# The Palladium(II)-Induced Oligomerization of Acetylenes: An Organometallic Detective Story

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One of the most fascinating chapters in organometallic chemistry concerns the interaction of transition-metal compounds with acetylenes. The number of different strange, unusual, and apparently unrelated types of molecules isolated from these reactions reminds one of the early days of organic natural product chemistry; the tale of the unravelling of their structures and of the elucidation of apparently tortuous mechanisms by which they are formed is reminiscent of a detective story. Clues abound, there are many red herrings, and the answer to the puzzle is seldom obvious even halfway through the problem.

Interest in the general area was dramatically awakened by Reppe's discovery of the tetramerization of acetylene to cyclooctatetraene by a nickel catalyst.[1] This was followed by extensive investigations of the structures of the multitude of complexes isolated from reactions of metal carbonyls and acetylenes, particularly by Hübel and his co-workers,[2] and many others. These studies showed that a number of complex processes occur during such reactions, many involving polynuclear intermediates, and even today our understanding of that particular story is only fragmentary.

I wish to draw attention here to the reactions of acetylenes with palladium(II) where it has now been possible to shed light on the details of the individual processes that occur, including the remarkable manner in which acetylenes are cyclotrimerized to benzenes via cyclopentadienylmethyl complexes.

Although these reactions have only been the subject of detailed study during the last 15 years, as early as 1894 F. C. Phillips, working at Western University in Allegheny, Pa., observed the formation of metal-containing dark-red precipitates when acetylene was bubbled into aqueous solutions of palladium chloride.[3] Virtually all acetylenes react readily with palladium chloride under ambient conditions to give red-brown complexes; single substances are usually obtained from disubstituted acetylenes, but the formation of complex mixtures in the reactions of most monosubstituted acetylenes and acetylene itself[4] has retarded the understanding of those systems.

For the disubstituted and a few monosubstituted acetylenes we have now been able to define relatively

Scheme I
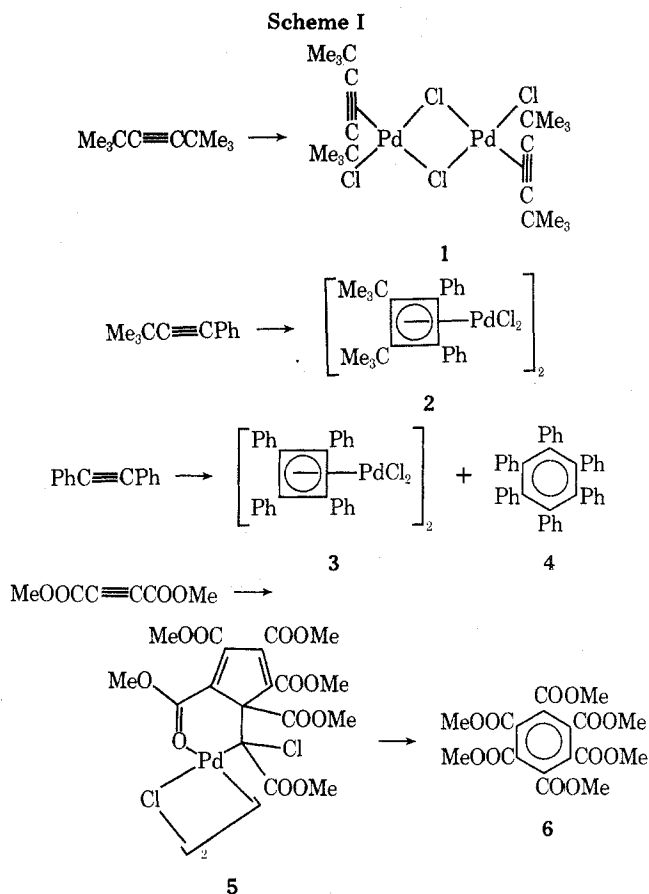


clearly nearly all the steps in a complicated overall process.

The usual starting material is the bis(benzonitrile) complex of palladium chloride, which is easily prepared and is readily soluble in common organic solvents.[5] Since benzonitrile binds only very loosely to $PdCl_2$ and appears to take little part in the subsequent reactions, the complex can be thought of as "solubilized $PdCl_2$". Undesirable side reactions are minimized by the use of aprotic solvents, but good coordinating solvents or better ligands than benzonitrile strongly retard the desired reactions.

The extent of reaction is very much governed by the size of the acetylenic substituents (Scheme I); for

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(1) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).

(2) W. Hübel, "Organic Synthesis via Metal Carbonyls", I. Wender and P. Pino, Ed., Vol. I, Interscience, New York, NY, 1967, p 273.

(3) F. C. Phillips, *Am. Chem. J.*, **16**, 255 (1894); *Z. Anorg Chem.*, **6**, 229 (1894).
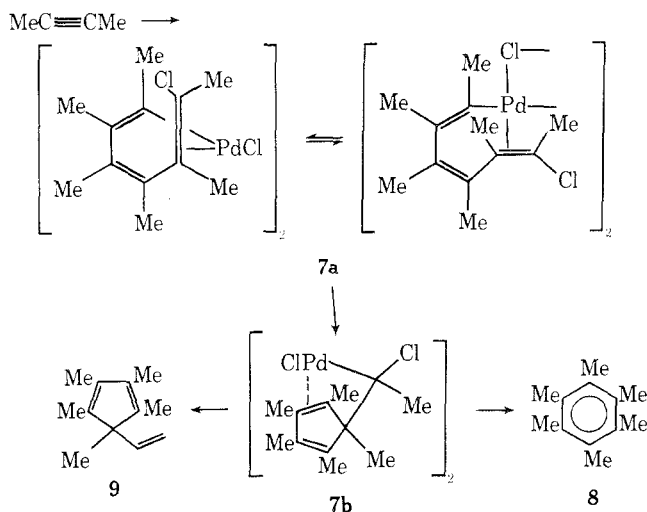
(4) H. Erdmann and O. Makowka, *Chem. Ber.*, **37** 2694 (1904); O. Makowka, *ibid.*, **41**, 824 (1908).

