

{2-[1-(2,6-Diisopropylphenylimino)ethyl]pyridyl}palladium Dibromide Polymorphs Originating from Different Br $\cdots\pi$ and C–H \cdots Br Contacts

Wenjuan Zhang,^[a] Xiubo Tang,^[a] Hongwei Ma,^[a] Wen-Hua Sun,^{*[a]} and Christoph Janiak^{*[b]}

Keywords: Palladium complexes / Polymorphism / Supramolecular interactions / C–H \cdots Br / Br $\cdots\pi$

{2-[1-(2,6-Diisopropylphenylimino)ethyl]pyridyl}palladium dibromide (**1**) was synthesized and crystallized as red crystals from chloroform in the monoclinic space group $P2_1/c$ or as yellow crystals from methanol in the triclinic space group $P\bar{1}$. Other solvents, such as THF and acetonitrile, gave mixtures of red and yellow crystals. With very little conformational dif-

ferences between the molecules in the dimorphs of **1** the crystal packing is a herringbone array in **1**-red and a parallel array in **1**-yellow, with the supramolecular interactions differing in the Br $\cdots\pi$ and C–H \cdots Br contacts.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

Studies on polymorphism are of timely interest.^[1–4] Polymorphism, the occurrence of different crystal structures for the same chemical entity,^[5] is of particular practical, and hence financial importance, in industrial processes where different physical properties of polymorphic forms can substantially alter the viability and quality of a product.^[6] Polymorphism can be associated with differences in molecular conformation, molecular orientation, crystal packing, solubility, color etc.^[7,8] Polymorphs provide information on conformational flexibility and are the basis for ab initio crystal structure predictions.^[9] However, it is very complex to rationalize how and why compounds are efficiently packed in different forms. The aggregation of flexible molecules depends on the compromise between intra- and intermolecular weak bonding interactions in the crystal (external or extra-molecular interactions).^[10,11] The transformation of different polymorphs may be triggered by the external stresses^[7,12] and governed by the intra- and intermolecular forces in the solid state.^[13]

Palladium complexes are widely used as catalysts for carbon–carbon coupling reactions.^[14,15] In our previous work, (pyridylimine)metal complexes showed good activity for ethylene oligomerization and polymerization.^[16] The com-

ound {2-[1-(2,6-diisopropylphenylimino)ethyl]pyridyl}-palladium dichloride, however, showed very low activity towards ethylene. Based on the improved activity observed with bromo rather than chloro analogues of the nickel complexes,^[17] the transformation of palladium chloride into the bromide was studied. The catalytic activity did not change, but for {2-[1-(2,6-diisopropylphenylimino)ethyl]pyridyl}-palladium dibromide different colors and crystal structures were observed when grown from different solvents. Here we report on the structural analysis of the title compound and discuss the basis of its polymorphism. There is need for the understanding of intermolecular interactions in the context of crystal packing in view of the ongoing difficulty involved in investigating and quantifying structural differences between polymorphs.^[6,7]

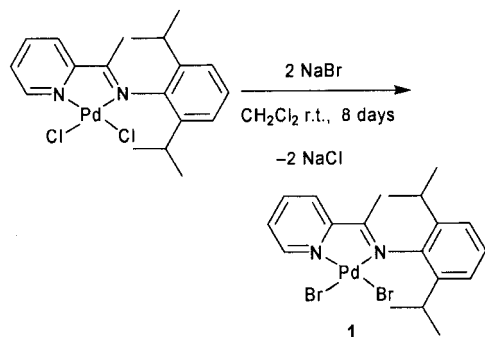
Results and Discussion

{2-[1-(2,6-Diisopropylphenylimino)ethyl]pyridyl}palladium dichloride was treated with NaBr to form its bromo analog **1** in 86% yield [Equation (1)].^[18] The resultant palladium dibromide complex **1** is stable in the solid state. Recrystallization of **1** from chloroform gave red, from methanol yellow crystals. Other solvents, such as THF and acetonitrile, gave mixtures of red and yellow colored crystals [Equation (2)]. Both crystal forms were confirmed to be of identical molecular composition by their elemental analyses and NMR spectra. The two forms must be of similar overall packing energy since they are concomitant dimorphs. The IR spectra of the solid yellow and red crystals showed some slight differences (Figure S1), and IR measurements were useful to investigate the crystal forms and the color, since most solvents gave mixtures of the two phases.

[a] Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China
Fax: +86-10-62618239
E-mail: whsun@iccas.ac.cn

[b] Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany
Fax: +49-761-2036147
E-mail: janiak@uni-freiburg.de

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.



(1)

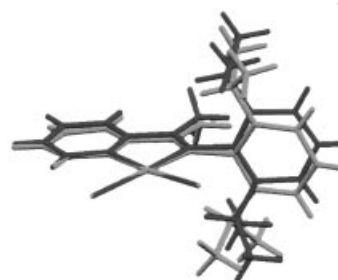
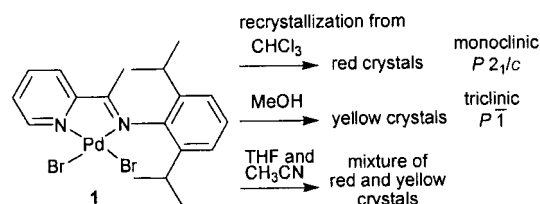


Figure 1. Overlay of the molecular structures of **1-red** (dark grey) and **1-yellow** (light grey) by specifying the atoms of the PdBr₂ moiety as three pairs in the two structures (RMS = 0.0159).



(2)

Both crystals, **1-red** and **1-yellow** feature the same palladium complex with a highly similar square-planar geometry around the metal atom and similar coordination features in terms of bond lengths and angles (Table 1). From an overlay of the molecules of **1-red** and **1-yellow** in Figure 1 the only obvious conformational difference between them is a different torsion of the isopropyl group with respect to the phenyl plane [defined by the angle H–C(*i*Pr)–C–C^{*ipso*}(Ph), see Table 1]. The very similar molecular structures provide little information as to the origin of their packing difference.

