Palladium(II) Complexes with Benzoxazol-2-ylidene Ligands: Crystal Structures of *trans*-Chloro(benzoxazol-2-ylidene)-bis(triphenylphosphine)palladium(II) Chloride and *cis*-Diiodo(benzoxazol-2-ylidene)(triphenylphosphine)palladium(II)

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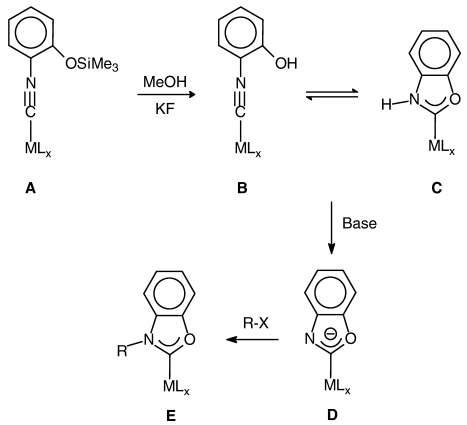
Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 60th birthday

The palladium(II) complexes *trans*-[PdCl(L)$(PPh_3)_2$]Cl, **5**, and *cis*-[PdI_2(L)PPh_3], **7**, (L = benzoxazol-2-ylidene) have been synthesized by treatment of the complexes *trans*-[$PdX_2(PPh_3)_2$] (**4**: X = Cl, **6**: X = I) with 2-(trimethylsiloxy)phenyl isocyanide **1**, and subsequent hydrolysis of the Si-O bond. The crystal structures of **5** and **7**$*CH_2Cl_2$ were established by X-ray diffraction. NMR and IR studies indicate, that the unexpected *cis*-configuration of **7** obtained from *trans*-[$PdI_2(PPh_3)_2$] is not the result of a solution equilibrium between the *cis*- and the *trans*-isomers.

Key words: Carbene Complexes, Palladium, Crystal Structures

Introduction

We have reported that complexes with a coordinated 2-(trimethylsiloxy)phenyl isocyanide ligand (**A**) react after hydrolytic O-$SiMe_3$ bond cleavage to give a mixture of products containing either the 2-hydroxyphenyl isocyanide ligand (**B**) or a benzoxazol-2-ylidene ligand (**C**) (Scheme 1). The reaction **A** → **B**/**C** has been studied at various metal centers like Cr [1], W [2], Re [3], Pd [4], and Fe [5] and non-metal centers [6] and has been reviewed [7]. The equilibrium between the isocyanide complex **B** and the carbene complex **C** resides on the isocyanide side for electron-rich complex fragments ML_x, where the isocyanide carbon atom is deactivated for an intramolecular nucleophilic attack by the hydroxyl oxygen atom by ($d \rightarrow \pi^*$) backbonding. However, complexes of type **B** are spontaneously converted into type **C** if ML_x is electron-poor [3]. The equilibrium between **B** and **C** can always be shifted to the carbene complex if the electronically disfavoured cyclization reaction is initiated by deprotonation of the hydroxyl function in **B**, thereby enhancing its nucleophilicity, and if the intermediate anionic ylide in **D** is subsequently alkylated to give the N-alkylated carbene complex **E** [8]. Species with the anionic ylidene ligand like in **D** have been isolated [9] and additional



Scheme 1.

methods for shifting the equlibrium between **B** and **C** have also been reported [1, 10]. More recently this type of carbene synthesis from β-functional phenyl isocyanides has been extended to include 2-aminophenyl isocyanide, thus leading to complexes with NH,NH heterocyclic carbene ligands [11, 12].

The N-alkylation of cationic, square-planar tetra (benzoxazol-2-ylidene) complexes of palladium(II) and platinum(II) (Scheme 2) proved difficult. For example, attempts to deprotonate complexes of type **F**

