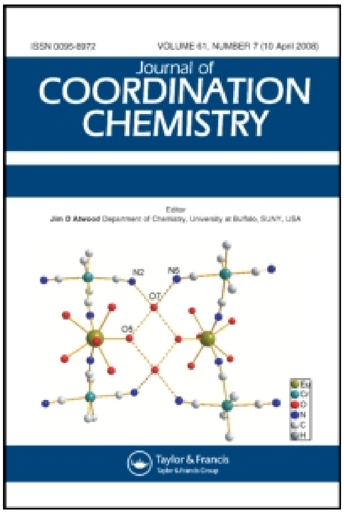

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The synthesis and structural characterization of a <i>N</i>-heterocyclic carbene-substituted palladacycle

Aytaç Gürhan Gökçe[a]; M. Emın Günay[b]; Muhıttın Aygün[a]; Bekır Çetınkaya[c]; Orhan Büyükgüngör[d]
[a] Department of Physics, Dokuz Eylul University, Buca-35160, ızmir, Turkey [b] Department of Chemistry, Adnan Menderes University, Aydın-09010, Turkey [c] Department of Chemistry, Ege University, Bornova-35100, İzmir, Turkey [d] Department of Physics, Ondokuz Mayıs University, Samsun-55139, Turkey

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The synthesis and structural characterization of a *N*-heterocyclic carbene-substituted palladacycle

AYTAÇ GÜRHAN GÖKÇE*†, M. EMİN GÜNAY‡, MUHİTTİN AYGÜN†,
BEKİR ÇETİNKAYA§ and ORHAN BÜYÜKGÜNGÖR¶

†Department of Physics, Dokuz Eylul University, Buca – 35160, İzmir, Turkey
‡Department of Chemistry, Adnan Menderes University, Aydın – 09010, Turkey
§Department of Chemistry, Ege University, Bornova – 35100, İzmir, Turkey
¶Department of Physics, Ondokuz Mayıs University, Samsun – 55139, Turkey

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Reaction of {[Pd(dmba)(μ-Cl)]$_2$} (dmba = $(CH_3)_2NCH_2C_6H_4$) with an *in situ* generated *N*-heterocyclic carbene (NHC = 1,3-dimesitylimidazolidin-2-ylidene) afforded crystals containing [chloro-(1,3-dimesitylimidazolidin-2-ylidene)(*N*,*N*-dimethylaminobenzyl-C^1,*N*) palladium(II)] (**VII**). Molecular and crystal structures of the title compound have been determined by single crystal X-ray diffraction technique. Complex **VII** crystallizes in space group $P\bar{1}$, with $a = 13.685(3)$ Å, $b = 13.590(2)$ Å, $c = 16.229(3)$ Å, $\alpha = 87.162(13)^\circ$, $\beta = 70.514(15)^\circ$, $\gamma = 84.153(16)^\circ$, $Z = 4$, $D_{\text{Calcd}} = 1.367\,\text{g cm}^{-3}$. There are two independent molecules in the asymmetric unit.

Keywords: Crystal structure; Palladacycle complex; *N*-Heterocyclic carbene; Imidazolinium salt; *N*,*N*-Dimethylbenzylamine; Palladium(II) complex

1. Introduction

During the last decade palladacycles such as **I**–**IV** (figure 1) have been extensively studied in figure 1 [1–4]. The possibility of modulating their steric and electronic properties by changing the nature of metallated carbon (sp^3 and sp^2), donor atom (L = N, P, S etc.), size of the linker (Y) and type of the ligand L$_n$ on the metal infers to this class of compounds various important applications such as catalytic precursors [5–12]. In addition, they are easy to synthesize, rather cheap and stable towards hydrolysis and oxidation.

Saturated *N*-heterocyclic carbene ligands, such as 1,3-diorganylimidazolidin-2-ylidenes, have proven to be very useful in a range of palladium-catalyzed reactions [13–18]. One important aspect of the NHC-based ligand is its thermal stability and lack of sensitivity to air and moisture. Our continuing interest in the development of NHC-related ligands in the Pd-catalysed C–C and C-heteroatom bond formation led us to explore the NHC-derived palladacycle (scheme 1).

