part of the ligands can coordinate in an intermolecular way to the next metal ion to form a dinuclear species formulated as **4**. However, this possibility was ruled out by a single crystal study on **3b** (see Fig. 1).

Yellow single crystals of **3b** suitable for diffraction were grown by slow diffusion of diethyl ether into a dichloromethane solution. A summary of crystallographic data is given in Table 2 and selected bond lengths and angles are listed in Table 3.

The palladium complex **3b** has a distorted square-planar geometry with the coordinated carbene carbon, imine nitrogen, phenolic oxygen and bromide ligands to the palladium.

The Pd(1)–C(13) and Pd(1)–N(3) bond lengths are 1.959(6) and 2.011(4) Å, respectively, which upon comparison to bond lengths of 2.035 Å for Pd–C and 2.051 Å for Pd–N in a imino–NHC system reported by Coleman's group [6b] are all smaller indicating stronger bonding. This could be due to tridentate chelating to the metal centre. The bite angle C(13)–Pd(1)–N(3) of 92.4(2)° is larger than those of other palladium(II)–NHC complexes [6b,11]. The bond lengths of Pd(1)–Br(1) and Pd(1)–O(1) are 2.4470(7), and 2.002(3) Å, respectively.

Table 4
The Suzuki coupling reaction of aryl halides with phenylboronic acid



Entry	**2** + $Pd(OAc)_2$ or **3**	X	Time (h)	Yield (%)[a]
1	**2a**	Br	0.5	82
2	**2b**	Br	0.5	92
3	**2c**	Br	0.5	98
4	**3a**	Br	0.5	97
5	**3b**	Br	0.5	96
6	**3c**	Br	0.5	97
7	**2c**	Br	1	99
8	**3a**	Br	1	99
9	**3b**	Br	1	99
10	**3c**	Br	1	99
11	**2a**	Br	2	88
12	**2b**	Br	2	99
13	**2a**	Cl	0.5	40
14	**2b**	Cl	0.5	45
15	**2c**	Cl	0.5	63
16	**3a**	Cl	0.5	48
17	**3b**	Cl	0.5	52
18	**3c**	Cl	0.5	59
19	**3a**	Cl	1	52
20	**3b**	Cl	1	57
21	**3c**	Cl	1	67
22	**3a**	Cl	2	57
23	**3b**	Cl	2	58
24	**3c**	Cl	2	73

Reaction conditions: 1.0 mmol of aryl halide; 1.5 mmol of phenylboronic acid; 1.0 mmol Cs_2CO_3; %1.0 Pd(Cat.) was used; 8.0 mL of 1,4-dioxane; temperature 80 °C.

[a] GC-yield using diethyleneglycol-di-*n*-butylether as internal standard.

3. Catalytic tests

The palladium-catalyzed reaction of aryl halides with arylboronic acids (the Suzuki reaction) is the most common method for C–C bond formation [13]. The reactions are usually carried out homogeneously in the presence of a base under inert atmosphere. The reactivity of the aryl halide component decreases sharply in the order X = I > Br > Cl and electron withdrawing substituents R are required for the chlorides to react [13,14].

The palladium-catalyzed cross-coupling reaction of phenylboronic acid with aryl halides has been summarized in Table 4. In order to find optimum conditions a series of experiments has been performed with 4-bromoacetophenone and phenylboronic acid as model compounds. For comparison to previous study [6b] Cs_2CO_3 [15] as a base and 1,4-dioxane as a solvent was used. The catalysts are generated in situ from $Pd(OAc)_2$ and salicylaldimine-imidazolium salts (**2**) or their isolated complexes **3** were prepared and compared under the same reaction conditions.

From the results in Table 4, it is evident that the complexes **3** and in situ formed catalyst systems here are more efficient than the related bidentate NHC–imine system [6b]. It is also clear that the NHC precursor **2c** and its isolated complex **3c** that contains the strongly electron donating pentamethyl substituent are the most effective of the catalysts. It is worth noting that isolated complexes **3a** and **3b** are more effective than the in situ generated forms of their imidazolium salts [16]. On the other hand in situ formed catalyst system **2c** + $Pd(OAC)_2$ gave better yields in the coupling reaction compared to the isolated carbene palladium(II) complex **3c**. Catalytic tests indicated that the performance increased with increasing electron donating and sterically hindered groups on NHC.

