# Synthesis and X-ray Crystal Structures of Acenaphthenequinone-based α-Diimine Palladium Complexes and a Novel V-shape Tripalladium Cluster

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**Abstract.** Partially fluorinated 1,4-Diazadiene ( $\alpha$ -Diimine) ligand 3,5-CF<sub>3</sub>-BIAN (1) formed from 3,5-bis(trifluoromethyl)aniline and acenaphthenequinone was used in the synthesis of palladium dichlorido complex 2 and its mono methyl chlorido palladium complex 3. Both complexes as well as side products of the reaction with methyl lithium such as trans-bis(3,5-bis(trifluoromethyl)aniline complex 4 and an interesting mixed valent trinuclear V-shaped

### Introduction

 $\alpha$ -Dimines are one of the most important ligand families, not only in coordination chemistry but also in catalysis. Thus the study on  $\alpha$ -diimines and their related catalytic reactions is a topic of general interest [1-4]. In 1995 Brookhart and his coworkers reported  $\alpha$ -diimine palladium(II)and nickel(II)-catalyzed olefin polymerizations and obtained high molecular weight polymers with a branched microstructure [5]. The copolymerization of ethylene or propylene with other  $\alpha$ -olefins and acrylates could be also catalyzed with the support of these ligands [6]. Mecking reported the catalytic olefin polymerization with ionic diimine palladium(II) and nickel(II) complexes in aqueous solution [7]. A Pd(OAc)<sub>2</sub>/1,4-diazabutadiene (DAB-R) system was developed for the Suzuki-Miyaura cross-coupling of various aryl bromides and activated aryl chlorides with arylboronic acids, and it was found that the best reactivity was attained if R is a cyclohexyl group with the stronger donating ability of alkyl substituents, making the ligand more electron-rich [8]. Cationic complexes [(ArN=CR-RC=NAr)Pt(CH<sub>3</sub>)(L)]<sup>+</sup>  $[BF_4]^-$  (Ar = aryl; R = H, CH<sub>3</sub>; L = water, trifluoroethanol) react smoothly with benzene at room temperature in trifluoroethanol to activate the C-H bond of benzene [9].

Herein, we report the synthesis and characterization of 1,2-bis-(3,5-bis-trifluoromethyl-phenylimino)-acenaphthene, 3,5-CF<sub>3</sub>-BIAN (1), 1,2-bis(3,5-bis-trifluoromethyl-phenylimino)acenaphthenedichloro-palladium(II),  $[PdCl_2(3,5-bis-trifluoromethyl-phenylimino)]$ 

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palladium cluster 5 with two bridging  $\mu^2$ , $\eta^3$ -N,CN' non-innocent BIAN ligands were structurally characterized by the single-crystal XRD method.

**Keywords:** Palladium; 1,4-Diazadienes; Metal cluster compounds; Crystal structures

 $CF_3$ -BIAN)] (2), and 1,2-bis(3,5-bis-trifluoromethylphenylimino)acenaphthene-methylchloropalladium(II), [Pd(Me)Cl(3,5-CF\_3-BIAN)] (3). The X-ray crystal structures of 2, 3, bis(3,5-di(trifluoromethyl)aniline)dichloropalladium(II) (4) and bi(1,2-bis(3,5-bis-trifluoromethyl-phenylimino)acenaphthene)-bis(dimethylsulfide)methylchlorotripalladium (5), which was obtained as an unexpected product, were determined by single-crystal diffraction method (Scheme 1).

#### **Results and Discussion**

#### 1 Synthesis

All air-sensitive and volatile materials were handled either in vacuo or under argon by using standard Schlenk techniques. The complex **2** was formed by the reaction of ligand **1** with palladium dichloride in CH<sub>3</sub>CN. The complex **4** was obtained together with complex **2**, in the same crystal cell. It is proposed that 3,5-di(trifluoromethyl)aniline was produced from partial decomposition of ligand **1**, therefore **4** was formed. The trinuclear compoud **5** was isolated as byproduct formed by reaction of ligand **1**,  $[PdCl_2(SMe_2)_2]$  and excessive methyl lithium. The crystals were isolated from the mother liquor at -20 °C. The yield of **5** is very low (< 1 % estimated).