(5) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).

example, if both substituents are bulky *tert*-butyl groups, no oligomerization occurs and only the 1:1 acetylene complex 1 is formed.[6] When one *tert*-butyl is replaced by the smaller phenyl substituent dimerization takes place and the cyclobutadiene complex 2 is the only product.[7,8] However, diphenylacetylene gives a mixture of the cyclobutadiene complex 3 and the benzenoid trimer 4.[9-12] The somewhat smaller carboxymethyl groups ensure that dimethyl acetylenedicarboxylate gives only trimer; in this case the Cl-bridged complex 5 is isolated; this gives the benzenoid hexamethyl mellitate (6) on heating or reaction with cyanide.[13,14]

In each of these cases no other significant products are found when the reactions are carried out in aprotic solvents. However, dimethylacetylene gives tetrameric materials of unknown structures in addition to the main product, $[Cl(Me_2C_2)_3PdCl]_2$ (7), of analogous stoichiometry to 5. We have not yet been able to completely characterize this complex, owing to its extreme lability, but two structures are currently being considered. In 7a a strain-free hexatrienyl ligand is $\sigma$ bonded to a palladium atom at one end and $\pi$ bonded at the other; it can exist in two forms with the $\pi$-bonded olefin either perpendicular to or in the same plane as the metal and the other ligands.[15] The other structure is one where internal cyclization of 7a has already occurred to give the rather strained 7b. $^1H$ NMR spectra do not distinguish between 7a and 7b, but recent $^{13}C$ NMR studies favor the latter.[16] 7 is

MeC≡CMe ⟶



7a



9     7b     8

easily decomposed to give either hexamethylbenzene (8) or vinylpentamethylcyclopentadiene (9).[17]

In contrast to the pronounced steric effects of the acetylenic substituents on the course of the reaction, their electronic effects appear minimal; the reaction of dimethyl acetylenedicarboxylate, for example, fits neatly into the sequence of substituent sizes.

In order to unravel further the strange events that lead to some acetylenes being catalytically transformed into benzenes, while others give trimer complexes and others again give only dimer complexes, we have searched for clues among the reaction intermediates.
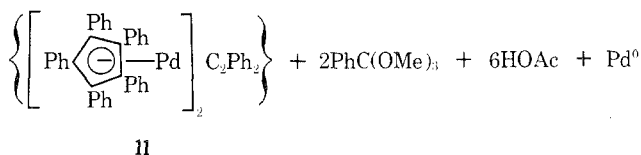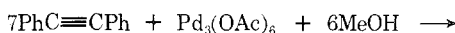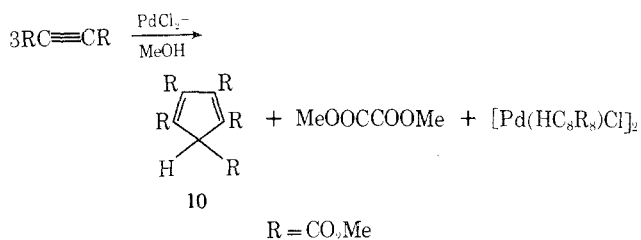
## Reaction Intermediates

(a) The first intermediate is undoubtedly an acetylene $\pi$ complex; one such, 1, has been isolated; another has been detected [(f), below].

(b) An early suggestion was that cyclobutadienes were intermediates in the formation of benzenes, for example:
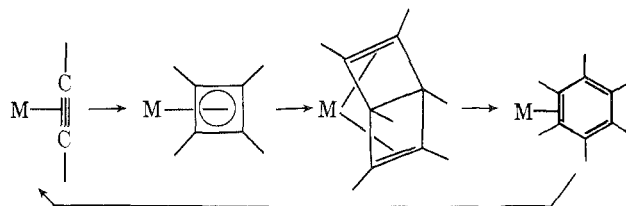


However, a number of experiments have shown this to be an unlikely path in the $PdCl_2$ reactions.[18,19]

(c) There is, on the other hand, strong evidence that complexes of the general form $[C_5R_5–CRCl–PdCl]_2$, containing a substituted cyclopentadiene as ligand, are intermediates in the benzene formation. One such example is 5 which is easily decomposed to hexamethyl mellitate. A number of other Pd(II)-induced reactions also give substituted cyclopentadienes, for example, vinylpentamethylcyclopentadiene (9) from 2-butyne, and 10 from dimethyl acetylenedicarboxylate.[20] The complex 11, containing the pentaphenylcyclopentadienyl ligand, has also

$$3RC\equiv CR \xrightarrow[\text{MeOH}]{PdCl_2^-}$$



$$+ \; MeOOCCOOMe \; + \; [Pd(HC_8R_8)Cl]_2$$

10

$$R = CO_2Me$$

$$7PhC\equiv CPh \; + \; Pd_3(OAc)_6 \; + \; 6MeOH \longrightarrow$$



$$+ \; 2PhC(OMe)_3 \; + \; 6HOAc \; + \; Pd^0$$

11

(6) T. Hosokawa, I. Moritani, and S. Nishioka, *Tetrahedron Lett.*, 3833 (1969). See also J. Chatt, L. A. Duncanson, and R. G. Guy, *J. Chem. Soc.*, 827 (1961); J. Chatt, R. G. Guy, L. A. Duncanson, and D. T. Thompson, *ibid.*, 5170 (1963); and G. R. Davies, W. Hewertson, R. H. B. Mais, P. G. Owston, and C. G. Patel, *J. Chem. Soc. A*, 1873 (1970).

