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Synthesis and structural study of $[\{Pd(C_6H_4CH_2N(CH_3)_2)\}_2(\mu\text{-}Br)(\mu\text{-}X)]$ complexes (X = hydroxide, amide or thiolate)

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Abstract

The mixed hydroxo-bromo bridged complex $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}OH)]$ (1) ($C_6H_4CH_2NMe_2$ = 2-[(dimethylamino)methyl]phenyl) has been prepared by addition of one equivalent of NBu_4OH to $[\{Pd(C_6H_4CH_2NMe_2)(\mu\text{-}O_2CMe)\}_2]$ in acetone–water solution, followed by addition of one equivalent of LiBr. Complex **1** reacts with arylamines or thiols in 1:1 mole ratio to yield the corresponding amido- or thiolato–bromo complexes $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}NHR)]$ (R = C_6H_5 (2), *p*-$MeOC_6H_4$ (3), *p*-$MeOC_6H_4$ (4)) or $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}SR)]$ (R = Et (5), ^{t}Bu (6), C_6H_5 (7), *p*-MeC_6H_4 (8)). The ^1H NMR data indicate a cis arrangement of the $C_6H_4CH_2NMe_2$ ligands. The crystal structure of compound **1** has been determined by X-ray diffraction. It crystallizes in the orthorhombic space group *Pbca* with a = 12.445(3), b = 18.029(3), c = 17.436(3) Å. Final R = 0.039 and R_w = 0.040 based on 2692 reflections.

Keywords: Palladium; Cyclometallated; Hydroxo; Amido; Thiolato; X-ray diffraction

1. Introduction

The binuclear hydroxo compounds $[\{MR_2(\mu\text{-}OH)\}_2]^{2-}$ (M = Ni, Pd or Pt; R = C_6F_5 or C_6Cl_5) and $[\{R(PPh_3)Pd(\mu\text{-}OH)\}_2]$ (R = C_6F_5 or C_6Cl_5) have proven to be excellent precursors for the synthesis of binuclear palladium or platinum complexes with double bridges (X = azolate, amide, methoxide or dicyanomethanide) by reaction between the di-μ-hydroxo complex and the corresponding protic acid HX [1–8]. Very recently we have described [9] the synthesis of the hydroxo carboxylato-bridged complex $[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CR)(\mu\text{-}OH)]$ ($CH_2C_9H_6N$ = 8-quinolylmethyl) and its reactivity towards amines and thiols to yield the corresponding amido– or thiolato–carboxylato complexes $[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CR)(\mu\text{-}X)]$ (X = amide or thiolate).

Complexes containing the $Pd(\mu\text{-}Br)(\mu\text{-}OH)Pd$ bridge are rare in the literature. The present work concerns the synthesis and structural study of the hydroxo–bromo-bridged complex $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}OH)]$ ($C_6H_4CH_2NMe_2$ = 2-[(dimethylamino)methyl]phenyl) and its reactivity towards amines and thiols to yield the corresponding amido– or thiolato–bromo complexes $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}X)]$ (X = amide or thiolate).

2. Results and discussion

Addition of one equivalent of NBu_4OH to $[\{Pd(C_6H_4CH_2NMe_2)(\mu\text{-}O_2CMe)\}_2]$ in acetone–water solution, followed by addition of one equivalent of LiBr, results in the formation of the hydroxo–bromo-bridged complex **1** (Scheme 1) in good yield (Table 1). The analytical data (Table 1) are in agreement with the proposed formula. The presence of the OH-bridged ligand is showed by an IR band at 3465 cm^{-1} and a high-field ^1H resonance at δ −1.70 (see Section 3). The observation of only one set of ^1H NMR resonances

