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SYNTHESIS AND STRUCTURE OF THE TRIPHENYLPHOSPHONIUM CYCLOPENTADIENYLIDE ADDUCT OF OLIGOMERIC TETRAKIS(METHOXYCARBONYL)PALLADIACYCLOPENTADIENE

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Summary

Addition of the triphenylphosphonium cyclopentadienylide to tetrakis(methoxycarbonyl)palladiacyclopentadiene yields the monomeric complex (cpylid)$[PdC_4(CO_2Me_4]$ NMR spectra of the cyclopentadienyl ring protons indicate unsymmetrical ring coordination. A crystallographic molecular structure determination has shown that intramolecular separations between phosphonium phenyl rings and palladiacycle methyl carboxylate groups restrict the Pd to the lower region of the ylide ring. Bond lengths within the ylide ring appear to indicate allylic coordination

Introduction

While the triphenylphosphonium cyclopentadienylide (cpylid) has been known for several years [1] its use as a ligand has been restricted to a narrow series of carbonyl complexes with Group VIA metals and their adducts [2—5]. Aromaticity of the cyclopentadienide ring serves to stabilize the zwitterionic form of the ylide [6]. Accordingly, spectroscopic evidence obtained for complexes of the form $M(cpylid)(CO)_3(M = Cr, Mo, W)$ indicate η^5-coordination for the ring with the ylide bonding ostensively as a substituted cyclopentadienyl ligand.

We now report the synthesis and structure of a new cpylide complex, (cpylid)

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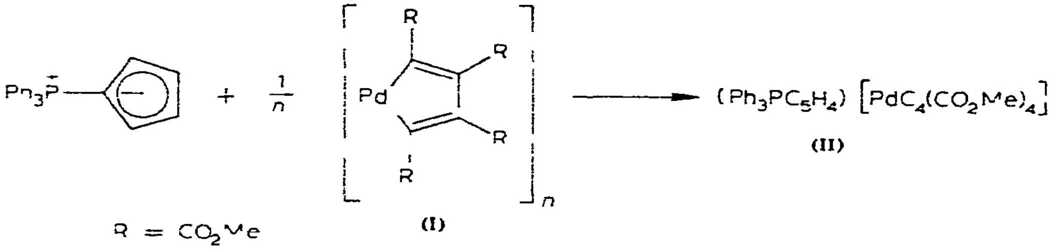
$[PdC_4(CO_2Me)_4]$, obtained by addition of the ligand to the oligomeric palladiacyclopentadiene complex $[PdC_4(CO_2Me)_4]_n$

Results and discussion

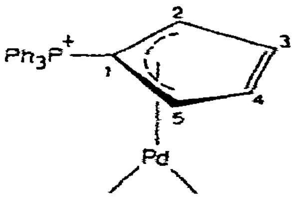
Oligomeric tetrakis(methoxycarbonyl)palladiacyclopentadiene (I) is readily formed by addition of dimethyl acetylenediacarboxylate to tris(dibenzylideneacetone)dipalladium [7—9] Treatment of I with neutral ligands has been reported to yield monomeric palladiacyclopentadiene complexes [10—12] For purposes of the present investigation the triphenylphosphonium cyclopentadienylide was used to form the complex (cpylid) $[PdC_4(CO_2Me)_4]$ (II) in 79% yield The NMR spectrum of the cyclopentadiene ring in II is considerably different



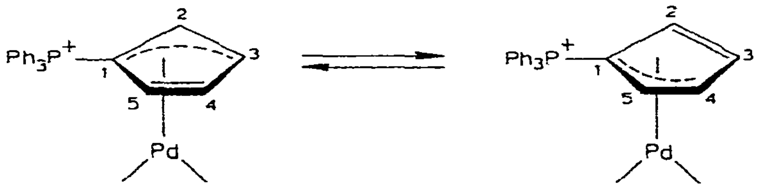
from spectra reported for the Cr, Mo and W carbonyl complexes [4] At 25°C ring proton resonances appear as two six line multiplets at δ 5 58 and 6.15 ppm ($\Delta\delta$ 0.57 ppm) (Fig 1) This AA'BB'X pattern differs considerably from the four line A_2B_2 patterns observed for the Cr, Mo and W complexes which exhibit smaller chemical shift differences ($\Delta\delta$ = 0 26 to 0 27 ppm) and no apparent coupling to the phosphorus Phosphorus coupling is clearly observed in the spectrum of II with J(P—H(a)) 3 6 Hz for the signal at δ 6.15 ppm and J(P—H(b)) 3.2 Hz for b protons at δ 5 58 ppm (Fig 2). Values of J(P—H(a)) 5 6 Hz and J(P—H(b)) 3.6 Hz have been reported for the free ylide where an AA'BB'X pattern is also observed with $\Delta\delta$ 0.17 ppm and assignment of a and b protons based on the magnitude of phosphorus coupling [13] The consistent increase in $\Delta\delta$ from free ligand and the *pentahapto* complexes to II is interpreted in terms of a decrease in coordination symmetry of the cyclopentadienylide ring

