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Synthesis and crystal structure of [1,3-*N,N*-bis{2,6-diisopropylphenyl}imidazol-2-ylidene]chloro-*N,N*-dimethylbenzylamine-2-*C,N*]palladium(II)

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Note

Synthesis and crystal structure of [1,3-*N,N*-bis{2,6-diisopropylphenyl}imidazol-2-ylidene]chloro- [*N,N*-dimethylbenzylamine-2-*C,N*]palladium(II)

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The title compound **1** has been synthesized and its structure has been determined by single-crystal X-ray methods. Crystal data: C₃₆H₄₈ClN₃Pd, *M* = 664.62, monoclinic, space group *P*2₁/*n* with *a* = 11.857(5), *b* = 21.042(8), *c* = 14.632(6) Å, β = 106.492(5), *Z* = 4, *V* = 3501(2) Å³, *D*_c = 1.261 g cm⁻³, μ(Mo-Kα) = 0.633 mm⁻¹, *F*(000) = 1392; final *R* and *wR* = 0.0412 and 0.0889, respectively, for 3265 observed reflections with *I* ≥ 2σ(*I*). The Pd(II) atom has distorted square planar geometry, due to the bulk of the isopropyl groups on the NHC ligand. Positioning of the carbenic carbon *trans* to the amino group and the metalated carbon *trans* to chlorine is consistent with the *trans* influence.

Keywords: *N*-Heterocyclic carbene; Cyclopalladation; X-ray structure

1. Introduction

Since the synthesis and isolation of stable *N*-heterocyclic carbenes (NHC) by Arduengo in 1991 [1], increasing attention has focussed on using them as ancillary ligands; they are alternatives to phosphines, and have been used for a variety of catalytic reactions, including the Suzuki–Miyaura reaction [2–4], the Kumada–Tamao–Corriu reaction [5], the Heck reaction [6–8], aryl amination involving aryl chlorides [9, 10], olefin metathesis [11–14] and olefin hydrogenation [15, 16]. Therefore, synthesis and characterization of *N*-heterocyclic carbene transition metal complexes are very attractive. We report here the preparation and crystal structure of [1,3-*N,N*-bis{2,6-diisopropylphenyl}imidazol-2-ylidene]chloro[*N,N*-dimethylbenzylamine-2-*C,N*]palladium(II).

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2. Experimental

2.1. Materials and measurements

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried using standard procedures. Flash chromatography was performed on silica gel (200–300 mesh) with ethylacetate/petroleum ether or methanol/dichloromethane. Bis(2,6-diisopropylphenyl)imidazolium chloride (**2**) [17] and di- μ -chloro-bis(*N,N*-dimethylbenzylamine-2-*C,N*)dipalladium(II) (**3**) [18] were prepared by the published literature methods.

2.2. Synthesis of **1**

A mixture of **2** (137 mg, 0.35 mmol), **3** (82 mg, 0.15 mmol), and NaO^tBu (29 mg, 0.30 mmol) was stirred in 3 cm³ of THF at room temperature for 1 h. The solvent was then removed under vacuum. The resulting solid was dissolved in dichloromethane, filtered through Celite, and purified by column chromatography (SiO₂, ethyl acetate/petroleum ether 1:10) to give a light yellow solid (193 mg, 96%). m.p. 243–244°. ¹H NMR (CDCl₃, 400 MHz): δ = 0.81 (d, 6H, *J* = 8.0 Hz), 1.02 (d, 6H, *J* = 8.0 Hz), 1.17 (d, 6H, *J* = 8.0 Hz), 1.48 (d, 6H, *J* = 8.0 Hz), 2.38 (s, 6H), 3.10–3.20 (m, 2H), 3.45 (s, 2H), 6.53 (d, 1H, *J* = 8.0 Hz), 6.77 (d, 1H, *J* = 8.0 Hz), 7.10–7.25 (m, 6H), 7.25–7.40 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ = 23.1, 23.2, 26.1, 26.3, 28.3, 29.0, 49.7, 72.6, 121.5, 122.6, 123.7, 124.0, 124.5, 125.3, 129.6, 136.1, 136.2, 144.7, 147.8, 147.9, 150.5, 177.5. IR (KBr, cm⁻¹): 3036, 2966, 2919, 2879, 2828, 1579, 1474, 1450, 1396, 1348, 1324, 1273, 1217, 1111, 1026, 993, 940, 870. MS (ESI) *m/z* (%): 628 [M–C1⁻] (100).