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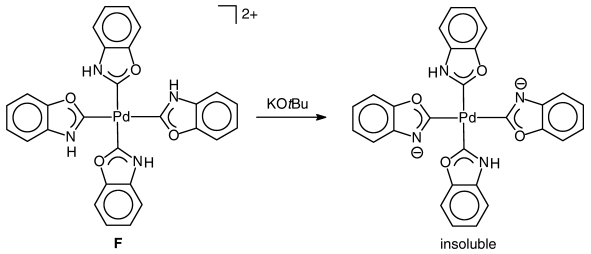
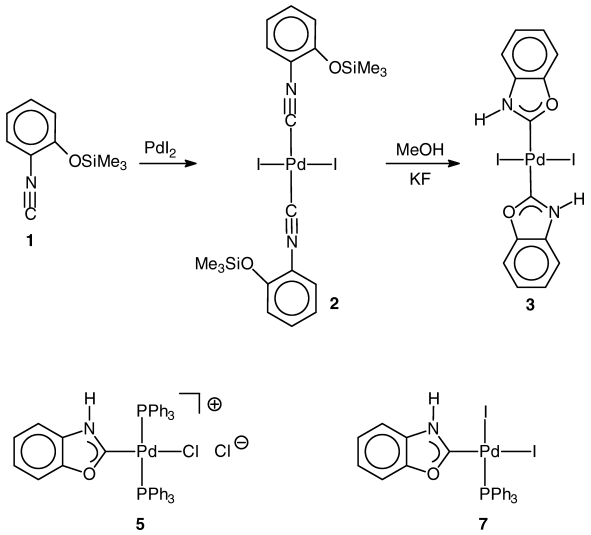


Scheme 2.



Scheme 3.

lead to complexes with both protonated and unprotonated ylidene ligands [4], which are insoluble in all organic solvents, and the subsequent N-alkylation is therefore not possible.

In this contribution we report on attempts to N-alkylate the known dicarbene complex **3** [4] obtained by intramolecular cyclization from the diisocyanide complex **2** [13] (Scheme 3). In addition, we present the preparation of the palladium complexes *trans*-[PdCl(L)$(PPh_3)_2$]Cl **5** and *cis*-[PdI_2(L)PPh_3] **7** (L = benzoxazol-2-ylidene) containing only one ylidene ligand (Scheme 3).

Results and Discussion

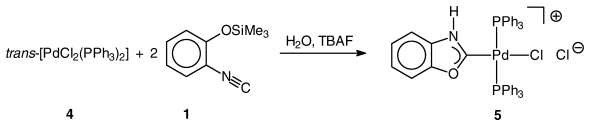
*Alkylation of trans-diiodo-bis(benzoxazol-2-ylidene)-palladium(II) (**3**)*

The reaction of PdI_2 with an excess of 2-trimethylsiloxyphenylisocyanide and subsequent O-$SiMe_3$ bond hydrolysis in the presence of a catalytic amount of *n*Bu_4NF yields the neutral complex *trans*-diiodo-bis(benzoxazol-2-ylidene)palladium(II) **3** [4] (Scheme 3). The N-alkylation of such coordinated benzoxazol-2-ylidenes has been described [1, 2, 5, 7, 10]. In analogy to the described methods, experiments were carried out to deprotonate complex **3** with various bases such as KO*t*Bu or Et_3N in DMF. Whilst evidence for the deprotonation of **3** could be obtained (for example Et_3NH^+ was detected in the ^1H NMR spectrum upon reaction of **3** with Et_3N, and the absorption for ν(NH) at 3200 – 3300 cm^{-1} was absent in the IR spectrum), no alkylation products could be isolated upon treatment of deprotonated **3** with alkyl halides. Regardless of the method employed for deprotonation/alkylation, all reaction products showed a similar elemental composition and were insoluble in all organic solvents and in water. Elemental analyses indicated the loss of iodine from the reaction products. One possible explanation for this behavior might be a nucleophilic attack of the deprotonated ylidene ligand at a second palladium center. The coordination of deprotonated benzoxazol-2-ylidene ligands at a second metal center *via* the ring nitrogen atom has been described [10]. As a result of such an attack one would expect loss of coordinated iodine. The resulting product would have an oligomeric structure, which correlates well with the insolubility of the substances which were isolated. This insolubility prevented a further characterization of the reaction products.

In order to prevent the formation of insoluble oligomeric products upon deprotonation of complexes with benzoxazol-2-ylidene ligands we initiated a study to synthesize palladium(II) complexes with only one benzoxazol-2-ylidene ligand. Bulky triphenylphosphine ligands were introduced, which are poor leaving groups and which enhance at the same time the solubility of the benzoxazol-2-ylidene complexes.

