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Distortion of cyclopentadienyl rings in η^5-cyclopentadienyl–palladium complexes: crystal structures of $[Pd(C_5H_5)Cl(PMe_2Ph)]$ and $[Pd(C_5H_5)(Ph_2PCH_2CH_2PPh_2)][PF_6]$

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Abstract

The structures of $[Pd(C_5H_5)Cl(PMe_2Ph)]$ and $[Pd(C_5H_5)(dppe)]PF_6$ (dppe = $Ph_2PCH_2CH_2PPh_2$) have been determined by X-ray analysis. Both are η^5-cyclopentadienyl compounds, with the Cp ring nearly perpendicular to the PdPCl or PdP_2 plane. Comparison of their molecular geometries with those of other cyclopentadienyl–palladium complexes of the types PdCpLL′ and $PdCpL_2$ reveals the existence of a complete range of ring–PdLL′ or ring–PdL_2 orientations and suggests that the usual assignment of structures of these types as either staggered or eclipsed is not realistic. Likewise, the patterns of long and short C–C bonds of the Cp rings do not in general follow the sequences expected for the idealized geometries, although large librational distortions of the C_5H_5 rings in most of the compounds limit the accuracy of these determinations. The lengths of the Pd–C(Cp) bonds appear to be much more dependent on the relative *trans* influences of L and L′ than on the ring orientations.

Key words: Palladium; Cyclopentadienyl; X-ray diffraction

1. Introduction

There has been considerable interest in the structures of metal cyclopentadienyl complexes $[M(\eta^5\text{-}C_5H_5)L_x]$, in which the symmetry of the C_5 ring is lowered by a metal orbital distribution of less than cylindrical symmetry. Low rotational barriers for the cyclopentadienyl rings, resulting in considerable librational motion of the rings expressed as large anisotropic displacement parameters of the carbon atoms, have limited the accuracy of many earlier structure determinations. A number of more accurate structure analyses have, however, recently been reported; they have been aided in some cases by measurement of the diffraction intensities at low temperature or by substitution of C_5H_5 by C_5Me_5.

Amongst complexes of the d^8 metal ions, several of the type $[M(C_5H_5)L_2]$ or $[M(C_5H_5)LL']$ have now been examined with sufficient accuracy to detect significant variations in the C–C and M–C bond lengths. In these complexes, L_2 or LL′ subtend angles at the metal ion of about 90°, and the planes containing the metal and the two ligand donor atoms are nearly perpendicular to the C_5 ring planes. The alignments of the ML_2 planes relative to the C_5 rings are usually described as eclipsed or staggered (Fig. 1), although it can be noted that these two conformations differ from each other by a rotation of the cyclopentadienyl ring about the metal–ring centroid vector of only 18°.

The compounds $[Co(C_5Me_5)(CO)_2]$ [1], $[Co(C_5H_5)(PEt_3)_2]$ [2] and $[Rh(C_5Me_5)(CO)_2]$ [3] fit the staggered conformation and their structural features include shorter than average C(1)–C(5), C(4)–C(5) and C(2)–C(3) bonds, with longer C(1)–C(2) and C(3)–C(4) bonds. In addition, M–C(1) and M–C(4) are shorter than the other metal–carbon bonds. This has been explained in terms of overlap of the empty metal d_{xz} orbital (in the ML_2 plane) with an e_1 ring π orbital, removing electron density from between C(1)–C(2) and C(3)–C(4). The filled d_{yz} orbital, on the contrary,

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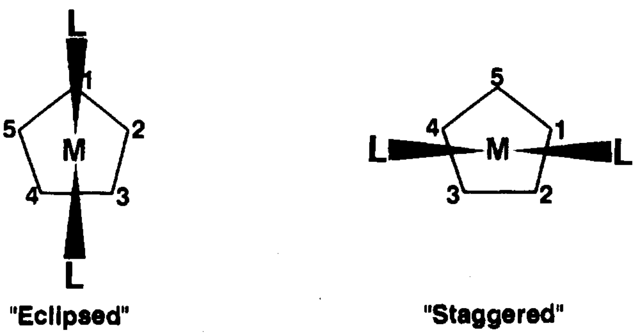

Fig. 1. Extreme conformations of ML_2 planes with respect to cyclopentadienyl rings in $CpML_2$ complexes: (a, left) the eclipsed conformation; (b, right) the staggered conformation.

overlaps with the other e_1 ring orbital but does not reduce its electron density.

