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ACETYLENES, CYCLOBUTADIENES AND PALLADIUM: A PERSONAL VIEW

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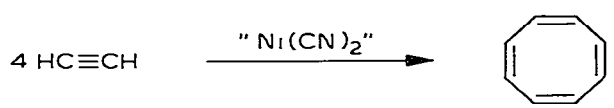
Thinking about it 21 years later, I cannot remember why I did not go to the "International Conference on Coordination Chemistry" that was held in London in April 1959. Although my own research work then was still in organo-boron chemistry, I had for some years been fascinated by the accounts of new types of organo-transition metal complexes that had been appearing in the literature in the 1950's. Perhaps I was still too bound-up in the organic chemistry I had done for my Ph.D. thesis and during the three subsequent years of my association with Michael Dewar at Queen Mary College in London; perhaps I was very involved in my personal affairs, in particular my marriage later that year.

Whatever the reason, I didn't go, but a few days later I met an old friend, the theoretician Leonello Paoloni, who had come over from Rome for the meeting. We met for dinner at the "New Shanghai" in Wardour Street, a favourite haunt of ours since it served Chinese food of an excellence and inexpensiveness unparalleled at that time. Leonello was full of the excitement of the meeting at which the flavour of the great things to come in organometallic chemistry was fully revealed for the first time. And while we were eating our egg-rolls he told me about the amazing results that had been described by Sternberg and Wender and by Hübel and his collaborators on the reactions of acetylenes with metal carbonyls [1]. Although the work of Reppe et al., in particular his cyclooctatetraene synthesis (equation 1) [2], was well-known these new results showing how acetylenes linked up with each other and with CO in stoicheiometric reactions to give defined complexes were now putting flesh on the earlier work [3].



(1)

I found all this very heady stuff but I cannot pretend that I was immediately converted. No, as often happens these things need time to grow, and the next year (1960) saw me as a Fulbright Fellow working with (the late) Al Blomquist

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at Cornell, still on organic chemistry. Al's chief interest had for some years been the synthesis of a cyclobutadiene and he had developed an ingenious route involving Diels-Alder addition to substituted 3,4-dimethylenecyclobutenes. The idea was good but unfortunately nature had not cooperated and other products were obtained. My project was still along this line however, and since the unsubstituted dimethylenecyclobutene had not yet been tried, I set to work to make this molecule by a series of standard synthetic steps.

During my year at Cornell I also read the current literature assiduously, in particular those papers dealing with organo-transition metal complexes, and the more I read the more intrigued I became. One day, I was finally hooked. I saw a short note in Angewandte Chemie by L. Malatesta in which he and his coworkers described a very simple route to a cyclobutadiene complex through the reaction of diphenylacetylene with palladium chloride in ethanol [4].

Cyclobutadienes had got into my blood by then and this looked like an extremely easy route to them; all that one needed was an acetylene and palladium chloride as precursors and then, in principle at least, it should be possible to simply detach the cyclobutadiene from its complex with some suitable reagent and the problem that had been engrossing many chemists since the time of Willstätter would be solved. Little did I know . . . .

I took these thoughts to Al Blomquist who, with his usual aimiability, had no objection to my trying this approach, even though he was rather dubious about its possible success, on the condition that I didn't neglect the dimethylenecyclobutene work. I agreed and set to work first to repeat Malatesta's reactions.

These were easy to reproduce and, apart from some minor modifications, we agreed with his general conclusions that in ethanol, diphenylacetylene was dimerised by palladium chloride * to a palladium complex (1) which could then be converted, with HCl, into the tetraphenylcyclobutadienepalladium chloride (2). The structure of this last complex we put onto a firm footing by comparing its IR spectrum with that of the related nickel complex that Hal Freedman, working at Dow, had just established [6] **. We also found that in aprotic solvents, diphenylacetylene was catalytically trimerised to hexaphenylbenzene and also gave directly a further tetraphenylcyclobutadienepalladium complex [7] which we later showed to be a salt (equation 2). We also showed

$$PhC{\equiv}CPh + PdCl_2(PhCN)_2 \rightarrow Ph_6C_6 + [Pd_2(C_4Ph_4)_2Cl_3]\tfrac{1}{2}[Pd_2Cl_6] \qquad (2)$$

that the cyclobutadiene 2 underwent a reversible reaction with ethanol to give a new complex (3) isomeric with 1 (Scheme 1). The story was completed a couple of years later when Larry Dahl and Oberansli in Wisconsin carried out the X-ray structure of the intermediate complex in the Malatesta reaction and showed it to be the *endo*-ethoxytetraphenylcyclobutenyl complex 1 [8]. They also identified complex 3 as the *exo*-ethoxy isomer.

