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Synthesis of cyclometallated complexes of Pd^{II}. The X-ray crystal structure of di- μ -bromo-bis[*N*-(3,4-dimethoxybenzylidene)cyclohexylamino-C6, *N*]dipalladium(II)

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Abstract

The structure of the cyclometallated bromo-bridged palladium(II) dimer complex $[\text{Pd}\{\overline{3,4}(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{NCy}\}(\text{Br})]_2$ is described. This is the first example of a structurally characterised cyclometallated bromo-bridged dimer. Crystals were triclinic, space group $P\bar{1}$ with $a = 788.7(2)$, $b = 911.0(3)$, $c = 1480.4(4)$ pm, $\alpha = 96.94(2)$, $\beta = 91.57(2)$, $\gamma = 101.85(2)^\circ$, $Z = 1$, $U = 1.0322(5)$ nm³, $R = 0.0688$, $R_w = 0.790$, for 3280 independent reflections with $F > 4.0\sigma(F)$. The structure is a centrosymmetric palladium dimer with two asymmetrically bridging bromine atoms and non-bonding Pd...Pd distance of 363.1(5) pm. The synthesis of the iodo-bridged analogue and the reactions of these two dimers and the chloro-bridged analogue with various tertiary phosphines are also described.

Introduction

Cyclometallation is an extensively researched area of organometallic chemistry which is covered in various general reviews [1–4]. Palladium(II) compounds, in particular, readily cyclometallate a variety of organic ligands. One of the more interesting problems that often arises is that of determining whether cyclometallated palladium complexes are dimeric or polymeric in nature and this is particularly so for complexes with Schiff bases [5–17]. Elemental analyses and spectroscopic results (IR and NMR) alone are not sufficient to resolve this problem and mass spectrometry is not always possible because the volatility of such complexes is often low. Single crystals have been grown for several of the more soluble acetato-bridged complexes and X-ray diffraction studies [5–10] have confirmed that all of these complexes are dimeric. Despite problems associated with the lower solubility of chloro-bridged analogues several structures of such complexes have been reported [11–15]. However, with the exception of a non-cyclometallated bromine dimer [16] there are no structurally characterised examples of bromo- or iodo-bridged com-

pounds. We have already reported the synthesis of $[\text{Pd}\{\overline{3,4-(\text{MeO})}_2\text{C}_6\text{H}_2\text{C(H)=N-Cy}\}(\text{Br})_2]$ together with several other related acetato, chloro- and bromo-bridged complexes [7,17]. Since then we have succeeded in obtaining single crystals of this complex which we report in detail here. Additional chemistry relating to the reactivity of this compound, together with that of the chloro- and iodo-bridged analogues, with tertiary phosphines has been carried out and this is also described.

Results and discussion

The title complex was prepared as described previously [17]. Suitable crystals were obtained by slowly evaporating a chloroform solution. The molecular structure and its numbering scheme are shown in Fig. 1. Final fractional co-ordinates are listed in Table 1 while selected interatomic distances and angles are given in Table 2.

The complex, which crystallises as a 1 : 1 chloroform solvate, is a centrosymmetric palladium dimer with two asymmetrically bridging bromine atoms. The nitrogen atom and a C-phenyl atom of each of the Schiff bases are *trans* to the di- μ -bromo-bridge unit so that these two cyclometallated ligands are in an overall antiparallel arrangement similar to that observed in other related dimers [5–15]. The asymmetry, which is also observed in related chloro-bridged dimers [15], results from the differing *trans* influence of the phenyl carbon and nitrogen atoms of the coordinated imine ligand. Thus the Pd–Br bond *trans* to C(4) is 256.5(4) pm whereas that *trans* to N(1) is 243.9(3) pm, a difference of over 12 pm. The Pd(1)–C(4) bond length of 199.8(10) pm (based on the covalent radius values of 131 pm for palladium and 77.1 pm for carbon [18]); this shortening, which has been observed in other analogous complexes [9], is attributed to partial multiple bonding character in the Pd–C(phenyl) linkage. The Pd(1)–N(1) length of 204.8(9) is slightly longer than the calculated single bond value of 201 pm (calculated covalent radius of N(sp^2) = 70 pm; palladium as above).