The structures of a few palladium cyclopentadienyls have also been described. Most have the added complication of differing L and L′ ligands, and have been assigned the eclipsed conformation (Fig. 1). $[Pd(C_5Me_5)Cl(PPr^i_3)]$ [4] and $[Pd(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(PPr^i_3)]$ [5] are typical, with shorter C(2)–C(3) and C(4)–C(5) bonds, rationalized in terms of the reversal of the relative population of the two e_1 orbitals caused by the rotation of the intersecting planes. A feature of both these structures is that the Pd–C(1) bond is 0.09–0.12 Å shorter than any of the other Pd–C bonds, leading to the description of the attachment mode of the cyclopentadienyl rings as $\eta^1\eta^4$ rather than η^5. EHT molecular orbital calculations on $[Pd(C_5H_5)(CH_3)(PH_3)]$ offered an explanation of this phenomenon [5]. However, a recent report on the related structure $[Pd(C_5H_5)(P\{OPh\}_2OC_6H_4)]$ [6] suggested to us that other factors might play a role. In $[Pd(C_5H_5)(P\{OPh\}_2OC_6H_4)]$ the sites of the P and C donor atoms are interchanged relative to their positions in $[Pd(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(P^iPr_3)]$ and there is no obvious shortening of the Pd–C(1) bond; indeed, the Pd–C distances of 2.28–2.35 Å show only slight variations.

We have recently examined a number of cyclopentadienyl–palladium compounds [7–9], and scrutiny of these led to the conclusion that simple descriptions of the geometry of these compounds as eclipsed or staggered were inadequate. We have therefore reassessed a number of the more accurate structure determinations of $Pd(\eta^5\text{-}C_5R_5)$ derivatives (R = H or Me) [4–11]. We also report here two additional structures of this type, namely those of $[Pd(C_5H_5)Cl(PMe_2Ph)]$ and $[Pd(C_5H_5)(dppe)]PF_6$, thus extending the series available for comparison. The chloro complex contains ligand atoms which are very dissimilar in character, whereas the dppe complex contains two identical donor groups.

2. Results and discussion

Structural results for $[PdCp(dppe)]PF_6$ and $[PdCpCl(PMe_2Ph)]$ are presented in Tables 1 and 2. Table 3 contains a summary of important geometric features in all mononuclear PdCpLL′ complexes which have been characterized by diffraction analysis. In an attempt to compare the individual structures with the idealized staggered and eclipsed conformations of the PdCpLL′ moiety (Fig. 1) we have adopted the following procedure in compiling Table 3. For each structure we have calculated the ten L– or L′–Pd–C(Cp)–C torsion angles (where C(Cp) is the centroid of the cyclopentadienyl ring). The smallest of these is designated ω_1, and ω_2 and ω_3 are then defined as shown in Fig. 2. Values of 0°, 36° and −36° respectively for these torsion angles characterize an exactly eclipsed conformation whereas the idealized staggered conformation would give rise to angles of 18°, 54° and −18° respectively.

Our study of the $[PdCp(dppe)]^+$ cation 7 (Fig. 3) reveals that it adopts an intermediate geometry which is closer to staggered than eclipsed, with ω_1, ω_2 and ω_3 values of 11.0°, 55.0° and −17.6° respectively (ω_1 being defined by P(1)–Pd–C(Cp)–C(1)). However, the variations in the Pd–C distances are more typical of the

TABLE 1. Selected bond lengths and angles for $[(C_5H_5)Pd(Ph_2PCH_2CH_2PPh_2)][PF_6]$

	Bond length (Å)		Bond length (Å)
Pd–P(1)	2.244(2)	Pd–P(2)	2.254(2)
Pd–C(1)	2.245(11)	Pd–C(2)	2.315(15)
Pd–C(3)	2.297(10)	Pd–C(4)	2.321(11)
Pd–C(5)	2.332(9)	P(1)–C(6)	1.831(6)
P(1)–C(8)	1.818(6)	P(1)–C(14)	1.801(7)
P(2)–C(7)	1.835(7)	P(2)–C(20)	1.822(6)
P(2)–C(26)	1.814(5)	C(1)–C(2)	1.413(20)
C(1)–C(5)	1.396(17)	C(2)–C(3)	1.379(21)
C(3)–C(4)	1.345(16)	C(4)–C(5)	1.294(15)
C(6)–C(7)	1.528(8)		
	Bond angle (°)		Bond angle (°)
P(1)–Pd–P(2)	86.3(1)	P(1)–Pd–C(Cp)	134.8
P(2)–Pd–C(Cp)	138.8	Pd–P(1)–C(6)	107.0(3)
Pd–P(1)–C(8)	114.6(3)	Pd–P(1)–C(14)	116.1(2)
C(6)–P(1)–C(8)	104.9(3)	C(6)–P(1)–C(14)	105.4(3)
C(8)–P(1)–C(14)	107.8(3)	Pd–P(2)–C(7)	108.1(2)
Pd–P(2)–C(20)	112.8(2)	Pd–P(2)–C(26)	119.1(2)
C(7)–P(2)–C(20)	104.5(3)	C(7)–P(2)–C(26)	106.3(3)
C(20)–P(2)–C(26)	105.0(3)	C(2)–C(1)–C(5)	108.1(11)
C(1)–C(2)–C(3)	103.8(12)	C(2)–C(3)–C(4)	109.3(10)
C(3)–C(4)–C(5)	111.4(10)	C(1)–C(5)–C(4)	107.1(10)
P(1)–C(6)–C(7)	108.7(4)	P(2)–C(7)–C(6)	108.6(4)

Cp is the centroid of the cyclopentadienyl ring defined by C(1) to C(5).

