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Palladium(II) and platinum(II) complexes formed from C_6H_4-1,3-$(CH_2PCy_2)_2$ (Cy = Cyclohexyl); crystal and molecular structures of [PdX{C_6H_3-2,6-$(CH_2PCy_2)_2$}], X = Cl and Br

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Abstract

The reaction of C_6H_4-1,3-$(CH_2PCy_2)_2$ (Cy = cyclohexyl) with [$PdCl_2(NCPh)_2$] gave mainly [$PdCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$ which was converted into [PdCl{C_6H_3-2,6-$(CH_2PCy_2)_2$}] on prolonged reflux, whereas C_6H_4-1,3-$(CH_2PCy_2)_2$ reacted with [$PdBr_2(PPh_3)_2$] to give mainly [PdBr{C_6H_3-2,6-$(CH_2PCy_2)_2$}]. Only [$PtCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$ was formed in the analogous reaction with [$PtCl_2(NCPh)_2$]. X-ray analysis showed that [PdCl{C_6H_3-2,6-$(CH_2PCy_2)_2$}] and [PdBr{C_6H_3-2,6-$(CH_2PCy_2)_2$}] are isostructural. Both molecules display a conformation of the terdentate PCP ligand that is different from that recently reported for several related molecules. It is concluded that the conformation adopted by C_6H_3-2,6-$(CH_2PR_2)_2$ ligands appears to be dominated by the steric demand of the phosphorus substituents.

Keywords: Palladium; Platinum; Metallation; Crystal structure; Chelate Conformation

1. Introduction

As part of our studies on the use of the sterically demanding terdentate ligand C_6H_3-2,6-$(CH_2PCy_2)_2$ to stabilise complexes in unusual coordination numbers or with weak ligands [1,2], we have prepared the compounds [PdX{C_6H_3-2,6-$(CH_2PCy_2)_2$}] (X = Cl or Br; Cy = cyclohexyl) by the reactions of C_6H_4-1,3-$(CH_2PCy_2)_2$ with the appropriate palladium(II) precursors. The recent reports of the crystal structures of the related complexes [MCl{C_6H_3-2,6-$(CHRPPh_2)_2$}] (M = Pd or Pt; R = H, Me or $CHOCMe_2OCH_2$) [3], reveal interesting contrasts between these and the structures of our complexes, and prompts us to report this work.

2. Results and discussion

The diphosphine C_6H_4-1,3-$(CH_2PCy_2)_2$ [1] reacted with [$PdCl_2(NCPh)_2$] under reflux in 2-methoxyethanol to produce the yellow powder [$PdCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$ (71%) and colourless [PdCl{C_6H_3-2,6-$(CH_2PCy_2)_2$}] (17%). Prolonged refluxing of the [$PdCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$ in 2-methoxyethanol caused further conversion into [PdCl{C_6H_3-2,6-$(CH_2PCy_2)_2$}]. In contrast, C_6H_4-1,3-$(CH_2PCy_2)_2$ and [$PtCl_2(NCPh)_2$] produced only [$PtCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$, and this resisted conversion into the metallated complex, even after 4 days of refluxing in a trifluoroacetic acid/chloroform mixture, conditions known to promote metallation in other complexes with this type of ligand [4]. We have previously reported

Table 1
Selected spectroscopic parameters for the compounds formed from C_6H_4-1,3-$(CH_2PCy_2)_2$

Compound	$\delta^{31}P$ /ppm	δCH_2 ('J') [a] /ppm (/Hz)
[NiBr{C_6H_3-2,6-$(CH_2PCy_2)_2$}]	51.9	3.08 (t, 7.91)
[PdCl{C_6H_3-2,6-$(CH_2PCy_2)_2$}]	52.4 (s)	3.17 (t, 8.52)
[PdBr{C_6H_3-2,6-$(CH_2PCy_2)_2$}]	52.7 (s)	3.21 (t, 8.49)
[$PdCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_2$	25.0 (s)	3.84 (s, br)
[$PdBr_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$	22.6 (m)	3.51 (s, br)
[$PtCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_2$	16.8 (s) [b]	3.52 (s, br)

[a] 'J' = $|^2J_{(P-H)} + {}^4J_{(P-H)}|$.
[b] $J_{(P_t-P)}$ = 2407.2 Hz.

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that the reaction between C_6H_4-1,3-$(CH_2PCy_2)_2$ and $NiBr_2$ produced only [NiBr{C_6H_3-2,6-$(CH_2PCy_2)_2$}] [1].