Table 1. Selected bond lengths [Å] and angles [°] in the dimorphs of **1**.

	1-red	1-yellow
Pd1–N1	2.039(4)	2.039(7)
Pd1–N2	2.040(4)	2.023(6)
Pd1–Br1	2.3811(8)	2.3955(12)
Pd1–Br2	2.3993(7)	2.4038(17)
N1–Pd1–N2	79.5(2)	79.6(3)
N1–Pd1–Br1	95.8(1)	95.4(2)
N1–Pd1–Br2	175.0(1)	173.3(2)
N2–Pd1–Br1	174.7(1)	174.8(2)
N2–Pd1–Br2	95.6(1)	95.2(2)
Br1–Pd1–Br2	89.10(3)	89.92(5)
Torsion angle:		
H–C(<i>i</i> Pr)–C–C ^{<i>ipso</i>} (Ph)	1.7(7), 14.4(7)	23(1), 25(1)
Interplanar angle:		
PdN ₂ C ₂ heterocycle to Ph	86.8(1)	83.3(3)

Each dimorph contains dimeric units (see parts a and b in Figure 2) which may be seen as “building blocks” of both structures. The differences in the intra-dimer, intermolecular distances are provided in Table 2. In the comparative packing of Pd and other transition metal polymorphs the weak interactions of interest (see Supporting Information) are Pd···Pd and Pd···Br contacts. The Pd···Pd separation in

1-red and **1-yellow** is quite similar. Also it is much longer than Pd···Pd separations which are discussed as differentiating factors in other Pd polymorphs (typically much less than 4.0 Å, see Supporting Information). The Br³···PdN₂C₂ heterocycle contact given by the Br³···N2 distance is shorter by 0.3 Å in **1-red** than in **1-yellow**. It has been suggested that an active electron delocalization within a metal–N–heterocyclic chelate ring could exhibit some degree of “metalloaromaticity”^[25,19,20] so that a Br³···π contact could be invoked.^[21]

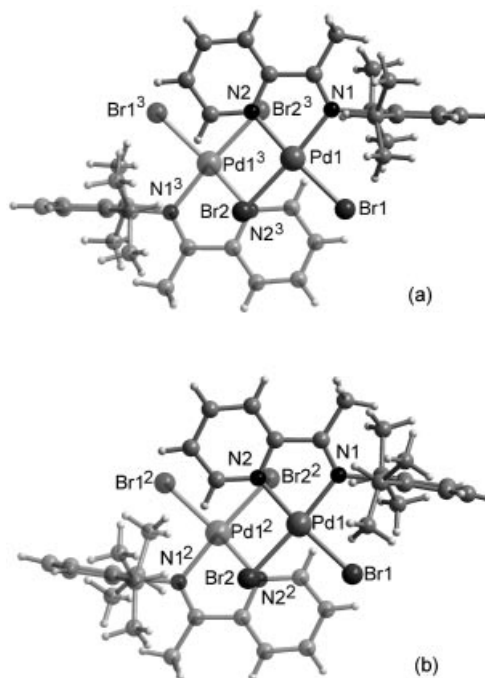


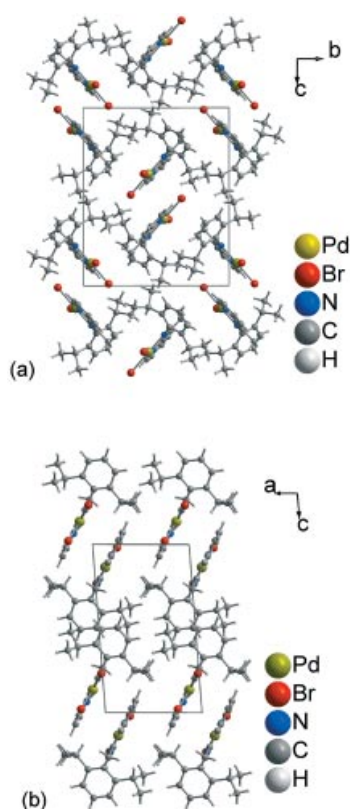
Figure 2. Dimeric units in (a) **1-red** and (b) **1-yellow**. For details, including symmetry transformations, see Tables 1 and 2.

The dimorphs are the result of two different ways of crystal packing of these dimeric building blocks. In **1-red** they form a herringbone array, in **1-yellow** they are parallel (Figure 3). The different packing of the dimeric building blocks must in turn be due to subtle differences in weak supramolecular interactions.

Table 2. Intermolecular distances in the “dimeric building blocks”.^[18a,9]

Contact	1-red	1-yellow
Pd...Pd [Å]	4.446(1) ⁽³⁾	4.329(2) ⁽²⁾
Pd...Br2 [Å]	3.820(1) ⁽³⁾	3.846(2) ⁽²⁾
Plane PdN ₂ C ₂ ...PdN ₂ C ₂ plane: Centroid...centroid [Å]	5.903(3) ⁽³⁾	6.047(2)
Interplanar separation [Å]	3.500 ⁽³⁾	3.494 ⁽²⁾
Interplanar angle [°]	0.0 ⁽³⁾	0.0 ⁽²⁾
Angle between the centroid vector and the normal to the plane [°]	53.6	54.7
Br2...N2	3.480(4) ⁽³⁾	3.780(8) ⁽²⁾

Symmetry transformations: ⁽²⁾ 2 - x, 2 - y, -z; ⁽³⁾ -x, -y, -z.

Figure 3. Packing of the dimeric building blocks in the dimorphs. (a) “herringbone” array in **1**-red and (b) parallel array in **1**-yellow.