*Reaction of 2-(trimethylsiloxy)phenyl isocyanide (**1**) with trans-[$PdCl_2(PPh_3)_2$] (**4**)*

trans-Dichloro-bis(triphenylphosphine)palladium(II) **4** was synthesized according to a method described in [14] from $PdCl_2$ and PPh_3 in acetonitrile. The ^{31}P NMR spectrum of the product (in $CDCl_3$) showed a singlet at $\delta = 24.46$ ppm. This confirms that only one, namely the *trans*-isomer was obtained [14]. The reaction of *trans*-[$PdCl_2(PPh_3)_2$] with two equivalents of 2-(trimethylsiloxy)phenyl isocyanide in THF at −40 °C and subsequent Si-O hydrolysis gave exclusively the monocarbene complex **5** (Scheme 4).



Scheme 4.

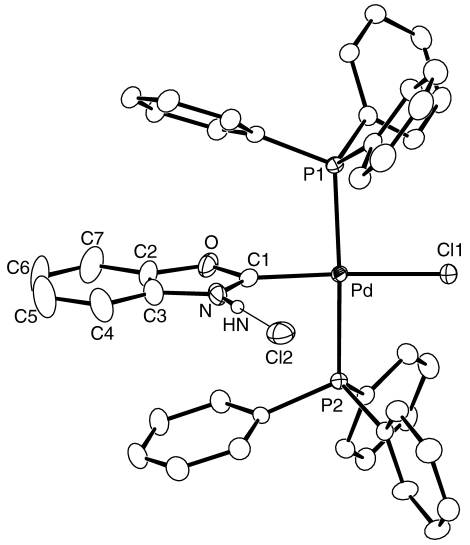


Fig. 1. Molecular structure of **5** (hydrogen atoms on calculated positions have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd-Cl1 2.3445(12), Pd-P1 2.3523(8), Pd-P2 2.3467(8), Pd-C1 1.961(2), O-C1 1.355(3), O-C2 1.405(3), N-C1 1.319(3), N-C3 1.400(3), C2-C3 1.363(4), C2-C7 1.398(4), C3-C4 1.388(4), N-HN 0.97(4), HN···Cl2 2.02(4); Cl1-Pd-P1 92.10(2), Cl1-Pd-P2 90.86(2), Cl1-Pd-C1 172.59(7), P1-Pd-P2 174.92(2), P1-Pd-C1 89.17(6), P2-Pd-C1 88.42(6), C1-O-C2 106.3(2), C1-N-C3 109.8(2), Pd-C1-O 124.9(2), Pd-C1-N 125.4(2), O-C1-N 109.7(2), O-C2-C3 108.9(2), N-C3-C2 105.3(2); dihedral angle between planes made up from (Pd,Cl1,P1,P2,C1) and (O,C1,N,C3,C2) 85.8°.

Experiments with a larger excess of the isocyanide, or the reaction of **5** with the isocyanide, did not lead to the substitution of the second chloro ligand.

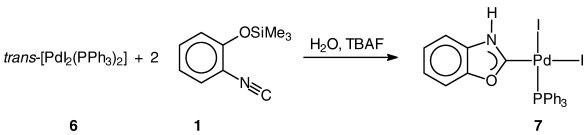
The presence of the benzoxazol-2-ylidene ligand in **5** was confirmed by the singlet at $\delta = 16.95$ ppm for the N-H proton in the ^{1}H NMR spectrum. The ^{31}P NMR spectrum showed a small shift to higher field for the phosphorus resonance ($\delta = 21.18$ ppm) compared to complex **4**. The molecular ion $[PdCl(L)PPh_3]^+$ (L = benzoxazol-2-ylidene) was detected in the FAB mass spectrum (positive ions) at $m/z = 786$, showing the calculated isotope distribution. In addition, peaks corresponding to the successive loss of the carbene ligand L, Cl and PPh_3 were also observed. Complex **5** could be crystallized from a concentrated solution in methanol, and its molecular structure determined by X-ray diffraction (Fig. 1). This analysis confirmed the assignment, that **5** is indeed the expected *trans*-bisphosphine monocarbene complex.