The following year (1961—1962) both Al Blomquist and I went to Harvard,

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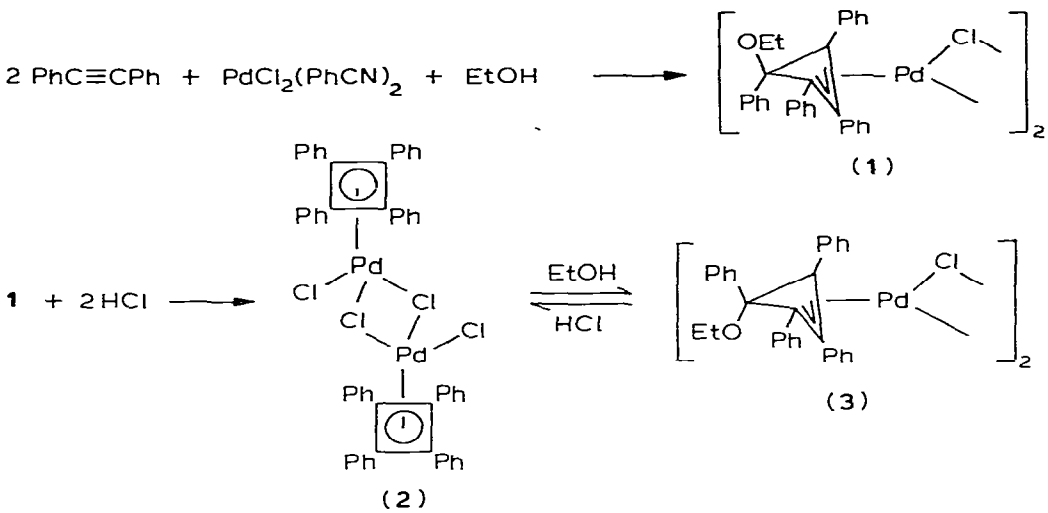
* We used the Kharach complex $PdCl_2(PhCN)_2$ [5].

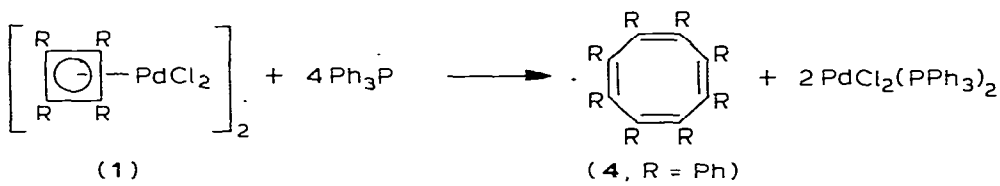
** Recently Phil Ridgwell in Sheffield has shown that our assumed structure for 2 was correct by carrying out an X-ray structure determination on the closely related complex derived from bis-(*p*-methoxyphenyl)acetylene.

SCHEME 1



Al as a visiting Professor and I to work with Gordon Stone. By this time I was really very excited about organo-transition metal chemistry and as Gordon had one of the liveliest and most active groups in North America in this field, this was the logical place to go to learn more. My year at Harvard was a very fruitful one and it allowed me to consolidate my rather fragmentary knowledge in the, at that time, still relatively new field of transition metal chemistry. Research proceeded more slowly and our first efforts to extend the Malatesta reaction to simpler acetylenes were very frustating and mirrored the early work in this area already described by Erdmann and Makowka in 1904 [9]. It rapidly became clear that this field would require long and patient work to uncover.

On the more positive side we did, in collaboration with Hal Freedman, show that the tetraphenylcyclobutadiene was liberated from its palladium complex by reaction with triphenylphosphine [10]. The product was not, unfortunately, the cyclobutadiene but a dimer thereof which Pawley, Lipscomb and Freedman subsequently identified as octaphenylcyclooctatetraene (4) [11].