(7) T. Hosokawa and I. Moritani, *Tetrahedron Lett.*, 3021 (1969).

(8) M. Avram, I. G. Dinulescu, G. D. Mateescu, E. Avram, and C. D. Nenitzescu, *Rev. Roum. Chim.*, 14, 1181 (1969).

(9) L. Malatesta, G. Santarella, L. M. Vallarino, and F. Zingales, *Angew. Chem.*, 72, 34 (1960).

(10) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, 84, 2329 (1962).

(11) P. M. Maitlis, D. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, 43, 470 (1965); D. Pollock and P. M. Maitlis, *J. Organometal. Chem.*, 26, 407 (1971).

(12) L. M. Vallarino and G. Santarella, *Gazz. Chim. Ital.*, 94, 952 (1964).

(13) M. Avram, I. G. Dinulescu, G. D. Mateescu, and C. D. Nenitzescu, *Rev. Roum. Chim.*, 14, 1191 (1969).

(14) D. M. Roe, C. Calvo, N. Krishnamachari, K. Moseley, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 436 (1973); D. M. Roe, C. Calvo, N. Krishnamachari, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 78 (1975).

(15) H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Am. Chem. Soc.*, 92, 2276 (1970).

(16) B. E. Mann and P. M. Maitlis, unpublished results.

(17) H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Am. Chem. Soc.*, 92, 2285 (1970).

(18) D. Pollock and P. M. Maitlis, *Can. J. Chem.*, 44, 2673 (1966).
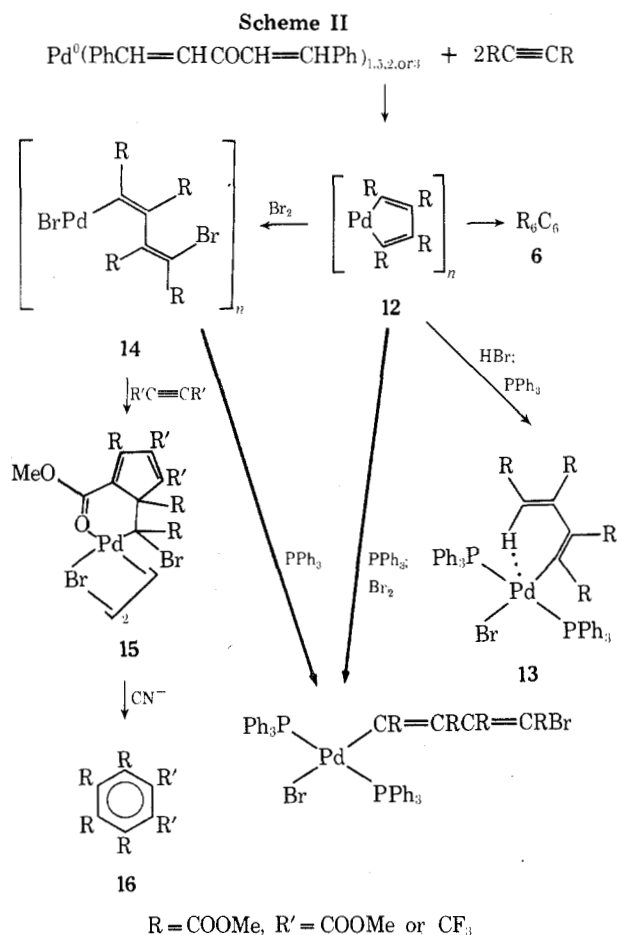
(19) G. M. Whitesides and W. J. Ehmann, *J. Am. Chem. Soc.*, 91, 3800 (1969).

(20) A. Konietzny, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 78 (1975).

been isolated from reactions of diphenylacetylene under appropriate conditions.[21]

(d) Evidence concerning precursors to the trimer complexes comes from a variety of reactions. For example, in a study of the reactions of the *zerovalent* palladium–olefin $\pi$ complexes $Pd(DBA)_n$ [DBA = dibenzylideneacetone][22] with dimethyl acetylenedicarboxylate, the first product was identified as the metallocycle **12**.[23] This also reacts further to give the benzene **6** by a different path from the one under discussion here, but one which has been well established for electrophilic acetylenes and low-oxidation-state metal complexes.[24]

The complex **12** was characterized in a number of ways (Scheme II),[14] including by reaction with HBr, followed by triphenylphosphine to give the $\sigma$-butadienyl complex **13**. The x-ray determination of **13** and its NMR spectrum[25] indicated that there is interaction between the $\delta$ hydrogen on the butadiene and the metal; the estimated H···Pd distance is 2.3 Å compared with an expected van der Waals contact of

3.1 Å, and the hydrogen is in the fifth (axial) coordination site.

Reaction of the metallocycle **12** with 1 equiv of bromine also cleaved one Pd–C bond to give **14**, characterized as its bis(triphenylphosphine) adduct. The complex **14** reacted with dimethyl acetylenedicarboxylate or bis(trifluoromethyl)acetylene to give the bromide-bridged complexes **15** (R = COOMe or $CF_3$), analogous to **5**, which on decomposition gave the appropriate benzenes **16**.[14]

(e) The synthesis of trimer complexes from a $\sigma$-butadienyl complex (**14** → **15**) suggested that $\sigma$-butadienyl complexes might in general be intermediates in the trimerization reactions. Positive support for this hypothesis came from a detailed analysis of the reactions of $PdCl_2$ and *tert*-butylacetylene.

