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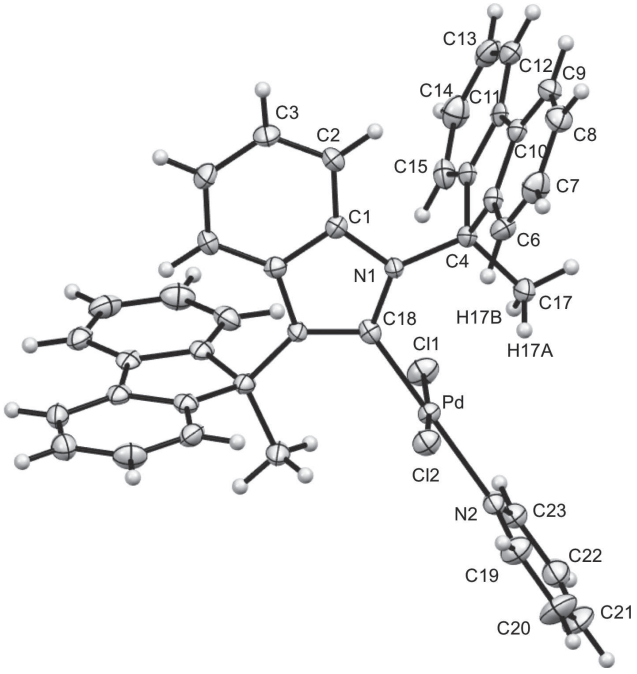
Matthieu Teci, Eric Brenner, Dominique Matt* and Loïc Toupet

Crystal structure of *trans*-dichlorido[1,3-bis (9-methyl-9H-fluoren-9-yl) benzimidazol-2-ylidene](pyridine)palladium(II) – a compound with anagostic CH–Pd interactions, $C_{40}H_{31}Cl_2N_3Pd$



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Abstract

$C_{40}H_{31}Cl_2N_3Pd$, orthorhombic, *Pnma* (no. 62), $a = 16.7821(7)$, $b = 14.1436(8)$, $c = 11.1431(5)$ Å, $V = 3205.9(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0394$, $wR_{ref}(F^2) = 0.0817$, $T = 150$ K.

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***Corresponding author: Dominique Matt,** UMR7177 CNRS-Université de Strasbourg, Laboratoire de Chimie Inorganique Moléculaire et Catalyse, 4 rue Blaise Pascal, 67070 STRASBOURG cedex, France, e-mail: dmatt@unistra.fr

Matthieu Teci and Eric Brenner: UMR7177 CNRS-Université de Strasbourg, Laboratoire de Chimie Inorganique Moléculaire et Catalyse, 4 rue Blaise Pascal, 67070 STRASBOURG cedex, France

Loïc Toupet: Institut de Physique de Rennes, Université de Rennes 1-CNRS UMR 6251, 35042 Rennes Cedex, France

Table 1: Data collection and handling.

Crystal:	Colourless, prism, size 0.07×0.09×0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.80 cm^{-1}
Diffractometer, scan mode:	CCD Saphire 3 Xcalibur, ω scan
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24740, 3612
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2188
$N(param)_{refined}$:	223
Programs:	CryAlis^{PRO} [4], SIR-97 [5], SHELX [6], PLATON [7]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	8*d*	0.7793	0.3881	0.2451	0.029
H(3)	8*d*	0.7054	0.3177	0.1032	0.033
H(6)	8*d*	0.7428	0.4157	0.5715	0.032
H(7)	8*d*	0.6551	0.5209	0.5519	0.037
H(8)	8*d*	0.6809	0.6200	0.4159	0.034
H(9)	8*d*	0.7936	0.6165	0.2951	0.029
H(12)	8*d*	0.9289	0.5827	0.1749	0.031
H(13)	8*d*	1.0468	0.5299	0.0993	0.037
H(14)	8*d*	1.0972	0.4137	0.1734	0.040
H(15)	8*d*	1.0305	0.3462	0.3271	0.033
H(17A)	8*d*	0.9015	0.3950	0.6314	0.039
H(17B)	8*d*	0.9437	0.4691	0.5714	0.039
H(17C)	8*d*	0.9847	0.3850	0.5629	0.039
H(19)	4*c*	0.9111	0.2500	0.9125	0.038
H(20)	4*c*	0.9703	0.2500	1.1005	0.057
H(21)	4*c*	1.1100	0.2500	1.1131	0.048
H(22)	4*c*	1.1841	0.2500	0.9380	0.039
H(23)	4*c*	1.1192	0.2500	0.7552	0.032

