Acetylenes and Noble Metal Compounds. Part XI.[1a] Reactions of Dimethyl Acetylenedicarboxylate with Dibenzylideneacetone–Palladium and –Platinum Complexes: Pallada- and Platina-cyclopentadienes

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Dimethyl acetylenedicarboxylate (RC_2R) reacted with the zerovalent dibenzylideneacetone (dba) palladium complexes to give the palladacyclopentadiene, $[Pd(C_4R_4)]_n$, characterised as the adducts $Pd(C_4R_4)L_2$ [L = Ph_3P, $(PhO)_3P$, *p*-toluidine; L_2 = $Ph_2PCH_2CH_2PPh_2$, bipy and phen]. $[Pd(C_4R_4)]_n$ reacted with bromine to give $Br(CR)_4Br$, with air and $Pd(PhCN)_2Cl_2$ to give the furan R_4C_4O, and with acetylenes $R'C_2R'$ to give the benzenes $R_4R'_2C_6$ (R' = COOMe or Ph). The platinum analogue, $[Pt(C_4R_4)]_n$, has also been detected and was characterised as $[Pt(C_4R_4)(Ph_3P)_2]$. The mechanism of the formation of the metallacyclopentadienes and benzenes is discussed.

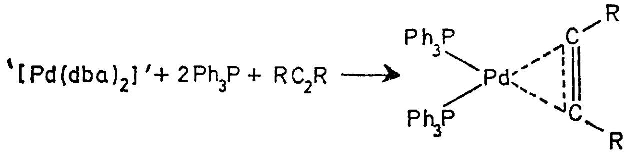
OUR investigation of the reactions of various acetylenes with $PdCl_2$ has led us to propose a mechanism for the cyclotrimerisation of acetylenes that involves a series of stepwise insertions.[1b] It was of considerable interest, therefore, to compare these reactions with those undergone by palladium(0).

Since it was known that palladium metal heterogeneously catalysed the cyclotrimerisation of dimethyl acetylenedicarboxylate (dma) [2] (*vide infra*), it seemed very probable that this would also occur homogeneously with zerovalent complexes. The only reactions of acetylenes with Pd^0 that had been reported at the time we began these experiments were those in which tris- or tetrakis-(triphenylphosphine)palladium reacted with hexafluorobut-2-yne and dimethyl acetylenedicarboxylate (dma) to give the monoacetylene π-complexes, $[Pd(Ph_3P)_2(acetylene)]$.[3]

The phosphine–palladium(0) complexes had the disadvantages (i), that reaction occurred readily only as far as the monoacetylene complex, which was then rather inert towards further reaction and (ii), that in these reactions triphenylphosphine was liberated which was itself very reactive towards dma.[4] The complex 'bis(dibenzylideneacetone)palladium(0), $[Pd(dba)_2]$,' [5] and its platinum analogue,[6] suffered from neither of these disadvantages and also allowed us the possibility of directly comparing the reactions of the two metals.†

To establish the relationship of the reactions described below to that of the phosphine complex '$[Pd(dba)_2]$' was reacted with two equivalents of triphenylphosphine, followed by dma, to give the monoacetylene complex (I) [3] in high yield. The complex $[Pd(RC_2R)(Ph_2PCH_2CH_2PPh_2)]$ was prepared analogously.

Palladacyclopentadienes $[Pd(C_4R_4)]_n$ *and* $[Pd(C_4R_4)L_2]$.—Reaction of dma with '$[Pd(dba)_2]$' (no phosphine present) occurred rapidly at +20° in a variety of solvents



(I)
(R = COOMe)

but was cleanest in warm acetone. The yellow-brown product, $[PdC_4R_4]_n$ (II; R = COOMe), was only appreciably soluble in complexing solvents and the n.m.r. spectra of such solutions showed only two singlets of equal intensity (Table 1).

The complex (II) also gave adducts (III) with monodentate ligands and (IV) with bidentate ligands (Scheme 1). Most of these showed, apart from the L or L_2 resonances, two singlets in the n.m.r. in the methoxycarbonyl region (Table 1). All the data were consistent with their formulation as palladacyclopentadienes.

Additional evidence for the presence of two linked C_2R_2 units in (II) came from the reaction with bromine which afforded palladium bromide and 1,4-dibromo-1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-diene (V).

The complex (II) was also slightly soluble in water, the solubility being considerably enhanced by halide ion; the complexes (VIa) and (VIb) were isolated from these solutions.

The complexes (IVb) and (IVc) were anomalous in that the methoxycarbonyl resonances were coincident in

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† It has been shown that crystals of solvated $[Pd_2(dba)_3]$ can be isolated from solutions of $[Pd(dba)_2]$, the structures of which indicate that the metal atoms are each trigonally co-ordinated to one double bond of each of the three dba ligands.[7] Recent studies indicate a similar process to occur in $[Pt(dba)_2]$.[8] We have also prepared $[Pd(dba)_3]$, which has also been independently synthesised by Pierpont who has determined its crystal structure.[9] Until the structures of $M(dba)_2$ and the details of their behaviour in solution are fully resolved we refer to them as '$[Pd(dba)_2]$', *etc.*; it is, however, clear that only complexes of Pd^0 and Pt^0 are present.

