Chemistry of Metallacyclobutanones. Part 2.[1] Synthesis and Ring Inversion of some Highly Puckered Metallacyclobutan-3-one (Slipped Oxodimethylenemethane) Complexes of Palladium; Crystal Structures of 2,4-Bis(methoxycarbonyl)-1,1-bis(triphenylphosphine)palladacyclobutan-3-one, 2,4-Bis(methoxycarbonyl)-1,1-bis(triphenylarsine)palladacyclobutan-3-one, and 1,1-(2′,2″-Bipyridyl)-2,4-bis(methoxycarbonyl)palladacyclobutan-3-one†

Raymond D. W. Kemmitt,* Peter McKenna, David R. Russell,* and Lesley J. S. Sherry
Department of Chemistry, The University, Leicester LE1 7RH

The reactions of the zerovalent palladium complex $[Pd_2(dba)_3]\cdot CHCl_3$ (dba = dibenzylideneacetone, PhCH=CH–C(O)–CH=CHPh), in the presence of a donor ligand L and dioxygen, with esters of 3-oxopentanedioic acid (RCH_2COCH_2R) in diethyl ether, afford, in high yield, the palladacyclobutan-3-one compounds $[Pd(CHRCOCHR)L_2]$ [R = CO_2Me, L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, or $AsPh_3$, L_2 = 2,2′-bipyridyl (bipy); R = CO_2Et, L = PPh_3 or $AsPh_3$, L_2 = bipy; R = CO_2Pr^n, L_2 = bipy]. The compounds $[Pd(CHRCOCHR)L_2]$ (R = CO_2Me or CO_2Et, L = PPh_3 or $AsPh_3$) are also formed upon treatment of benzene solutions of $[PdL_4]$ with RCH_2COCH_2R in the presence of air. Treatment of the ketone $MeO_2CCH_2COCH_2CO_2Me$ with either $[Pd(O_2)(PPh_3)_2]$ in benzene or $[Pd(OCO_3)(PPh_3)_2]$ in ethanol also affords $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$. Spectroscopic data (i.r. and n.m.r.) for the new compounds are reported, and discussed in relation to their structures, which were firmly established for $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}L_2]\cdot H_2O$ [L = PPh_3 (**3a**), L = $AsPh_3$ (**3e**), and L_2 = bipy (**3f**)] by single-crystal *X*-ray diffraction studies. Crystals of (**3a**) are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters a = 11.995(5), b = 17.72(1), c = 10.30(1) Å, α = 94.7(1), β = 110.8(1), and γ = 102.84(2)°. The structure was refined to R 0.055 (R' 0.060) for 5 093 reflections having $7 \leqslant 2\theta \leqslant 54°$ (Mo-K_α *X*-radiation) collected at room temperature. Crystals of (**3e**) are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters a = 12.219(6), b = 17.56(1), c = 10.44(1) Å, α = 93.3(1), β = 110.8(1), and γ = 103.56(2)°. The structure was refined to R 0.043 (R' 0.046) for 6 025 reflections having $7 \leqslant 2\theta \leqslant 54°$ collected at room temperature. Crystals of (**3f**) are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell with lattice parameters a = 8.43(1), b = 14.594(6), c = 14.170(6) Å, and β = 92.1(1)°. The structure was refined to R 0.043 (R' 0.032) for 4 000 reflections having $7 \leqslant 2\theta \leqslant 60°$ collected at room temperature. The three molecules contain a highly puckered palladacyclobutan-3-one ring [fold angles 53.3(2) for (**3a**), 52.3(4) for (**3e**), and 51.3(3)° for (**3f**)] with a weak transannular Pd–C bond [Pd–C(2) 2.389(7) for (**3a**), 2.384(6) for (**3e**), and 2.374(3) Å for (**3f**)]. The molecules can be alternatively formulated with slipped η^3-oxodimethylenemethane ligands. Variable-temperature ^1H n.m.r. data for the compounds $[Pd(CHRCOCHR)L_2]$ (R = CO_2Me, L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, or $AsPh_3$; L_2 = bipy) are interpreted in terms of inversion of the palladacyclobutan-3-one ring through a planar transition state.

We have shown that the 3-oxopentanedioates (**1**) react with tertiary phosphine complexes of platinum(0) in the presence of air to give novel organoplatinum complexes which can be formulated either as the platinacyclobutan-3-one species (**2a**) or the slipped oxodimethylenemethane species (**2b**).[1] In this paper we demonstrate that analogous palladium complexes can be obtained by the reactions of the esters RCH_2COCH_2R [R = CO_2Me (**1a**), CO_2Et (**1b**), or CO_2Pr^n (**1c**)] with zero-valent palladium complexes in the presence of dioxygen as reported in a preliminary communication.[2] An interesting structural feature of the species (**2**), if they are viewed as platinacyclobutan-3-ones, is the extent of the non-planarity of the metallacyclic ring and the presence of a transannular Pt–CO interaction. Such interactions have been invoked in platinacyclobutanes[3] and in mechanisms for the isomerisation of platinacyclobutane complexes[4,5] although *X*-ray crystallographic studies have shown that the ground-state structures of these systems contain essentially planar four-membered rings.[3,6,7] It seemed possible that palladacyclobutan-3-ones, like the complexes (**2a**) might also exhibit ring puckering and that the nature of the peripheral ligands in the complexes might exert an influence on the extent of non-planarity of the ring. It was for these reasons that the work described in this paper was carried out.

Results and Discussion

Reaction of $[Pd(PPh_3)_4]$ suspended in diethyl ether with an excess of dimethyl 3-oxopentanedioate (**1a**) in the presence of air affords in almost quantitative yield a white microcrystalline air-stable solid formulated as the palladacyclobutan-3-one (**3a**) on the basis of microanalysis and spectroscopic properties. The formation of (**3a**) presumably occurs *via* attack of (**1a**) on the dioxygen compound $[Pd(O_2)(PPh_3)_2]$[8] or peroxycarbonate compound $[Pd(OCO_3)(PPh_3)_2]$,[9] both of which would be formed under the reaction conditions. In agreement with this

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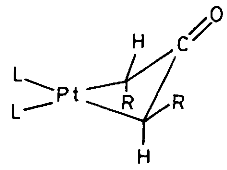
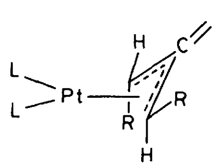
† [1,3-Bis(methoxycarbonyl)-2-oxopropane-1,3-diyl]bis(triphenylphosphine)palladium, [1,3-bis(methoxycarbonyl)-2-oxopropane-1,3-diyl]bis(triphenylarsine)palladium, and (2′,2″-bipyridyl-*NN′*)[1,3-bis(methoxycarbonyl)-2-oxopropane-1,3-diyl]palladium.

Supplementary data available (No. SUP 56092, 13 pp.): thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



(2a)



(2b)

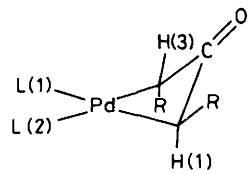
L = PPh_3, $PMePh_2$, or PMe_2Ph

we find that (**3a**) results from the reaction of (**1a**) with either $[Pd(O_2)(PPh_3)_2]$ or $[Pd(OCO_3)(PPh_3)_2]$, the formation of the palladacyclobutan-3-one probably occurring *via* a mechanism similar to that proposed for analogous platinum compounds.[1]

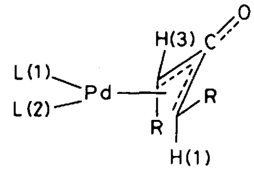
In reactions of (**1a**) with $[Pt(PPh_3)_4]$ suspended in diethyl ether in the presence of air a high yield of the peroxy-ring compound $[Pt\{OOC(CH_2CO_2Me)_2O\}(PPh_3)_2]$ is formed in addition to the platinacyclobutan-3-one (**2a**).[1] However, analogous reactions involving $[Pd(PPh_3)_4]$ only yield the palladacyclobutan-3-one (**3a**). Previous studies have shown that ketones give unstable adducts with $[Pd(O_2)(PPh_3)_2]$[9] and a peroxy-ring complex formed from (**1a**) and $[Pd(O_2)(PPh_3)_2]$ would also presumably be unstable.

Having fully characterised (**3a**) we wished to establish whether related palladium complexes containing a range of donor ligands could be isolated. Accordingly reactions between the ketones (**1**) and $[Pd_2(dba)_3]\cdot CHCl_3$[10–12] (dba = dibenzylideneacetone*) in the presence of a donor ligand L and dioxygen were investigated. In this manner the complexes (**3a**)—(**3j**) were isolated. It is known that a variety of phosphorus-, arsenic-, and nitrogen-donor ligands, L, effect displacement of the dab ligands in $[Pd_2(dba)_3]$ to give zero-valent palladium complexes of the ligands L,[13–15] which in the presence of dioxygen would generate the complexes $[Pd(O_2)L_2]$. Abstraction of hydrogen from the ketones (**1**) by these dioxygen complexes could then lead to the palladacyclobutan-3-ones (**3**). In addition some of the complexes (**3**) were also obtained by the reaction of the ketones (**1**) with the zero-valent palladium complexes $[PdL_4]$ (L = PPh_3 or $AsPh_3$) in the presence of air (see Experimental section).