2.3. Crystallography

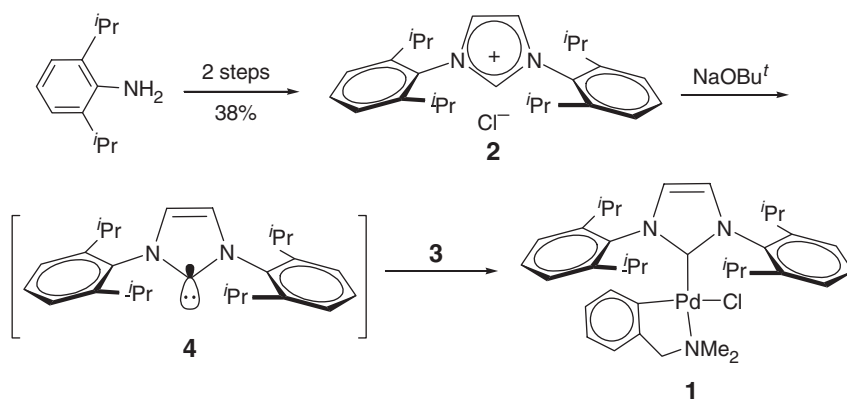
Crystals suitable for X-ray analysis were obtained by layering petroleum ether onto a dichloromethane solution of the complex at 0°C. A colourless crystal of dimensions of 0.22 × 0.21 × 0.05 mm³ was mounted on a glass fibre in a random orientation. Intensity data were collected by a BRUKER SMART 1000 CCD diffractometer equipped with a graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) using an ω scan mode in the range 1.74 ≤ θ ≤ 27.62° at 273(2) K. A total of 8072 reflections was collected with 5297 being unique (R_{int} = 0.0801), of which 3265 with $I > 2\sigma(I)$ were used in structure calculations. Lattice determination and data collection were carried out using SMART version 5.625 software. Data reduction and absorption corrections were performed with SAINT version 6.45 and SADABS version 2.03. The structure was solved by direct methods and difference Fourier syntheses. Non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters. All calculations were carried out with the SHELXT-97 software package.

3. Results and discussion

1,3-*N,N*-Bis(2,6-diisopropylphenyl)imidazolium chloride (**2**), prepared from 2,6-diisopropylaniline in two steps [17], is the precursor of 1,3-*N,N*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**4**). The NHC **4** is easily produced via **2** by a strong base such as

sodium *tert*-butoxide (scheme 1), and can break the chlorine bridges of the palladium dimer to form an analogue of **1** [19]. We were pleased to find that **1** could be prepared more conveniently by mixing the three components together in the same time with higher yield (96%). The complex **1** was characterized by IR, ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ -NMR and MS spectroscopies. The downfield signal in the ^1H NMR spectrum of **2** at 11 ppm for H-2 of imidazolium disappeared in the spectrum of **1**, indicating the successful transformation of the salt into the carbene. A single downfield signal in the $^{13}\text{C}\{^1\text{H}\}$ -NMR of **1** at 177.5 ppm for C-2 of the imidazole moiety was present for the carbene carbons coordinated to palladium(II), consistent with assignments in the literature [19].

Selected bond distances and angles for the complex are given in table 1 and the molecular structure is depicted in figure 1. The Pd(II) ion is located in a distorted square planar environment with the NHC ligand *trans* to the amino group, as expected according to *trans* influence. The distorted configuration, indicated by a C(31)–Pd(1)–Cl(1) bond angle of $172.83(9)^\circ$ and a C(11)–Pd(1)–N(1) angle of $171.43(12)^\circ$,



Scheme 1. Synthesis of complex **1**.

Table 1. Selected bond distances (Å) and angles ($^\circ$) with estimated standard deviation in parenthesis for the complex.

Pd(1)–C(11)	1.994(3)
Pd(1)–C(31)	1.997(3)
Pd(1)–N(1)	2.142(3)
Pd(1)–C(11)	2.3911(12)
C(11)–N(2)	1.365(4)
C(11)–N(3)	1.366(4)
C(11)–Pd(1)–C(31)	95.19(12)
C(11)–Pd(1)–N(1)	171.43(12)
C(31)–Pd(1)–N(1)	82.46(12)
C(11)–Pd(1)–C(11)	91.95(8)
C(31)–Pd(1)–C(11)	172.83(9)
N(1)–Pd(1)–C(11)	90.56(9)
N(2)–C(11)–N(3)	104.3(2)
N(2)–C(11)–Pd(1)	122.4(2)
N(3)–C(11)–Pd(1)	133.3(2)

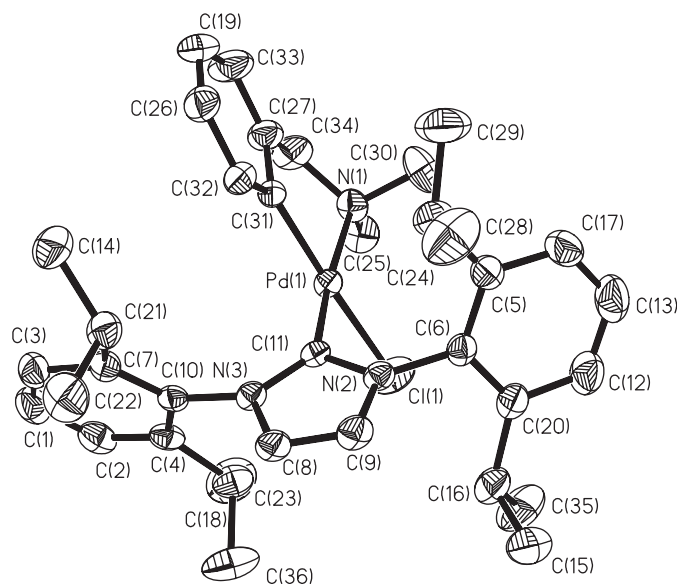


Figure 1. Molecular structure of the complex showing the atom numbering scheme.

probably results from the steric requirements of the NHC ligand. The Pd(1)–Cl(1) bond length of 2.3911(12) Å, longer than that in its palladium(II) precursor (2.327(1) Å) [18], is due to a combination of the *trans* influence of the metalated carbon atom and the steric bulk of the NHC ligand. The distance between Pd and carbenic carbon (Pd(1)–C(11), 1.994(3) Å) is very close to that in a recently synthesized analogue (1.992 Å) [19].

Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 295435. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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