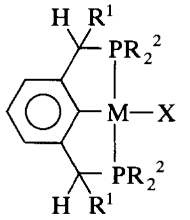
Table 1 lists NMR spectroscopic data characteristic of the two types of complex. The chelate ring CH_2 groups on the terdentate ligand complexes show pseudotriplets [5] near δ 3.2 with $|^2J_{(P-H)} + {}^4J_{(P-H)}|$ about 8 Hz in the ^1H NMR spectra, a feature typical of complexes of this geometry [1,3,6]. The ^{31}P NMR spectra of these complexes reveal singlets near δ52. The non-metallated complexes, however, have ^{31}P NMR resonances about 20 ppm; their ^1H NMR $CH_2(P)$ group resonances are broad singlets near 3.5 ppm; and in addition the chloride complexes have single ν(M-Cl) vibrations in their IR spectra (at 342 cm^{-1} for the Pd complex and 335 cm^{-1} for Pt) typical of *trans* dichlorides [6].

The failure to obtain metallated platinum complexes would seem to be in conflict with some previous reports that Pt compounds undergo such reactions more readily than their Pd analogues [7,8]. The explanation probably lies in the failure of product [$PtCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$, in which each bidentate ligand C_6H_4-1,3-$(CH_2PCy_2)_2$ spans two metal centres, to rearrange to *trans*-spanning monomers [$PtCl_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}] prior to metallation [9,10]. The kinetic inertness of the platinum complexes (several orders of magnitude greater than for Pd or Ni analogues) would inhibit the rearrangement. We observe that *trans*-[$PdBr_2(PPh_3)_2$] reacts with C_6H_4-1,3-$(CH_2PCy_2)_2$ in ethanol over 19.5 h to produce good yields of [PdBr{C_6H_3-2,6-$(CH_2PCy_2)_2$}] and only small amounts of [$PdBr_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$. Nucleophilic attack of the displaced PPh_3 is likely to catalyse the rearrangement of the latter to its *trans*-spanning monomeric analogue. Rimml and Venanzi [9] similarly observed that C_6H_4-1,3-$(CH_2PPh_2)_2$ and [$PtCl_2(PPh_3)_2$] gave a higher proportion of metallated to polymeric product than did the analogous reaction between C_6H_4-1,3-$(CH_2PPh_2)_2$ and $PtCl_2$ or $PtBr_2$.

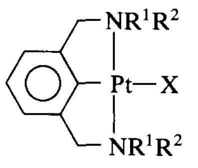
The extent of oligomerisation of non-metallated [MX_2{C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$ is unknown, but we note that for the chloride derivatives the ^{31}P NMR spectrum of each contains a singlet, indicative of only one species. In line with similar observations on related complexes [4,8,11], we tentatively suggest that for these complexes $n = 2$, assigning them as *trans-trans*-[MCl_2{C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_2$ to account for their single ν(M-Cl). [$PdBr_2${C_6H_4-1,3-$(CH_2PCy_2)_2$}]$_n$ has several ^{31}P resonances near δ 22.6, however, and is presumably a mixture of species.

2.1. Structures of compounds [PdX{C_6H_3-2,6-$(CH_2PCy_2)_2$}]

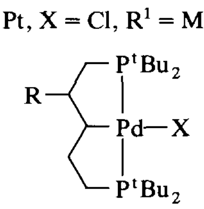
We have examined the crystal structures of [PdX{C_6H_3-2,6-$(CH_2PCy_2)_2$}] (X = Cl and Br). The compounds are isomorphous and isostructural. Indeed, the [Pd{C_6H_3-2,6-$(CH_2PCy_2)_2$}] units are virtually indistinguishable, indicating that substitution of Cl (van der Waals radius 1.80 Å) by the larger Br (van der Waals radius 1.95 Å) has no obvious effect on the rest of the structure despite the presence of bulky Cy



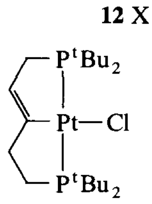
1 M = Ni, X = Br, R^1 = H, R^2 = Cy [1]
2 M = Pd, X = Cl, R^1 = H, R^2 = Cy
3 M = Pd, X = Br, R^1 = H, R^2 = Cy
4 M = Pd, X = Cl, R^1 = H, R^2 = Ph [3]
5 M = Pt, X = CO_2H, R^1 = H, R^2 = Ph [14]
6 M = Pt, X = Cl, R^1 = Me, R^2 = Ph [3]
7 M = Pt, X = Cl, R^1 = Me, R^2 = Ph [3]



8 X = Br, R^1 = R^2 = Me [15]
9 X = I, R^1 = R^2 = Me [16]
10 X = (p-tol)N = CHNH(p-tol)$^+$ $CF_3SO_3^-$; R^1 = R^2 = Me [17]
11 X = (p-tol)N = CHN(p-tol), R^1 = R^2 = Me [17]
12 X = I, R^1, R^2 = $(CH_2)_{10}$ [18]



