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# Synthesis and molecular structures of $\alpha$ -diimines and their zinc and palladium dichloride complexes

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#### Abstract

Three  $\alpha$ -diimines, 2,3-dimethyl-*N*,*N'*-bis(cyclohexyl)-diaza-1,4-butadiene, Cy-DAD (1), (DAD = diaza-1,4-butadiene), bis{2,8-(4-methoxyphenylimino)} acenaphthene, *p*-OMe-BIAN (3), (BIAN = 2,8-bis(arylimino)acenaphthene) and bis{2,8-(2,6-di-isopropylphenylimino)} acenaphthene, 2,6-<sup>i</sup>Pr-BIAN (4), were synthesised either via their zinc complexes, as a template, or by the direct reaction of the appropriate primary amine with the diketone. Compound 1 is a non-constrained analogue of the rigid, bidentate nitrogen ligands 3 and 4. Syntheses of the zinc and palladium complexes of 3 and 4, namely 2, 5, 6 and 7, are also reported herein. All compounds have been characterised spectroscopically, and the molecular structures of 1, 3, 4, ZnCl<sub>2</sub> (*p*-OMe-BIAN)  $\cdot \frac{1}{2}$ CH<sub>2</sub>Cl<sub>2</sub> (2), PdCl<sub>2</sub>(*p*-OMe-BIAN) (6) and PdCl<sub>2</sub>(2,6-<sup>i</sup>Pr-BIAN) (7) have been determined by single-crystal X-ray diffraction. Compound 1 adopts a *transoid* geometry and possesses a crystallographic inversion centre midway along the N=C-C=N backbone. Compounds 3 and 4 are inherently *cisoidal* and X-ray analysis highlights a twofold axis through the backbone. The Pd(II) centres of 6 and 7 both adopt square planar geometries whilst 6 contains four molecules per asymmetric unit and 1/2 molecule of benzonitrile per Pd atom and complex 7 is isomorphous with the known structure of PdCl(Me)(2,6-<sup>i</sup>Pr-BIAN). The Zn complex 2 is pseudo tetrahedral as expected for Zn(II).

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#### 1. Introduction

Over the past decade there has been considerable interest in alternative ligands to phosphines, for the development of late transition metal catalysts. Examples of this include the substantial development by Brookhart and co-workers [1] of  $\alpha$ -diimine ligands for nickel and palladium catalysed olefin polymerisation and recent developments in the zinc catalysed ring-opening polymerisation of epoxides and  $\varepsilon$ -caprolactone reported by Bochmann and co-workers [2]. Furthermore, other bi-

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dentate nitrogen donor ligands have been used in many catalytic studies including the enantioselective carbonylation of olefins [3], hydrogenation and hydrosilylation [4], the borylation of alkanes and alkenes [5], diboration [6] and reduction of nitrobenzene to aniline [7]. Routes to the diimines have been previously developed by Elsevier and co-worker [8a], Fukuda and co-worker [8b] and Dieck and Dietrich [8c].

Whilst most studies of the  $\alpha$ -diimines have concentrated on the reactivity of their complexes, very little crystallographic information has been obtained. We report herein the synthesis and structural characterisation of *p*-OMe-BIAN (3), 2,6-<sup>*i*</sup>Pr-BIAN (4), Cy-DAD (1), ZnCl<sub>2</sub>(*p*-OMe-BIAN)  $\cdot \frac{1}{2}$ CH<sub>2</sub>Cl<sub>2</sub> (2), PdCl<sub>2</sub>(*p*-OMe-BIAN) (6) and PdCl<sub>2</sub>(2,6-<sup>*i*</sup>Pr-BIAN) (7) (shown in

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Scheme 1). Although the structure of 2,6-<sup>*i*</sup>Pr-BIAN has been published previously [9a,9b] we note that the space group reported was wrong [9c].

