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Palladium complexes with bridged and unbridged benzimidazolin-2-ylidene ligands

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Abstract

Two equivalents of *N*,*N*′-dimethylbenzimidazolyl iodide (**1**) react with $Pd(OAc)_2$ to yield the complex *cis*-bis(*N*,*N*′-dimethylbenzimidazoli-2-ylidene)diiodo palladium (**2**). The potentially bidentate ligand 1,1′-methylene-bis(*N*-methylbenzimidazolyl) diiodide (**3**) reacts with $Pd(OAc)_2$ to yield the complex [1,1-methylene-bis(*N*-methylbenzimidazolin-2-ylidene)]diiodo palladium (**4**) with a bidentate carbene ligand. Both complexes were characterised by ^1H- and ^{13}C-NMR spectroscopy. The X-ray crystal structures of **2** and **4** reveal that methylene-bridging of the benzimidazolin-2-ylidene ligands leads to palladium complexes with a reduced $C_{carbene}-Pd-C_{carbene}$ angle (91.3(2) in **2** vs. 83.7(3)° in **4**). In addition, the angles between the planes of the carbene ligands and the PdC_2I_2 plane are reduced from almost perpendicular in **2** (83.06(10) and 79.84(13)°) to 54.4(2) and 51.8(2)° in **4**, while comparable bond distances in **2** and **4** are identical within experimental error. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Many carbene complexes have been reported since the first planned synthesis of a complex with a heteroatom-stabilized carbene ligand by Fischer in 1964 [1]. Meanwhile various procedures for the introduction of such carbene ligands into transition metal complexes have been described [2].

The development of free and stable nucleophilic *N*-heterocyclic carbenes [3] opened new ways for the synthesis of carbene complexes. One possibility to introduce *N*-heterocyclic carbene ligands, mostly of the imidazolin-2-ylidene type, into metal complexes is the reaction of the free carbene with an appropriate transition metal fragment either with or without substitution of a two-electron ligand at the metal centre [4]. An interesting variation of this reaction is the reaction of a dialkylated imidazolium ion with bases (NaH) under in situ generation of the free carbene and subsequent reaction with transition metal complexes [5]. The presence of basic ligands in a metal complex will also initiate the formation of carbene complexes from imidazolium salts and this was indeed the first method to generate chromium [6] and mercury [7] complexes of *N*-heterocyclic carbenes. The preparation of stable *N*-heterocyclic carbenes and their metal complexes has recently been reviewed [8].

Alternatively, metal complexes with *N*-heterocyclic carbenes, mostly of the saturated imidazolidin-2-ylidene type, can be obtained by the reaction of electron-rich enetetramines with transition metal complexes under C=C bond cleavage [9].

Access is much more limited to complexes containing carbene ligands derived from benzimidazol. The first free stable carbene of this type, *N*,*N*′-bis(2,2-dimethylpropyl)benzimidazolin-2-ylidene, was only isolated in 1998 from the corresponding thione [10]. The *N*,*N*′-dialkylation of benzimidazol with very bulky substituents (^{t}Bu, neopentyl) is not possible and the deprotonation of *N*,*N*′-dimethyl-substituted benzimidazolium salts does not yield a free carbene, but instead an enetetramine [11].

However, some complexes containing benzimidazolin-2-ylidene ligands are known. Among these are a

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homoleptic gold(I)–dicarbene complex obtained by phase transfer catalysis deprotonation of a *N*,*N*′-dialkylated benzimidazolium bromide in the presence of Au(SMe$_2$)Cl [12]. Complexes containing CH$_2$-bridged bidentate imidazolin-2-ylidene-benzimidazolin-2-ylidene ligands have been synthesised from the corresponding diazolium salts and $K_4[M_4(\mu\text{-}OCH_3)_4(CO)_{12}]$ (M = Cr, Mo, W) [5b] in moderate yield. More recently the intramolecular cyclization reaction of coordinated 2-aminophenylisocyanide was shown to yield complexes containing NH,NH-benzimidazolin-2-ylidene ligands [13], which can be *N*,*N*′-dialkylated as we reported for the corresponding benzoxazolin-2-ylidene complexes obtained from 2-hydroxyphenylisocyanide [14].