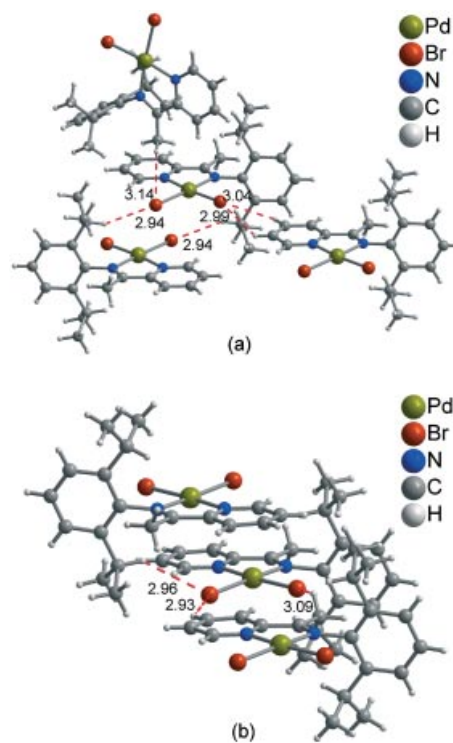
The aromatic ligand system in **1** would suggest the presence of differentiating π - π and C-H... π interactions.^[22-25] There are no significant π - π contacts, however, in that they exhibit rather long centroid-centroid distances (>4.7 Å) together with large slip angles (>35°) and vertical displacements (>3.0 Å) between the ring centroids. No C-H... π contacts (with H...centroid < 3.0 Å) can be found with PLATON in **1**-yellow and only one such interaction is observed in **1**-red onto the pyridyl plane with symmetry transformation $-x, 1/2 + y, 1/2 - z$ and $d[\text{H}\cdots\text{centroid}] = 2.97 \text{ \AA}$, $d[\text{H}\cdots\perp] = 2.89 \text{ \AA}$, and $\angle[\text{CH}\cdots\text{centroid}] = 132^\circ$.^[23]

More obvious are differences in the intermolecular C-H...Br hydrogen bonding interactions between the molecules in **1**-red and **1**-yellow, respectively. Table 3 provides a list and Figure 4 a pictorial presentation of the C-H...Br hydrogen bonding. The molecules of **1**-red have 12 C-H...Br interactions with H...Br < 3.20 Å (2×6 unique C-H...Br contacts). The molecules of **1**-yellow feature only 6 of such C-H...Br interactions. Often C-H...Br contacts are noted in the packing discussion of bromine containing

Table 3. Intermolecular C-H...Br hydrogen bonds in the dimorphs of **1**.^[a]

C-H...Br	H...Br [Å]	C...Br [Å]	C-H...Br [°]
1-red ^[b]			
C-H17A...Br1 ^(1')	3.04(1)	3.630(5)	122.9(3)
C-H18A...Br1 ^(1')	2.99(1)	3.612(5)	125.4(3)
C-H14B...Br2 ⁽²⁾	3.14(1)	3.457(6)	101.5(4)
C-H8B...Br2 ⁽⁴⁾	3.18(1)	4.078(8)	156.2(5)
C-H9A...Br2 ⁽⁴⁾	3.13(1)	4.047(8)	160.1(5)
C-H10A...Br2 ⁽³⁾	2.94(1)	3.760(6)	142.0(3)
1-yellow ^[c]			
C-H17A...Br2 ^(1')	2.93(1)	3.64(1)	133.8(7)
C-H14B...Br2 ⁽²⁾	3.09(1)	3.58(1)	113.5(6)
C-H10A...Br1 ^(1')	2.96(1)	3.784(9)	142.4(5)

[a] With H...Br less than 3.20 Å. [b] Plus symmetry-related set of C-H...Br bonds to Br1 and Br2. Symmetry relations: ^(1') $-1 + x, y, z$; ⁽²⁾ $-x, 0.5 + y, 0.5 - z$; ⁽³⁾ $-x, -y, -z$; ⁽⁴⁾ $x, -0.5 - y, 0.5 + z$. [c] Plus symmetry-related set of C-H...Br bonds to Br1 and Br2. Symmetry relations: ^(1') $x, -1 + y, z$; ⁽²⁾ $2 - x, 2 - y, -z$.

Figure 4. Molecules in **1** with selected surrounding intermolecular C-H...Br contacts. (a) **1**-red, (b) **1**-yellow. For further details, including symmetry transformations, see Table 3.

molecules,^[26] including the differentiation of polymorphs^[27] as well as related *cis*-(dibromo)metal^[28] and other (multibromo)metal complexes.^[29,30] The range of the C–H···Br contacts observed in **1** matches the range observed and discussed for the packing in the compound [Ph₂S=N=SPh₂]₂[Pd₂Br₆].^[30] C–H···Br contacts may not be as widely known as C–H···O/N,^[31,32] C–H···F^[33] or C–H···Cl hydrogen bonds^[34] but the role of C–H···Br–M interactions in crystalline species has been recognized as structure-directing factors.^[35]

A packing analysis with PLATON^[36] of structurally related Pd polymorphs of PdCl₂(2,2'-bipy),^[37] PdCl₂(N)₂,^[38] PdCl(C[^]N)(P),^[39] PdCl(P)₃,^[40] [Ph₄P]₂[PdCl₃(N)]₂,^[41] PdI₂(PMe₂Ph)₂,^[42] and PdCl₂(cod)^[43] revealed the absence of “strong” N/O–H···O/N hydrogen bonds. Only weaker supramolecular interactions could be found, predominantly C–H···Cl hydrogen bonds together with some C–H···π and occasionally π···π interactions. We see this absence of strong intermolecular interactions, which would tend to favor only one packing arrangement, as the basis for the formation of polymorphs.

A search in the Cambridge Structure Database (CSD)^[44] retrieved 11899 entries with one or more intermolecular (C–)H···Br distances within the range 2.6–3.3 Å. The total of 65000 intermolecular C–H···Br contacts within the 11899 different CSD Refcodes shows that such interactions are not unusual.^[35] The frequency distribution of H···Br distances (Figure 5) shows an onset at about 2.6 Å with a steady increase in the number of contacts to ca. 3.1 Å where the curve levels off. There is no clustering of structures. The experimental C–H···Br angles fall between 100° and 180° (Figure 6). There is a preference for linearity with shorter H···Br distances. In **1** the intermolecular C–H···Br hydrogen bonds start at 2.93 Å below the sum of the van der Waals radii of H (1.20 Å) and Br (1.85 Å). The C–H···Br parameter in **1** fit well with the statistical analysis.

