Structure of $[\overline{\mathrm{Pd}\{\mathrm{C}_5(\mathrm{CO}_2\mathrm{Me})_4(\mathrm{C}}\mathrm{O}_2\mathrm{Me})\mathrm{C}(\mathrm{CO}_2\mathrm{Me})\mathrm{Cl}\}\{\mathrm{acac}\}]$ and the Intermediacy of a σ-Butadienyl Complex in the $\mathrm{Pd}^{\mathrm{II}}$-Induced Trimerisation of Dimethyl Acetylenedicarboxylate

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Summary The structure of the complex, $[\overline{\mathrm{Pd}\{\mathrm{C}_5(\mathrm{CO}_2\mathrm{Me})_4(\mathrm{CO}_2}\text{-}\mathrm{Me})\mathrm{C}(\mathrm{CO}_2\mathrm{Me})\mathrm{Cl}\}\mathrm{Cl}]_2$, obtained from reaction of dimethyl acetylenedicarboxylate (dma) and $\mathrm{Pd(PhCN)_2Cl_2}$, has been established spectroscopically and confirmed by *X*-ray analysis of the acetylacetonate; such complexes were also obtained by reaction of a σ-butadienyl complex with dma.

Avram *et al.*[1] have reported the synthesis of a complex, $[Pd(R_6C_6)Cl_2]_n$ (I; R = CO_2Me), from dimethyl acetylenedicarboxylate (dma) and $[Pd(PhCN)_2Cl_2]$. A reinvestigation of this complex and of some of the degradation reactions reported by Avram showed that (I) was a dimer with a Pd_2Cl_2 bridge (which could be split by triphenylphosphine, for example); that the second chlorine in each half of the dimer was bonded to carbon; and that in the i.r. spectrum there was, apart from the normal ester ν_{CO} at 1746 cm^{-1}, a strong band (ν_{CO}) at 1638 cm^{-1} which we assign to a metal-complexed ester.

On reaction with thallium acetylacetonate a new complex, $[Pd(R_6C_6Cl)acac]$ (II), was formed with a similar i.r. spectrum to (I). This reaction was readily reversed with HCl.

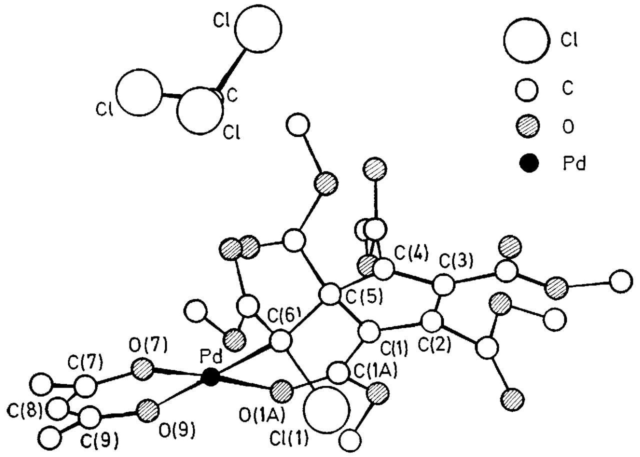
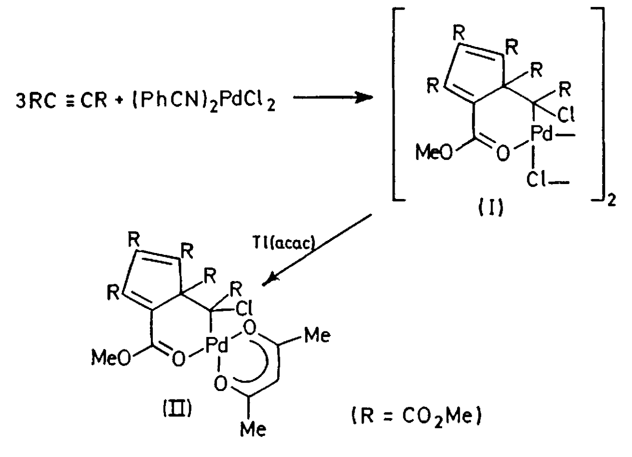


FIGURE. *The structure of* $[Pd\{C_6(CO_2Me)_4(CO_2Me)C(CO_2Me)Cl\}\{acac\}],0{\cdot}66CHCl_3$. *Bond lengths:* Pd–O(1A) 2·05(1), Pd–O(7) 2·00(1), Pd–O(9) 2·02(1), Pd–C(6) 2·04(1) (all other distances to Pd > 2·89 Å), C(1)–C(2) 1·36(2); C(2)–C(3) 1·47(2), C(3)–C(4) 1·37(2), C(4)–C(5) 1·52(2), C(5)–C(1) 1·53(2) C(1)–C(1A) 1·44(2), C(1A)–O(1A) 1·23(2), C(5)–C(6) 1·54(2), and C(6)–Cl 1·80(1) Å.