Here we present the preparation of a CH$_2$-bridged bis(*N*-methyl-benzimidazolyl) salt together with the synthesis of the corresponding dicarbene palladium complex. In addition, the molecular structures of palladium complexes containing two bridged or non-bridged benzimidazolin-2-ylidene ligands are compared.

2. Results and discussion

2.1. Synthesis and characterisation

The reaction of two equivalents of *N*,*N*′-dimethylbenzimidazolyl iodide **1** with Pd(OAc)$_2$ yields *cis*-bis(*N*,*N*′-dimethylbenzimidazolin-2-ylidene)diiodo palladium(II) **2** as a yellow powder. By the same procedure, [1,1′-methylene-bis(*N*-methylbenzimidazolin-2-ylidene)]-diiodo palladium(II) **4** could be synthesised, from 1,1′-methylene-bis(*N*-methylbenzimidazolyl) diiodide **3** as the carbene precursor. The procedure used for obtaining **2** and **4** has been employed previously for the synthesis of palladium(II) complexes with two imidazolin-2-ylidene ligands [5c,d]. However, **4** is the first bridged bis(benzimidazolin-2-ylidene) complex known to date (see Scheme 1).

The iodo salts used in the syntheses have been described. *N*,*N*′-dimethylbenzimidazolyl iodide **1** was first reported in 1901 by Fischer [15], and 1,1′-methylene-bis(*N*-methylbenzimidazolyl) diiodide **3** by Elguero et al. [16] in 1983. However, neither has been used in organometallic synthesis, and their ability to act as carbene precursors has not been studied systematically.

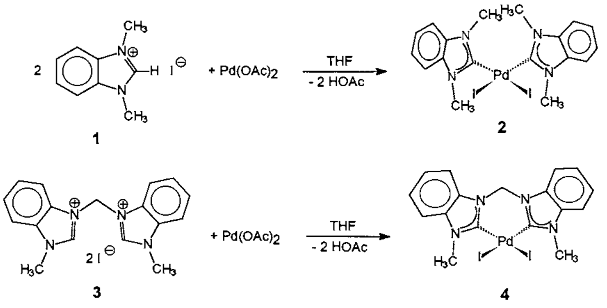
The ^{13}C-NMR resonance for the C2 carbon atom in free imidazolin-2-ylidenes is normally observed around $\delta = 220$ [3], for saturated *N*-heterocyclic imidazolidin-2-ylides around $\delta = 240$ [17] and for the only known stable benzimidazolin-2-ylidene at $\delta = 231.5$ ppm [10]. The substituents at the nitrogen atoms in the ylidenes exert almost no influence [8]. Upon coordination, the ^{13}C-NMR resonance for C2 is normally shifted upfield relative to the free carbene. For *cis*-bis(imidazolin-2-ylidene)diiodo palladium complexes values of $\delta = 168.2$ (unbridged ylidenes) and $\delta = 185.5$ ppm (CH$_2$-bridged ylidenes) [5c,d] were reported. A similar behaviour was observed for **2** (δ(C2) = 172.06 ppm) and **4** (δ(C2) = 175.14 ppm) relative to the free benzimidazolin-2-ylidene ($\delta = 231.5$ ppm) [10]. However, the difference in the upfield shifts for unbridged und bridged bis(benzimidazol-2-ylidenes) is not as pronounced as for the imidazolin-2-ylidene ligands.

2.2. Molecular structure of complexes 2 and 4

The results of X-ray structure investigations of **2** and **4** are illustrated in Fig. 1. Selected bond lengths and angles are listed in Table 1.

The carbene ligands in **2** are arranged in *cis*-fashion around an almost planar palladium atom (sum of angles around Pd 360.5°). The same, almost planar *cis*-arrangement was observed for bis(*N*,*N*′-dimethylimidazolin-2-ylidene)diiodo palladium [5c,d]. However, the geometry of both complexes differs from that of bis(*N*-methylbenzoxazolin-2-ylidene)diiodo palladium synthesised from the corresponding 2-hydroxyphenylisocyanide complex, where the two carbene ligands are coordinated in a *trans*-arrangement [18].