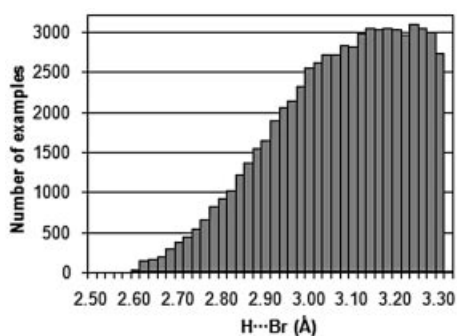


Figure 5. Histogram (frequency distribution) of the (C–)H···Br distance distribution from a CSD search.^[44]

The packing difference in the dimorphs of **1** also extends to their color. We note that in better investigated compounds of platinum with aromatic ligands, the emission properties are often affected by the extent of Pt···Pt and π–π contacts.^[45] There exists a yellow and red polymorph of [PtCl₂(2,2'-bipy)],^[46] of {Ti[(C₄H₉N₄)Pt(CN)₂]_n},^[47] in other polymorphic forms a color difference of red (orange)

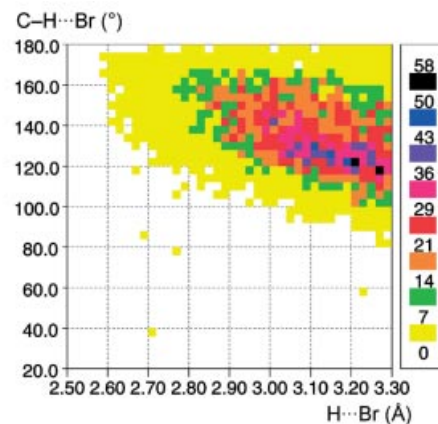


Figure 6. Scatterplot for the C–H···Br angle vs. (C–)H···Br distance distribution from a CSD search.^[44]

and yellow for the modifications is often noted, e.g. in [Co₂(ibdpt)₂(MeCN)₂(H₂O)₂](ClO₄)₄,^[48] 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile (ROY),^[6,49] Tl^I picrate,^[5,50] and [RhCl(CO)₂(Hpz^{dp})].^[51]

Conclusions

Compound {2-[1-(2,6-diisopropylphenylimino)ethyl]pyridyl}palladium dibromide (**1**) crystallizes as a red form from chloroform and as a yellow polymorph from methanol. Its polymorphism is traced to packing differences due to Br···π contacts between the Br···PdN₂C₂ heterocycle together with different C–H···Br bonds.

Experimental Section

General: All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The IR spectra were obtained on a Perkin–Elmer FT-IR 2000 spectrophotometer by using the KBr disc in the range of 4000–400 cm^{–1}. The ¹H NMR spectra were recorded on a Bruker DMX-300 instrument with TMS as the internal standard. Elemental analyses were performed on a Flash EA 1112 microanalyzer.

THF and toluene were refluxed over sodium/benzophenone until the purple color appeared and distilled under nitrogen prior to use. Pd(CH₃CN)₂Cl₂ was prepared in a manner similar to that reported for the benzonitrile analogue,^[52] and 2-[1-(2,6-diisopropylphenylimino)ethyl]pyridine was synthesized as described.^[53] All other chemicals were obtained commercially and used without further purification unless stated otherwise.

X-ray Crystallography: Crystals of the red and yellow phases were selected and mounted on the tip of a glass fiber by means of hydrocarbon oil. Data collection: RIGAKU R-AXIS RAPID IP CCD area detector at 293(2) K with graphite monochromated Mo-*K*_α radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was performed. Structure analysis and refinement: The structure was solved by direct methods (SHELXS-97);^[54] refinement was done by full-matrix least-squares on *F*² using the SHELXL-97 program suite.^[54] All non-hydrogen positions were

refined with anisotropic temperature factors. Hydrogen atoms were placed at calculated positions with an appropriate riding model (AFIX 43 for aromatic CH, AFIX 13 for aliphatic CH and AFIX 33 for CH₃) and an isotropic temperature factor of $U_{\text{eq}}(\text{H}) = 1.2 U_{\text{eq}}(\text{CH})$ and $1.5 U_{\text{eq}}(\text{CH}_3)$. Details of the X-ray structure determinations and refinements are provided in Table 4. Graphics were drawn with DIAMOND.^[55]

Table 4. Crystal data and structure refinement for **1-red** and **1-yellow**.

Compound	1-red	1-yellow
Empirical formula	C ₁₉ H ₂₄ Br ₂ N ₂ Pd	C ₁₉ H ₂₄ Br ₂ N ₂ Pd
M [g mol ⁻¹]	546.62	546.62
Crystal size [mm]	0.31 × 0.17 × 0.16	0.34 × 0.05 × 0.04
θ range [°]	2.01–27.48	2.56–27.48
h ; k ; l range	0, 13; –15, 16; –20, 20	0, 11; –9, 11; –18, 18
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a [Å]	10.191(2)	9.029(2)
b [Å]	12.763(3)	9.236(2)
c [Å]	15.704(3)	14.029(3)
α [°]	90	81.24(3)
β [°]	95.59(3)	89.66(3)
γ [°]	90	61.10(3)
V [Å ³]	2032.9(7)	1009.3(3)
Z	4	2
D_{calcd} [g cm ⁻³]	1.786	1.799
$F(000)$	1072	536
μ [mm ⁻¹]	4.847	4.881
Max./min. transmission	0.5147/0.3141	0.8287/0.2876
Reflections collected	18905	7537
Independent reflections	4656 ($R_{\text{int}} = 0.0471$)	4282 ($R_{\text{int}} = 0.0452$)
Obsd. refl. [$I > 2\sigma(I)$]	3367	2487
Parameters refined	217	217
Max./min. $\Delta\rho$ [e Å ⁻³]	0.799/–1.241	0.917/–0.899
R_1/wR_2 [$I > 2\sigma(I)$] ^[a]	0.0387/0.1052	0.0554/0.1355
R_1/wR_2 (all refl.) ^[b]	0.0585/0.1176	0.1108/0.1718
Goodness-of-fit on F^2 ^[c]	0.993	1.026
Weight. scheme w ; hkl ^[d]	0.0681/0.0000	0.0880/0.0000

[a] Largest difference peak and hole. [b] $R_1 = [\sum(|F_o| - |F_c|)]/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goodness-of-fit = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\max(F_o^2 \text{ or } 0) + 2F_c^2]/3$.