At 20° *tert*-butylacetylene gave only trimer products: 1,3,5-tri-*tert*-butylbenzene (**17**) was formed in acetone, while the complex $[Cl(Me_3CC_2H)_3PdCl]_2$ was obtained in benzene or dichloromethane.[26] The latter complex exists as a mixture of the $\pi$-allylic isomers **18a** and **18b** in dynamic equilibrium.[27] All attempts to generate **17** from **18** were wholly unsuccessful, and these trimer complexes do *not* appear to be intermediates in the formation of the benzene **17**.

**Scheme II**



R = COOMe, R′ = COOMe or $CF_3$



The trimerization to **18** takes place in two stages. At −10° a fast reaction occurs wherein *three* molecules of *tert*-butylacetylene combine with $PdCl_2(PhCN)_2$ to give an unstable intermediate, **19**, in which two acetylenes have linked. Addition of the chelate ligand $MeSCH_2CH_2SMe$ to the solution containing **19** gives the stable $\sigma$-butadienyl complex **20**,

(21) E. Ban, P-T. Cheng, T. Jack, S. C. Nyburg, and J. Powell, *J. Chem. Soc., Chem. Commun.*, 368 (1973).

(22) Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, *Chem. Commun.*, 1065 (1970); K. Moseley and P. M. Maitlis, *ibid.*, 982 (1971); M. C. Mazza and C. G. Pierpont, *J. Chem. Soc., Chem. Commun.*, 207 (1973); T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organometal. Chem.*, **65**, 253 (1974).

(23) K. Moseley and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 169 (1974).

(24) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **7**, P22 (1967); **21**, 431 (1970); J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1967); J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968); S. McVey and P. M. Maitlis, *J. Organometal. Chem.*, **19**, 169 (1969).
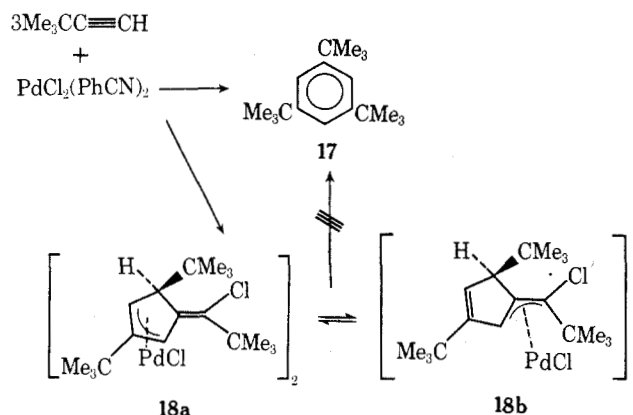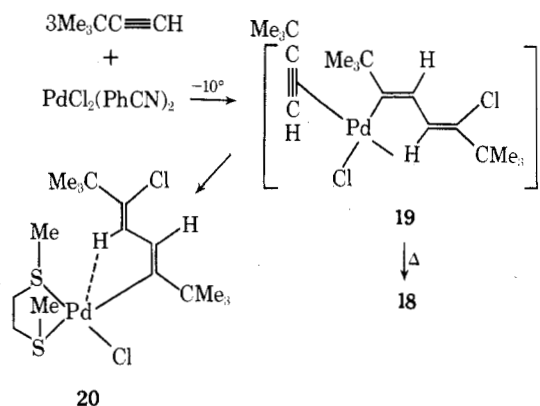
(25) D. M. Roe, P. M. Bailey, K. Moseley, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1274 (1972).

(26) M. Avram, E. Avram, G. D. Mateescu, I. G. Dinulescu, F. Chiraleu, and C. D. Nenitzescu, *Chem. Ber.*, **102**, 3996 (1969).

(27) P. M. Bailey, B. E. Mann, A. Segnitz, K. L. Kaiser, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 530 (1974)

the structure of which has been determined.[28] In **19** the third acetylene is presumably weakly π bonded and is displaced by the sulfur chelate; the structure shown is suggested. When the solution containing **19** is allowed to warm up, the second, slower, stage in the trimerization occurs in which a further acetylene is slowly taken up and the trimer complexes **18** are formed in high yield. The intermediacy of the σ-butadienyl complex in the formation of 1,3,5-tri-*tert*-butylbenzene (**17**) is demonstrated by the reaction of **20**-$d_2$ with *tert*-butylacetylene in the presence of Ag+ (to remove Cl− and thereby to create a vacant site at Pd) to give **17**-$d_2$.[28]
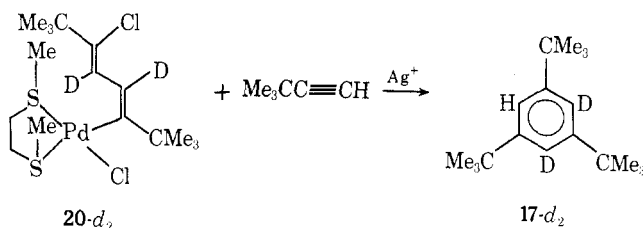


(f) An investigation of the reaction of PdCl$_2$(PhCN)$_2$ with 2-butyne indicated that the first intermediate was an acetylene complex, [Me-C$_2$Me(PdCl$_2$)$_2$]$_n$, stable only at −50°. The rate-determining step in the further reaction was independent of 2-butyne concentration and hence was likely to be a rearrangement of the π-acetylene complex.[15] The internal addition of Pd–Cl to the coordinated acetylene to give a σ-(β-chlorovinyl) complex is such a step for which there are many analogies.[29]

If subsequent reactions occur by fast insertions of further coordinated acetylenes into the Pd–vinyl σ bond, then a chain, ClPd(R$_2$C$_2$)$_n$Cl, will be built up. The stereochemistry of the σ-butadienyl ligand in the complex **20** is of particular interest since it shows that this does indeed happen in the initial stages of reaction and that the first step is a cis insertion of the coordinated acetylene into the Pd–Cl bond, which is followed in the second step by another cis insertion into the resultant Pd–vinyl σ bond.