The angle between the two carbene ligands (C1–Pd–C10) in **2** is slightly widened from the ideal value for square-planar complexes to 91.3(2) and the angle between the iodo ligands to 95.79(2)°. The planes of the five-membered carbene rings are bent towards each other and form an interplane angle of 89.7(2)°. Both carbene ring planes are oriented almost perpendicular to the PdC$_2$I$_2$ plane (83.06(10) und 79.84(13°). This is probably due to the steric demand of the methyl groups at the nitrogen atoms, however, the angles between the carbene planes and the PdC$_2$I$_2$ plane measure only 70.5 and 69.4° in the bis(*N*,*N*′-dimethylimidazolin-2-ylidene)diiodo palladium complex [5c]. The Pd–C$_{carbene}$ bond lengths in **2** are almost identical and measure 1.987(4) and 1.989(4) Å, respectively. These values are almost identical to the corresponding distances in the



Scheme 1.

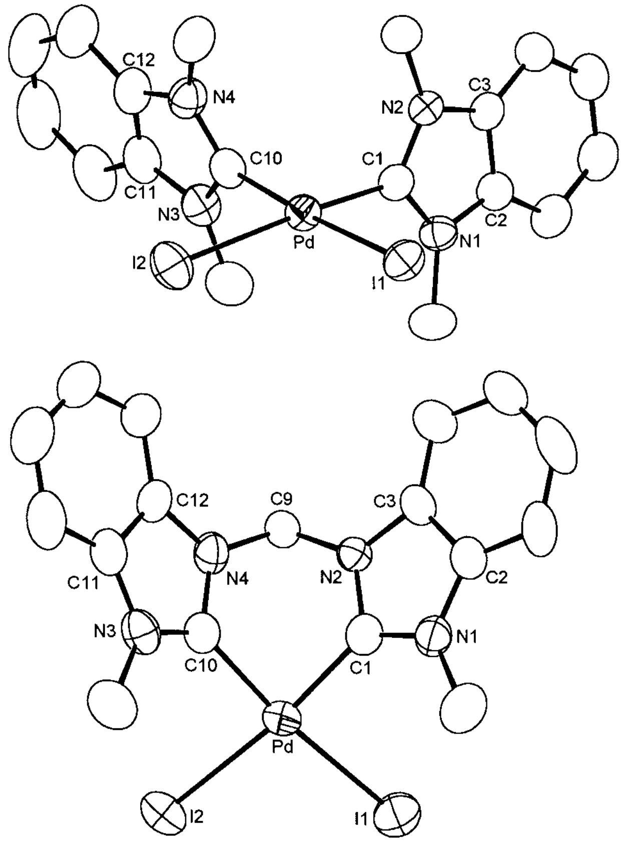


Fig. 1. Molecular structures of complexes **2** (upper) and **4** (lower, the disordered DMSO molecule is not depicted).

bis(imidazolin-2-ylidene) homologue (1.990(3) and 1.997(3) Å [5a]). Both rings of the carbene ligands in **2** are planar within experimental error. Compared to the free stable benzimidazol-2-ylidene [10], the angles N1–C1–N2 and N3–C10–N4 in **2** are widened upon coordination to 106.4(3) and 106.1(4)°. These values are slightly larger than observed in coordinated imidazolin-2-ylidene ligands [8].

Complex **4** crystallizes with one molecule of DMSO per asymmetric unit. The molecular structure consists of an almost square-planar coordinated (sum of angles around palladium 359.3°) palladium atom. The angle between the two carbene ligands (C1–Pd–C10) in **4** is reduced to 83.7(3) from 91.3(2)° in **2**. This small value, apparently caused by the methylene bridge between the benzimidazolin-2-ylidene ligands, is one of the smallest values observed in square-planar palladium bis(ylidene) complexes. However, it compares well with the equivalent angle in the methylene bridged octahedral (imidazolin-2-ylidene-benzimidazolin-2-ylidene) tungsten complex (79.2(3) and 80.6(3)° [5b]). Both the angle between the carbene planes (72.6(3)°) and the angles between the carbene planes and the PdC_2I_2 plane (54.4(2) and 51.8(2)°) are significantly reduced compared to the unbridged complex **2**. This reflects the steric distortion caused by the methylene bridge between the two benzimidazolin-2-ylidene groups. Both the Pd–C distances and the N–C–N angles in the carbene ligands in **4** fall in the range observed for the unbridged complex **2** and for *cis*-bis(imidazolin-2-ylidene)diiodo palladium complexes [5].