The availability of a range of palladacyclobutan-3-one complexes of (**3**) made it possible to examine the effects of the donor ligand L on the extent of ring puckering. Single-crystal *X*-ray diffraction studies were therefore undertaken on the complexes $[Pd(CHRCOCHR)(PPh_3)_2]\cdot H_2O$ (**3a**), $[Pd(CHRCOCHR)(bipy)]\cdot H_2O$ (**3f**) (bipy = 2,2′-bipyridyl), and $[Pd(CHRCOCHR)(AsPh_3)_2]\cdot H_2O$ (**3e**). The results of the *X*-ray work are summarised in Tables 1 and 2. The molecular structures are shown in Figures 1—3. All three complexes crystallise with one molecule of water per molecule of compound and although there is some disordering about the solvent molecule present in (**3a**) and (**3e**) the i.r. and ^1H n.m.r. spectra of these complexes show absorptions which can be assigned to water. In the triphenylphosphine and triphenylarsine complexes the water is incorporated in a 'hole' in the lattice with no short intermolecular contacts between the palladium complex and the water molecule. However, in the bipyridyl derivative (**3f**) the water molecule present is weakly hydrogen-bonded to the ring carbonyl, the O(1)···O(6) distance being 2.76 Å. These data indicate that the oxygen of the ring carbonyl in (**3f**) may be more basic than that in both the phosphine and arsine derivatives and it is noteworthy that the corresponding carbonyl oxygen in the related complexes $[Pd\{CH(CO_2Et)COCH_2\}(Ph_2PCH{=}CHPPh_2)]$ can behave as a donor ligand and co-ordinate to metal ions.[16] Attempts to obtain water-free samples of (**3a**), (**3e**), and (**3f**) using strictly anhydrous conditions during the preparations of the complexes have not been successful. This would tend to indicate that water is a product of the reaction of the ketones RCH_2COCH_2R with the dioxygen complexes $[Pd(O_2)L_2]$.



(**3a**) L = PPh_3, R = CO_2Me
(**3b**) L = $PMePh_2$, R = CO_2Me
(**3c**) L = PMe_2Ph, R = CO_2Me
(**3d**) L = PEt_3, R = CO_2Me
(**3e**) L = $AsPh_3$, R = CO_2Me
(**3f**) L_2 = bipy, R = CO_2Me
(**3g**) L = PPh_3, R = CO_2Et
(**3h**) L = $AsPh_3$, R = CO_2Et
(**3i**) L_2 = bipy, R = CO_2Et
(**3j**) L_2 = bipy, R = CO_2Pr^n



(4)

The co-ordination about palladium in all three complexes is essentially square planar, the twist angles between the XPdX (X = P, As, or N) and CPdC planes being 8.9(2), (**3a**), 7.1(2), (**3e**), and 5.9(2)°, (**3f**): Table 3. Moreover, in common with the platinum analogue of (**3a**) which has a highly non-planar Pt–C–C–C ring,[1] the complexes (**3a**), (**3e**), and (**3f**) also have puckered palladacyclobutan-3-one rings in the solid state, as measured by the fold angle between planes C(1)–Pd–C(3) and C(1)–C(2)–C(3), Table 4. A consequence of the large fold angles is that the Pd–C(2) distances in the complexes (**3a**), (**3e**), and (**3f**) are only 2.389(7), 2.384(6), and 2.374(3) Å respectively. Although these distances are larger than the sum of the covalent radii [C(sp^2) 0.76, Pd 1.31 Å],[17,18] considerable orbital interaction must occur between Pd and C(2) in (**3a**), (**3e**), and (**3f**). The orientation of PdC_3 ring atoms is thus reminiscent of an η^3-allyl metal complex and a bonding description of these three complexes can be considered to include a contribution from the slipped oxodimethylenemethane structure (**4**) analogous to (**2b**). Indeed the C(1)–C(2) and C(2)–C(3) distances are in the range for co-ordinated olefinic double bonds.[19] The C(2)–O(1) bonds are also longer than the C=O bonds C(4)–O(2) and C(6)–O(4) and they are inclined by 12.2(7), (**3a**), 11.2(5), (**3e**), and 12.0(3)°, (**3f**), out of the C(1)C(2)C(3) planes towards the palladium (Table 3).

Overall the geometry of the palladacyclobutan-3-one rings in the three palladium complexes bears a strong resemblance to the platinacyclobutan-3-one complex $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$[1] with one methoxycarbonyl substituent occupying a pseudo-axial position and the other a pseudo-equatorial position in each complex. Furthermore, as in the platinacyclobutan-3-one, the axial hydrogen atom in the

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* 1,5-Diphenylpenta-1,4-dien-3-one.

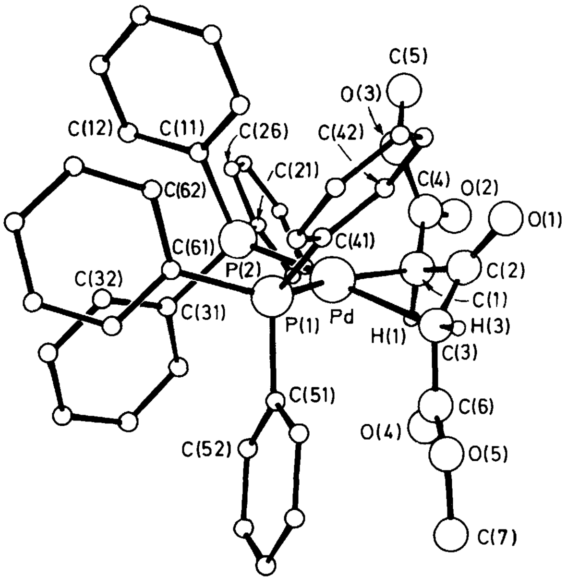

Figure 1. Molecular structure of $[\mathrm{Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2}]$ (**3a**), showing the crystallographic numbering

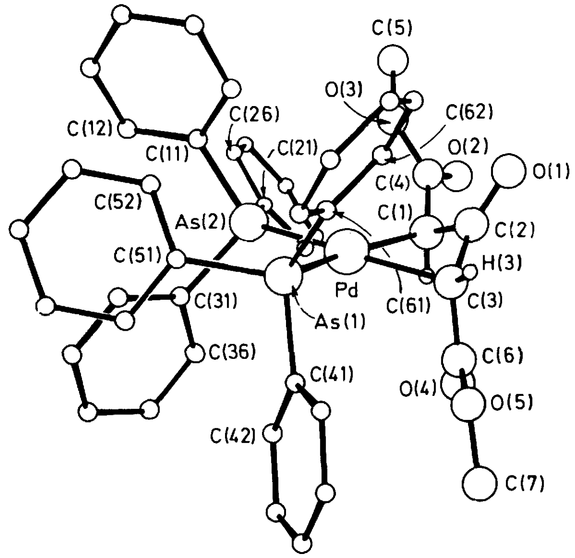

Figure 2. Molecular structure of $[\mathrm{Pd\{CH(CO_2Me)COCH(CO_2Me)\}(AsPh_3)_2}]$ (**3e**), showing the crystallographic numbering

complexes (**3a**), (**3e**), and (**3f**) is closer to the metal than the equatorial hydrogen [Pd–H(1) 2.55(17), (**3a**), 2.48(4), (**3e**), 2.42(4), (**3f**); Pd–H(3) 2.95(5), (**3a**), 2.84(3), (**3e**), 2.67(4) Å, (**3f**)]. The palladium–carbon bonds Pd–C(1) and Pd–C(3) for the three complexes (**3a**), (**3e**), and (**3f**) decrease in length in the order $\mathrm{PPh_3} > \mathrm{AsPh_3} >$ bipy, consistent with the expected decrease in *trans* influence of these ligands.[20] The average palladium–carbon bond lengths are 2.15, 2.13, and 2.09 Å for (**3a**), (**3e**), and (**3f**) respectively. However, the transannular palladium–carbon bond distances Pd–C(2) remain fairly constant in the range 2.39—2.37 Å indicating the tendency of the palladium to maintain its interaction with the ring carbonyl group in all three complexes.

The ^{1}H n.m.r. spectra of several of the palladacyclobutan-3-one complexes, measured at low temperature, showed the expected features for the illustrated static structure (*e.g.* see Figure 4), with two resonances for the methyl protons and two resonances for the CH protons, the CH resonance at higher field being assigned to the equatorial hydrogen by analogy with related platinum systems.[1] Furthermore, the magnitude of the coupling of the CH protons in the complexes (**3a**)—(**3c**) to the *cis* and *trans* phosphorus nuclei suggest that the three-bond couplings (*cis*-P–Pd–C–H) are under dihedral angle control as in analogous platinum complexes.[1,21] Thus in each complex the equatorial hydrogen H(3) couples to both its *cis* and *trans* phosphorus ligand atoms by a similar magnitude and appears as a triplet [the L(1)–Pd–C(3)–H(3) torsion angles are −26(6), (**3a**), −34(3), (**3e**), and 44(3)°, (**3f**)]. However, the lower field CH resonance, assigned to the axial hydrogen H(1), shows no discernible coupling to its *cis* phosphorus ligand and appears as a doublet due to *trans* phosphorus coupling only [the

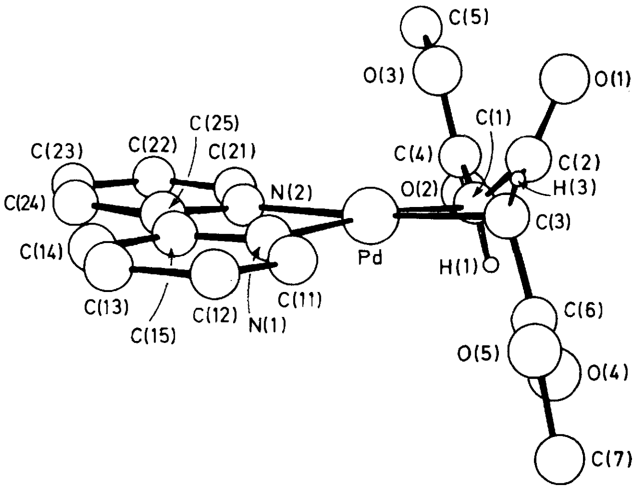

Figure 3. Molecular structure of $[\mathrm{Pd\{CH(CO_2Me)COCH(CO_2Me)\}(bipy)}]$ (**3f**), showing the crystallographic numbering