The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	4*c*	0.95068(2)	0.25	0.64360(3)	0.0223(2)	0.0182(2)	0.0163(2)	0.0	−0.0028(2)	0.0
Cl(1)	4*c*	1.07039(7)	0.25	0.5390(1)	0.0250(8)	0.0403(8)	0.0257(7)	0.0	0.0025(6)	0.0
Cl(2)	4*c*	0.82284(7)	0.25	0.7254(1)	0.0242(7)	0.0290(7)	0.0246(7)	0.0	0.0016(6)	0.0
N(1)	8*d*	0.8665(2)	0.3139(2)	0.4298(2)	0.025(2)	0.013(2)	0.018(2)	−0.002(1)	−0.007(1)	0.000(1)
N(2)	4*c*	1.0095(3)	0.25	0.8145(4)	0.021(3)	0.017(2)	0.024(2)	0.0	−0.006(2)	0.0
C(1)	8*d*	0.8193(2)	0.2904(2)	0.3323(3)	0.023(2)	0.019(2)	0.017(2)	−0.002(2)	−0.002(2)	−0.001(1)
C(2)	8*d*	0.7782(2)	0.3327(2)	0.2463(3)	0.034(2)	0.014(2)	0.024(2)	0.001(2)	−0.002(2)	0.001(2)
C(3)	8*d*	0.7354(2)	0.2907(2)	0.1622(3)	0.033(2)	0.025(2)	0.024(2)	0.003(2)	−0.011(2)	0.003(2)
C(4)	8*d*	0.8894(2)	0.3973(2)	0.4465(3)	0.023(2)	0.017(2)	0.016(2)	−0.004(2)	−0.003(2)	0.000(2)
C(5)	8*d*	0.8196(2)	0.4533(2)	0.4422(3)	0.019(2)	0.019(2)	0.020(2)	−0.003(2)	−0.003(2)	−0.004(2)
C(6)	8*d*	0.7530(2)	0.4559(2)	0.5149(3)	0.034(2)	0.028(2)	0.017(2)	−0.004(2)	−0.004(2)	0.001(2)
C(7)	8*d*	0.7016(2)	0.5185(2)	0.5034(3)	0.028(2)	0.038(3)	0.027(2)	−0.001(2)	0.008(2)	−0.007(2)
C(8)	8*d*	0.7169(2)	0.5775(2)	0.4222(3)	0.031(2)	0.024(2)	0.030(2)	0.003(2)	−0.005(2)	−0.000(2)
C(9)	8*d*	0.7833(2)	0.5756(2)	0.3505(3)	0.031(2)	0.019(2)	0.023(2)	−0.003(2)	−0.006(2)	0.003(2)
C(10)	8*d*	0.8349(2)	0.5134(2)	0.3604(3)	0.023(2)	0.021(2)	0.017(2)	−0.006(2)	−0.005(2)	−0.002(2)
C(11)	8*d*	0.9091(2)	0.4952(2)	0.2961(3)	0.025(2)	0.019(2)	0.019(2)	−0.012(2)	−0.008(2)	−0.002(2)
C(12)	8*d*	0.9492(2)	0.5350(2)	0.2056(3)	0.034(2)	0.026(2)	0.019(2)	−0.007(2)	−0.007(2)	0.001(2)
C(13)	8*d*	1.0189(2)	0.5035(2)	0.1614(3)	0.036(2)	0.039(2)	0.018(2)	−0.011(2)	0.002(2)	−0.004(2)
C(14)	8*d*	1.0491(3)	0.4341(2)	0.2056(3)	0.029(2)	0.038(2)	0.032(2)	−0.004(2)	0.004(2)	−0.008(2)
C(15)	8*d*	1.0100(2)	0.3939(2)	0.2965(3)	0.031(2)	0.020(2)	0.031(2)	−0.001(2)	−0.001(2)	−0.006(2)
C(16)	8*d*	0.9401(2)	0.4256(2)	0.3408(3)	0.026(2)	0.018(2)	0.019(2)	−0.009(2)	−0.005(2)	−0.002(2)
C(17)	8*d*	0.9338(2)	0.4130(2)	0.5635(3)	0.034(2)	0.019(2)	0.025(2)	−0.005(2)	−0.011(2)	0.001(2)
C(18)	4*c*	0.8935(3)	0.25	0.4896(4)	0.013(3)	0.016(3)	0.023(3)	0.0	0.001(2)	0.0
C(19)	4*c*	0.9676(3)	0.25	0.9174(5)	0.028(4)	0.040(4)	0.027(3)	0.0	−0.003(3)	0.0
C(20)	4*c*	1.0021(4)	0.25	1.0300(5)	0.060(5)	0.063(5)	0.019(3)	0.0	−0.001(3)	0.0
C(21)	4*c*	1.0842(4)	0.25	1.0372(5)	0.048(4)	0.044(4)	0.028(4)	0.0	−0.019(3)	0.0
C(22)	4*c*	1.1275(4)	0.25	0.9351(5)	0.036(4)	0.027(3)	0.035(4)	0.0	−0.007(3)	0.0
C(23)	4*c*	1.0879(3)	0.25	0.8263(5)	0.032(3)	0.023(3)	0.025(3)	0.0	−0.005(3)	0.0

