Crystal and Molecular Structure of $[Pd_3\{C_3Ph(p\text{-}MeOC_6H_4)_2\}_2(acac)_2]$, derived from a Tri-arylcyclopropenium Salt and a Palladium(0) Complex †

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The crystal and molecular structure of $[Pd_3\{C_3Ph(p\text{-}MeOC_6H_4)_2\}_2(acac)_2]$ (2) {obtained from $[Pd_2(PhCH{:}CHCOCH{:}CHPh)_3(CHCl_3)]$ and $[C_3Ph(p\text{-}MeOC_6H_4)_2]Br$ followed by reaction of the product with Tl(acac)} has been determined. Crystals are monoclinic, space group $C2/c$ (C^6_{2h}, No. 15) with a = 14.99(1), b = 21.88(2), c = 18.98(2) Å, β = 90.5(1)°, U = 6 227 Å^3, and Z = 4; R = 0.060 for 2 259 independent reflections. The compound is composed predominantly (67%) of enantiomers of one isomer which arises from the addition of the $C_3R^1R^2_2$ moiety (R^1 = phenyl, R^2 = p-MeOC$_6$H$_4$) to Pd(1) by ring-opening of the CR^2–CR^2 bond [$R^2C(1)$–$C(2)R^1$ = 1.370(17); $R^1C(2)$–$C(3)R^2$ = 1.443(19); $R^2C(1) \cdots C(3)R^2$ = 2.116(17) Å]. Pd(1) is also O,O′-bonded to the acac (pentanedionato) ligand. Two such units are linked by Pd(2) such that the three Pd atoms form a triangular framework [Pd(1)–Pd(2) = 2.662(2) Å; Pd(1)–Pd(1′) = 4.769(2) Å; Pd(1)–Pd(2)–Pd(1′) = 127°], the two halves of the molecule being related by a two-fold axis of symmetry through Pd(2). The structure may be viewed either as having the acyclic $C_3R^1R^2_2$ ligands bridging Pd(1)–Pd(2) [and Pd(2)–Pd(1′)] or as two palladiacyclobutenyl ligands [$>Pd(1)C_3R^1R^2_2$] π^4-bonded to Pd(2). The presence of other isomers of (2) (33%) is deduced from the electron densities in the p-positions of the C_3-aryl substituents; these isomers arise from cleavage of CR^1–CR^2 bonds in the original $C_3R^1R^2_2$ salt.

THE following paper describes the chemistry of a novel series of palladium and platinum complexes (1) derived from reaction of triarylcyclopropenium salts with zerovalent palladium and platinum olefin complexes.[1]

$$\begin{array}{l} \underset{(\text{dba} = \text{PhCH:CHCOCH:CHPh})}{[M_2(\text{dba})_3(\text{solvent})]} + [C_3R^1R^2_2]^+Br^- \longrightarrow \underset{(1)\ M = Pd,\ Pt;\ R^1 = R^2 = Ph}{[M_3(C_3R^1R^2_2)_2Br_2]} \\ \qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow \text{Tl(acac)};\ \begin{array}{l} R^1 = Ph,\ R^2 = p\text{-MeOC}_6H_4 \\ R^1 = R^2 = p\text{-MeOC}_6H_4 \end{array} \\ \qquad\qquad\qquad\qquad\qquad\qquad [M_3(C_3R^1R^2_2)(acac)_2] \end{array}$$

In order to establish the structures of these compounds, the pentanedionato (acetylacetonato, acac) derivative $[Pd_3\{C_3Ph(p\text{-}MeOC_6H_4)_2\}_2(acac)_2]$, (2), was studied by single-crystal X-ray diffraction. The compound (2) was obtained by reaction of $[Pd_3\{C_3Ph(p\text{-}MeOC_6H_4)_2\}_2Br_2]$ with Tl(acac). A preliminary communication on part of this work has appeared.[2]

EXPERIMENTAL

A crystal of the compound of approximate dimensions 0.020 × 0.020 × 0.007 cm was selected from a batch grown from a solution in chloroform–diethyl ether–light petroleum (b.p. 40—60 °C) (1 : 1 : 2 v/v). A good single crystal could not be found; the one used had a small crystal embedded in it with an orientation very different from that of the main crystal, and such that the diffraction peaks did not appear to interfere.