TABLE 2. Selected bond lengths and angles for $[(C_5H_5)PdCl(PMe_2Ph)]$

	Bond length (Å)		Bond length (Å)
Pd-Cl	2.340(1)	Pd-P	2.217(1)
Pd-C(9)	2.340(4)	Pd-C(10)	2.179(3)
Pd-C(11)	2.340(3)	Pd-C(12)	2.385(4)
Pd-C(13)	2.378(4)	P-C(1)	1.802(3)
P-C(2)	1.819(4)	P-C(3)	1.815(3)
C(3)-C(4)	1.393(4)	C(3)-C(8)	1.383(4)
C(4)-C(5)	1.387(5)	C(5)-C(6)	1.384(7)
C(6)-C(7)	1.378(6)	C(7)-C(8)	1.393(5)
C(9)-C(10)	1.433(5)	C(9)-C(13)	1.366(6)
C(10)-C(11)	1.431(4)	C(11)-C(12)	1.346(5)
C(12)-C(13)	1.441(5)		
	Bond angle (°)		Bond angle (°)
Cl-Pd-P	90.7(1)	Cl-Pd-C(Cp)	133.9
P-Pd-C(Cp)	135.4	Pd-P-C(1)	113.9(2)
Pd-P-C(2)	115.6(2)	Pd-P-C(3)	113.8(1)
C(1)-P-C(2)	103.4(2)	C(1)-P-C(3)	105.7(2)
C(2)-P-C(3)	103.2(2)	P-C(3)-C(4)	121.9(3)
P-C(3)-C(8)	119.1(3)	C(4)-C(3)-C(8)	119.0(3)
C(3)-C(4)-C(5)	120.5(3)	C(4)-C(5)-C(6)	119.7(4)
C(5)-C(6)-C(7)	120.3(4)	C(6)-C(7)-C(8)	119.8(4)
C(3)-C(8)-C(7)	120.5(3)	C(10)-C(9)-C(13)	107.0(3)
C(9)-C(10)-C(11)	107.5(3)	C(10)-C(11)-C(12)	107.4(3)
C(11)-C(12)-C(13)	109.1(3)	C(9)-C(13)-C(12)	108.2(3)

C(Cp) is the centroid of the cyclopentadienyl ring defined by C(9)–C(13).

pattern expected for an eclipsed conformation: the Pd–C(1) distance of 2.245(11) Å appears distinctly shorter than the remaining Pd–C bond lengths of 2.297(10)–2.332(9) Å. This does not seem to be a consequence of a distortion of the Cp ring from planarity since the maximum displacement of a carbon atom from the ring plane is only 0.032(15) Å and involves C(2). The slight asymmetry in the P–Pd–C(Cp) angles (134.8 and 138.8°) suggests that the Cp ring tilts so as to bring C(1) closer to the metal atom. The ring C–C distances show significant variations (from 1.29(2)–1.41(2) Å) which do not correspond to the pattern considered typical of either staggered or eclipsed geometries.

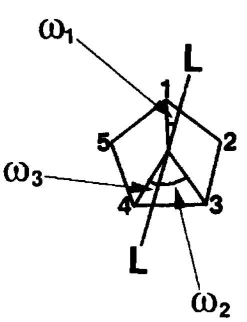

Fig. 2. Definition of cyclopentadienyl ring orientations: ω_1 is the smallest of the ten L–Pd–ring centroid–C(ring) torsion angles and ω_2 and ω_3 the smallest torsion angles involving the second donor atom L′.

These results for 7 (the PF_6^- salt) agree with those reported for the $CF_3SO_3^-$ salt (9 in Table 3) by Bachechi *et al.* [11]. The two salts are nearly isomorphous and libration of the Cp ring about the Pd–C(Cp) vector is substantial in both structures (see Fig. 3). The libration appears to be a somewhat greater problem in 9 where the ring C–C distances (1.29(2)–1.60(4) Å) suggest systematic error in the positions of the ring C atoms, as do the ω_1, ω_2 and ω_3 values of 12.9°, 45.2° and −35.7° respectively. The ω_1 torsion angle in 9 involves P(1) and C(28) and the P(1)–Pd–C(Cp) angle of 132° is less obtuse than that of 141° involving P(2) (*cf.* 7). In

TABLE 3. Geometrical features of [PdCpLL′]