The zwitterionic structure for the ylide may be represented in terms of delocalized allylic structures within the ring. Divalent palladium has a strong affinity for allylic ligands, and such coordination may contribute to the unusually large separation between a and b proton resonances. Three potential modes of allylic coordination exist:

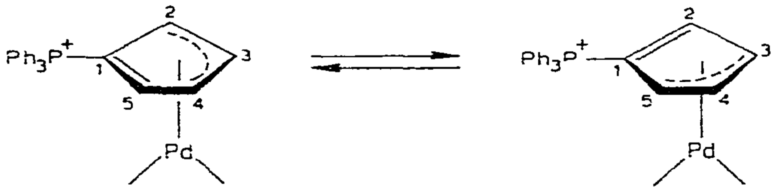
(1) Rigid, symmetrical η^3-coordination:



(2) Fluxional phosphonium-η^3-allyl coordination.



(3) Fluxional vinylphosphonium-η^3-allyl coordination



Since the plane of the cyclopentadiene ring in all forms above would be normal to the palladiacyclopentadiene plane, differentiation between various coordination geometries would amount to displacement of the Pd from the ring center with slight alteration of ring carbon—carbon distances from values consistent

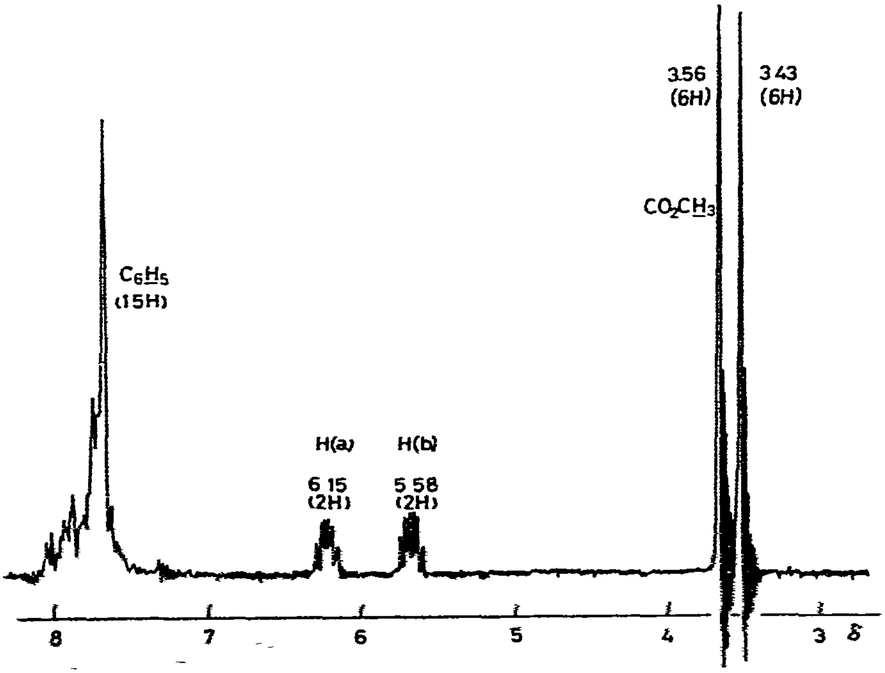


Fig. 1. The NMR spectrum of {cpylid [PdC$_4$(CO$_2$Me)$_4$]} in CDCl$_3$ at 25°C.