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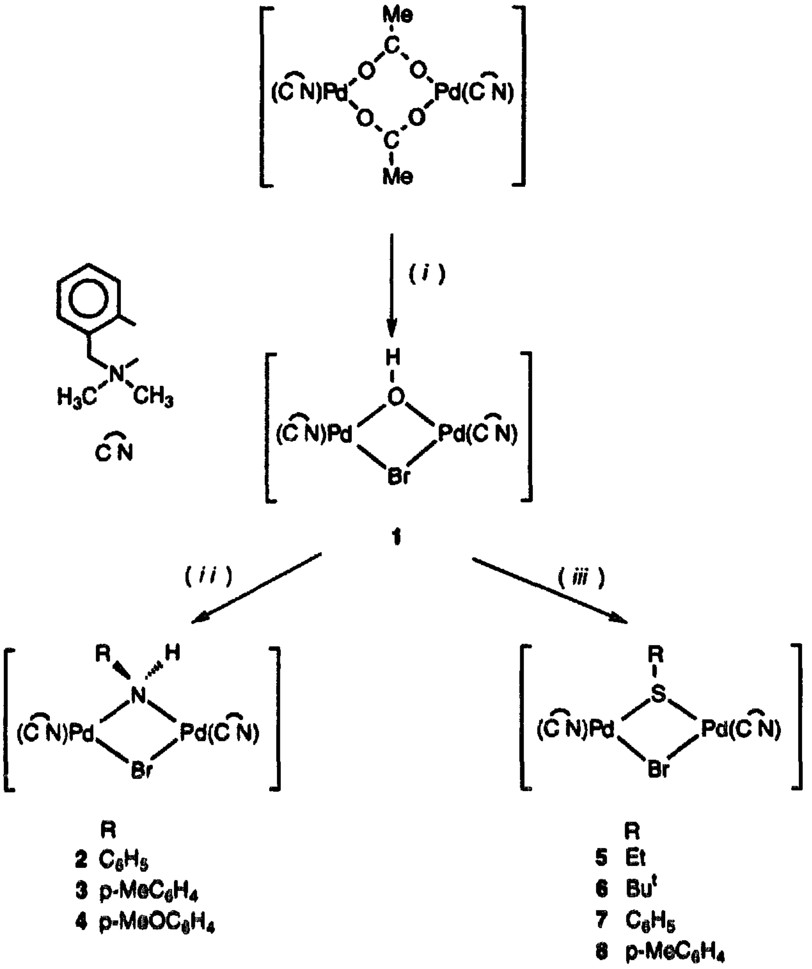

Scheme 1. (*i*) OH^-, Br^-; (*ii*) NH_2R; (*iii*) RSH.

for the $C_6H_4CH_2NMe_2$ ligands in complex **1** indicates a cis arrangement for these groups.

The crystal structure of complex **1** has been established by X-ray diffraction, and a view of the molecule is depicted in Fig. 1. Atomic coordinates and selected intramolecular distances and angles are shown in Tables 2 and 3 respectively. The molecule consists of a binuclear (Pd) structure bridged by an OH group and a Br atom. Fig. 1 shows the cisoid arrangement of the cyclometallated ligands and the arrangement of the bridges so that the Br atom is trans to carbon.

The Pd atoms are in approximately square-planar coordination (maximum deviations from the mean plane defined by all of them being 0.0762(6) Å for Pd1 and 0.0443(6) Å for the Pd2 atom), the two planes forming an angle of 13° between them. The angles around the Pd atoms deviate from the square disposition due to the bite of the bidentate $C_6H_4CH_2NMe_2$ ligand. Phenyl

Table 1
Analytical data, yields and physical properties for the new complexes

Complex	Yield	M.p. [a]	Analysis (%) [b]				IR bands [c]
	(%)	(θ/°C)	C	H	N	S	(cm⁻¹)
1 [d]	67	156	37.1 (37.4)	4.3 (4.4)	4.7 (4.9)		3465 ν(OH)
2	92	188	44.2 (44.1)	4.7 (4.6)	6.2 (6.4)		3330 ν(NH)
3	68	183	44.8 (45.0)	4.8 (4.8)	6.0 (6.3)		3330 ν(NH)
4	88	194	43.6 (43.9)	4.5 (4.7)	6.0 (6.2)		3340 ν(NH)
5	60	191	38.7 (38.6)	4.8 (4.7)	4.4 (4.5)	5.0 (5.2)	
6	66	195	40.7 (40.6)	5.2 (5.1)	4.3 (4.3)	4.9 (4.9)	
7	89	188	42.8 (43.0)	4.3 (4.4)	4.0 (4.2)	4.6 (4.8)	
8	88	172	43.6 (43.9)	4.5 (4.6)	4.0 (4.1)	4.4 (4.4)	

[a] With decomposition. [b] Calculated values in parentheses. [c] In Nujol mulls. [d] Analysis of Br = 13.6 (13.8)%.