Still, this reaction gave me an idea. It however was by then too late to try it out at Harvard since my time was up and Gordon was also leaving to take up the Readership in Inorganic Chemistry at my old college in London.

During my year at Harvard I had been approached by several Universities as a potential faculty member and I finally went, in the autumn of 1962, to McMaster University in Hamilton, Canada, to join Ron Gillespie in building up the inorganic side of the chemistry department there. The next ten years at McMaster were very happy and productive. I learnt the truth of the saying that

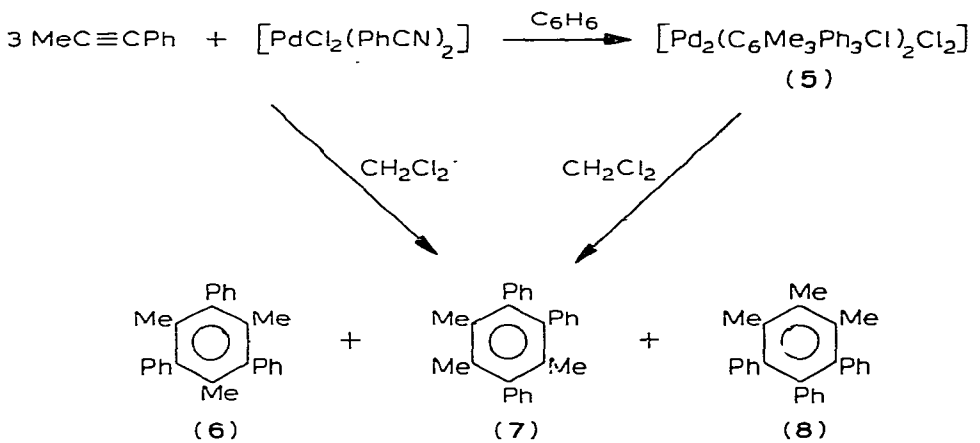
the only way to really learn a subject is to teach it, and the research work went well, though in a rather unexpected direction.

Since the acetylene-palladium chloride reactions were clearly going to be difficult to disentangle and since I now had the responsibility for supervising a postgraduate student, David Pollock, and making sure that he got some useful results quickly, we tried to use the easily accessible tetraphenylcyclobutadiene-palladium chloride as a starting material for synthesising other tetraphenylcyclobutadiene-metal complexes. We were lucky almost immediately and we showed that we could carry out ligand exchange reactions of the type shown in equation 3.

$$[Pd_2(C_4Ph_4)_2Cl_4] + 2\,Ni(R_3P)_2Cl_2 \rightarrow [Ni_2(C_4Ph_4)_2Cl_4] + Pd(R_3P)_2Cl_2 \qquad (3)$$

Even better was the ligand transfer reaction which we developed very shortly thereafter when Marguerite Games came to join me [12]. This was basically the reaction between $[Pd_2(C_4Ph_4)_2Cl_4]$ and metal carbonyls which resulted in the transfer (often in high yield) of the cyclobutadiene from palladium onto the other metal (iron, nickel, cobalt and others). Avi Efraty and Bob Bruce who came a little later were very successful in extending this work to other cyclobutadienes and other metals and also to cyclopentadienyl ligand transfer [13].

Meanwhile, what of the acetylene reactions? They were going slowly, and it wasn't until Hans Dietl and Horst Reinheimer (both from Munich) joined me in the late 1960's that we really began to make progress. Hans Dietl showed that methyl(phenyl)acetylene (phenylprop-1-yne) gave trimers catalytically via a very unstable complex (5) when reacted with $PdCl_2(PhCN)_2$ [14]. An interest-