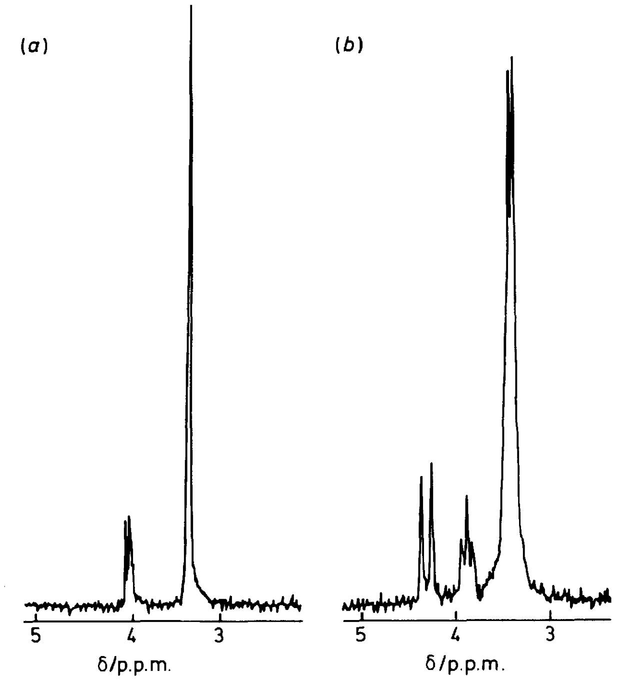

Figure 4. ^{1}H N.m.r. spectrum of $[\mathrm{Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PMe_2Ph)_2}]$ (**3c**), recorded at 100 MHz in $\mathrm{CD_2Cl_2}$: (*a*) at 25 °C, (*b*) at − 90 °C

Table 1. Selected intramolecular bond lengths (Å) in [Pd{CH(CO_2Me)COCH(CO_2Me)}(PPh_3)$_2$]·H_2O (**3a**), [Pd{CH(CO_2Me)COCH(CO_2Me)}($AsPh_3$)$_2$]·H_2O (**3e**), and [Pd{CH(CO_2Me)COCH(CO_2Me)}(bipy)]·H_2O (**3f**), with estimated standard deviations in parentheses

	(**3a**)		(**3e**)		(**3f**)
Pd–P(1)	2.343(1)	Pd–As(1)	2.437	Pd–N(1)	2.076(3)
Pd–P(2)	2.316(2)	Pd–As(2)	2.404(1)	Pd–N(2)	2.106(4)
Pd–C(1)	2.135(6)	Pd–C(1)	2.125(5)	Pd–C(1)	2.103(3)
Pd–C(2)	2.389(7)	Pd–C(2)	2.384(6)	Pd–C(2)	2.374(3)
Pd–C(3)	2.165(7)	Pd–C(3)	2.152(5)	Pd–C(3)	2.085(3)
CH(CO_2Me)COCH(CO_2Me) ligands					
C(1)–C(2)	1.467(9)		1.482(7)		1.471(5)
C(2)–C(3)	1.492(8)		1.473(6)		1.471(5)
C(2)–O(1)	1.224(8)		1.231(7)		1.242(4)
C(1)–H(1)	1.076(17)		0.95(4)		0.92(4)
C(1)–C(4)	1.469(9)		1.467(7)		1.465(5)
C(4)–O(2)	1.191(8)		1.200(6)		1.203(5)
C(4)–O(3)	1.367(9)		1.342(7)		1.331(5)
O(3)–C(5)	1.484(12)		1.463(9)		1.442(6)
C(3)–C(6)	1.488(9)		1.473(7)		1.476(5)
C(3)–H(3)	1.08(5)		1.02(3)		0.96(4)
C(6)–O(4)	1.188(7)		1.203(5)		1.208(4)
C(6)–O(5)	1.341(7)		1.331(6)		1.342(4)
O(5)–C(7)	1.475(10)		1.465(8)		1.443(6)
Triphenylphosphine ligands		Triphenylarsine ligands		Bipyridyl ligand	
P(1)–C(41)	1.828(5)	As(1)–C(41)	1.932(4)	N(1)–C(11)	1.345(6)
P(1)–C(51)	1.835(5)	As(1)–C(51)	1.946(4)	N(1)–C(15)	1.354(6)
P(1)–C(61)	1.835(4)	As(1)–C(61)	1.942(3)	N(2)–C(21)	1.333(6)
P(2)–C(11)	1.821(4)	As(2)–C(11)	1.921(3)	N(2)–C(25)	1.360(6)
P(2)–C(21)	1.834(3)	As(2)–C(21)	1.933(3)		
P(2)–C(31)	1.843(5)	As(2)–C(31)	1.953(4)		

L(2)–Pd–C(1)–H(1) torsion angles are −88(3), (**3a**), −87(3), (**3e**), and 100(2)°, (**3f**)]. Evidence that P(1), P(2), and H(3) can be treated as 'first order' with similar P–H couplings is provided by ^{1}H-{^{31}P} decoupled spectra of the dimethylphenylphosphine complex (**3c**). Thus in a selective ^{1}H-{^{31}P} decoupled n.m.r. spectrum of (**3c**), irradiation of the P(1) resonance caused the H(1) signal to collapse to a singlet; however, on irradiation of the P(2) resonance, the H(1) signal remained unchanged as a doublet. Irradiation of either P(1) or P(2) caused the H(3) signal to appear as a doublet. Furthermore the broad-band ^{1}H-{^{31}P} decoupled n.m.r. spectrum of (**3c**), measured at 360 MHz in CD_2Cl_2 at −90 °C, exhibited resonances for the CH protons at δ 4.29 [s, H(1)] and 3.86 p.p.m. [s, H(3)].

Upon warming to room temperature the Me and CH ring signals in the ^{1}H n.m.r. spectra of the palladacyclobutan-3-ones (**3a**)—(**3f**) undergo reversible changes (*e.g.* see Figure 4). Thus the two methyl resonances observed at low temperature collapsed to a singlet, while the two CH signals collapsed to a single resonance (Figure 4). These results are consistent with an inversion of the ring through a planar structure such that there is a rapid interconversion of all equatorial substituents to axial and all axial ones to equatorial. The free energies of activation, $\Delta G_{Tc}^{\ddagger}$, calculated for this process from the coalescence temperatures of the CH protons using the Gutowsky–Holm equations[22] are given in Table 4. The same values are also obtained from the coalescence temperatures of the methyl protons. These values of $\Delta G_{Tc}^{\ddagger}$ are larger than those found for analogous platinum(II) complexes.[1] The *X*-ray data for the complexes (**3a**), (**3e**), and (**3f**) (Tables 1 and 2) indicate that palladacyclobutan-3-ones have shorter transannular metal–carbon bonds and are more highly puckered than corresponding platinacyclobutan-3-ones and as shown in Table 4 the free energy of activation for ring inversion does increase as the fold angle increases.

The room-temperature ^{13}C-{^{1}H} n.m.r. spectra of the palladacyclobutan-3-ones containing tertiary phosphine ligands (**3a**)—(**3c**) exhibited the expected features for the time-averaged planar ring structure. Moreover, since the α- and β-carbons of the ring exhibit coupling to the phosphorus-31 nuclei it is clear that the temperature-dependent ^{1}H n.m.r. spectra observed for these complexes are not due to phosphine dissociation. These complexes contain chemically equivalent but magnetically non-equivalent phosphorus nuclei and the spectra of their ring α-carbons are second order and appear as the A part of an AXX′ spin system (X = ^{31}P).[23,24] The signal due to the ring α-carbons of analogous platinum tertiary phosphine complexes appears as a doublet of doublets with a small central feature and accompanying platinum-195 satellites.[1] However, the observed triplet nature of the ring α-carbons of the palladium complexes (**3a**)—(**3c**) may be due to the ^2J(PP) virtual coupling constants being larger for the palladium complexes than those for the platinum complexes. Thus the observed ^2J(PP) coupling for the rigid forms of [Pt{CH(CO_2Me)COCH(CO_2Me)}(PPh_3)$_2$] and (**3c**) are 11 and 36 Hz respectively. Similarly the value of ^2J(PP) for [Pt{CH_2COCH(COMe)}{P(C_6H_4Cl-*p*)$_3$}$_2$] is 11 Hz,[25] but for analogous palladium complexes values of ^2J(PP) are in the range 9—27 Hz.[16] The ^{13}C-{^{1}H} spectrum of (**3c**) exhibits two resonances for the methyl carbons of the PMe_2Ph ligands, since due to the chiral nature of the ring α-carbons in the complexes (**3**) the two methyls attached to each phosphorus are always non-equivalent. These resonances appear as the A part of an AXX′ spin system (X = ^{31}P). Similarly two sets of phenyl-carbon resonances are observed in the spectrum of the $PMePh_2$ complex (**3b**).