(g) The argument can be taken a step further, and if the first acetylene were also able to cis insert into a Pd–C σ bond, that reaction should be faster than the insertion into Pd–Cl. Hence the expected product from "PhPdCl" would be of the form [ClPd(C$_2$R$_2$)$_n$Ph]. When "PhPdCl" [prepared in situ from PdCl$_2$(PhCN)$_2$ and HgPh$_2$[30]] and dimethylacetylene were allowed to react, the product (**21**) was of the anticipated type except that a H-transfer reaction had also occurred. The structure of **21** showed



**21**
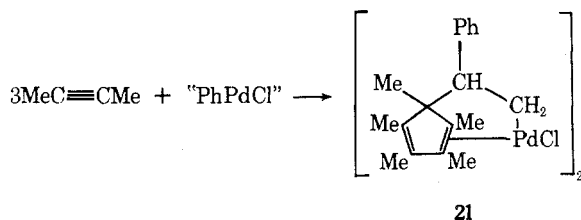
(28) B. E. Mann, P. M. Bailey, and P. M. Maitlis, *J. Am. Chem. Soc.*, **97**, 1275 (1975).

(29) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. II, Academic Press, New York, NY, 1971, p 151.

(30) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518 (1968).

that another trimer complex, containing a η$^2$-cyclopentadiene, had been formed.[31]

(h) The structure adopted by the trimer complex depends critically on the nature of the acetylenic substituents. Two of the four square-planar coordination sites on the metal are filled by a Cl$_2$ bridge, one by the σ bond to carbon, but in order to stabilize the molecule the fourth site must also be occupied. Models show that coordination to one of the cyclopentadiene double bonds as in **22** is possible but leads to a very strained system which is clearly not an energy minimum. It is possible that this mode of stabilization is actually adopted by the dimethylacetylene trimer complex, **7b**, which explains why it is very labile. However, for the dimethyl acetylenedicarboxylate trimer complexes **5** and **15**, an ester carbonyl is conveniently situated to form a Pd–O bond in a six-membered chelate ring; this gives a quite stable complex.



**22**
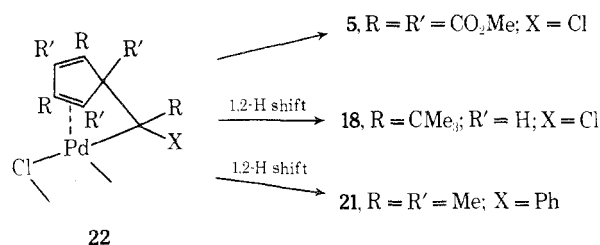
In the case of the *tert*-butylacetylene trimer complex, the intermediate **22** (R = CMe$_3$, R′ = H, X = Cl) stabilizes itself in the π-allylic form **18** after a 1,2 hydrogen shift. A similar type of shift but in a different direction occurs for **22** (R = R′ = Me, X = Ph) to give **21**; this leads to a system where the metal can now coordinate to a cyclopentadiene double bond in a strain-free ring.

The form that the trimer complex adopts also influences the decomposition to the benzene. Thus the dimethyl acetylenedicarboxylate complexes **5** and **15** and the 2-butyne complex **7** readily decompose to the appropriate benzenes, but the *tert*-butylacetylene trimer complex **18** has undergone an apparently irreversible H shift and does not give the benzene. Similarly **21** cannot be decomposed to a benzene.
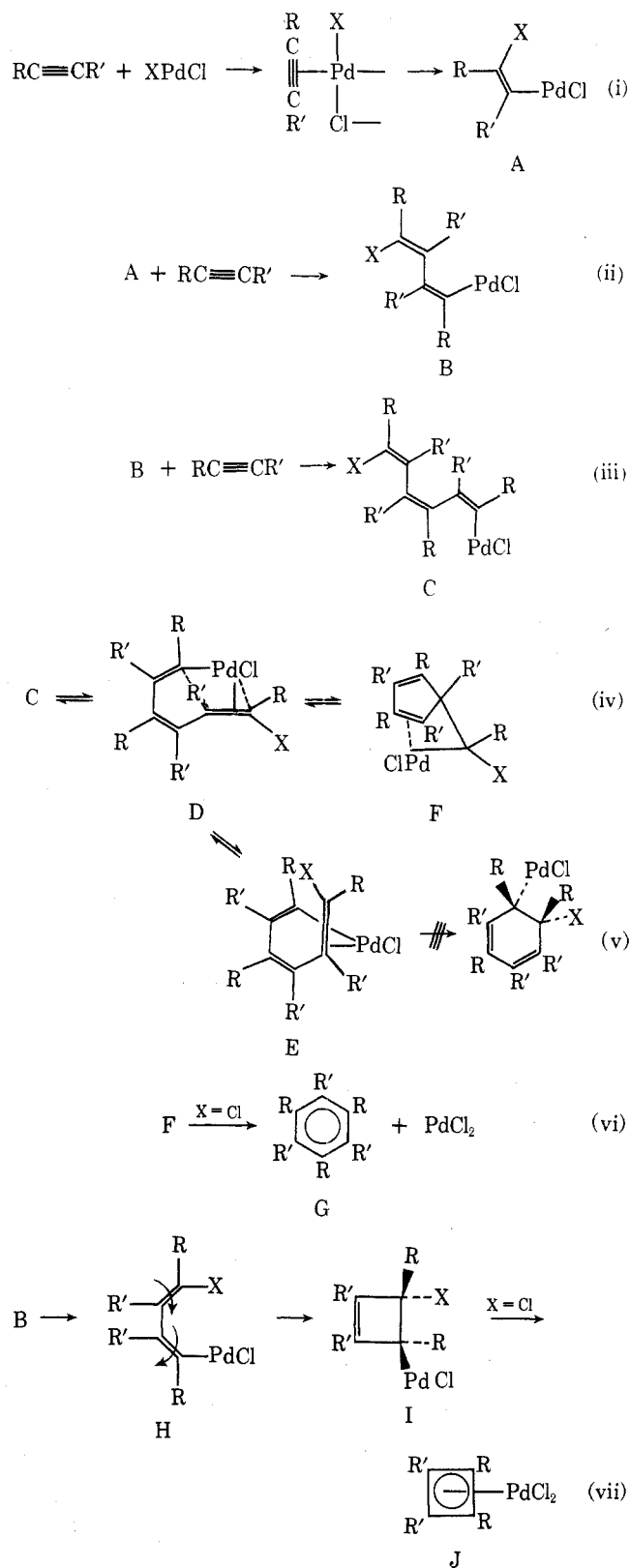
## Reaction Mechanisms