Crystal Data.—$C_{56}H_{52}O_8Pd_3$ [$(C_2H_5)_2O$ of crystallisation], M = 1 246.4; monoclinic, a = 14.99(1), b = 21.88(2), c = 18.98(2) Å, β = 90.5(1)°, U = 6 227 Å^3, Z = 4; space group $C2/c$ (C^6_{2h}, No. 15) from systematic absences; ρ(calc.) = 1.329, ρ(obs.) = 1.38 g cm^{-3}; Mo-K_α radiation, λ = 0.710 69 Å. The cell constants were determined from least-squares fit to the setting angles of 104 reflections centred manually.

Three-dimensional X-ray data (6.5° < 2θ < 50°) were collected with the crystal mounted along the b-axis using Mo-K_α radiation (graphite monochromator) and a Stoe STADI-2 diffractometer by the moving-crystal stationary-counter method. Variable-width scans were measured with a background count at each extremity of the scan. 2 259 Independent reflections were collected with $I_{obs.} \geqslant 3\sigma(I_{obs.})$ and the structure was solved using Patterson and Fourier methods. Lorentz and polarisation corrections were applied, no allowance being made for extinction or absorption since μ = 8.92 cm^{-1}. The central palladium atom lies on the

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† No reprints available.

[1] A. Keasey and P. M. Maitlis, *J.C.S. Dalton*, following paper.

[2] A. Keasey, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1977, 178.

crystallographic C_2 axis, so that only half the molecule is unique. Block-diagonal least-squares refinement has finally reduced R to 0.060, with anisotropic temperature factors for all non-hydrogen atoms which do not show disordering (those atoms which are disordered have been left as isotropic). Individual atom refinement was allowed initially, then the phenyl rings were treated as groups of fixed geometry, and finally the entire p-($-OC_6H_4C-$) units were treated as fixed geometry groups (using the O-phenyl and C-phenyl distances obtained from the individual atom refinement) as was the pentanedionato-ligand. This gave the structure shown for compound (2) (Figure 1).

At a fairly advanced stage of the refinement ($R = 0.076$) a difference-Fourier synthesis showed some areas of small electron density. One of these was found to be in the *para*-position of the phenyl ring (B) attached to the central carbon [C(2)] of the C_3 ligand. This suggested that the two methoxy-groups present on each [$C_3Ph(p\text{-}MeOC_6H_4)_2$] ligand were to some extent disordered over the *para*-positions of all three aryl substituents.

The populations of the three p-methoxy-oxygens [O(A), O(B), O(C)] were manually adjusted using the criterion that the total electron density should correspond to two oxygen atoms and that all should have similar isotropic temperature factors. Each of the two methoxy-carbons [Me(A), Me(C)] on the two end rings (A,C) was given the same population factor as the oxygens [O(A), O(C)] to which it is attached. Although this treatment is only an approximation (since a different type of disorder could also be associated with these atoms), it was found that it gave sensible isotropic temperature factors for Me(A) and Me(C) though they were higher than the isotropic temperature factors of O(A) and O(C) respectively. The relative populations of O(A), O(B), and O(C) were found to be 0.97 : 0.33 : 0.70. No localised region of electron density could be found for the central methoxy-carbon [Me(B)] but this is not surprising since only a very small amount of electron density is involved and since this methyl could also be further disordered.

Although the atoms in the groups were assigned anisotropic thermal parameters, the presence of disorder in these sites means that these anisotropic values reflect to some extent the disorder associated with the atoms common to both phenyl and p-methoxyphenyl substituents as well as the thermal vibration.

The other area of electron density on the difference-Fourier synthesis was remote (>3.8 Å) from the atoms of the complex and could be resolved into six peaks. They were initially introduced into the structure-factor calculation as full carbon atoms but their populations had to be manually reduced to 0.4 so as to give reasonable isotropic temperature factors after refinement. A further difference-Fourier synthesis at this stage showed that some electron density in this part of the cell was still unaccounted for but since the density was remote and clearly reflected the presence of solvent of crystallisation further computation was not felt to be justified. In view of the method of preparation of the crystals of (2) the solvent of crystallisation is probably severely disordered diethyl ether, the disordering possibly being due to the methoxy-disorder discussed above.

