

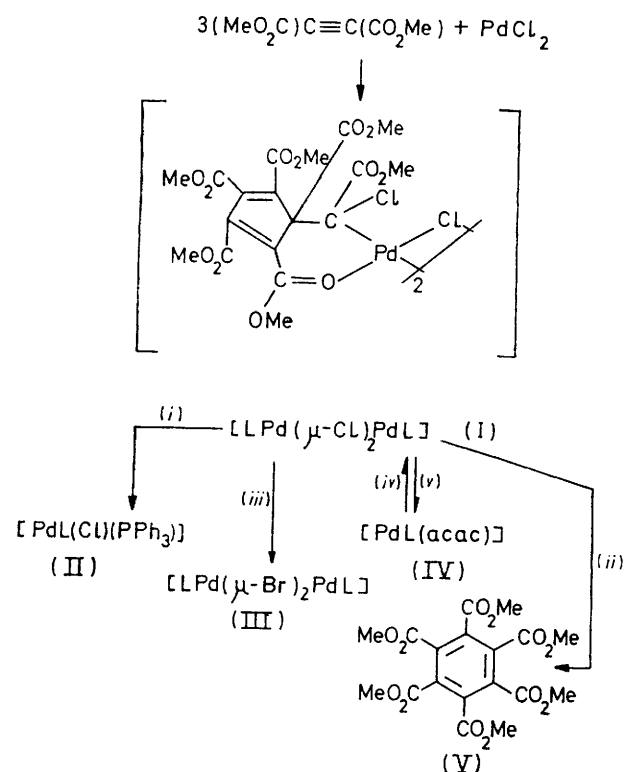
Acetylenes and Noble Metal Compounds. Part XII.¹ Reactions of Dimethyl Acetylenedicarboxylate with Palladium(II) Chloride and the Structure of {[Chloro(methoxycarbonyl)(1,2,3,4,5-pentakismethoxycarbonylcyclopenta-2,4-dienyl)-2-MeOCO]methyl}(pentane-2,4-dionato)-palladium(II)²

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The structure of the complex $[LPd(\mu-Cl)_2PdL]$ [I; $L = -CCl(CO_2Me) \cdot C_5(CO_2Me)_4C(OMe):O^-$], obtained from cyclotrimerisation of dimethyl acetylenedicarboxylate with $PdCl_2$, has been determined spectroscopically and with the aid of X-ray structure analysis of $[PdL(acac)]$ (IV; $acac = \text{pentane-2,4-dionato}$). The organic ligand contains pentakis(methoxycarbonyl)cyclopenta-2,4-diene bearing a $-C(CO_2Me)(Cl)Pd$ substituent at C(1). Two further co-ordination sites of the square-planar Pd atom are occupied by $acac$ and the remaining one by the ester carbonyl group $[O(2a)]$ attached to C(2). This interaction forms a non-planar six-membered ring. The bond lengths $Pd-C(6)$ [2.038(14)], $Pd-O(2a)$ [2.052(10)], and the $Pd-acac$ lengths $Pd-O(7)$ [1.995(10)] and $Pd-O(9)$ [2.024(11) Å], are normal. Thermal or aqueous-cyanide decomposition of complex (I) affords hexamethyl mellitate. Analogues of (I) and (I), such as $[XIII; L' = -CBr(CO_2Me) \cdot C_5(CO_2Me)_4C(OMe):O^-]$ and $[L''Pd(\mu-Br)_2PdL'']$ [XIIb; $L'' = -CBr(CO_2Me) \cdot C_5(CO_2Me)_3(CF_3)_2C(OMe):O^-]$, have been obtained by reaction of the σ -buta-1,3-dienyl complex $[Pd\{C_4(CO_2Me)_4Br\}Br]_n$ (IX) with dimethyl acetylenedicarboxylate and hexafluorobut-2-yne respectively. Reaction of complex (XIIb) with aqueous cyanide gives 1,2,3,4-tetrakis-(methoxycarbonyl)-5,6-bis(trifluoromethyl)benzene. The structures of some degradation products from complex (I) have been reformulated as 1-substituted pentakis(methoxycarbonyl)cyclopenta-2,4-dienes $C_5(CO_2Me)_5-C(CO_2Me)(Cl)X$ ($X = H, Cl, \text{ or } Br$).

In continuation of the investigation of reactions of acetylenes with palladium(II) chloride we now report



(i), PPh_3 ; (ii), CN^- or heat; (iii), Br^- ; (iv), HCl ; (v), $acac$

on the complex $[LPd(\mu-Cl)_2PdL]$ [I; $L = -CCl(CO_2Me) \cdot C_5(CO_2Me)_4C(OMe):O^-$ obtained from reaction of di-

¹ Part XI, K. Moseley and P. M. Maitlis, *J.C.S. Dalton*, 1974, 169.

² A preliminary account of this work has been given by D. M. Roe, C. Calvo, N. Krishnamachari, K. Moseley, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1973, 436.

methyl acetylenedicarboxylate (dma) with bis(benzonitrile)dichloropalladium in benzene. This complex was first prepared in 1969^{3,4} when Avram *et al.*³ suggested it to be a η -complex of hexakis(methoxycarbonyl)bicyclo[2.2.0]hexa-2,5-diene. Our chemical and spectroscopic studies led to the conclusion that (I) was a di- μ -chloro-bridged dimer with an extremely asymmetric organic ligand which also contained a strong $Pd-O:COMe$ interaction in a chelate ring. Mechanistic considerations, based on previous work on related systems, led to the proposal of the structure shown below.⁵ This is now confirmed by an X-ray crystal-structure study of complex (IV) which also reveals the stereochemistry of the organic ligand.

RESULTS AND DISCUSSION

Structure of Complex (I) and its Derivatives.—*Chemical studies.* Osmometric molecular-weight measurements showed (I) to be a dimer ($n = 2$, Table 1) and reaction with triphenylphosphine gave the monomeric $[PdL(Cl)(PPh_3)]$, (II). A metathesis reaction with lithium bromide replaced only two of the four chlorides in complex (I) giving $[LPd(\mu-Br)_2PdL]$, (III). This suggested that (I) and (III) are dimers with di- μ -chloro- and di- μ -bromo-bridges, and that the non-exchangeable chlorides are carbon bonded. This was confirmed by isolation of the monomeric pentane-2,4-dionate $[PdL(acac)]$, (IV); brief treatment of this complex with HCl regenerated (I). Only the mono(triphenylphosphine) complex, (II), could be isolated; addition of further triphenylphosphine caused complicated changes in the n.m.r. spectrum, associated with the formation of a number of intermediates in the decomposition to the final products hexamethyl mellitate [(V), 80%] and

³ M. Avram, I. D. Dinulescu, G. D. Mateescu, and C. D. Nitulescu, *Rev. Roumaine Chim.*, 1969, **14**, 1191.

⁴ H. Reinheimer and P. M. Maitlis, unpublished work.