Compound	L-Pd-L′ angle (°)	Plane Intersect Angle (°)	L	L′	ω_1[a]	ω_2	ω_3	Pd-C(1) (Å)	Pd-C(2) (Å)	Pd-C(3) (Å)	Pd-C(4) (Å)	Pd-C(5) (Å)	Reference
1 $PdCpCl(PMe_2Ph)$	90.7(1)	89.3	P	Cl	0.2	38.7	−36.5	2.179(3)	2.340(3)	2.385(4)	2.378(4)	2.340(4)	This work
2 $PdCp(\eta^1\text{-}Cp)(P^iPr_3)$	96.1(2)	87.3	C	P	1.2	41.6	−33.7	2.260(10)	2.350(9)	2.347(7)	2.373(7)	2.390(8)	[5]
3 $[PdCp(SbPh_3)_2]PF_6$	96.47(5)	86.7	Sb	Sb	1.8	31.9	−37.5	2.232(10)	2.304(10)	2.254(10)	2.280(10)	2.314(10)	[10]
4 $PdCp\{P(OPh)_2(OC_6H_4)\}$	80.2(2)	87.9	P	C	2.9	42.5	−28.3	2.347(9)	2.314(7)	2.347(7)	2.284(7)	2.301(7)	[6]
5 $[PdCp(PMe_2Ph)_2]ClO_4$ (A)	95.7(1)	87.7	P	P	4.2	45.5	−28.7	2.259(7)	2.301(8)	2.301(8)	2.307(8)	2.343(6)	[9]
6 $PdCp^*Cl(P^iPr_3)$ [b]	94.9(1)	89.7	P	Cl	9.1	42.2	−32.9	2.218(4)	2.395(4)	2.403(3)	2.341(4)	2.351(4)	[4]
7 $[PdCp(dppe)]PF_6$	86.3(1)	85.2	P	P	11.0	55.0	−17.6	2.245(11)	2.332(9)	2.321(11)	2.297(10)	2.315(15)	This work
8 $PdCp(C_6H_4N_2Ph)(PCy_3)$	92.4(2)	86.8	P	C	12.4	42.3	30.7	2.337(5)	2.382(5)	2.336(5)	2.303(6)	2.385(6)	[7]
9 $[PdCp(dppe)CF_3SO_3$	86.4(1)	85.7	P	P	12.9	45.2	−35.7	2.287(18)	2.334(22)	2.344(17)	2.317(20)	2.318(19)	[11]
10 $PdCp(C_6H_4N_2Ph)$	78.7(1)	87.4	C	N	15.2	45.8	−27.7	2.167(3)	2.264(3)	2.397(3)	2.407(3)	2.336(3)	[8]
11 $[PdCp(PMe_2Ph)_2]ClO_4$ (B)	98.0(1)	89.9	P	P	18.7	51.5	−19.1	2.270(6)	2.341(6)	2.331(7)	2.252(8)	2.324(6)	[9]

[a] standard deviations in torsion angles range up to 0.7°.

[b] $Cp^* = \eta^5 - C_5Me_5$.

consequence, the Pd–C(28) distance of 2.28(2) Å is shorter than the other Pd–C bond lengths of 2.32(2)–2.35(2) Å. This difference was not considered significant by Bachechi *et al.* [11].

The Pd(dppe) units in **7** and **9** are virtually identical. The Pd–P distances, the P–Pd–P bond angle and the P–C–C–P torsion angle in **7** (2.244(2) Å, 2.254(2) Å, 86.3(1)° and 50.1(4)° respectively) agree well with corresponding values in **9** (2.250(2) Å, 2.266(3) Å, 86.4(1)° and 51°). Broadly similar results have been reported for other palladium–diphosphine complexes [12,13].

The reduction in the local symmetry of the PdLL′ unit from C_{2v} in **7** and **9** to C_s in [PdCpCl(PMe$_2$Ph)], (**1**) is accompanied by a distinct change in the nature of the Pd–cyclopentadienyl interaction. Compound **1** adopts a virtually ideal eclipsed conformation (ω_1, ω_2 and ω_3 are 0.2°, 38.7° and −36.5° respectively) with P–Pd–C(Cp)–C(10) defining ω_1 (see Fig. 4). The Pd–C bond lengths in **1** vary much more sharply than they do in **7** or **9**; thus the Pd–C(10) distance of 2.179(3) Å is only slightly longer than the σ-Pd–C bond length of 2.130(7) Å in [PdCp(η^1-Cp) (P^{i}Pr$_3$)] (**2**) and is much shorter than the Pd–C(9) and Pd–C(11) distances (2.340(4) Å and 2.340(3) Å respectively). The Pd–C(12) and Pd–C(13) bond lengths of 2.385(4) Å and 2.378(4) Å respectively are longer still. These variations appear to be a consequence of a significant distortion of the Cp ring from planarity; the ring is folded by 8.8° about the C(9)–C(11) vector into a symmetrical envelope conformation, thereby bringing C(10) closer to the metal atom. The ring torsion angle across C(12)–C(13) is −0.9(3)°, indicating that C(9), C(11), C(12) and C(13) are coplanar to within experimental error, whereas the torsion angles across C(9)–C(10) and C(10)–C(11) are −9.0(3)° and 8.6(3)° respectively.