Atomic scattering factors were taken from reference 3. Programs used were part of the Sheffield X-ray system and calculations were performed on the Sheffield University ICL 1906S computer. Atomic co-ordinates are given in Table 1, selected interatomic distances and angles in Table 2, and least-squares planes in Table 3. Tables of thermal parameters and observed and calculated structure factors are listed as Supplementary Publication No. SUP 22338 (44 pp.).*

TABLE 1

Atomic co-ordinates $\times 10^4$ [except $\times 10^5$ for Pd(1) and Pd(2)]

Atom	X	Y	Z
Pd(1)	483(8)	4 668(6)	12 447(6)
Pd(2)	0(0)	10 076(8)	25 000(0)
C(1)	126(6)	1 379(4)	1 449(7)
C(2)	997(7)	1 379(5)	1 675(9)
C(3)	1 059(7)	738(6)	1 847(8)
C(A1)	−531(5)	1 874(3)	1 314(4)
C(A2)	−371(5)	2 462(4)	1 571(4)
C(A3)	−988(5)	2 927(3)	1 444(4)
C(A4)	−1 766(5)	2 804(3)	1 059(4)
C(A5)	−1 926(5)	2 217(4)	802(4)
C(A6)	−1 308(5)	1 751(3)	929(4)
O(A)	−2 359(6)	3 251(4)	937(7)
Me(A)	−2 290(16)	3 832(11)	1 288(12)
C(B1)	1 657(5)	1 863(4)	1 673(6)
C(B2)	1 772(6)	2 220(5)	1 071(5)
C(B3)	2 407(7)	2 686(4)	1 070(5)
C(B4)	2 928(5)	2 795(4)	1 670(6)
C(B5)	2 813(6)	2 438(5)	2 271(5)
C(B6)	2 177(7)	1 972(4)	2 273(5)
O(B)	3 538(7)	3 243(5)	1 668(9)
C(C1)	1 843(5)	399(4)	2 127(5)
C(C2)	2 700(6)	549(4)	1 901(5)
C(C3)	3 437(5)	230(4)	2 164(5)
C(C4)	3 318(5)	−239(4)	2 653(5)
C(C5)	2 462(6)	−389(4)	2 879(5)
C(C6)	1 724(5)	−70(4)	2 616(5)
O(C)	4 026(7)	−545(6)	2 906(8)
Me(C)	3 914(23)	−952(17)	3 410(18)
O(1)	338(5)	−465(4)	1 130(5)
O(2)	−1 093(5)	344(4)	608(5)
Me(4)	219(9)	−1487(3)	808(10)
C(4)	−142(6)	−843(3)	789(6)
C(5)	−924(6)	−726(4)	421(6)
C(6)	−1 342(5)	−165(4)	352(5)
Me(6)	−2 196(7)	−122(7)	−72(7)
X(1)	4 393(34)	1 349(23)	392(26)
X(2)	4 550(33)	1 783(23)	695(25)
X(3)	5 000(33)	1 761(22)	1 324(26)
X(4)	5 815(32)	1 392(23)	1 337(25)
X(5)	5 973(30)	999(21)	892(23)
X(6)	5 114(38)	848(27)	328(30)

RESULTS AND DISCUSSION

The unit cell of the compound contains pairs of centrosymmetrically related enantiomers; the essential features of the molecule are shown in Figure 1 and may be summarised as follows.

Three Pd atoms are arranged in a triangular fashion and a crystallographic two-fold symmetry axis passes through the central metal atom, Pd(2). This relates the primed and unprimed atoms in the molecule and the discussion will, therefore, mostly be concerned with one half of the molecule since only one half is unique.