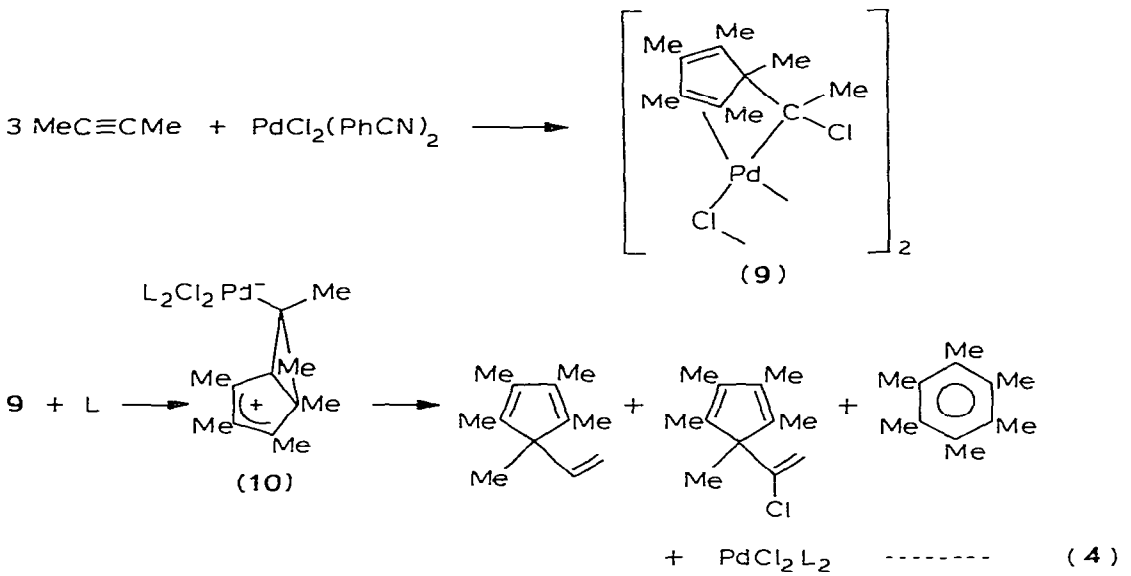


ing and novel result, which reflected the great care that Hans Dietl brought to the project, was the isolation of small amounts of the trimer 8 in addition to 6 and 7. The trimer 8 was a totally unexpected product since, formally at least, it could only be formed if the C≡C bond of an acetylene were broken. This was the first indication that we could expect some substantial rearrangements in the overall reaction path.

Horst Reinheimer took this work a stage further in the analogous reaction with dimethylacetylene (but-2-yne) and was able to isolate and partially characterise the intermediate complex $[Pd_2Cl_2(C_6Me_6Cl)_2]$ (9) and, with Jamie

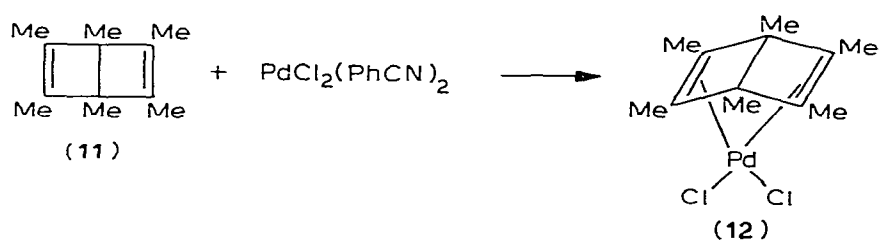
Moffatt, was able to show in some detail how this complex decomposed to give hexamethylbenzene, vinylpentamethylcyclopentadiene and chlorovinylpentamethylcyclopentadiene [15] (Scheme 2). He also showed that in the reaction

SCHEME 2



represented by equation 4 an intermediate could be detected which underwent fluxional behaviour; one form of this is represented by **10**. A dynamic process involving related species could account for the isolation of the trimer 8 in the Dietl reaction.

At about this time, Schäfer and Hellmann working at Chemische Werke Hüls in Germany reported the preparation of hexamethyl "Dewar" benzene (hexamethylbicyclo[2.2.0]hexadiene) (**11**), from butyne [16], some of the chemistry of which appeared to be intriguingly similar to that exhibited by our complex **9** derived from but-2-yne. They kindly sent us a sample and we prepared one of the first "Dewar" benzene complexes (**12**) with it [17].