with a completely delocalized structure Also, the energy requirement for interconversion of limiting structures in fluxional forms (2) and (3) would be quite minimal. To examine the possibility of a fluxional structure for II NMR spectra of the ring were taken over the temperature range from 25°C to −97°C at which point crystallization from solution occurs The results of this study are summarized in Table 1 While the AA′ BB′ pattern remains essentially unchanged the positions of the a and b proton resonances and $\Delta\delta$ show a slight temperature dependence While this may possibly indicate a fluxional structure, the magnitude of the spectral change over the temperature range does not permit unambiguous interpretation

To identify the geometry of II in the solid state a crystallographic molecular structure determination has been carried out Views of the complex molecule are presented in Fig 3 and 4 with atomic positional and thermal parameters contained in Table 2 Intramolecular bonding parameters are contained in Table 3 As anticipated from the spectral properties of the complex the Pd is bound unsymmetrically to the ring. The longer Pd—C distances are associated with the ylidic carbon C(1) and the adjacent ring carbon C(2) with values of 2 447(6) and 2 429(6) Å, respectively Shorter values of 2 399(6), 2 334(6) and 2 340(6) Å are found to carbons C(3), C(4) and C(5). These values together with the bonding pattern within the ring are consistent with a localized coordination geometry described by form (3) Carbon—carbon bond lengths for bonds C(2)—C(3) and C(1)—C(5) approach single bond values, while the other lengths within the ring are consistent with delocalized multiple bonds The P—C(1) length of 1 776(9) Å is shorter than P—C lengths for the phenyl carbons which range from 1 80 to 1.81 Å, but substantially longer than the value of 1.718(2) Å reported for the free ylide [14] The unsymmetrical coordination to the ring appears certainly related to close intramolecular contacts between phosphonium phenyl rings and methyl carboxylate substituents associated with palladiacyclopentadiene carbons C(6) and C(9) Steric interactions between these groups eliminate forms (1) and (2) as potential geometries for the complex and suggest that regular *pentahapto* coordination to the Pd in (cpylid)[$PC_4(CO_2Me)_4$] is unlikely

The structural features of the palladiacycle moiety are similar to those of

(continued on p 99)

TABLE 1

THE TEMPERATURE DEPENDENCE OF THE CHEMICAL SHIFT DIFFERENCE BETWEEN PROTONS H(a) AND H(b)[a]

Temperature (°C)	Chemical shift (δ ppm)		
	H(a) (H(2 5))	H(b) (H(3,4))	Δδ (ppm)
−97	6 24	5 86	0 38
−90	6 23	5 84	0 39
−78	6 19	5 79	0 40
−58	6 15	5 72	0 43
−42	6 14	5 70	0 44
−5	6 13	5 68	0 45
25	6.12	6.67	0 45
	(6 15)[b]	(5 58)[b]	(0 57)[b]

[a] Measured in the solvent mixture $(CD_3)_2CO/CDCl_3$ = 5/1 vol. [b] Measured in $CDCl_3$.

TABLE 2. FINAL STRUCTURAL PARAMETERS AND GROUP PARAMETERS FOR (cpylid) [PdC$_4$(CO$_2$Me)$_4$]

