

Synthesis and Structural Characterization of *trans*-Bis[1,3-bis(methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]dichloropalladium(II)

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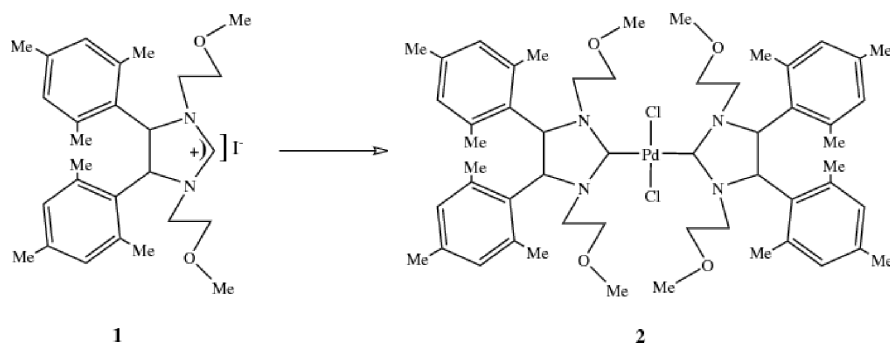
A Pd(II) complex of a new *N*-heterocyclic carbene (NHC) ligand with bulky substituents and functionalized methoxy-donor side arms has been synthesized and characterized by elemental analyses, ¹H and ¹³C NMR, and IR spectroscopy. Molecular and crystal structures of the title complex have been determined by single crystal X-ray diffraction. The compound crystallizes in the monoclinic space group *P*2₁/*c*, with *a* = 15.927(2), *b* = 8.489(2), *c* = 20.309(5) Å, β = 99.213(2)°, *Z* = 2, *D*_x = 1.253 g cm⁻³. The palladium atom is situated on an inversion center. There are several weak intramolecular C–H···N/O interactions.

Key words: Bulky Substituents, *N*-Heterocyclic Carbene, Palladium(II) Complex, Imidazolidin-2-ylidene, Methoxy-donor

Introduction

The first metal complexes of *N*-heterocyclic carbenes (NHCs) were reported independently in 1968 by Wanzlick [1] and Öfele [2], and Lappert and co-workers continued investigations in this area [3–5]. After the isolation and crystallographic characterization of stable *N*-heterocyclic carbenes by Arduengo [6–10], increasing attention has focused on using these compounds as ancillary ligands for transition-metal complexes. Interestingly, most studies focusing on catalysts incorporating NHC ligands have revolved around the platinum group metals. In many instances simple substitution reaction routes involving replacement of phosphines by NHC ligands lead to higher catalytic activity as well as improved thermal stability of the resulting organometallic complexes. In contrast to metal-phosphine complexes, NHC's form metal complexes that have high stability towards heat, moisture and oxygen. Numerous publications related to their metal coordination chemistry and their catalytic properties were reported in recent years [11–18].

The ancillary NHC ligand coordinated to the metal center has a number of important roles in homogeneous catalysis, such as providing a stabilizing effect and governing activity and selectivity by alteration of steric and electronic parameters. The number, nature and position of the substituents on the nitrogen atom(s) and/or NHC ring have been found to play a crucial role in tuning the catalytic activity. Much work has focused on the study of structure-reactivity relationships in NHC complexes. Thus, useful information has been collected about the influence of several structural factors, including the steric bulkiness around the carbene carbon atom [19], the presence of electron-withdrawing groups in the imidazole backbone [20], or the presence or absence of unsaturation at the C₄–C₅ bond in the imidazole/dihydroimidazole series [21]. There is only limited information on the effect of steric bulkiness at the C₄, C₅ positions. In view of the growing importance of palladium complexes as catalysts for C–C and C-heteroatom bond formation, we have synthesized and structurally characterized the title compound **2**, which incorporates mesityl groups.



Scheme 1. Reagents and conditions: (i) Ag_2O , CH_2Cl_2 , r. t.; (ii) $\text{PdCl}_2(\text{NCMe})_2$, CH_2Cl_2 , r. t.