The dynamic behaviour of the palladacyclobutan-3-ones (**3**) in solution results in the CH groups of the four-membered ring appearing as equivalent protons in their room-temperature ^{1}H

Table 2. Selected bond angles (°) in [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$]·H$_2$O (**3a**), [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$]·H$_2$O (**3e**), and [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(bipy)]·H$_2$O (**3f**), with estimated standard deviations in parentheses

(**3a**)		(**3e**)		(**3f**)	
Pd(1)–Pd–P(2)	102.2(1)	As(1)–Pd–As(2)	100.4	N(1)–Pd–N(2)	79.0(1)
Pd(2)–Pd–C(1)	98.9(2)	As(2)–Pd–C(1)	98.4(1)	N(2)–Pd–C(1)	108.2(1)
Pd(1)–Pd–C(3)	91.1(1)	As(1)–Pd–C(3)	92.9(1)	N(1)–Pd–C(3)	104.3(1)
C(1)–Pd–C(3)	68.4(2)	C(1)–Pd–C(3)	68.7(2)	C(1)–Pd–C(3)	68.8(1)
CH(CO$_2$Me)COCH(CO$_2$Me) ligands					
C(1)–C(2)–C(3)	109.5(6)		109.5(5)		107.1(3)
C(1)–C(2)–O(1)	126.0(6)		125.3(4)		126.9(3)
C(3)–C(2)–O(1)	122.6(5)		123.7(4)		124.1(3)
Pd–C(1)–C(2)	80.8(3)		80.6(3)		81.2(2)
Pd–C(1)–H(1)	99(4)		101(3)		99(2)
Pd–C(1)–C(4)	125.9(5)		125.2(4)		122.0(3)
H(1)–C(1)–C(4)	114(3)		114(2)		114(2)
H(1)–C(1)–C(2)	115(3)		117(3)		113(2)
C(4)–C(1)–C(2)	116.8(6)		115.7(5)		122.2(3)
Pd–C(2)–O(1)	131.1(5)		132.9(4)		133.4(3)
Pd–C(2)–C(1)	61.9(4)		61.6(3)		61.1(2)
Pd–C(2)–C(3)	62.9(4)		62.7(3)		60.4(2)
C(1)–C(4)–O(2)	124.6(7)		123.2(6)		124.0(4)
C(1)–C(4)–O(3)	112.4(5)		113.2(4)		114.1(3)
O(2)–C(4)–O(3)	123.0(7)		123.6(5)		121.9(4)
C(4)–O(3)–C(5)	113.6(6)		116.2(5)		116.6(3)
Pd–C(3)–C(2)	79.2(4)		79.9(3)		81.8(2)
Pd–C(3)–H(3)	128(5)		124(2)		118(2)
Pd–C(3)–C(6)	105.8(5)		105.0(4)		105.7(2)
H(3)–C(3)–C(6)	104(4)		111(2)		112(2)
C(2)–C(3)–C(6)	119.6(4)		120.8(4)		122.9(3)
C(2)–C(3)–H(3)	119(5)		114(2)		114(2)
C(3)–C(6)–O(5)	109.6(4)		110.6(3)		109.7(3)
C(3)–C(6)–O(4)	128.1(6)		127.9(4)		127.6(3)
O(4)–C(6)–O(5)	122.2(6)		121.5(5)		122.7(3)
C(6)–O(5)–C(7)	114.5(5)		115.4(4)		116.9(3)
Triphenylphosphine ligands		Triphenylarsine ligands		Bipyridyl ligand	
Pd–P(1)–C(41)	109.3(1)	Pd–As(1)–C(41)	111.1(1)	Pd–N(1)–C(11)	125.6(3)
Pd–P(1)–C(51)	125.6(1)	Pd–As(1)–C(51)	127.0(1)	Pd–N(1)–C(15)	115.1(3)
Pd–P(1)–C(61)	109.5(1)	Pd–As(1)–C(61)	109.7(1)	C(11)–N(1)–C(15)	119.4(4)
C(41)–P(1)–C(61)	109.5(2)	C(41)–As(1)–C(61)	108.6(1)	Pd–N(2)–C(21)	127.0(3)
C(41)–P(1)–C(51)	102.7(2)	C(41)–As(1)–C(51)	100.6(2)	Pd–N(2)–C(25)	113.8(3)
C(51)–P(1)–C(61)	99.4(2)	C(51)–As(1)–C(61)	98.2(1)	C(21)–N(2)–C(25)	119.1(4)
Pd–P(2)–C(11)	114.0(1)	Pd–As(2)–C(11)	114.3(1)		
Pd–P(2)–C(21)	119.3(2)	Pd–As(2)–C(21)	120.1(1)		
Pd–P(2)–C(31)	107.9(2)	Pd–As(2)–C(31)	110.2(1)		
C(11)–P(2)–C(21)	103.1(2)	C(11)–As(2)–C(21)	102.9(1)		
C(11)–P(2)–C(31)	107.8(2)	C(11)–As(2)–C(31)	105.2(2)		
C(21)–P(2)–C(31)	103.8(2)	C(21)–As(2)–C(31)	102.5(1)		

n.m.r. spectra. At 100 MHz the ^{1}H n.m.r. spectra of the CH ring protons of the tertiary phosphine complexes appear as simple first-order doublets (see Figure 4), with coupling to only one phosphorus ligand (presumably the one *trans*) being observed. However, at 400 MHz the CH protons of the complex (**3c**) appear as a second-order filled-in doublet of an AA′XX′ (X = ^{31}P) spin system. The room-temperature ^{1}H n.m.r. spectra of the methyl groups attached to phosphorus in the complexes (**3b**) and (**3c**) also exhibit second-order effects, the phosphorus methyl groups appearing as filled-in doublets. In the 400-MHz ^{1}H n.m.r. spectrum of (**3c**) the diastereotopic PMe$_2$ groups appear as two filled-in doublets. At 100 MHz a multiplet is observed for the PMe$_2$ groups, whilst at 60 MHz the PMe$_2$ groups appear equivalent and exhibit one filled-in doublet.

The i.r. spectra of the palladacyclobutan-3-one complexes normally exhibit five maxima in the range 1 750—1 500 cm^{-1} (Table 5). The two higher frequency bands occur in regions which can be associated with ν(CO) of the ester substituents, and thus the band in the region 1 620—1 588 cm^{-1} can be assigned to ν(CO) of the ring carbonyl. In analogous platinum complexes,[1] the value of ν(CO)$_{\text{ring}}$ occurs in the region 1 648—1 617 cm^{-1}. Since transannular metal–CO interactions would be expected to weaken the ring C=O bond and hence lower the values of ν(CO)$_{\text{ring}}$, the i.r. data provide further evidence for stronger metal–CO interactions in palladium complexes than in platinum complexes as has been shown by the *X*-ray data.

Finally we note that these and earlier studies[1] establish that the oxodimethylenemethane ligand system η^3-CHRCOCHR (R = ester function) forms stable complexes with both palladium(II) and platinum(II) which are considerably more robust than the related trimethylenemethane complex, [Pd{η^3-CH$_2$C(=CH$_2$)CH$_2$}(PPh$_3$)$_2$].[26] Furthermore, in contrast to the palladium(II) complexes (**3**), complexes of the oxodimethylenemethanes η^3-CH$_2$COCHR (R = acyl or ester function) do not exhibit temperature-dependent n.m.r. spectra.[16,25]

Experimental

The techniques used have been previously described.[1] For n.m.r. measurements, chemical shifts (δ p.p.m.) are relative to SiMe$_4$

Table 3. Equations of some least-squares planes in the form $Ax + By + Cz = D$, where x,y, and z are fractional co-ordinates, with distances of relevant atoms from these planes for the complexes (**3a**), (**3e**), and (**3f**)

		Distances (Å) of atoms		
Plane (1)[a]	Equation	C(1)	C(2)	C(3)
(**3a**)	$2.7273x - 17.6782y + 1.4319z = -3.6080$	0.192	0.687	−0.180
(**3e**)	$-2.7657x - 17.4968y - 1.4381z = 3.5972$	−0.165	−0.693	0.131
(**3f**)	$-6.5863x + 8.1711y + 4.3119z = 0.5401$	0.124	−0.677	−0.121
Plane (2)[b]		Pd	O(1)	
(**3a**)	$-7.6868x - 10.2434y + 5.5807z = -1.9537$	1.427	0.259	
(**3e**)	$7.6882x + 10.0797y - 5.6617z = 1.9987$	−1.397	−0.238	
(**3f**)	$-2.8958x + 12.2510y - 5.7845z = -0.4805$	−1.348	−0.259	

[a] Plane (1): Pd, L(1), L(2). [b] Plane (2): C(1), C(2), C(3).

Table 4. Fold angles and free energies of activation for the barrier to ring inversion for some palladacyclobutan-3-ones

Complex	Fold angle (°)	$\Delta G_{Tc}^{\ddagger}$(CH)[a]/ kJ mol^{-1}	$\Delta G_{Tc}^{\ddagger}$(Me)[a]/ kJ mol^{-1}
(**3a**)	53.3(2)	50.7	51.1
(**3b**)		42.1	41.9
(**3c**)		43.5	43.2
(**3d**)		[b]	45.0
(**3e**)	52.3(4)	44.3	44.4
(**3f**)	51.3(3)	40.5	40.3

[a] $\Delta G_{Tc}^{\ddagger}$ values accurate to ± 1 kJ mol^{-1}. [b] Value not obtained due to overlap with methyl signal of CO_2Me group.

for the ^1H and ^{13}C-{^1H} spectra and to $[P(OH)_4]^+$ in D_2O (external) for ^{31}P-{^1H} spectra unless otherwise stated. The quoted i.r. spectra (1 750—1 500 cm^{-1}) were recorded as KBr discs. Light petroleum refers to that fraction of b.p. 40—60 °C. The compounds $[Pd(PPh_3)_4]$,[27] $[Pd(O_2)(PPh_3)_2]$,[28] $[Pd(OCO_3)(PPh_3)_2]$,[9] and $[Pd_2(dba)_3]\cdot CHCl_3$[11] were prepared as described in the literature. Analytical data, yields, and melting points for the new complexes are given in Table 6.