[1] (a) Part X, T. Hosokawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1973, **95**, 4914. (b) See, for example, P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971, vol. II, p. 47 *et seq.*; P. M. Maitlis, *Pure Appl. Chem.*, 1972, **30**, 427; 1973, **33**, 489.

[2] D. Bryce-Smith, *Chem. Ind.*, 1964, 239.

[3] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879.

[4] See, for example, M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc. (C)*, 1968, 2795; N. E. Waite, J. C. Tebby, R. S. Ward, and D. H. Williams, *ibid.*, 1969, 1100; E. M. Richards, J. C. Tebby, R. S. Ward, and D. H. Williams, *ibid.*, p, 1542; N. E. Waite, J. C. Tebby, R. S. Ward, M. A. Shaw, and D. H. Williams, *ibid.*, 1971, 1620.

[5] Y. Takahashi, T. Ho, S. Sakai, and Y. Ishii, *Chem. Comm.*, 1970, 1065.

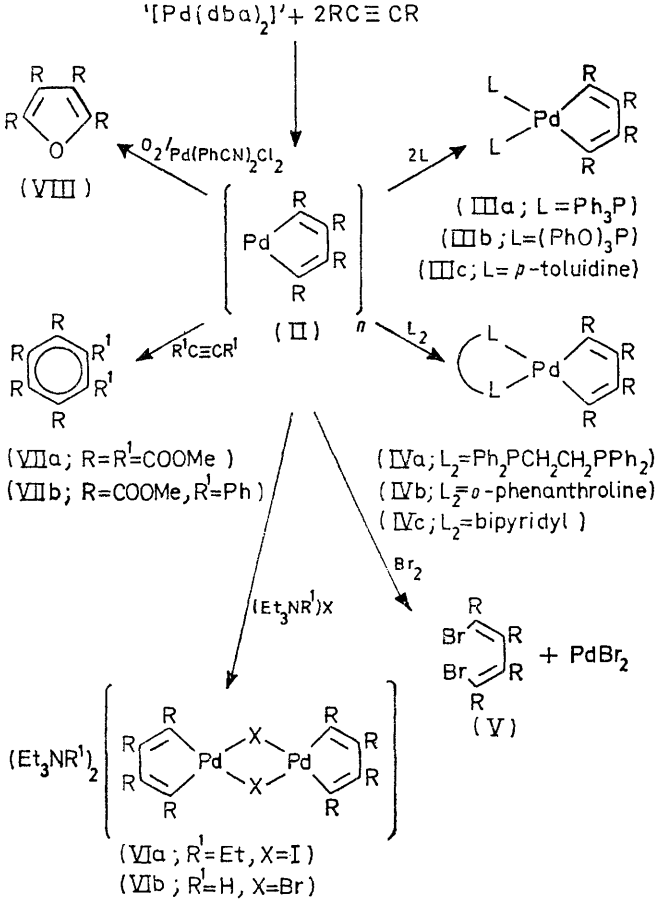
[6] K. Moseley and P. M. Maitlis, *Chem. Comm.*, 1971, 982.

[7] M. C. Mazza and C. G. Pierpont, *J.C.S. Chem. Comm.*, 1973, 207; T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organometallic Chem.*, in press.

[8] B. E. Mann, A. Sonoda, and P. M. Maitlis, unpublished results.

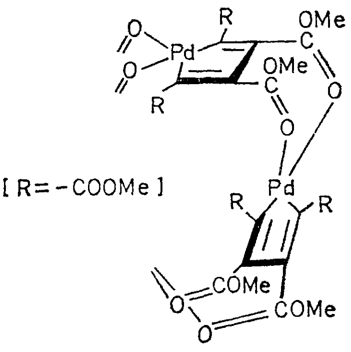
[9] C. G. Pierpont, personal communication.

$CDCl_3$ solution (even at 100 MHz; no splitting was observed either on heating or on cooling to —70°) but they were resolved in other solvents (*e.g.* CD_2Cl_2). The chemical shift of one of the pairs of methoxycarbonyl groups was relatively insensitive to the nature of L (or L_2) and occurred in all the complexes between δ 3·62 and 3·75; the other came at higher field and varied quite significantly (δ 2·66—3·75 in $CDCl_3$) with L or L_2. This can best be explained if the lower field resonance arises from the methoxycarbonyls on the β-carbons of the palladacyclopentadienes, which are little influenced by non-bonded interactions to L. The higher field resonance is then due to the methoxycarbonyls on the α-carbons and the magnitude of its shift from the 'normal' (δ *ca.* 3·7, that of a β-COOMe) is roughly related to the size of L (or L_2) and its interaction with the α-COOMe. Thus, phen and bipy are very compact ligands while Ph_3P and $Ph_2PCH_2CH_2PPh_2$, which give the largest deviations, are much larger and can interact more.