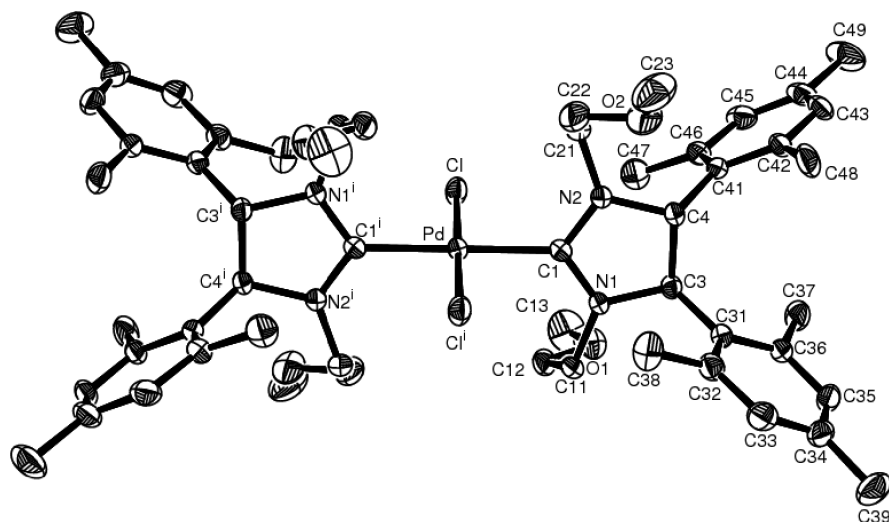


Fig. 1. An ORTEP-III view [22] of the molecular structure of 2. Displacement ellipsoids are shown at the 30% probability level and hydrogen atoms have been omitted for clarity.

Results and Discussion

The complex was prepared according to Scheme 1. Elemental analyses and NMR spectra of the product are in agreement with the proposed structure. The clearest spectroscopic evidence identifying 2 as a carbene complex is the appearance of a highly deshielded ^{13}C NMR singlet for the carbene C atom at 197.9 ppm. The IR spectrum shows a strong band at 1499 cm^{-1} attributable to $\nu(\text{CN}_2)$. The absorption bands in the region $1420\text{--}1660\text{ cm}^{-1}$ are due to skeletal vibrations of the aromatic rings.

The molecular structure of the title complex is shown in Fig. 1. Crystals of $[\text{PdCl}_2(\text{C}_{27}\text{H}_{38}\text{N}_2\text{O}_2)_2]$ are monoclinic, space group $P2_1/c$. The Pd atom is four-coordinated by two C atoms of the NHC rings and two Cl atoms in *trans* positions. The palladium atom lies on a center of inversion, thus one half of the molecule represents the asymmetric unit. The bond angles at the Pd atom involving *cis* pairs of substituents are $90.33(15)^\circ$ for C1-Pd-Cl and $89.67(15)^\circ$

for C1-Pd-Cl^i [i]: $-x, -y, -z$]. The dihedral angle between the plane of the NHC ring and the coordination plane ($\text{Pd/C1/Cl/Cl}^i/\text{Cl}^i$) is $75.8(3)^\circ$.

The Pd–Cl bond lengths ($2.3560(15)\text{ \AA}$) are slightly larger than the sum of the individual covalent radii ($d_{\text{Pd-Cl}} = 2.273\text{ \AA}$) [23] but compare well with the range observed for other related Pd complexes [24–29]. The Pd–C_{carb} bond lengths ($2.026(5)\text{ \AA}$) are slightly smaller than the sum of the individual covalent radii ($d_{\text{Pd-C}} = 2.055\text{ \AA}$) [23]. In this regard it is worth noting that a theoretical study [30] revealed that a shortening of a metal–carbene bond of up to 4% can be ascribed to the change in the hybridization state of the carbene carbon atom as a consequence of enhanced *s*-character of the in-plane carbene lone pair orbital in metal–NHC complexes. Selected interatomic distances and bond and torsion angles for the title complex 2 are listed in Table 1.