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	−0.14561(11)	0.21412(4)	0.00972(7)	0.01732(16)	0.00249(2)	0.00727(7)	−0.00092(6)	0.00686(8)	−0.00061(3)
P	−0.2927(4)	0.0684(1)	−0.1220(2)	0.0157(5)	0.0020(1)	0.0073(2)	−0.0002(2)	0.0058(3)	−0.0001(1)
C(1)	−0.1665(14)	0.1109(5)	−0.0135(8)	0.0159(24)	0.0023(3)	0.0061(9)	0.0007(7)	0.0037(12)	−0.0006(4)
C(2)	−0.0212(14)	0.1264(5)	0.0141(9)	0.0128(20)	0.0022(3)	0.0074(9)	−0.0009(7)	0.0023(11)	−0.0002(4)
C(3)	0.0549(18)	0.1494(6)	0.1191(11)	0.0258(29)	0.0023(3)	0.0110(14)	−0.0006(8)	0.0083(17)	0.0005(5)
C(4)	−0.0532(18)	0.1503(5)	0.1465(10)	0.0266(30)	0.0023(3)	0.0090(11)	−0.0006(8)	0.0085(17)	−0.0002(5)
C(5)	−0.1006(15)	0.1289(5)	0.0665(9)	0.0196(24)	0.0026(3)	0.0055(9)	−0.0002(7)	0.0084(13)	−0.0005(4)
C(6)	−0.2884(15)	0.2703(5)	0.0007(9)	0.01993(24)	0.0019(3)	0.0079(9)	−0.0002(7)	0.0084(13)	−0.0005(4)
C(7)	−0.2966(14)	0.3213(6)	−0.0464(8)	0.0136(21)	0.0030(4)	0.0067(9)	−0.0001(8)	0.0052(11)	−0.0010(4)
C(8)	−0.1935(15)	0.3252(6)	−0.0794(8)	0.0175(24)	0.0026(3)	0.0056(8)	−0.0011(7)	0.0055(2)	0.0001(4)
C(9)	−0.1095(15)	0.2770(6)	−0.0594(9)	0.0183(23)	0.0031(4)	0.0069(9)	−0.0015(8)	0.0074(12)	−0.0005(4)
C(10)	−0.3885(15)	0.2550(5)	0.0337(9)	0.0209(24)	0.0019(3)	0.0091(10)	−0.0001(7)	0.0096(14)	0.0001(4)
C(11)	−0.4177(17)	0.2540(6)	0.1757(10)	0.0304(32)	0.0040(4)	0.0111(12)	−0.0036(10)	0.0149(17)	−0.0007(5)
C(12)	−0.4067(16)	0.3675(6)	−0.0713(9)	0.0237(27)	0.0038(4)	0.0068(10)	0.0009(9)	0.0078(14)	0.0011(5)
C(13)	−0.3167(18)	0.4004(7)	−0.0602(13)	0.0244(32)	0.0047(5)	0.0194(18)	0.0047(11)	0.0144(21)	0.0009(8)
C(14)	−0.1740(15)	0.3798(6)	−0.1220(10)	0.0168(24)	0.0043(4)	0.0082(11)	−0.0014(9)	0.0054(13)	0.0008(6)
C(15)	−0.0816(35)	0.4672(12)	−0.1048(21)	7.9(7)^c					
C(15)	−0.2361(32)	0.4461(10)	−0.2541(22)	6.4(6)^c					
C(16)	0.0013(16)	0.2722(8)	−0.0894(10)	0.0167(25)	0.0050(6)	0.0083(11)	−0.0031(11)	0.0069(14)	−0.0000(6)
C(17)	0.1104(20)	0.2173(7)	−0.1569(14)	0.0350(37)	0.0045(5)	0.0214(19)	0.0037(12)	0.0236(24)	0.0011(8)
O(1)	−0.3279(10)	0.2697(3)	0.1330(6)	0.0265(18)	0.0026(2)	0.0086(6)	−0.0023(5)	0.0097(9)	−0.0008(3)
O(2)	−0.5057(10)	0.2286(3)	−0.0155(6)	0.0229(16)	0.0035(2)	0.0115(7)	−0.0027(5)	0.0107(9)	−0.0016(3)
O(3)	−0.4956(11)	0.3591(4)	−0.0364(7)	0.0337(22)	0.0037(3)	0.0131(8)	0.0016(6)	0.0155(12)	0.0017(4)
O(4)	−0.4188(13)	0.4104(5)	−0.1188(8)	0.0436(28)	0.0055(3)	0.0199(11)	0.0065(8)	0.0221(16)	0.0063(5)
O(5)	−0.0807(16)	0.4157(7)	−0.0547(10)	6.0(3)^c					
O(5)′	−0.2583(16)	0.3914(6)	−0.2201(10)	4.6(3)^c					
O(6)	−0.2056(20)	0.3747(9)	−0.2166(12)	5.9(4)^c					
O(6)′	−0.1226(22)	0.4243(8)	−0.0671(13)	8.5(5)^c					
O(7)	0.0597(14)	0.3159(5)	−0.1004(8)	0.0385(28)	0.0051(3)	0.0169(11)	−0.0041(8)	0.0205(16)	−0.0027(5)
O(8)	0.0111(12)	0.2217(4)	−0.1203(8)	0.0209(21)	0.0033(3)	0.0171(10)	0.0015(6)	0.0170(13)	0.0006(4)

Group	$x_c{}^d$	y_c	z_c	ϕ	θ	ρ
R1	−0.3444(7)	−0.0519(3)	−0.0467(5)	2.176(11)	2.234(7)	−0.894(10)
R2	−0.6201(7)	0.1220(2)	−0.2738(4)	−0.282(7)	−2.459(5)	0.184(6)
R3	−0.1494(7)	0.0513(3)	−0.2538(4)	−2.900(6)	−2.928(6)	1.211(6)