3. Experimental

3.1. General procedures

N,*N*′-Dimethylbenzimidazolyl iodide (**1**) [15] and 1,1′-methylene-bis(*N*-methylbenzimidazolyl) diiodide (**3**) [16] were synthesised according to literature procedures. All reactions were carried out in an atmosphere of dry argon. Solvents were dried and distilled under an inert atmosphere prior to use. NMR spectra were recorded on a Bruker AM 250 spectrometer. Mass spectra were obtained using a Finnigan MAT 112 or MAT 711 spectrometer. Elemental analyses were performed on an Elementar Vario EL elemental analyser at the Institut für Anorganische und Analytische Chemie, Freie Universität Berlin.

Table 1
Selected bond lengths (Å) and angles (°) for **2** and **4**·DMSO

	2	**4**·DMSO
Bond lengths		
Pd–I1	2.6371(5)	2.6456(8)
Pd–I2	2.6805(5)	2.6410(8)
Pd–C1	1.987(4)	1.990(8)
Pd–C10	1.989(4)	1.991(7)
N1–C1	1.353(5)	1.350(10)
N1–C2	1.388(6)	1.384(10)
N2–C1	1.359(5)	1.358(10)
N2–C3	1.392(5)	1.391(9)
N2–C9		1.434(9)
N3–C10	1.359(6)	1.333(10)
N3–C11	1.377(6)	1.393(10)
N4–C10	1.352(6)	1.360(10)
N4–C12	1.394(6)	1.402(10)
N4–C9		1.449(10)
C2–C3	1.391(6)	1.387(11)
C11–C12	1.385(8)	1.386(11)
Bond angles		
I1–Pd–I2	95.79(2)	92.54(3)
I1–Pd–C1	88.32(11)	91.3(2)
I1–Pd–C10	175.53(13)	172.1(2)
I2–Pd–C1	172.63(12)	172.2(2)
I2–Pd–C10	85.09(12)	91.8(2)
C1–Pd–C10	91.3(2)	83.7(3)
C1–N1–C2	110.8(3)	110.4(6)
C1–N2–C3	110.2(3)	110.3(6)
C10–N3–C11	110.4(4)	111.4(6)
C10–N4–C12	110.7(4)	109.7(6)
N1–C1–N2	106.4(3)	106.5(6)
N3–C10–N4	106.1(4)	106.7(6)

3.2. Synthesis of cis-bis(N,N′-dimethylbenzimidazolin-2-ylidene)-diiodo palladium (2)

A sample of 220 mg (0.803 mmol) *N*,*N*′-dimethylbenzimidazolyl iodide (**1**) and 90 mg (0.401 mmol) of palladium acetate were suspended in 15 ml of THF and stirred overnight at room temperature (r.t.). The orange suspension turned first dark brown and lightened up to pale yellow after a few hours. The volatiles were removed in vacuo and the residue was washed several times with dichloromethane. The residue was recrystallized from acetonitrile to give yellow crystals of **2**. Yield: 146 mg (56%). Anal. Calc. for $C_{18}H_{20}N_4I_2Pd$: C, 33.13; H, 3.09; N, 8.59. Found: C, 33.13; H, 3.40; N, 7.96%. ^{1}H-NMR (250 MHz, CD_3CN): 4.02 (s, 12H, CH_3), 7.72–7.86 (m, 8H, Ar-H). ^{13}C-NMR (62.9 MHz, DMSO-d_6): 35.75 (CH_3), 110.84, 123.21, 134.44 (Ar-C), 172.06 (NCN). MS (+FAB, relative intensity %) *m*/*e*: 652 (24, M^+), 525 (50, $C_{18}H_{20}N_4IPd$).