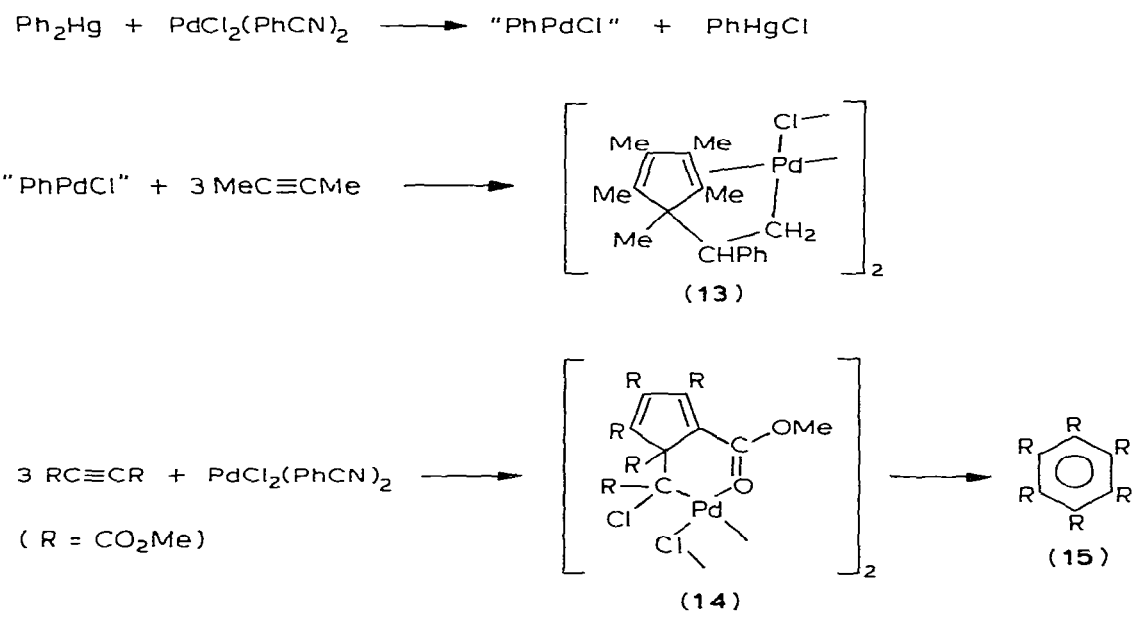


Although we soon realised that the parallel between the chemistry of the "Dewar" benzene complex **12** and our $[Pd_2Cl_2\{C_6Me_6Cl\}_2]$ complex (**9**) was more apparent than real, the "Dewar" benzene (**11**) led us into another very remarkable field. John Kang, who had joined me in 1967 and was working on rhodium chemistry, saw the bottle of hexamethyl "Dewar" benzene and thought it might be interesting to see what happened when it was reacted with

rhodium trichloride. Indeed it was and this led to the development of a whole new area of rhodium chemistry, but that is a different story [18].

Back on the acetylene front, David Roe from London and Takahiro Hosokawa from Osaka *, with the essential help of our friendly neighbourhood crystallographer, Cris Calvo (who has, sadly, since died), finally showed that acetylenes with medium-sized substituents reacted with palladium complexes to give complexes (13, 14) containing acetylene trimers in which the ligand had the basic form of a σ-palladiamethylpenta-substituted cyclopentadiene (Scheme 3) [21,22].