#### 2. Experimental

#### 2.1. General

All chemicals were commercially available and were used as received. <sup>1</sup>H NMR spectra were obtained using a 400 MHz Bruker Avance and Mercury-200, Unity-300 and Inova-500 MHz Varian spectrometers; coupling constants are given in Hz. Mass spectra were obtained with Micromass AutoSpec (EI) and Micromass-LCT (ES) spectrometers. The elemental analyses were carried out with an Exeter Analytical Inc. CE-440 elemental analyser.

#### 2.2. Synthesis of (Cy-DAD) (1)

The compound 2,3-dimethyl-N,N'-bis(cyclohexyl)diaza-1,4-butadiene was prepared in a similar manner to that used by Dieck and Dietrich [8c]. Cyclohexylamine (20.25 ml, 180 mmol) was added dropwise to a cooled (0 °C) mixture of butane-2,3-dione (7.8 ml, 90 mmol), molecular sieves (10 g, 4 Å) and formic acid (1 ml, 98%) in chloroform (100 ml). After stirring for one day, the mixture was filtered and the chloroform removed in vacuo. The remaining yellow-white solid was re-crystallised from ethanol yielding colourless plates suitable for Xray diffraction. Yield: 8.9 g, 40%. (Found: C, 77.40; H, 11.60; N, 11.28. C<sub>16</sub>H<sub>28</sub>N<sub>2</sub> requires: C, 77.36; H, 11.36; N, 11.28%). ES-MS [m/z]: 248 [M]<sup>+</sup>, 205 [M – C<sub>3</sub>H<sub>7</sub>]<sup>+</sup>,

# 166 $[M - C_6H_{10}]^+$ . <sup>1</sup>H NMR [CD<sub>2</sub>Cl<sub>2</sub>, 200 MHz]: $\delta$ 3.5 (m, 4H, CH<sub>2</sub>), 2.05 (s, 6H, CH<sub>3</sub>), 1.8 (m, 4H, CH<sub>2</sub>), 1.65 (m, 4H, CH<sub>2</sub>), 1.4 (m, 8H, CH<sub>2</sub>).

#### 2.3. Synthesis of $ZnCl_2(p$ -OMe-BIAN) $\cdot \frac{1}{2}CH_2Cl_2$ (2)

This complex was synthesised in a similar manner to that described in the literature [8a]. A mixture of acenaphthenequinone (2.00 g, 11 mmol), anhydrous ZnCl<sub>2</sub> (1.71 g, 12.5 mmol) and 4-methoxyaniline was heated to 170 °C in a closed Young's-tap tube for 4 h. The mixture was then cooled to 20 °C and transferred to a beaker with Et<sub>2</sub>O (2  $\times$  50 ml) and glacial acetic acid (2  $\times$  50 ml). Aluminium foil was placed over the beaker and the following day the red precipitate which had formed was collected by filtration and washed with  $Et_2O$  (5 × 20 ml). Crystals suitable for X-ray diffraction studies were grown from CH<sub>2</sub>Cl<sub>2</sub>. Yield: 5.51 g, 95%. (Found: C, 56.49; H, 3.71; N, 5.09.  $C_{26}H_{20}Cl_2N_2O_2Zn \cdot \frac{1}{2}CH_2Cl_2$  requires: C, 55.72; H, 3.71; N, 4.90%). This suggests that CH<sub>2</sub>Cl<sub>2</sub> may be slowly evaporating from the crystal lattice.) ES-MS [CH<sub>2</sub>Cl<sub>2</sub>, m/z]: 528 [M]<sup>+</sup>, 391  $[M - H - ZnCl_2]^+$ . <sup>1</sup>H NMR [DMSO; 200 MHz]:  $\delta$ 8.12 (d, 2H, J = 8.3, C<sub>10</sub>H<sub>6</sub>), 7.57 (dd, 2H, J = 8.3, 7.2,  $C_{10}H_6$ ), 7.09 (s, 8H,  $C_6H_4$ ), 6.96 (d, 2H, J = 7.2, C<sub>10</sub>H<sub>6</sub>), 3.85 (s, 6H, OMe).