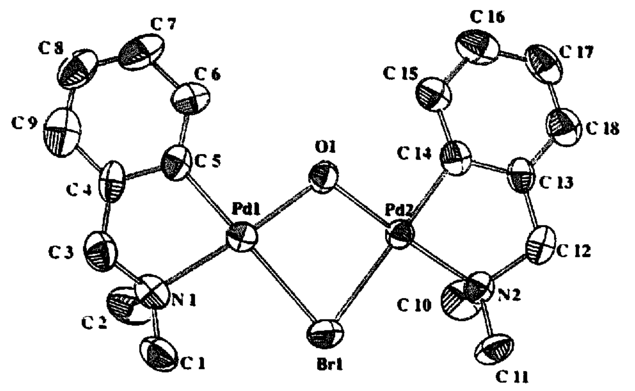

Fig. 1. An ORTEP [10] drawing of the compound **1** showing 50% probability ellipsoids and the atom-labelling scheme. Hydrogen atoms are omitted for clarity.

rings are planar. Structures containing the M(μ-Br)(μ-OH)M bridge are not common in the literature, and to the best of our knowledge, the Pd(μ-Br)(μ-OH)Pd bridge is the first to be characterized in a diffraction study. The angles on the Br and O atoms are 78.23(3)° and 106.8(2)°. The Pd–O distance (2.029(5) and 2.034(5) Å) is slightly shorter than that found in $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$ (2.077(6) and 2.068(6) Å, the PdOPd angle being 98.8(0.4)°) [1].

Crystal packing presents a partial stacking pattern of aromatic interactions [11] forming chains along the *a* axis (see Fig. 2). The two phenyl groups involved in the interaction present an interplanar angle of 21.2°, a lateral offset of 5.39 Å and a distance between centroids of 6.02 Å.

Mixed amide complexes of the types *anti*-$[\{Pd(C_6F_5)(PPh_3)\}_2(\mu\text{-}NHR)(\mu\text{-}OH)]$ and *cis*-$[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}O_2CR')(\mu\text{-}NHR)]$ ($CH_2C_9H_6N$ = 8-quinolylmethyl) have been previously reported [6,9]. Addition of amine RNH_2 to a solution of the hydroxo–bromo complex **1** in chloroform gives (70–90% yields; Table 1) the corresponding bromo-amido-bridged complexes $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}NHR)]$ (R = C_6H_5 **2**, *p*-MeC_6H_4 **3**, *p*-$MeOC_6H_4$ **4**) with the concomitant release of water (Scheme 1). These complexes gave satisfactory partial elemental analyses (Table 1), and the IR spectra (Table 1) show a weak absorption at ca. 3330 cm^{-1} assigned to the N–H stretching vibration.

The ^{1}H NMR spectra (see Section 3) of complexes **2**–**4** show two singlet resonances for the N–Me groups and an AB quartet for the CH_2 protons of bonded $C_6H_4CH_2NMe_2$, since they are diastereotopic due to the two different substituents in the amide ligand with the lack of a symmetry plane in the Pd–O–Pd–N core; no dynamic behaviour is observed at room temperature [12]. These data also suggest a cis arrangement of the $C_6H_4CH_2NMe_2$ ligands. The NMR patterns observed for the aromatic proton signals of the RNH group indicate that rotation about the C–N bond is rapid on the ^{1}H NMR time scale.

Table 2

Atomic parameters (× 10^4) for compound **1**; coordinates and thermal parameters as U_{eq} [a]