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*Corresponding author. Email: aytac.gokce@deu.edu.tr

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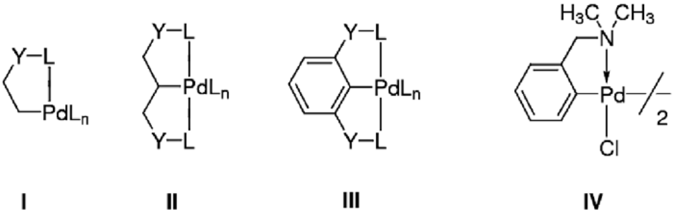
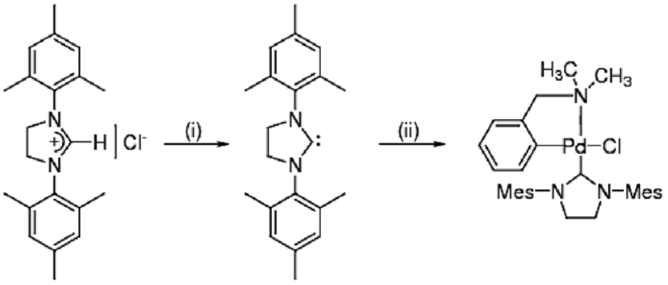


Figure 1. Generalized palladacyclic structure (L = donor, Y = Linker group).



V **VI** **VII**

Scheme 1. Reagents and conditions: (i) NaH, THF, 25°C; (ii) $[Pd(dmba)(\mu\text{-}Cl)]_2$, 4 h, 65°C.

2. Experimental section

2.1. *Materials and method*

All reactions and manipulations of air-sensitive materials were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received. Compounds **IV** and **V** were prepared according to literature methods [19–21]. ^1H and ^{13}C NMR spectra were recorded on a Varian mercury +400 MHz spectrometer. Elemental analysis was performed via CHNS-932 (LECO) in TUBITAK Microlab and melting point was determined by electrothermal melting point detection apparatus.

2.2. *Synthesis of the title complex and analytical characterization*

To a suspension of imidazolinium salt (**V**, 0.500 g, 1.46 mmol) in THF was added NaH (0.069 g, 2.87 mmol). The mixture was stirred for 12 h at 25°C and suspension was filtered. Palladacycle dimer (**IV**, 0.350 g, 0.634 mmol) was added to the solution. The solution was heated under reflux for 4 h. Upon cooling to room temperature, hexane (10 mL) was added to the mixture. The resulting solid was filtered off and then recrystallized from CH_2Cl_2–Et_2O (2 mL, 6 mL). Yield: 0.258 g, 70%; m.p.: 235–237°C. Anal. Calcd for $C_{30}H_{38}ClN_3Pd$: C, 61.86; H, 6.58; N, 7.21. Found: C, 61.94; H, 6.70; N, 7.01.

Table 1. Crystal data and details of the structure refinement for the title complex.

Chem. form.	$C_{30}H_{38}N_3PdCl$
Color/shape	Colorless/prismatic
Formula weight	582.48
Crystal system	Triclinic
$F(000)$	1208
Space group	$P\bar{1}$
Cell constants (Å, °)	
a	13.685(3)
b	13.590(2)
c	16.229(3)
α	87.162(13)
β	70.514(15)
γ	84.153(16)
Cell volume (Å^3)	2830.1(9)
Formula units/unit cell	4
D_{Calcd} (g cm^{-3})	1.367
μ (Mo-Kα) (mm^{-1})	0.772
Diffractometer/meas. method	STOE IPDS II/rotation
λ (Mo-Kα) (Å)	0.71073
Crystal size (mm^3)	0.620 × 0.447 × 0.190
Calculated $T_{\min}/T_{\max}$	0.6546/0.8755
Temperature (K)	293(2)
Unique reflections measured	13302
Independent/observed reflections	13302/10737
Data/restrain/parameters	13302/0/647
Final R indices [$I > 2\sigma(I)$]	$R = 0.0271/R_w = 0.0687$
R indices (all data)	$R = 0.0404/R_w = 0.0652$
Goodness-of-fit (GoF) on F^2	1.004
Highest peak (e Å^{-3})	0.312
Deepest hole (e Å^{-3})	−0.690
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.0000P]$ where $P = [F_o^2 + 2F_c^2]/3$