SCHEME 3

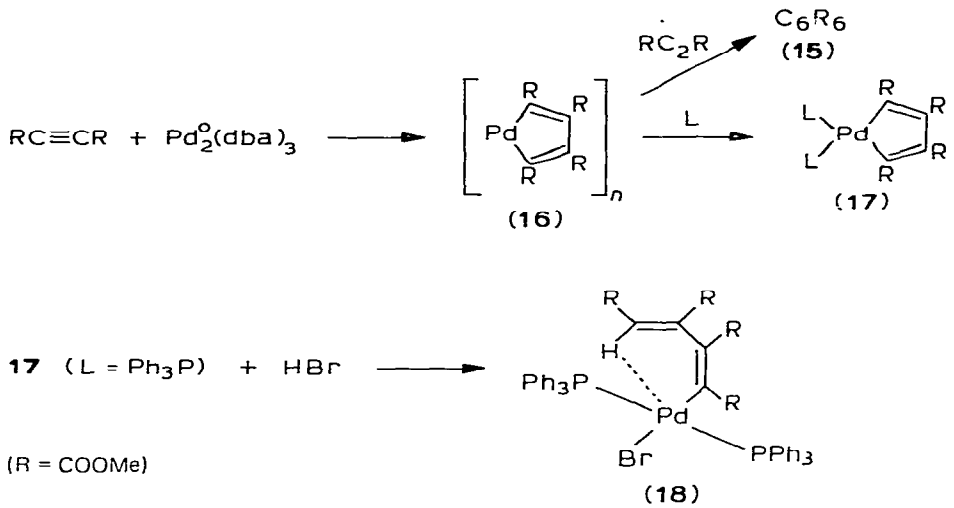


This put our previous somewhat speculative thoughts on a firm foundation and allowed us to make sense of a large number of reactions, and to propose a scheme for the cyclo-oligomerisation of acetylenes induced by Pd^{II} which, with only minor variations, is the one described below.

Another line of work in this area which had an interesting outcome was started by Keith Moseley who reacted the dibenzylideneacetone-palladium(0) complex, that had been reported by Ishii and his collaborators [23], with dimethyl acetylenedicarboxylate. The initial product, $[Pd\{C_4(CO_2Me)_4\}]_n$ (16) and its derivatives, $L_2PdC_4(CO_2Me)_4$, (17), were interesting examples of metallacyclopentadiene complexes [24]. We also showed that the benzenoid trimer, hexamethyl mellitate (15), could be formed from the acetylene either through a Pd^{II}-induced path, via 14, or a Pd^0-induced path, via 16 (Scheme 4).

* This was by no means Takahiro's only contribution in this area. He had also, together with I. Moritani, prepared the first stable acetylene-Pd^{II} complex and another cyclobutadiene complex [19,20]. Both these results were of great value to our subsequent analyses of the overall reaction mechanisms.

SCHEME 4



More surprising was our discovery that, on reaction of $[(Ph_3P)_2PdC_4(CO_2Me)_4]$ with HBr we obtained a complex, for which Pam Bailey found the structure (18), and which showed the vinyl CH to be coupled to the two phosphines and to be at unusually low field in the ^1H NMR spectrum [25]. This was one of the first observations of a "non-bonded" M···H—C interaction and the NMR chemical shift was in nice agreement with a theoretical prediction that had been made by Buckingham [26].