Atom	*x*	*y*	*z*	U_{eq}
Pd1	722(0)	1176(0)	834(0)	34(0)
Pd2	−1380(0)	733(0)	−185(0)	33(0)
Br1	−1111(1)	667(1)	1285(1)	55(0)
N1	1297(6)	1506(4)	1901(4)	44(2)
N2	−3028(5)	583(3)	−177(4)	37(1)
O1	223(4)	945(3)	−248(3)	41(1)
C1	852(9)	2257(6)	2059(6)	65(3)
C2	1006(8)	1013(6)	2531(5)	60(3)
C3	2478(8)	1555(6)	1856(6)	57(2)
C4	2767(6)	1802(4)	1073(6)	46(2)
C5	2063(6)	1643(4)	479(5)	40(2)
C6	2300(7)	1856(4)	−263(5)	43(2)
C7	3229(8)	2205(5)	−433(7)	62(3)
C8	3954(8)	2342(5)	144(8)	63(3)
C9	3746(8)	2154(5)	881(8)	64(3)
C10	−3519(8)	1312(5)	−67(7)	59(2)
C11	−3423(7)	60(6)	403(5)	51(2)
C12	−3321(7)	287(5)	−952(6)	52(2)
C13	−2610(6)	621(4)	−1539(5)	39(2)
C14	−1587(6)	812(4)	−1302(5)	39(2)
C15	−855(7)	1092(5)	−1810(5)	46(2)
C16	−1142(9)	1161(6)	−2568(6)	59(3)
C17	−2187(9)	979(5)	−2811(5)	57(3)
C18	−2895(8)	710(6)	−2303(6)	57(2)

[a] $U_{eq} = (1/3)\Sigma[U_{ij}a_i^* a_j^* a_i a_j \cos(a_i,a_j)] \times 10^3$.

Table 3
Selected intramolecular distances (Å) and angles (deg) for **1** with estimated standard deviations in parentheses

Bonds			
Pd1–Br1	2.582(1)	N1–C1	1.489(13)
Pd1–N1	2.080(7)	N1–C2	1.459(12)
Pd1–O1	2.029(5)	N1–C3	1.475(12)
Pd1–C5	1.969(8)	N2–C10	1.462(11)
Pd2–Br1	2.588(1)	N2–C11	1.467(12)
Pd2–N2	2.069(6)	N2–C12	1.498(12)
Pd2–O1	2.034(5)	C3–C4	1.480(15)
Pd2–C14	1.969(8)	C12–C13	1.481(13)
Angles			
O1–Pd1–C5	93.1(3)	C2–N1–C3	108.9(7)
N1–Pd1–C5	82.4(3)	C10–N2–C11	110.3(7)
Br1–Pd1–O1	86.6(1)	C11–N2–C12	108.1(6)
Br1–Pd1–N1	97.6(2)	N1–C3–C4	108.0(8)
O1–Pd2–C14	93.5(3)	C3–C4–C5	118.2(8)
N2–Pd2–C14	83.5(3)	C3–C4–C9	124.2(9)
Br1–Pd2–O1	86.3(2)	C5–C4–C9	117.4(8)
Br1–Pd2–N2	96.7(2)	N2–C12–C13	109.5(7)
C1–N1–C2	108.8(7)	C12–C13–C14	116.4(7)
C1–N1–C3	109.0(7)	C12–C13–C18	123.9(8)

Addition of thiols RSH to a solution of the hydroxo–bromo complex **1** in chloroform yields the corresponding bromo–thiolate-bridged complexes $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}SR)]$ (R = Et **5**, ^{t}Bu **6**, C_6H_5 **7**, p-MeC_6H_4 **8**) (Scheme 1). The analytical data and yields for these compounds are presented in Table 1. The related mixed thiolato–carboxylato-bridged complexes *cis*-$[\{Pd(CH_2C_9H_6N)\}_2(\mu\text{-}SR)(\mu\text{-}O_2CR)]$ ($CH_2C_9H_6N$ = 8-quinolylmethyl) [9] and *cis*-$[\{Pd(L\text{-}L)\}_2(\mu\text{-}SR)(\mu\text{-}O_2CR)]$ (L–L = *ortho*-palladated imine ligand) [13] have been recently reported.

The NMR data for the complexes **5**, **7** and **8** show a unique singlet resonance for N–Me protons and also a singlet for the CH_2 protons of bonded $C_6H_4CH_2NMe_2$, which suggests again the cis arrangement of the $C_6H_4CH_2NMe_2$ ligands. However, the NMR spectrum of complex **6** exhibits an AB quartet resonance for the CH_2 protons and two singlet resonances for the N–Me protons, which is in agreement with a slower rotation caused by the bulkier ^{t}Bu group.