2.3. *Physical measurements*

^{1}H NMR ($CDCl_3$): δ 2.24 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 2.35 (s, 6H, CH_3), 2.66 (s, 6H, $N(CH_3)_2$), 3.44 (s, 2H, $CH_2N(CH_3)_2$), 3.95–4.10 (m, 4H, NCH_2CH_2N), 6.73 (s, br, 2H, mesityl), 6.76–6.87 (m, 3H, orthometallated phenyl ring), 6.95 (s, br, 2H, mesityl), 7.16 (d, 1H, $J = 2.4$ Hz, orthometallated phenyl ring). ^{13}C NMR ($CDCl_3$): δ 20.13, 20.58, 21.16 (s, CH_3), 49.95 (s, CH_2), 51.98 (s, CH_2), 72.35 (s, CH_2), 121.50, 123.23, 124.04, 129.00, 129.85, 135.46, 136.63, 137.71, 138.03, 138.96, 147.82, 149.28 (s, Ar), 204.35 (s, carbene C).

2.4. *Crystal structure determination*

A colorless crystal with dimensions of 0.620 × 0.447 × 0.190 mm^3 was selected for the crystallographic study. The diffraction intensity data were collected at room temperature on a STOE IPDS II diffractometer using graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). A summary of crystallographic data and details of the structure refinement are listed in table 1. The cell parameters were determined using X-AREA software [22] on the setting angles of 74633 reflections [$1.99° < \theta < 27.97°$]. Absorption correction was achieved by the integration method via X-RED software [22].

A total of 48165 reflections were collected for $h_{\min} = -17$, $h_{\max} = 17$, $k_{\min} = -17$, $k_{\max} = 17$, $l_{\min} = -21$, $l_{\max} = 21$. The crystal structure was solved by SHELXS-97 [23]. The refinement (on F^2) was carried out by full-matrix least squares techniques using the SHELXL-97 program [24]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding atoms, with C–H distances of 0.93 Å for aromatic H atoms, 0.96 Å for methyl H atoms and 0.97 Å for methylene H atoms.

3. Results and discussion

We chose to synthesize the NHC adduct of palladacyclic complex based on *ortho*-metalated *N*,*N*-dimethylbenzylamine. The parent palladacycle is present both in solution and the solid state as the neutral halogen dimer, which can be cleaved by nucleophiles. As ligand saturated NHC, 1,3-dimesitylimidazolidin-2-ylidene, was used, the proton attached to C_2 in the corresponding imidazolinium salt (**V**) was acidic enough to react easily with NaH. The free carbene (**VI**), generated *in situ*, was treated with the dimer palladacycle (**IV**). The complex prepared in this work has been characterized by a range of techniques.

For **VII**, the ^{1}H NMR spectrum showed that in solution only one isomer, involving the NHC ligand *trans* to $N(CH_3)_2$, was present. Iyer and Jayanthi briefly reported on [(dmba)PdCl(NHC)] (NHC = 1,3-diphenylimidazolidin-2-ylidene) and assumed it to posses a *cis* configuration of the NHC to Cl. No analytical data were, however, provided and no further evidence for this conclusion has been presented [9]. Compared with the dimer palladacycle the ^{1}H NMR signals assigned to dmba are shifted to high field due to the higher σ-donor ability of NHC. The formula of complex **VII** with one NHC ligand is clearly supported by $^{13}C\{^1H\}$ NMR in which a singlet at 204.35 ppm ($CDCl_3$) was observed.

An ORTEP3 [25] view of the title complex is shown in figure 2. The title compound crystallizes in space group $P\bar{1}$ with two independent molecules in the asymmetric unit.