13 R = Me, X = Cl [11]
14 R = H, X = Me [19]
15 R = H, X = $OH_2^+BPh_4^-$ [19]



16 [20]

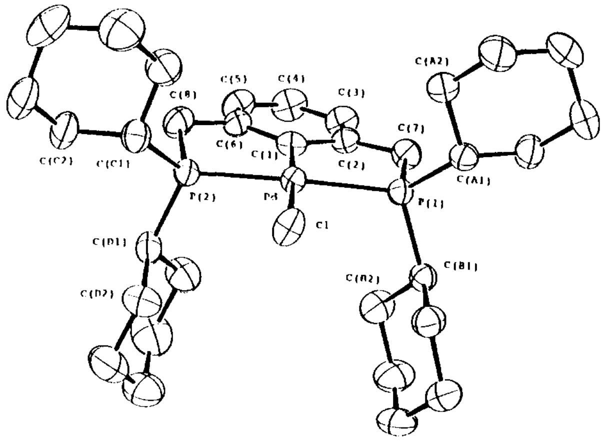


Fig. 1. View of the molecule [PdCl{C_6H_3-2,6-(CH_2PCy_2)$_2$}]. 50% Probability ellipsoids are displayed, and hydrogen atoms are omitted.

Table 2
Selected lengths (Å) and angles (°) for [PdCl(2,6-(PCy_2-CH_2)$_2$(C_6H_3))]

(a) Bond lengths			
Pd–Cl	2.427 (2)	Pd–P (1)	2.294 (2)
Pd–P (2)	2.266 (2)	Pd–C (1)	2.012 (6)
P(1)–C(7)	1.826(7)	P(2)–C(8)	1.824(7)
C(1)–C(2)	1.426(9)	C(1)–C(6)	1.421(8)
C(2)–C(3)	1.380(9)	C(2)–C(7)	1.497(9)
C(3)–C(4)	1.389(9)	C(4)–C(5)	1.385(10)
C(5)–C(6)	1.375(9)	C(6)–C(8)	1.490(9)
	P–C(Cy)	1.821(7)–1.836(6)	
(b) Bond angles			
Cl–Pd–P(1)	98.2(1)	Cl–Pd–P(2)	94.4(1)
Cl–Pd–C(1)	177.0(2)	P(1)–Pd–P(2)	165.5(1)
P(1)–Pd–C(1)	84.7(2)	P(2)–Pd–C(1)	82.8(2)
Pd–P(1)–C(7)	102.6(2)	Pd–P(1)–C(A1)	122.5(2)
Pd–P(1)–C(B1)	112.7(2)	Pd–P(2)–C(8)	104.1(3)
Pd–P(2)–C(C1)	118.2(3)	Pd–P(2)–C(D1)	114.9(2)
Pd–C(1)–C(2)	121.0(4)	Pd–C(1)–C(6)	122.1(5)
C(2)–C(1)–C(6)	116.9(5)	C(1)–C(2)–C(7)	119.2(5)
C(1)–C(6)–C(8)	118.8(6)	P(1)–C(7)–C(2)	111.2(4)
P(2)–C(8)–C(6)	108.6(4)		
(c) Torsion angles			
P(2)–Pd–P(1)–C(7)	35.7(3)	P(1)–Pd–P(2)–C(8)	−44.4 (3)
P(1)–Pd–C(1)–C(2)	0.9(5)	P(1)–Pd–C(1)–C(6)	179.1(5)
C(1)–Pd–P(1)–C(7)	5.1(3)	P(2)–Pd–C(1)–C(2)	−171.7(5)
P(2)–Pd–C(1)–C(6)	6.6(5)	C(1)–Pd–P(2)–C(8)	−13.7(3)
Pd–P(1)–C(7)–C(2)	−10.4(4)	Pd–P(2)–C(8)–C(6)	19.8(4)
Pd–C(1)–C(2)–C(7)	−8.7(5)	Pd–C(1)–C(6)–C(8)	5.8(5)
C(1)–C(2)–C(7)–P(1)	12.7(5)	C(1)–C(6)–C(8)–P(2)	−17.7(5)

substituents on the phosphorus atoms. Accordingly, we describe fully the main features only of the chloride (see Fig. 1 and Table 2), and comment only on the bromide to the extent that it differs from the chloride.