#### 2 Spectral characteristics

The <sup>1</sup>H NMR spectrum of compound **1** shows three signals at 8.02, 7.48, and 6.85 ppm corresponding to positions a, b and c, respectively (Scheme 2), of the acenaphthenequinone backbone, and at 7.79 and 7.60 ppm for the  $C_6H_3$  benzene protons (positions d and e). On complexation to the palladium atom, a downfield shift is observed for all of the



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Fig. 1 ORTEP representation of complexes 2 and 4





Scheme 2 Assignment of proton position

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#### 3 Crystal structures

Complex 2 (shown in Fig. 1) lies in the crystal cell with complex 4 together. The palladium atom Pd1 in 2 is in square-planar coordination with a cis configuration. The sum of internal angles of the chelating ring with the value of 539.4° indicates all of the five atoms of the chelating ring are in one plane. The sum of four angles N2-Pd1-N1 =  $80.8(3)^{\circ}$ , N2-Pd1-Cl2 = 92.4(2)°, N1-Pd1-Cl1 = 95.6(2)°



Fig. 2 ORTEP representation of complex 3

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Fig. 3 Ball and Stick representation of complex 5

In the crystal cell complex **4** next to molecule **2** can be found. The central Pd2 atom has an absolute square-planar coordination with *trans* configuration. Both Pd-Cl and Pd-N bond distances for the aniline palladium chlorido complexes are in the expected range [10]. C29-N3-Pd2 = 113.4(6)° indicates a nitrogen atom in sp<sup>3</sup> hybridization state. Angles Cl1'-Pd2-Cl1A and N3-Pd2-N3A are exactly 180°. The sum of four angles N3-Pd2-Cl1' = 88.9(2), N3-Pd2-Cl1A = 91.1(2), N3a-Pd-Cl1' = 88.9(2) and N3a-Pd2-Cl1A = 91.1(2)° with the value of 360° also implies that all of the five atoms Pd2, N3, N3a, Cl1' and Cl1A are in one coordination plane.

Bis(3,5-di(trifluoromethyl)aniline)dichloropalladium(II) is of importance because the notable analogy between the coordination chemistry of platinum(II) and palladium(II) compounds has advocated studies of Pd<sup>II</sup> complexes as anti-tumor drugs [11]. Recent advances in this field have focused on Pd<sup>II</sup> compounds bearing diamino bidentate ligands [12].

Complex 2 can be methylated by MeLi in ether to give complex 3 (Fig. 2). The crystal structure of 3 was determined at 193(2) K in space group P2<sub>1</sub>/c. The symmetry in complex 3 is lower than that in complex 2. In trans position to methyl group the Pd1-N2 distance of 2.227(4) Å is significantly larger than Pd1-N1 = 2.052(3) Å being *trans* to the chlorido ligand indicating a stronger *trans* influence of the methyl group. Therefore a relatively small bite angle N1-Pd1-N2 = 78.27(14)° is formed, while in complex 2 the bite angle N1-Pd1-N2 is  $80.8(3)^{\circ}$ . There are no remarkable differences of the other bond lengths apart from Pd1-N2 between complexes **2** and **3**. Two sets of trifluoromethyl groups, C20, F4, F5, F6 and C27, F7, F8, F9 are disordered in the crystal lattice.