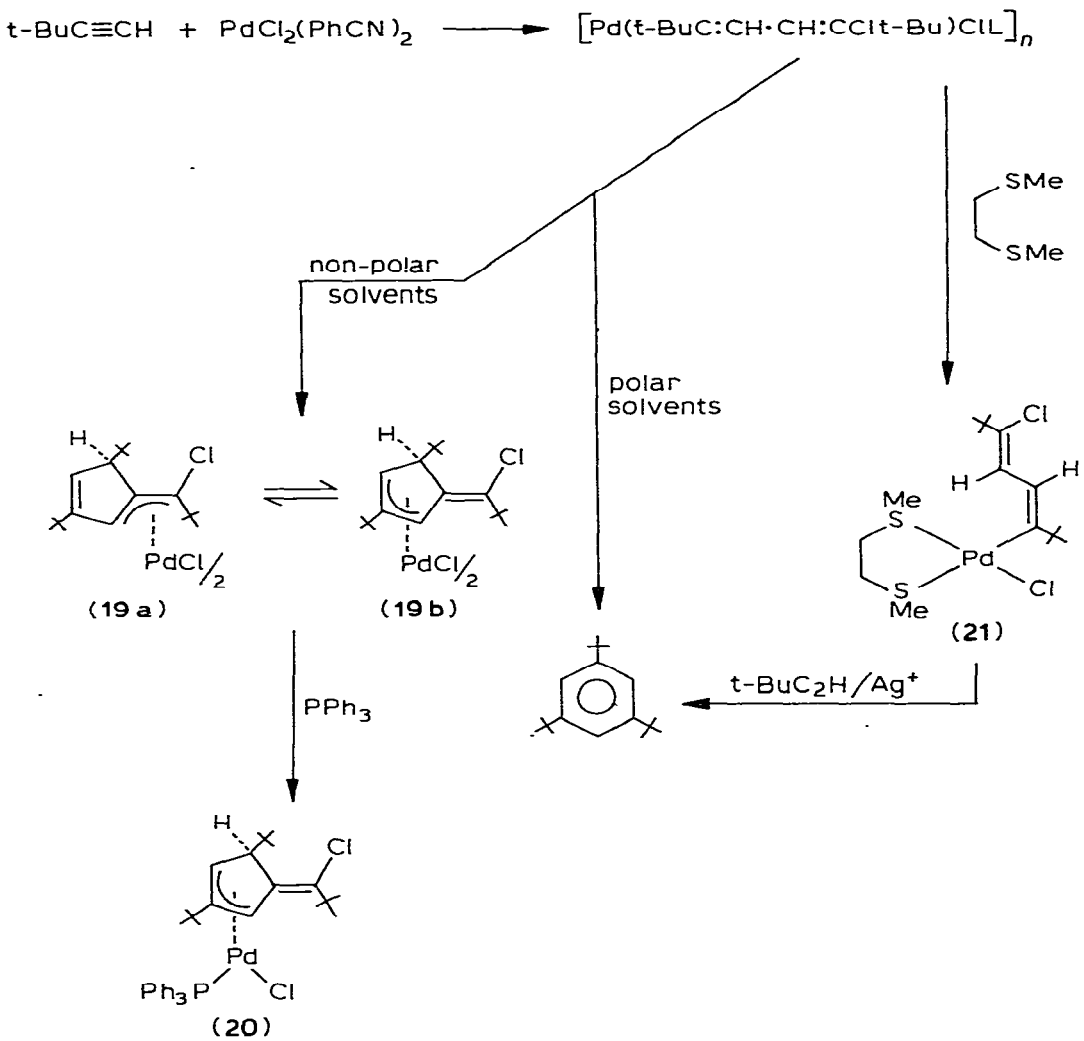
In 1972 I took up the Chair of Inorganic Chemistry in Sheffield. During the following years I was asked many times why I had moved back to England. There were many reasons, but a higher salary was certainly not one of them. I remember going into the office of Dick Tomlinson, then our Departmental Chairman at McMaster, and telling him of my decision. He tried to dissuade me with a number of arguments and then gave up, baffled. Finally he said, "Look, will you stay if we lower your salary to match their offer?"

I had one unexpected bonus in the presence in Sheffield of Pamela Bailey, a crystallographer with whom I quickly established an extremely fruitful collaboration. One of the first results of this collaboration was the structure of a derivative (20) of the complex $[Pd_2\{(t\text{-}Bu)_3C_6H_3Cl\}_2Cl_2]$ (**19a** ⇌ **19b**), originally prepared by Avram and Nenitzescu [27] from t-butylacetylene (3,3-dimethylbut-1-yne), which revealed how an asymmetrically (mono-) substituted acetylene reacted [28]. A more detailed understanding of this reaction was achieved by Brian Mann who, with characteristic insight, discovered that it could be slowed down and an intermediate (21) trapped in which only two acetylenes were linked tail to tail (Scheme 5) [29].

This showed, again, that the oligomerisation process was stepwise and that the acetylenes linked in such a manner that the first step was effectively a Markownikow addition of "Pd—Cl" to the triple bond whereas subsequent steps involved anti-Markownikow addition, i.e. where the carbon bearing the largest substitutuent was also attached to the metal.