The terminal palladium, Pd(1), is O,O′-bonded to the pentanedionato (acac) ligand and the C_3 ligand bridges Pd(1)–Pd(2). The angle Pd(1)–Pd(2)–Pd(1′) is 127.2°, Pd(1)–Pd(2) [2.662(2) Å] is well within the range

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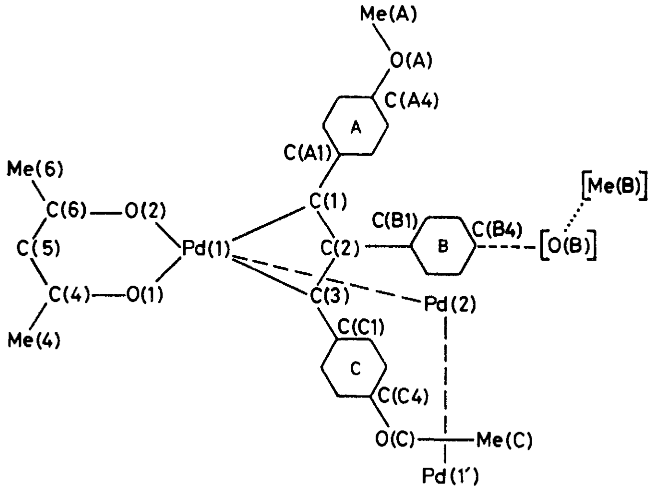
* See Notice to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue, for details of the Scheme.

[3] 'International Tables for X-Ray Crystallography,' vol 4, Kynoch Press, Birmingham, 1974.

(2.531—2.699 Å)[4] reported for Pd–Pd metal–metal bonds but there is no significant bonding between Pd(1) and Pd(1′) [4.769(2) Å].

TABLE 2

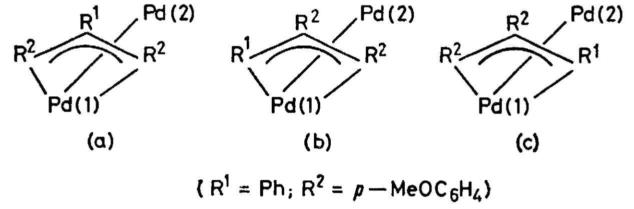
Selected bond lengths (Å) and angles (°) of complex (2) (e.s.d.s in parentheses)



Pd(1)–C(1)	2.037(11)	Pd(1)–Pd(2)	2.662(2)
Pd(1)–C(2)	2.579(14)	Pd(1)–Pd(1′)	4.769(2)
Pd(1)–C(3)	1.981(13)	Pd(2)–C(1)	2.164(11)
Pd(1)–O(1)	2.096(8)	Pd(2)–C(2)	2.321(14)
Pd(1)–O(2)	2.104(8)	Pd(2)–C(3)	2.106(13)
C(1)–C(2)	1.370(17)	C(3)–C(C1)	1.485(16)
C(1)–C(3)	2.116(17)	O(1)–C(4)	1.270(12)
C(1)–C(A1)	1.485(13)	C(4)–C(5)	1.384(13)
C(2)–C(3)	1.443(19)	C(5)–C(6)	1.384(13)
C(2)–C(B1)	1.450(16)	C(6)–O(2)	1.270(12)
Pd(1)–Pd(2)–Pd(1′)	127.2(1)	C(A1)–C(1)–C(2)	133.1(9)
O(1)–Pd(1)–O(2)	89.1(4)	C(A1)–C(1)–C(3)	168.7(8)
O(2)–Pd(1)–C(1)	106.3(3)	C(1)–C(2)–C(3)	97.5(1.0)
O(1)–Pd(1)–C(3)	101.2(4)	C(1)–C(2)–C(B1)	130.3(1.1)
C(1)–Pd(1)–C(3)	63.5(3)	C(3)–C(2)–C(B1)	131.9(1.1)
		C(C1)–C(3)–C(2)	128.1(1.1)
		C(C1)–C(3)–C(1)	168.0(1.0)

The cyclopropenium unit from which (2) is derived has undergone ring-opening on complexing to the metal and while C(1)–C(2) [1.370(17) Å] and C(2)–C(3) [1.443(19) Å] are in the range expected for co-ordinated olefinic double bonds,[5] there can be little bonding between C(1) and C(3) [2.116(17) Å].[6] The angle C(1)–C(2)–C(3) has opened correspondingly from 60° for $C_3R_3^+$ to 97.5(9)° in the complex.