The NHC ring (weighted average ring bond length 1.436 \AA) adopts a twisted conformation (puckering pa-

Table 1. Selected geometrical parameters (Å, deg) for **2**.

| Distances | | | |
|-----------------|-----------|-----------------|-----------|
| Pd–C1 | 2.4227(8) | Pd2–C12 | 2.3987(7) |
| Pd–C1 | 1.991(2) | Pd2–C31 | 1.978(2) |
| Pd–N3 | 2.141(2) | Pd2–N6 | 2.141(2) |
| Pd–C22 | 2.005(2) | Pd2–C52 | 2.007(2) |
| C1–N1 | 1.340(3) | C31–N4 | 1.349(2) |
| C1–N2 | 1.343(3) | C31–N5 | 1.337(2) |
| C2–N1 | 1.475(3) | C32–N4 | 1.484(3) |
| C3–N2 | 1.479(3) | C33–N5 | 1.473(3) |
| C2–C3 | 1.508(3) | C32–C33 | 1.504(3) |
| C13–N1 | 1.435(3) | C43–N4 | 1.431(2) |
| C4–N2 | 1.434(3) | C34–N5 | 1.437(2) |
| C28–N3 | 1.489(4) | C58–N6 | 1.480(3) |
| Angles | | | |
| Cl–Pd–C22 | 172.2(1) | Cl2–Pd2–C52 | 173.0(1) |
| C1–Pd–N3 | 170.2(1) | C31–Pd2–N6 | 170.4(1) |
| C1–Pd–C22 | 92.9(1) | C31–Pd2–C52 | 92.6(1) |
| C1–Pd–Cl | 94.9(1) | C31–Pd2–Cl2 | 94.2(1) |
| N3–Pd–Cl | 90.6(1) | N6–Pd2–Cl2 | 91.2(1) |
| C22–Pd–N3 | 81.6(1) | C52–Pd2–N6 | 81.8(1) |
| N1–C1–N2 | 108.1(2) | N5–C31–N4 | 108.0(2) |
| N1–C1–Pd | 120.7(2) | N4–C31–Pd2 | 131.2(1) |
| N2–C1–Pd | 131.1(1) | N5–C31–Pd2 | 120.7(1) |
| Dihedral angles | | | |
| N1–C2–C3–N2 | –16.9(2) | N4–C32–C33–N5 | –16.1(2) |
| Pd–C1–N1–C13 | –4.3(3) | Pd2–C31–N4–C43 | 17.1(3) |
| Pd–C1–N2–C4 | 15.6(3) | Pd2–C31–N5–C34 | –11.0(3) |
| C22–C27–C28–N3 | –27.5(3) | C52–C57–C58–N6 | –26.3(2) |
| Pd–C2–C27–C28 | 3.7(3) | Pd2–C52–C57–C58 | 3.0(2) |

Table 2. Weak intramolecular hydrogen-bonding (Å, deg) in **2**.

| D–H...A | D–H | H...A | D...A | D–H...A |
|---------------|------|-------|----------|---------|
| C4–H4...O2 | 0.98 | 2.58 | 3.101(8) | 114 |
| C38–H38B...N1 | 0.96 | 2.41 | 2.908(8) | 112 |
| C38–H38D...N1 | 0.96 | 2.19 | 2.908(8) | 131 |
| C47–H47B...N2 | 0.96 | 2.56 | 3.024(9) | 110 |
| C47–H47D...N2 | 0.96 | 2.30 | 3.024(9) | 132 |

D: donor, A: acceptor.

average NHC plane is 0.072(6) Å. The phenyl rings are planar with maximum deviations of $-0.023(7)^\circ$ for C34 and $0.009(7)^\circ$ for C43, respectively. The dihedral angle between these ring planes is $56.0(3)^\circ$.