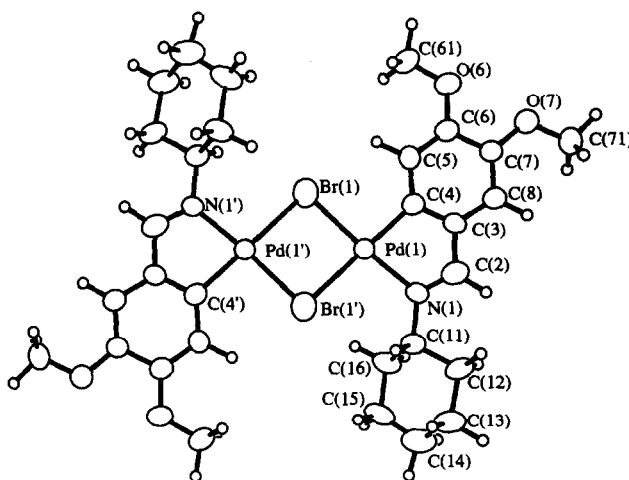


Fig. 1. ORTEP drawing of the molecular structure of $[(\text{MeO})_2\text{C}_6\text{H}_2\text{CHN}(\text{C}_6\text{H}_{11})\text{PdBr}]_2$ showing numbering system used.

Table 1

Non-hydrogen atom co-ordinates ($\times 10^4$)

	x	y	z
Pd(1)	12196.4(7)	1028.1(7)	4883.9(4)
Br(1)	9923(2)	1201(2)	5936(1)
N(1)	12198(9)	992(8)	4036(4)
C(11)	14090(11)	-11(9)	3162(5)
C(12)	15804(13)	-49(11)	2750(6)
C(13)	15524(15)	-1223(13)	1890(6)
C(14)	14207(17)	-875(14)	1185(7)
C(15)	12660(15)	-667(12)	1610(7)
C(16)	12861(13)	428(10)	2491(6)
C(2)	15558(12)	1990(10)	4309(6)
C(3)	15495(10)	2982(9)	5166(5)
C(4)	13946(10)	2730(9)	5565(5)
C(5)	13771(10)	3616(9)	6367(5)
C(6)	15137(10)	4719(9)	6776(5)
O(6)	15118(8)	5623(7)	7578(4)
C(61)	13587(12)	5470(12)	8037(6)
C(7)	16766(10)	4967(9)	6348(5)
O(7)	18041(8)	6088(7)	6796(4)
C(71)	19657(12)	6363(12)	6385(7)
C(8)	16933(11)	4097(10)	5537(5)
Cl(1S)	9359(5)	2003(5)	999(3)
Cl(2S)	11099(8)	5138(5)	1153(4)
Cl(3S)	12600(7)	2828(7)	143(3)
C(1S)	11387(16)	3281(13)	1069(8)

Each palladium atom adopts a distorted square-planar geometry with the distortion most noticeable in the C(4)–Pd(1)–M(1) angle of $81.4(4)^\circ$; the sum of angles about the palladium atom is 360.2° . Steric repulsion between the bromine bridge atoms and the bulky cyclohexyl groups forces the Pd₂Br₂ unit into an almost planar configuration. This is in contrast to the less sterically hindered chloro-bridged complex [Pd{CH₂C(CH₃)C=NOH}CH₃}Cl]₂ [11] which is folded across the Cl–Cl vector. This steric repulsion also produces a slight twist of the Schiff base ligand relative to the bromine bridges [the angle between the planes defined by Pd(1)N(1)C(4) and Pd(1)Br(1)Br(1') is $6.4(1)^\circ$] so that, overall, the dimer is slightly buckled. The C=N distance of 127.5(12) pm is somewhat longer than the value of 123.7(3) pm which is observed for a related free ligand [19]; this lengthening is characteristic of a co-ordinated Schiff base ligands [26] where the nitrogen atom is involved in a σ bond to a metal atom. The combination of the Pd₂Br₂ unit planarity and the long bromine bridge bonds produces an inter-palladium distance of 363.1(5) pm which is even longer than the non-bonded Pd...Pd distance of 354.9(9) pm observed for the dibromo-bridged complex [(Me₂S)PdBr₂]₂ [15] and excludes the possibility of a metal–metal bond in this complex.