SCHEME 1

The complexes (IIIa and c), (IVa—c), and (VIa) all showed (Table 2) two very strong bands [ν(CO)] at 1705 ± 20 cm^{-1} (which frequently overlapped to appear as one very strong band with a shoulder), together with a number of weak to medium bands [ν(C=C)] between 1500 and 1620 cm^{-1}. The dibromide (V) also showed one very strong ν(CO) at 1730 cm^{-1}. By contrast, the palladiacyclopentadiene (II) showed, in addition to these, a strong band at 1620 cm^{-1} (in Nujol) which we ascribe to a co-ordinated ester ν(CO) in agreement with the work of Lappert.[10] In KBr this band was considerably reduced in intensity. These results can best be explained if units of (II) are bound together by two ester oxygens filling the two vacant (*cis*) co-ordination sites on the palladium of an adjacent molecule. One way in which this could occur is as shown but other possibilities exist in which different methoxycarbonyl groups co-ordinate or where cross-linking can occur.* In KBr the reduced intensity of this lower frequency ν(CO) arises from some degree of depolymerisation owing to the formation of $K_2[Pd(C_4R_4)Br_2]$ or similar species.



Lappert [10] has also noted that when the ester carbonyl is co-ordinated ν(COOMe) moves to higher frequencies. In Nujol, complex (II) shows very strong bands at 1260 and 1290 as well as a strong one at 1210 cm^{-1}. This compares with very strong bands at 1210 in (IIIa) and 1215 cm^{-1} in (VIa), for example, and again suggests that some of the esters in (II) are co-ordinated. In none of the complexes is there any significant change in the bands assigned to ν(C=C).

Reactions of $[Pd(C_4R_4)]_n$ *with Acetylenes.*—The most interesting reaction of (II) occurred with acetylenes. When (II) was heated in dma as solvent hexamethyl mellitate (VIIa) was obtained catalytically, 60 equivalents of dma being trimerised per equivalent of (II) (these conditions were *not* optimised). A similar, but non-catalytic, reaction occurred when (II) was reacted with diphenylacetylene and the terphenyl (VIIb) was obtained.

The reaction to give (VIIa) is effectively catalytic in (II) and is obviously related to the heterogeneous cyclotrimerisation of dma to hexamethyl mellitate on palladium on carbon [2] and it may be presumed that (II) is an intermediate there too. This is an interesting example of a parallel between a heterogeneous and a homogeneous catalytic process.

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* Models show that if the mode of bonding illustrated is utilised then a fairly rigid cyclic trimer can be built up in this way. This agrees well with the result from our chloroform molecular weight measurement.

[10] M. F. Lappert, *J. Chem. Soc.*, 1961, 817.

When the adduct (IIIa) was treated with one equivalent of dma a complex with empirical formula $[Pd(C_4R_4)(Ph_3P)]_n$ was isolated. This could be converted back to (IIIa) by reaction with one equivalent of triphenylphosphine. The forward reaction is a consequence of the lability of triphenylphosphine in (IIIa); since the liberated ligand can react irreversibly with dma[4] (*vide infra*) the equilibrium (1) is displaced to the right. The existence of an equilibrium of this type was

$$[Pd(C_4R_4)(Ph_3P)_2] \rightleftharpoons [Pd(C_4R_4)(Ph_3P)]_n + nPh_3P \quad (1)$$

also suggested by molecular weight measurements on (IIIa) which gave low results.

TABLE 1

N.m.r. Spectra [a]

	Complex	COOMe [b]	Other
(II)	$[Pd(C_4R_4)]_n$	3·50, 3·58 [c] 3·84, 3·90 [d] 3·66, 3·74 [e]	
(IIIa)	$[Pd(C_4R_4)(Ph_3P)_2]$	2·72, 3·63	7·25(m,phenyl)
(IIIb)	$[Pd(C_4R_4)\{(PhO)_3P\}_2]$	3·36, 3·64	7·07(m,phenyl)
(IIIc)	$[Pd(C_4R_4)(p\text{-toluidine})_2]$	3·55, 3·75	2·17(s,CH_3), 4·88(s, br,NH_2), 6·83(s, aromatic)
(IVa)	$[Pd(C_4R_4)(Ph_2PCH_2CH_2PPh_2)]$	2·66, 3·62	1·88(s,CH_2), 2·20(s,CH_2), 7·56(m,br,phenyl)
(IVb)	$[Pd(C_4R_4)(o\text{-phen})]$	3·76 3·60, 3·71 [c] 3·68, 3·71 [f]	7·84, 8·61(m,aromatic)
(IVc)	$[Pd(C_4R_4)(bipy)]$	3·75 3·55, 3·63 [c] 3·66, 3·68 [f] 3·58, 3·59 [g]	7·88, 8·61(m, aromatic)
(V)	[BrCR=CRCR=CRBr]	3·76, 3·90	
(VIa)	$[Et_4N)_2[Pd_2(C_4R_4)_2I_2]$	3·54, 3·66	1·32(t,CH_3), 3·48(q,CH_2)
(VIb)	$(Et_3NH)_2[Pd_2(C_4R_4)_2Br_2]$	3·60, 3·73	1·44(t,CH_3), 3·52(q,CH_2)
(VIIb)	$[C_6R_4Ph_2]$	3·63, 3·72 [e]	
(VIII)	$[\overline{C_4R_4O}]$	3·90, 3·92	
	$[Pt(C_4R_4)(Ph_3P)_2]$	2·63, 3·62	7·2(m,br,phenyl)

[a] In δ, in $CDCl_3$ unless otherwise stated. [b] Singlets of equal intensity. [c] In $(CD_3)_2SO$. [d] In $(CD_3)_2CO$. In PhCN. [f] In CD_2Cl_2. [g] In $CDCl_3$–C_6H_6 (1 : 2).