Source of material

The title compound was prepared according to a method reported elsewhere [1]. Crystals were obtained by slow evaporation of a $CDCl_3$ solution of the complex.

Discussion

The title complex shows a *trans* configuration of the two chlorido ligands, in a somewhat distorted square-planar geometry around the palladium centre (Cl—Pd—Cl: 172.87(5)°; C18—Pd—N2: 178.2(2)°). The palladium atom lies slightly out of the plane defined by the five-membered N-heterocyclic carbene ring, providing a pitch angle of 8.1° of the C18—Pd vector. The Pd,Cl,Cl,C,N coordination plane (together with the pyridine ring) constitutes a symmetry plane of the whole molecule. The fluorenyl planes, which are nearly orthogonal to the carbenic plane (dihedral angle 88.9°), are both folded back towards the C6 ring of the benzimidazolyl unit. This feature orientates the two methyl groups towards the d_{z^2} orbital, with four hydrogen atoms coming close to the metal atom (Pd—H17A 2.623 Å; Pd—H17C 2.548 Å). The corresponding CH$\cdots$Pd separations are characteristic of anagostic M$\cdots$H—C interactions [2]. In keeping with such electrostatic interactions, the ^{1}H NMR signal of the CH_3 groups appears at significantly lower field than that seen for the same protons in the benzimidazolium precursor used for the preparation of the complex ($\delta = 4.02$ vs. 2.96 ppm). Note that, as shown by NMR solution studies, the methylfluorenyl groups do not rotate about the corresponding N1—C4 bonds [1]. The Pd—Cl (2.323(1) and 2.331(1) Å), Pd—C18 (1.966(5) Å), and Pd—N2 (2.144(4) Å) bond lengths are comparable to those found in related *trans*-[$PdCl_2$(NHC)(pyridine)] complexes [1, 3].

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