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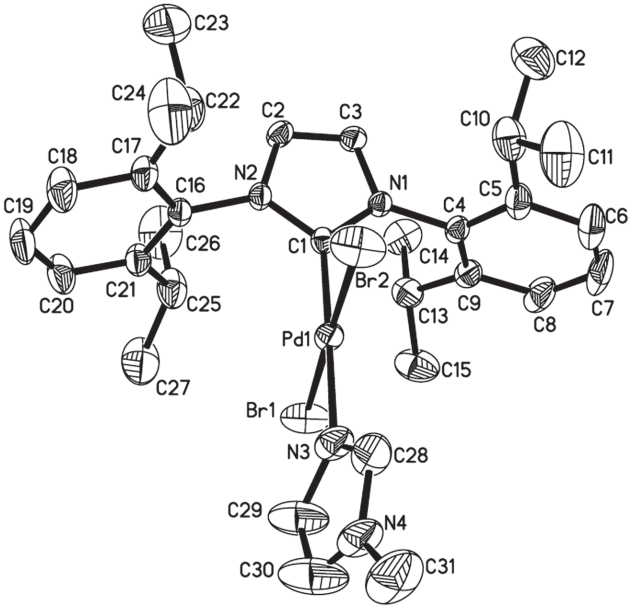
The crystal structure of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)-dibromido-(1-methyl-1*H*-imidazole-κ^{1}N)palladium(II) – ethyl acetate – water (1/1/1), $C_{31}H_{42}Br_2N_4Pd$



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Abstract

$C_{31}H_{42}Br_2N_4Pd$, monoclinic, $P2_1/c$, $a = 12.3093(14)$Å, $b = 15.2805(18)$ Å, $c = 20.3205(17)$ Å, $\beta = 112.213(5)°$, $V = 3538.5(7)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0540$, $wR_{ref}(F^2) = 0.1528$, $T = 298(2)$K.

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The metal complex of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow blocks
Size:	0.31 × 0.25 × 0.23 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	28.1 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	52.°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	27750, 6941, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5517
$N(param)_{refined}$:	352
Programs:	SHELX [3], PLATON [4], Bruker programs [5]

Source of material

The title product was prepared by modification of the literature known methods [1, 2]. Under a nitrogen atmosphere, 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazolium bromide (0.7 mmol), palladium acetate (0.7 mmol), sodium bromide (0.7 mmol), potassium carbonate (0.7 mmol), tetrahydrofuran (5.0 mL) and 1-methylimidazole (2.5 mmol) were successively added into a Schlenk tube. The mixture was stirred under reflux for 12 h. Then it was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to give the pure product in 42% yield as yellow solid. Crystals suitable for X-ray diffraction were grown in a mixture of ethyl acetate and petroleum ether. mp 275 °C (decomposed). **^{1}H NMR** (500 MHz, $CDCl_3$, TMS) δ