Preparation of $[Pd(AsPh_3)_4]$.—$AsPh_3$ (2.50 g, 8.2 mmol) was added to a stirred suspension of $[Pd_2(dba)_3]\cdot CHCl_3$ (1.0 g, 0.97 mmol) in diethyl ether (50 cm^3) under dinitrogen. After stirring for 4 h a white microcrystalline solid was filtered off, washed with diethyl ether (3 × 10 cm^3) and dried *in vacuo* to give $[Pd(AsPh_3)_4]$ (2.49 g, 97%), m.p. 85—100 °C (decomp.) [lit.,[29] 80—100 °C (decomp.)]. It was also identified by comparison of its i.r. spectrum with that of an authentic sample.

Preparation of Palladacyclobutan-3-ones from Tris(dibenzylideneacetone)dipalladium: General Method.—An excess of ligand was added to a stirred suspension of $[Pd_2(dba)_3]\cdot CHCl_3$ (0.50 g, 0.48 mmol) in diethyl ether (50 cm^3) containing the required 3-oxopentanedioic acid dialkyl ester (1.0 cm^3) under oxygen for 16—72 h. The resulting off-white microcrystalline solid was collected, recrystallised, and dried *in vacuo* at 40 °C.

(*i*) A mixture of the palladium complex, triphenylphosphine (0.60 g, 2.29 mmol), and 3-oxopentanedioic acid dimethyl ester was stirred for 16 h under oxygen. Recrystallisation from dichloromethane–diethyl ether gave white microcrystals of $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]\cdot H_2O$ (0.70 g). N.m.r.: ^1H (100 MHz, [$^2H_1$]chloroform), δ 7.35—7.10 (30 H, m, Ph), 4.11 [2 H, d, CH, ^3J(PH) 3.9], 2.95 (6 H, s, Me), and 2.39 (H_2O); ^1H (100 MHz, [$^2H_1$]chloroform, −50 °C), 7.4—7.0 (30 H, m, Ph), 4.54 [1 H, d, CH, ^3J(PH) 10.3], 3.71 [1 H, t, CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ 4.2], 3.14 (3 H, s, Me), 3.06 (H_2O), and 2.82 (3 H, s, Me); ^1H-{^{31}P} (60 MHz, irradiated at 24.291 14 MHz, [$^2H_1$]chloroform), 7.35—7.10 (30 H, m, Ph), 4.12 (2 H, s, CH), 2.96 (6 H, s, Me), and 2.40 (H_2O); ^{13}C-{^1H} 174.42 [t, CO, ring, ^3J(PC) 5.1], 170.91 (s, CO, CO_2Me), 133.91 [t, second order, Ph, C-β, $|^2J(PC) + {}^4J(PC)|$ 13.0], 131.22 (d, second order, Ph, C-α, $|^1J(PC) + {}^3J(PC)|$ 42.7], 130.13 (s, Ph, C-δ), 128.12 [t, second order, Ph, C-γ, $|^3J(PC) + {}^5J(PC)|$ 10.9], 61.82 [t, second order, CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 47.3 Hz], and 50.3 [s, Me, CO_2Me]; ^{31}P-{^1H} (24 MHz, dichloromethane), 26.2 p.p.m. (s).

(*ii*) A mixture of the palladium complex, triphenylphosphine (0.60 g, 2.29 mmol), and 3-oxopentanedioic acid diethyl ester was stirred for 24 h. Recrystallisation from dichloromethane–diethyl ether gave white microcrystals of $[Pd\{CH(CO_2Et)COCH(CO_2Et)\}(PPh_3)_2]\cdot H_2O$ (0.73 g). N.m.r.: ^1H (100 MHz, [$^2H_1$]chloroform), δ 7.3—7.1 (30 H, m, Ph), 4.09 [2 H, d, CH, ^3J(PH) 3.6], 3.38 [4 H, d of d of q, second order AB spin system, CH_2, ^3J(HH) 7.2, ^2J(HH) 9.0, $\delta_A - \delta_B$ 0.60 p.p.m.], 2.08 (s, H_2O), and 0.77 [6 H, t, Me, ^3J(HH) 7.2 Hz]; ^{31}P-{^1H} (24 MHz, dichloromethane), 26.4 p.p.m. (s).

(*iii*) A mixture of the palladium complex, triphenylarsine (1.00 g, 3.27 mmol), and 3-oxopentanedioic acid dimethyl ester was stirred for 40 h. Recrystallisation from dichloromethane–diethyl ether gave white microcrystals of $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(AsPh_3)_2]\cdot H_2O$ (0.77 g). N.m.r.: ^1H (100 MHz, [$^2H_2$]dichloromethane), δ 7.4—7.1 (30 H, m, Ph), 4.22 (2 H, s, CH), 2.96 (6 H, s, Me), and 2.34 (s, H_2O); ^1H (100 MHz, [$^2H_2$]dichloromethane, −90 °C), 7.6—7.1 (30 H, m, Ph), 4.48 (1 H, s, CH), 4.00 (1 H, s, CH), 2.97 (3 H, s, Me), 2.82 (s, H_2O), and 2.79 p.p.m. (3 H, s, Me).

(*iv*) A mixture of the palladium complex, triphenylarsine (1.00 g, 3.27 mmol), and 3-oxopentanedioic acid diethyl ester was stirred for 48 h. Recrystallisation from dichloromethane–diethyl ether gave white microcrystals of $[Pd\{CH(CO_2Et)COCH(CO_2Et)\}(AsPh_3)_2]\cdot 0.5H_2O$ (0.76 g). N.m.r.: ^1H (100 MHz, [$^2H_1$]chloroform), δ 7.3—7.1 (30 H, m, Ph), 4.33 (2 H, s, CH), 3.42 [4 H, d of d of q, second-order AB spin system, CH_2, ^3J(HH) 6.6, ^2J(HH) 10.5, $\delta_A - \delta_B$ 0.56 p.p.m.], 1.99 (s, H_2O), and 0.77 p.p.m. [6 H, t, Me, ^3J(HH) 6.6 Hz].

(*v*) A mixture of the palladium complex, 2,2′-bipyridyl (0.40 g, 2.56 mmol), and 3-oxopentanedioic acid dimethyl ester was stirred for 48 h. Recrystallisation from methanol–diethyl ether gave yellow microcrystals of $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(bipy)]\cdot 0.5H_2O$ (0.37 g). N.m.r.: ^1H (100 MHz, [$^2H_4$]methanol), δ 8.4—8.1 (6 H, m, bipy), 7.6—7.5 (2 H, m, bipy), 4.07 (2 H, s, CH), and 3.70 (6 H, s, Me); ^1H {100 MHz, [$^2H_2$]dichloromethane–[$^2H_4$]methanol (1:1),–90 °C}, 8.6—7.2 (8 H, m, bipy), 4.49 (1 H, s, CH), 3.89 (3 H, s, Me), 3.67 (1 H, s, CH), and 3.60 p.p.m. (3 H, s, Me).

Table 5. I.r. spectra (1 750—1 500 cm^{-1}) of some palladacyclobutan-3-one complexes $[\overline{\mathrm{Pd(CHRCOC}}\mathrm{HR)L_2}]^a$

R	L	ν(CO)$_{ester}$/cm^{-1}	ν(CO)$_{ring}$/cm^{-1}	ν(ligand)/cm^{-1}
CO_2Me	PPh_3	1 708vs, 1 686s	1 592s	1 579s, 1 569s
CO_2Et	PPh_3	1 699s, 1 677s	1 588s	1 574s, 1 566s
CO_2Me	$AsPh_3$	1 711vs, 1 688s	1 597s	1 580s, 1 571s
CO_2Et	$AsPh_3$	1 705s, 1 680vs	1 615s	1 588s, 1 569s
CO_2Me	bipy^b	1 710s (sh), 1 686vs, 1 676vs	1 607s	1 599s, 1 585s
CO_2Et	bipy^b	1 706vs, 1 679vs	1 615s (sh)	1 600vs, 1 563s
CO_2Pr^n	bipy^b	1 717vs, 1 696s (sh), 1 680(sh)	1 620s	1 599s, 1 563m
CO_2Me	$PMePh_2$	1 717vs, 1 666s	1 598s	1 572m
CO_2Me	PMe_2Ph	1 684s, 1 667s	1 599vs	1 572, 1 560m
CO_2Me	PEt_3	1 670s (sh), 1 658vs	1 605s	1 589s (sh)

^{a} Recorded as KBr discs. ^{b} bipy = L_2.

Table 6. Preparations, yields, melting points, and analytical data^a

Complex	M.p. (θ_c/°C)	Yield (%)	Analysis (%)	
			C	H
(**3a**)·H_2O	173—174^b	88	62.9 (62.9)	4.9 (4.9)
(**3b**)	179—181^b	91	58.1(58.4)	5.0 (5.1)
(**3c**)	166—167^b	84	49.8 (49.8)	5.5 (5.5)
(**3d**)	158—160	48	42.4 (42.8)	7.0 (7.6)
(**3e**)·H_2O	175—177^b	88	56.3 (56.8)	4.5 (4.4)
(**3f**)·0.5 H_2O^c	228—229^b	86	45.7 (46.0)	3.8 (3.9)
(**3g**)·H_2O	146—148	89	63.9 (63.8)	5.2 (5.2)
(**3h**)·0.5 H_2O	135—139	85	58.1 (58.2)	4.9 (4.7)
(**3i**)·0.25 H_2O^d	140—142	82	49.0 (48.8)	4.4 (4.4)
(**3j**)·0.25 H_2O^e	119—122	81	50.9 (50.9)	4.9 (5.0)

^{a} Calculated values are given in parentheses. ^{b} With decomposition. ^{c} N = 6.3 (6.3)%. ^{d} N = 5.8 (6.0)%. ^{e} N = 5.6 (5.7)%.