TABLE 2

I.r. spectra [a]

	Complex	ν(CO)	ν(C=C)
(II)	$[Pd(C_4R_4)]_n$	1725vs, 1710sh, 1620s [b] 1710vs, 1680vs, 1610m [c]	1570ms, 1550m [b] 1555m [c]
(V)	[BrCR=CRCR=CRBr]	1730vs, 1625w	1600m
(IIIa)	$[Pd(C_4R_4)(Ph_3P)_2]$	1715vs, 1615w 1710sh, 1700vs, 1620w [b]	1550m 1555m-w [b]
(IIIe)	$[Pd(C_4R_4)(p\text{-toluidine})_2]$	1710vs, 1680vs, 1615m	1550s, 1510m
(IVa)	$[Pd(C_4R_4)(Ph_2PCH_2CH_2PPh_2)]$	1715vs, 1690vs, 1610vw	1550m,br
(IVb)	$[Pd(C_4R_4)(o\text{-phen})]$	1710sh, 1690vs	1560m, 1500w
(IVc)	$[Pd(C_4R_4)(bipy)]$	1705sh, 1685vs	1590m, 1550m
(VIa)	$(Et_4N)_2[Pd_2(C_4R_4)_2I_2]$	1725sh, 1695vs [b]	1550m [b]

[a] In cm^{-1}, in chloroform except where indicated. [b] In Nujol. [c] In KBr.

The reactions of (I), (II), (IIIa), and $[Pd(C_4R_4)(PPh_3)]_n$ with an excess of dma (≥10 equivalents) at 35° in benzonitrile–benzene (1 : 5) were also studied by n.m.r. In each case darkening of the solution was accompanied by the growth of a peak corresponding to hexamethyl mellitate, in addition to others. Very similar results but faster rates of reaction were obtained using benzene alone as solvent, but here solubility problems only allowed examination of the behaviour of (I) and (IIIa) towards dma. In contrast to the report of Ito *et al.*,[11] under our conditions we could obtain no evidence for the formation of appreciable amounts of either (IIIa) or $[Pd(C_4R_4)PPh_3]_n$ from (I).

In the reactions of dma and (I) we observed an induction period which coincided with a decrease in the intensity of the signal owing to the complexed acetylene. Thereafter, during the slow catalytic formation of hexamethyl mellitate the intensity of this signal remained constant. This evidence seems to rule out a process such as:

$$\text{(I)} \xrightarrow[k_1]{\text{dma}} \text{(IIIa) or } [Pd(C_4R_4)(PPh_3)]_n \xrightarrow[k_2]{\text{dma}} C_6R_6$$

where $k_2 > k_1$. One alternative is that the observed formation of hexamethyl mellitate arises from the presence of traces of metal (probably solubilised in some way) which arise by partial decomposition of (I):

$$\text{(I)} \longrightarrow Pd(solv)_x \xrightarrow[k_3]{\text{dma}} \text{(II)} \xrightarrow[k_4]{\text{dma}} C_6R_6$$

and that under conditions where (II) is solubilised it reacts with a large excess of dma such that $k_4 > k_3$.

Other Reactions of $[Pd(C_4R_4)]_n$.—The palladacyclopentadiene (II) did not react in benzene with carbon monoxide at 20° and 1 atmos; reaction did occur under

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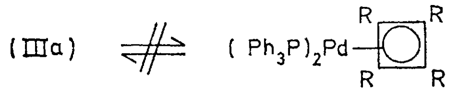
[11] Ts. Ito, S. Hasegawa, Y. Takahashi, and Y. Ishii, *J.C.S. Chem. Comm.*, 1972, 629.

these conditions in tetrahydrofuran and also in benzene (80 °C, 70 atmos) to give metal and polymeric organic products that could not be characterised.

The complex (II) was inert to air or oxygen; however, in air (II) reacted with dichlorobis(benzonitrile)palladium to give the furan (VIII). It is interesting that dichloro(tetraphenylcyclobutadiene)palladium dimer reacted with triphenylphosphine in air to give tetraphenylfuran [12] and it seems likely that these reactions are related.

The possibility that an equilibrium might exist between the palladacyclopentadiene (IIIa) and a cyclobutadiene complex [such as (IX)] was also investigated. However, there was no change in a sample of solid (IIIa) that had been heated at 140° for 4 h nor were the n.m.r. spectra of solutions of (IIIa) in $(CD_3)_2SO$ and of (IVc) in *o*-dichlorobenzene changed up to 140°, above which temperature decomposition began to occur.



