The Cyclotetramerisation of Dimethyl Acetylenedicarboxylate and the *X*-Ray Structure of $[Pd\{H(C_8(CO_2Me)_8)\}Cl(pyridine)_2]$, an Unusual Five-co-ordinate Palladium(II) Complex

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Summary Reaction of dimethyl acetylenedicarboxylate with $PdCl_2$ in methanol yields $[Pd\{HC_8(CO_2Me)_8\}Cl]_2$, which gives monomeric and non-conducting adducts $[Pd\{HC_8(CO_2Me)_8\}ClL_2]$; an *X*-ray structure determination of the adduct (L = pyridine) shows it to contain five-co-ordinate Pd^{II}.

The structure of the complex (I), obtained from reaction of dimethyl acetylenedicarboxylate (dma) and palladium chloride [as $PdCl_2(PhCN)_2$] in aprotic solvents, has been determined.[1] This complex contains a trimer of the acetylene. By contrast, when the reaction of dma and $PdCl_2$ (molar ratio 7—18:1) was carried out in methanol (24 h; 20 °C) a new complex (II) was obtained as yellow crystals (52%, based on Pd) which was shown to have the formula $[Pd\{HC_8(CO_2Me)_8\}Cl]_2$ and therefore to contain a tetramer of dma. From the mother liquor it was also possible to isolate substantial amounts of the cyclopentadiene (III) as the sodium salt, $Na[C_5(CO_2Me)_5]$, as well as hexamethyl mellitate, dimethyl oxalate, and a mixture of compounds of unknown structure of common formula $[C_6(CO_2Me)_6H_2]$. Under these conditions the formation of complex (I) could not be detected. Using a ratio of $PdCl_2$: dma of 0·5 : 1, (III) was the major product.

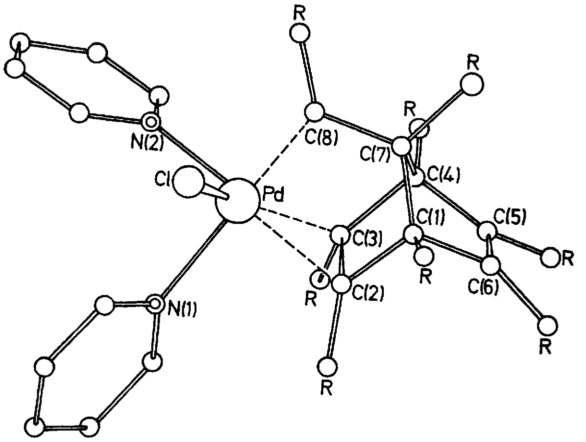
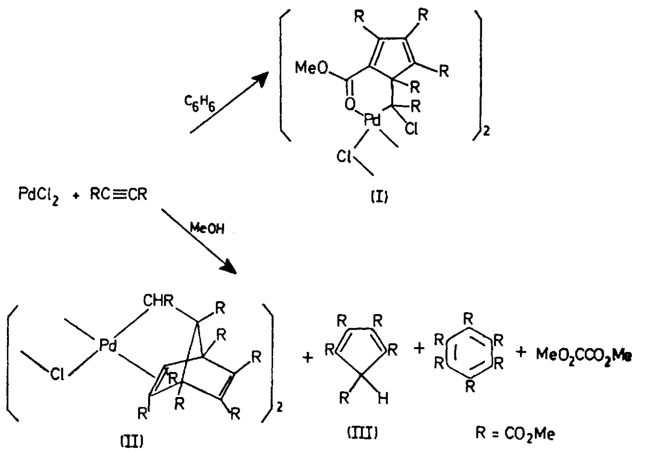


Figure. The structure of $[Pd\{HC_8(CO_2Me)_8\}Cl(pyridine)_2]$ (R = CO_2Me). Bond lengths (with e.s.d.s in parentheses): Pd–Cl 2·509(4); Pd–N(1) 2·191(13); Pd–N(2) 2·226(14); Pd–C(2) 2·090(14); Pd–C(3) 2·139(13); Pd–C(8) 2·043(14); C(2)–C(3) 1·47(2); C(5)–C(6) 1·33(2); all C–C single bond lengths 1·52—1·58-(2) Å. Bond angles: C(8)PdN(1) 174; C(8)PdN(2) 95; N(1)-PdN(2) 87; ClPdC(8) 88; ClPdN(1) 86; ClPdN(2) 92; ClPdC(2) 112; ClPdC(3) 152; N(2)PdC(2) 156; N(2)PdC(3) 115°.