The cation of **5** shows a slightly distorted square-planar coordination geometry around the palladium atom. The angles C1-Pd-Cl and P1-Pd-P2 measure 172.59(7)° and 174.92(2)°, respectively. The chloride counter ion is hydrogen-bonded to the N-H group of the ylidene ligand [HN···Cl2 2.04(4) Å]. Finally, the dihedral angle between the almost planar benzimidazol-2-ylidene ligand and the Pd,P1,P2,Cl1,C1 plane measures 85.8°.

*Reaction of 2-(trimethylsiloxy)phenylisocyanide (**1**) with trans-[PdI$_2$(PPh$_3$)$_2$] (**6**)*

The surprising observation that only one chloride ligand could be substituted in *trans*-$[PdCl_2(PPh_3)_2]$ prompted us to repeat the experiment with *trans*-$[PdI_2(PPh_3)_2]$ **6**. Complex **6** was synthesized by the reaction of PdI_2 with two equivalents of triphenylphosphine in acetonitrile as described for the preparation of **4**. The ^{31}P NMR spectrum of **6** measured at low temperature showed just one resonance at $\delta = 13.84$ ppm which clearly indicated that a uniform reaction product was obtained. No indications for a *cis/trans* isomer equilibrium in solution were found. Since no ^{31}P NMR data for either the *cis* or the *trans* isomer have been published, we confirmed the *trans* configuration for **6** by determination of the lattice constants and space group of its dichloromethane solvate and compared the results with the published data for *trans*-$[PdI_2(PPh_3)_2]$*$2CH_2Cl_2$ [ref. 15]: $a = 11.922$ [11.884], $b = 20.432$ [20.399], $c = 8.35$ [8.331] Å, $\beta = 95.18$ [94.896]°, space group $P2_1/c$ [$P2_1/c$].

The reaction of *trans*-$[PdI_2(PPh_3)_2]$ with two equivalents of **1** in chloroform at −40 °C and the subsequent Si-O bond cleavage yielded exclusively *cis*-diiodo(benzoxazol–2–ylidene)–(triphenylphosphine)



Scheme 5.

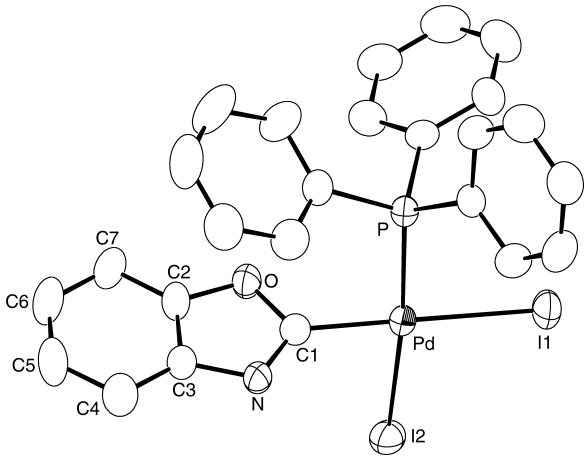


Fig. 2. Molecular structure of **7** (hydrogen atoms on calculated positions have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd-C1 1.962(5), Pd-P 2.2797(14), Pd-I1 2.6500(9), Pd-I2 2.6562(9), O-C1 1.346(5), O-C2 1.392(6), N-C1 1.305(6), N-C3 1.394(6), C2-C3 1.364(7), C2-C7 1.367(7), C3-C4 1.375(7); I1-Pd-I2 92.50(3), I1-Pd-P 91.05(4), I1-Pd-C1 177.69(13), I2-Pd-P 171.71(4), I2-Pd-C1 85.79(13), P-Pd-C1 90.45(13), C1-O-C2 107.9(4), C1-N-C3 111.6(4), Pd-C1-O 121.9(3), Pd-C1-N 130.1(3), O-C1-N 108.0(4), C3-C2-O 108.3(4), C7-C2-O 127.9(5), C2-C3-N 104.3(4); dihedral angle between planes made up from (Pd,I1,I2,P,C1) and (O,C1,N,C3,C2) 73.0°.

palladium(II) **7** (Scheme 4). In the ^{31}P NMR spectrum of **7**, only one singlet at $\delta = 16.32$ ppm was observed. Yellow needles of $\mathbf{7}{*}CH_2Cl_2$ crystallized from a dichlormethane/*n*-hexane solution and were used for an X-ray diffraction study. The molecular structure of **7** (Fig. 2) is considerably different from that of **5**. One phosphine ligand was substituted by one carbene ligand and the iodine atoms occupy *cis*-positions at the metal center. The distortion of the ideal square-planar coordination geometry around Pd is small (max 8°), similar to that in **5**.