The Pd–ligand bond lengths in the chloride are fairly typical of those found in square planar Pd(II) complexes with *trans*-$P_2ClC(sp^2)$ donor sets. In the majority of such complexes Pd–C is in the range 1.97–2.03 Å; the value found here is 2.012(6) Å. The Pd–P(1) and Pd–P(2) distances [2.294(2) and 2.266(2) Å] show a slight but significant difference (as do the corresponding values in the bromide) but both values compare well with recently compiled mean Pd–PR_3 bond lengths of 2.287–2.315 Å [12]. The same compilation gave a mean of 2.326 Å for 224 Pd–Cl bond lengths. The value found here [2.427(2) Å] is substantially greater; this seems mainly attributable to the high *trans*-influence of σ-phenyl, but we note that the mean length of 19 Pd–Cl(*trans* to C(sp^2)) bonds is 2.396 Å and that in [PdCl{C_6H_3-2,6-(CH_2PPh_2)$_2$}] the Pd–Cl distance is only 2.367(3) Å; thus steric pressure from the bulky Cy groups in [PdCl{C_6H_3-2,6-(CH_2PCy_2)$_2$}] cannot be excluded as a contributory factor in the weakening of the Pd–Cl bond. In the bromide, however, the *trans*-influence of σ-phenyl seems to account adequately for

Table 3
Selected distances(Å) and angles(°) in square planar complexes with PCP and NCP terdentate ligands

No.	M	X	L	M–C	M–X	L–M–L	C–M–X	M–L–C(chelate)	ω [a]	*R* and approx. point symmetry	
1	Ni	Br	P	1.909(5)	2.360(1)	167.6(1)	177.3(2)	103.6(2), 105.0(2)	4.1	Cy	Cs
2	Pd	Cl	P	2.012(6)	2.427(2)	165.5(1)	177.0(2)	102.6(2), 104.1(3)	5.0	Cy	Cs
3	Pd	Br	P	2.009(8)	2.514(2)	165.6(1)	177.1(3)	102.4(3), 104.2(3)	5.0	Cy	Cs
4	Pd	Cl	P	1.998(8)	2.307(3)	162.0(1)	178.7(3)	101.0(4), 101.3(3)	19.8	Ph	C_2
5	Pt	CO_2H	P	2.066(3)	2.058(3)	161.9(1)	176.8(2)	104.6(2), 102.8(2)	11.4	Ph	C_2
6	Pt	Cl	P	2.00(2)	2.368(6)	163.4(2)	178.5(6)	101.4(8), 100.4(7)	17.0	Ph	C_2
7	Pt	Cl	P	2.003(9)	2.384(2)	163.1(1)	177.6(3)	103.0(3), 101.6(3)	14.7	Ph	C_2
8	Pt	Br	N	1.90(1)	2.526(2)	164.4(4)	177.4(4)	107.1(8), 108.3(9)	13.2	Me	C_2
9	Pt	I	N	1.933(6)	2.716(2)	163.3(2)	179.6(2)	108.4(4), 108.7(4)	9.5	Me	C_2
10	Pt	imine	N	1.91(1)	2.16(1)	163.0(4)	177.7(4)	107.7(9), 107.9(8)	–	Me	C_2
11	Pt	imide	N	1.914(6)	2.132(6)	163.2(1)	178.6(2)	107.6(3), 107.3(3)	–	Me	C_2
12	Pt	I	N	1.94(1)	2.734(1)	164.1(4)	173.4(3)	107.2(8), 108.4(8)	11.0	Me/alkyl	C_2
13	Pd	Cl	P	2.102(9)	2.428(3)	166.8(1)	175.9(3)	103.0(4), 103.6(3)	–	^{t}Bu	Cs
14	Pd	Me	P	2.129(4)	2.156(5)	166.2(1)	171.9(2)	103.6, 104.1	–	^{t}Bu	Cs
15	Pd	OH_2	P	2.056(6)	2.301(6)	167.1(1)	171.1(3)	102.7, 102.2	–	^{t}Bu	Cs
16	Pt	Cl	P	2.03(2)	2.404(4)	167.9(1)	176.9(5)	103.1(5), 102.3(6)	–	^{t}Bu	Cs

[a] Dihedral angle between metal coordination plane and that of the metallated phenyl ring.

the long Pd–Br distance [2.514(2) Å], which may be compared with a similar value [2.515(2) Å] in *trans*-[PdBr(*o*-tolyl)$(PPh_3)_2$] [13] and with a mean of 2.526 Å for all 11 reported Pd–Br(*trans* to C(sp^2)) bond lengths; these values contrast with the mean of 2.424 Å for eight Pd–Br bonds *trans* to a variety of donor atoms given in Ref. [12].