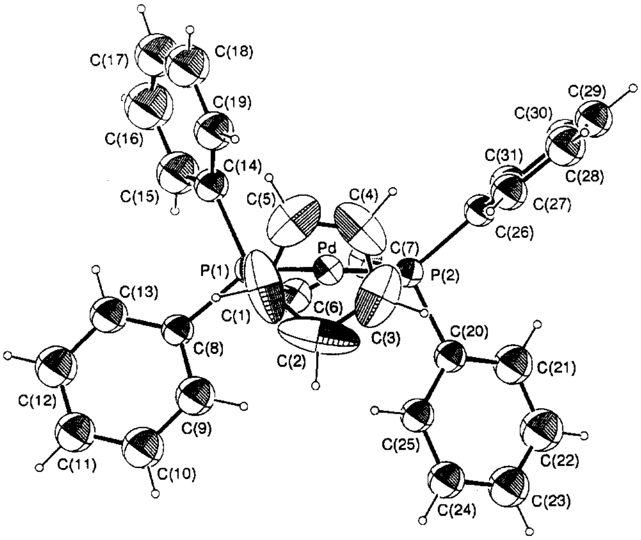

Fig. 3. A view of the structure of [(C$_5$H$_5$)Pd(Ph$_2$PCH$_2$CH$_2$PPh$_2$)][PF$_6$] showing 50% probability ellipsoids. Hydrogen atoms are represented by spheres of arbitrary size.

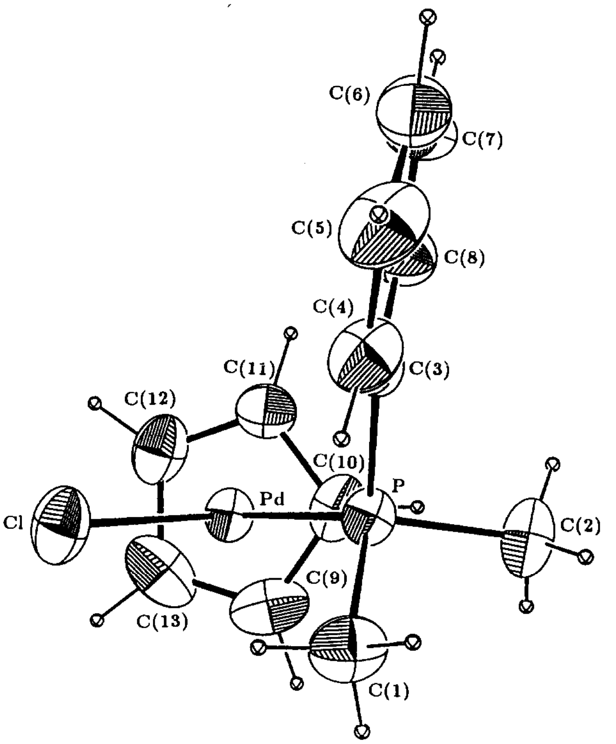

Fig. 4. A view of the structure of [(C$_5$H$_5$)PdCl(PMe$_2$Ph)]. 50% probability ellipsoids are shown except for hydrogen atoms which are represented by spheres of arbitrary size.

The cyclopentadienyl C–C bond lengths in **1** vary in a predictable fashion, given the nearly ideally eclipsed conformation adopted by the complex. The bonds radiating from C(10) (1.431(4) and 1.433(5) Å) are long and the planar C(11)–C(12)–C(13)–C(9) sequence shows butadiene-like bond length alternation (1.346(5), 1.441(5) and 1.366(6) Å). These bond length variations are less obscured by ring libration than is the case with **7** or **9** (*cf.* Figs. 3 and 4).

The Cl–Pd–C(Cp) and P–Pd–C(Cp) angles in **1** are nearly equal (133.9° and 135.4° respectively) and therefore do not seem to be a factor in the variations shown by the Pd–C distances. The Pd–P bond length of 2.217(1) Å in **1** is 0.03–0.05 Å shorter than the more typical distances found in **7** or **9**. The Pd–Cl bond length of 2.340(1) Å differs only slightly from the average value of 2.326 Å derived for 226 such distances in square-planar palladium(II) complexes [14].

The compounds in Table 3 are arranged in order of increasing ω_1. The angles L–Pd–L′ lie in the range

79–98° with values of less than 90° occurring exclusively in chelate complexes. The angles of intersection between the LPdL′ and mean cyclopentadienyl ring planes are all close to 90°. The description of these compounds as pseudo-square planar with the Cp rings occupying two adjacent coordination sites is thus justified.

Although some compounds have structures close to the idealized eclipsed or staggered conformations, scrutiny of Table 3 makes it clear that a complete range of conformations is represented. It is also apparent that neither idealized geometry is favoured by complexes with identical L_2, with widely different LL′, or by chelating ligands; so in general such classifications are not helpful for palladium compounds [PdCpLL′], a conclusion strengthened by our discovery of two quite different conformations within the unit cell of one compound (**5** and **11**) [9].

It might be expected that the sequence of C–C bond distances within the cyclopentadienyl rings would change from that expected for eclipsed conformations to that expected for staggered as Table 3 is descended but this is not observed, many C–C sequences not adhering to either pattern. It should be noted that, in all the structures, librational motion of the Cp ring is large.