As described in the Experimental section above, an examination of the *X*-ray data shows that in the crystal which was studied there is some disorder of the two methoxy-groups between the *p*-positions of the phenyls (A), (B), and (C) attached to C(1), C(2), and C(3) of the C_3 ligand. From the data it is clear that the major isomer present (67%) contains the arrangement (a) with *p*-methoxyphenyls on the terminal carbons C(1) and C(3) and phenyl on the central carbon C(2). The population analysis suggests the presence of other isomers containing the arrangements (b) and (c) to the extent of approximately 30 and 3% respectively. The existence of other isomers has also been inferred from the ^{1}H n.m.r. spectra of compound (2) and its platinum analogue.[1]



The carbon atoms bonding the aryl groups to the C_3 ligand are very nearly in the same plane [C(A1) −0.277. C(B1) +0.097, and C(C1) +0.012 Å] as the C_3 ligand and the three aryl groups are feathered with respect to each other [angles of aryl planes to C(1)–C(2)–C(3) plane, (A) 27°, (B) 50°, and (C) 37°]. All the four external angles, C(A1)–C(1)–C(2), C(1)–C(2)–C(B1), C(3)–C(2)–C(B1), and C(2)–C(3)–C(1) are close to 131°.

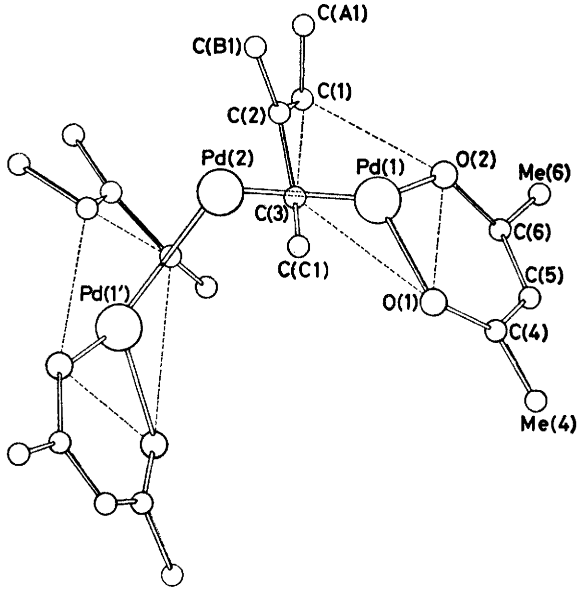


FIGURE 1 View of the molecule (2) projected in the plane Pd(1)–Pd(2)–Pd(1′). Phenyl and *p*-methoxyphenyl substituents are omitted for clarity; for more detail see diagram for Table 2

The C_3 ligand is asymmetrically placed with respect to Pd(1) and Pd(2); C(1) and C(3) are nearer to Pd(1) [2.037(11), 1.981(13) Å] than to Pd(2) [2.164(11), 2.106(13) Å] but C(2) is closer to Pd(2) [2.321(14) Å] than to Pd(1) [2.579(14) Å].

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[4] G. Allegra, C. T. Casagrande, A. Immirzi, L. Porri, and G. Vitulli, *J. Amer. Chem. Soc.*, 1970, **92**, 289; Y. Kobayashi, Y. Iitaka, and H. Yamazaki, *Acta Cryst.* (*B*), 1972, **28**, 899; E. Ban, P. T. Cheng, J. Jack, S. C. Nyburg, and J. Powell, *J.C.S. Chem. Comm.*, 1973, 368; H. Werner, D. Tune, G. Parker, C. Krüger, and D. J. Brauer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 185; A. Ducruix, H. Felkin, C. Pascard, and G. K. Turner, *J.C.S. Chem. Comm.*, 1975, 615; S. Z. Goldberg and R. Eisenberg, *Inorg. Chem.*, 1976, **15**, 535; B. R. Penfold and R. Colton, *J.C.S. Chem. Comm.*, 1976, 485; A. L. Balch, J. R. Boehm, H. Hope, and M. M. Olmstead, *J. Amer. Chem. Soc.*, 1976, **98**, 7431.

[5] S. D. Ittel and J. A. Ibers, *Adv. Organometallic Chem.*, 1976, **14**, 33.

[6] See, for example, discussion in A. Segnitz, E. Kelly, S. H. Taylor, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **124**, 113.