(*vi*) A mixture of the palladium complex, 2,2′-bipyridyl (0.40 g, 2.56 mmol), and 3-oxopentanedioic acid diethyl ester was stirred for 64 h. Recrystallisation from methanol–diethyl ether gave yellow microcrystals of $[\overline{\mathrm{Pd\{CH(CO_2Et)COC}}\mathrm{H(CO_2Et)\}}$-(bipy)]·0.25$H_2O$ (0.37 g). N.m.r.: ^{1}H (100 MHz, [$^2H_2$]dichloromethane), δ 8.5—8.0 (6 H, m, bipy), 7.5—7.3 (2 H, m, bipy), 4.14 [4 H, q, CH_2, ^3J(HH) 6.6], 3.82 (2 H, s, CH), 1.88 (s, H_2O), and 1.23 p.p.m. [6 H, t, CH_3, ^3J(HH) 6.6 Hz].

(*vii*) A mixture of the palladium complex, 2,2′-bipyridyl (0.40 g, 2.56 mmol), and 3-oxopentanedioic acid di-n-propyl ester was stirred for 72 h. Recrystallisation from methanol–diethyl ether gave yellow microcrystals of $[\overline{\mathrm{Pd\{CH(CO_2Pr^n)COC}}\mathrm{H}$ $\mathrm{(CO_2Pr^n)\}}$(bipy)]·0.25H_2O (0.39 g). N.m.r.: ^{1}H (100 MHz, [$^2H_1$]chloroform), δ 8.3—8.0 (6 H, m, bipy), 7.5—7.2 (2 H, m, bipy), 4.03 [4 H, t, CH_2, ^3J(HH) 6.6], 3.86 (2 H, s, CH), 2.10 (s, H_2O), 1.73 [4 H, septet, CH_2, ^3J(HH) 6.6], and 0.94 p.p.m. [6 H, t, CH_3, ^3J(HH) 6.6 Hz].

(*viii*) A mixture of the palladium complex, methyldiphenylphosphine (0.4 cm^3, 2.13 mmol), and 3-oxopentanedioic acid dimethyl ester was stirred for 16 h. Recrystallisation from dichloromethane–hexane gave white microcrystals of $[\overline{\mathrm{Pd\{CH(CO_2Me)COC}}\mathrm{H(CO_2Me)\}(PMePh_2)_2}]$ (0.60 g). N.m.r.: ^{1}H (100 MHz, [$^2H_2$]dichloromethane), δ 7.4—7.1 (20 H, m, Ph), 4.00 [2 H, d, CH, ^3J(PH) 4.3], 3.00 (6 H, s, CO_2Me), and 1.75 [6 H, d, second-order, PMe, |^2J(PH) + ^4J(PH)| 8.5]; ^{1}H (100 MHz, [$^2H_2$]dichloromethane, −90 °C), 7.6—7.0 (20 H, m, Ph), 4.36 [1 H, d, CH, ^3J(PH) 11.4], 3.78 [1 H, t, CH, |$^3J(PH)_{trans}$ + $^3J(PH)_{cis}$| 5.0], 3.02 (3 H, s, CO_2Me), 2.78 (3 H, s, CO_2Me), and 2.0—1.6 (6 H, m, PMe); ^{1}H-{^{31}P} (60 MHz, irradiated at 24.290 69 MHz), 7.4—7.1 (20 H, m, Ph), 4.00 (2 H, s, CH), 3.00 (6 H, s, CO_2Me), and 1.75 (6 H, s, PMe); ^{13}C-{^{1}H} 175.76 [t, CO, ring, ^3J(PC) 5.3], 171.21 (s, CO, CO_2Me), 132.66 [d, second order, Ph, C-α, |^1J(PC) + ^3J(PC)| 44.2], 132.36 [d, second order, Ph, C-α, |^1J(PC) + ^3J(PC)| value not obtainable due to overlap with C-β spectrum], 132.18 [t, second order, Ph, C-β, |^2J(PC) + ^4J(PC)| 13.7], 131.52 [t, second order, Ph, C-β, |^2J(PC) + ^4J(PC)| 13.7], 130.39 (s, Ph, C-δ), 129.98 (s, Ph, C-δ), 128.51 [t, second order, Ph, C-γ, |^3J(PC) + ^5J(PC)| 10.7], 128.38 [t, second order, Ph, C-γ, |^3J(PC) + ^5J(PC)| 10.7], 59.26 [t, second order, CH, |$^2J(PC)_{trans}$ + $^2J(PC)_{cis}$| 48.8], 50.10 (s, Me, CO_2Me), and 14.50 [t, second order, Me, PMe, |^1J(PC) + ^3J(PC)| 30.52 Hz]; ^{31}P-{^{1}H} (24 MHz, dichloromethane), 7.9 p.p.m. (s).

(*ix*) A mixture of the palladium complex, dimethylphenylphosphine (0.4 cm^3, 2.80 mmol), and 3-oxopentanedioic acid dimethyl ester was stirred for 16 h. Recrystallisation from dichloromethane–hexane gave white microcrystals of $[\overline{\mathrm{Pd\{CH(CO_2Me)COC}}\mathrm{H(CO_2Me)\}(PMe_2Ph)_2}]$ (0.45 g). N.m.r.: ^{1}H (400 MHz, [$^2H_1$]chloroform), δ 7.70—7.27 (10 H, m, Ph), 4.26 [d, second order, 2 H, CH, |$^3J(PH)_{trans}$ + $^3J(PH)_{cis}$| 4.9], 3.50 (6 H, s, CO_2Me), 1.47 [6 H, d, second order, PMe, |^2J(PH) + ^4J(PH)| 9.2], and 1.44 [6 H, d, second order PMe, |^2J(PH) + ^4J(PH)| 9.2]; ^{1}H (100 MHz, [$^2H_2$]dichloromethane, −90 °C), 7.5—7.1 (10 H, m, Ph), 4.45 [1 H, d, CH, ^3J(PH) 12.0], 3.96 [1 H, t, CH, $^3J(PH)_{trans}$ + $^3J(PH)_{cis}$| 5.8], 3.46 (3 H, s, CO_2Me), 3.41 (3 H, s, CO_2Me), and 1.65—1.35 (12 H, m, PMe); ^{1}H-{^{31}P} (60 MHz, irradiated at 24.290 28 MHz, dichloromethane), 7.4—7.2 (10 H, m, Ph), 4.13 (2 H, s, CH), 3.43 (6 H, s, CO_2Me), and 1.47 (12 H, s, PMe); ^{1}H-{^{31}P} (360 MHz, broad-band irradiation, [$^2H_2$]-dichloromethane, −90 °C), 4.29 (1 H, s, CH), 3.86 (1 H, s, CH), 3.44 (3 H, s, Me), and 3.38 (3 H, s, Me); ^{1}H-{^{31}P} {360 MHz, irradiated at 145.784 523 MHz [P(1)], −90 °C}, 4.29 (1 H, s, CH), 3.86 [1 H, d, CH, ^3J(PH) 4], 3.44 (3 H, s, Me), and 3.38 (3 H, s, Me); ^{1}H-{^{31}P} {360 MHz, irradiated at 145.784 072 MHz [P(2)], −90 °C}, 4.29 [1 H, d, CH, ^3J(PH) 11], 3.86 [1 H, d, CH, ^3J(PH) 4], 3.44 (3 H, s, Me), and 3.38 (3 H, s, Me); ^{13}C-{^{1}H} 175.52 [t, CO, ring, ^3J(PC) 5.4], 171.82 (s, CO, CO_2Me), 134.19 [d, second order, Ph, C-α, |^1J(PC) + ^3J(PC)| 43.1], 130.35 [t, second order, Ph, C-β, |^2J(PC) + ^4J(PC)| 12.21], 130.25 (s, Ph, C-δ), 128.54 [t, second order, Ph, C-γ, |^3J(PC) + ^5J(PC)| 9.9], 57.34 [t, second order, CH, |$^2J(PC)_{trans}$ + $^2J(PC)_{cis}$| 49.6], 50.32 (s, Me, CO_2Me), 15.35 [t, second order, Me, PMe, |^1J(PC) + ^3J(PC)| 28.6], and 14.15 [t, second order, Me, PMe, |^1J(PC) + ^3J(PC)| 27.1]; ^{31}P-{^{1}H} (24 MHz, dichloromethane), −7.5 (s); ^{31}P-{^{1}H} (145.8 MHz, [$^2H_2$]dichloromethane, external reference H_3PO_4 in D_2O at 0 °C, −90 °C), −4.23 {d, P(1), ^2J[P(2)P(1)] 36.0}, and −7.32 p.p.m. {d, P(2), ^2J[P(1)P(2)] 36.0 Hz}.