⁵ P. M. Maitlis, *Pure Appl. Chem.*, 1973, **33**, 489.

dichlorobis(triphenylphosphine)palladium(II). Complex (II) also decomposed slowly in chloroform solution. Hexamethyl mellitate was formed from complex (I) on heating or on treatment with aqueous cyanide.³

down to -70°C . These observations suggested that the complexes were relatively rigid and also ruled out any structures based on symmetrical ligands such as 'Dewar benzenes.'

TABLE 1
Analytical (%) and n.m.r. data

Compound	C ^a	H ^a	Halogen ^a	M ^{a,b}	N.m.r. data in CDCl ₃ (δ /p.p.m.) ^c CO ₂ Me	Other
[LPd(μ -Cl) ₂ PdL] (I) ^d	35.8 (35.8)	3.0 (3.0)		1 190 (1 206)	3.83(9), 3.92(3), 3.97(3), 4.18(3)	
[PdL(Cl)(PPh ₃) ₂] (II) ^d	49.5 (49.9)	3.9 (3.8)	Cl 8.3(8.2)	847 (866)	3.40(3), 3.72(6), 3.91(3), 3.96(3), 3.99(3)	Ph 7.4 (m, 15H)
[LPd(μ -Br) ₂ PdL] (III) ^d	34.2 (33.4)	2.6 (2.8)	Cl 5.4 (5.5) Br 12.1(12.3)		3.89(9), 3.93(3), 3.96(3), 4.06(3)	
[PdL(acac)] (IV) ^d	41.5 (41.6)	3.4 (3.8)	Cl 5.2 (5.3)	706 (665)	3.68(3), 3.78(6), 3.83(3), 3.87(3), 4.00(3)	acac 1.90(3) 1.93(3), 5.34(1)
[Pd{MeO ₂ C-C[C(CO ₂ Me)Br]-C(CO ₂ Me): C(CO ₂ Me)}Br] _n (IX)	26.6 (26.2)	2.4 (2.2)	Br 28.7(29.0)	740 ^e (550)	4.0 (v. broad)	
[Pd{BrC(CO ₂ Me):C(CO ₂ Me)-C(CO ₂ Me): C(CO ₂ Me)}(PPh ₃) ₂ Br] (X)	54.1 (53.8)	4.1 (3.9)	Br 15.0(14.9)	1 038 (1 072)	2.90(3), 3.42(3), 3.53(3), 3.76(3)	Ph 7.5 (m, 30H)
[Pd{MeO ₂ C-C ₆ (CF ₃) ₂ (CO ₂ Me) ₂ : C(CO ₂ Me)Br}Br] ₂ (XIIb)	27.1 (27.0)	1.8 (1.7)	Br 22.8(22.4)	1 267 (1 414)	3.78(3), 3.99(6), 4.13(3)	¹⁹ F two q [J(F-F) 12 Hz] 52.3, 56.1 ^f
[PdL'(acac)] (XIII) ^g	39.1 (38.9)	3.8 (3.5)	Br 11.4(11.3)		3.72(3), 3.78(3), 3.81(3), 3.85(3), 3.89(3), 4.02(3)	acac 1.91(3) 1.94(3), 5.32(1)
[L'Pd(μ -Cl) ₂ PdL'] (XIV) ^g	33.9 (33.4)	3.0 (2.8)	Cl 5.3(5.5) Br 12.0(12.3)		3.81(9), 3.92(3), 3.95(3), 4.08(3)	
[PdL'(Cl)(PPh ₃) ₂] (XV) ^g	48.2 (47.5)	3.8 (3.7)	Cl 3.7(3.9) Br 8.4 (8.8)		3.42(3), 3.71(6), 3.91(3), 3.97(3), 3.99(3)	Ph 7.4 (m, 15H)
[Pd{BrC(CO ₂ Me):C(CO ₂ Me)-C(CO ₂ Me): C(CO ₂ Me)}(PMePh ₂) ₂ Br]	48.2 (48.1)	4.1 (4.0)	Br 17.2(17.0)		3.00(3), 3.39(3), 3.73(3), 3.82(3)	Me 2.61 [3H, t, J(H-P) 4 Hz]; Ph 7.5 (m, 20H)
[Pd{BrC(CO ₂ Me):C(CO ₂ Me)-C(CO ₂ Me): C(CO ₂ Me)}(AsPh ₃) ₂ Br]	49.8 (49.7)	3.7 (3.6)	Br 12.5(13.8)		2.93(3), 3.48(3), 3.61(3), 3.78(3)	Ph 7.5 (m, 30H)
C ₆ (CF ₃) ₂ (CO ₂ Me) ₄ (XVI)	43.1 (43.5)	3.0 (2.7)		446 ^h (446)	3.92(6), 3.94(6)	¹⁹ F, 53.2 (s) ^f

acac = Pentane-2,4-dionato.

^a Calculated values in parentheses. ^b Determined osmometrically, in CHCl₃. ^c Relative intensities in parentheses. ^d L = -CCl(CO₂Me)-C₆(CO₂Me)₄-C(OMe);O-. ^e Determined osmometrically in acetone; calc. for $n = 1$. ^f P.p.m. upfield from external reference of CFCl₃. ^g L' = -CBr(CO₂Me)-C₆(CO₂Me)₄-C(OMe);O-. ^h Determined mass spectroscopically.

TABLE 2
I.r. spectra in CHCl₃ (cm⁻¹)

Compound	$\nu(\text{CO})$		$\nu(\text{C}=\text{C})$
	free	co-ordinated	
(I)	1 744vs, 1 690w (sh)	1 638m—s	1 617w (sh), 1 573vw
(I) ^a	1 746vs, 1 729vs, 1 692m	1 626vs	1 585w (sh)
(II)	1 732vs	1 663s	1 624w, 1 575w
(III) ^a	1 738vs, 1 685m (sh)	1 629vs	1 569m—w
(IV)	1 739vs, 1 696m	1 647m—s	b
(XIV) ^a	1 751vs, br, 1 690m (sh)	1 630vs	1 568m
(XV)	1 743vs	1 665s	1 623m—w, 1 576w
(XIII) ^a	1 758, 1 738vs, 1 693m	1 637m	1 608w
(XIIb)	1 748vs	1 660m	1 633w—m, 1 584w
C ₆ (CO ₂ Me) ₅ -C(CO ₂ Me)Cl ₂ (XIX; X = Cl)	1 747vs		1 624w, 1 580vw
BrC(CO ₂ Me):C(CO ₂ Me)-C(CO ₂ Me):C(CO ₂ Me)Br (XI)	1 740vs		1 635vw, 1 608w
(IX)	1 730vs	1 615m—s	1 585m (sh)
(X)	1 731vs, 1 698s (sh)		1 615m, 1 585w

^a In Nujol. ^b Obscured by bands arising from acac at 1 616m, 1 580vs, 1 560s, and 1 509m cm⁻¹.

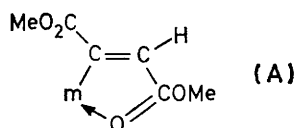
Spectroscopic studies. Spectra of the complexes (I)—(IV) were basically similar indicating a common organic ligand.