Compound **11** [9] has significantly shorter Pd–C(1) and Pd–C(4) bonds of 2.25 Å and 2.27 Å respectively compared to the other Pd–C(Cp) distances of 2.32–2.34 Å and thus closely resembles the staggered arrangement described and explained for [$CoCpL_2$] and [$RhCpL_2$] [1–3]. In the unsymmetrical complexes **1**, **2**, **6** and **10** the Pd–C(1) bond is 0.11–0.18 Å shorter than the mean Pd–C distance and in each case it is by far the shortest of the Pd–C bonds; this is explicable in terms of the fact that L′ exerts a lower *trans* influence than L. In the symmetrical complexes **3**, **5**, **7** and **9**, Pd–C(1) is still the shortest of the Pd–C distances but the differences between Pd–C(mean) and Pd–C(1) of 0.04–0.07 Å are appreciably smaller than those for the unsymmetrical complexes **1**, **2**, **6** and **10**. Finally, in the unsymmetrical complexes **4** and **8**, where L′ = C and L = P (contrast with **2**), the Pd–C bond lengths again reflect a *trans* influence with Pd–C(4) (*trans* to P) 0.02–0.05 Å shorter than Pd–C(1) (*trans* to C).

In conclusion, it appears that (i) the designation of the structures of these complexes as staggered or eclipsed is simplistic and unhelpful, a wide range of orientations being found, (ii) the dominant effect in determining Pd–C(Cp) distances is the *trans* influence of L and L′, any effects of ring orientation with respect to the PdLL′ plane being at best secondary, and (iii), the description of the ring bonding as $\eta^1\eta^4$ rather than η^5 [4,5] is clearly not generally applicable.

3. Experimental details

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WP200SY instrument. Microanalyses were performed at the University of Glasgow.

3.1. Preparation of [$Pd(C_5H_5)Cl(PMe_2Ph)$]

To a suspension of TlC_5H_5 (4.16 g, 15.4 mmol) in tetrahydrofuran (140 ml) was added [$Pd_2Cl_4(PMe_2Ph)_2$] (4.88 g, 7.74 mmol). The mixture was stirred for 30 min and then filtered to remove TlCl (3.43 g). Removal of the solvent left green [$Pd(C_5H_5)Cl(PMe_2Ph)$] (3.1 g (58%)), which was recrystallized from toluene (melting point, 104–106 °C). Anal. Found: C, 44.4; H, 4.7. $C_{13}H_{16}ClPPd$ calcd: C, 45.2; H, 4.7%. ^1H NMR: δ 1.86 (d, $J = 11.79$ Hz, CH_3); 5.60 (d, $J = 2.35$ Hz, C_5H_5) ppm. ^{31}P NMR: 8.55 ppm.

3.2. Preparation of [$Pd(C_5H_5)(dppe)$]PF_6 [10]

A mixture of [$PdCl_2(dppe)$] (2.5 g, 4.0 mmol) and $AgNO_3$ (1.38 g, 8.12 mmol) in 1:1 aqueous methanol

TABLE 4. Crystallographic data and refinement details for the complexes [$(C_5H_5)PdCl(PMe_2Ph)$] and [$(C_5H_5)Pd(Ph_2PCH_2CH_2PPh_2)$][$PF_6$]

Formula	$C_{13}H_{16}ClPPd$	$C_{31}H_{29}F_6P_3Pd$
Formula weight	345.10	714.90
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a (Å)	9.9092(6)	9.8281(5)
b (Å)	10.2707(5)	12.0773(8)
c (Å)	13.4742(6)	13.3808(7)
β (°)		110.760(4)
U (Å^3)	1371.3(1)	1485.1(2)
Z	4	2
D_{calc} (g cm^{-3})	1.672	1.598
$F(000)$	688	720
μ (cm^{-1})	16.2	8.3
Crystal (mm × mm × mm)	0.83 × 0.47 × 0.39	0.45 × 0.45 × 0.28
θ range (°)	2–30	2–30
h	0–13	$\overline{13}$–13
k	$\overline{14}$–14	$\overline{17}$–0
l	$\overline{19}$–19	0–18
Number of reflections measured	8371	4710
Number of unique reflections	3992	4541
Number of observed reflections	3784	4030
R_{int}	0.022	0.015
R	0.0270	0.0412
R_w	0.0355	0.0569
Number of parameters	147	250
$\lvert\Delta\rho\rvert_{max}$ (electrons Å^{-3})	0.70	0.70
η	1.03(6)	1.2(2)

(160 ml) was stirred for 45 min to give a yellow–green solution and a precipitate. Cyclopentadiene (1.6 ml) was added and the mixture turned red. AgCl was removed by filtration and addition of excess KPF_6 (0.91 g, 4.92 mmol) to the bright-red solution led to precipitation of pink $[Pd(C_5H_5)(dppe)]PF_6$ (0.45 g (15.7%)), which was recrystallized from 1 : 1 CH_2Cl_2–Et_2O. Anal. Found: C, 51.8; H, 3.9. $C_{31}H_{29}F_6P_3Pd$ calcd: C, 52.1; H, 4.1%. ^1H NMR: δ 2.83 (d, $J = 21.6$ Hz, CH_2); 6.09 (t, $J = 2.05$ Hz, C_5H_5) ppm. ^{31}P NMR: −15.97 (dppe); −145.5 (septet, PF_6^-) ppm.