Except for the cyclohexyl and methyl groups, the Schiff base ligand is almost planar (the maximum deviation of any of these atoms from their least squares plane is 2.8(3) pm). The overall dimensions of the Schiff base ligand compare favourably with those observed for a similar 2,4,6-trimethoxyphenyl analogue [5] of a palladium

Table 2

Selected bond lengths (pm) and angles ($^{\circ}$)^a

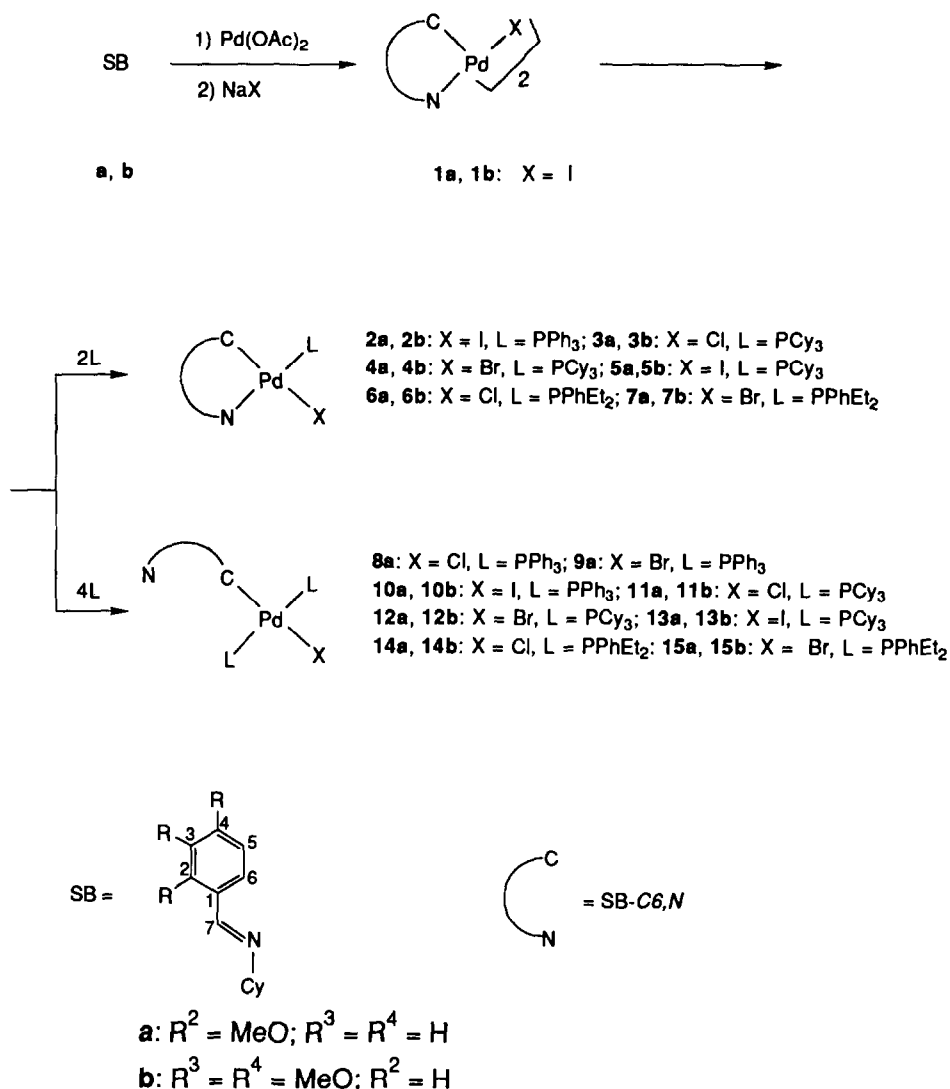
Br(1)–Pd(1)	243.9(3)	Br(1)–Pd(1')	256.5(4)
N(1)–Pd(1)	204.8(9)	C(4)–Pd(1)	199.8(10)
C(11)–N(1)	148.1(11)	C(2)–N(1)	127.5(12)
C(12)–C(11)	150.4(14)	C(16)–C(11)	151.3(13)
C(13)–C(12)	154.1(14)	C(14)–C(13)	155.6(17)
C(15)–C(14)	142.5(17)	C(16)–C(15)	152.6(14)
C(3)–C(2)	147.5(12)	C(4)–C(3)	136.1(12)
C(8)–C(3)	140.6(12)	C(5)–C(4)	137.9(12)
C(6)–C(5)	138.1(12)	O(6)–C(6)	136.4(10)
C(7)–C(6)	143.6(12)	C(61)–O(6)	139.2(12)
O(7)–C(7)	136.9(11)	C(8)–C(7)	138.2(12)
C(71)–O(7)	141.7(12)		
Br(1)–Pd(1)–Br(1')	97.0(2)	N(1)–Pd(1)–Br(1)	175.1(2)
N(1)–Pd(1)–Br(1')	97.7(3)		
C(4)–Pd(1)–Br(1)	94.1(3)	C(4)–Pd(1)–Br(1')	175.5(3)
C(4)–Pd(1)–N(1)	81.4(4)		
Pd(1)–Br(1)–Pd(1')	93.0(2)		
C(11)–N(1)–Pd(1)	124.7(6)	C(2)–N(1)–Pd(1)	113.1(7)
N(1)–C(2)–Pd(1)	142.2(4)	C(3)–C(2)–Pd(1)	75.5(6)
C(2)–C(3)–Pd(1)	74.1(6)	C(4)–C(3)–Pd(1)	40.6(4)
C(8)–C(3)–Pd(1)	163.6(6)		
C(3)–C(4)–Pd(1)	113.0(7)	C(5)–C(4)–Pd(1)	128.4(7)
C(2)–N(1)–C(11)	122.1(8)	C(3)–C(2)–N(1)	117.7(9)
C(12)–C(11)–N(1)	114.7(8)	C(16)–C(11)–N(1)	109.4(7)
C(4)–C(3)–C(2)	114.8(8)	C(8)–C(3)–C(2)	122.2(8)
C(8)–C(3)–C(2)	123.0(8)	C(5)–C(4)–C(3)	118.6(8)
C(6)–C(5)–C(4)	121.5(8)	C(7)–C(6)–C(5)	119.3(8)
C(8)–C(7)–C(6)	119.2(8)	C(7)–C(8)–C(3)	118.4(8)
Pd(1)···Pd(1')	363.1(5)		