#### 2.4. Synthesis of p-OMe-BIAN (3)

Compound 3 was prepared in a similar manner to that described in the literature [8a]. Thus, ZnCl<sub>2</sub>  $(p-OMe-BIAN) \cdot \frac{1}{2}CH_2Cl_2$  (2) (3.00 g, 5.25 mmol) was added to a solution of  $K_2CO_3$  (25.00 g, 180 mmol) in water (250 ml) and the mixture was heated at reflux with vigorous stirring. After 17 h, the solid was collected by filtration and washed with water  $(5 \times 30 \text{ ml})$  and then was extracted by soxhlet with ethanol for two days. On cooling, red crystals suitable for X-ray diffraction studies grew from solution. The reaction was filtered and the mother liquor concentrated to half volume to promote the formation of a second crop of crystals. Yield: 1.80 g, 81%. (Found: C, 79.32; H, 5.03; N, 7.17. C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 79.57; H, 5.14; N, 7.14%), EI-MS [CH<sub>2</sub>Cl<sub>2</sub>, m/z]: 391 [M - 1]<sup>+</sup>, 377 [M - CH<sub>3</sub>]<sup>+</sup>, 361  $[M - OCH_3]^+$ . <sup>1</sup>H NMR [DMSO; 200 MHz]:  $\delta$ 8.07 (d, 2H, J = 7.8, C<sub>10</sub>H<sub>6</sub>), 7.53 (dd, 2H, J = 7.8, 7.0,  $C_{10}H_6$ , 7.07 (apparent d, 8H, J = 3.1,  $C_6H_4$ ), 6.92 (d, 2H, J = 7.0,  $C_{10}H_6$ ), 3.83 (s, 6H, OMe).

#### 2.5. Synthesis of $(2,6^{-i}Pr-BIAN)$ (4)

This compound was prepared via a similar method to that of Fukuda and co-workers [8b]. Acenaphthenequinone (1.35 g, 7.4 mmol) was dissolved in acetonitrile (65 ml) and glacial acetic acid (12 ml) and heated to reflux. 2,6-Diisopropylaniline (3 ml, 16 mmol) was added dropwise and the mixture refluxed for 1.5 h. After cooling to room temperature the yellow solid was filtered, washed with hexane and re-crystallised with hexane/CH<sub>2</sub>Cl<sub>2</sub> to yield crystals suitable for X-ray diffraction. Yield: 3.15 g, 85%. (Found: C, 86.20; H, 7.98; N, 5.65 C<sub>36</sub>H<sub>40</sub>N<sub>2</sub> requires: C, 86.35; H, 8.05; N, 5.59%). EI-MS [CH<sub>2</sub>Cl<sub>2</sub>, *m*/*z*]: 500 [M]<sup>+</sup>, 457 [M - C<sub>3</sub>H<sub>7</sub>]<sup>+</sup>, 340 [M - C<sub>6</sub>H<sub>3</sub>(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> + 1]<sup>+</sup>. <sup>1</sup>H NMR [CD<sub>2</sub>Cl<sub>2</sub>; 400 MHz]: $\delta$  7.91 (d, 2H, *J* = 8.3, C<sub>10</sub>H<sub>6</sub>), 7.58 (dd, 2H, *J* = 8.3, 7.1, C<sub>10</sub>H<sub>6</sub>), 7.3 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 6.69 (d, 2H, *J* = 7.1, C<sub>10</sub>H<sub>6</sub>), 2.98 (sept, 2H, *J* = 6.8, CHCH<sub>3</sub>), 1.30 (d, 6H, *J* = 6.8, CH<sub>3</sub>), 1.0 (d, 6H, *J* = 6.8, CH<sub>3</sub>).