4. Conclusion

Simple method is now available for the preparation of Pd(II) complexes that are coordinated by salicylaldiminato-carbene ligands. The Schiff base, derived from the condensation of 3,5-*t*-butylsalicylaldehyde with commercially available *N*-(3-aminopropyl)imidazole was quaternized with benzyl halides, and then the resulting salts were reacted with palladium(II) acetate to give the corresponding κ^3-*C*,*N*,*O*(*N*-salicylaldiminato–NHC)palladium(II) complexes. These complexes have been found to be active catalysts for the Suzuki–Miyaura cross-coupling of activated aryl bromides and chlorides with aryl boronic acids, using 1,4-dioxane as solvent.

5. Experimental

5.1. General considerations

Syntheses were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. All reagents were purchased from Aldrich and Merck. The solvents, Et_2O, pentane/hexane and toluene over Na and CH_2Cl_2 over P_2O_5 were distilled prior to use. ^1H and ^{13}C NMR spectra were recorded at 297 K using a Varian AS-400 spectrometer operating at 400 MHz (^1H), 100.56 MHz (^{13}C). Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer Spectrum RXI FT-IR spectrometer as KBr pellets. The starting Schiff base was prepared by known method [10].

5.2. Synthesis of 1-[3-(3,5-di-tert-butyl-2-hydroxyphenyl)propylimino]-3-(benzyl)imidazolium chloride (**2a**)

A solution of the *N*-[1-(3-aminopropyl)imidazole]-3,5-di-*tert*-butylsalicylaldimine (341 mg, 1.0 mmol) in toluene (10 mL) and benzyl halide (1.0 mmol) were heated for 12 h under reflux. *n*-Hexane (15 mL) was added to the solution in order to obtain a pale-yellow solid. Recrystallization from CH_2Cl_2 (5 mL)\Et_2O (10 mL) at 25 °C, gave pale yellow crystals of **2**. 92% yield (431 mg). M.p. 166–167 °C. ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 1.26 (s, 9H, C_6H_2-5-C(CH_3)$_3$); 1.38 (s, 9H, C_6H_2-3-C(CH_3)$_3$); 2.35 (m, 2H, CH_2–CH_2–CH_2); 3.79 (t, $J = 5.8$ Hz, 2H, im–N–CH_2–); 4.46 (t, $J = 6.9$ Hz, 2H, –CH=N–CH_2); 5.38 (s, 2H, –CH_2–Ph); 7.11 (d, $J = 2.8$ Hz, 1H, N–CH=CH–N); 7.36 (d, $J = 2.4$ Hz, 1H, N–CH=CH–N); 7.16 (t, $J = 1.6$ Hz, 1H, *m*-C_6H_5); 7.39 (t, $J = 1.8$ Hz, 1H, *m*′-C_6H_5); 7.28–7.33 (m, 5H, Ar–CH); 8.42 (s, 1H, –CH=N); 10.95 (s, 1H, N–CH–N); 13.24 (s, 1H, –OH). ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm) 167.96 (N–CH–N); 157.89 (CH=N); 140.77; 138.17; 136.77; 133.01; 129.63; 129.17; 127.47; 126.60; 122.32; 121.84; 117.83; 56.48 (CH_2–C_6H_5); 53.47 (–CH=N–CH_2–); 48.76 (im–N–CH_2–); 35.19 (CH_2–CH_2-CH_2); 34.38 (C_6H_2-5-C(CH_3)$_3$); 31.69 (C_6H_2-5-C(CH_3)$_3$); 31.12 (C_6H_2-3-C(CH_3)$_3$); 29.62 (C_6H_2-3-C(CH_3)$_3$).