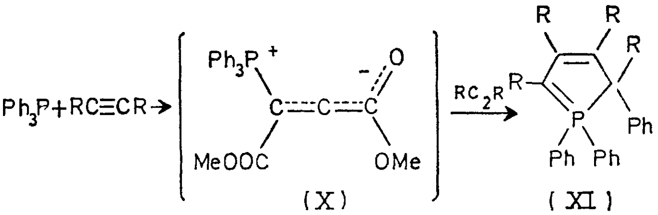
(IX)

Tetrakis(methoxycarbonyl)platinacyclopentadiene.— Attempts to prepare the platinum analogue of (II) by reaction of dma with either ' $[Pt(dba)_2]$ ' or ' $[Pt(dba)_3]$ ' in a variety of solvents were unsuccessful. Reaction occurred and an orange solid could in each case be isolated but this showed a broad resonance in the n.m.r. spectrum. This material may be related to $[Pt(C_4R_4)]_n$ since, when the reaction was carried out in benzonitrile–benzene (1 : 5), a solution was obtained which showed two resonances in the n.m.r. (δ 4·0, 4·08) close to those for (II). On addition of triphenylphosphine to this solution the adduct $[Pt(C_4R_4)(Ph_3P)_2]$, analogous to (IIIa), was obtained which was fully characterised.

Comparison of the reactions of ' $[Pt(dba)_2]$ ' and ' $[Pd(dba)_2]$ ' with dma under similar conditions showed that the Pt complex reacted more slowly to give $[Pt(C_4R_4)]_n$ but that this reacted more readily than (II) with further dma to give hexamethyl mellitate (VIIIa).

Mechanism of the Di- and Tri-merisation of dma. The formation of metallacyclopentadienes by reaction of acetylenes with metal complexes is well known, though it has not hitherto been reported for Pd or Pt; for example, Collman *et al.*[13] described the formation of rhoda- and irida-cyclopentadienes from Rh^I and Ir^I complexes and dma.

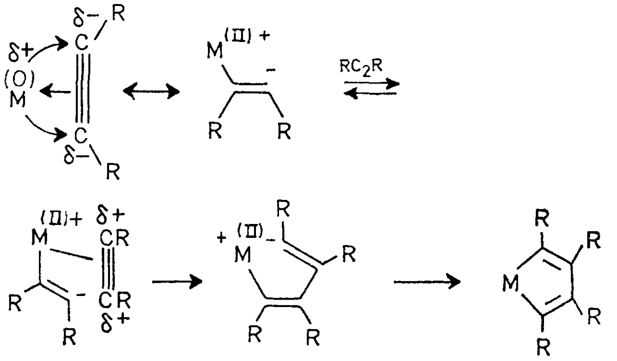
A wide variety of nucleophiles, in fact, react with acetylenes bearing electron-withdrawing substituents and when the nucleophile has no active hydrogen a common path involves the co-dimerisation of two molecules of the acetylene with one of the nucleophile to give cyclic products.[14] For example, the major product of the reaction of dma with triphenylphosphine in non-polar solvents and at high dma : phosphine ratios is the phosphole (XI). This is postulated to arise through attack by the dipolar intermediate (X) on another molecule of dma, followed by a 1,2-migration of a phenyl from phosphorus to carbon.[4]



(X) (XI)

For this reason, when working with acetylenes such as dma it is highly desirable to avoid the use of phosphines and similar ' stabilising ' ligands on the metal. As we observed in the reaction of (IIIa) and dma, side reactions occur which can complicate and seriously obscure the main reaction paths.

The nucleophilicity of the metal, at least for the Pd^0 and Pt^0 complexes described here, must act as the driving force for their reactions to give the metallacyclopentadienes.* The first step is probably the formation of a π-acetylene complex of the metal in the zerovalent state and we envisage the further reaction to proceed through a series of dipolar intermediates and transition states (Scheme 2).[15] Similar types of intermediates have been proposed in the reaction of $[Pt(Ph_3P)_2O_2]$ with acetone to give $[\overline{\mathrm{Pt(OCMe_2O{\cdot}O}})(\mathrm{Ph_3P})_2]$ [16] and in the reactions of Fe^0, Ru^0, and Os^0 complexes with fluoro-olefins and -acetylenes.[17] Owing to the present uncertainty over the natures of the dba complexes in solution it is, however, not yet possible to specify how many metal atoms are involved in our reactions.



Scheme 2

The last step in the cyclotrimerisation, that of the reaction of dma (or other acetylenes) with the metallacyclopentadiene has not yet been resolved. We had

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* This may not always be the case; for example, Rh^I complexes will also react with acetylenes *not* bearing electron-withdrawing substituents to give rhodacyclopentadienes.[15]

[12] P. M. Maitlis and F. G. A. Stone, *Proc. Chem. Soc.*, 1962, 330.

[13] J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 1968, **7**, 1298.

[14] E. Winterfeldt, *Angew. Chem. Internat. Edn.*, 1967, **6**, 423.

[15] S. McVey and P. M. Maitlis, *J. Organometallic Chem.*, 1969, **19**, 169.

[16] R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Comm.*, 1968, 1498.

[17] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2975 and 2981.

earlier shown that the *tetrahapto*-benzene complex, $[Rh(C_5Me_5)\{C_6(COOMe)_6\}]$ [which can be made from dma and $Rh(C_5Me_5)(dba)$ [18]], is fluxional and undergoes a series of 1,2-shifts of the metal with respect to the ring on heating; this is accompanied by a slow decomposition to hexamethyl mellitate.[19]

Browning *et al.*[20] have recently isolated and characterised the *dihapto*-benzene complex $[Pt(Et_3P)_2\{C_6(CF_3)_6\}]$, analogues of which may well be intermediates in the Pd and Pt reactions. Presumably the *dihapto*-bonding here is preferred over the *tetrahapto*-bonding since platinum(0) prefers to be three-co-ordinate.