(a) The ¹H n.m.r. spectra (Table 1), though in part masked by accidental coincidences, showed that the six methoxycarbonyl groups were all non-equivalent and suggested that a very asymmetric ligand was present. No significant changes in the spectra with temperature were observed, that of complex (IV) being invariant

(b) In the carbonyl region of the i.r. spectra, all the complexes showed the expected very strong absorptions at ca. 1 740 cm⁻¹ (Table 1) due to the ester carbonyl groups. These bands were often broad with shoulders, both at higher and lower frequencies, which were sometimes split (particularly in Nujol mulls) into separate very strong bands, e.g. for complex (I) at 1 746, 1 729, and 1 692 cm⁻¹. The complexes also showed weak bands, assigned to $\nu(\text{C}=\text{C})$, usually at ca. 1 620 and 1 570

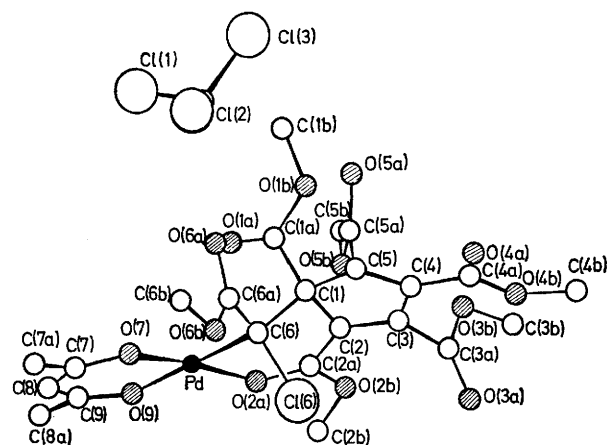
cm^{-1} . In addition, we observed a medium to strong band in the complexes (I), (III), and (IV) at *ca.* 1 640 cm^{-1} and in (II) at 1 663 cm^{-1} (in CHCl_3) which we ascribe to $\nu(\text{CO})$ of an ester carbonyl group co-ordinated to the metal atom.^{6,7} It is especially significant that this band remains even in the triphenylphosphine complex (II).

The formation of chelate complexes with adducts of dma is not uncommon particularly when the adduct results from *trans*-addition of transition-metal hydrides. In these cases five-membered rings of the type (A) [for example, where $m = \text{Re}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_7)$,⁸ $\text{Mn}(\text{CO})_4$,⁹ or $\text{Ru}(\text{C}_5\text{H}_5)(\text{PPh}_3)$ ¹⁰] are formed and $\nu(\text{CO})$, co-ordinated) is in the region 1 500–1 600 cm^{-1} .



The far-i.r. spectrum of complex (I) showed three very strong bands at 256, 283, and 290 cm^{-1} in the region $\nu(\text{Pd}-\text{Cl})$ and one at 356 cm^{-1} which we assign to $\delta(\text{OCO})$.⁶ The absence of strong bands between 290 and 350 cm^{-1} suggested that the observed bands arise from a di- μ -chloro-bridge and that there are no terminal $\text{Pd}-\text{Cl}$ bonds present. As expected, the triphenylphosphine complex (II) showed a strong band at 312 cm^{-1} arising from $\nu(\text{Pd}-\text{Cl})$, terminal). There was also a very strong band at 228 cm^{-1} in complex (I) and in (III) which may be due to $\nu(\text{Pd}-\text{O})$.⁶

Description of the Crystal Structure of Complex (IV).—The molecular geometry is shown in projection down the



The molecular geometry of complex (IV)

[100] axis in the Figure; bond lengths and angles are given in Tables 3 and 4. The crystal consists of ribbons running along $b + c$ and $-b + c$ containing molecules of complex separated by centrosymmetrically related pairs of CHCl_3 molecules (ignoring fractional occupancy). The ribbons intersect and share these CHCl_3 pairs.

⁶ W. L. Driessen, W. L. Groeneveld, and F. W. van der Wey, *Rec. Trav. chim.*, 1970, **89**, 353.

⁷ M. F. Lappert, *J. Chem. Soc.*, 1961, 817.

⁸ M. Dubeck and R. A. Schell, *Inorg. Chem.*, 1964, **3**, 1757.

TABLE 3

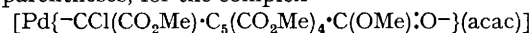
Bond lengths (Å), estimated standard deviations in parentheses, for the complex



Pd-C(6)	2.038(14)	C(7)-O(7)	1.265(19)
Pd-O(2a)	2.052(10)	C(9)-O(9)	1.280(19)
Pd-O(7)	1.995(10)	C(1a)-O(1a)	1.205(16)
Pd-O(9)	2.024(11)	C(1a)-O(1b)	1.315(16)
Cl(6)-C(6)	1.804(15)	C(1b)-O(1b)	1.507(21)
C(1)-C(2)	1.526(19)	C(2a)-O(2a)	1.229(18)
C(1)-C(5)	1.515(19)	C(2a)-O(2b)	1.314(15)
C(1)-C(6)	1.536(19)	C(2b)-O(2b)	1.486(18)
C(2)-C(3)	1.364(20)	C(3a)-O(3b)	1.202(16)
C(3)-C(4)	1.473(20)	C(3a)-O(3b)	1.325(16)
C(4)-C(5)	1.370(20)	C(3b)-O(3b)	1.489(19)
C(7)-C(8)	1.415(22)	C(4a)-O(4a)	1.216(16)
C(8)-C(9)	1.388(15)	C(4a)-O(4b)	1.306(16)
C(1)-C(1a)	1.534(17)	C(4b)-O(4b)	1.475(18)
C(2)-C(2a)	1.436(20)	C(5a)-O(5a)	1.227(16)
C(3)-C(3a)	1.469(17)	C(5a)-O(5b)	1.321(16)
C(4)-C(4a)	1.446(18)	C(5b)-O(5b)	1.463(18)
C(5)-C(5a)	1.451(17)	C(6a)-O(6a)	1.219(15)
C(6)-C(6a)	1.501(16)	C(6a)-O(6b)	1.310(15)
C(7)-C(7a)	1.521(24)	C(6b)-O(6b)	1.467(18)
C(9)-C(9a)	1.516(25)		

TABLE 4

Selected bond angles (°), estimated standard deviations in parentheses, for the complex