In the solution, from which the crystals of complex 3were obtained, dark brown prisms were also found in very small amount. The structure of this single crystalline species was determined by single crystal X-ray diffraction. The compound crystallizes in space group P1. The asymmetric unit of 5.Et<sub>2</sub>O.0.5 pentane comprises two molecules of complex 5, two molecules of diethyl ether and one of pentane. In complex 5 three palladium atoms and two 1,2-bis-(3,5-bis-trifluoromethyl-phenylimino)-acenaphthene ligands can be found. The latter adopts a rather unusual bridging  $\mu^2$ -N,NC coordination mode. In addition, a chlorido ligand at Pd3, a methyl group at Pd2 and two dimethyl sulfide ligands are identified as monodentate ligands. While Pd2 and Pd3 show a coordination close to square-planar, the coordination at the central atom Pd1 is better described as close to tetrahedral. The coordination of the carbon atoms C1 and C29 of both diimine units indicates, that a certain degree of anionic charge density is located on these carbon donor atoms. This is in accord with the assumption, that these non-innocent ligands might be coordinated in either their monoanion radical oxidation state or in their diamagnetic fully reduced dianionic form. Recently we have established that the 3,5-CF<sub>3</sub>-BIAN ligand is prone to coordinate in its radical anionic oxidation state to nickel and cobalt [13]. As there are only two other anionic ligands available within the trinuclear complex, a chlorido group at Pd3 and a methyl group at Pd2, the oxidation states in 5 could be described within the limits of three options: A) Pd2 and Pd3 could be considered as in formal +1 oxidation state, while Pd1 as in formal oxidation state zero, then BIAN would be neutral [BIAN]<sup>0</sup>; B) Pd2 and Pd3 could be considered as in formal +2 oxidation state, while Pd1 as in formal oxidation state zero, then both BIAN would be a radical anion [BIAN]<sup>-</sup>; finally C) Pd1, Pd2 and Pd3 could be considered as in formal +2 oxidation state, then both BIAN would be a dianion [BIAN]<sup>2-</sup>. Option B) tends to be the best description taking into account the square planar coordination of the metal in d<sup>8</sup> configuration and close to tetrahedral coordination of Pd1 in d<sup>10</sup> configuration. However as a matter of fact, it is impossible to fully assign the metal and ligand oxidation states (and metal valence electron count) with the data in our hands. However we would like to exclude the diamagnetic closed-shell option C), as the dark brown-black color of 5 is in accord with a mixed valence compound as well as with charge transfer phenomena within the metal ligand core. The elongation of Pd2-N4, 2.176(4) Å, in comparison with Pd2-N3, 2.078(4) Å, is a result from the strong *trans* influence of the methyl group. For the same reason Pd1-N1, 2.189(4) A, trans to C29 of BIAN is notable longer than Pd1-N2, 2.083(4) Å, Pd3-N1, 2.097(4) Å, and Pd1-N3, 2.108(5) Å, in complex 5 as well as Pd1-N1, 2.050(7) Å, Pd1-N2, 2.036(7) Å, in complex 2

and Pd1-N1, 2.052(3) Å, in complex 3. Comparing C29-N3, 1.411(6) Å, and C1-N1, 1.385(7) Å, with all of the other carbon-nitrogen bond lengths of imine functions in this paper indicates elongation of these two imine (C=N)bonds, which fall in between a typical C-N double bond (1.287 Å) and a (C-N) single bond (1.471 Å) [10]. Again this is well in accord with a reduced ligand oxidation state and the  $\eta^2$ -coordination of two of the imine (C=N) bonds to the palladium atoms. C1, N1, C29, and N3 can be considered as atoms with sp<sup>3</sup> hybridization and tetrahedral coordination, while the other carbon and nitrogen atoms in DIAN are considered as sp<sup>2</sup> hybridized with trigonal arrangement. The Pd3-C1-N1 plane is approximately orthogonal to the chelate plane N2-C11-C1-N1-Pd1 (dihedral angle 91.7°) and the Pd1-C29-N3 plane is nearly perpendicular to the chelate plane N3-C29-C39-N4-Pd2 (dihedral angle 84.3°).