#### 2.6. Synthesis of $ZnCl_2(2,6^{-i}Pr-BIAN)$ (5)

This zinc complex was prepared using a different method to that published by Asselt et al. [8a]. Thus, 2,6-'Pr-BIAN (4) (2 g, 3.99 mmol) was added in one portion to a stirring solution of anhydrous ZnCl<sub>2</sub> (0.544 g, 3.99 mmol) in glacial acetic acid (50 ml). The yellow-orange solid which formed was collected by filtration, washed with  $Et_2O(3 \times 30 \text{ ml})$  and dried in air. The product was recrystallised by layering Et<sub>2</sub>O over CH<sub>2</sub>Cl<sub>2</sub>. Yield: 2.34 g, 92%. (Found: C, 67.77; H, 6.33; N, 4.42. C<sub>36</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>2</sub>Zn requires: C, 67.88; H, 6.33; N, 4.40%). EI-MS  $[CH_2Cl_2, m/z]$ : 600  $[M - Cl + 1]^+$ 500  $[M - ZnCl_2]^+$ , 457  $[M - ZnCl_2 - C_3H_7]^+$ , 340  $[M - ZnCl_2 - C_3H_7]^+$  $Cl_2 - C_6H_3(C_3H_7)_2 + 1]^+$ . <sup>1</sup>H NMR [CD<sub>2</sub>Cl<sub>2</sub>; 200 MHz]:  $\delta$  8.17 (d, 2H, J = 7.9, C<sub>10</sub>H<sub>6</sub>), 7.58 (dd, 2H,  $J = 7.9, 7.4, C_{10}H_6$ , 7.46 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 6.75 (d, 2H, J = 7.4, C<sub>10</sub>H<sub>6</sub>), 3.26 (sept, 2H, J = 6.8, CHCH<sub>3</sub>), 1.36  $(d, 6H, J = 6.8, CH_3), 0.87 (d, 6H, J = 6.8, CH_3).$ 

#### 2.7. Synthesis of $PdCl_2(p-OMe-BIAN) \cdot \frac{1}{2}C_6H_5CN$ (6)

Cyclooctene (0.341 ml, 2.61 mmol) was added in one portion to a stirring solution of  $PdCl_2(NCPh)_2$ (0.5 g, 1.324 mmol) in benzonitrile (10 ml). A solution of p-OMe-BIAN (3) (1.023 g, 2.608 mmol) in benzonitrile (10 ml) was then added and the reaction was stirred for 2 h. The solid formed was collected by filtration, washed with Et<sub>2</sub>O and recrystallised from refluxing CH<sub>2</sub>Cl<sub>2</sub>/benzonitrile. Yield: 0.511 g, 67%. (Found: С, 3.64; N, 56.65; Η, 5.64.  $C_{26}H_{20}Cl_2N_2O_2Pd \cdot \frac{1}{2}C_6H_5CN$  requires: C, 57.02; H, 3.65; N, 5.64%). EI-MS [CH<sub>2</sub>Cl<sub>2</sub>, m/z]: 570 [M]<sup>+</sup>, MHz]:  $\delta$  8.27 (d, 2H, J = 8.4, C<sub>10</sub>H<sub>6</sub>), 7.63 (dd, 2H, J = 8.4, 7.3,  $C_{10}H_6$ ), 7.34 (d, 4H, J = 8.7,  $C_6H_4$ ), 7.13 (d, 4H, J = 8.7, C<sub>6</sub>H<sub>4</sub>), 6.73 (d, 2H, J = 7.3, C<sub>10</sub>H<sub>6</sub>), 3.86 (s, 6H, OMe).