C(6)-Pd-O(2a)	90.5(6.0)	C(3)-C(4)-C(4a)	125.9(1.1)
C(6)-Pd-O(7)	92.1(6.0)	C(3)-C(4)-C(5)	109.2(1.2)
O(2a)-Pd-O(9)	83.5(4.0)	C(3a)-C(3)-C(4)	121.1(0.9)
O(7)-Pd-O(9)	94.0(4.0)	C(4)-C(5)-C(1)	110.0(1.2)
C(1)-C(6)-C(6a)	110.3(0.9)	C(4)-C(5)-C(5a)	123.3(1.1)
C(1)-C(6)-Cl(6)	107.8(0.8)	C(4a)-C(4)-C(5)	124.8(1.1)
C(1)-C(6)-Pd	112.6(9.0)	C(5)-C(1)-C(1a)	112.0(1.0)
C(2)-C(1)-C(5)	101.8(0.9)	C(5a)-C(5)-C(1)	123.3(0.8)
C(2)-C(1)-C(6)	110.7(1.1)	C(6a)-C(6)-Pd	108.9(0.9)
C(2)-C(2a)-O(2a)	124.3(1.2)	C(7)-C(8)-C(9)	127.1(1.2)
C(2)-C(2a)-O(2b)	114.7(1.0)	C(7)-O(7)-Pd	122.5(0.9)
C(2)-C(3)-C(3a)	126.9(1.1)	C(9)-O(9)-Pd	123.8(0.9)
C(2)-C(3)-C(4)	108.6(1.2)	C(8)-C(7)-O(7)	127.5(1.2)
C(2a)-C(2)-C(1)	123.6(1.0)	C(8)-C(9)-O(9)	124.8(1.2)
C(2a)-C(2)-C(3)	126.1(1.3)	Cl(6)-C(6)-Pd	106.3(0.8)
C(2a)-O(2a)-Pd	129.4(9.0)	O(2a)-C(2a)-O(2b)	120.9(1.1)
C(3)-C(2)-C(1)	110.2(1.1)		

The chloroform molecules lie in chains running parallel to a , consisting of pairs of molecules, separated by 3.8 Å; the pairs along a are separated by over 4 Å. Adjacent ribbons along a pack to form sheets. Molecules in neighbouring sheets show some short interactions which may be significant. The acac groups between centrosymmetrically related molecules are *ca.* 3.5 Å apart. In addition, the chlorine atom Cl(6) in one molecule lies 3.69 Å from C(7a) of an adjacent molecule, and therefore at least one of the hydrogen atoms of this methyl group must lie *ca.* 0.5 Å closer to the chlorine, leading to a Cl(6)···H separation less than the sum of the van der Waals radii.

There are no interactions between the chloroform chlorine atoms and oxygens on the complex, but one of the chlorines is within van der Waals distance of the chlorine Cl(6). Furthermore, there are a number of $\text{CHCl}_3 \cdots \text{H}_3\text{C}-$ interactions which probably bind the solvent molecules into the structure. If the solvent

⁹ B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. (A)*, 1969, 2766.

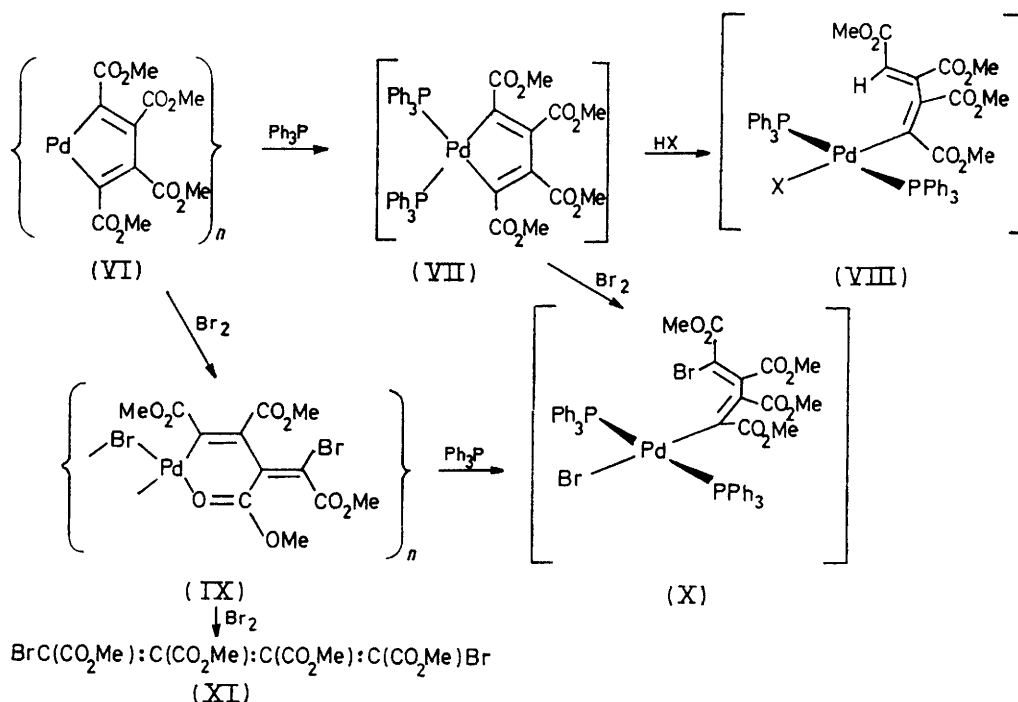
¹⁰ T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.

were to be removed the structure would most certainly collapse along the diagonals of the *bc* face. It is not clear why there is only 0.66 molecule (on average of) CHCl_3 per molecule of complex (IV). The large standard errors for the x atomic parameter probably reflect the fact that the disorder resulting from the fractional average occupancy of the solvent primarily affects the [100] direction.

The complex itself consists of a planar [maximum deviation from least-squares plane being 0.041 Å at C(2)] pentakis(methoxycarbonyl)cyclopentadiene, where C(1) also bears a $-\text{C}(\text{CO}_2\text{Me})(\text{Cl})\text{Pd}$ group. One further co-ordination site on the metal is occupied by the ester carbonyl group at C(2), forming a considerably bent six-membered ring, deviations from the least-squares plane

that bond lengths and angles are very normal and show no evidence for strain in the molecule; this implies that the structure of complex (IV) represents a distinct energy minimum.

It is interesting to note that, although Cl(6) is far from being in an axial position with respect to the co-ordination plane of the metal, the non-bonded distance $\text{Pd} \cdots \text{Cl}(6)$ (3.08 Å)¹¹ is considerably less than the sum of the van der Waals radii (3.8 Å). While it is not clear whether any significant interaction exists between Pd and Cl(6), this point is relevant to a discussion of the modes of decomposition of the molecule to hexamethyl mellitate. In view of the similarities between complexes (IV) and (I), and the ease of their interconversion, (I) must possess the same organic ligand.



being +0.153 (Pd), +0.024 [O(2a)], -0.080 [C(2a)], -0.080 [C(2)], +0.343 [C(1)], and -0.360 Å [C(6)]. The remaining co-ordination sites are occupied by acac, and the atoms C(6), O(2a), O(7), and O(9) are in the same plane as the metal. The Pd-C(6) σ -bond length (Table 3) is normal,¹¹⁻¹⁴ as are the bond lengths Pd-O(2a), Pd-O(7), and Pd-O(9), and the lengthening expected in Pd-O(9), because it is *trans* to Pd-C(6), is only just significant (3 σ). It is particularly interesting that the distance between the metal atom and the ester carbonyl group [O(2a)] is very similar to the other Pd-O bond lengths and is only slightly (5 σ) longer than Pd-O(7). This suggests that all the Pd-O bonds are similar in strength and indeed we were unable to break the Pd-O(2a) bond without destroying the whole complex. In other respects the structure is remarkable only in

¹¹ P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971, vol. 1, pp. 38-39.

¹² D. M. Roe, P. M. Bailey, K. Moseley, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1972, 1273.