5.3. Synthesis of 1-[3-(3,5-di-tert-butyl-2-hydroxyphenyl)propylimino]-3-(2,4,6-trimethylbenzyl)imidazolium bromide (**2b**)

Compound **2b** was prepared in the same way as **2a** from *N*-[1-(3-aminopropyl)imidazole]-3,5-di-*tert*-butylsalicylaldimine (**1**) (341 mg, 1.0 mmol) and 2,4,6-trimethylbenzyl bromide (213 mg, 1.0 mmol) to give pale yellow crystals. 89% yield (494 mg). M.p. 135–137 °C. ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 1.27 (s, 9H, C_6H_2-5-C(CH_3)$_3$); 1.39 (s, 9H, C_6H_2-3-C(CH_3)$_3$); 2.20 (s, 6H, C_6H_2-*o*-(CH_3)$_2$); 2.25 (s, 3H, C_6H_2-*p*-CH_3); 2.39 (m, 2H, CH_2–CH_2–CH_2); 3.78 (t, $J = 6.0$ Hz, 2H, im–N–CH_2–); 4.57 (t, $J = 7.0$ Hz, 2H, CH=N–CH_2); 5.45 (s, 2H, –CH_2–C_6H_2–(CH_3)$_3$); 6.88 (s, 2H; C_6H_2–(CH_3)$_3$); 6.81 (s, 1H, C_6H_2-*p*-CH); 7.13 (d, $J = 2.4$ Hz, 1H, N–CH=CH–N); 7.36 (d, $J = 2.4$ Hz, 1H, N–CH=CH–N); 7.40 (s, 1H, C_6H_2-*o*-CH); 8.47 (s, 1H, –CH=N); 10.53 (s, 1H, N–CH–N); 13.29 (s, 1H, –OH). ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm) 167.95 (N–CH–N);

157.92 (*C*H=N); 140.71; 138.25; 137.34; 136.65; 130.17; 127.52; 126.58; 125.42; 122.28; 120.95; 117.85; 56.21 (*C*H_2–$C_6H_2(CH_3)_3$); 48.80 (–CH=N–*C*H_2–); 48.15 (im–N–*C*H_2–); 35.19 (CH_2–*C*H_2–CH_2); 34.36 (C_6H_2-5-*C*$(CH_3)_3$); 31.69 (C_6H_2-5-C(*C*$H_3)_3$); 31.29 (C_6H_2-3-*C*$(CH_3)_3$); 29.61 (C_6H_2-3-C(*C*$H_3)_3$); 21.22 (C_6H_2-*p*-*C*H_3); 20.06 (C_6H_2-*o*-(*C*$H_3)_2$).

5.4. Synthesis of 1-[3-(3,5-di-tert-butyl-2-hydroxyphenyl)propylimino]-3-(2,3,4,5,6-pentamethylbenzyl)imidazolium bromide (**2c**)

Compound **2c** was prepared in the same way as **2a** from *N*-[1-(3-aminopropyl)imidazole]-3,5-di-*tert*-butylsalicylaldimine (**1**) (341 mg, 1.0 mmol) and 2,3,4,5,6-pentamethylbenzyl bromide (241 mg, 1.0 mmol) to give pale yellow crystals. 86% yield (501 mg). M.p. 170–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.26 (s, 9H, C_6H_2-5-C(C$H_3)_3$); 1.36 (s, 9H, C_6H_2-3-C(C$H_3)_3$); 2.13 (s, 6H, C_6H_0-*o*-(C$H_3)_2$); 2.16 (s, 6H, C_6H_0-*m*-(C$H_3)_2$); 2.20 (s, 3H, C_6H_0-*p*-CH_3); 2.38 (m, 2H, CH_2–CH_2–CH_2); 3.76 (t, $J = 6.4$ Hz, 2H, im–N–CH_2–); 4.56 (t, $J = 7.2$ Hz, 2H, CH=N–CH_2); 5.50 (s, 2H, –CH_2–$C_6H_0(CH_3)_5$); 6.86 (t, $J = 1.6$ Hz, 1H, C_6H_2-*p*-C*H*); 7.12 (s, 1H, C_6H_2-*o*-C*H*); 7.35 (d, $J = 2.4$ Hz, 1H, N–C*H*=CH–N); 7.49 (d, $J = 1.6$ Hz, 1H, N–CH=C*H*–N); 8.47 (s, 1H, –C*H*=N); 10.19 (s, 1H, N–C*H*–N); 13.31 (s, 1H, –O*H*). ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm) 167.90 (N–*C*H–N); 158.0 (*C*H=N); 140.7; 137.5; 136.7; 136.7; 134.0; 133.7; 127.5; 126.5; 125.5; 122.4; 121.2; 117.9; 56.2 (*C*H_2–$C_6H_0(CH_3)_5$); 49.3 (–CH=N–*C*H_2–); 48.7 (im–N–*C*H_2–); 35.2 (CH_2–*C*H_2–CH_2); 34.4 (C_6H_2-5-*C*$(CH_3)_3$); 31.7 (C_6H_2-5-C(*C*$H_3)_3$); 31.4 (C_6H_2-3-*C*$(CH_3)_3$); 29.5 (C_6H_2-3-C(*C*$H_3)_3$); 17.4 (C_6H_0-*p*-*C*H_3); 17.1 (C_6H_0-*o*-(*C*$H_3)_2$); 17.0 (C_6H_0-*m*-(*C*$H_3)_2$).