The small bite angles of the terdentate ligand lead to substantial departure of the Pd coordination from ideal square planar geometry, most notably through the closure of the P–Pd–P angle to 165.5(1)°. This arises partly from an in-plane narrowing of the P–Pd–C angles and opening of the Cl–Pd–P angles, and partly from a deviation of the Pd coordination towards tetrahedral [the displacements of P(1), P(2), Cl and C(1) from the $PdP_2ClC(1)$ coordination plane are respectively 0.088(2), 0.092(2), −0.047(1), and −0.078(6) Å]. The chelate ring Pd–P–C angles [102.6(2) and 104.1(3)°] are also smaller than would be expected for non-chelating phosphines.

The two chelate rings adopt rather flat envelope conformations with methylene carbons at the flap positions. The ring containing P(2) is noticeably more puckered than that containing P(1) but otherwise corresponding bond lengths and angles in the two rings agree well, apart from the previously noted small difference in Pd–P lengths. The near C_s point symmetry of the molecule is revealed, inter alia, by the opposite signs of corresponding torsion angles in the two chelate rings (see Table 2). Although the ligand geometry constrains the σ-bonded aromatic ring to be nearly parallel to the Pd coordination plane it is tilted symmetrically out of this plane by 5° so that the Pd–C(1)–C(2)–C(3) and Pd–C(1)–C(6)–C(5) torsion angles are 174.8(8) and −174.8(8)°, and the Pd atom lies 0.17 Å from the C(1)–C(6) plane.

Salient structural features of [PdCl{C_6H_3-2,6-$(CH_2PCy_2)_2$}] and [PdBr{C_6H_3-2,6-$(CH_2PCy_2)_2$}] are compared with those of related PCP and NCN terdentate ligand complexes in Table 3 (compounds **1–12**) [1,3,11,13–19]. At first sight the most striking feature of these complexes is their similarity: thus the C–M–X angle is close to linear in all cases, whereas the P–M–P or N–M–N angle has closed to 162–168°. The cyclohexyl complexes **1–3**, however, are conformationally different from the other complexes **4–12** in that they have near C_s symmetry and fairly small phenyl/coordination plane dihedral angles, ω. Complexes **4–12** have C_2 rather than C_s symmetry and ω is not only larger but arises from a rotation of the phenyl ring about the M–C bond rather than from a tilting of the M–C bond out of the plane of the phenyl ring. In consequence, the PR_2 groups are nearly eclipsed (Fig. 2, projection A,) in the Cy complexes [Cl–Pd–P–C torsion angles for rings A to D are respectively −55.9(3), 73.4(3), 45.9(3) and −82.6(3)°] but are staggered (Fig. 2, projection B) in the other related complexes, with axial R groups pointing normal to the coordination plane and equatorial R groups lying close to the plane.

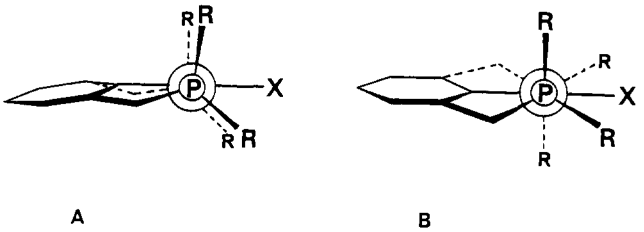


Fig. 2. Conformations adopted by molecules **1–12**. Projection A: C_s symmetry, with eclipsed ring substituents; Projection B: C_2 symmetry, with staggered ring substituents.

The eclipsed conformation found in the Cy complexes avoids steric congestion of the halide ligand: the shortest intramolecular Cl ··· H and Cl ··· C contacts in the chloride complex [2.93 Å and 3.74 Å] are virtually identical to the shortest intermolecular contacts of the same type. In the bromide complex, **3**, intraligand Br ··· H and Br ··· C contacts are actually longer than the shortest intermolecular contacts of comparable type. We conclude that ligands of the PCP and NCN type have sufficient conformational flexibility to adopt either C_2 or C_s conformations when attached to square planar metal ions and that bulky substituents on P are likely to favour the C_s conformation found in our Cy complexes rather than the C_2 conformation typical of the phenyl complexes **4–7** or the less hindered NCN complexes **8–12**.

Compounds **13–16** (Table 3) [11,19,20] are close relatives of the PCP ligand complexes discussed. Though without the constraint of the central aryl group, all have five-member chelate ring systems which adopt envelope conformations, and all contain terminal *tert*-butyl groups which have very high steric demand. Except for the in-built asymmetry arising from the methyl ring-substituent in **13** and the double bond in **16** these complexes adopt a largely C_s conformation, (see Fig. 2, projection A) with eclipsed *t*-Bu groups when viewed along the P–P axis and the envelope conformations of the five-member rings folded to the same side of the coordination plane. It is reasonable to conclude, therefore, that the conformations adopted by all of these PCP and NCN complexes are dictated by the interactions of the P- or N-atom substituents with the other coordinated ligands.