Other Routes to Complexes analogous to (I).—The formation and some reactions of the palladacyclopentadiene (VI) and its adducts such as (VII) have recently been reported.^{1,12} In particular, complex (VII) undergoes cleavage of a Pd-C bond on treatment with acid (1 equiv.); an X-ray determination of (VIII; X = Br) confirmed the structure.¹² Complex (VII) also reacted with bromine (1 equiv.) to give (X). Alternatively, (X) could be prepared by addition of bromine to (VI) [1 equiv.; excess of bromine gave PdBr_2 and (XI)] to give (IX), followed by triphenylphosphine. The intermediate (IX) was isolated and could, in part, be characterised. Although the n.m.r. spectrum was uninformative, as it consisted only of a broad band with closely overlapping and unresolvable peaks, the i.r. spectrum showed, in addition to the normal ester

¹³ T. Hosokawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1973, **95**, 4914.

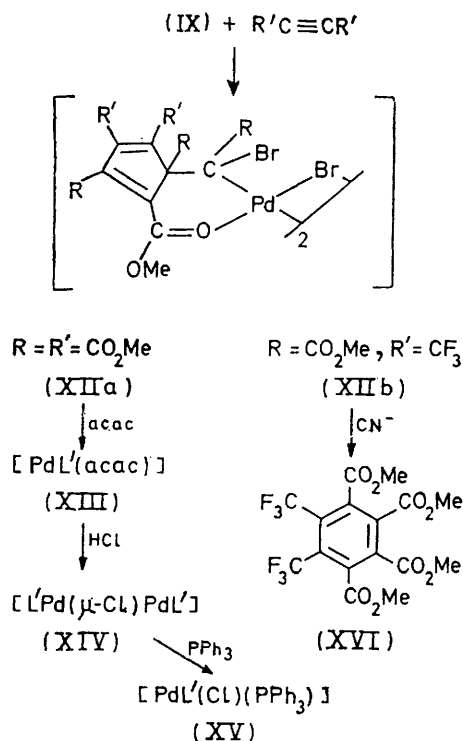
¹⁴ A. Segnitz, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1973, 698.

$\nu(\text{CO})$ at 1730 vs cm^{-1} , another band at 1615 ms cm^{-1} which, by analogy to complexes (I)—(IV), we assign to a co-ordinated ester. The fully characterised triphenylphosphine adduct (X) showed $\nu(\text{CO, free})$ virtually unchanged and there was no band in the region of $\nu(\text{CO, co-ordinated})$ (Table 2). The structure shown for complex (IX) is tentatively suggested; molecular-weight measurements were inconclusive since the complex was only sparingly soluble in non-co-ordinating

from unco-ordinated ester groups and double bonds, a band at 1660 cm^{-1} due to $\nu(\text{CO, co-ordinated})$. Further evidence for the structure shown came from decomposition by aqueous cyanide to give compound (XVI), which again has two trifluoromethyl groups adjacent, and this structure fits in well with the proposed mechanism for the trimerisation (see below).

Mechanism of the Cyclotrimerisation.—The reactions described here emphasise the difference between the Pd^{II} - and Pd^0 -induced trimerisation reactions. In the former only Pd^{II} intermediates appear to be involved and reaction proceeds by a series of stepwise insertions, while in the latter the individual steps are also associated with changes in formal oxidation state, $\text{Pd}^0 \rightarrow \text{Pd}^{\text{II}}$.¹ A link between the two processes is provided by the ring opening of the palladacyclopentadiene, (VI), to give the σ -buta-1,3-dienyl complex, (IX).

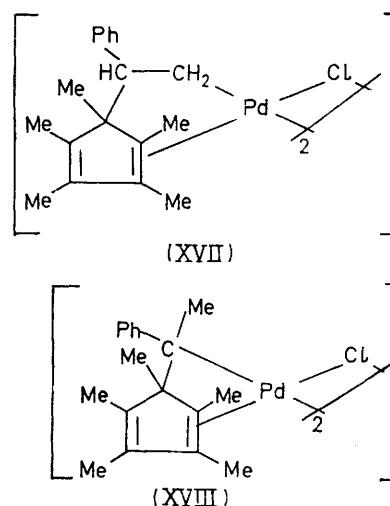
The structure of complex (I) and its analogues is of considerable interest as it provides the first conclusive evidence for the intermediacy of a cyclopentadiene complex in cyclotrimerisation of an acetylene to the benzene. It is also reminiscent of that of the complex (XVII) which was obtained by reaction of 'phenyl-palladium chloride' and but-2-yne.¹³ There are two points of difference between complexes (I) and (XVII). In complexes (IV) and (I), Pd is σ -bonded to C(6), which was originally one of the acetylenic carbon atoms of a dma molecule, whereas in (XVII) it is *not* bonded to the corresponding carbon atom but to a carbon that was originally a methyl group, a 1,2-H shift having occurred. Secondly, in complex (XVII) Pd is also η -bonded to a cyclopentadiene double bond, a feature that is absent in (I) and (IV), where the fourth co-ordination site is occupied by an ester oxygen atom. The reasons for these differences are clear. In order



solvents, but a determination in acetone, in which it may well have partially depolymerised, suggested that n could be 2.

The triphenylphosphine complex (X) reacted with acetylenes with difficulty to give a mixture of products, some of which may well have arisen from reaction with dissociated Ph_3P .^{1,5} However, complex (IX) reacted quite smoothly, in particular with dma, to give a red oil (XIIa) which was characterised by conversion to the pentane-2,4-dionate, $[\text{PdL}'(\text{acac})]$ (XIII), the dimeric chloride (XIV), and its triphenylphosphine adduct (XV). The spectroscopic properties of complexes (XIII), (XIV), and (XV) corresponded very closely to those of (IV), (I), and (II), respectively, and support the assigned structures; (XIV) also reacted with aqueous cyanide to give hexamethyl mellitate, (V). Complex (IX) also underwent reaction with hexafluorobut-2-yne to give (XIIb), which was characterised by analysis and spectroscopically (Tables 1 and 2).

The ^{19}F n.m.r. spectrum of complex (XIIb) showed two quartets [$J(\text{F-F})$ 12 Hz] which indicated the presence of two *cis*- CF_3 groups on a double bond.¹⁵ The similarity of this complex to (I) was evident from the i.r. spectrum which showed, in addition to bands arising

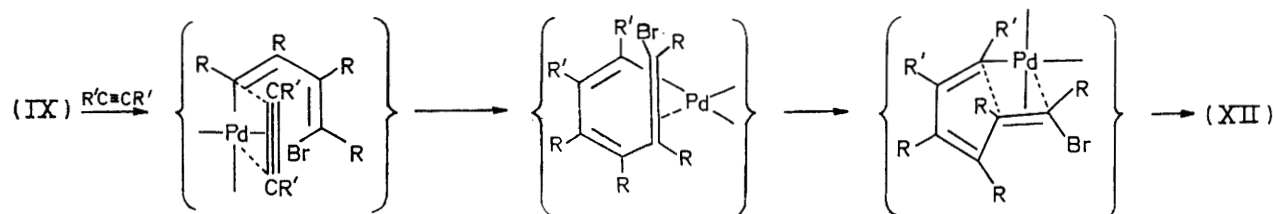


to obtain a stable strain-free molecule, Pd needs to bridge at least four carbon atoms as in complex (XVII) and the alternative structure (XVIII) would be very

¹⁵ R. D. W. Kemmitt, B. Y. Kimura, and G. W. Littlecott, *J.C.S. Dalton*, 1973, 636.