5.5. Synthesis of 1-[3-(3,5-di-tert-butyl-2-oxophenyl)propyliminato]-3(benzyl)imidazol-2-ylidenechloropalladium(II) (**3a**)

A solution of the 1-[3-(3,5-di-*tert*-butyl-2-hydroxyphenyl)propylimino]-3-(benzyl)imidazolium chloride (**2a**) (234 mg, 0.5 mmol) in toluene (8 mL) and $Pd(OAc)_2$ (112 mg, 0.5 mmol) were heated for 12 h under reflux. The color of the solution turned from red to yellow. The solution was evaporated to half of its initial volume in vacuo. *n*-Hexane (10 mL) was added in order to precipitate the product. The precipitated solid was filtered via cannula and washed several times with Et_2O. The desired compound was recrystallized from CH_2Cl_2 (3 mL):Et_2O (12 mL). 92% yield (285 mg). M.p. 273–275 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm)^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.27 (s, 9H, C_6H_2-5-C(C$H_3)_3$); 1.48 (s, 9H, C_6H_2-3-C(C$H_3)_3$); 1.94–2.04 (m, 2H, CH_2–CH_2–CH_2); 2.83 (td, $J = 3.6$, 4.0, 4.0 Hz, 1H, CH=N–CH_2–); 3.50–3.54 (dd, $J = 3.6$, 4.0 Hz, 1H, CH=N–CH'_2–); 4.09–4.14 (dd, $J = 6.8$, 6.4 Hz, 1H, im–N–CH_2); 5.61 (td, $J = 5.2$, 4.8, 5.2 Hz, 1H, im–N–CH'_2); 5.35 (d, $J = 14.8$ Hz, 1H, –CH_2–C_6H_5); 6.17 (d, $J = 14.8$ Hz, 1H, –CH'_2–C_6H_5); 6.84 (d, $J = 2.0$ Hz, 1H, N–CH=C*H*–N); 6.88 (d, $J = 2.0$ Hz, 1H, N–C*H*=CH–N); 6.95 (d, $J = 2.8$ Hz, 1H; 6-C_6H_2); 7.30–7.35 (m, 3H, *o,p*-C_6H_5); 7.43 (d, $J = 2.4$ Hz, 1H, 4-$C_6H'_2$); 7.47–7.49 (dd, $J = 1.6$, 1.6 Hz, 2H, *m*-C_6H_5); 7.60 (s, 1H, C*H*=N).^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm) 164.4 (*C*H=N); 163.9 (2-C_6H_2); 157.7 (Pd–*C*); 141.2 (3-C_6H_2); 136.7 (4-C_6H_2); 135.5 (1-C_6H_5); 130.7 (5-C_6H_2); 129.1 (*o*-C_6H_5); 128.9 (*m*-C_6H_5); 128.6 (*p*-C_6H_5); 127.8 (6-C_6H_2); 122.7 (N-*C*H=CH–N); 120.9 (N–CH=*C*H–N); 117.9 (1-C_6H_2); 62.6 (–CH=N–*C*H_2–); 54.9 (*C*H_2–C_6H_5); 45.8 (im–N–*C*H_2–); 35.9 (C_6H_2-3-*C*$(CH_3)_3$); 34.0 (C_6H_2-5-*C*$(CH_3)_3$); 32.7 (CH_2–*C*H_2–CH_2); 31.6 (C_6H_2-3-C(*C*$H_3)_3$); 29.8 (C_6H_2-5-C(*C*$H_3)_3$).