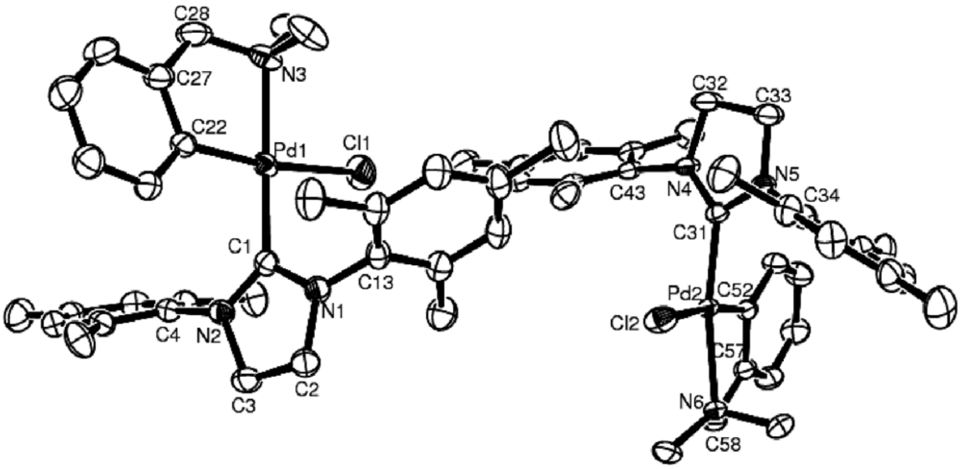


Figure 2. An ORTEP3 view of the title compound. Displacement ellipsoids are shown at the 30% probability level and hydrogen atoms have been omitted for clarity.

In both moieties the geometry at palladium is distorted square-planar (sum of angles around Pd 359.95° for moiety 1 and 359.82° for moiety 2) with the chlorine atoms (Cl1 and Cl2) *trans* to the Pd1–C22 and Pd2–C52 bonds of the dmba ligands and the NHC ligands *trans* to the Pd1–N3 and Pd2–N6 bonds, that is expected for four-coordinate Pd(II) complexes. The maximum deviation of the coordination plane formed by Pd1/Cl1/C1/N3/C22 atoms in moiety 1 is −0.079(2) Å for C22. C52 atom has a maximum deviation of −0.066(2) Å from Pd2/Cl2/C31/N6/C52 coordination plane in moiety 2. The dihedral angle between the plane of the NHC ring and the coordination plane is 70.82(1)° for moiety 1 and 75.46(1)° for moiety 2. Bond distances and angles in the coordination sphere of Pd are in the expected range and in accord with reported Pd(II) structures [26–28]. Selected interatomic distances, bond and torsion angles for **VII** are listed in table 2.

Although both C–N bonds in the NHC rings are single bond, their bond distances are different. The bond distances between carbene C and N atoms in the NHC ring are shorter than N1–C2, N2–C3, N4–C32 and N5–C33 bonds (see table 2). For instance, N1–C1 and C2–N1 bond distances are 1.340(3) and 1.475(3) Å, respectively, possibly indicative of a greater partial double-bond character due to partial electron donation by N to the carbene C-atom donor [29, 30]. Theoretical study indicates that the stability of these carbenes is due to electron donation from the nitrogen lone pairs into the formally vacant $p(\pi)$ orbital of the carbene C atom (herein C1 and C31) [31]. The five-membered rings (Pd1/C22/C27/C28/N3 and Pd2/C52/C57/C58/N6) are adapted to envelop conformation on N3 and N6 in moiety 1 and 2, respectively. The dihedral angles between the two trimethylphenyl ring planes are 45.83(11) and 39.22(11)° for moiety 1

Table 2. Selected geometrical parameters (Å, °) for **VII**.

Pd1–Cl1	2.4227(8)	Pd2–Cl2	2.3987(7)
Pd1–C1	1.991(2)	Pd2–C31	1.978(2)
Pd1–N3	2.141(2)	Pd2–N6	2.141(2)
Pd1–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)
Cl1–Pd1–C22	172.20(6)	Cl2–Pd2–C52	172.99(5)
C1–Pd1–N3	170.19(8)	C31–Pd2–N6	170.37(7)
C1–Pd1–C22	92.85(8)	C31–Pd2–C52	92.62(7)
C1–Pd1–Cl1	94.90(6)	C31–Pd2–Cl2	94.17(5)
N3–Pd1–Cl1	90.62(7)	N6–Pd2–Cl2	91.22(5)
C22–Pd1–N3	81.58(9)	C52–Pd2–N6	81.81(7)
N1–C1–N2	108.05(17)	N5–C31–N4	107.98(16)
N1–C1–Pd1	120.74(15)	N4–C31–Pd2	131.16(14)
N2–C1–Pd1	131.14(14)	N5–C31–Pd2	120.73(13)
N1–C2–C3–N2	−16.9(2)	N4–C32–C33–N5	−16.1(2)
Pd1–C1–N1–C13	−4.3(3)	Pd2–C31–N4–C43	17.1(3)
Pd1–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)
Pd1–C2–C27–C28	3.7(3)	Pd2–C52–C57–C58	3.0(2)

Table 3. The intra- and intermolecular weak hydrogen-bonding geometry (Å, °) for the title compound.