The mechanism of acetylene oligomerization induced by PdCl$_2$ is therefore seen to involve a series of stepwise cis insertions of coordinated acetylenes as shown in Scheme III (i) into a Cl–Pd bond giving A, and (ii) into a vinyl–Pd bond giving a σ-butadienyl–Pd complex (B).[32] Where trimers are formed a further acetylene cis insertion (iii) then occurs to give a σ-hexatrienyl–Pd complex (C) which can then undergo an internal cis insertion, (iv) to give the substituted palladiamethylcyclopentadiene (F = **22**).

The relative rates of reactions i–iv determine the observed products and are themselves determined by the sizes of the acetylenic substituents. Thus when R

(31) T. Hosokawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Am. Chem. Soc.*, **95**, 4914 (1973).

(32) Scheme III is considerably oversimplified; for example, it is very likely that the cis insertion in steps i, ii, and even iii is accompanied, and may even be promoted by, the coordination of a further acetylene. The question of the coordination numbers of intermediates such as A, B, C, H, etc., is open, but it is most likely to be four, with one site possibly binding a solvent molecule weakly.

**Scheme III**

$$RC\equiv CR' + XPdCl \longrightarrow \quad \underset{A}{\quad} \longrightarrow R{-}C{=}C{-}PdCl \quad (i)$$

$$A + RC\equiv CR' \longrightarrow \quad \underset{B}{\quad} \quad (ii)$$

$$B + RC\equiv CR' \longrightarrow \quad \underset{C}{\quad} \quad (iii)$$

$$C \rightleftharpoons \quad \underset{D}{\quad} \rightleftharpoons \quad \underset{F}{\quad} \quad (iv)$$

$$\underset{E}{\quad} \nRightarrow \quad \quad (v)$$

$$F \xrightarrow{X=Cl} \quad \underset{G}{\quad} + PdCl_2 \quad (vi)$$

$$B \longrightarrow \underset{H}{\quad} \longrightarrow \underset{I}{\quad} \xrightarrow{X=Cl}$$

$$\underset{J}{\quad}{-}PdCl_2 \quad (vii)$$

= R' = *tert*-butyl no appreciable reaction in sense i occurs and there is no oligomerization, whereas for R = R' = COOMe or Me the steric restraints are smaller and reactions i–iv proceed readily.
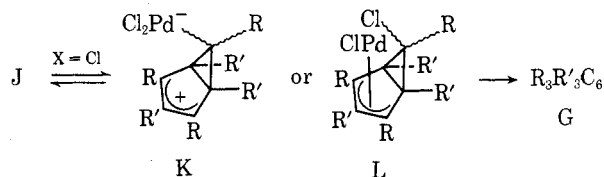
The intermediate cases, where R = Ph and R' = *t*-Bu or Ph, are of considerable interest since cyclobutadiene complexes are formed. We believe that this can be best understood by considering the inter-

actions between Pd and R' on the $\gamma$ carbon of the $\sigma$-butadienyl ligand (B) which, when R' is large, forces the diene to adopt the s-cis (H) rather than the s-trans conformation (B). A large $\alpha$ substituent, R, will also adversely affect both the complexation of another acetylene to B or H and the rate of the cis insertion to C. Here an alternative path will be favored, which is postulated to involve a conrotatory cyclization of H to give the $\sigma$-cyclobutene (I), the $\pi$-cyclobutenyl, and finally, when X = Cl, the $\pi$-cyclobutadiene complex (J) (step vii).[33]

In the absence of large substituents $\alpha$ and $\gamma$ in B the hexatrienyl complex C can be built up. This is particularly likely if R' on the $\gamma$ carbon is either very small (hydrogen, methyl) or of such a nature (e.g., $CO_2Me$) as to interact with the metal, and thus to stabilize B relative to H. It is probable that even a $\gamma$ hydrogen may interact sufficiently with the metal to stabilize B; evidence in favor of Pd···H–C interactions has come from the NMR spectra and the x-ray structures of complexes **13** and **20**,[25,28] and quite strong metal···H–C interactions of this type are also reported.[34]

If R and R' in C are small, it should in principle be possible for the cis-insertion reactions to continue to give tetramers and finally polyenes and their complexes.[35] However, if $\beta$-R' and $\epsilon$-R' are large enough to repel each other significantly, then the molecule will twist about the $\delta,\epsilon$ bond to conformer D. Conformer D is well arranged for an internal cyclization to F, as discussed above.