[a] Estimated standard deviations of the least significant figures are given in parentheses [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ [c] Atoms associated with the disordered methyl carboxylate group [d] x_c, y_c and z_c are the fraction coordinates of the rigid group centers The angles ϕ, θ and ρ are in radians and have been defined previously [18]

TABLE 3

BONDING PARAMETERS FOR (cpylid) [$PdC_4(CO_2Me)_4$]

Atoms	Distance (Å)	Atoms	Distance (Å)
Pd—C(1)	2.447(6)	C(2)—C(3)	1.47(1)
Pd—C(2)	2.429(6)	C(3)—C(4)	1.42(2)
Pd—C(3)	2.399(6)	C(4)—C(5)	1.39(1)
Pd—C(4)	2.334(6)	C(1)—C(5)	1.46(1)
Pd—C(5)	2.340(6)	P—C(1)	1.776(9)
Pd—C(6)	1.955(5)	C(6)—C(7)	1.38(1)
Pd—C(9)	1.984(5)	C(7)—C(8)	1.44(1)
C(1)—C(2)	1.40(1)	C(8)—C(9)	1.37(1)

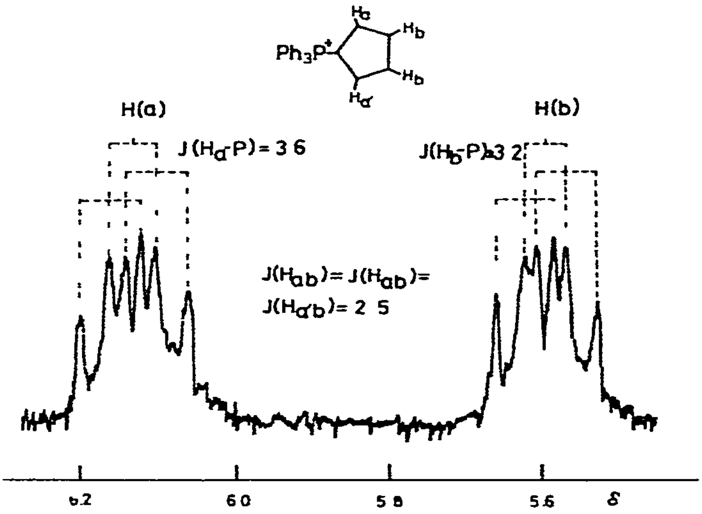


Fig. 2. Proton signals of the cyclopentadienylide ring at 25°C in $CDCl_3$

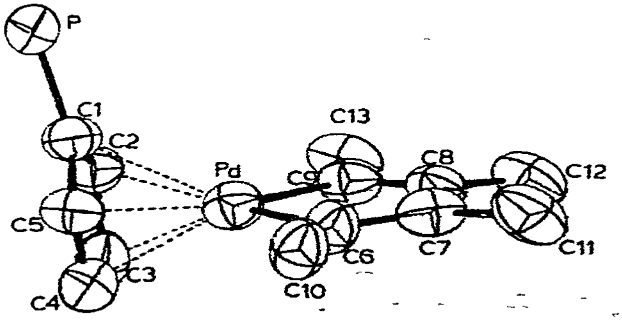


Fig. 3. A view of the inner coordination geometry of (cpylid) [$PdC_4(CO_2Me)_4$].

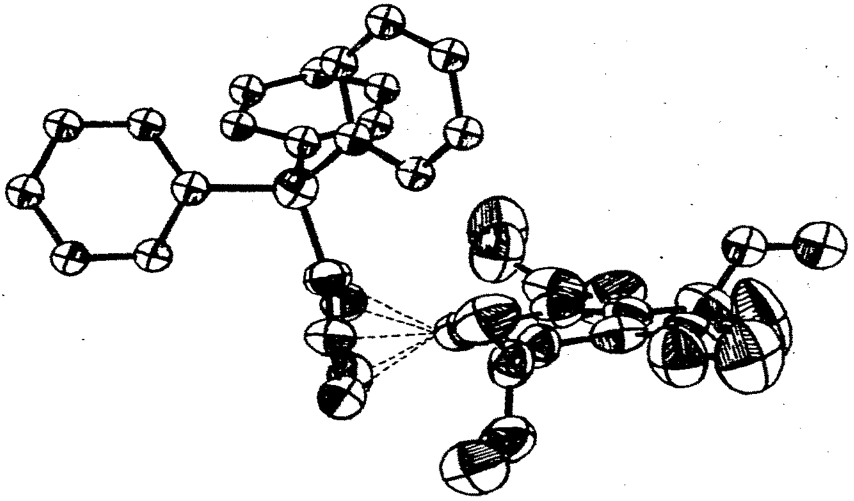


Fig. 4. Perspective view of the complete (cpylid) [$PdC_4(CO_2Me)_4$] molecule.