The formation of the *cis*-complex **7** from the *trans*-configurated starting material **6** is remarkable. For square-planar complexes of the type $[PdX_2L_2]$ (X = halogen), equilibria have been observed between the two possible stereoisomers. Newkome *et al.* showed that *cis*-dichlorobis(di-2-pyridylphenylphosphine)palladium(II) can be converted into the *trans*-isomer on heating solutions containing excess phosphine [14]. Georgiev *et al.* detected a *cis/trans* equilibrium for $[PdCl_2\{PPh_2CH_2C(O)CH_3\}_2]$ in solution by using ^{31}P NMR spectroscopy [16]. A five-coordinate transition state has been discussed by Nelson *et al.* [17] for the *cis/trans* interconversion. It is unlikely that such an equilibrium is the source of the observed configurational change during the reaction **6** → **7**, as both the starting material **6** and the product **7** show only one resonance in the ^{31}P NMR spectra. We assume, that the geometry change takes place during the substitution of one phosphine ligand by the isocyanide. Unfortunately, the initially formed isocyanide complex could not be isolated.

Table 1. Crystal and data collection details for **5** and $\mathbf{7}{*}CH_2Cl_2$.

	5	$\mathbf{7}{*}CH_2Cl_2$
Crystal habit	colorless cubes	yellow needles
Crystal size, mm	$0.4 \times 0.4 \times 0.4$	$0.6 \times 0.1 \times 0.06$
Formula	$C_{43}H_{35}NCl_2OP_2Pd$	$C_{25}H_{20}NI_2OPPd{*}CH_2Cl_2$
Fw, amu	820.96	826.52
a, Å	12.569(8)	9.816(5)
b, Å	23.171(7)	12.926(3)
c, Å	12.690(6)	13.057(4)
α, deg	90	63.67(2)
β, deg	90.90(5)	76.17(4)
γ, deg	90	72.71(3)
V, Å^3	3695(5)	1406.6(9)
Space group	$P2_1/n$	$P\bar{1}$
Z	4	2
μ, mm^{-1}	0.769	3.121
Abs. corr.	none	empirical, 6Ψ-scans
2θ Range, deg	5 to 56	4 to 50
Unique data	8890	4914
Obsvd. ($I > 2\sigma(I)$)	6694	4126
R(observed),%	2.79, $R_w = 6.36$	3.23, $R_w = 7.71$
R(all),%	5.45, $R_w = 7.09$	4.40, $R_w = 8.27$
GOF	1.043	1.053
No. of variables	455	307
Res. el. dens., e/Å^3	$0.471/-0.456$	$0.756/-0.886$

Experimental Section

All experiments were carried out in an argon atmosphere using standard Schlenk techniques. All solvents were dried by standard methods and distilled prior to use. Correct elemental analyses were obtained for all reported compounds using a Vario EL elemental analyzer. NMR spectra were recorded on Bruker AM 250 and Jeol λ 400 instruments. Mass spectra were measured with Finnigan MAT 112 and MAT 711 spectrometers. Ligand **1** [2] and complexes **2** and **3** [4] were prepared according to published methods.

*Preparation of trans-dichloro-bis(triphenylphosphine)-palladium(II), (**4**):* A sample of 299 mg (1.686 mmol) of $PdCl_2$ was suspended in 40 ml of warm acetonitrile. A solution of 890 mg (3.39 mmol) of triphenylphosphine in 20 ml of acetonitrile was added at room temperature and the mixture was stirred for one hour. The yellow precipitate formed

was isolated by filtration, washed with small amounts of acetonitrile and dried *in vacuo*. Yield 1.10 g (1.567 mmol, 93%). – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.70$ (m, 12 H, Ar-H), 7.37(m, 18 H, Ar-H). ^{13}C NMR (63 MHz, $CDCl_3$): $\delta =$ 128.0, 128.06, 130.50, 135.05 (Ar-C). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 24.46$.