^a Primed atoms are related by the symmetry operator (2.0 – x, – y, 1.0 – z).

dimer with acetate bridges although the large e.s.d.'s preclude any detailed comparison.

As for the title complex, the acetato, chloro- and bromo-bridged precursors used in the subsequent reactions (shown in Scheme 1) were prepared as reported previously [7,17]. The iodo-bridged complexes $[\text{Pd}\{2\text{-MeOC}_6\text{H}_3\text{C}(\text{H})=\text{NCy}\}(\text{I})]_2$ and $[\text{Pd}\{3,4\text{-(MeO)}_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{NCy}\}(\text{I})]_2$ (**1a** and **1b** respectively) were prepared as air-stable solids from the reaction of the corresponding acetato-bridged complex with sodium iodide (see Experimental, Table 3 and Scheme 1). The IR spectra of both **1a** and **1b** have two Pd–X_b bands confirming that, in both cases, the Pd₂I₂ bridging unit is asymmetric. The NMR data (Table 4) is consistent with the proposed structures with the unequivocal assignment of the phenyl ring protons from chemical shift data and coupling constants confirming the position of palladation [20].

Treatment of these halide-bridged dimers with the tertiary phosphines triphenyl-, tricyclohexyl- and diethylphenylphosphine in a 1 : 2 or 1 : 4 dimer : phosphine molar



Scheme 1

ratio produces the cyclometallated and non-cyclometallated monomers shown in Scheme 1. All complexes have been fully characterised by microanalysis (C,H and N), IR and both ¹H and ³¹P NMR spectroscopy. The possibility of the non-cyclometallated complexes being ionic, i.e. the Schiff base remaining cyclometallated and the phosphine displacing a halogen anion to produce a 1 : 1 electrolyte, is excluded by the low molar conductivity of all of these complexes in dry acetonitrile at 20 °C.

In the case of the cyclometallated monomers (**2a–7a, 2b–7b**) both the H(7) and H(5) protons (see Scheme 1) are coupled to the phosphorus atom (Table 4). However, since the non-cyclometallated monomers (**8a–15a, 10b–15b**), in principle, have no Pd–N bond, the metallated phenyl ring can rotate about the Pd–C vector

