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Dibromo(1,1′-dimethyl-3,3′-methylene-diimidazoline-2,2′-diylidene)palladium(II)

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Key indicators

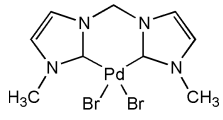
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.034
wR factor = 0.095
Data-to-parameter ratio = 16.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title N-heterocyclic carbene (NHC)-palladium complex, [$PdBr_2(C_9H_{12}N_4)$], an important precursor for catalytic reactions, exhibits a slightly distorted square-planar geometry at the Pd center, with two Br atoms in *cis* position, and is isostructural with the Pt analog [Muehlhofer, Strassner, Herdtweck & Hermann (2002). *J. Organomet. Chem.* **660**, 121–126].

Comment

Metal complexes of imidazolin-2-ylidenes, also known as *N*-heterocyclic carbene (NHC) complexes, have recently gained attention because of their extraordinary catalytic properties (Herrmann, 2002). Dicarbenepalladium(II) dihalides have recently been shown to be efficient catalysts for various C—C and C—N coupling reactions, in particular, the activation of chloroarenes in the Heck reaction (Herrmann *et al.*, 1995, 1998). Dicationic complexes are active in the copolymerization of ethylene and carbon monoxide; this has, for example, been shown for a Pd (NHC) bis(acetonitrile) complex, which has already been structurally characterized (Gardiner *et al.*, 1999). Very recently, a new application for the title complex, (I), was found; Lautens & Mancuso (2002) reported catalytic activity in the silylstannation cyclization of 1,6-enynes.



(I)

The title complex exhibits extraordinary stability, thermally as well as against strong acidic media, which allows its use under the harsh conditions necessary for methane activation. Compound (I) is currently the most active precursor complex for the homogeneously catalysed C—H activation of methane in its conversion to methanol (Muehlhofer, Strassner & Herrmann, 2002).

The title compound is structurally similar to other mono- (Herrmann *et al.*, 1999) and dichelating NHC complexes (Muehlhofer, Strassner, Herdtweck & Herrmann, 2002) of palladium and platinum and is isostructural with its Pt analog (Muehlhofer, Strassner, Herdtweck & Herrmann, 2002). The *N*-heterocyclic carbene ligand exhibits a bowl shape, thereby differentiating between the upper and lower sides of the complex (Fig. 1). The Pd—Br distances of 2.4999 (6) and 2.4942 (6) Å, as well as the Pd—$C_{carbene}$ bond lengths of 1.983 (5) and 1.971 (5) Å, are in the expected ranges. The Br—Pd—Br angle of 92.64 (2)° differs only slightly from that in the corresponding platinum complex (Muehlhofer, Strassner, Herdtweck & Herrmann, 2002), where the Pt—Br distances

are essentially the same [2.4976 (11) and 2.4883 (13) Å] and the Pt—$C_{carbene}$ distances are slightly shorter [1.963 (10) and 1.950 (10) Å]. Due to the larger size of the metal, the Br—Pt—Br angle decreases to 91.14 (4)°, whereas the $C_{carbene}$—Pd—$C_{carbene}$ angle of 83.2 (2)° in (I) is almost the same as the value of 83.8 (4)° for $C_{carbene}$—Pt—$C_{carbene}$.

Experimental

The title compound, first reported by Herrmann *et al.* (1999), was synthesized in a manner similar to the literature procedure; the only difference was that it was not necessary to heat the reaction mixture to 393 K as previously described. The reaction was complete after 4 h at 353 K. The procedure used is as follows: the title compound was obtained by heating a suspension of palladium(II) acetate and 1,1′-dimethyl-3,3′-methylenediimidazolium bromide in dimethyl sulfoxide for 4 h at 353 K. The solvent was removed and the residue washed twice with tetrahydrofuran. The compound was recrystallized from acetonitrile and crystals were grown by slow evaporation of the solution.

Crystal data

$[PdBr_2(C_9H_{12}N_4)]$	D_x = 2.214 Mg m^{-3}
M_r = 442.45	Mo Kα radiation
Monoclinic, $P2_1/n$	Cell parameters from 2524 reflections
a = 8.5614 (1) Å	θ = 2.5–25.3°
b = 16.0701 (2) Å	μ = 7.40 mm^{-1}
c = 10.2978 (2) Å	T = 293 (1) K
β = 110.4670 (7)°	Fragment, colorless
V = 1327.36 (3) Å^3	0.46 × 0.28 × 0.15 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	2130 reflections with $I > 2\sigma(I)$
φ and ω rotation scans	R_{int} = 0.060
Absorption correction: multi-scan (*DENZO*; Nonius, 2001), T_{min} = 0.103, T_{max} = 0.330	θ_{max} = 25.3°
	$h = -10 \rightarrow 10$
	$k = -19 \rightarrow 19$
23418 measured reflections	$l = -12 \rightarrow 12$
2422 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.4868P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.095	$\Delta\rho_{max}$ = 1.00 e Å^{-3}
S = 1.06	$\Delta\rho_{min}$ = −0.78 e Å^{-3}
2422 reflections	
147 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Pd—Br1	2.4999 (6)	Pd—C1	1.983 (5)
Pd—Br2	2.4942 (6)	Pd—C6	1.971 (5)
Br1—Pd—Br2	92.64 (2)	Br2—Pd—C1	91.62 (15)
Br1—Pd—C1	174.34 (15)	Br2—Pd—C6	171.56 (15)
Br1—Pd—C6	92.09 (15)	C1—Pd—C6	83.2 (2)

All H atoms were placed in calculated positions, with C—H distances ranging from 0.93 to 0.97 Å and included in the refinement in riding-motion approximation with $U_{iso} = 1.2U_{eq}$ of the carrier atom

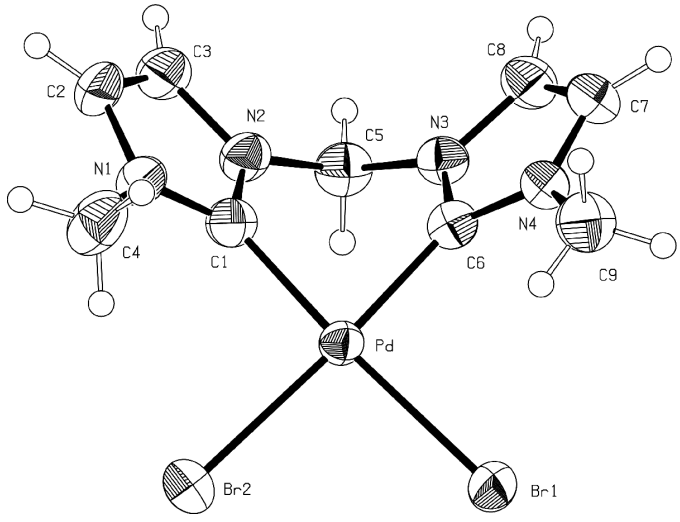


Figure 1
A perspective view of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Data collection: *KappaCCD Control Software* (Nonius, 2001); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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