CCDC-271437 (for **1-red**) and -271438 (for **1-yellow**) contain 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.

{2-[1-(2,6-Diisopropylphenylimino)ethyl]pyridyl}palladium Dibromide (1): The pyridylimine C₅H₈N-2-CMe = NAr [Ar = 2,6-*i*Pr-2-C₆H₃] reacted with Pd(CH₃CN)₂Cl₂ in dichloromethane to yield a yellow precipitate of air-stable {2-[1-(2,6-diisopropylphenylimino)ethyl]pyridyl}palladium dichloride. According to literature,^[18] the yellow precipitate (0.0525 g, 0.115 mmol) and NaBr (1.182 g, 11.5 mmol) were mixed in CH₂Cl₂ (10 mL) and refluxed for 8 d. After cooling, water (10 mL) was added to remove the excess NaBr, and the organic phase was separated and the aqueous phases extracted with CH₂Cl₂ (3 × 5 mL). The combined organics were dried with Na₂SO₄, concentrated and layered with *n*-hexane. The precipitate obtained (0.0540 g, 86%) was dried in vacuo. Differently colored crystals were obtained from diffusion of diethyl ether into a chloroform solution (→ red crystals) or a methanol solution (→ yellow crystals) or a tetrahydrofuran or acetonitrile solution (→ mixtures of red and yellow crystals) of the precipitate. The differently colored crystals were confirmed to be of identical molecular composi-

tion by their elemental analyses and NMR spectra. C₁₉H₂₄Br₂Pd (518.61): calcd. C 41.75, H 4.43, N 5.12; found C 41.79, H 4.45, N 5.22. ¹H NMR (300 MHz, CDCl₃): δ = 9.86 (d, J = 5.20 Hz, 1 H, pyridyl-H), 8.21 (t, J = 1.09 Hz, 1 H, pyridyl-H), 7.90 (d, J = 7.75 Hz, 1 H, pyridyl-H), 7.81 (t, J = 6.93 Hz, 1 H, pyridyl-H), 7.32 (t, J = 7.35 Hz, 1 H, phenyl-H), 7.25 (d, J = 7.35 Hz, 2 H, phenyl-H), 3.09 [dd, J = 6.89 Hz, 2 H, -CH(CH₃)₂], 2.25 (s, 3 H, CH₃-C=N), 1.42 (d, J = 6.67 Hz, 6 H, CH₃), 1.12 (d, J = 6.81 Hz, 6 H, CH₃) ppm; the isopropyl methyl groups are chemically different due to their orientation to the “front” or “rear” of the PdBr₂ reference moiety in connection with the hindered rotation of the phenyl group around the C–N bond.

Supporting Information (see also the footnote on the first page of this article): Infrared spectra of **1-red** and **1-yellow**, a Table with a description and comparison of the palladium polymorphs.

Acknowledgments

We are greatly thankful to the National Natural Science Foundation of China for financial assistance under GrantNo. 20272062 and to the University of Freiburg.

- [1] Recent work on polymorphs: a) A. Kuhn, P. Diaz-Carrasco, M. E. A. de Dompablo, F. Garcia-Alvarado, *Eur. J. Inorg. Chem.* **2007**, 3375–3384; b) L. Yu, *CrystEngComm* **2007**, *9*, 847–851; c) S. Schnabel, C. Röhr, *Z. Naturforsch., Teil B* **2007**, *62*, 1235–1245; d) F. P. A. Fabbiani, L. T. Byrne, J. J. McKinnon, M. A. Spackman, *CrystEngComm* **2007**, *9*, 728–731; e) M. Gobel, T. M. Klapötke, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1006–1017; f) B. M. Casari, V. Langer, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1074–1081; g) M. F. Davis, W. Levason, M. E. Light, R. Ratnani, G. Reid, K. Saraswat, M. Webster, *Eur. J. Inorg. Chem.* **2007**, 1903–1910; h) E. F. Paulus, F. J. J. Leusen, M. U. Schmidt, *CrystEngComm* **2007**, *9*, 131–143; i) E. M. Zerbe, C. Wolper, S. R. Pinol, P. G. Jones, A. Blaschette, *Z. Anorg. Allg. Chem.* **2007**, *633*, 593–602; j) S. Busi, R. Fröhlich, M. Lahtinen, R. Sillanpää, K. Rissanen, *Z. Naturforsch., Teil B* **2007**, *62*, 35–43; k) O. Mundt, G. Becker, J. Baumgarten, H. Riffel, A. Simon, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1687–1709; l) M. Neukirch, B. Blaschkowski, M. Haberlen, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1799–1803; m) Z. Deutsch, J. M. Rubin-Preminger, J. Bernstein, J. Y. Becker, *CrystEngComm* **2006**, *8*, 41–50; n) K. Roth, *Chem. Unserer Zeit* **2006**, *40*, 398–406.
- [2] Recent work on polymorphs involving high-pressure crystallization: a) F. P. A. Fabbiani, D. R. Allan, S. Parsons, C. R. Pulham, *CrystEngComm* **2005**, *7*, 179–186; b) F. P. A. Fabbiani, D. R. Allan, W. I. F. David, S. A. Moggach, S. Parsons, C. R. Pulham, *CrystEngComm* **2004**, *6*, 504–511.
- [3] Recent experimental and theoretical work on polymorphs: a) P. McArdle, K. Gilligan, D. Cunningham, R. Dark, M. Mahon, *CrystEngComm* **2004**, *6*, 303–309; b) T. C. Lewis, D. A. Tocher, G. M. Day, S. L. Price, *CrystEngComm* **2003**, *5*, 3–9; c) A. T. Anghel, G. M. Day, S. L. Price, *CrystEngComm* **2002**, *4*, 348–355; d) M. A. Spackman, J. J. McKinnon, *CrystEngComm* **2002**, *4*, 378–392.
- [4] Recent work on pseudo-polymorphs: a) D. Braga, K. Rubini, L. Maini, *CrystEngComm* **2004**, *6*, 236–238; b) D. Bellamy, N. G. Connelly, G. R. Lewis, A. G. Orpen, *CrystEngComm* **2002**, *4*, 51–58.
- [5] F. H. Herbstein, *Cryst. Growth Des.* **2004**, *4*, 1419–1429.
- [6] J. J. McKinnon, F. P. A. Fabbiani, M. A. Spackman, *Cryst. Growth Des.* **2007**, *7*, 755–769.
- [7] J. Bernstein, *Polymorphism in Molecular Crystals*, Clarendon Press, Oxford, **2002**.
- [8] a) D. Braga, F. Grepioni, *Chem. Soc. Rev.* **2000**, *29*, 229; b) S. Haddad, R. D. Willett, *Inorg. Chem.* **2001**, *40*, 2457; c) J. Dunitz, J. Bernstein, *Acc. Chem. Res.* **1995**, *28*, 193.