## 2.8. Synthesis of $PdCl_2(2,6^{-i}Pr-BIAN)$ (7)

This complex was prepared and crystallised as for **6** with the following quantities of materials: cyclooctene (0.166 ml, 1.27 mmol), PdCl<sub>2</sub>(NCPh)<sub>2</sub> (0.244 g, 0.637 mmol) in benzonitrile (10 ml) and 2,6<sup>-*i*</sup>Pr-BIAN (0.319 g, 0.637 mmol) in benzonitrile (10 ml). Yield: 0.314 g, 72%. (Found: C, 63.62; H, 5.95; N, 4.13. C<sub>36</sub>H<sub>40</sub> Cl<sub>2</sub>N<sub>2</sub>Pd requires: C, 63.77; H, 5.95; N, 4.13%.) EI-MS [CH<sub>2</sub>Cl<sub>2</sub>, *m*/*z*]: 500 [M – PdCl<sub>2</sub>]<sup>+</sup>, 457 [M – PdCl<sub>2</sub> – C<sub>3</sub>H<sub>7</sub>]<sup>+</sup>, 340.1 [M – PdCl<sub>2</sub> – C<sub>6</sub>H<sub>3</sub>(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> + 1]<sup>+</sup>. <sup>1</sup>H NMR [CD<sub>2</sub>Cl<sub>2</sub>; 200 MHz]:  $\delta$  8.18 (d, 2H, *J* = 8.4, C<sub>10</sub>H<sub>6</sub>), 7.69 (m, 6H, C<sub>6</sub>H<sub>3</sub>), 7.41 (dd, 2H, *J* = 8.4, 7.2, C<sub>10</sub>H<sub>6</sub>), 6.55 (d, 2H, *J* = 7.2, C<sub>10</sub>H<sub>6</sub>), 3.50 (sept, 2H, *J* = 6.8, CHCH<sub>3</sub>), 1.52 (d, 6H, *J* = 6.8, CH<sub>3</sub>).

#### 2.9. X-ray crystallography

X-ray diffraction experiments were performed on Bruker 3-circle diffractometers with SMART 6000 CCD area detectors, using graphite-monochromated Mo K $\alpha$  radiation ( $\bar{\lambda} = 0.71073$  Å). The low temperature of the crystals was maintained with Cryostream (Oxford Cryosystems) open-flow N<sub>2</sub> cryostats. The structures were solved by direct methods and refined by full-matrix least squares against  $F^2$  of all reflections, using SHELXTL software [10]. All non-H atoms were refined with anisotropic ADP and all H atoms were located by difference Fourier synthesis and refined isotropically. The absolute structure of **5** has been determined from the anomalous dispersion of sulfur, the Flack parameter converging at 0.26(16) [11]. Crystal data and experimental details are given in Table 1.

#### 3. Results and discussion

#### 3.1. Crystal structures

Molecule 1 (shown in Fig. 1) lies at a crystallographic inversion centre, the C(1)-N=C(7)-C(7')=N'-C(1') moiety is planar, and *transoid* with respect to the central C(7)-C(7') bond; the C(1)-N-C(7)-C(7') torsion angle is  $-179.95(7)^{\circ}$ . This *E*, s-*trans-E* conformation has been observed in CyN=CHCH=NCy [12] and is typical for previously reported 2,3-dimethyl-azabutadienes [13], while their analogues with larger substituents in the 2,3-positions usually adopt *gauche* conformations. The cyclohexyl ring adopts a chair conformation. The bond distances are usual, and indicative of localised C=N double bonds.

In the structure of  $2 \cdot \frac{1}{2}$ CH<sub>2</sub>Cl<sub>2</sub>, molecule 2 (Fig. 2) has no crystallographic symmetry, while the CH<sub>2</sub>Cl<sub>2</sub> is chaotically disordered around an inversion centre. The