The bridging BIAN coordination mode holds the palladium atoms in rather close proximity with distances Pd1-Pd3 = 3.172, Pd1-Pd2 = 3.307, and Pd2-Pd3 = 4.609 Å. The angle Pd1-Pd2-Pd3 is approximately 90.7°. This arrangement in complex 5 can be envisaged as a V-shape tripalladium cluster bridged with two nitrogen atoms of the imine groups. Tripalladium clusters were well reviewed by Kovala-Demertzi [14]. In most of the tripalladium clusters with 42 valence electrons the bridging groups are halogenido, carbonyl, sulfur, amines and nitriles as well as other non-redox active ligands. If we assume option A) as realistic valence state description, complex 5 would have a 44 valence electron count, which would be responsible for the relatively long Pd-Pd bond length. On the other hand it is well documented, that the large size of the bridging ligand leads to much larger Pd-Pd bond lengths [15, 16]. An analogous tetraruthenium cluster with bridging  $\mu^2$ ,  $\eta^3$ -N, CN' diimine coordination mode has been reported by Staal et al. [17]. We assume, that in our experiment, methyl lithium has acted as reducing agent for palladium and / or the BIAN ligand.

#### Conclusion

 $\alpha$ -Diimine ligand 1 (3,5-CF<sub>3</sub>-BIAN) formed from 3,5-bis(trifluoromethyl)aniline and acenaphthenequinone, its palladium dichlorido complex 2 and its mono methyl chlorido palladium complex 3 were synthesized. Complex 2 and 3 were characterized by single-crystal XRD method. While in both, 2 and 3, the palladium atom has a square-planar cis coordination, bis(3,5-bis(trifluoromethyl)aniline)dichloropalladium(II) 4 reveals a trans square-planar arrangement. The reaction of chlorido palladium complex 2 with methyl lithium leads to an interesting and unexpected side product formed via a redox reaction: The XRD structure of the brown-black mixed valent trinuclear cluster di(1,2bis(3,5-bis-trifluoromethyl-phenylimino)acenaphthene)bis(dimethylsulfide)methylchlorotripalladium 5 reveals a V-shape palladium core with two bridging  $\mu^2$ ,  $\eta^3$ -N, CN' BIAN ligands.

#### **Experimental Section**

#### 1 General procedures and materials

All chemicals were commercially available and were used as received. Complexes 2, 3 and 5 were prepared and handled under nitrogen atmosphere. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR were performed using a Bruker ARX 300. Mass spectra were obtained with Varian MAT CH7 spectrometer. The elemental analyses were carried out with a CHN-Rapid elemental analyzer (Heraeus) at the Marburg analytical service lab.

### 2 X-ray crystallography

X-ray diffraction experiments were performed on a STOE IPDS-II diffractometer, using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  A). The low temperature of the crystal was maintained with cryostream open-flow N<sub>2</sub> cryostats. The collected data have been corrected for absorption effects. The structures were solved by direct methods and refined by the full-matrix least square method against F<sup>2</sup> of all unique reflections, using SHELX software [18]. The H atoms were introduced at calculated positions and refined using the riding model. The crystal of **3** was twinned. Only data of one twin domain were used for the structure determination of **3**. Selected crystal data and experimental details are given in Table 1.