- [9] A. Gavezzotti, *CrystEngComm* **2002**, 343–347; A. Gavezzotti, *Acc. Chem. Res.* **1994**, 27, 309.
- [10] D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, 98, 1375.
- [11] P. J. Dyson, *Inorg. Chem.* **1994**, 33, 3218.
- [12] J. Bernstein, A. T. Hagler, *J. Am. Chem. Soc.* **1978**, 100, 673.
- [13] Z. Dega-Szafran, A. Katrusiak, M. S. Szafran, *J. Mol. Struct.* **2002**, 610, 229.
- [14] a) C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, 33, 314; b) P. W. N. M. van Leeuwen, P. C. J. Kaner, J. N. H. Reek, P. Dierkes, *Chem. Rev.* **2000**, 100, 2741; c) C. A. Bessel, P. Aggarwal, A. C. Marschilok, K. J. Takeuchi, *Chem. Rev.* **2001**, 101, 1031.
- [15] Pd complexes in olefin polymerization: a) C. Janiak, P.-G. Lassahn, V. Lozan, *Macromol. Symp.* **2006**, 236, 88–99; b) V. Lozan, P.-G. Lassahn, C. Zhang, B. Wu, C. Janiak, G. Rheinwald, H. Lang, *Z. Naturforsch., Teil B* **2003**, 58, 1152–1164; c) P.-G. Lassahn, C. Tzschucke, W. Bannwarth, C. Janiak, *Z. Naturforsch., Teil B* **2003**, 58, 1063–1068; d) P.-G. Lassahn, V. Lozan, B. Wu, A. S. Weller, C. Janiak, *Dalton Trans.* **2003**, 4437–4450; e) P.-G. Lassahn, V. Lozan, C. Janiak, *Dalton Trans.* **2003**, 927–935; f) B. Berchtold, V. Lozan, P.-G. Lassahn, C. Janiak, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, 40, 3604–3614; g) C. Janiak, P.-G. Lassahn, *Polym. Bull.* **2002**, 47, 539–546; h) C. Janiak, P.-G. Lassahn, *J. Mol. Catal. A* **2001**, 166, 193–209.
- [16] a) W.-H. Sun, X. Tang, T. Gao, B. Wu, W. Zhang, H. Ma, *Organometallics* **2004**, 23, 5037; b) X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen, W. Chen, *J. Organomet. Chem.* **2005**, 690, 1570.
- [17] L. Timo, L. Kristian, L. Jonas, *Macromol. Rapid Commun.* **1999**, 20, 487.
- [18] S. Paavola, R. Kivekas, *J. Organomet. Chem.* **2002**, 657, 187.
- [19] H. Masui, *Coord. Chem. Rev.* **2001**, 219–221, 957.
- [20] For evidence of metalloaromaticity in aromatic α,α' -diimine-copper(II) chelates, see: a) E. Craven, C. Zhang, C. Janiak, G. Rheinwald, H. Lang, *Z. Anorg. Allg. Chem.* **2003**, 629, 2282–2290; b) A. Castiñeiras, A. G. Sicilia-Zafra, J. M. González-Pérez, D. Choquesillo-Lazarte, J. Niclós-Gutiérrez, *Inorg. Chem.* **2002**, 41, 6956.
- [21] C–Br $\cdots\pi$ contact: M. Enamullah, A. K. M. Royhan Uddin, A.-C. Chamayou, C. Janiak, *Z. Naturforsch., Teil B* **2007**, 62, 807–817.
- [22] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.
- [23] a) M. Nishio, *CrystEngComm* **2004**, 6, 130; b) M. Nishio, M. Hirota, Y. Umezawa, *The CH π interaction (Evidence, Nature and consequences)*, Wiley-VCH, **1998**; c) Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa, M. Nishio, *Bull. Chem. Soc. Jpn.* **1998**, 71, 1207; d) C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M. J. Kolm, T. G. Scharmann, O. M. Zipffel, *Eur. J. Inorg. Chem.* **2000**, 1229–1241.
- [24] a) H. H. Monfared, Z. Kalantari, M.-A. Kamyabi, C. Janiak, *Z. Anorg. Allg. Chem.* **2007**, 633, 1945–1948; b) B. Wu, X. Huang, Y. Xia, X.-J. Yang, C. Janiak, *CrystEngComm* **2007**, 9, 676–685; c) B. Wisser, Y. Lu, C. Janiak, *Z. Anorg. Allg. Chem.* **2007**, 633, 1189–1192; d) B. Wisser, C. Janiak, *Acta Crystallogr., Sect. E* **2007**, 63, o2871–2872.
- [25] X.-J. Yang, F. Drepper, B. Wu, W.-H. Sun, W. Haehnel, C. Janiak, *Dalton Trans.* **2005**, 256–267; and supplementary material therein.
- [26] a) L. Wang, Y. Zhang, C. R. Lu, D. C. Zhang, *Acta Crystallogr., Sect. C* **2004**, 60, o696–o698; b) R. J. Bowen, M. A. Fernandes, P. W. Gitari, M. Layh, *Acta Crystallogr., Sect. C* **2004**, 60, o113–o114; c) W. T. A. Harrison, R. A. Howie, M. Jaspars, S. M. S. V. Wardell, J. L. Wardell, *Polyhedron* **2003**, 22, 3277–3288; d) P. A. Iyere, W. Y. Boadi, D. Atwood, S. Parkin, *Acta Crystallogr., Sect. B* **2003**, 59, 664–669; e) T. Hamann, D. Henschel, I. Lange, O. Moers, A. Blaschette, P. G. Jones, *Z. Naturforsch., Teil B* **2002**, 57, 1051–1065; f) P. Dastidar, H. Krupitsky, Z. Stein, I. Goldberg, *J. Includ. Phen. Mol. Recognition. Chem.* **1996**, 24, 241–262.