The bond lengths between carbene C and N atoms in the NHC ring are shorter than the N1–C3 and N2–C4 bonds (see Table 1). N1–C1 and C3–N1 bond lengths of 1.333(7) and 1.483(6) Å, respectively, are indicative of a greater partial double-bond character due to partial electron donation from N to the carbene C-atom [31–32], as also corroborated by theoretical studies [33–34].

The Pd atoms are located at the corners and the *bc* face centers of the monoclinic unit cell as shown in Fig. 2. There are five weak intramolecular interactions in the crystal structure. The details of the weak intramolecular hydrogen bonds are given in Table 2.

Experimental Section

Materials and methods

The 1,3-bis(2-methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl)imidazolidinium iodide (**1**) was prepared according to a known method [35]. NMR spectra were recorded at 297 K on a Varian spectrometer at 400 MHz (^1H) and 100.56 MHz (^{13}C). Infrared spectra were recorded as KBr pellets in the range $400\text{--}4000\text{ cm}^{-1}$ on a ATI UNICAM 2000 spectrometer. Elemental analyses were carried out by the analytical service of TUBITAK with a Carlo Erba Strumentazione Model 1106 apparatus.

Synthesis of bis[1,3-bis(2-methoxyethyl)-4,5-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene]dichloropalladium(II) (**2**)

Ag_2O (0.12 g, 0.5 mmol) was added to a solution of **1** (0.55 g, 1 mmol) in CH_2Cl_2 (10 mL). The suspension became clear after stirring for 2 h at r.t. with exclusion of light. Thereafter $\text{PdCl}_2(\text{NCMe})_2$ (0.13 g, 0.5 mmol) was added. The resultant solution was stirred for 48 h at r.t. and filtered through celite. The volume of the filtrate was reduced to 5 mL under vacuum. Then, hexane (10 mL) was added and the mixture was filtered. The yellow solid

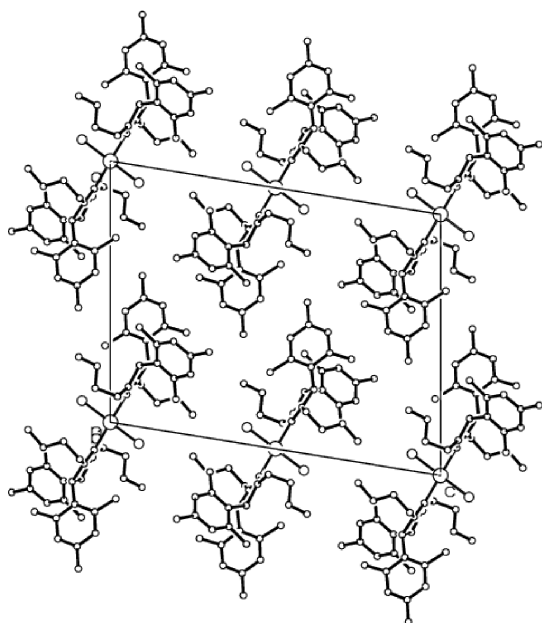


Fig. 2. Packing pattern in the crystal structure of **2** as seen along the *b* axis. H atoms have been omitted for clarity.

rameters $q_2 = 0.123(6)$ Å and $\varphi = 130(3)^\circ$) of the C3–C4 bond. The maximum deviation of C3 from the

Table 3. Crystal data and details of the structure refinement for the title complex.

| | |
|---|---|
| Chem. form. | PdCl ₂ (C ₂₇ H ₃₈ N ₂ O ₂) ₂ |
| Color / shape | yellow / prismatic |
| Formula weight | 1022.49 |
| Crystal system | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> , Å | 15.927(2) |
| <i>b</i> , Å | 8.489(2) |
| <i>c</i> , Å | 20.309(5) |
| β , deg | 99.213(2) |
| Cell volume, Å ³ | 2710.4(10) |
| <i>Z</i> | 2 |
| <i>D</i> _x , g cm ⁻³ | 1.253 |
| <i>F</i> (000), e | 1080 |
| μ (MoK α), mm ⁻¹ | 0.486 |
| Scans | ω -2 θ scan |
| λ (MoK α), Å | 0.71073 |
| Calculated <i>T</i> _{min} / <i>T</i> _{max} | 0.909 / 0.953 |
| Independent/observed reflections | 5290 / 3057 |
| Data / parameters | 5290 / 290 |
| <i>R</i> / <i>wR</i> [<i>I</i> \geq 2 σ (<i>I</i>)] | 0.056/0.163 |
| <i>R</i> / <i>wR</i> (all data) | 0.141/0.128 |
| Goodness-of-fit (GoF) on <i>F</i> ² | 1.037 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 4.4059P]$ where $P = [F_o^2 + 2F_c^2]/3$ |
| $\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³ | 0.66/−0.53 |