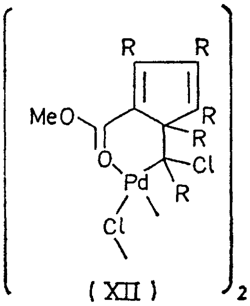
It is of considerable interest to contrast the reactions of dma with Pd^0 reported here with those of Pd^{II}. In the latter case both Avram *et al.*[21] and ourselves [22] found that dma reacts with dichlorobis(benzonitrile)palladium to give a complex $[C_6R_6PdCl_2]_n$ which we have now shown to be a dimer with the structure (XII).[23] This is probably also formed by a stepwise process, but in this case by a series of *cis*-insertion reactions of dma, first into a Pd–Cl bond and then into vinylic–Pd bonds, followed by a ring closure. We ascribe this difference in reaction to the very different natures of the complexes involved and to their different oxidation states. The end product for both the Pd^0 and the Pd^{II} reactions is hexamethyl mellitate, which can be obtained from (XII) either on heating or on treatment with aqueous cyanide.

TABLE 3

Analytical data [a]

	Complex [b]	C	H	Other	*M*
$Pd(dba)_3$	$Pd(C_{17}H_{14}O)_3$	75·1(75·7)	5·4(5·2)		
' $Pt(dba)_2$ '	$Pt(C_{17}H_{14}O)_2$	61·3(61·5)	4·2(4·2)		593 [c] (663)
' $Pt(dba)_3$ '	$Pt(C_{17}H_{14}O)_3$	68·1(68·2)	4·6(4·7)	O,5·6(5·3)	450 [c] (897)
	$[Pd(R_2C_2)(Ph_2PCH_2CH_2PPh_2)]$	61·6(62·3)	5·0(4·9)		
(II)	$[Pd(C_4R_4)]_n$	37·0(36·9)	3·1(3·1)		1240 [c] (391) [d]
(IIIa)	$[Pd(C_4R_4)(Ph_3P)_2]$	63·0(63·0)	4·6(4·6)	P,6·9(6·8)	566 [c] (914)
(IIIb)	$[Pd(C_4R_4)\{(PhO)_3P\}_2]$	57·4(57·0)	4·2(4·2)		
(IIIc)	$[Pd(C_4R_4)(p\text{-toluidine})_2]$	51·7(51·7)	4·8(5·0)	N,4·5(4·6)	
(IVa)	$[Pd(C_4R_4)(Ph_2PCH_2CH_2PPh_2)]$	57·8(57·9)	4·8(4·6)		
(IVb)	$[Pd(C_4R_4)(o\text{-phen})$	50·3(50·5)	3·3(3·5)	N,4·9(4·9)	
(IVc)	$[Pd(C_4R_4)(bipy)]$	48·2(48·4)	3·8(3·7)	N,5·0(5·1)	543 [c] (546)
	$[Pd(C_4R_4)(Ph_3P)]_n$	55·5(55·2)	4·7(4·1)		
(V)	[BrCR=CRCR=CRBr]	32·8(32·4)	3·0(2·7)	Br,35·8(36·0)	
(VIa)	$(Et_4N)_2[Pd_2(C_4R_4)_2I_2]$	36·4(37·1)	4·9(5·4)	I,19·6(19·6)	
(VIb)	$(Et_3NH)_2[Pd_2(C_4R_4)_2Br_2]$	37·6(37·9)	4·8(4·9)	Br,14·2(14·0)	
(VIIb)	$[C_6R_4Ph_2]$	67·5(67·5)	5·0(4·8)		462 [e] (462)
(VIII)	$[\overline{C_4R_4O}]$	47·7(48·0)	4·1(4·0)		300 [e] (300)
	$[Pt(C_4R_4)(Ph_3P)_2]$	57·1(57·4)	4·4(4·2)	P,6·2(6·2)	

[a] Required values in parentheses. [b] In the formulae R = COOMe. [c] Osmometric in chloroform. [d] Calculated for $n = 1$. [e] Mass spectroscopic.



(XII)

EXPERIMENTAL

All experiments were conducted under an atmosphere of nitrogen unless otherwise stated. Removal of solvent was carried out using a rotary evaporator with a bath temperature ⩽25°. N.m.r. and i.r. spectra are collected in Tables 1 and 2; analytical data in Table 3.

' *Bis(dibenzylideneacetone)platinum.*'—A hot solution of potassium tetrachloroplatinate (1·5 g, 3·6 mmol) in water (20 ml) was added to a well stirred refluxing solution of dibenzylideneacetone (2·4 g, 10 mmol) and sodium acetate (3 g) in ethanol (100 ml) under nitrogen. The solution rapidly turned dark and deposited a deep purple solid. The reaction was continued for 10 min, the mixture was cooled and the product filtered off to give the deep blue-purple microcrystalline ' bis(dibenzylideneacetone)platinum ' (1·5 g, 63%, m.p. 172—176° decomp.).