TABLE 5. Fractional atomic coordinates and isotropic displacement parameters for $[(C_5H_5)Pd(Ph_2PCH_2CH_2PPh_2)][PF_6]$

	x	y	z	U [a] (Å^2)
Pd	−0.23701(3)	−0.25000	−0.23135(2)	0.034
P(1)	−0.11942(13)	−0.40677(16)	−0.24051(10)	0.036
P(2)	−0.36600(13)	−0.27645(15)	−0.40617(10)	0.034
P(3)	−0.24784(20)	−0.41388(24)	−0.77904(16)	0.062
F(1)	−0.1292(14)	−0.5036(13)	−0.7426(10)	0.189
F(2)	−0.1882(16)	−0.3945(15)	−0.6586(9)	0.215
F(3)	−0.3735(12)	−0.3418(13)	−0.8093(19)	0.287
F(4)	−0.1366(15)	−0.3401(21)	−0.7894(17)	0.369
F(5)	−0.3424(15)	−0.5017(17)	−0.7628(17)	0.282
F(6)	−0.2963(24)	−0.4464(20)	−0.8934(9)	0.318
C(1)	−0.1077(11)	−0.1798(12)	−0.0702(8)	0.102
C(2)	−0.1248(16)	−0.0914(12)	−0.1429(13)	0.132
C(3)	−0.2730(16)	−0.0731(8)	−0.1827(7)	0.096
C(4)	−0.3376(8)	−0.1405(10)	−0.1329(9)	0.085
C(5)	−0.2436(14)	−0.2033(8)	−0.0640(6)	0.088
C(6)	−0.1579(6)	−0.4350(5)	−0.3823(4)	0.046
C(7)	−0.3192(6)	−0.4134(5)	−0.4439(4)	0.044
C(8)	0.0777(5)	−0.3978(5)	−0.1815(4)	0.039(1)
C(9)	0.1418(8)	−0.3039(7)	−0.2029(6)	0.058(2)
C(10)	0.2945(9)	−0.2937(8)	−0.1643(7)	0.066(2)
C(11)	0.3768(8)	−0.3751(7)	−0.1048(6)	0.060(2)
C(12)	0.3153(9)	−0.4654(8)	−0.0785(7)	0.066(2)
C(13)	0.1624(7)	−0.4789(6)	−0.1194(6)	0.053(1)
C(14)	−0.1752(6)	−0.5294(5)	−0.1889(4)	0.043(1)
C(15)	−0.1442(9)	−0.6341(8)	−0.2165(7)	0.068(2)
C(16)	−0.1918(10)	−0.7324(11)	−0.1785(8)	0.089(3)
C(17)	−0.2719(9)	−0.7161(8)	−0.1132(7)	0.073(2)
C(18)	−0.3004(10)	−0.6129(8)	−0.0807(8)	0.072(2)
C(19)	−0.2504(8)	−0.5206(7)	−0.1184(6)	0.057(2)
C(20)	−0.3160(6)	−0.1803(5)	−0.4922(4)	0.039(1)
C(21)	−0.4052(8)	−0.1627(7)	−0.5971(6)	0.058(2)
C(22)	−0.3599(9)	−0.0952(8)	−0.6638(7)	0.071(2)
C(23)	−0.2291(9)	−0.0419(8)	−0.6233(7)	0.064(2)
C(24)	−0.1387(7)	−0.0583(6)	−0.5193(5)	0.052(1)
C(25)	−0.1817(6)	−0.1264(6)	−0.4535(5)	0.044(1)
C(26)	−0.5631(5)	−0.2710(4)	−0.4520(4)	0.038(1)
C(27)	−0.6304(7)	−0.1955(6)	−0.4080(5)	0.050(1)
C(28)	−0.7806(8)	−0.1868(7)	−0.4441(6)	0.060(2)
C(29)	−0.8658(6)	−0.2548(8)	−0.5262(4)	0.052(1)
C(30)	−0.7986(7)	−0.3302(6)	−0.5729(6)	0.055(1)
C(31)	−0.6479(7)	−0.3384(6)	−0.5356(5)	0.052(1)

[a] U is the isotropic displacement parameter for C(8) to C(31). For other atoms both here and in Table 6 $U = \frac{1}{3}\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i^*a_j^*(\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

TABLE 6. Fractional coordinates and equivalent isotropic displacement parameters for $[(C_5H_5)PdCl(PMe_2Ph)]$

	x	y	z	U (Å^2)
Pd	0.18217(1)	−0.00146(2)	0.06745(1)	0.031
Cl	0.13900(9)	−0.14158(7)	0.20064(5)	0.053
P	0.36753(7)	−0.11170(6)	0.02976(5)	0.033
C(1)	0.3423(3)	−0.2850(3)	0.0202(2)	0.051
C(2)	0.4457(3)	−0.0696(3)	−0.0881(2)	0.053
C(3)	0.5037(3)	−0.0902(3)	0.1183(2)	0.037
C(4)	0.5648(3)	−0.1956(3)	0.1655(2)	0.049
C(5)	0.6756(4)	−0.1770(4)	0.2267(3)	0.067
C(6)	0.7256(4)	−0.0527(5)	0.2414(2)	0.067
C(7)	0.6634(3)	0.0529(4)	0.1979(3)	0.065
C(8)	0.5518(4)	0.0340(3)	0.1367(2)	0.053
C(9)	0.0488(4)	0.0893(3)	−0.0580(2)	0.057
C(10)	0.1780(3)	0.1499(3)	−0.0458(2)	0.047
C(11)	0.1733(3)	0.2241(2)	0.0440(2)	0.045
C(12)	0.0569(4)	0.1946(3)	0.0903(2)	0.053
C(13)	−0.0215(3)	0.1095(3)	0.0278(3)	0.062