3.3. Synthesis of [1,1′-methylene-bis(N-methylbenzimidazolin-2-ylidene)]diiodo palladium (4)

A 250 mg (0.472 mmol) sample of 1,1′-methylene-bis(*N*-methylbenzimidazolyl) diiodide **3** and 107 mg (0.477 mmol) of palladium acetate were suspended in 15 ml of THF. The mixture was heated to reflux for 8 h and then stirred for 24 h at r.t. The colour changed to dark brown. The volatiles were removed in vacuo, and the residue was washed with dichloromethane until the washing solution stayed colourless. The residue was recrystallized from dimethylsulfoxide to yield a bright yellow powder of **4**. Yield: 200 mg (67%). Anal. Calc. for $C_{17}H_{16}N_4I_2Pd$: C, 32.08; H, 2.53; N, 8.80. Found: C, 32.26; H, 2.33; N, 8.48%. ^{1}H-NMR (250 MHz, DMSO-d_6): 4.08 (s, 6H, CH_3), 6.82 (d, 2H, CH_2), 7.43, 7.60, 8.13 (m, 8H, Ar-H). ^{13}C-NMR (62.9 MHz, DMSO-d_6): 37.39 (CH_3), 56.99 (CH_2), 110.40, 110.85, 123.97, 124.20, 132.44, 134.02 (Ar-C), 175.14 (NCN). MS (+FAB, relative intensity %) *m*/*e*: 636 (4%, M^+). 509 (100, $C_{17}H_{16}N_4IPd$).

3.4. X-ray crystal structures of 2 and 4·DMSO

Crystals of **2** were obtained from an acetonitrile solution; those of **4**·DMSO were grown from a DMSO solution at r.t.

3.4.1. Selected crystallographic details for 2

Size of data crystal 0.40 × 0.40 × 0.38 mm, formula $C_{18}H_{20}N_4I_2Pd$, $M_r = 652.58$ amu, triclinic, space group $P\bar{1}$, $a = 8.3806(12)$, $b = 9.1030(10)$, $c = 15.1032(12)$ Å, $\alpha = 78.980(7)$, $\beta = 89.280(10)$, $\gamma = 70.260(10)°$, $V = 1062.8(2)$ Å^3, $Z = 2$, $D_{calc} = 2.039$ g cm^{-3}, Mo–K$_\alpha$ radiation, ($\lambda = 0.71073$ Å, graphite monochromator), μ (Mo–K$_\alpha$) = 3.79 mm^{-1}. Symmetry-independent diffraction data (3687) were measured at 20(2)°C in the 2θ-range 5–50°. Structure solution with Patterson and refinement with Fourier methods, refinement (on F^2) of positional parameters of all non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms on calculated positions (d(C–H) = 0.95 Å [19]) with $U_{eq(H)} = 1.3U_{eq(C)}$. $R = 0.032$, $Rw = 0.087$ for 3405 absorption corrected (seven ψ-scans) structure factors $I \geq 2\sigma(I)$ and 227 refined parameters. Neutral atomic scattering factors were used and all scattering factors were corrected for anomalous dispersion. All calculations were carried out with the SHELXS program package [20].

3.4.2. Selected crystallographic details for 4·DMSO

Size of data crystal 0.37 × 0.37 × 0.35 mm, formula $C_{19}H_{22}N_4I_2OPdS$ (**4**·DMSO), $M_r = 714.67$ amu, monoclinic, space group $P2_1/n$, $a = 7.0475(4)$, $b = 14.0084(14)$, $c = 24.072(3)$ Å, $\beta = 90.110(7)°$, $V = 2376.5(4)$ Å^3, $Z = 4$, $D_{calc} = 1.997$ g cm^{-3}, Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å, graphite monochromator), μ (Mo–K$_\alpha$) = 3.483 mm^{-1}. Symmetry-independent diffraction data (3083) were measured at 20(2)°C in the 2θ-range 3–45°. Structure solution with Patterson and refinement (on F^2) with Fourier methods, refinement of positional parameters of all non-hydrogen atoms with anisotropic thermal parameters (except for the positional parameters of a disordered DMSO molecule per asymmetric unit, which were refined isotropically, no hydrogen positions were calculated for the DMSO molecule). Other hydrogen atoms on calculated positions (d(C–H) = 0.95 Å [19]) with $U_{eq(H)} = 1.3U_{eq(C)}$. $R = 0.040$, $Rw = 0.106$ for 2598 absorption corrected (six ψ-scans) structure factors $I \geq 2\sigma(I)$ and 238 refined parameters. Neutral atomic scattering factors were used and all scattering factors were corrected for anomalous dispersion. All calculations were carried out with the SHELXL-97 program package [20].

4. Supplementary material

Further details of the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk) on quoting the depository numbers CCDC-116875 (for **4**·DMSO) and CCDC-116876 (for **2**).

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