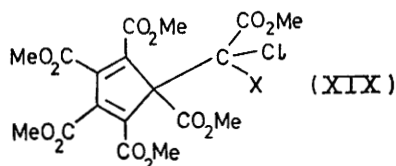
strained. In complex (I) a stable strain-free six-membered chelate ring can be formed between the metal atom and O(2a), and it is clearly impossible for a 1,2-H shift [in the manner of (XVIII) \rightarrow (XVII)] to occur. Furthermore, a double bond bearing two electron-withdrawing substituents such as $-\text{CO}_2\text{Me}$ is only expected to bond relatively weakly to Pd in the $+II$ oxidation state.¹⁶

The formation of complexes analogous to (I) by reaction of the σ -buta-1,3-dienyl complex (IX) with acetylenes provides further evidence for a path which has been proposed for reactions of $\text{Pd}^{II}\text{-X}$ with acetylenes.^{5,13} Presumably complex (IX) has a co-ordination site which can be made available with sufficient ease to allow the reaction [giving (XII)] to proceed. In the absence of evidence to the contrary for our systems (*cf.* ref. 10), we regard reactions such as (IX) \rightarrow (XII) as occurring by the usual path of co-ordination (of an acetylene) followed by *cis*-migration to give a σ -*cis,cis,cis*-hexa-1,3,5-trienyl intermediate which then undergoes internal cyclising *cis*-migration with the co-ordinated olefin to give the cyclopentadiene:



This type of process leads directly to the structure proposed for complex (XIIb), in which the trifluoromethyl groups are adjacent on a double bond, and also permits chelation of the metal atom to the same ester carbonyl group as in (I) and (IV). Under the conditions we have explored, hexafluorobut-2-yne does not react with PdCl_2 but the results reported here imply that, if a co-ordination site can be made available, it will 'insert' into a Pd-C bond.

The structure established for complex (I) also necessitates revision of those proposed for the organic degradation products.³ The compounds $\text{C}_6(\text{CO}_2\text{Me})_6\text{HCl}$, $\text{C}_6(\text{CO}_2\text{Me})_6\text{Cl}_2$, and $\text{C}_6(\text{CO}_2\text{Me})_6\text{BrCl}$ [which were obtained by hydrogenation, chlorination, and bromination respectively of (I)] were all formulated as substituted cyclohexa-1,3-dienes. The n.m.r. spectrum reported for $\text{C}_6(\text{CO}_2\text{Me})_6\text{Cl}_2$ ³ (four singlets with intensities in the ratio 2:1:2:1) does not agree with this compound being either *cis*- or *trans*-5,6-dichloro-1,2,3,4,5,6-hexakis(methoxycarbonyl)cyclohexa-1,3-diene, but is in good agreement with structure (XIX);



$\text{X} = \text{Cl}$). By analogy, the other compounds are re-assigned as (XIX; $\text{X} = \text{H}$) and (XIX; $\text{X} = \text{Br}$), in agreement with their reported n.m.r. spectra³ and other properties. These compounds are, in fact, good models for the spectroscopic properties to be expected from the ligand L in complexes such as (I); for example, (XIX; $\text{X} = \text{Cl}$) shows only a band due to unco-ordinated CO at $1\,747\text{ cm}^{-1}$ in the carbonyl region.

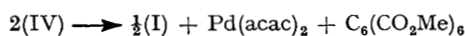
EXPERIMENTAL

All preparations were carried out under an atmosphere of nitrogen. Analytical, n.m.r., and i.r. spectroscopic data are given in Tables 1 and 2.

The complex $[\text{LPd}(\mu\text{-Cl})_2\text{PdL}]$ [I; $\text{L} = \text{MeO}_2\text{C-C}_3(\text{CO}_2\text{Me})_4\text{C}(\text{CO}_2\text{Me})\text{Cl}$] was prepared by the method of Avram³ from bis(benzonitrile)dichloropalladium and dimethyl acetylenedicarboxylate (dma) in benzene. The initial product had high chlorine analyses (Found: Cl, 13.4, 13.6%) probably due to the presence of extra PdCl_2 .¹⁷ This was removed and the complex purified by dissolving it in methanol and allowing it to crystallise. On heating complex (I) *in vacuo* hexamethyl mellitate (82%) was obtained. The complexes $[\text{LPd}(\mu\text{-Br})_2\text{PdL}]$ (III) [80%;

m.p. 165°C (decomp.)] and $[\text{PdL}(\text{Cl})(\text{PPh}_3)]$ (II) [99%; m.p. $228\text{--}229^\circ\text{C}$ (decomp.)] were prepared by standard methods from (I) (see also below).

{[Chloro(methoxycarbonyl)(1,2,3,4,5-pentakis(methoxycarbonyl)cyclopenta-2,4-dienyl)-2-MeOCO]methyl}(pentane-2,4-dionato)palladium(II), (IV).—Complex (I) (1.4 g, 2 mmol) dissolved in tetrahydrofuran (thf) (20 cm^3) was treated with a solution of potassium pentane-2,4-dionate (2 mmol) in thf for 20 min at 20°C . Removal of the solvent gave an orange solid which was crystallised from dichloromethane-diethyl ether to give microcrystals [1.4 g, 90% yield, m.p. $145\text{--}147^\circ\text{C}$ (decomp.)]. The crystal-structure determination was carried out on a crystal of approximate dimensions $0.3 \times 0.3 \times 0.3\text{ mm}$ grown from chloroform at 0°C ; the crystal contained chloroform of crystallisation. Some difficulties were encountered in growing suitable crystals since the complex underwent slow disproportionation at ambient temperatures and occasionally an eutectic of $\text{Pd}(\text{acac})_2$ and (IV) was obtained. N.m.r. studies in solution (30°C) indicated the disproportionation:



Crystal data. $\text{C}_{23}\text{H}_{25}\text{ClO}_{14}\text{Pd}$, $M = 667.28$, Monoclinic, $a = 8.78(1)$, $b = 21.15(2)$, $c = 16.76(2)\text{ \AA}$, $\beta = 93.0(1)^\circ$, $Z = 4$, $D_o = 1.594$, $D_m = 1.55\text{ g cm}^{-3}$.^{*} The space group

^{*} Calculated and measured for the solvated crystal.

¹⁶ Ref. 8, pp. 123–130.

¹⁷ See, for example, P. M. Maitlis, D. Pollock, M. L. Games, and W. J. Pryde, *Canad. J. Chem.*, 1965, **43**, 470; H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 2276.

$P2_1/c$ was uniquely determined from precession and Weissenberg photographs; conditions limiting possible reflections were $h0l$ (l even) and $0k0$ (k even).