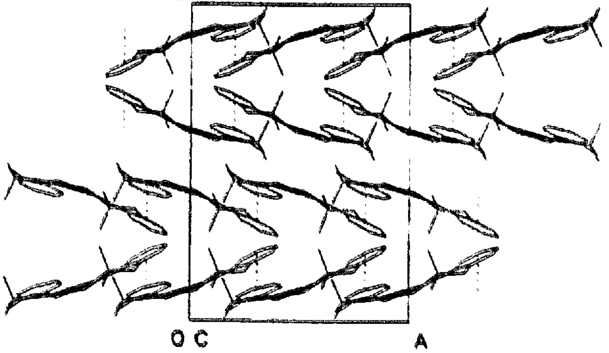

Fig. 2. Crystal packing of the compound **1** showing aromatic interactions as dotted lines.

3. Experimental details

The C, H, N, S analyses were performed with a Carlo Erba model EA 1108 microanalyser. The Br analyses were performed in the microanalyses service of the Centro de Investigación y Desarrollo of the CSIC, Barcelona, Spain. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1} and the solid sample under nitrogen flow (100 ml min^{-1}). The NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using $SiMe_4$ as standard. Infrared spectra were recorded on a Perkin–Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. Solvents were dried by the usual methods. The starting complex $[\{Pd(C_6H_4CH_2NMe_2)(\mu\text{-}O_2CMe)\}_2]$ was prepared by the procedure described in Ref. [14].

3.1. Synthesis of the complexes

3.1.1. Complex 1

To a solution of $[\{Pd(C_6H_4CH_2NMe_2)(\mu\text{-}O_2CMe)\}_2]$ (205.5 mg, 0.343 mmol) in acetone (1 cm^3) was added 20% $[NBu_4]OH(aq)$ (0.45 cm^3, 0.343 mmol), with constant stirring. Addition of LiBr (29.8 mg, 0.343 mmol) yielded a white suspension, which was stirred at room temperature for 5 min. After partial evaporation of the solvent under reduced pressure, the white complex **1** was filtered off and air-dried.

^{1}H NMR ($CDCl_3$): δ 7.0–6.9 (m, 8H, arom. of dmba), 3.71 (s, 4H, NCH_2), 2.69 (s, 12H, NCH_3), −1.70 (s, OH).

3.1.2. Complexes 2–4

The appropiate amine NH_2R (0.1037 mmol) was added to a solution of $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}OH)]$ (60 mg, 0.1037 mmol) in chloroform (2 cm^3), and the solution was stirred for 1 h. After partial evaporation of the solvent under reduced pressure, the addition of hexane caused the precipitation of white or yellowish solids which were filtered off and air-dried.

Complex **2**: ^{1}H NMR ($CDCl_3$): δ 7.78 (d, 2H, H_o of C_6H_5NH, *J* 7.8), 7.10 (m, 3H, H_m + H_p of C_6H_5NH), 7.0–6.9 (m, 8H, arom. of dmba), 3.90 (d, 2H, NCH_2, *J* 13.7), 3.67 (d, 2H, NCH_2, *J* 13.7), 2.79 (s, 6H, NCH_3), 2.66 (s, 6H, NCH_3).

Complex **3**: ^{1}H NMR ($CDCl_3$): δ 7.66 (d, 2H, H_o of MeC_6H_4NH, *J* 8.2), 7.0–6.9 (m, 10H, H_m of MeC_6H_4NH + arom. of dmba), 3.90 (d, 2H, NCH_2, *J* 13.7), 3.66 (d, 2H, NCH_2, *J* 13.7), 2.80 (s, 6H, NCH_3), 2.66 (s, 6H, NCH_3), 2.48 (s, 3H, CH_3 of MeC_6H_4NH).

Complex **4**: ^{1}H NMR ($CDCl_3$): δ 7.70 (d, 2H, H_o of $MeOC_6H_4NH$, *J* 8.7), 7.0–6.9 (m, 8H, arom. of dmba), 6.66 (d, 2H, H_m of $MeOC_6H_4NH$, *J* 8.7), 3.89 (d, 2H, NCH_2, *J* 13.7), 3.70 (s, 3H, CH_3 of $MeOC_6H_4NH$), 3.65 (d, 2H, NCH_2, *J* 13.7), 2.79 (s, 6H, NCH_3), 2.65 (s, 6H, NCH_3).