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Pd1	0.14518(3)	0.67241(2)	0.639188(19)	0.04001(13)
Br1	0.13610(8)	0.57655(4)	0.73290(4)	0.0813(2)
Br2	0.15002(8)	0.76699(5)	0.54533(4)	0.0838(2)
N1	0.0412(3)	0.8253(2)	0.68820(18)	0.0323(7)
N2	0.2285(3)	0.8271(2)	0.73475(19)	0.0349(8)
N3	0.1579(4)	0.5614(3)	0.5819(3)	0.0631(13)
N4	0.1551(5)	0.4750(4)	0.4956(4)	0.0781(17)
C1	0.1374(3)	0.7792(3)	0.6912(2)	0.0326(8)
C2	0.1895(4)	0.9023(3)	0.7563(2)	0.0418(10)
H2	0.2361	0.9456	0.7858	0.050*
C3	0.0733(4)	0.9016(3)	0.7273(3)	0.0409(10)
H3	0.0230	0.9442	0.7324	0.049*
C4	−0.0813(4)	0.8001(3)	0.6539(2)	0.0385(10)
C5	−0.1468(4)	0.8320(4)	0.5859(3)	0.0542(13)
C6	−0.2645(5)	0.8076(5)	0.5576(4)	0.0768(19)
H6	−0.3109	0.8257	0.5119	0.092*
C7	−0.3139(5)	0.7581(5)	0.5947(4)	0.088(2)
H7	−0.3929	0.7433	0.5742	0.105*
C8	−0.2483(5)	0.7302(4)	0.6613(4)	0.0694(17)
H8	−0.2831	0.6962	0.6859	0.083*
C9	−0.1301(4)	0.7516(3)	0.6936(3)	0.0462(11)
C10	−0.0992(6)	0.8948(5)	0.5475(3)	0.0698(17)
H10	−0.0133	0.8937	0.5697	0.084*
C11	−0.1356(8)	0.8736(8)	0.4684(4)	0.118(3)
H11A	−0.1162	0.8138	0.4631	0.176*
H11B	−0.0948	0.9116	0.4479	0.176*
H11C	−0.2187	0.8820	0.4447	0.176*
C12	−0.1414(8)	0.9873(5)	0.5547(4)	0.100(3)
H12A	−0.2250	0.9905	0.5305	0.149*
H12B	−0.1047	1.0287	0.5342	0.149*
H12C	−0.1209	1.0007	0.6041	0.149*
C13	−0.0624(5)	0.7272(4)	0.7711(3)	0.0573(13)
H13	0.0209	0.7241	0.7786	0.069*
C14	−0.0763(7)	0.7977(5)	0.8192(3)	0.0741(17)
H14A	−0.0478	0.8522	0.8085	0.111*
H14B	−0.0323	0.7823	0.8678	0.111*
H14C	−0.1577	0.8036	0.8118	0.111*
C15	−0.0976(7)	0.6382(5)	0.7908(5)	0.089(2)
H15A	−0.0400	0.6194	0.8354	0.134*
H15B	−0.1022	0.5964	0.7546	0.134*
H15C	−0.1727	0.6429	0.7947	0.134*
C16	0.3520(4)	0.8043(3)	0.7597(2)	0.0368(9)
C17	0.4208(4)	0.8409(3)	0.7260(3)	0.0482(11)
C18	0.5397(5)	0.8190(5)	0.7531(4)	0.0691(17)
H18	0.5886	0.8426	0.7323	0.083*
C19	0.5854(5)	0.7637(5)	0.8094(4)	0.0766(19)
H19	0.6643	0.7483	0.8253	0.092*
C20	0.5171(5)	0.7305(4)	0.8429(3)	0.0665(16)
H20	0.5505	0.6939	0.8820	0.080*
C21	0.3987(4)	0.7505(3)	0.8197(3)	0.0484(11)
C22	0.3750(5)	0.9074(5)	0.6671(3)	0.0700(17)
H22	0.2893	0.9018	0.6462	0.084*
C23	0.4036(8)	0.9991(5)	0.6965(5)	0.107(3)
H23A	0.3606	1.0118	0.7261	0.160*
H23B	0.3822	1.0402	0.6580	0.160*
H23C	0.4862	1.0035	0.7241	0.160*
C24	0.4206(7)	0.8946(8)	0.6078(4)	0.115(3)
H24A	0.5000	0.9154	0.6233	0.172*
H24B	0.3724	0.9269	0.5666	0.172*
H24C	0.4184	0.8336	0.5962	0.172*
C25	0.3274(5)	0.7202(5)	0.8624(3)	0.0715(18)
H25	0.2452	0.7152	0.8298	0.086*
C26	0.3342(9)	0.7885(7)	0.9181(4)	0.114(3)
H26A	0.4137	0.7934	0.9514	0.171*
H26B	0.2846	0.7713	0.9427	0.171*
H26C	0.3085	0.8440	0.8954	0.171*
C27	0.3663(7)	0.6319(6)	0.8976(5)	0.114(3)
H27A	0.3654	0.5897	0.8623	0.171*
H27B	0.3138	0.6135	0.9198	0.171*
H27C	0.4444	0.6366	0.9328	0.171*
C28	0.1329(5)	0.5562(5)	0.5140(4)	0.0725(17)
H28	0.1035	0.6021	0.4822	0.087*
C29	0.1982(9)	0.4798(5)	0.6075(5)	0.102(3)
H29	0.2231	0.4629	0.6549	0.123*
C30	0.1963(11)	0.4279(6)	0.5536(6)	0.122(4)
H30	0.2197	0.3697	0.5570	0.146*
C31	0.1391(9)	0.4481(6)	0.4246(5)	0.117(3)
H31A	0.2143	0.4398	0.4215	0.176*
H31B	0.0963	0.4925	0.3914	0.176*
H31C	0.0959	0.3942	0.4135	0.176*