Table 3
Microanalytical, colour, yield and IR data

	Colour	Yield (%)	Analytical data, found (calcd.)(%)			IR data (cm ⁻¹) ^a		
			C	H	N	$\nu(\text{C}=\text{N})$ ^b	$\nu(\text{Pd}-\text{X}_b)$	$\nu(\text{Pd}-\text{X}_l)$
1a	yellow	72	37.2(37.4)	4.1(4.0)	3.0(3.1)	1608s	142w 132w	
2a	yellow	78	53.6(54.0)	5.1(5.7)	2.1(2.0)	1612s		150m
3a	yellow	74	60.2(60.2)	7.7(8.0)	2.3(2.2)	1620s		280m
4a	yellow	87	56.4(56.2)	7.6(7.5)	2.0(2.0)	1622s		228w
5a	yellow	65	52.6(52.6)	6.8(7.0)	1.9(1.9)	1608m		150w
6a	yellow	64	55.1(55.0)	6.3(6.3)	2.6(2.7)	1609m		295m
7a	yellow	63	50.9(50.7)	5.5(5.8)	2.3(2.5)	1607m		210m
8a	yellow	66	68.3(68.0)	5.7(5.5)	1.6(1.5)	1622m		290m
9a	yellow	62	64.6(64.8)	5.4(5.2)	1.7(1.5)	1621m		202w
10a	yellow	66	61.7(61.6)	4.8(5.0)	1.6(1.4)	1620m		150m
11a	yellow	81	65.5(65.3)	9.3(9.2)	1.5(1.5)	1625m		285m
12a	yellow	90	62.4(62.3)	8.7(8.8)	1.5(1.5)	1621m		205m
13a	yellow	85	59.3(59.4)	8.5(8.4)	1.3(1.4)	1624m		147w
14a	yellow	79	59.2(59.1)	7.1(7.0)	1.9(2.0)	1623m		293m
15a	yellow	82	55.7(55.6)	6.6(6.6)	1.9(1.9)	1625m		204m
1b	yellow	80	37.1(37.5)	4.3(4.2)	2.8(2.9)	1610m	140w 128w	
2b	yellow	64	53.5(53.4)	4.7(4.6)	1.8(1.8)	1610m		148w
3b	yellow	79	59.2(59.2)	8.0(7.9)	2.1(2.3)	1611m		287m
4b	yellow	71	56.0(55.6)	7.8(7.5)	1.9(2.0)	1615m		225m
5b	yellow	67	52.3(52.1)	7.1(7.0)	2.0(1.8)	1610m		148w
6b	yellow	73	54.1(54.2)	6.4(6.4)	2.5(2.5)	1607m		293m
7b	yellow	75	50.1(50.1)	5.8(5.9)	2.4(2.3)	1605m		201m
10b	yellow	61	61.2(60.9)	5.3(5.0)	1.6(1.4)	1639m		151w
11b	yellow	67	62.7(63.0)	9.0(9.4)	1.6(1.5)	1638m		289m
12b	yellow	62	58.7(58.8)	9.3(9.0)	1.4(1.3)	1639m		222m
13b	yellow	70	68.3(68.0)	8.4(8.3)	1.6(1.5)	1640m		148w
14b	yellow	75	58.4(58.3)	7.0(7.0)	1.8(1.9)	1641m		296m
15b	yellow	78	54.9(54.9)	6.5(6.6)	1.7(1.8)	1637m		204m

^a s, strong; m, medium; w, weak. ^b $\nu(\text{C}=\text{N})$ values (in cm⁻¹): a, 1637m; b, 1647s.

so that its plane is at 90° to the palladium co-ordination plane, these couplings are absent [21,22].

In the ¹H NMR spectra of complexes **2b** and **10b** the resonance of the methoxy group C(4) (see Scheme 1) is shifted by ca. 1 ppm to lower frequency when compared to the parent halide-bridged dimer **1b** due to shielding effects of the phosphine phenyl rings [20], indicating that the phosphine is *trans* to the nitrogen atom in the palladium co-ordination geometry.

The presence of a single phosphorus resonance in the ³¹P-{¹H} NMR spectra of **8a–15a** and **10b–15b** together with the very weak band at ca. 550 cm⁻¹ in the IR spectra [23], indicates a P–Pd–P *trans* geometry in these complexes. The IR spectra of these complexes also have rather low values for the Pd–X stretching mode (ca. 295–280 (X = Cl), 225–205 (X = Br), 150 cm⁻¹ (X = I)); cf. standard values of 370–345 (X = Cl), 285–265 (X = Br) [24], 190–170 cm⁻¹ (X = I) [25]), since the Pd–X_l bond is subject to a large *trans* influence from a phenyl carbon atom. There may be some weak Pd···N interaction since values for the C=N stretching mode

(see Table 4) are somewhat smaller than those found for the corresponding free ligands [26].