Structure determination. Intensity data were collected on a Syntex PI automatic diffractometer using graphite-monochromatised Mo- K_α radiation and the θ – 2θ mode of scan at a variable scan rate. A total of 3366 unique reflections in the range $0 \leq 2\theta \leq 45^\circ$ were collected, of which 2396 had intensities above three standard deviations as calculated from counting statistics. These 2396 reflections were used in subsequent computations and refinement. The data were corrected for Lorentz and polarisation effects, but not for absorption ($\mu = 9.06 \text{ cm}^{-1}$). The position of the palladium atom was derived from a three-dimensional Patterson function. Combination of a few successive Fourier and Fourier-difference syntheses led to determination of all the remaining atom positions. Most of these calculations were carried out using the 'X-ray 71' system of programs,¹⁸ although the refinement was carried out using a full-matrix least-squares program written for a CDC 6400 computer by J. S. Stephens of this laboratory. Atomic-scattering curves for Pd, Cl, O, and C were obtained using the expressions of Cromer and Mann,¹⁹ and those for Pd and Cl were corrected for dispersion.²⁰ A weighting function $\omega = (38.07 - 0.8206|F_o| + 0.00762|F_o|^2)^{-1}$, chosen such that $\langle \omega(|F_o| - |F_c|)^2 \rangle$ would be independent of the local average $\langle |F_o| \rangle$, was used in the refinement. The data were corrected for secondary extinction effects according to the method of Zachariasen,²¹ by including the parameter g as a variable in the refinement; the final value of g found was 0.5195×10^{-7} . Refinement was terminated when the maximum shift in any parameter was less than a third of the standard error in that parameter. The final R value was 0.071 and the final weighted R_w value, defined by $R_w = [\Sigma \omega(|F_o| - |F_c|)^2 / \Sigma \omega |F_o|^2]^{1/2}$, was 0.085. Final atomic parameters are listed in Table 5, and a list of selected bond distances and angles in the structure are given in Tables 3 and 4. A Table of observed and calculated structure factors is given in Supplementary Publication No. SUP 21045 (3 pp.).*

Poly[bromo(4-bromo-3-methoxycarbonyl-O-1,2,4-trimethoxycarbonylbuta-1,3-dienyl)palladium(II)] (IX).—Bromine (57 μl , 1 mmol) was added dropwise to a well stirred suspension of $\{\text{Pd}[\text{C}_4(\text{CO}_2\text{Me})_4]\}_n$ (VI) (0.39 g, 1 mmol) in dichloromethane (50 cm^3) at -78°C under an argon atmosphere. The solid dissolved with a darkening in colour and the resulting solution was stirred for 0.5 h at -78°C and was then allowed to warm to $+20^\circ\text{C}$. It was filtered, and the solvent evaporated from the filtrate until the volume was 2 cm^3 . Addition of diethyl ether gave a yellow precipitate (60%) identified as (IX). Chromatography of the diethyl ether filtrate on Florisil gave a colourless oil (7%) that was identified as $\text{BrC}(\text{CO}_2\text{Me})\cdot\text{C}(\text{CO}_2\text{Me})\cdot\text{C}(\text{CO}_2\text{Me})\cdot\text{C}(\text{CO}_2\text{Me})\text{Br}$, (XI), by n.m.r. spectroscopy.¹

Reactions of Complex (IX).—To give bromo(4-bromo-1,2,3,4-tetrakis(methoxycarbonylbuta-1,3-dienyl)bis(triphenylphosphine)palladium(II), (X). Triphenylphosphine (0.13 g, 0.5 mmol) was added to a stirred suspension of complex

(IX) (0.11 g, 0.2 mmol) in dichloromethane (20 cm^3). Most of the solid dissolved and, after stirring for 1 h at 20°C , the solution was filtered (to remove some $[\text{Pd}(\text{PPh}_3)_2\text{Br}_2]$) and the filtrate was added to light petroleum (50 cm^3) whereupon a bright yellow precipitate of complex (X) [0.18 g, 90%, m.p. 195°C (decomp.)] was obtained. The PMePh_2 (50%) and AsPh_3 derivatives (70%) were obtained analogously. Complex (X) was also prepared by addition of bromine (6 μl , 0.1 mmol) to a solution of $[\text{Pd}(\text{PPh}_3)_2\{\text{C}_4(\text{CO}_2\text{Me})_4\}]$ (VII) (0.08 g, 0.1 mmol) in dichloromethane (10 cm^3) at -78°C under an argon atmosphere. The resulting solution was stirred at -78°C for 1 h, allowed to warm to $+20^\circ\text{C}$, filtered, and most of the solvent removed. Addition of light petroleum gave a solid (80 mg) which was shown to be (X) by n.m.r. spectroscopy.

To give complexes (XIII)–(XV). (a) Dma (95 μl , 1.5 mmol) was added to a suspension of complex (IX) (0.55 g, 1 mmol) in dichloromethane (60 cm^3). The solid dissolved and the solution became deep red. After 10 min the solution was filtered and concentrated (to 5 cm^3) and light petroleum (50 cm^3) was added to give an oily red precipitate of $[\text{L}'\text{Pd}(\mu\text{-Br})_2\text{PdL}']$ (XIIa) (0.5 g, 75%). Although this material was homogeneous as indicated by n.m.r. spectroscopy, all attempts to crystallise or purify it without decomposition failed. It was therefore converted to $[\text{PdL}'(\text{acac})]$ (XIII), $[\text{L}'\text{Pd}(\mu\text{-Cl})_2\text{PdL}']$ (XIV), and $[\text{PdL}'(\text{Cl})(\text{PPh}_3)]$ (XV) which were all characterised.

(b) Potassium pentane-2,4-dionate (70 mg, 0.5 mmol) was added to a solution of complex (XIIa) (0.35 g, 0.5 mmol) in thf (20 cm^3). The solution became lighter in colour and was stirred for 10 min. The solvent was then removed, the residue extracted with dichloromethane ($2 \times 10 \text{ cm}^3$), and the resulting solution was chromatographed on a short Florisil column, to give, after removal of solvent, orange crystals of complex (XIII) [yield after recrystallisation from methanol, 0.2 g (65%); m.p. 149 – 151°C]. Hydrogen chloride gas was bubbled in a slow stream through a solution of complex (XIII) (0.1 g) in dichloromethane (10 cm^3) for 10 s. The colour darkened and a brown precipitate of complex (XIV) (75 mg, 80%, m.p. $>240^\circ\text{C}$) was obtained on the addition of diethyl ether (20 cm^3) to the solution.

(c) Complex (XIV) was converted into the mono(triphenylphosphine) complex (XV) (75%, m.p. $>240^\circ\text{C}$) by reaction with one equivalent of triphenylphosphine in dichloromethane. Addition of excess of triphenylphosphine gave an insoluble yellow solid $[\text{Pd}(\text{PPh}_3)_2(\text{Br})\text{Cl}]$ (?) and an organic product, identified as hexamethyl mellitate (85%) after crystallisation following chromatography on Florisil. A similar reaction occurred with complex (XIIa) and excess of triphenylphosphine.