other metallocycles [15]. Much interest has been devoted to the observed disparity (usually 0.03—0.04 Å) between metal—carbon bond lengths within metallocycle rings [16]. A similar difference is found in the $PdC_4(CO_2Me)_4$ ring where Pd—C distances of 1.955(5) and 1.984(5) Å are found. The carbon—carbon bond lengths within the ring appear to indicate that $d\pi$—$p\pi$ bonding is an important effect in palladiacycles as in related rhodacycles [17].

Experimental

Materials

Triphenylphosphonium cyclopentadienylide was prepared by the procedure of Ramirez [1]. Tetrakis(methoxycarbonyl)palladiacyclopentadiene was prepared by treating excess dimethyl acetylenedicarboxylate with tris(dibenzylideneacetone)dipalladium(0) in acetone [10—12]. NMR spectra were recorded on a JEOL-C-60HL spectrometer using tetramethylsilane as an internal standard.

Preparation of (triphenylphosphonium cyclopentadienylide)tetrakis(methoxycarbonyl)palladiacyclopentadiene (II)

Triphenylphosphonium cyclopentadienylide (130 mg; 0.40 mmol) and tetrakis(methoxycarbonyl)palladiacyclopentadiene (I) (153 mg; 0.40 mmol) were suspended in dry acetone (20 ml). The mixture was stirred at room temperature for 1 h. The suspension gradually became a brown solution which was then filtered to remove metallic palladium. The filtrate was condensed under reduced pressure and ethyl ether added dropwise to the reaction mixture. Complex II was isolated as a yellow powder in 79% yield (224 mg). Recrystallization from methanol gave brownish orange prisms. M.p. 170—171°C dec. Anal. Found: C, 58.65; H, 4.50. $C_{35}H_{31}O_8Pd$ calcd.: C, 58.63; H, 4.36%.

Structure determination

Photographic examination of crystals of (cpylid) [$PdC_4(CO_2Me)_4$] indicated monoclinic symmetry with an extinction pattern consistent with space group $P2_1/c$. A crystal was mounted and aligned on a Picker automated diffractometer. The angular settings of 18 strong reflections centered using Mo-K_α radiation (λ 0.7107 Å) were used to give refined lattice constants of a 10.596(3), b 23.519(5), c 15.547(3) Å and β 123.27(4)°. An experimental density of 1.46(1) g cm^{-3} agrees with a calculated value of 1.468 g cm^{-3} for four molecules per unit cell. Data were collected by the θ—2θ scan technique. The intensities of a total of 5128 independent reflections were measured, of which 3027 were observed, corrected for absorption effects, and included in the refinement. The structure was solved by conventional Patterson and Fourier techniques *. Phenyl rings were refined as rigid groups with an assumed carbon—carbon bond length of 1.392 Å. The oxygen and methyl carbon atoms associated with palladiacyclopentadiene carbon C(12) were found to suffer from a two fold rotational disorder. Atoms with occupancy factors of 0.5 were placed in the six disordered positions (4 oxygen, 2 carbon) with an assumed C=O length of 1.24 Å, and C—O lengths of 1.36 and 1.46 Å for the carboxylate and methyl carbons. The disordered atoms were refined with isotropic thermal parameters throughout the refinement, all other nongroup atoms were refined anisotropically. Group carbon atoms were refined with individual isotropic thermal parameters. Upon completion of the refinement the conventional R factor was 0.086. A final difference Fourier revealed only diffuse regions of residual electron density in the vicinity of the methyl carboxylate groups. An expanded account of the structure determination and a complete table of the final atomic positional and thermal parameters of the structure, and a table containing the F_0 and $|F_c|$ values for the 3027 reflections used in the refinement is available **.

Acknowledgments

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