3. Experimental details

NMR spectra were recorded on Bruker AM200 or SW200 instruments operating in the Fourier transform mode. IR spectra were recorded as KBr discs on a Phillips FTIR spectrophotometer. Microanalyses were performed at Glasgow University Chemistry Department microanalytical laboratory. Reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. C_6H_4-1,3-$(CH_2PCy_2)_2$ was synthesised as previously described [1].

3.1. Reaction of C_6H_4-1,3-$(CH_2PCy_2)_2$ with $[PdCl_2(NCPh)_2]$

$[PdCl_2(NCPh)_2]$ (0.5 g, 1.3 mmol) was added to a suspension of C_6H_4-1,3-$(CH_2PCy_2)_2$ (0.87 g, 1.74 mmol) in 2-methoxyethanol. The mixture was refluxed for 25 min, then allowed to cool, and the solvent was removed to leave a yellow powder. Extraction with hot ethanol (50 ml) left $[PdCl_2\{C_6H_4\text{-}1,3\text{-}(CH_2PCy_2)_2\}]_n$ as a yellow powder (0.63 g, 71%), m.p. 236°. Anal. Found: C, 56.9; H, 7.7; Cl, 10.75, $C_{32}H_{52}Cl_2P_2Pd$. Calc.: C, 56.85; H, 7.8; Cl, 10.5%.

Cooling and reducing the volume of ethanol solution gave $[PdCl\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}]$ as white microcrystals (0.18 g, 17%) m.p. 216–219°. Salient NMR spectroscopic parameters are in Table 1.

3.2. Conversion of $[PdCl_2\{C_6H_4\text{-}1,3\text{-}(CH_2PCy_2)_2\}]_n$ to $[PdCl\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}]$

A suspension of $[PdCl_2\{C_6H_4\text{-}1,3\text{-}(CH_2PCy_2)_2\}]_n$ (0.16 g, 0.12 mmol) in 2-methoxyethanol (20 ml) was refluxed for 48 h. After cooling, the solution was filtered to remove unchanged $[PdCl_2\{C_6H_4\text{-}1,3\text{-}(CH_2PCy_2)_2\}]_n$ (0.08 g) as a yellow-green solid, and the solution yielded $[PdCl\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}]$ (0.06 g, 43%) as an off-white powder.

3.3. Reaction of C_6H_4-1,3-$(CH_2PCy_2)_2$ with *trans*-$[PdBr_2(PPh_3)_2]$

To a solution of C_6H_4-1,3-$(CH_2PCy_2)_2$ (0.30 g, 0.60 mmol) in ethanol (35 ml) was added *trans*-$[PdBr_2(PPh_3)_2]$ (0.22 g, 0.28 mmol). After 16 h refluxing then cooling of the mixture, a pale yellow precipitate of $[PdBr_2\{C_6H_4\text{-}1,3\text{-}(CH_2PCy_2)_2\}]_n$ was produce (0.03 g, 12%, m.p. 204–208°; dec. at 240°; NMR spectroscopic parameters are in Table 1). Further standing and concentration of the solution yielded $[PdBr\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}]$ (0.14 g, 72%) as colourless crystals, m.p. 240–241° (phase change at 148–151°). Anal. Found: C, 56.0; H, 7.4. $C_{32}H_{51}BrP_2Pd$ Calc.: C, 56.2; H, 7.5%.

3.4. Reaction of C_6H_4-1,3-$(CH_2PCy_2)_2$ with $[PtCl_2(NCPh)_2]$

To a solution of C_6H_4-1,3-$(CH_2PCy_2)_2$ (1.79 g, 3.95 mmol) in 2-methoxyethanol (25 ml) was added $[PtCl_2(NCPh)_2]$ (1.59 g, 3.37 mmol). The clear yellow solution rapidly gave a pale yellow precipitate, and the mixture was refluxed for 18 h and then cooled. Removal of the solvent from the solution left $[PtCl_2\{C_6H_4\text{-}1,3\text{-}(CH_2PCy_2)_2\}]_n$ as a white powder (2.19 g, 85%), m.p. 218–222° (dec). Anal. Found: C, 50.6; H, 6.8; Cl, 8.3. $C_{32}H_{52}Cl_2P_2Pt$. Calc.: C, 50.25; H, 6.9; Cl, 9.3%. Spectroscopic parameters are in Table 1.

A sample of $[PtCl_2\{C_6H_4\text{-}1,3\text{-}(CH_2PCy_2)_2\}]_n$ was refluxed in a $CF_3COOH/CHCl_3$ mixture for 4 days, but apart from a slight darkening of the supernatant liquid, no change was observed.