5.6. Synthesis of 1-[3-(3,5-di-tert-butyl-2-oxophenyl)propyliminato]-3-(2,4,6- trimethylbenzyl)imidazol-2-ylidenebromopalladium(II) (**3b**)

Compound **3b** was prepared in the same way as **3a** from 1-[3-(3,5-di-*tert*-butyl-2-hydroxyphenyl)propylimino]-3-(2,-4,6- trimethylbenzyl)imidazolium bromide (**2b**) (277 mg, 0.5 mmol) and $Pd(OAc)_2$ (112 mg, 0.5 mmol) with 12 h refluxing to give yellow crystals. 89% yield (293 mg). M.p. 291–292 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.27 (s, 9H, C_6H_2-5-C(C$H_3)_3$); 1.49 (s, 9H, C_6H_2-3-C(C$H_3)_3$); 1.98–2.08 (m, 2H, CH_2–CH_2–CH_2); 2.92 (s, 9H, C_6H_2–(C$H_3)_3$); 2.35 (s, 1H, im–N–CH_2–); 2.92 (t, $J = 10.8$ Hz, 1H, im–N–CH'_2–); 3.56 (d, $J = 10.4$ Hz, 1H, CH=N–CH_2); 4.09–4.14 (dd, $J = 6.8$, 6.0 Hz, 1H, CH=N–CH'_2); 5.63 (d, $J = 14.8$ Hz, 1H, –CH_2–C_6H_2–$(CH_3)_3$); 5.83 (d, $J = 14.8$ Hz, 1H, –CH'_2–C_6H_2–$(CH_3)_3$); 6.42 (s, 1H, N–CH=C*H*–N); 6.83 (s, 1H, N–C*H*=CH–N); 6.89 (s, 2H; C_6H_2–$(CH_3)_3$); 6.92 (s, 1H, C_6H_2-*p*-C*H*); 7.43 (s, 1H, C_6H_2-*o*-C*H*); 7.68 (s, 1H, –C*H*=N). ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm) 164.2 (*C*H=N); 163.6; 155.9 (Pd–*C*); 141.2; 138.8; 138.3; 135.4; 130.7; 129.7; 128.5; 128.1; 121.4; 120.7; 117.7; 62.3 (*C*H_2–$C_6H_2(CH_3)_3$); 50.7 (–CH=N–*C*H_2–); 45.8 (im–N–*C*H_2–); 35.9 (CH_2–*C*H_2–CH_2); 34.0 (C_6H_2-5-*C*$(CH_3)_3$); 31.6 (C_6H_2-5-C(*C*$H_3)_3$); 32.8 (C_6H_2-3-*C*$(CH_3)_3$); 29.8 (C_6H_2-3-C(*C*$H_3)_3$); 21.3 (C_6H_2-*p*-*C*H_3); 20.1 (C_6H_2-*o*-(*C*$H_3)_2$).

5.7. Synthesis of 1-[3-(3,5-di-tert-butyl-2-oxophenyl)propyliminato]-3-(2,3,4,5,6-pentamethylbenzyl)imidazol-2-ylidenebromopalladium(II) (**3c**)

Compound **3c** was prepared in the same way as **3a** from 1-[3-(3,5-di-*tert*-butyl-2-hydroxyphenyl)propylimino]-3-(2,3,- 4,5,6-pentamethylbenzyl)imidazolium bromide (**2c**) (291 mg, 0.5 mmol) and $Pd(OAc)_2$ (112 mg, 0.5 mmol) to give orange-yellow crystals. 71% yield (207 mg). M.p. >282 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.21 (s, 9H, C_6H_2-5-C(C$H_3)_3$); 1.43 (s, 9H, C_6H_2-3-C(C$H_3)_3$); 1.89–2.07 (m, 2H, CH_2–CH_2–CH_2); 2.15 (s, 6H, C_6H_0-*o*-(C$H_3)_2$); 2.19 (s, 3H, C_6H_0-*p*-CH_3); 2.20 (s, 6H,