D–H···A	D–H	H···A	D···A	∠D–H···A
C3–H3B···Cl2[a]	0.97	2.78	3.534(3)	135
C29–H29C···Cl1	0.96	2.77	3.218(4)	109
C12–H12A···Cl1	0.96	2.81	3.576(4)	138
C49–H49A···Cl2	0.96	2.61	3.493(3)	153
C42–H42C···Cl2	0.96	2.70	3.460(4)	136
C60–H60C···Cl2	0.96	2.74	3.232(3)	112
C10–H10B···N2	0.96	2.47	2.928(3)	109
C12–H12C···N2	0.96	2.57	2.912(3)	101
C51–H51B···N4	0.96	2.54	2.917(3)	103

D: donor, A: acceptor. Symmetry transformation used to generate equivalent atoms: (a) $-x$, $1-y$, $1-z$.

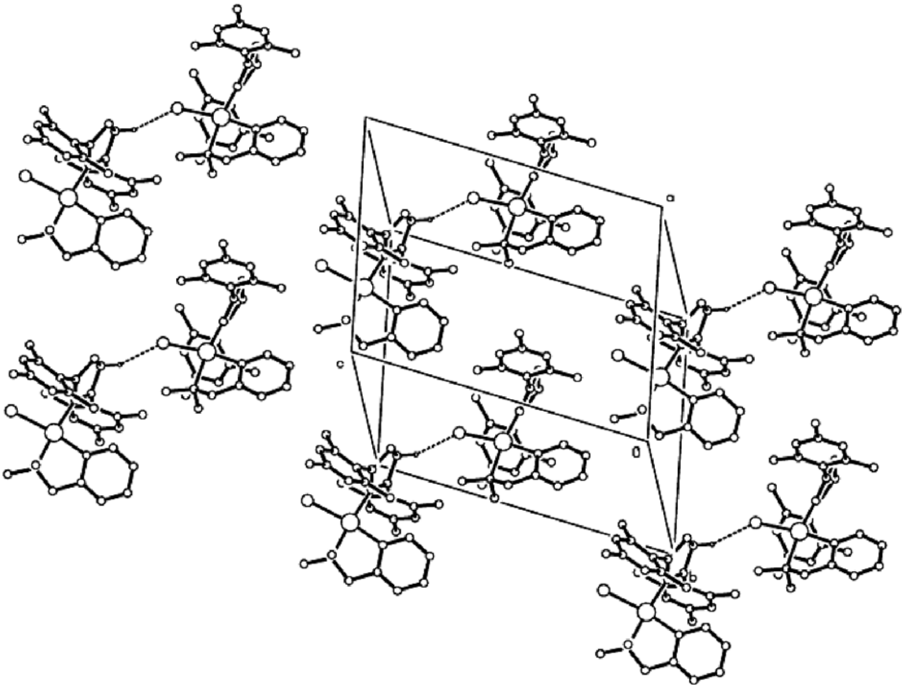


Figure 3. Part of the crystal structure of the title compound, showing the intermolecular hydrogen bonds. For the sake of clarity, H atoms except H3B have been omitted.

and 2, respectively. Pd–N bond (2.141 Å) *trans* to NHC is shorter than Pd–N$(CH_3)_2$ bond (2.150 Å) *trans* to PPh_3 in [Pd(dmba)(Cl) (PPh_3)] [20].

Examination of the structure of the title compound with PLATON [32] showed that there was a solvent-accessible void (108 Å^3) in the region around (1/2, 0, 1/2). The reflection (*hkl*) data were modified using the SQUEEZE option of PLATON. Although the empty space seemed large enough to accommodate small solvent molecules, the spaces are too constricted to hold any molecule larger than water. Since no water was present during the synthesis or recrystallization, and since little electron density in the area of the void is found, we conclude that the voids are empty.