' Bis(dibenzylideneacetone)palladium ' [5] (67%) was obtained as deep red-purple microcrystals by a similar reaction.

' *Tris(dibenzylideneacetone)platinum.*'—A solution of potassium tetrachloroplatinate (0·5 g, 1·2 mmol) in water (40 ml) was added to a solution of dibenzylideneacetone (4·0 g, 17 mmol) and sodium acetate (2·5 g) in ethanol (180 ml) and the resultant solution was stirred (4 h, at 40°). The solution was cooled and the canary-yellow microcrystalline precipitate of ' tris(dibenzylideneacetone)-platinum ' was filtered off; yield 1·2 g (54%). Both the bis- and the tris-complex reacted with carbon monoxide in benzene (20°, 1 atmos.) to give metal and dba.

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Tris(dibenzylideneacetone)palladium.—A solution of sodium tetrachloropalladate (0·3 g, 1 mmol) dissolved in water (40 ml) was added to a suspension of dibenzylideneacetone (1·0 g, 4·0 mmol) in ethanol (60 ml). The resultant suspension was then stirred (20—25°, 10 days), after which the solid was filtered off and washed with ethanol to give yellow tris(dibenzylideneacetone)palladium (0·6 g, 75%, m.p. 151° decomp.).

The same complex can also be prepared at higher temperatures and with shorter reaction times (37°, 2 days) in about the same yield; however, this product is then darker in colour and less pure.

$[Pd(R_2C_2)(Ph_3P)_2]$, *Complex* (I).—Triphenylphosphine (0·10 g, 0·38 mmol) was slowly added to a well stirred suspension of $[(dba)_2Pd]$ (0·10 g, 0·18 mmol) in dry benzene (10 ml) at 20°. To this red solution was added dimethyl acetylenedicarboxylate (60 μl) whereupon a colour change to yellow occurred. Removal of the solvent and crystallisation from ether at 0° gave cream crystals of $[Pd(R_2C_2)(Ph_3P)_2]$ (94 mg, 70%) identified by i.r. and n.m.r. spectra. $[Pd(R_2C_2)(Ph_2PCH_2CH_2PPh_2)]$ (pale orange, 63%, m.p. 151—154° decomp.) was prepared analogously.

$[Pd(C_4R_4)]_n$, *Complex* (II).—Dimethyl acetylenedicarboxylate (0·76 g, 5·3 mmol) was added dropwise to a suspension of $[Pd(dba)_2]$ (1 g, 1·7 mmol) in acetone (10 ml). The resultant solution was warmed (50° for 5 min) when a colour change occurred and a yellow precipitate formed. The solution was cooled and the yellow palladacyclopentadiene (II, 0·65 g, 95%) was filtered off. The complex could not be recrystallised; its solubility properties varied somewhat from one sample to another but it was at best only slightly soluble in acetone, chloroform, THF, and other weakly co-ordinating solvents. One sample was sufficiently soluble in chloroform for a molecular weight determination (Table 3).

$Pd(C_4R_4)(Ph_3P)_2$, *Complex* (IIIa).—Triphenylphosphine (0·15 g, 0·6 mmol) was added to a stirred suspension of $[Pd(C_4R_4)]_n$ (0·1 g, 0·25 mmol) in benzene (5 ml) at 20°. The solid slowly dissolved to give a clear yellow solution from which a white solid slowly precipitated after 0·5 h. This was filtered off and crystallised from dichloromethane–ether to give cream needles of $[Pd(C_4R_4)(Ph_3P)_2]$ (164 mg, 70%, m.p. 150° decomp.).

Prepared analogously were $[Pd(C_4R_4)\{(PhO)_3P\}_2]$ (IIIb, white, 65%, m.p. 154—157°), $[Pd(C_4R_4)(p\text{-toluidine})_2]$ (IIIc, yellow, 66%, m.p. 170—174°); $[Pd(C_4R_4)(Ph_2PCH_2CH_2PPh_2)]$ (IVa) (cream, 74%, m.p. 250—252°); $[Pd(C_4R_4)(phen)]$ (IVb) (yellow, 87%, m.p. 242—244°); and $[Pd(C_4R_4)(bipy)]$ (IVc) (pale yellow, 75%, m.p. 219—221°).

Reaction of $[Pd(C_4R_4)(Ph_3P)_2]$ (IIIa) *with Dimethyl Acetylenedicarboxylate.*—Dimethyl acetylenedicarboxylate (25 μl, 0·2 mmol) was added to a suspension of $[Pd(C_4R_4)(Ph_3P)_2]$ (0·2 g, 0·2 mmol) in benzene (4 ml). The mixture was stirred for 8 h at 20°; the yellow precipitate was then filtered off and crystallised from dichloromethane–ether to give yellow crystals of $[Pd(C_4R_4)(Ph_3P)]_n$ (113 mg, 79%). On addition of one equivalent of triphenylphosphine to a solution of this complex the original complex, $[Pd(C_4R_4)(Ph_3P)_2]$, was regenerated quantitatively.