The n.m.r. spectra of (I) and (II) showed considerable asymmetry in the organic ligand[‡] and were consistent with their formulation as shown in Scheme 1.



SCHEME 1

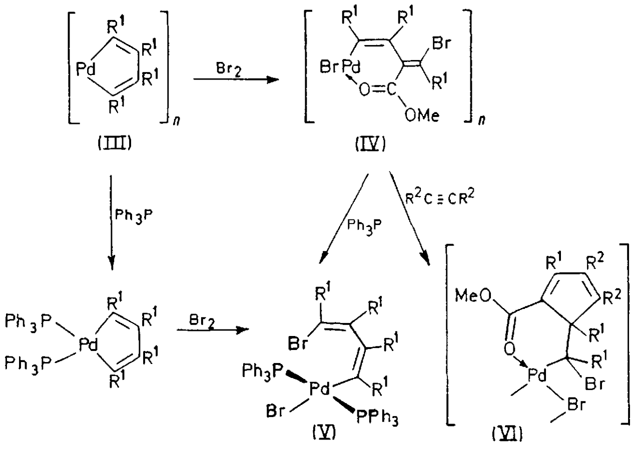
The structure shown was found to be correct by an *X*-ray structure determination of a crystal of (II) grown from chloroform solution. *Crystal data:* $C_{23}H_{25}ClO_{14}Pd,0{\cdot}66CHCl_3$, M = 746·88, monoclinic, a = 8·78(1), b = 21·15(2), c = 16·76(2) Å, β = 93·0(1)°, Z = 4, D_c 1·594, D_m = 1·55 g cm^{-3}, space group $P2_1/c$.

The structure was solved from Patterson and electron density maps using 2391 observed reflections of 3366 unique reflections measured with graphite monochromatised Mo-K_α radiation on a Syntex automatic diffractometer. It was refined to a conventional R of 0·071.

The structure of (II) is shown in the Figure together with some important bond lengths. The metal atom is bound to C(6) by a normal σ-bond, to the two oxygens of the acetylacetonate, and to the ketonic oxygen [O(1A)] of the ester group on C(1). This latter interaction forms another 6-membered ring, but one which is considerably twisted. Bond lengths are normal, in particular Pd–O(1A) is hardly significantly longer than Pd–O(7) or Pd–O(9). The bond angles about Pd are 84 [∠O(1A)PdO(9)], 94, 92, and 90°.

The molecules in the structure are held together by a hydrogen-bonding network involving chloroform molecules [about 0·66 $CHCl_3$ per molecule of (II)] which have become entrapped in the crystal lattice during crystallisation.

Complexes of this type are also formed in a different series of reactions (Scheme 2). The palladiacyclopentadiene (III)[2] is cleaved by one equivalent of bromine to give the σ-butadienyl-complex (IV) [ν_{CO} 1620(s) and 1732(vs) cm^{-1}], characterised as the bis(triphenylphosphine) complex (V) [ν_{CO} 1732(vs) cm^{-1}; δ 2·95, 3·43, 3·57, 3·78 (all s, 3H, CO_2Me), and 7·5 (m, 30H, phenyl)].[3] The complex (IV) reacted readily with dimethyl acetylenedicarboxylate to give (VI; $R^1 = R^2 = CO_2Me$), characterised as the acetylacetonate which was virtually identical to (II). Both it, (I) and (II) gave hexamethyl mellitate on reaction with aqueous cyanide.



SCHEME 2

Complex (IV) also reacted with hexafluorobut-2-yne to give a complex which was identified, from its spectroscopic properties, as (VI; $R^1 = CO_2Me$, $R^2 = CF_3$) and which gave tetramethyl 1,2-bis(trifluoromethyl)benzene-3,4,5,6-tetracarboxylate with aqueous cyanide.

[‡] (I) has resonances (all s) at δ 3·83(9H), 3·92(3H), 3·97(3H), and 4·18(3H); (II) at δ 1·90(3H), 1·93(3H), 3·68(3H), 3·78(6H), 3·83 (3H), 3·87(3H), 4·00(3H), and 5·34(1H) and was unchanged down to −70°.

These reactions provide additional support for the proposal that the Pd^{II}-induced oligomerisations of acetylenes are stepwise processes that proceed through σ-butadienyl intermediates.[4] The organic degradation products of (I), which were originally believed to have cyclohexadiene skeletons,[1] must now be reformulated as 5-substituted pentakis(methoxycarbonyl)cyclopentadienes (*e.g.* C_5R_5-CHClR, $C_5R_5CCl_2R$, *etc.*), as a consequence of the structure that we have established for (I). These structures are also in better agreement with the spectroscopic data on these compounds.[1,5]

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