- [27] a) J. R. Anaconda, J. Gomez, D. Lorono, *Acta Crystallogr., Sect. C* **2003**, 59, o277–o280; b) P. G. Jones, V. Lozano, *Acta Crystallogr., Sect. E* **2003**, 59, o632–o634.
- [28] X. P. Shen, A. H. Yuan, *Acta Crystallogr., Sect. E* **2004**, 60, m1074–m1075.
- [29] a) M. Baby Mariyatra, K. Panchanatheswaran, A. E. Goeta, *Acta Crystallogr., Sect. E* **2002**, 58, m694–m696; b) C. Hasselegren, S. Jagner, I. Dance, *Chem. Eur. J.* **2002**, 8, 1269–1278; c) F. Neve, A. Crispini, *Cryst. Growth Des.* **2001**, 1, 387–393.
- [30] S. H. Dale, M. R. J. Elsegood, L. M. Gilby, K. E. Holmes, P. F. Kelly, *Acta Crystallogr., Sect. C* **2005**, 61, m40–m42.
- [31] a) G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*, IUCr Oxford Science, **1999**; b) G. R. Desiraju, *Acc. Chem. Res.* **2002**, 35, 565; c) M. Mascal, *Chem. Commun.* **1998**, 303; d) T. Steiner, *Chem. Commun.* **1997**, 727; e) G. R. Desiraju, *Acc. Chem. Res.* **1996**, 29, 441.
- [32] C. Janiak, T. G. Scharmann, *Polyhedron* **2003**, 22, 1123–1133.
- [33] G. Althoff, J. Ruiz, V. Rodríguez, G. López, J. Pérez, C. Janiak, *CrystEngComm* **2006**, 8, 662–665.
- [34] a) B. Wisser, C. Janiak, *Z. Anorg. Allg. Chem.* **2007**, 633, 1796–1800; b) H. K. Fun, S. Chantrapromma, Z. L. Lu, A. A. Neverov, R. S. Brown, *Acta Crystallogr., Sect. E* **2006**, 62, m3225–m3227; c) M. E. Gunay, M. Aygun, A. Kartal, B. Cetinkaya, E. Kendi, *Cryst. Res. Technol.* **2006**, 41, 615–621; d) X. F. Wang, S. L. Deng, L. S. Long, R. B. Huang, L. S. Zheng, *J. Incl. Phenom. Macrocycl. Chem.* **2006**, 54, 295–298; e) S. R. Ban, X. Yang, W. B. Chen, X. F. Cheng, H. B. Song, *Acta Crystallogr., Sect. E* **2006**, 62, o1713–o1714; f) D. Lorono-Gonzalez, *Acta Crystallogr., Sect. E* **2006**, 62, o1735–o1737; g) V. Balamurugan, R. Mukherjee, *Inorg. Chim. Acta* **2006**, 359, 1376–1382; h) H. Xu, Y.-L. Song, L.-W. Mi, H.-W. Hou, M.-S. Tang, Y.-L. Sang, Y.-T. Fan, Y. Pan, *Dalton Trans.* **2006**, 838–845; i) K. Ravikumar, B. Sridhar, M. Mahesh, V. V. N. Reddy, *Acta Crystallogr., Sect. E* **2006**, 62, o318–o320; j) X.-W. Yang, A.-Y. Li, K.-M. Zhu, X.-Q. Zhou, D.-Z. Liu, *Acta Crystallogr., Sect. E* **2005**, 61, o4144–o4145; k) N. Stanley, P. T. Muthiah, P. Luger, M. Weber, S. J. Geib, *Inorg. Chem. Commun.* **2005**, 8, 1056–1059; l) W. Imhof, K. Halbauer, H. G. Gørls, *Acta Crystallogr., Sect. E* **2005**, 61, m1995–m1997; m) Y. Qu, X. M. Sun, *Acta Crystallogr., Sect. E* **2005**, 61, m2121–m2123; n) W. Imhof, K. Halbauer, H. Gørls, *Acta Crystallogr., Sect. E* **2005**, 61, m2130–m2132.
- [35] F. Neve, A. Crispini, *Cryst. Growth Des.* **2001**, 1, 287–393.
- [36] A. L. Spek, *Acta Crystallogr. A* **1990**, 46, C34. PLATON Version 29-11-98. Windows implementation: L. J. Farrugia, University of Glasgow, Scotland, **1998**.
- [37] Refcodes SOXZUA, SOXZUA01: a) M. Maekawa, M. Munakata, S. Kitagawa, M. Nakamura, *Anal. Sci.* **1991**, 7, 521–522; b) A. J. Canty, B. W. Skelton, P. R. Traill, A. H. White, *Aust. J. Chem.* **1992**, 45, 417–422.
- [38] Bis[μ -3,5-bis(dimethylaminomethyl)pyridine-*N,N'*]dichloropalladium(II), Refcodes NUSYIJ, NUSYIJ01: a) A. L. Spek, M.-C. Lagunas, G. van Koten, *Private Communication*, **1998**; b) M.-C. Lagunas, R. A. Gossage, W. J. J. Smeets, A. L. Spek, G. van Koten, *Eur. J. Inorg. Chem.* **1998**, 163–168.
- [39] Chloro-((*S,R*)-2-[1-[isopropyl(methyl)amino]ethyl]phenyl-*C,N*)-((*S*)-methyl(*tert*-butyl)phenylphosphane)palladium(II), Refcodes XOZQOS, XOZQOS02: Yu. K. Grishin, N. A. Kataeva, A. V. Churakov, L. G. Kuz'mina, V. V. Dunina, personal communication, **2002**.
- [40] Bis[$(\mu$ -diphenylphosphido)chloro(diphenylphosphane)palladium(II)] dichloromethane, Refcodes KUXSOL, KUXSOL01: T. Gebauer, G. Frenzen, K. Dehnicke, *Z. Naturforsch., Teil B* **1992**, 47, 1505–1512.
- [41] Bis(tetraphenylphosphonium)(μ -1,3,2,4-dithiadiazetane-1,3-diylo)-bis(trichloro-palladium), Refcodes KOJGAR, KOJGAR01: a) P. F. Kelly, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *Polyhedron* **1991**, 10, 2337–2340; b) V. C. Ginn, P. F. Kelly, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1992**, 963–968.