Table 1 Crystal data and experimental parameters

Complex	2 + 4	3	5	
Formula C <sub>78</sub> H <sub>46</sub> Cl <sub>6</sub> F <sub>36</sub> N <sub>6</sub>	$_{3}O_{2}Pd_{3}(2x2\cdot4\cdot2x)$	CH <sub>3</sub> COCH <sub>3</sub> )		
	C29H15ClF12N2F	Pd(3)		
	$C_{67.5}H_{55}ClF_{24}N_4OPd_3S_2(5 \cdot Et_2O \cdot 0.5C_5H_{12})$			
Formula Weight	2311.08	761.28	1812.92	
T/K	193(2)	193(2)	193(2)	
Crystal system	triclinic	monoclinic	triclinic	
Space group	ΡĪ	$P2_1/c$	ΡĪ	
alÅ	11.843(2)	12.3947(12)	14.3485(11)	
b/Å	14.318(3)	24.388(2)	16.5772(12)	
c/Å	15.001(3)	9.1324(10)	16.7856(12)	
$\alpha /^{\circ}$	85.702(15)		80.744(6)	
βl°	67.475(13)	93.307(8)	72.335(6)	
γ/°	72.411(14)		69.277(6)	
V/Å <sup>3</sup>	2237.5(7)	2756.0(5)	3551.8(5)	
Ζ	1	4	2	
$\rho_{\rm calcd}/{\rm Mgm^{-3}}$	1.715	1.835	1.695	
$\mu / \text{mm}^{-1}$	0.899	0.876	0.956	
Data collection range /°	1.47 - 25.00	2.38 - 25.50	1.57 - 26.07	
Total reflections	21981	22907	59758	
Unique reflections	7463	3564	13787	
Reflections $I > 2\sigma(I)$	3044	2228	8681	
Parameters	603	434	1045	
R <sub>int</sub>	0.1678	0.0802	0.1051	
$R(F, I > 2\sigma(I))$	0.0569	0.0347	0.0463	
$wR(F^2, \text{ all data})$	0.0919	0.0814	0.1106	

# 3 Synthesis

# Preparation of (3,5-CF<sub>3</sub>-BIAN) (1)

3,5-Bis(trifluoromethyl)aniline (20.0 g, 87.3 mmol) and acenaphthenequinone (6.14 g, 33.8 mmol) were dissolved in 160 mL of toluene. To this solution 10-camphorsulfonic acid (0.26 g, 1.12 mmol) as catalyst was added. The mixture was refluxed 10 h with a water separator. After separating of water the solution was filtrated through  $Al_2O_3$  and Celite. The volatiles were removed in vacuo. The resulting solid was washed with pentane or petrolether and dried at 80 °C for 2 h in vacuo. The diimine product was obtained as yellow crystals (16.5 g, 80 %). m.p.: 175.0-176.5 °C. Anal. Calc. for  $C_{28}H_{12}F_{12}N_2$  (604.4 g/mol): C, 55.64; H, 2.00; N, 4.63. Found: C, 55.65; H, 2.34; N, 4.92 %.

<sup>1</sup>**H NMR** (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  6.85 (d, J = 7.3 Hz, 2H, C<sub>10</sub>H<sub>6</sub>), 7.48 (t, J = 7.7 Hz, 2H, C<sub>10</sub>H<sub>6</sub>), 7.60 (s, 4H, C<sub>6</sub>H<sub>3</sub>), 7.79 (s, 2H, C<sub>6</sub>H<sub>3</sub>), 8.02 (d, J = 8.3 Hz, 2H, C<sub>10</sub>H<sub>6</sub>) ppm. <sup>13</sup>**C NMR** (50.3 MHz, CDCl<sub>3</sub>): 162.3 (s, C=N), 153.2 (s, C-N=C), 142.4 (s, C-C=N), 133.1 (quartet, C-CF<sub>3</sub>, <sup>2</sup>J (C, F) = 34 Hz), 123.2 (quartet, CF<sub>3</sub>, <sup>1</sup>J (C, F) = 273 Hz), 131.6, 130.4, 128.2, 127.4, 123.9, 118.9, 118.3 (s, C and CH) ppm. <sup>19</sup>**F NMR** (188.3 MHz, CDCl<sub>3</sub>): -16.4 (s, CF<sub>3</sub>) ppm. **EI-MS**: m/z = 604 M+.