The mode by which F generates the benzene G is not yet clear; it is likely that a bicyclo[3.1.0]hexenyl complex is intermediate, but it is not known whether this has the form K or L since there are precedents for each.[37,38] Both K and L may be expected to ex-

$$J \underset{\xrightarrow{X=Cl}}{\rightleftharpoons} \quad \underset{K}{\quad} \quad or \quad \underset{L}{\quad} \longrightarrow R_3R'_3C_6 \quad \underset{G}{\quad}$$

hibit fluxionality which can be described as arising from the cyclopropane ring moving around the perimeter of the $C_5$ ring. If this occurs prior to ring opening and formation of the benzene, it will lead to

(33) It is unlikely that the species H, I, and J are in equilibrium with appreciable amounts of a palladiacyclopentadiene such as

$$\underset{R'}{\quad} PdCl_2$$

as this would be a complex of Pd(IV) (and hence probably octahedral) and would be expected to be of significantly higher energy than any of the other species, given the ligands likely to be involved.

(34) F. A. Cotton and A. G. Stanislowski, *J. Am. Chem. Soc.*, **96**, 5074 (1974).

(35) It is not clear whether oligomerization of this type occurs in practice since all the tetramers that have so far been isolated and characterized are clearly derived from F.[36]

(36) P. M. Bailey, B. E. Mann, and P. M. Maitlis, unpublished results.

(37) For example, R. F. Childs, M. Sakai, B. D. Parrington, and S. Winstein, *J. Am. Chem. Soc.*, **96**, 6403 (1974); H. Hogeveen, P. W. Kwant, E. P. Schudde, and P. A. Wade, *ibid.*, **96**, 7518 (1974), and references therein.

(38) For example, A. Maercker, P. Gütlein, and H. Wittmayr, *Angew. Chem., Int. Ed. Engl.*, **12**, 774 (1973); D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, NY, 1965, Chapter 6, and references therein. See also D. J. Mabbott, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 521 (1975), and ref 31.

scrambling and would account for the observations that methyl(phenyl)acetylene gives rise to 3% 1,2,3-trimethyl-4,5,6-triphenylbenzene, and that $CH_3C{\equiv}CCD_3$ gives 10% of 1,2,3-tris(trideuteriomethyl)-4,5,6-trimethylbenzene.[15,19]

There is no evidence which suggests that the allowed disrotatory cyclization of a hexatriene (e.g., E) to a dihydrobenzene occurs (step v). For example, the precursor E, where R = Me₃C and R′ = H, could only undergo such a cyclization to give, after elimination of Pd–Cl, 1,2,4-tri-*tert*-butylbenzene; this was not detected, and only the 1,3,5 isomer 17 was formed. Clearly the internal cyclizing cis insertion D → F represents a much lower energy path.

Although the reactions of acetylenes with PdCl₂ in protic solvents have not yet been extensively investigated, one such reaction does call for comment. Diphenylacetylene reacted in ethanol to give the cyclobutenyl complex 23, *exclusively* with the *endo*-ethoxy stereochemistry shown. Reaction with HCl gave the cyclobutadiene complex 3 which in turn underwent nucleophilic attack by ethanol to give only the *exo*-ethoxycyclobutenyl complex 24.[9-12,39]
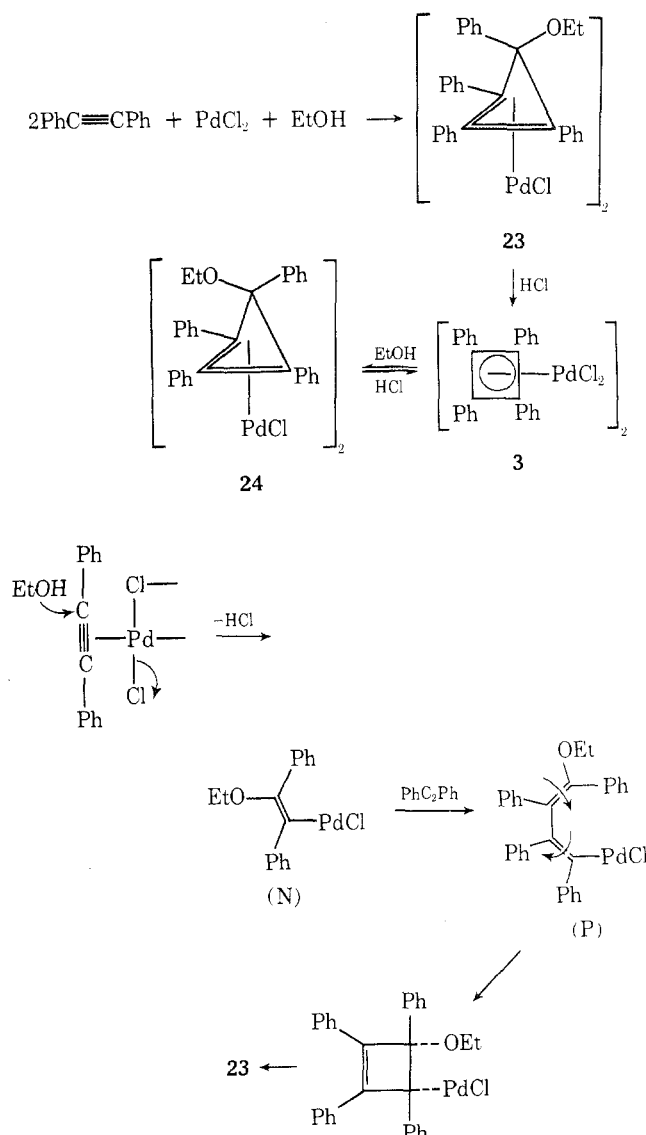


A plausible route to 23 involves nucleophilic attack on coordinated diphenylacetylene by *uncoordinated* ethanol (or ethoxide) to give N in which the σ-vinyl is now trans (compare A); further reaction gives the σ-butadienyl complex P which undergoes stereospecific conrotatory cyclization to the *endo*-ethoxy σ-cyclobutenyl complex followed by rearrangement to the π-cyclobutenyl 23.