Table 1 Crystal data and experimental parameters

Compound	1	2	3	4	6	7
Formula	C16H28N2	$C_{26}H_{20}N_2O_2Cl_2Zn \cdot \frac{1}{2}CH_2Cl_2$	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	C36H40N2	$C_{26}H_{20}N_2O_2Cl_2Pd \cdot \frac{1}{2}C_7H_5N$	C <sub>36</sub> H <sub>40</sub> N <sub>2</sub> Cl <sub>2</sub> Pd
Formula weight	248.40	571.17	392.44	500.70	621.30	678.00
T (K)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c \ (\# 14)$	$P2_1/c$ (# 14)	Pbcn (# 60)	<i>C</i> 2/ <i>c</i> (# 15)	$P2_1/n \ (\# \ 14)$	Pbca (# 61)
a (Å)	14.076(5)	12.402(1)	19.851(4)	15.414(2)	19.360(3)	11.429(1)
b (Å)	5.8507(7)	11.736(1)	8.913(1)	8.860(1)	23.573(4)	21.330(1)
<i>c</i> (Å)	9.222(2)	17.574(2)	10.936(2)	21.452(3)	23.871(4)	26.984(1)
β (°)	93.81(2)	95.99(1)	90	93.56(1)	105.93(1)	90
$V(Å^3)$	757.8(3)	2543.9(4)	1934.9(6)	2923.8(7)	10476(3)	6578.1(5)
Ζ	2	4	4	4	16	8
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.089	1.491	1.347	1.137	1.576	1.369
$\mu (\text{mm}^{-1})$	0.06	1.31	0.09	0.07	0.94	0.75
$2\theta_{\max}$ (°)	60	60	58	58	60	60
Total reflections	10 161	31 064	30 778	19 346	158 533	86 119
Unique reflections	2211	7424	2569	4261	30 528	9562
Reflections $I > 2\sigma(I)$	2006	5762	2159	3053	18 993	7306
Parameters	138	330	177	181	1349	394
R <sub>int</sub>	0.071	0.035	0.034	0.059	0.063	0.052
$R(F, I > 2\sigma(I))$	0.040	0.035	0.038	0.053	0.037	0.033
$wR$ ( $F^2$ , all data)	0.119	0.103	0.110	0.156	0.114	0.092



Fig. 1. Molecular structure of 1. Atoms generated by the inversion centre are primed.

Zn atom has a distorted tetrahedral coordination with two Cl ligands and a nearly-planar chelating diazabutadiene moiety N(1)C(11)-C(12)N(2). In similar complexes with phenyl (and especially substituted phenyl) groups at the N atoms, the phenyl rings usually adopt a perpendicular orientation with respect to the diazabutadiene plane (plane A).



Fig. 2. Molecular structure of **2** in the crystal of  $2 \cdot \frac{1}{2}$ CH<sub>2</sub>Cl<sub>2</sub>.

In 2, the phenyl rings form angles of 54.1° and 57.7° with the A plane and  $13.1^{\circ}$  between themselves. Thus, the molecule has an approximate mirror plane perpendicular to the acenaphthene plane (violated, however, by opposite orientations of the methyl groups) but loses the mirror plane coinciding with the acenaphthene plane. The two Cl ligands are sterically non-equivalent: Cl(2) faces more overcrowding than Cl(1), with the following results: (i) the Zn-Cl(2) bond is 0.017 Å longer than Zn-Cl(1); (ii) the Zn atom tilts out of the A plane by 0.12 Å in the direction of Cl(1); (iii) the N–Zn–Cl(1) angles are wider than N-Zn-Cl(2), averaging 116.5° and  $110.2^{\circ}$ , respectively; (iv) the naphthalene moiety is tilted out of the A plane by  $5.1^{\circ}$  towards Cl(2), i.e., in the direction of less hindrance on its side. Distortions (ii), (iii) and (iv) together make the angle between the acenaphthene plane and the Zn-Cl(2) bond 70.9° compared to 44.5° for Zn–Cl(1).

Molecule **3** lies on a crystallographic twofold axis, passing through atoms C(5), C(6) and the midpoint of the C(7)–C(7') bond (Fig. 3(a)). The diazabutadiene moiety is planar, and the phenyl rings are inclined to its plane (*A*) by 57.6°; hence, the molecule has no local mirror symmetry but adopts a twisted overall conformation. The *A* and naphthalene planes form an angle  $\varphi = 6.0^\circ$ , while the N–C(8) bond is tilted out of plane *A* in the opposite direction, with the torsion angles C(7')–C(7)–N–C(8) 11.0° and C(2)–C(1)···N–C(8) 15.5°.