(*x*) A mixture of the palladium complex, triethylphosphine (0.3 cm^3, 2.04 mmol), and 3-oxopentanedioic acid dimethyl ester was stirred for 16 h. Recrystallisation from dichloromethane–hexane gave white microcrystals of $[\overline{\mathrm{Pd\{CH(CO_2Me)COC}}\mathrm{H}$-$\mathrm{(CO_2Me)\}(PEt_3)_2}]$·$H_2O$ (0.25 g). N.m.r.: ^{1}H (100 MHz, [$^2H_2$]dichloromethane), δ 3.98 [2 H, d, CH, ^3J(PH) 4.4], 3.66 (6 H, s, Me, CO_2Me), 2.49 (s, H_2O), 1.93—1.64 (12 H, m, CH_2,

Table 7. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(PPh$_3$)$_2$]·H$_2$O (**3a**)							
Pd	0.027 27(4)	0.239 27(3)	0.382 36(4)	C(31)	−0.067 4(4)	0.327 37(20)	0.611 7(5)
P(1)	−0.183 95(13)	0.195 00(9)	0.238 12(15)	C(32)	−0.189 5(4)	0.302 83(20)	0.601 3(5)
P(2)	0.023 69(14)	0.256 84(9)	0.606 09(15)	C(33)	−0.256 4(4)	0.357 86(20)	0.602 1(5)
O(1)	0.206 7(5)	0.156 7(3)	0.268 8(5)	C(34)	−0.201 2(4)	0.437 48(20)	0.613 3(5)
O(2)	0.416 2(5)	0.268 4(4)	0.616 1(6)	C(35)	−0.079 0(4)	0.462 05(20)	0.623 7(5)
O(3)	0.251 8(5)	0.168 5(3)	0.587 9(5)	C(36)	−0.012 1(4)	0.407 02(20)	0.622 8(5)
O(4)	0.161 5(6)	0.382 9(3)	0.259 3(6)	C(41)	−0.226 1(4)	0.266 4(2)	0.124 0(4)
O(5)	0.022 8(5)	0.327 9(3)	0.044 8(5)	C(42)	−0.193 6(4)	0.343 8(2)	0.193 5(4)
C(1)	0.222 8(5)	0.263 3(4)	0.440 1(6)	C(43)	−0.227 1(4)	0.402 2(2)	0.117 4(4)
C(2)	0.181 1(5)	0.217 3(3)	0.298 2(7)	C(44)	−0.293 3(4)	0.383 4(2)	−0.028 4(4)
C(3)	0.076 1(5)	0.242 2(3)	0.199 3(6)	C(45)	−0.325 8(4)	0.306 0(2)	−0.097 9(4)
C(4)	0.308 6(6)	0.236 3(4)	0.556 4(7)	C(46)	−0.292 3(4)	0.247 5(2)	−0.021 7(4)
C(5)	0.335 5(10)	0.141 0(6)	0.707 7(11)	C(51)	−0.311 2(3)	0.172 3(2)	0.300 4(4)
C(6)	0.095 1(6)	0.325 3(4)	0.177 0(7)	C(52)	−0.320 7(3)	0.108 0(2)	0.369 5(4)
C(7)	0.039 3(10)	0.407 2(5)	0.007 6(9)	C(53)	−0.413 9(3)	0.089 3(2)	0.421 9(4)
C(11)	−0.046 3(4)	0.167 05(17)	0.654 4(4)	C(54)	−0.497 6(3)	0.134 7(2)	0.405 3(4)
C(12)	−0.099 8(4)	0.167 00(17)	0.754 6(4)	C(55)	−0.488 1(3)	0.198 9(2)	0.336 2(4)
C(13)	−0.155 7(4)	0.095 91(17)	0.783 0(4)	C(56)	−0.394 9(3)	0.217 7(2)	0.283 7(4)
C(14)	−0.158 2(4)	0.024 86(17)	0.711 2(4)	C(61)	−0.215 1(4)	0.099 62(19)	0.129 1(4)
C(15)	−0.104 8(4)	0.024 94(17)	0.611 0(4)	C(62)	−0.120 7(4)	0.062 50(19)	0.148 3(4)
C(16)	−0.048 8(4)	0.095 99(17)	0.582 6(4)	C(63)	−0.146 0(4)	−0.011 77(19)	0.070 2(4)
C(21)	0.169 7(3)	0.298 1(3)	0.759 2(4)	C(64)	−0.265 6(4)	−0.048 87(19)	−0.027 3(4)
C(22)	0.256 6(3)	0.363 0(3)	0.752 5(4)	C(65)	−0.359 9(4)	−0.011 73(19)	−0.046 6(4)
C(23)	0.367 1(3)	0.395 8(3)	0.889 0(4)	C(66)	−0.334 7(4)	0.062 50(19)	0.031 6(4)
C(24)	0.390 4(3)	0.363 9(3)	0.992 3(4)	H(1)	0.246(5)	0.326 0(8)	0.446(6)
C(25)	0.303 5(3)	0.299 0(3)	0.999 0(4)	H(3)	0.024(8)	0.208(5)	0.095(4)
C(26)	0.193 1(3)	0.266 1(3)	0.882 5(4)	O(6)	0.493 2(10)	0.489 2(7)	0.615 3(13)
(*b*) [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$]·H$_2$O (**3e**)							
Pd	0.036 21(3)	0.242 04(2)	0.373 81(3)	C(33)	−0.253 0(3)	0.361 66(18)	0.594 4(4)
As(1)	−0.180 73(4)	0.196 12(3)	0.232 33(5)	C(34)	−0.197 6(3)	0.442 72(18)	0.612 8(4)
As(2)	0.030 41(4)	0.259 81(3)	0.601 17(5)	C(35)	−0.075 6(3)	0.469 35(18)	0.630 0(4)
O(1)	0.219 0(3)	0.160 3(2)	0.271 7(4)	C(36)	−0.009 1(3)	0.414 48(18)	0.628 9(4)
O(2)	0.416 4(4)	0.272 7(3)	0.606 5(5)	C(41)	−0.231 2(3)	0.270 4(2)	0.109 6(4)
O(3)	0.253 7(4)	0.174 2(3)	0.585 2(4)	C(42)	−0.203 6(3)	0.348 4(2)	0.172 7(4)
O(4)	0.171 2(4)	0.384 3(2)	0.238 2(5)	C(43)	−0.239 4(3)	0.405 8(2)	0.092 8(4)
O(5)	0.020 5(3)	0.326 1(2)	0.039 7(4)	C(44)	−0.302 7(3)	0.385 1(2)	−0.050 3(4)
C(1)	0.227 9(4)	0.267 8(3)	0.433 1(5)	C(45)	−0.330 3(3)	0.307 1(2)	−0.113 4(4)
C(2)	0.188 6(4)	0.220 0(3)	0.294 8(5)	C(46)	−0.294 5(3)	0.249 8(2)	−0.033 5(4)
C(3)	0.085 7(4)	0.242 7(3)	0.195 4(5)	C(51)	−0.313 7(2)	0.170 90(20)	0.297 8(3)
C(4)	0.309 9(5)	0.239 9(4)	0.549 4(5)	C(52)	−0.323 4(2)	0.105 67(20)	0.367 4(3)
C(5)	0.330 1(8)	0.142 8(5)	0.700 2(8)	C(53)	−0.414 4(2)	0.086 59(20)	0.420 7(3)
C(6)	0.099 3(5)	0.324 6(3)	0.165 6(5)	C(54)	−0.495 7(2)	0.132 77(20)	0.404 6(3)
C(7)	0.028 3(7)	0.404 5(4)	−0.002 9(7)	C(55)	−0.485 9(2)	0.198 00(20)	0.335 1(3)
C(11)	−0.045 7(3)	0.164 77(15)	0.653 6(3)	C(56)	−0.394 9(2)	0.217 07(20)	0.281 7(3)
C(12)	−0.098 4(3)	0.165 81(15)	0.752 2(3)	C(61)	−0.216 5(3)	0.094 32(16)	0.121 0(3)
C(13)	−0.156 2(3)	0.094 73(15)	0.782 3(3)	C(62)	−0.123 9(3)	0.057 11(16)	0.140 9(3)
C(14)	−0.161 4(3)	0.022 56(15)	0.713 8(3)	C(63)	−0.149 0(3)	−0.017 74(16)	0.066 8(3)
C(15)	−0.108 8(3)	0.021 49(15)	0.615 3(3)	C(64)	−0.266 7(3)	−0.055 39(16)	−0.027 3(3)
C(16)	−0.050 9(3)	0.092 58(15)	0.585 2(3)	C(65)	−0.359 3(3)	−0.018 18(16)	−0.047 2(3)
C(21)	0.179 5(3)	0.303 0(2)	0.761 5(3)	C(66)	−0.334 2(3)	0.056 68(16)	0.026 9(3)
C(22)	0.267 5(3)	0.367 7(2)	0.754 4(3)	H(1)	0.249(4)	0.324(2)	0.438(5)
C(23)	0.375 5(3)	0.399 5(2)	0.669 4(3)	H(3)	0.038(3)	0.203 1(19)	0.107(3)
C(24)	0.395 4(3)	0.366 7(2)	0.991 5(3)	O(10)*	0.488 8(9)	0.473 6(7)	0.591 7(11)
C(25)	0.307 4(3)	0.302 0(2)	0.998 6(3)	O(11)*	0.494 8(14)	0.469 7(10)	0.375 2(19)
C(26)	0.199 4(3)	0.270 2(2)	0.883 6(3)	O(12)*	0.476 8(14)	0.458 4(9)	0.454(2)
C(31)	−0.064 5(3)	0.333 80(18)	0.610 5(4)	O(13)*	0.558 0(13)	0.451 0(8)	0.340 6(14)
C(32)	−0.186 5(3)	0.307 21(18)	0.593 3(4)				
(*c*) [Pd{CH(CO$_2$Me)COCH(CO$_2$Me)}(bipy)]·H$_2$O (**3f**)							
Pd	0.271 97(4)	0.089 91(2)	0.370 30(2)	C(3)	0.390 7(4)	0.201 0(2)	0.313 2(2)
N(1)	0.356 5(4)	0.084 5(3)	0.509 7(2)	C(4)	0.132 4(4)	0.041 6(3)	0.168 2(2)
N(2)	0.156 5(4)	−0.028 4(3)	0.418 1(3)	C(5)	0.181 9(6)	−0.100 9(3)	0.096 3(4)
O(1)	0.457 0(3)	0.127 24(20)	0.168 55(18)	C(6)	0.301 5(4)	0.283 1(2)	0.341 2(2)
O(2)	−0.000 3(4)	0.039 3(2)	0.133 8(2)	C(7)	0.315 2(7)	0.411 9(3)	0.443 5(4)
O(3)	0.236 2(3)	−0.025 37(19)	0.154 7(2)	C(11)	0.455 0(6)	0.145 6(3)	0.551 9(3)
O(4)	0.172 8(3)	0.308 13(20)	0.311 1(2)	C(12)	0.510 1(6)	0.136 0(4)	0.644 5(3)
O(5)	0.386 4(4)	0.329 83(19)	0.407 21(19)	C(13)	0.458 3(6)	0.061 7(4)	0.695 6(4)
C(1)	0.192 7(4)	0.115 0(3)	0.230 2(2)	C(14)	0.353 4(6)	−0.000 2(4)	0.653 6(3)
C(2)	0.355 2(4)	0.150 9(2)	0.224 9(2)	C(15)	0.304 4(5)	0.012 3(3)	0.559 9(3)

Table 7 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(21)	0.059 2(5)	−0.083 1(4)	0.367 7(3)	C(25)	0.196 2(5)	−0.051 0(3)	0.509 0(3)
C(22)	−0.003 1(6)	−0.162 9(4)	0.404 3(4)	H(1)	0.119(4)	0.160(2)	0.242(2)
C(23)	0.035 8(7)	−0.185 9(4)	0.496 7(4)	H(3)	0.502(5)	0.207(3)	0.328(3)
C(24)	0.136 7(6)	−0.129 9(4)	0.549 3(4)	O(6)	0.770 8(5)	0.174 6(3)	0.204 9(4)

* Disordered site for H_2O.