Spectroscopic investigation of complex (II) (^{1}H n.m.r. and i.r.) revealed that the organic ligand $\{HC_8(CO_2Me)_8\}$, was asymmetric and that the complex was a Pd_2Cl_2-bridged dimer [ν(Pd–Cl) 310 cm^{-1}]. The dimer was cleaved on reaction with donor ligands; with ammonia and aromatic amines it formed 1:2 complexes, $[Pd\{HC_8(CO_2Me)_8\}ClL_2]$ (L = pyridine, γ-picoline, ammonia; L_2 = *o*-phenanthroline, bipyridyl), but 1:1 complexes, $[Pd\{HC_8(CO_2Me)_8\}ClL']$, with triphenylphosphine and triphenyl phosphite. On reaction with Na(acac) or $Na(C_5H_5)$, (II) formed $[Pd\{HC_8(CO_2Me)_8\}acac]$ and $[Pd\{HC_8(CO_2Me)_8\}C_5H_5]$ respectively. There was no i.r. evidence for internal $Pd \leftarrow O{=}C$ co-ordination in any of these complexes, as had been found for (I) and its derivatives, and none of the complexes were ionised in acetonitrile.



The *X*-ray structure determination of $[Pd\{HC_8(CO_2Me)_8\}Cl(pyridine)_2]$ was undertaken. *Crystal data:* $C_{34}H_{35}ClN_2O_{16}Pd$, M = 869·51, monoclinic, a = 11·588(5), b = 15·54(1), c = 10·362(5) Å, β = 105·1(1)°, U = 1801 Å^3, D_c = 1·603 g cm^{-3}, Z = 2, space group $P2_1$. Three-dimensional *X*-ray data were collected with the crystal mounted along the b axis, using Mo-K_α radiation (graphite monochromator) and a Stoe STADI 2 diffractometer. 3476 independent reflections were collected with $I_{obs} \geqslant 3\sigma(I_{obs})$; the structure was solved using Patterson and Fourier methods. Block-diagonal least-squares refinement has reduced R to 0·054, allowing anisotropic thermal vibration for the palladium and chlorine atoms.

The structure of the complex is shown (Figure). The organic ligand is derived from a 7-substituted 1,2,3,4,5,6,7-heptakismethoxycarbonylbicyclo[2,2,1]heptadiene where the metal is σ-bonded to the carbon [C(8)] attached to C(7) and π-bonded to the 2,3-double bond. This is clear from the considerable lengthening of the 2,3-bond [1·47(2) Å] by comparison with the 5,6-bond [1·33(2) Å), as well as the fact that the ester carbons attached to C(2) and C(3) are 0·73 and 0·86 Å respectively below the plane defined by C(1), C(2), C(3), and C(4) whereas the ester carbons attached to C(5) and C(6) are only 0·12 and 0·20 Å below the equivalent plane defined by C(1), C(5), C(6), and C(4). There is no bonding interaction between any of the carbonyl oxygens and the metal.

The co-ordination about the metal is very unusual in that it represents a case of the rare five-co-ordination for Pd^{II}. It is best described as distorted trigonal bipyramidal with C(8) and N(1) axial, and N(2), Cl, and the C(2)–C(3) bond approximately equatorial. The Pd–C(2), –C(3) and –C(8) bond lengths are normal[2] but both the Pd–N(1) and Pd–N(2) as well as the Pd–Cl bond lengths are considerably lengthened over usual values; indeed the Pd–Cl distance is in the range of Pd–Cl bridging rather than terminal. Nevertheless, this complex has no conductance in acetonitrile and there is no tendency, even in polar solvents, to form the four-co-ordinate cation, $[Pd\{HC_8(CO_2Me)_8\}(pyridine)_2]^+$.

Based on these results, we propose the structure shown for (II); the general relationship between (I), (II), and (III) is fairly clear and the details are being investigated.

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