3.5. X-ray Analysis of $[PdX\{C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2\}]$ $X = Cl$ or Br

Measurements were made at 24°C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatised Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, using

Table 4
Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for $[PdCl(2,6\text{-}(PCy_2CH_2)_2(C_6H_3))]$

Atom	*x*	*y*	*z*	*U*
Pd	0.19908(4)	0.22156(2)	0.21558(3)	0.030
Cl	0.08040(13)	0.28800(8)	0.31688(8)	0.039
P(1)	0.39576(13)	0.22614(9)	0.28100(8)	0.031
P(2)	0.02373(14)	0.19047(9)	0.13887(9)	0.034
C(1)	0.2893(5)	0.1665(3)	0.1277(3)	0.034
C(2)	0.4221(5)	0.1511(3)	0.1362(3)	0.036
C(3)	0.4806(6)	0.1085(3)	0.0788(4)	0.046
C(4)	0.4135(7)	0.0804(3)	0.0109(4)	0.052
C(5)	0.2857(7)	0.0973(3)	0.0001(4)	0.049
C(6)	0.2241(6)	0.1395(3)	0.0560(3)	0.037
C(7)	0.4987(6)	0.1850(3)	0.2052(4)	0.042
C(8)	0.0874(6)	0.1585(4)	0.0416(3)	0.046
C(A1)	0.4724(6)	0.3100(3)	0.3109(3)	0.037
C(A2)	0.4448(6)	0.3673(3)	0.2462(4)	0.047
C(A3)	0.5034(7)	0.4390(4)	0.2713(4)	0.059
C(A4)	0.6464(7)	0.4324(4)	0.2903(5)	0.067
C(A5)	0.6773(6)	0.3751(4)	0.3530(4)	0.059
C(A6)	0.6169(6)	0.3035(4)	0.3288(4)	0.050
C(B1)	0.4075(5)	0.1677(3)	0.3721(3)	0.035
C(B2)	0.3548(7)	0.0941(3)	0.3513(4)	0.053
C(B3)	0.3645(8)	0.0445(4)	0.4237(5)	0.066
C(B4)	0.2963(8)	0.0734(4)	0.4968(4)	0.067
C(B5)	0.3454(6)	0.1469(4)	0.5195(4)	0.054
C(B6)	0.3401(6)	0.1983(3)	0.4470(4)	0.046
C(C1)	−0.0940(6)	0.2590(3)	0.1144(3)	0.040
C(C2)	−0.2060(6)	0.2338(4)	0.0593(4)	0.050
C(C3)	−0.2991(6)	0.2947(4)	0.0430(4)	0.059
C(C4)	−0.2362(8)	0.3572(4)	0.0036(4)	0.067
C(C5)	−0.1249(8)	0.3830(4)	0.0567(5)	0.072
C(C6)	−0.0298(7)	0.3234(4)	0.0773(4)	0.058
C(D1)	−0.0623(6)	0.1128(3)	0.1774(4)	0.041
C(D2)	−0.1360(7)	0.1279(4)	0.2552(4)	0.056
C(D3)	−0.2078(7)	0.0620(4)	0.2839(5)	0.069
C(D4)	−0.1190(8)	0.0000(4)	0.2992(5)	0.076
C(D5)	−0.0418(9)	−0.0165(4)	0.2222(6)	0.081
C(D6)	0.0288(7)	0.0503(4)	0.1921(5)	0.058

colourless prismatic crystals. Similar experimental methods were used for both analyses. Details for the chloro-complex are given below, followed by values for the bromo-complex in square brackets if different.

3.5.1. Crystal data

$C_{32}H_{51}ClP_2Pd[C_{32}H_{51}BrP_2Pd]$, M = 639.58 [684.03], monoclinic, space group $P2_1/c$, a = 10.496(1) [10.478(1)] Å, b = 18.800(2) [18.889(2)] Å, c = 16.123(2) [16.245(2)] Å, β = 91.568(6) [91.077(7)]°, V = 3180.1(5) [3214.7(5)] Å^3, Z = 4, D_c = 1.336 [1.413] g cm^{-3}, μ(Mo $K\alpha$) = 7.8 [19.2] cm^{-1}.

3.5.2. Measurements

Cell dimensions are based on the setting angles of 24 [22] reflections with 2.0 [9.6] < θ(Mo $K\alpha$) < 14.0 [23.4]°. The intensities of 7032 [5810] reflections with 2.0 < θ(Mo $K\alpha$) < 25.0°, h 0–12, k $\overline{22}$–22, l $\overline{19}$–19 [h $\overline{12}$–12, k 0–22, l $\overline{19}$–0] were estimated from $\omega/2\theta$ scans and corrected for Lp and absorption effects (empirical correction factors on F 0.90 [0.83]–1.09 [1.09]) [21]. On averaging 1135 [209] duplicate measurements (R_{int} = 0.023 [0.033]) intensities for 5615 [5410] unique reflections were obtained. Further calculations used only the 3272 [2520] unique reflections with $I > 3\sigma(I)$.