7.75 (s, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 7.5 Hz, 4H), 7.24 (s, 1H), 7.12 (s 2H), 6.53 (t, J = 1.5 Hz, 1H), 3.47 (s, 3H), 3.29 (hept, J = 6.5 Hz, 4H), 1.48 (d, J = 6.5 Hz, 12H), 1.10 (d, J = 6.5 Hz, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.1, 146.7, 139.9, 135.5, 130.5, 130.0, 125.12, 124.0, 119.0, 33.9, 28.8, 26.3, 23.5. **IR** (neat) nujol 3134, 2965, 2926, 2858, 1537, 1461, 1407, 1382, 1348, 1278, 1228, 1208, 1110, 1082, 947, 854, 828, 803, 767, 760, 738, 706, 656 cm^{-1}. **MS (ESI)**: 655 $[M-Br]^+$. **HRMS (ESI)** calcd. for $C_{31}H_{42}BrN_4Pd$ $[M-Br]^+$: 655.1628; found: 655.1630. Anal. calcd. for $C_{31}H_{42}Br_2N_4Pd$: C, 50.53%; H, 5.74%; N, 7.60%; found: C, 50.73%; H, 5.82%; N, 7.48%.

Experimental details

All hydrogen atoms attached to C atoms were introduced using the HFIX command in the SHELXL program [3]. The C—H distances of CH_3 were restrained to 0.96 Å with U_{iso} values to be $1.5U_{eq}$(C). Vinylic and aromatic C—H distances were restrained to 0.93 Å with U_{iso} values to be $1.2U_{eq}$(C). The C—H distances of the isopropyl groups were restrained to 0.98 Å with U_{iso} values to be $1.2U_{eq}$(C). The dataset was massaged using the program SQUEEZE [4]. The residual electron density was assigned to a molecule of the ethyl acetate solvent and one water molecule is present in the crystal [55 e per asymmetric unit; a molecule of ethyl acetate would give 46e and one water molecule gives 10e]

Discussion

During the past years, N-heterocyclic carbene-palladium complexes have been proven efficient catalysts in the traditional cross-coupling reactions [6–10]. For instance, the synthesis of [1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-2(3*H*)-ylidene]palladium complex, from easily available starting materials in a one-pot procedure was reported [1]. In addition, the applications of this complex have been fully investigated in Suzuki-Miyaura coupling [2, 11–18], C—N coupling [1, 19–21], α-arylation of carbonyl compounds [22–26], Hiyama coupling [27], Mizoroki-Heck reaction [28] and direct C—H bond functionalization of heteroaromatic compounds [29–33]. As its analogue, initial studies on the catalytic activity of the title complex showed that it is also an efficient catalyst in the C—N coupling between primary and secondary amines with aryl chlorides at very low catalyst loadings, implying that the anions on the complex may have no effect on the catalytic activity. Therefore, it may draw the conclusion that the title product may be also a good catalyst in the above mentioned and other relevant reactions catalyzed by the NHC—Pd(II)-Im complex, and will also find its new applications in organic synthesis [34].

The title complex shows a slightly distorted square-planar coordination geometry with the two bromido ligands perpendicular to the plane of the NHC ligand and the 1-methylimidazole *trans* to it. For instance, the bond angles for C(1)—Pd(1)—N(3) is 177.63(18)°, C(1)—Pd(1)—Br(2) is 87.05(12)°, N(3)—Pd(1)—Br(2) is 91.00(16)°, C(1)—Pd(1)—Br(1) is 93.03(12)°, N(3)—Pd(1)—Br(1) is 88.95(15)°, and Br(2)—Pd(1)—Br(1) 178.87(3)°. The bond lengths are all in the expected ranges.

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