C_6H_0-*m*-(CH_3)$_2$); 3.48–3.52 (dd, $J = 3.6$, 3.6 Hz, 1H, CH=N–CH_2); 4.00–4.05 (q, $J = 6.9$ Hz, 1H, CH=N–CH'_2); 2.87 (td, $J = 3.2$, 3.6, 3.6 Hz, 1H, im–N–CH_2–); 5.65 (td, $J = 9.6$, 5.2, 4.8 Hz, 1H, im–N–CH'_2–); 5.67 (d, $J = 15.2$ Hz, 1H, –CH_2–C_6H_2–(CH_3)$_3$); 5.83 (d, $J = 15.2$ Hz, 1H, –CH'_2–C_6H_2–(CH_3)$_3$); 6.39 (d, $J = 1.6$ Hz, 1H, N–C*H*=CH–N); 6.42 (d, $J = 1.6$ Hz, 1H, N–CH=C*H*–N); 6.85 (d, $J = 2.4$ Hz, 1H, C_6H_2-*p*-C*H*); 7.36 (d, $J = 2.4$ Hz, 1H, C_6H_2-*o*-C*H*); 7.61 (s, 1H, –C*H*=N). ^{13}C NMR (100.56 MHz, $CDCl_3$, δ ppm) 163.9 (*C*H=N); 163.2; 154.8 (Pd–*C*); 140.9; 138.5; 137.2; 136.1; 133.9; 133.4; 130.7; 128.7; 121.8; 117.7; 116.7; 62.3 (*C*H$_2$–C_6H_0(CH_3)$_5$); 51.9 (–CH=N–*C*H$_2$–); 45.8 (im–N–*C*H$_2$–); 35.9 (CH$_2$–*C*H$_2$–CH$_2$); 34.8 (C_6H_2-5-*C*(CH_3)$_3$); 32.8 (C_6H_2-5-C(*C*H$_3$)$_3$); 32.8 (C_6H_2-3-*C*(CH_3)$_3$); 29.9 (C_6H_2-3-C(*C*H$_3$)$_3$); 17.3 (C_6H_0-*p*-*C*H$_3$); 17.1 (C_6H_0-*o*-(*C*H$_3$)$_2$); 17.0 (C_6H_0-*m*-(*C*H$_3$)$_2$).

5.8. General procedure for the Suzuki–Miyaura coupling reaction

Catalyst (1.0 mmol% of Pd), aryl halide (1.0 mmol), phenyl boronic acid (1.5 mmol), Cs_2CO_3 (1 mmol), diethyleneglycol-di-*n*-butylether as internal standard (30 mg), 1,4-dioxane (8 mL) were added to a small Schlenk tube and the mixture was heated at 80 °C in an oil bath. At the end, the mixture was cooled, extracted with Et_2O, filtered through a pad of silica gel with repeated washings and concentrated. The purity of the compounds was checked by GC and yields are based on aryl halide.

5.9. X-ray structural analyses of **3b**

A yellow crystal of **3b** suitable for data collection was mounted on glass fibres and data collection was performed on a STOE IPDS II diffractometer with graphite monochromated Mo Kα radiation at 296 K. The structures were solved by direct-methods using SHELXS-97 [17] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [18] from within the WINGX [19,20] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon were placed in calculated positions (C–H = 0.93–0.97 Å) and treated using a riding model with $U = 1.2$ times the U value of the parent atom for CH, CH_2 and CH_3. Molecular diagrams were created using ORTEP-III [21]. Geometric calculations were performed with PLATON [22]. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2.

6. Supplementary material

CCDC 662986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors are grateful to TÜBİTAK (106T364) and Harran University (HUBAK-703) for research fund and for support. The authors wish to acknowledge the Faculty of Arts and Sciences, Ondokuz May±s University, Turkey, for the use of the Stoe IPDS-II diffractometer (purchased from Grant No. F279 of the University Research Fund).