3.1.3. Complexes 5 and 6

The appropiate thiol RSH (0.1037 mmol) was added to a solution of $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}OH)]$ (60 mg, 0.1037 mmol) in chloroform (2 cm^3). The resulting solution was stirred for 1 h. Partial evaporation of the solvent under reduced pressure, followed by addition of hexane, caused the precipitation of white or yellowish solids which were filtered off and air-dried.

Complex **5**: ^{1}H NMR ($CDCl_3$): δ 7.55 (m, 2H, arom. dmba), 6.90 (m, 6H, arom. dmba), 3.81 (s, 4H, NCH_2), 2.70 (s, 12H, NCH_3), 2.64 (q, 2H, CH_2S, *J* 7.3), 1.61 (t, 3H, CH_3CH_2S, *J* 7.3).

Complex **6**: ^{1}H NMR ($CDCl_3$): δ 7.74 (m, 2H, arom. dmba), 6.89 (m, 6H, arom. dmba), 4.15 (d, 2H, NCH_2, *J* 13.6), 3.45 (d, 2H, NCH_2, *J* 13.6), 2.73 (s, 6H, NCH_3), 2.63 (s, 6H, NCH_3), 1.56 (s, 9H, ^{t}BuS).

3.1.4. Complexes 7 and 8

The appropiate thiol RSH (0.1037 mmol) was added to a solution of $[\{Pd(C_6H_4CH_2NMe_2)\}_2(\mu\text{-}Br)(\mu\text{-}OH)]$ (60 mg, 0.1037 mmol) in chloroform (2 cm^3). The resulting solution was stirred for 30 min, during which time complexes **7** and **8** precipitated and were filtered off and air-dried.

Complex **7**: ^{1}H NMR ($CDCl_3$): δ 8.07 (m, 2 H, H_o C_6H_5S), 7.60 (m, 2H, arom. dmba), 7.05 (m, 3H, H_{m+p} C_6H_5S), 6.89 (m, 6H, arom. dmba), 3.83 (s, 4H, NCH_2), 2.74 (s, 12H, NCH_3).

Complex **8**: ^{1}H NMR ($CDCl_3$): δ 7.97 (d, 2H, H_o p-MeC_6H_4S, *J* 8.1), 7.61 (m, 2H, arom. dmba), 6.87 (m, 8H, H_m *p*-MeC_6H_4S + arom. dmba), 3.82 (s, 4H, NCH_2), 2.73 (s, 12H, NCH_3), 2.15 (s, 3H, *p*-MeC_6H_4S).

3.2. Crystal structure determination of complex 1

Suitable crystals were grown from dichloromethane–hexane. Crystal data: $Pd_2BrON_2C_{18}H_{25}$, orthorhombic, *Pbca*, $a = 12.445(3)$, $b = 18.029(3)$, $c = 17.436(3)$ Å, $V = 3912.1(12)$ Å^3, $D_c = 1.967$ g cm^{-3}, $M = 579.12$, $F(000) = 2264$, $\mu = 38.472$ cm^{-1}, $Z = 8$.

5102 reflections up to $\theta = 28°$ (4710 independent) were measured on an Enraf Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation and using ω–2θ scan mode. 2692 reflections were considered as observed with $I > 3\sigma(I)$ criterion. Scattering factors and anomalous dispersion coefficients were taken from Ref. [15]. The heavy-atom (Pd) method and DIRDIF [16] system were followed by normal Fourier synthesis. Most of the H atoms were found on a difference map; others were located at the calculated positions [17].

Full-matrix least squares refinements [18], 217 variables, 2475 degrees of freedom, ratio of freedom 12.4, non-H atoms anisotropic, H atoms isotropic. Least squares weights were applied so as to give no trends in $\langle w\Delta^2F\rangle$ vs. $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$ with $w = K/(\sigma_1^2\sigma_2^2)$ where $K = 1$, $\sigma_1 = f(F_o)$ and $\sigma_2^2 = g(\sin\theta/\lambda)$ [19]. Final R and R_w were 0.039 and 0.040 respectively. Geometrical calculations were performed with PARST [20] and CSU [21] on a VAX 6410.

Additional material from the authors or the Cambridge Crystallographic Data Centre comprises tables of H coordinates, thermal parameters, bond distances and bond angles. Structure factors tables are available from the authors.

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