TABLE 3

Equations of, and angles between, planes in complex (2) [a]

Set			
1	Pd(1)–O(1)–O(2):	$-0.5452X - 0.2032Y + 0.8133Z =$	1.6854
2	Pd(1)–C(1)–C(3):	$+0.5685X + 0.1255Y - 0.8131Z =$	−1.7631
3	O(1)–C(4)–C(5)–C(6)–O(2):	$-0.5347X - 0.1841Y + 0.8247Z =$	1.6956
4	C(1)–C(2)–C(3):	$+0.3067X - 0.1978Y - 0.9310Z =$	−3.1065
5	Pd(2)–C(1)–C(3):	$+0.5569X + 0.7476Y + 0.3620Z =$	+3.3439
6	Pd(2)–C(1′)–C(3′):	$-0.5569X + 0.7476Y - 0.3620Z =$	−0.0470
7	Pd(1′)–O(1′)–O(2′):	$-0.5452X + 0.2032Y + 0.8133Z =$	6.0772
8	Pd(1)–C(2)–C(5):	$0.6021X - 0.6283Y + 0.4927Z =$	0.5539
9	Pd(1′)–C(2′)–C(5′)	$-0.8225X - 0.5676Y + 0.0378Z =$	−0.2017
10	Pd(1)–Pd(2)–Pd(1′)	$-0.9993X - 0.0000Y - 0.0388Z =$	−0.1441
11	Plane of ring A:	$-0.4785X - 0.2336Y + 0.8465Z =$	1.5434
12	Plane of ring B:	$-0.6891X + 0.6446Y + 0.3312Z =$	1.9868
13	Plane of ring C:	$0.0805X + 0.6608Y + 0.7463Z =$	3.8093

Angles (°) between planes:

Set	1	2	3	4	5	6	7	8	9	10	11	12
2	175.4											
3	1.4	176.1										
4	152.2	25.0	153.6									
5	99.3	83.3	97.9	108.3								
6	98.2	85.9	98.0	89.0	83.2							
7	23.4	161.0	22.3	164.7	81.8	80.7						
8	78.5	97.9	78.5	98.6	87.5	169.5	93.2					
9	53.5	124.7	54.9	100.1	150.3	88.9	68.7	96.9				
10	59.1	122.4	59.8	105.7	124.8	55.2	59.1	128.4	34.9			
11	4.6	171.7	4.5	152.7	97.7	102.4	25.6	74.0	56.1	63.6		
12	59.1	125.5	58.5	130.3	77.4	41.8	39.1	131.0	77.7	47.5	62.6	
13	64.6	118.6	63.2	143.2	36.0	79.7	45.8	89.9	114.4	96.3	64.0	51.9

[a] Equations are given in the form, $lX + mY + nZ = d$, where X, Y, and Z are co-ordinates in Å referred to the axes a, b, and c^*.

The pentanedionato-ligand is attached to Pd(1) in a conventional manner; all bond lengths are normal, and the atoms are virtually co-planar since the dihedral angle between the plane including O(1)–O(2)–C(6)–C(5)–C(4) and that through Pd(1)–O(1)–O(2) is only 1.4°. Furthermore, the plane defined by Pd(1)–O(1)–O(2) is virtually coplanar with Pd(1)–C(1)–C(3) (dihedral angle 4.6°); C(1)–C(2)–C(3) makes an angle of 155° with Pd(1)–C(1)–C(3).

In considering the bonding of the C_3 ligands to the Pd_3 framework it is instructive to look at it from two different viewpoints. The first is to consider each C_3 ligand as a μ-η^3-allylic unit which bridges the Pd(1)–Pd(2) metal–metal bond and contributes 5 electrons to the cluster. In this sense the structure resembles those of two nickel complexes (6) [7] and (7) [8] (very brief accounts of which have quite recently been published) except that there the C_3 ligands bridge Ni–Ni bonds very nearly perpendicularly. In complex (2) the C_3 plane lies at an angle of 71° to the Pd(1)–Pd(2) axis. This difference probably arises because of the greater asymmetry of our palladium complex but it also encourages an alternative view of complex (2).