When the monomeric complexes change from being cyclometallated to being non-cyclometallated, i.e. when a second phosphine is added, the phosphorus resonance in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum is shifted to lower frequency; for the PPh_3 complexes this shift is ca. 16 ppm, for the PCy_3 complexes ca. 20 ppm and ca. 23 ppm for the PPhEt_2 complexes (Table 4). The ^{31}P chemical shifts are in the order $\delta \text{P}(\text{PPh}_3) > \delta \text{P}(\text{PCy}_3) > \delta \text{P}(\text{PPhEt}_2)$ for both the cyclometallated and non-cyclometallated monomers. We are not yet certain whether this trend is due to the change in basicity of the phosphine ligands [27] or steric effects or a combination of the two.

Experimental

The general procedures and apparatus used were the same as described previously [7]. The preparation of the Schiff base ligands and of the acetato-, chloro- and bromo-bridged dimer complexes has already been described elsewhere [17].

*Preparation of $[\text{Pd}\{3,4-(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{NCy}\}(\text{I})]_2$ (**1a**).* Aqueous NaI (ca. 10^{-2} mol l^{-1}) was added to a solution of the acetato-bridged dimer (100 mg, 0.13 mmol) in acetone (5 cm^3). The product immediately precipitated out as a yellow solid. The solution was then stirred for an hour and the solid filtered off and dried in vacuo. Compound **1b** was prepared similarly.

*Preparation of $[\text{Pd}\{3,4-(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{NCy}\}(\text{I})(\text{PPh}_3)]$ (**2a**).* PPh_3 (8.8 mg, 0.02 mmol) was added to a suspension of **1a** (15 mg, 0.01 mmol) in acetone (5 cm^3). The mixture was stirred for 2 h by which time it had become clear. The complex was then precipitated out by addition of a 1:3 acetone water mixture, filtered off and dried in vacuo. Compounds **3a–7a** and **2b–7b** were prepared similarly.

*Preparation of $[\text{Pd}\{3,4-(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{NCy}\}(\text{I})(\text{PPh}_3)_2]$ (**10a**).* The complex was synthesised following a similar procedure to that of **2a** but using a dimer/phosphine ratio of 1:4. Complexes **8a–15a** and **10b–15b** were prepared similarly.

Single crystal X-ray diffraction analysis. All crystallographic measurements were carried out on a Nicolet P3/F diffractometer operating in the ω scan mode using graphite monochromated Mo-K_α radiation following a standard procedure [28]. The data-set was corrected for absorption empirically once the structure had been determined [29].

The structure, which possesses a crystallographic inversion centre, was determined via standard heavy atom techniques and refined by fullmatrix least-squares using the SHELX program system [30]. All non-hydrogen atoms (including those of the unique solvate molecule) were refined with anisotropic thermal parameters. All hydrogen atoms were included in calculated positions and were refined with an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]$ was used in which the parameter g was varied in refinement to obtain a flat analysis of variance with increasing $\sin \theta$ and $(F/F_{\text{max}})^{1/2}$. Final non-hydrogen atomic co-ordinates are given in Table 1.

Crystal data. $\text{C}_{30}\text{H}_{40}\text{Br}_2\text{N}_2\text{O}_4\text{Pd}_2 \cdot 2\text{CHCl}_3$, $M = 1104.06$ (includes both solvate molecules), triclinic, $P1$, $a = 788.7(2)$, $b = 911.0(3)$, $c = 1480.8(4)$ pm, $\alpha = 96.94(2)$, $\beta = 91.57(2)$, $\gamma = 101.85(2)^\circ$, $U = 1.0322(5)$ nm^3 , $Z = 1$, $D_x = 1.78$ Mg m^{-3} , $\lambda(\text{Mo-K}_\alpha) = 71.069$ pm, $\mu = 32.06$ cm^{-1} , $F(000) = 554.0$.