Reaction of $[Pd(C_4R_4)]_n$ *with an Excess of Bromine.*—A solution of bromine (0·65 g, 4 mmol) in dichloromethane (3 ml) was added dropwise to a suspension of $[Pd(C_4R_4)]_n$ (0·15 g, 0·4 mmol) in dichloromethane (15 ml) at 0°. The solid dissolved to give a deep red solution from which a brown solid ($PdBr_2$) was rapidly deposited. The solution was filtered and the solvent removed to give, after chromatography on Florisil in ether, 1,4-dibromo-1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-diene (V) as a viscous colourless oil (170 mg). The molecular ion was not detectable in the mass spectrum, the largest ions in which corresponded to loss of OCH_3 from $C_{12}H_{12}O_8Br_2$ (Found, 414·86796, 412·87042, and 410·87257; $(C_{11}H_9O_7{}^{81}Br_2)^+$ requires 414·86751, $(C_{11}H_9O_7{}^{79}Br^{81}Br)^+$ requires 412·86951, and $(C_{11}H_9O_7{}^{79}Br_2)^+$ requires 410·87152). The compound underwent no rearrangement on heating (155°, 24 h) in *o*-dichlorobenzene.

$(Et_4N)_2[Pd_2(C_4R_4)_2I_2]$, *Complex* (VIa).—Potassium iodide (0·2 g, 1·2 mmol) was added to a suspension of $[Pd(C_4R_4)]_n$ (0·2 g, 0·5 mmol) in water (10 ml). The solid dissolved to give a yellow solution; to this was added tetraethylammonium chloride (0·2 g) whereupon a thick pale yellow precipitate formed. Crystallisation from dichloromethane–ether gave pale yellow crystals of $(Et_4N)_2[Pd_2(C_4R_4)_2I_2]$ (0·3 g, 44%, m.p. 242—244° decomp.). $(Et_3NH)_2[Pd_2(C_4R_4)_2Br_2]$ (VIb) (80%, m.p. 220—221° (decomp.) was prepared similarly.

Reaction of $[Pd(C_4R_4)]_n$ *with Acetylenes.*—(i) *With dimethyl acetylenedicarboxylate.* A mixture of dma (1·5 ml, 12 mmol) and $[Pd(R_4C_4)]_n$ (50 mg, 0·13 mmol) was heated in a sealed evacuated tube. The complex slowly dissolved to give a red solution until, at 70°, the mixture rapidly turned black and solidified. The tube was cooled and opened and the solid was extracted with ether and crystallised from methanol to give hexamethyl mellitate (VIIIa, 1·1 g, 64% based on dma, m.p. 184—186°). A small residue of metal remained. An analogous reaction occurred in benzene (60°, 5 h).

(ii) *With diphenylacetylene.* Under the same conditions as above, diphenylacetylene reacted with $[Pd(C_4R_4)]_n$ to give tetramethyl *o*-terphenyl-1′,2′,3′,4′-tetracarboxylate (VIIIb) (63%, m.p. 208—210°).

2,3,4,5-*Tetrakis(methoxycarbonyl)furan* (IX).—$[Pd(C_4R_4)]_n$ (80 mg, 0·2 mmol) was added to a solution of dichlorobis(benzonitrile)palladium (80 mg, 0·2 mmol) in benzene (10 ml) to give a dark brown solution. This was stirred in air for 3 days; it was then poured into ether (50 ml) to precipitate a greyish solid; addition of triphenylphosphine to a solution of this material gave dichlorobis(triphenylphosphine)palladium (180 mg, 50%). No other identifiable material was obtained from this fraction.

The ether–benzene filtrate was chromatographed (Florisil, eluted with ether) to give, after crystallisation from methanol, colourless crystals of 2,3,4,5-tetrakis(methoxycarbonyl)furan (25 mg, 45%, m.p. 106—107°).

No reaction occurred on stirring a suspension of $[Pd(C_4R_4)]_n$ in benzene in air by itself.

$[Pt(C_4R_4)(Ph_3P)_2]$.— Tris(dibenzylideneacetone)platinum (0·10 g, 0·11 mmol) was added to dma (15 μl, 0·12 mmol) in benzene (3 ml) and benzonitrile (0·5 ml) and the solution was stirred at 40° for 15 min. Further dma (15 μl, 0·12 mmol) was then added and the reaction was continued for a further 20 min. The red solution was filtered and triphenylphosphine (0·15 g) was added to the filtrate, followed by ether (80 ml). A cream solid was precipitated which, after crystallisation from dichloromethane–ether, afforded $[Pt(C_4R_4)(Ph_3P)_2]$ (0·06 g, 55%, m.p. 232—235° decomp.).

When the above reaction was repeated but without the addition of triphenylphosphine, an orange solid (0·03 g) was obtained which showed a broad complex resonance in the n.m.r. spectrum at δ 3·65. Addition of triphenylphosphine to this solution caused the appearance of small peaks at δ 2·62 and 3·6, which are probably due to $[Pt(C_4R_4)(Ph_3P)_2]$, as well as a stronger peak at δ 3·88 which may be due to hexamethyl mellitate. These bands were superimposed on a broad resonance.

We thank Mr. R. MacDonald, Dr. B. E. Mann, and Dr. D. M. Roe for experimental assistance, the National Research Council of Canada for support, and Johnson, Matthey for the loan of palladium and platinum salts.

[3/1273 *Received*, 18*th June*, 1973]