The alternative approach is to regard Pd(1) as di-σ-(1,3-η-) bonded to the C_3 unit, which in turn is π- (1-3-η-) bonded to Pd(2). The bonding of the C_3 unit to Pd(1) is then very similar to that found in the iridium complex $[Ir(1,3\text{-}\eta\text{-}C_3Ph_3)(Me_3P)_2(CO)Cl]^+$ (5).[9] This view is supported by the planarity of the (acac)Pd(1)C(1)C(3) unit, and the short Pd(1)–C(1) and Pd(1)–C(3) bonds, the lengths of which are characteristic of Pd–C(sp^2) σ-bonds.[10] Similarly, the Pd(2)–C(1) and Pd(2)–C(3) bonds are longer and are characteristic of those between Pd and η^3-allylically bonded carbons,[10] but Pd(2)–C(2) is sig-

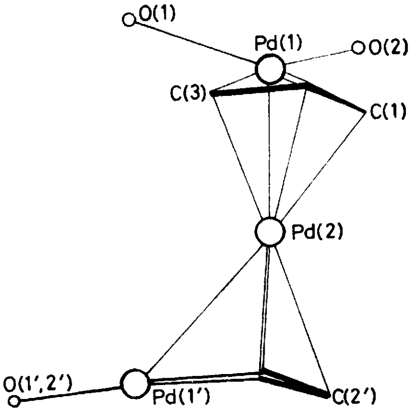


FIGURE 2 View of the molecule (2) along the edge of the Pd(1′)–O(1′)–O(2′) plane; phenyl and *p*-methoxyphenyl substituents and remaining parts of the acac ligands are omitted for clarity

[7] R. G. Posey, G. P. Khare, and P. D. Frisch, *J. Amer. Chem. Soc.*, 1977, **99**, 4863.

[8] H. Hoberg and C. Krüger, *Angew. Chem. Internat. Edn.*, 1977, **16**, 183.

[9] R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, 1972, **11**, 2237.

[10] See, for example, P. M. Maitlis, ' The Organic Chemistry of Palladium,' Academic Press, New York, 1971, vol. I, p. 38; T. Hosokawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1973, **95**, 4914; B. E. Mann, P. M. Bailey, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1975, **97**, 1275; D. J. Mabbott, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1975, 521; E. A. Kelley, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1977, 289; P. M. Bailey, S. H. Taylor, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1978, **100**, 4711.

nificantly longer (0.19 Å, 13σ) and suggests a rather weaker bonding of the metal to C(2) than is usual in normal mononuclear η^3-allylic complexes.

Pd(2) may then be regarded as octahedrally co-ordinated, the co-ordination sphere being made up of two π-allylically bonded units [C(1)–C(2)–C(3) and C(1′)–C(2′)–C(3′)], each occupying two co-ordination sites, the remaining two being taken up with bonds to Pd(1) and Pd(1′) respectively. Figure 2 illustrates this view and also shows the relative orientations of the two η^3-allylic units, while Figure 3 illustrates the relative positions of Pd(1) and Pd(2) to the allyl plane.

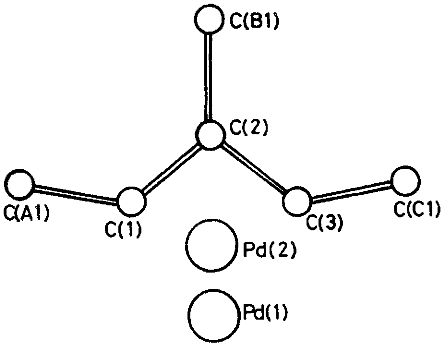


FIGURE 3 View of the allylic plane [C(1)–C(2)–C(3)] with respect to Pd(1) (out-of-plane distance −0.80 Å) and Pd(2) (out-of-plane distance +1.71 Å); substituents on the C_3 ligand and acac atoms omitted for clarity

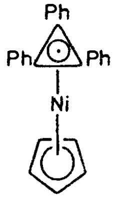
Such a view of the molecule suggests that Pd(1) and Pd(1′) are then best regarded as 15-electron atoms. Since n.m.r. studies show (2) (and the related molecules discussed in ref. 1 which have the same structure) to be diamagnetic, both Pd(1) and Pd(1′) must pair their odd electrons with Pd(2) which then becomes an 18-electron atom. This accounts for the presence of the metal–metal bonds in the complex.