Table 4
 $^1\text{H}^a$ and $^{31}\text{P}^c$ (^1H)^b NMR data for the ligands and complexes^c

	$\delta(\text{H}(7))$	$\delta(\text{H}(2))$	$\delta(\text{H}(3))$	$\delta(\text{H}(4))$	$\delta(\text{H}(5))$	$\delta(\text{MeO})$	$^3J(\text{H}(3)\text{H}(4))$	$^3J(\text{H}(4)\text{H}(5))$	$^4J(\text{PH}(7))$	$^4J(\text{PH}(5))$	$\delta(\text{P})$
a^d	8.74s		6.87d	7.34td	6.96t	3.84s	8.0	8.0			
1a	8.24s		6.46d	6.90t	6.93d	3.71s	8.0	8.0			
2a	8.63d		6.38d	6.51t	5.90t	3.76s	8.0	8.0	8.5	8.0	42.4s
3a	8.40d		6.45d	6.93t	6.80dd	3.72s	8.0	8.0	7.9	3.3	38.0s
4a	8.42d		6.44d	6.94t	6.81dd	3.72s	8.0	8.0	7.6	3.5	37.8s
5a	8.52d		6.52d	7.03t	6.85dd	3.80s	8.0	8.0	6.4	3.5	38.1s
6a	8.49d		6.50d	7.01t	6.85dd	3.81s	8.0	8.0	6.3	6.9	33.5s
7a	8.42d		6.48d	6.95t	6.79dd	3.79s	8.0	8.0	6.1	7.0	34.0s
8a	8.56s		6.38d	6.49t	5.97d	3.76s	7.5	7.5			27.1s
9a	8.51s		6.30d	6.43t	5.88d	3.69s	8.0	8.0			27.4s
10a	8.63s		6.37d	6.51t	5.90d	3.69s	8.0	8.0			26.9s
11a	8.70s		6.44d	6.66t	6.80d	3.71s	7.4	7.3			18.3s
12a	8.69s		6.51d	6.61t	6.77d	3.74s	8.0	8.0			18.2s
13a	8.71s		6.32d	6.51t	6.79d	3.76s	8.0	8.0			18.5s
14a	8.65s		6.53d	6.80t	6.10d	3.80s	8.1	8.0			12.3s
15a	8.66s		6.49d	6.82t	6.05d	3.75s	7.5	7.4			11.1s
b^c	8.23s	7.41d			6.87d	3.95s					
					3.91s						
1b	7.83s	7.27s			6.84s	3.92s					
					3.81s						
2b	8.11d	6.83s			5.86d	3.77s			7.8	6.9	41.7s
					3.83s						

3b	7.94d	6.96d	6.87d	3.94s	7.7	3.2	38.3s
				3.91s			
4b	7.95d	6.86s	6.87d	3.88s	8.5	5.6	38.5s
				3.80s			
5b	8.02d	6.84s	6.85d	3.88s	7.4	5.2	38.1s
				3.84s			
6b	7.86d	7.10s	6.70d	3.91s	6.2	6.8	35.5s
				3.05s			
7b	7.91d	6.95s	6.73d	3.78s	6.1	7.1	36.2s
				3.00s			
10b	8.11s	6.83s	5.87s	3.77s			25.0s
				2.83s			
11b	9.53s	7.44s	6.99s	3.88s			17.9s
				3.80s			
12b	9.51s	7.39s	6.99s	3.88s			17.8s
				3.80s			
13b	9.44s	7.40s	6.98s	3.89s			18.1s
				3.87s			
14b	8.10s	7.39s	6.77s	3.85s			12.6s
				3.10s			
15b	8.20s	7.31s	6.78s	3.87s			12.8s
				3.07s			

^a Measured at 250 MHz. Chemical shifts (δ) in ppm (± 0.01 ppm) relative to high frequency of SiMe₃; coupling constants in Hz (± 0.1 Hz). ^b Measured at 100.6 MHz. Chemical shifts (δ) in ppm (± 0.1 ppm) relative to high frequency of 85% H₃PO₄. ^c s, singlet; d, doublet; dd, doublet of doublets; t, triplet; td, triplet of doublets. ^d δ (H(6)) = 7.95dd, ³J(H(6)H(5)) = 7.7 Hz, ⁴J(H(6)H(4)) = 1.8 Hz. ^e δ (H(6)) = 7.14 dd, ³J(H(6)H(5)) = 8.2 Hz, ⁴J(H(6)H(2)) = 1.8 Hz.

Data collection. Scan widths $1.8^\circ + \alpha$ -doublet splitting, scan speeds $2.0 - 29.3^\circ \text{ min}^{-1}$, $4.0 < 2\theta < 50.0^\circ$. 3733 data collected, 3280 with $I > 4.0\sigma(I)$ considered observed, $T = 290 \text{ K}$.

Structure refinement. Number of parameters = 224, $g = 0.0008$, $R = 0.0668$, $R_w = 0.0790$.

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