# Preparation of [PdCl<sub>2</sub>(3,5-CF<sub>3</sub>-BIAN)] (2)

PdCl<sub>2</sub> (0.826 g, 4.66 mmol) was dissolved in 40 mL of acetonitrile under refluxing. To this solution  $\alpha$ -diimine ligand (3,5-CF<sub>3</sub>-BIAN) (1) in 30 mL of acetonitrile was added. The mixture was refluxed for 2h, and then filtrated. The palladium complex crystallized at 6 °C as yellow needle crystals from this filtrate and was dried at 50 °C in vacuo. Yield: 2.70 g (74 %). Anal. Calc. for C<sub>28</sub>H<sub>12</sub>Cl<sub>2</sub>F<sub>12</sub>N<sub>2</sub>Pd (781.7 g/mol): C, 43.02; H, 1.55; N, 3.58. Found: C, 43.03; H, 1.85; N, 3.70 %.

<sup>1</sup>**H NMR** (300.1 MHz, CD<sub>3</sub>CN):  $\delta$  6.91 (d, J = 7.5 Hz, 2H, C<sub>10</sub>H<sub>6</sub>), 7.61 (t, J = 7.9 Hz, 2H, C<sub>10</sub>H<sub>6</sub>), 8.03 (s, 4H, C<sub>6</sub>H<sub>3</sub>), 8.23 (t, J = 0.6 Hz, 2H, C<sub>6</sub>H<sub>3</sub>), 8.32 (d, J = 8.0 Hz, 2H, C<sub>10</sub>H<sub>6</sub>) ppm. <sup>13</sup>**C NMR** (75.5 MHz, d6-DMSO): 176.8 (s, C=N), 132.6, 132.4, 131.3, 129.6, 129.3, 128.7, 125.5, 125.3, 125.1, 123.0 (s, C and CH) ppm. <sup>19</sup>**F NMR** (188.3 MHz, CD<sub>3</sub>CN): -58.5 (s, CF<sub>3</sub>) ppm.

#### Preparation of [Pd(Me)Cl(3,5-CF<sub>3</sub>-BIAN)] (3)

To a suspension PdCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub> (0.268 g, 0.886 mmol) in 30 mL of diethyl ether methyl lithium (0.65 mL, 0.96 mmol, 1.47 mol/L in diethyl ether) was drop wise added at -60 °C. During warm-up time to -40 °C the reaction solution became clear. Then methanol (0.5 mL) was added in order to remove the residual methyl lithium. After 10 min. diimine ligand 1 (0.535 g, 0.886 mmol) was added to the solution at -40 °C. The mixture was gradually warmed up to the ambient temperature and then continuously stirred for 2 h. The volatiles were removed in vacuo. The resulting dark brown solid was extracted with diethyl ether and at -20 °C dark brown crystals were obtained from the ether solution. Yield: 56 mg (0.073 mmol, 8.2 %). Anal. Calc. for C<sub>29</sub>H<sub>17</sub>ClF<sub>12</sub>N<sub>2</sub>Pd (763.31 g/mol): C, 45.63; H, 2.67; N, 3.67. Found: C, 45.50; H, 2.41; N, 3.83 %.

<sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.04 (s, 3H, PdCH<sub>3</sub>), 6.92 (d, J = 7.3 Hz, 2H, C<sub>10</sub>H<sub>6</sub>), 7.54 (t, J = 7.8 Hz, 2H, C<sub>10</sub>H<sub>6</sub>), 7.81 (s, 4H, C<sub>6</sub>H<sub>3</sub>), 8.00 (s, 2H, C<sub>6</sub>H<sub>3</sub>), 8.18 (d, J = 8.3 Hz, 2H, C<sub>10</sub>H<sub>6</sub>) ppm. <sup>19</sup>F NMR (188.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -61.7 (s, CF<sub>3</sub>) ppm.

A crop of a few black-brown single crystals of compound 5 were obtained from the pentane layered ethereal mother liquid of preparation of 3.

**Supplementary data:** Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre with CCDC-266671 (complex **3**), CCDC-266672 (complex

2 and 4) and CCDC-266673 (complex 5). These data can be obtained free of charge via http://www.ccdc.ac.uk. (or from the Cambridge CB2 1EZ, U. K.; fax (+44) 1223-336-033 and email deposit@ccdc.cam.uk).

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