Molecule 4 also has crystallographic  $C_2$  symmetry (Fig. 3(b)). Bulky <sup>*i*</sup>Pr groups enforce a more perpendicular orientation of the phenyl rings, which are inclined



Fig. 3. Molecular structures of **3** (a) and **4** (b). Atoms generated by the twofold axis in each structure are primed.

by 78.7° to the *A* plane, and the twist of the molecule is correspondingly smaller than in **3**, with the angles  $\varphi = 2.8^{\circ}$ , C(7')–C(7)–N–C(8) 3.5° and C(2)–C(1)···N–C(8) 5.1°.

While this work was in progress, the crystal structure of **4** was determined [9a,9b] at room temperature in space group *Cc* (No. 9), with the molecule in a general position. The lattice parameters reported, a = 15.587(2)Å, b = 8.856(2) Å, c = 21.780(7) Å,  $\beta = 93.85(2)^{\circ}$ , V = 2999.7 Å<sup>3</sup>, were identical with our results (allowing for thermal expansion). A search for additional symmetry, performed on the atomic coordinates (ref. code WUSLIF) deposited at the CSD, using PLATON software [14], revealed the missing inversion centre with the coordinates (-0.030, 0, -0.212). Thus, the structure [9a,9b] is identical with the one reported herein, in the correct space group *C2/c* (No. 15) as already pointed out by Marsh [9c].

The asymmetric unit of  $\mathbf{6} \cdot \frac{1}{2}$ PhCN comprises four molecules of the complex and two of benzonitrile, all of them devoid of crystallographic symmetry (Fig. 4(a)). Acenaphthene systems of all molecules **6** in the structure are approximately parallel to the  $(1\ 0\ -1)$ plane, and the four independent Pd atoms (although not the rest of the molecules) are related by peculiar pseudo-symmetrical operations, viz: (i) x, y, z; (ii) x, y + 1/2, z; (iii) 1/2 - x, y - 1/4, 1 - z; (iv) 1/2 - x, y - 1/4, 1 - z. The geometry and conformation of inde-



Fig. 4. Molecular structures of 6 (a) (one of the four independent molecules in the crystal of  $6 \cdot \frac{1}{2}$  PhCN) and 7 (b).

pendent molecules is similar, with square-planar coordination of the Pd atom. Phenyl rings are approximately normal to the diazabutadiene moiety (interplanar angles  $74.8^{\circ}$ - $89.9^{\circ}$ ). The acenaphthene moiety in molecule (ii) is practically planar and in three others show minor twist, of the same order as in molecule **4**.

The crystal structure of **7** (Fig. 4(b)) is isomorphous with that of chloro-bis $\{2,8-(2,6-di\text{-isopropylphenylimi-no})$ -acenaphthene-N,N)-methylpalladium [5], which differs from **7** by a substitution of a methyl group for one of the chloro-ligands. The asymmetric unit comprises one molecule, without crystallographic symmetry. Molecule **7** is similar to **6** in the nearly perpendicular orientation of the phenyl rings (dihedral angles of 83.3° and 82.6° with plane *A*) and other conformational features.

The ionic radius of square-planar  $Pd^{2+}$  (0.64 Å) exceeds that of tetrahedral  $Zn^{2+}$  (0.60 Å) [20]. In fact, the Pd–Cl bond distances in **6** and **7** exceed Zn–Cl in **2** by an average of 0.065 Å, while the Pd–N bonds are actually *shorter* than Zn–N, by ca. 0.035 Å (Table 2). This is probably due to  $d\pi \rightarrow p\pi$  back donation in the Pd complexes. The resulting  $\pi$  delocalisation in the chelate ring is indicated by small but significant lengthening of C=N bonds and shortening of the intermediate C–C bond in the Pd complexes compared to the free molecules, while coordination with Zn affects these distances insignificantly. It is noteworthy that coordination with