Strong support for this proposal[40] has come from the observation that the rearrangement P → 23 is reversible, and in particular that in the presence of β-diketonate ligands there is an equilibrium between 24 and 25.[41]



R = CH₃, CF₃
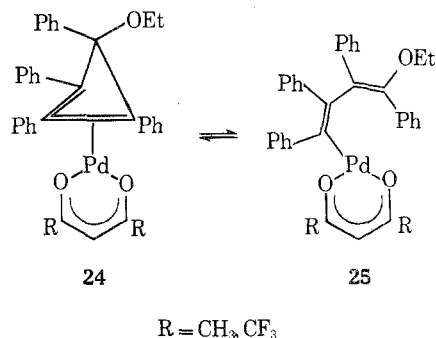
## Conclusion

A number of paths have previously been proposed for the metal-induced oligomerization of acetylenes[42] including: (i) reactions via metallocyclopentadienes, for example, 12,[23,24,33] (ii) reactions via cyclobutadienes and Dewar benzenes;[43] (iii) stepwise reactions initiated by metal hydride intermediates;[44] and (iv) concerted processes whereby three acetylenes come together at a metal atom and then combine.[45]

The work described here establishes the existence of another path for such reactions and also shows that even an apparently simple process such as the coming together of three acetylenes to give a benzene is actually of considerable complexity since the most obvious "commonsense" path is not necessarily the one that nature adopts.

Although the broad outlines of the processes are clear, many intriguing problems remain; among them are the mechanisms by which the cyclopentadienyl-methyl–metal complexes, such as 5, are converted to the benzenes, and the natures and modes of formation of the tetramers and their complexes. A further point of considerable interest is the qualitative observation that two molecules of PdCl₂ appear to be involved in many of the processes described; however, it is at present not clear whether both are necessary or whether the isolation of complexes containing, for example, (LPdCl·PdCl₂)ₙ arises merely from solubili-

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ty considerations. The catalytic utilization of these reactions for the production not only of benzenoid trimers but also of novel and otherwise difficult of access dimers and tetramers is being pursued.
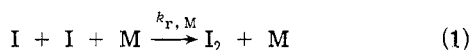
# Why Atoms Recombine More Slowly as the Temperature Goes Up

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It is now a little over 20 years since a series of experiments using flash-photolysis techniques[1-3] showed decisively that the reaction

$$I + I + M \xrightarrow{k_{r,M}} I_2 + M \qquad (1)$$

went more slowly as the temperature was increased. At about the same time, it was becoming evident from many shock-tube dissociation experiments that the reverse reactions, i.e.

$$X_2 + M \xrightarrow{k_{d,M}} X + X + M \qquad (2)$$
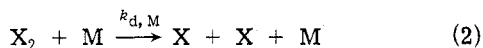
probably had Arrhenius temperature coefficients considerably less than the known spectroscopic dissociation energies ($D_0$), and it is now generally accepted that this is the case.[4,5] By Arrhenius temperature coefficient we mean

$$"E" = -R^{-1}d(\ln k_{d,M})/d(1/T) \qquad (3)$$

Since the rate quotient law

$$k_{d,M}/k_{r,M} = K_c \qquad (4)$$

holds virtually exactly even for these systems,[6,7] this means that to a good degree of approximation

$$E_{d,M} - E_{r,M} = D_0 \qquad (5)$$

where $E_{d,M}$ and $E_{r,M}$ are the Arrhenius temperature coefficients of $k_{d,M}$ and $k_{r,M}$, respectively, and $K_c$ is the equilibrium constant of the dissociation at the temperature in question. Thus, since $E_{d,M}$ is less than $D_0$, these shock-tube data also imply a negative temperature coefficient (i.e., $E_{r,M}$ negative) for the recombination reaction, but a much more severe one than was found in the flash-photolysis experiments, as shown in Figure 1.[8-11]

*There is no one single explanation of this behavior,* and over the last 20 years at least half a dozen different ideas have been proposed,[5] all of which are probably valid to some extent, but which can only ex-

plain the magnitudes of the trends shown in Figure 1 with difficulty. However, it has recently become apparent that a very simple form of collision theory gives recombination rate constants for all diatomic molecules *similar in form* to those found in practice. The principal feature of this treatment is that it takes account of the rotational motion of the recombining atoms in a way which is already commonplace in molecular-beam or ion-reaction work,[12-14] and as such is rather similar to the orbiting resonance theory,[15] but without tunneling.[16] Of course, rotational effects have been included in previous discussions of this problem[5]—typical is the work of Palmer and Hornig,[17] which is a form of Hinshelwood–Lindemann theory, but can only account for the observed behavior of some systems by assuming more degrees of rotational freedom than the molecule can possess.

Another approach to the problem is the chaperon mechanism which invokes the pre-equilibrium

$$M + X \rightleftharpoons MX \qquad (6)$$

followed by

$$X + MX \rightleftharpoons X_2 + M \qquad (7)$$
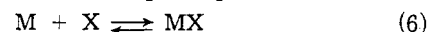
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