was recrystallized from dichloromethane (3 mL)/diethyl ether (9 mL). Yield: 0.389 g; 76 %, m.p.: 298–300 °C. PdCl₂C₅₄H₇₆N₄O₄: calcd. C 63.43, H 7.49, N 5.48; found C 63.06, H 7.86, N 5.73. – ¹H NMR (CDCl₃): δ = 1.73 (s, 12 H, 2,4,6-(CH₃)₃C₆H₂), 2.22 (s, 12 H, 2,4,6-(CH₃)₃C₆H₂), 2.49 (s, 12 H, 2,4,6-(CH₃)₃C₆H₂), 3.13–3.20 (m, 4 H, NCH₂CH₂OCH₃), 3.34 (s, 12 H, NCH₂CH₂OCH₃), 3.65–3.68 (m, 4 H, NCH₂CH₂OCH₃), 4.28–4.34 (m, 4 H, NCH₂CH₂OCH₃), 4.69 (m, 4 H, NCH₂CH₂OCH₃), 5.73 (s, 4 H, NCHCHN), 6.66 (s, 4 H, 2,4,6-(CH₃)₃C₆H₂), 6.85 (s, 4 H, 2,4,6-(CH₃)₃C₆H₂). – ¹³C NMR (CDCl₃): δ = 20.0, 20.6, 21.1 (2,4,6-(CH₃)₃C₆H₂), 46.8 (NCH₂CH₂OCH₃), 58.9 (NCH₂CH₂OCH₃), 68.3 (NCHCHN), 73.9 (NCH₂CH₂OCH₃), 129.2, 130.1, 131.7, 137.6, 138.3, 138.6 (2,4,6-(CH₃)₃C₆H₂), 197.9 (s, C_{carb} Pd).

Crystal structure determination

A suitable sample of size 0.20 × 0.20 × 0.10 mm³ was chosen for the crystallographic study and carefully mounted on the goniometer of a Nonius CAD-4 diffractometer [36]. All diffraction measurements were performed at r.t. (293 K) using graphite monochromated MoK α radiation (λ = 0.71073 Å). The systematic absences and intensity symmetries indicated the monoclinic space group *P*2₁/*c*. A total of 5488 reflections (5290 unique) within the θ range 1.30° < θ < 25.79° were collected in the ω -2 θ scanning mode with *R*_{int} = 0.0438. The intensities were corrected for Lorentz and polarization effects and an absorption correction was applied by the multiscan method [37]. The cell parameters were determined by using CRYSDA [38]. An extinction correction was not applied. The structure was solved by Direct Methods using SHELXS-97 [39]. The refinement was carried out by full-matrix least-squares methods on the positional and anisotropic temperature parameters of the non-hydrogen atoms, corresponding to a total of 290 crystallographic parameters using the SHELXL-97 program [39]. All H atoms were refined using appropriate riding models, with C–H distances of 0.97 Å for CH₂, 0.96 Å for CH₃, 0.98 Å for methine and 0.93 Å for aromatic groups. The structure was refined to *R*₁ = 0.056 for all 5290 data used in the refinement process. The methyl H atoms were refined as idealized disordered methyl groups with two positions rotated from each other by 60° and equivalent site-occupation factors (0.50). Other details of the data collection conditions and parameters of the refinement process are summarized in Table 3.

Supplementary data

CCDC 643518 contains 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.

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