- [42] Refcodes IMPPPD, IMPPPD01: a) N. A. Bailey, R. Mason, *J. Chem. Soc. A* **1968**, 2594–2605; b) J. M. Jenkins, B. L. Shaw, *J. Chem. Soc. A* **1966**, 770–775.
- [43] Refcodes CYOCPD, CYOCPD01, CYOCPD02: a) L. Benchekroun, P. Herpin, M. Julia, L. Saussine, *J. Organomet. Chem.* **1977**, *128*, 275–290; b) M. F. Rettig, R. M. Wing, G. R. Wiger, *J. Am. Chem. Soc.* **1981**, *103*, 2980–2986; c) R. Kumar, A. W. Maverick, F. R. Fronczek, J. R. Doyle, N. C. Baenziger, M. A. M. Howells, *Acta Crystallogr., Sect. C* **1993**, *49*, 1766–1767.
- [44] CSD Version 5.28 (November 2006) with 3 updates (January 2007, May 2007, August 2007). The search for C–H···Br contacts was limited to intermolecular contacts in “not disordered” structures with “3D coordinates determined” and “no errors”.
- [45] a) F. Yang, P. E. Fanwick, C. P. Kubiak, *Inorg. Chem.* **2002**, *41*, 4805; b) P. Vitoria, J. I. Beitia, J. M. Gutiérrez-Zorrilla, E. R. Sáiz, A. Luque, M. Insausti, J. J. Blanco, *Inorg. Chem.* **2002**, *41*, 4396; c) R. Büchner, C. T. Cunningham, J. S. Field, R. J. Haines, D. R. McMillin, G. C. Summerton, *J. Chem. Soc., Dalton Trans.* **1999**, 711; d) M. Kato, C. Kosuge, K. Morii, J. S. Ahn, H. Kitagawa, T. Mitani, M. Matsushita, T. Kato, S. Yano, M. Kimura, *Inorg. Chem.* **1999**, *38*, 1638; e) M. Kato, C. Kosuge, S. Yano, M. Kimura, *Acta Crystallogr., Sect. C* **1998**, *54*, 612.
- [46] a) R. H. Herber, M. Croft, M. J. Coyer, B. Bilash, A. Sahiner, *Inorg. Chem.* **1994**, *33*, 2422–2426; b) R. S. Osborn, D. Rogers, *J. Chem. Soc., Dalton Trans.* **1974**, 1002–1004.
- [47] J. R. Stork, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2005**, *127*, 6512–6513.
- [48] ibdpt = 4-isobutyl-3,5-bis(2-pyridyl)-4H-1,2,4-triazole: M. H. Klingele, P. D. W. Boyd, B. Moubaraki, K. S. Murray, S. Brooker, *Eur. J. Inorg. Chem.* **2005**, 910–918.
- [49] S. Chen, I. A. Guzei, L. Yu, *J. Am. Chem. Soc.* **2005**, *127*, 9881–9885; L. Yu, *J. Phys. Chem. A* **2002**, *106*, 544–550.
- [50] a) M. Botoshansky, F. H. Herbstein, M. Kapon, *Acta Crystallogr., Sect. B* **1994**, *50*, 589–596; b) F. H. Herbstein, M. Kapon, S. Wielinski, *Acta Crystallogr., Sect. B* **1977**, *33*, 649–654.
- [51] Hpzd^{dp} = 3-[4-(decyloxy)phenyl]pyrazole: M. C. Torralba, M. Cano, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, *J. Organomet. Chem.* **2001**, *633*, 91–104.
- [52] J. R. Doyle, P. E. Slade, H. B. Jonassen, *Inorg. Synth.* **1960**, *6*, 218.
- [53] S. P. Meneghetti, P. J. Lutz, J. Kress, *Organometallics* **1999**, *18*, 2734.
- [54] G. M. Sheldrick, *SHELXS-97*, *SHELXL-97*, Programs for Crystal Structure Analysis, University of Göttingen, Germany, **1997**.
- [55] K. Brandenburg, Diamond (Version 3.1f), *Crystal and Molecular Structure Visualization*, Crystal Impact, K. Brandenburg & H. Putz GbR, Bonn, Germany, **2007**.

Received: March 12, 2008

Published Online: May 14, 2008