The bend (of 127°) of the Pd–Pd–Pd framework, which is at first sight surprising, now comes as a logical consequence of (i) the steric requirements of the six-co-ordinate Pd(2), and (ii) the need for the two {(acac)-Pd(1)C(1)C(2)C(3)} units to minimise their interactions especially when the three aryl groups attached to the C_3 ligands are considered. As Figure 2 infers, the aryl groups on the C_3 ligands are interleaved with each other and the units can be thought of as two gear wheels each bearing three cogs (aryl groups) which mesh together. The racemisation of compound (2) and related complexes,[1] which is observed by n.m.r. spectroscopy, then occurs by a one-cog movement of the two gear wheels with respect to each other.

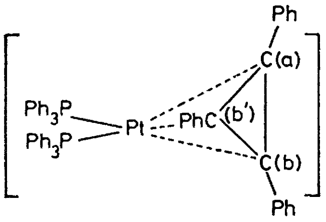
Normal η^3-allylic complexes are found to have the allylic unit at an angle of 110—120° to the co-ordination plane of the metal rather than perpendicular to it. Kettle and Mason suggested that this was because two forms of bonding were possible, the π- (η^3-) and the di-σ-(1,3-η^2-), and that the structure actually adopted was a compromise between these two forms which minimised the overall energy of the molecule.[11] Clearly a very similar description of the bonding would be entirely appropriate for compound (2).

It is also instructive to compare the various types of bonding of C_3R_3 ligands to transition metals that have been reported since they show a unique set of trends. The complexes investigated range from the symmetrical (all C–C bonds equivalent) η^3-binding in (3)[12] *via* the asymmetrically η^3-bonded in complex (4)[13] [where although Pt–C_a (2.48 Å) is greater than Pt–C_b (2.09 Å) and C_a–C_b (1.39 Å) is less than C_b–$C_{b'}$ (1.58 Å) there is obviously still bonding between C_b and $C_{b'}$], to the ring-opened 1,3-η-bonded iridium complex (5)[9] where there is no longer a bond between the two carbons σ-bonded to Ir.

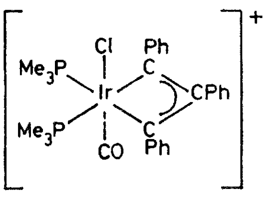
Clearly complex (2) [and complexes (6) and (7)] represents a type of bonding in-between (4) and (5) and illustrates that the effect of increasing the electron density at a ligand by co-ordination of an electron-rich metal atom can be to cause C–C bond cleavage.



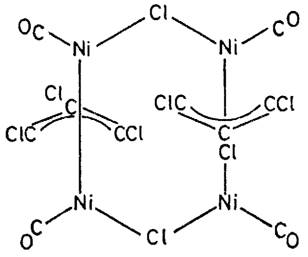
(3)



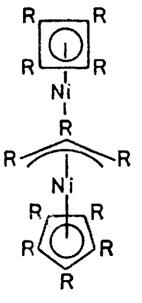
(4)



(5)



(6)



(7) R = Ph

In this context, however, a word of caution is needed. Although we have prepared $[Pt_3\{C_3(p\text{-}MeOC_6H_4)_3\}_2(Ph_3P)_4]^{2+}$ (8)[1] which is formally two molecules of (4;

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[11] R. Mason and S. F. A. Kettle, *J. Organometallic Chem.*, 1966, **5**, 573.

[12] M. D. Rausch, R. M. Tuggle and D. L. Weaver, *J. Amer. Chem. Soc.*, 1970, **92**, 4981; R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, 1971, **10**, 1504, 2599.

[13] M. D. McClure and D. L. Weaver, *J. Organometallic Chem.*, 1973, **54**, C59.

p-$MeOC_6H_4$ in place of Ph on C) with one Pt joining them there was no indication that (8) could be induced to break up to give (4), for example even in the presence of a large excess of triphenylphosphine. Similarly, attempts to prepare (8) from reaction of (4) with Pt^0 complexes were without success. Kinetic factors appear therefore to allow the independent existence of two such similar entities as (4) and (8).

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