PEt_3), and 1.21—0.91 (18 H, m, CH_3, PEt_3); ^1H (100 MHz, [$^2H_2$]dichloromethane, −85 °C), 4.22 [1 H, d, CH, $^3J(PH)$ 10.6 Hz], 3.67 (shoulder on side of CO_2Me signal, CH), 3.65 (3 H, s, Me, CO_2Me), 3.50 (3 H, s, Me, CO_2Me), 1.95—1.66 (12 H, m, CH_2, PEt_3), and 1.19—0.93 (18 H, m, CH_3, PEt_3); $^{31}P-\{^1H\}$ (24 MHz, dichloromethane), 18.0 p.p.m. (s).

*Preparation of Metallacyclobutan-*3-*ones from Tetrakis-*(*ligand*)*palladium*(0): *General Method.*—A mixture of the metal(0) complex and the 3-oxopentanedioic acid dialkyl ester (0.5 cm^3) in benzene (30 cm^3) was stirred in a flask open to the air for 16—48 h. Addition of diethyl ether (100 cm^3) to the reaction mixture afforded a fine white solid which was recrystallised from dichloromethane–light petroleum and dried *in vacuo* (0.4 mmHg) at 40 °C.

(*i*) $[Pd(PPh_3)_4]$ (0.50 g, 0.43 mmol) and 3-oxopentanedioic acid dimethyl ester were stirred for 16 h and gave white microcrystals of $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]\cdot H_2O$ (0.34 g, 96%) identified by its i.r. and ^1H n.m.r. spectra.

(*ii*) $[Pd(PPh_3)_4]$ (0.50 g, 0.43 mmol) and 3-oxopentanedioic acid diethyl ester were stirred for 24 h and gave white microcrystals of $[Pd\{CH(CO_2Et)COCH(CO_2Et)\}(PPh_3)_2]\cdot H_2O$ (0.34 g, 94%) identified by its i.r. and ^1H n.m.r. spectra.

(*iii*) $[Pd(AsPh_3)_4]$ (0.50 g, 0.38 mmol) and 3-oxopentanedioic acid dimethyl ester were stirred for 40 h and gave white microcrystals of $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(AsPh_3)_2]\cdot H_2O$ (0.32 g, 93%) identified by its i.r. and ^1H n.m.r. spectra.

(*iv*) $[Pd(AsPh_3)_4]$ (0.50 g, 0.38 mmol) and 3-oxopentanedioic acid diethyl ester were stirred for 48 h and gave white microcrystals of $[Pd\{CH(CO_2Et)COCH(CO_2Et)\}(AsPh_3)_2]\cdot 0.5H_2O$ (0.32 g, 92%) identified by its i.r. and ^1H n.m.r. spectra.

*Preparation of Palladacyclobutan-*3-*ones from Peroxocarbonatobis*(*triphenylphosphine*)*palladium*(II): *General Method.*—A suspension of $[Pd(OCO_3)(PPh_3)_2]\cdot C_6H_6$ in ethanol (40 cm^3) containing the 3-oxopentanedioic acid dialkyl ester was stirred and slowly heated to 45—55 °C until a clear solution had formed. The resulting solution was filtered and the filtrate was evaporated under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane followed by addition of diethyl ether gave, after standing for 16 h, a white crystalline solid which was recrystallised from dichloromethane–light petroleum and dried *in vacuo* (0.4 mmHg) at 40 °C.

(*i*) $[Pd(OCO_3)(PPh_3)_2]\cdot C_6H_6$ (0.20 g, 0.26 mmol) and 3-oxopentanedioic acid dimethyl ester (0.3 cm^3, 2.0 mmol) gave white microcrystals of $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]\cdot H_2O$ (0.12 g, 58%) identified by its i.r. and ^1H n.m.r. spectra.

(*ii*) $[Pd(OCO_3)(PPh_3)_2]\cdot C_6H_6$ (0.20 g, 0.26 mmol) and 3-oxopentanedioic acid diethyl ester (0.3 cm^3, 1.6 mmol) gave white microcrystals of $[Pd\{CH(CO_2Et)COCH(CO_2Et)\}(PPh_3)_2]\cdot H_2O$ (0.10 g, 46%) identified by its i.r. and ^1H n.m.r. spectra.

Reaction of $[Pd(O_2)(PPh_3)_2]$ *with* 3-*Oxopentanedioic Acid Dimethyl Ester.*—A solution of $[Pd(O_2)(PPh_3)_2]$ (0.20 g, 0.30 mmol) in benzene (10 cm^3) containing 3-oxopentanedioic acid dimethyl ester (0.2 cm^3, 1.4 mmol) was stirred for 1 h under oxygen. Addition of diethyl ether (40 cm^3) to the reaction mixture afforded a white microcrystalline solid which was recrystallised from dichloromethane–hexane, dried *in vacuo*, and identified as $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]\cdot H_2O$ (0.11 g, 44%) by its i.r. and ^1H n.m.r. spectra.

X-*Ray Crystal Structures.*—(*a*) $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]\cdot H_2O$ (**3a**). The crystal was mounted in air. The cell dimensions were determined from an oscillation photograph about the *c* axis of the crystal and from its optimized counter angles for zero- and upper-layer reflections on a Weissenberg diffractometer. Intensity data were collected at room temperature on a Stoe Weissenberg diffractometer using an ω-scan technique in the range $7 \leqslant 2\theta \leqslant 54°$. The 5 093 reflections, collected from Weissenberg layers *hk* (0—12), having $I \geqslant 3\sigma(I)$, were corrected for Lorentz and polarisation effects. Subsequent calculations were carried out using the computer program SHELX.[30]

Crystal data. $C_{43}H_{38}O_5P_2Pd\cdot H_2O$, M = 821.4, triclinic, a = 11.995(5), b = 17.72(1), c = 10.30(1) Å, α = 94.7(1), β = 110.8(1), γ = 102.84(2)°, U = 1 962.6 Å^3, Z = 2, D_c = 1.40 g cm^{-3}, $F(000)$ = 844, space group $P\bar{1}$, Mo-K_α *X*-radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 5.28 cm^{-1}.

The structure was solved by conventional Patterson and difference-Fourier techniques. Scattering factors were taken from ref. 31. In the final stages of block-matrix least-squares refinement all non-hydrogen atoms, except the oxygen atom in the water molecule, were given anisotropic thermal parameters. All the phenyl rings including hydrogen atoms were treated as rigid bodies with D_{6h} symmetry (C–C 1.395, C–H 1.08 Å). The hydrogen-atom positions for H(1) and H(3) were located from a difference-Fourier map and were refined with isotropic thermal parameters. Final cycles employed a weight $w = k/(\sigma^2F + gF^2)$, where k = 1.087, g = 0.0034. Final R [= $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$] and R' [= $\Sigma w(||F_o| - |F_c||)/\Sigma w|F_o|$] values are 0.0548, 0.0597. The atomic co-ordinates for all three structures are given in Table 7.

(*b*) $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(AsPh_3)_2]\cdot H_2O$ (**3e**). Conditions were as for (**3a**), except: 6 025 reflections from Weissenberg layers *hk*(0—13); weighting parameter k = 1.394, g = 0.0012. Final R and R' values are 0.0426, 0.0455.

Crystal data. $C_{43}H_{38}As_2O_5Pd\cdot H_2O$, M = 909.3, triclinic, a = 12.219(6), b = 17.56(1), c = 10.44(1) Å, α = 93.3(1), β = 110.8(1), γ = 103.56(2)°, U = 2 010.7 Å^3, Z = 2, D_c = 1.51 g cm^{-3}, $F(000)$ = 936, space group $P\bar{1}$, μ(Mo-K_α) = 20.39 cm^{-1}.

(*c*) $[Pd\{CH(CO_2Me)COCH(CO_2Me)\}(bipy)]\cdot H_2O$ (**3f**). Conditions were as for (**3a**), except: crystal mounted about the *a* axis; intensity data were collected in the range $7 < 2\theta < 60°$ for 4 000 reflections from Weissenberg layers (0—10)*kl*; final weighting parameters, k = 1, g = 0.000 083. Rinal R and R' values are 0.0425, 0.0320.

Crystal data. $C_{17}H_{16}N_2O_5Pd\cdot H_2O$, M = 453.1 monoclinic, a = 8.43(1), b = 14.594(6), c = 14.170(6) Å, β = 92.1(1)°, U = 1 742.1 Å^3, Z = 4, D_c = 1.73 g cm^{-3}, $F(000)$ = 872, space group $P2_1/c$, μ(Mo-K_α) = 9.82 cm^{-1}.

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