References

[1] (a) D.J. Cardin, B. Çetinkaya, M.F. Lappert, Chem. Rev. 72 (1972) 545;
(b) W.A. Herrmann, C. Köcher, Angew. Chem., Int. Ed. Engl. 36 (1997) 2162;
(c) D. Bourrissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39;
(d) L. Jafarpour, S.P. Nolan, Adv. Organomet. Chem. 46 (2001) 181;
(e) W.A. Herrmann, Angew. Chem., Int. Ed. 41 (2002) 1290;
(f) M.C. Perry, K. Burgess, Tetrahedron: Asym. 14 (2003) 951;
(g) R.E. Douthwaite, Coord. Chem. Rev. 251 (2007) 702;
(h) L.H. Gade, S. Bellemin-Laponnaz, Coord. Chem. Rev. 251 (2007) 718;
(i) E. Colacino, J. Martinez, F. Lamaty, Coord. Chem. Rev. 251 (2007) 726;
(j) J.A. Mata, M. Poyatos, E. Peris, Coord. Chem. Rev. 251 (2007) 841;
(k) F.E. Hahn, Angew. Chem., Int. Ed. 45 (2006) 1348;
(l) S.P. Nolan, in: *N*-heterocyclic Carbenes in Synthesis, Wiley-VCH, Weinheim, Germany, 2006;
(m) F. Glorius Topics in Organometallic Chemistry, vol. 21, Springer, Berlin/Heidelberg, Germany, 2007;
(n) T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18;
(o) H.M. Lee, D.C. Smith, Z.J. He, E.D. Stevens, C.S. Yi, S.P. Nolan, Organometallics 20 (2001) 794;
(p) M. Poyatos, P. Uriz, J.A. Mata, C. Claver, E. Fernandez, E. Peris, Organometallics 22 (2003) 440;
(r) I. Özdemir, B. Çetinkaya, S. Demir, N. Gürbüz, Catal. Lett. 97 (2004) 37;
(s) I. Özdemir, M. Yiğit, E. Çetinkaya, B. Çetinkaya, Tetrahedron Lett. 45 (2004) 5823.
[2] (a) D.S. McGuinness, K.J. Cavell, Organometallics 19 (2000) 741;
(b) A.A.D. Tulloch, A.A. Danopoulos, R.P. Tooze, S.M. Cafferkey, S. Kleihenz, M.B. Hursthouse, Chem. Commun. (2000) 1247;
(c) A.A.D. Tulloch, A.A. Danopoulos, G.J. Tizzard, S.J. Colles, M.B. Hursthouse, R.S. Hay-Motherwell, W.B. Motherwell, Chem. Commun. (2001) 1270;
(d) P.L. Chiu, C.L. Lai, C.F. Chang, C.H. Hu, H.M. Lee, Organometallics 24 (2005) 6169;
(e) F.E. Hahn, M.C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, Organometallics 24 (2005) 6458;
(f) A.M. Magill, D.S. McGuinness, K.J. Cavell, G.J.P. Britovsek, V.C. Gibson, A.J.P. White, D.J. Williams, A.H. White, B.W. Skelton, J. Organomet. Chem. 617 (2001) 546;
(g) J.C.C. Chen, I.J.B. Lin, Organometallics 19 (2000) 5113;
(h) E. Peris, J. Mata, J.A. Loch, R.H. Crabtree, Chem. Commun. (2001) 201;
(i) A.A.D. Tulloch, S. Winston, A.A. Danopoulos, G. Eastham, M.B. Hursthouse, Dalton Trans. (2003) 699;
(j) M. Poyatos, J.A. Mata, E. Falomir, R.H. Crabtree, E. Peris, Organometallics 22 (2003) 1110;
(k) M. Poyatos, E. Mas-Marzá, J.A. Mata, M. Sanaú, E. Peris, Eur. J. Inorg. Chem. (2003) 1215;
(l) A.A. Danopoulos, J.A. Wright, W.B. Motherwell, S. Ellwood, Organometallics 23 (2004) 4807;