Table 5
Fractional coordinates and isotropic displacement parameters(Å^2) for non-hydrogen atoms in $[PdBr(2,6\text{-}(PCy_2CH_2)_2(C_6H_3))]$.

Atom	x	y	z	U
Pd	0.20004(5)	0.22071(3)	0.21688(3)	0.031
Br	0.07584(8)	0.28924(5)	0.32109(5)	0.056
P(1)	0.39680(17)	0.22527(11)	0.28136(11)	0.035
P(2)	0.02499(18)	0.19025(10)	0.14062(12)	0.036
C(1)	0.2922(7)	0.1670(3)	0.1293(4)	0.035
C(2)	0.4228(7)	0.1513(4)	0.1367(4)	0.040
C(3)	0.4841(7)	0.1087(4)	0.0798(5)	0.046
C(4)	0.4164(9)	0.0815(4)	0.0139(5)	0.055
C(5)	0.2897(9)	0.0976(4)	0.0027(5)	0.052
C(6)	0.2276(7)	0.1398(4)	0.0592(5)	0.040
C(7)	0.5009(7)	0.1842(4)	0.2049(5)	0.045
C(8)	0.0891(7)	0.1594(4)	0.0441(4)	0.045
C(A1)	0.4736(7)	0.3098(3)	0.3107(4)	0.036
C(A2)	0.4457(7)	0.3657(4)	0.2461(5)	0.052
C(A3)	0.5031(9)	0.4373(4)	0.2725(5)	0.063
C(A4)	0.6469(9)	0.4308(5)	0.2901(6)	0.070
C(A5)	0.6768(8)	0.3742(5)	0.3529(5)	0.062
C(A6)	0.6158(7)	0.3036(4)	0.3287(5)	0.050
C(B1)	0.4093(6)	0.1676(4)	0.3722(4)	0.039
C(B2)	0.3431(8)	0.1975(4)	0.4478(5)	0.051
C(B3)	0.3493(8)	0.1462(5)	0.5200(5)	0.061
C(B4)	0.3003(8)	0.0731(5)	0.4969(6)	0.065
C(B5)	0.3671(9)	0.0441(4)	0.4239(6)	0.073
C(B6)	0.3564(8)	0.0944(4)	0.3507(5)	0.056
C(C1)	−0.0626(7)	0.1133(4)	0.1794(4)	0.041
C(C2)	−0.1392(8)	0.1291(4)	0.2562(5)	0.054
C(C3)	−0.02095(9)	0.0626(5)	0.2839(6)	0.072
C(C4)	−0.1192(10)	0.0016(5)	0.3001(7)	0.087
C(C5)	−0.0416(9)	−0.0145(5)	0.2255(7)	0.084
C(C6)	0.0293(8)	0.0516(4)	0.1957(6)	0.061
C(D1)	−0.0926(6)	0.2592(4)	0.1154(4)	0.038
C(D2)	−0.2028(7)	0.2343(4)	0.0595(5)	0.053
C(D3)	−0.2957(8)	0.2946(5)	0.0415(5)	0.069
C(D4)	−0.2293(9)	0.3566(5)	0.0030(6)	0.076
C(D5)	−0.1194(9)	0.3821(4)	0.0573(6)	0.073
C(D6)	−0.0257(7)	0.3237(4)	0.0792(5)	0.056

3.5.3. Structure analysis

The structures were solved by Patterson and Fourier methods. Refinement on F with w = $1/\sigma^2(F)$ of 325 parameters (Table 4 [Table 5]) converged (Δ/σ < 0.084 [0.005]) at R = 0.036 [0.037], R_w = 0.048 [0.036], S = 2.0 [1.1]. Anisotropic U_{ij} were used for all non-H atoms. H-atom positions were calculated using stereochemical criteria with C–H = 1.00 [0.96]Å and U(H) = 1.2U_{eq}(C). Final $\Delta\rho$ values were −0.24 [−0.43] to +0.98 [+0.42] e Å^{-3}. The GX package was used for all calculations [22]. Scattering factors and anomalous dispersion corrections were taken from Ref. [23].

Tables of hydrogen atom coordinates and anisotropic displacement parameters, and complete lists of bond lengths and angle have been deposited at the Cambridge Crystallographic Data Centre.

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