To give di- μ -bromo-bis[$\{\text{bromo}(\text{methoxycarbonyl})[1,2,3\text{-trismethoxycarbonyl-4,5-bis}(\text{trifluoromethyl})\text{cyclopenta-2,4-dienyl-2-MeOCO}\}\text{methyl}\}$ palladium(II)], (XIIb). A solution of complex (IX) was prepared *in situ* by treatment of (VI) (0.4 g, 1 mmol) with bromine (57 μl) in a mixture of toluene (50 cm^3) and dichloromethane (15 cm^3) at -78°C under an argon atmosphere. A slow stream of hexafluorobut-2-yne gas was bubbled into this solution for 15 min; the solution was then allowed to warm to -20°C , at which temperature it was left stirring for 12 h under a

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

¹⁸ J. M. Stewart, G. J. Kruger, F. A. Kundell, and J. C. Baldwin, 'X-Ray 71 System,' Computer Science Center, University of Maryland.

¹⁹ D. J. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

²⁰ International Tables for X-Ray Crystallography, vol. 3, Kynoch Press, Birmingham, 1962.

²¹ W. H. Zachariasen, *Acta Cryst.*, 1963, **16**, 1139.

−78 °C condenser. The resulting solution was then allowed to warm to +20 °C over 18 h. The light red solution was filtered (to remove a small amount of PdBr₂), the filtrate concentrated to 10 cm³, and light petroleum (50 cm³) added. The precipitate obtained was crystallised

resulting solution chromatographed on Florisil to give 1,2,3,4-tetrakisethoxycarbonyl-5,6-bis(trifluoromethyl)-benzene (XV) (75 mg, 80%, m.p. 122–123 °C) after crystallisation from methanol. The same compound was obtained (78%), together with [Pd(PPh₃)₂Br₂] (85%),

TABLE 5

Final positional co-ordinates (Å) and thermal parameters (Å²), with estimated standard deviations in parentheses, for the complex [Pd{MeO₂C·C₅(CO₂Me)₄·C(CO₂Me)Cl}(acac)]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>		
Pd	0.4452(1)	0.08796(4)	0.11422(6)			
O(9)	0.2790(10)	0.0266(4)	0.0768(5)	0.043(2)		
C(9)	0.2983(14)	−0.0333(6)	0.0722(7)	0.034(3)		
C(9a)	0.1590(18)	−0.0732(7)	0.0491(9)	0.057(4)		
C(8)	0.4376(16)	−0.0640(6)	0.0846(8)	0.042(3)		
C(7)	0.5789(14)	−0.0365(6)	0.1106(7)	0.035(3)		
C(7a)	0.7201(17)	−0.0784(7)	0.1159(9)	0.052(4)		
O(7)	0.6054(10)	0.0210(4)	0.1269(5)	0.039(2)		
C(6)	0.5943(13)	0.1568(6)	0.1531(7)	0.027(3)		
C(6a)	0.7284(14)	0.1263(6)	0.1974(7)	0.028(3)		
O(6a)	0.7201(11)	0.1133(4)	0.2678(5)	0.045(2)		
O(6b)	0.8450(10)	0.1113(4)	0.1556(5)	0.041(2)		
C(6b)	0.9712(18)	0.0749(7)	0.1941(9)	0.059(4)		
C(5)	0.6241(14)	0.2596(6)	0.2347(7)	0.032(3)		
C(5a)	0.7651(15)	0.2542(6)	0.2837(8)	0.037(3)		
O(5a)	0.7752(11)	0.2567(5)	0.3568(6)	0.056(3)		
O(5b)	0.8841(10)	0.2463(4)	0.2398(5)	0.044(2)		
C(5b)	1.0314(18)	0.2440(8)	0.258(1)	0.062(4)		
C(4)	0.5615(14)	0.3165(6)	0.2112(7)	0.033(3)		
C(4a)	0.6348(15)	0.3783(6)	0.2248(8)	0.037(3)		
O(4a)	0.650(11)	0.3834(5)	0.2529(6)	0.051(3)		
O(4b)	0.5449(10)	0.4247(4)	0.2012(5)	0.047(2)		
C(4b)	0.6084(18)	0.4894(7)	0.2054(9)	0.058(4)		
C(3)	0.4148(14)	0.3052(6)	0.1666(7)	0.033(3)		
C(3a)	0.3146(15)	0.3554(6)	0.1329(8)	0.034(3)		
O(3a)	0.3191(11)	0.3776(4)	0.0671(6)	0.049(2)		
O(3b)	0.2154(10)	0.3711(4)	0.1862(5)	0.041(2)		
C(3b)	0.1077(19)	0.4233(8)	0.1629(10)	0.066(5)		
C(2)	0.3932(14)	0.2414(6)	0.1593(7)	0.030(3)		
C(2a)	0.2758(14)	0.2107(6)	0.1103(7)	0.031(3)		
O(2a)	0.2782(10)	0.1546(4)	0.0911(5)	0.038(2)		
O(2b)	0.1651(10)	0.2482(4)	0.0833(5)	0.041(2)		
C(2b)	0.0474(19)	0.2202(8)	0.0267(10)	0.064(5)		
C(1)	0.5203(13)	0.2059(5)	0.2062(7)	0.027(3)		
C(1a)	0.4417(15)	0.1743(6)	0.2754(7)	0.033(3)		
O(1a)	0.3559(11)	0.1298(5)	0.2692(6)	0.050(3)		
O(1b)	0.4643(11)	0.2073(5)	0.3414(6)	0.055(3)		
C(1b)	0.3899(20)	0.1838(9)	0.415(1)	0.072(5)		
Cl(6)	0.6533(4)	0.1970(2)	0.0651(2)			
C(CHCl ₃)	0.7877(19)	0.1021(7)	0.4516(9)	0.021(4)		
Cl(3)	0.7619(7)	0.1500(2)	0.5347(3)			
Cl(2)	0.9798(6)	0.0892(3)	0.4387(3)			
Cl(1)	0.6907(8)	0.0308(3)	0.4652(4)			
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Pd	0.0315(6)	0.0228(5)	0.0404(6)	−0.0008(6)	−0.0003(4)	−0.0002(5)
Cl(6)	0.045(2)	0.036(2)	0.037(2)	0.000(2)	0.005(2)	0.003(1)
Cl(3)	0.062(4)	0.040(3)	0.053(3)	−0.009(3)	0.022(3)	−0.024(2)
Cl(2)	0.033(3)	0.088(4)	0.047(3)	0.006(3)	0.005(3)	−0.003(3)
Cl(1)	0.082(5)	0.038(5)	0.082(4)	−0.023(3)	0.011(4)	−0.020(3)

from diethyl ether–light petroleum to give complex (XIIb) (0.49 g, 70%). The mother liquors were shown (by n.m.r. spectroscopy) to contain only compounds (XI) and (XVI).

Potassium cyanide (66 mg, 1 mmol) was added to a solution of complex (XIIb) (0.14 g, 0.2 mmol) in methanol (10 cm³). A brown precipitate was formed immediately, filtered off, and the filtrate was evaporated to dryness. The residue was extracted with diethyl ether and the

by reaction of complex (XIIb) with a small excess of triphenylphosphine.

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