(m) A.A. Danopoulos, J.A. Wright, W.B. Motherwell, Chem. Commun. (2005) 784;
(n) M. Yiğit, B. Yiğit, I. Özdemir, E. Çetinkaya, B. Çetinkaya, Appl. Organometal. Chem. 20 (2006) 322.
[3] R.E. Douthwaite, J. Houghton, B. Kariuki, Chem. Commun. (2004) 698.
[4] (a) M. Frøseth, A. Dhindsa, H. Røise, M. Tilset, J. Chem. Soc., Dalton Trans. (2003) 4516;
(b) L.G. Bonnet, R.E. Douthwaite, Organometallics 22 (2003) 4187;
(c) M. Frøseth, K.A. Netland, C. Rømming, M. Tilset, J. Organomet. Chem. 690 (2005) 6125;
(d) K.S. Coleman, S. Dastgir, G. Barnett, M.J.P. Alvite, A.R. Cowley, M.L.H. Green, J. Organomet. Chem. 690 (2005) 5591;
(e) I.S. Edworthy, M. Rodden, S.A. Mungur, K.M. Davis, A.J. Blake, C. Wilson, M. Schroder, P.L. Arnold, J. Organomet. Chem. 690 (2005) 5710.
[5] M. Frøseth, K.A. Netland, K.W. Törnroos, A. Dhindsa, M. Tilset, J. Chem. Soc., Dalton Trans. (2005) 1664.
[6] (a) K.S. Coleman, H.T. Chamberlayne, S. Tuberville, M.L.H. Green, A.R. Cowley, J. Chem. Soc., Dalton Trans. (2003) 2917;
(b) S. Dastgir, K.S. Coleman, A.R. Cowley, M.L.H. Green, Organometallics 25 (2006) 300.
[7] B.D. Clercg, F. Verpoort, J. Organomet. Chem. 672 (2003) 11.
[8] W. Li, H. Sun, M. Chen, Z. Wang, D. Hu, Q. Shen, Y. Zhang, Organometallics 24 (2005) 5925.
[9] J.F. Larrow, E.N. Jacobsen, Y. Gao, Y. Hong, X. Nie, C.M. Zepp, J. Org. Chem. 59 (1994) 1939.
[10] E. Tas, M. Aslanoglu, M. Guler, M. Ulusoy, J. Coord. Chem. 57 (2004) 583.
[11] A. Flahaut, J.P. Baltaze, S. Roland, P. Mangeney, J. Organomet. Chem. 691 (2006) 3498.
[12] R. K±l±nçarslan, H. Karab±y±k, M. Ulusoy, M. Aygün, B. Çetinkaya, O. Büyükgüngör, J. Coord. Chem. 59 (2006) 1649.
[13] (a) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(b) A.J. Suzuki, J. Organomet. Chem. 576 (1999) 147;
(c) S.P. Stanforth, Tetrahedron 54 (1998) 263;
(d) G.T. Crisp, Chem. Soc. Rev. 27 (1998) 427;
(e) N.J. Whitcombe, K.K. Hii, S.E. Gibson, Tetrahedron 57 (2001) 7449.
[14] (a) A.F. Littke, G.F. Fu, Angew. Chem., Int. Ed. 41 (2002) 4176;
(b) R.B. Bedford, S.L. Hazewood, M.E. Limmeat, Chem. Commun. (2002) 2610.
[15] C. Zhang, J. Huang, M.L. Trudell, S.P. Nolan, J. Org. Chem. 64 (1999) 3804.
[16] (a) A. Fürstner, A. Leitner, Synlett 2 (2001) 290;
(b) I. Özdemir, S. Demir, B. Çetinkaya, Tetrahedron 61 (2005) 9791.
[17] G.M. Sheldrick, SHELXS-97 – A Program for Automatic Solution of Crystal Structures, University of Göttingen, Germany, 1997.
[18] G.M. Sheldrick, SHELXL-97 – A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[19] L.J. Farrugia, WINGX – A Windows Program for Crystal Structure Analysis, University of Glasgow, 1998.
[20] L.J. Farrugia, J. Appl. Cryst. 30 (1999) 837.
[21] L.J. Farrugia, Appl. Crystallogr. 30 (1997) 565.
[22] A. L. Spek, PLATON – A Multipurpose Crystallographic Tool, Utrecht, Utrecht University, The Netherlands, 2005.