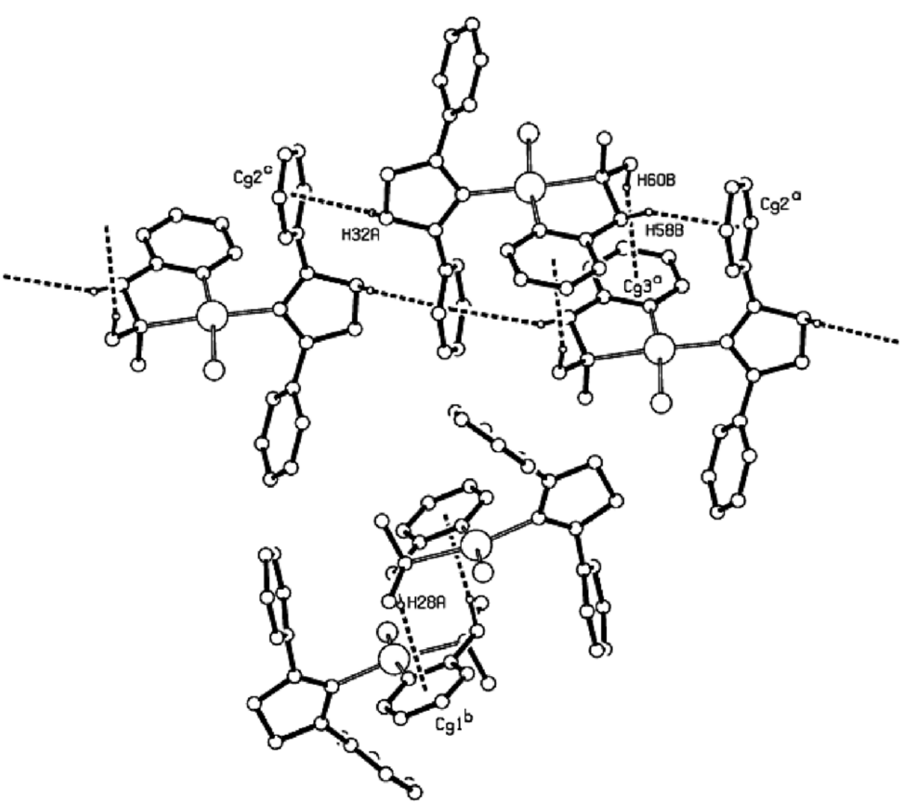


Figure 4. Part of the crystal structure of the title compound, showing C–H···π hydrogen-bonding interactions. For clarity, the methyl C atoms bonded to phenyl rings and H atoms bonded to atoms not involved in the motif shown have been omitted.

Table 4. C–H···π interaction geometry (Å, °) for the title compound.

X–H···Cg	X–H	H···Cg	X···Cg	X–H···Cg
C28–H28A···Cg1[b]	0.97	2.695	3.663(3)	175.10
C32–H32A···Cg2[c]	0.97	2.773	3.614(3)	145.42
C58–H58B···Cg2[a]	0.97	2.681	3.542(3)	148.15
C60–H60B···Cg3[a]	0.96	2.852	3.738(3)	153.85

Cg1, Cg2 and Cg3 are the centroids of C22···C27, C43···C48 and C52···C57 rings, respectively. Symmetry codes: (b) $1-x$, $-y$, $-z$; (c) $1-x$, $1-y$, $1-z$.

Table 3 shows the intra and intermolecular interactions for the title compound. There are eight C–H···Cl and C–H···N type intramolecular interactions in the crystal structure. Intermolecular hydrogen bonds exists between H3B in the NHC ring and Cl2 as shown in figure 3. The intermolecular hydrogen bonds affect the conformation of NHC rings. Thus, both NHC rings adopt twisted conformation on their C–C single bonds (C2–C3 and C32–C33). Intermolecular C–H···π interactions between molecules and their closest neighbors within the crystal lattice are also present (figure 4 and table 4).

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 294445. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336-033; Email: deposit@ccdc.cam.ac.uk).

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