3.3. Crystal structures of $[(C_5H_5)PdCl(PMe_2Ph)]$ and $[(C_5H_5)Pd(Ph_2PCH_2CH_2PPh_2)]$ $[PF_6]$

Similar experimental and computational methods were used for both structures (Table 4). Measurements were made at 23°C with Mo Kα X-rays ($\lambda = 0.710$ 69 Å) on an Enraf–Nonius CAD4 diffractometer fitted with a graphite monochromator. Cell dimensions were obtained from least-squares treatments of the setting angles of 20 or more high-angle reflections. Intensities were determined from ω–2θ scans and were corrected for Lorentz, polarization and absorption [15] effects. For $[(C_5H_5)PdCl(PMe_2Ph)]$ a correction was also made for a linear decay of 10% in the mean intensity of the standard reflections over the course of the experiment. The structures were solved by Patterson and Fourier methods. They were then refined on F with $w = 1/\sigma(F)^2$ to convergence ($\Delta/\sigma \leqslant 0.18$) by the full-matrix least-squares method using reflections with $I \geqslant 3\sigma(I)$; the data set for $[(C_5H_5)PdCl(PMe_2Ph)]$ included 1626 Friedel pairs. Isotropic displacement parameters were refined for phenyl carbon atoms in $[(C_5H_5)Pd(Ph_2PCH_2CH_2PPh_2)][PF_6]$. Otherwise, anisotropic displacement parameters were refined for non-H atoms and allowance was made for the scattering of the H atoms. Methylene and phenyl H atoms were initially positioned using stereochemical criteria whereas methyl group orientations were deduced from difference syntheses. Subsequently, H atoms were constrained to ride on their parent C atoms with a C–H distance of 0.96 Å and $U(H) = 1.2U(C)$. The absolute structure was established in both cases by refining a Rodgers [16] η parameter (see Table 4) and for $[(C_5H_5)PdCl(PMe_2Ph)]$ an isotropic extinction parameter $g = 0.36(3) \times 10^3$ was also refined. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 17 and the calculations were performed on a VAX3600 with the GX package [18]. Final atomic parameters are presented in Tables 5 and 6.

4. Deposited material

Atomic parameters and bond length and angle listings have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Any request for copies of this material should include the full literature citation for this paper.

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References

1 L.R. Byers and L.F. Dahl, *Inorg. Chem., 19* (1980) 277.

2 R.L. Harlow, R.J. McKinney and J.F. Whitney, *Organometallics, 2* (1983) 1839.

3 D.L. Lichtenberger, C.H. Blevins and R.B. Ortega, *Organometallics, 3* (1984) 1614.

4 H.-J. Kraus, H. Werner and C. Krüger, *Z. Naturforsch., 38b* (1983) 733.

5 H. Werner, H.-K. Kraus, U. Schubert, K. Ackermann and P. Hofmann, *J. Organomet. Chem., 250* (1983) 517.

6 A. Albinati, S. Affolter and P.S. Pregosin, *Organometallics, 9* (1990) 379.

7 G.K. Anderson, R.J. Cross, L. Manojlović-Muir, K.W. Muir and M. Rocamora, *Organometallics*, 7 (1988) 1520.

8 G.K. Anderson, R.J. Cross, K.W. Muir and L. Manojlović-Muir, *J. Organomet. Chem., 362* (1989) 225.

9 L. Manojlović-Muir, R.J. Cross and R.W. Hoyle, *Acta Crystallogr., Sect. C, 49* (1993) 1603.

10 N.K. Roberts, B.W. Skelton, A.H. White and S.B. Wild, *J. Chem. Soc., Dalton Trans.*, (1982) 2093.

11 F. Bachechi, R. Lehmann and L.M. Venanzi, *J. Crystallogr. Spectrosc. Res., 18* (1988) 721.

12 See especially W.L. Steffen and G.J. Palenik, *Inorg. Chem., 15* (1976) 2432; D.H. Farrer and G. Ferguson, *J. Crystallogr. Spectrosc. Res., 12* (1982) 465.

13 *International Tables for Crystallography*, Vol. C, Kluwer, Dordrecht, 1992, p. 765.

14 *International Tables for Crystallography*, Vol. C, Kluwer, Dordrecht, 1992, p. 774.

15 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A39* (1983) 158.

16 D. Rodgers, *Acta Crystallogr., Sect. A37* (1981) 734.

17 *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, 1974, pp. 99, 119.

18 P.R. Mallinson and K.W. Muir, *J. Appl. Crystallogr., 18* (1985) 51.