*Preparation of trans-chloro(benzoxazol-2-ylidene)bis(triphenylphosphine)palladium (II) chloride, (**5**):* A sample of 0.6 ml (3.134 mmol, 2.2 eq) of **1** was injected into a solution of 1.020 g (1.453 mmol) of **4** in 150 ml of THF at −40 °C. After stirring for one hour, a few crystals of Bu_4NF along with 0.1 ml of water were added to the solution. A colorless solid precipitated immediately. After stirring for an additional 10 min the solid product was separated by filtration, washed several times with THF and dried *in vacuo*. Yield 1.005 g (1.224 mmol, 84%). Suitable crystals for X-ray structure determination were obtained by cooling a saturated solution of **5** in methanol. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.3 - 7.1$ (m, 22 H, Ar-H), 7.80 (m, 12 H, Ar-H), 16.95 (s, 1 H, N-H). – ^{31}P NMR (161 MHz, $CDCl_3$): $\delta =$ 21.18. – FAB-MS (positive ions, $CHCl_3$/nitrophenol): *m/z* (%) = 786 (8) $[PdCl(PPh_3)_2(L)]^+$, 748 (9) $[Pd(PPh_3)_2(L)]^+$, 630 (2) $[Pd(PPh_3)_2]^+$, 524 (4) $[PdCl(PPh_3)(L)]^+$, 489 (16) $[Pd(PPh_3)(L)]^+$, 263 (41) $[PdCl(L)+H]^+$; L = benzoxazol-2-ylidene ligand.

*Preparation of trans-diiodobis(triphenylphosphine)palladium(II), (**6**):* Complex **6** was synthesized as described for **4** as a red-brown powder. Yield 92%. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.66$ (m, 12 H, Ar-H), 7.36 (m, 18 H, Ar-H). – ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 13.84$. FAB-MS (positive ions, $CHCl_3$/nitrophenol): *m/z* (%): 884 (1) $[PdI_2(PPh_3)_2]^+$, 757 (37) $[PdI(PPh_3)_2]^+$, 630 (26) $[Pd(PPh_3)_2]^+$, 368 (22) $[Pd(PPh_3)]^+$.

*Preparation of cis-diiodo(benzoxazol-2-ylidene)(triphenylphosphine)palladium(II), (**7**):* Complex **7** was synthesized as described for **5** from 310 mg (0.35 mmol) of **6** in 40 ml of chloroform and 0.15 ml (0.784 mmol, 2.2 eq) of 2-trimethylsiloxyphenyl isocyanide **1**. To separate **7** from unreacted **6**, the crude reaction product was suspended in toluene and the insoluble **7** was isolated by filtration. Yield 180 mg (0.24 mmol, 70%). Yellow needles of $\mathbf{7}^*CH_2Cl_2$ were obtained by recrystallization from CH_2Cl_2/*n*-hexane at −18 °C. – ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 14.63$ (s, 1 H, N-H), 7.78 – 7.12 (19 H, m, Ar-H). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 16.32$. IR (KBr): $\tilde{\nu}$ [cm^{-1}] 3050 (w, N-H), 1433 (vs), 1094 (vs).

*X–ray structure determination of **5** and $\mathbf{7}*CH_2Cl_2$ [18]:*

Suitable crystals were selected and mounted on a CAD-4 diffractometer equipped with a sealed Mo X-ray tube ($\lambda =$ 0.71073 Å) and a nitrogen cooling device for data collection at 153(2) K. Both structures were solved by standard Patterson and Fourier methods. All non hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms (except HN in **5**) reside on calculated positions (d(C-H) = 0.95 Å, d(N-H) = 0.87 Å [19]) with U_{eq}(H) = 1.3 U_{eq}(C). HN in **5** was located by Fourier procedures and its positional parameters were refined with isotropic displacement parameters. Selected crystallographic data are listed in Table 1. ORTEP [20] plots are presented in Figures 1 and 2. All calculations were carried out using the SHELX-97 [21] programs.

Acknowledgement

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[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 206018 & 206019. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44) 1223-336033; e-mail: deposit@ccdc.ac.uk).

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