Table 2 Bond distances (Å) in diimine ligands and their complexes

	M–Cl	M–N	C=N	C–C	$N{\cdots}N$
1	_	_	1.281(1)	1.510(1)	
2	2.2013(6)	2.085(2)	1.281(3)	1.520(3)	2.713(3)
	2.2180(6)	2.071(2)	1.285(3)	_	_
3	_	_	1.277(1)	1.527(2)	2.815(2)
4	_	_	1.280(1)	1.530(2)	2.812(2)
6					
Minimum	2.2731(7)	2.033(2)	1.275(3)	1.495(3)	2.652(3)
Maximum	2.2817(7)	2.055(2)	1.295(3)	1.499(3)	2.664(3)
Average	2.277(3)	2.041(8)	1.289(6)	1.497(2)	2.660(5)
7	2.2665(5)	2.053(2)	1.293(2)	1.486(3)	2.679(2)
	2.2689(5)	2.051(2)	1.292(2)	_	-

Zn reduces the transannular  $N \cdots N$  distance by ca. 0.1 Å compared to free molecules, and coordination with Pd reduces it by 0.15 Å.

### 3.2. <sup>1</sup>H NMR properties

The <sup>1</sup>H NMR spectrum of compound **3** shows three signals at  $\delta$  8.07, 7.53 and 6.92 corresponding to positions **A**, **B** and **C**, respectively (see Fig. 5) of the acenaphthenequinone backbone, and an apparent doublet (AB spin system) at  $\delta$  7.07 for the C<sub>6</sub>H<sub>4</sub> aromatic protons. On complexation to Zn, a very small downfield shift is observed for all of these signals and the apparent doublet collapses to a singlet, i.e., the two chemical environments lead to absolutely coincident signals. When Pd occupies the cavity, a more pronounced effect is observed. The signals relating to protons at positions **A** and **B** move downfield while that of **C** moves upfield. The major difference, however, is the splitting of the C<sub>6</sub>H<sub>4</sub> AB signal into two doublets.

These effects may well be due to the Pd–N interaction being stronger than the analogous Zn–N interaction. Very little change is observed in the shift of the methoxy signal. An increase in all of the coupling constants is also observed in complexation of **3** to either Zn or Pd.

The proton signals of compound 4 exhibit very similar behaviour to that observed in 3. While the <sup>1</sup>H signals at positions A and C move upfield and downfield as described for 3, the signal for the protons at posi-



Fig. 5. Assignment of acenaphthenequinone proton positions.

tion **B** does not shift on complexing to Zn but moves upfield when **4** is bound to Pd. As in compound **3**, it is the <sup>1</sup>H signals for the aryl side arm that show the most significant shifts. The C<sub>6</sub>H<sub>3</sub> signal remains a multiplet regardless of complexation; however, it moves downfield on binding to Zn (0.16 ppm) and Pd (0.39 ppm). This is also the case for the CH of the <sup>*i*</sup>Pr groups. There are two signals present for the methyl groups in compound **4** ( $\Delta \delta = 0.3$  ppm), indicative of restricted rotation. The magnitude of separation increases on complexation to Zn ( $\Delta \delta = 0.49$ ppm) and Pd ( $\Delta \delta = 0.52$  ppm).

#### 4. Conclusions

Three  $\alpha$ -diimines have been synthesised and two of these have been complexed to both ZnCl<sub>2</sub> and PdCl<sub>2</sub>. The <sup>1</sup>H NMR spectra have been compared and compounds **1**, **2**, **3**, **4**, **6** and **7** have been structurally characterised by single-crystal X-ray diffraction, revealing the changes resulting from coordination to both tetrahedral Zn(II) and square-planar Pd(II) metal centres.

#### 5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic data centre, CCDC Nos. 236150–236155. Copies of this data may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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