Brian Mann also found that the tail-to-tail dimer was an intermediate in the

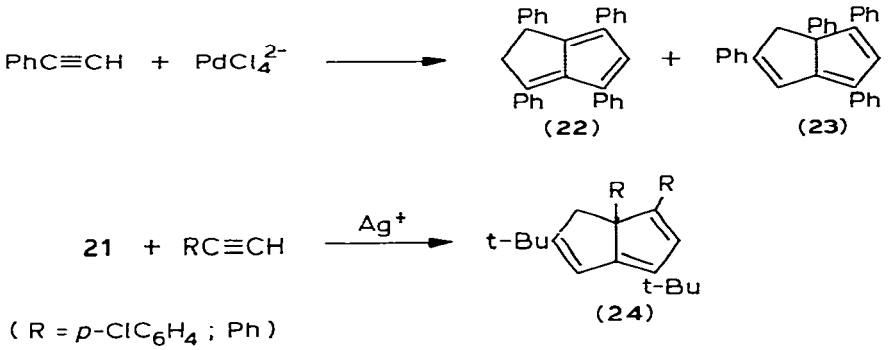
SCHEME 5



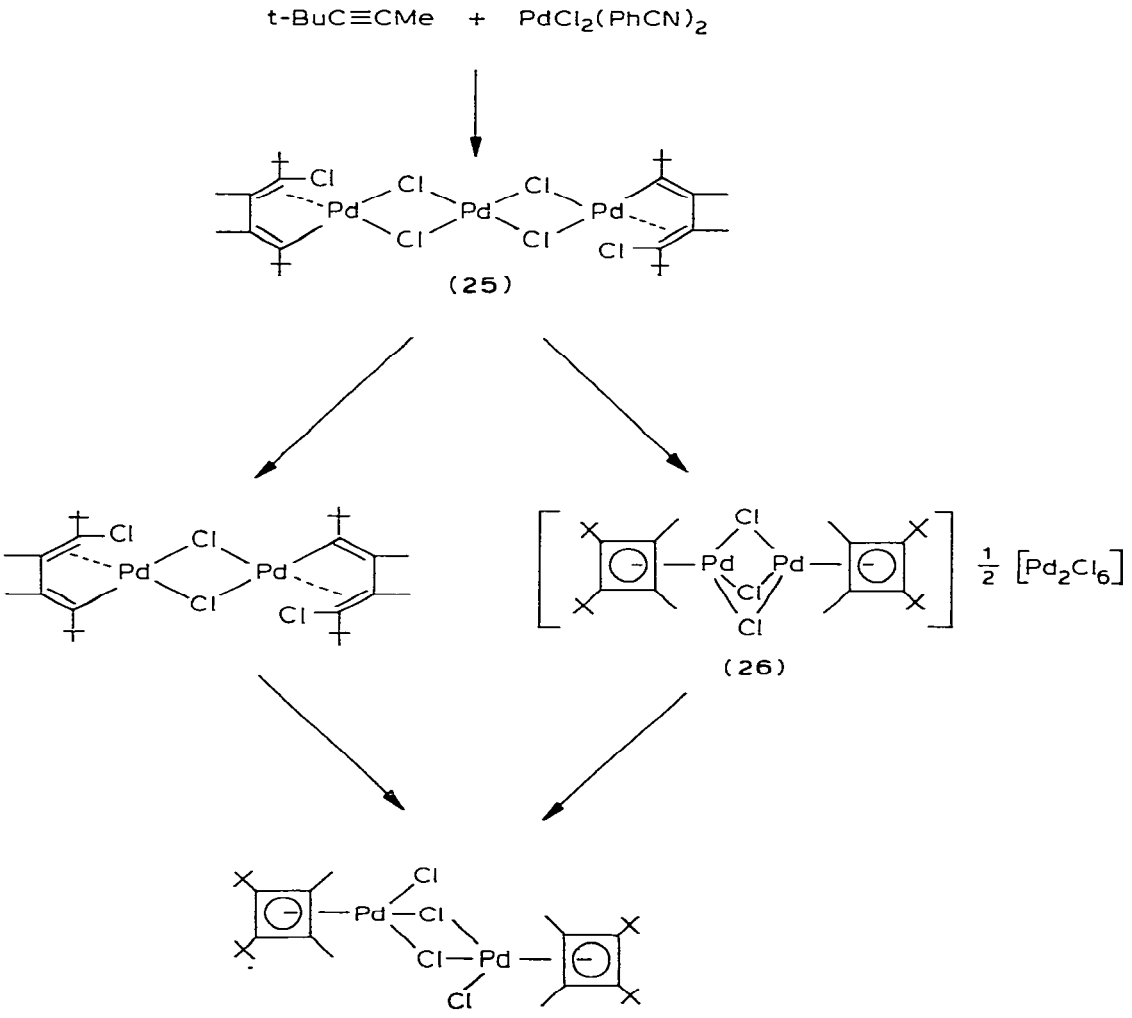
(catalytic) formation of only 1,3,5-tri-t-butylbenzene. This again implicated a rearrangement step in the overall trimerisation sequence since the tributylbenzene isomer isolated contained only acetylene fragments linked head-to-tail.

During my year at Harvard I had looked at the reaction, amongst others, of (mono-) phenylacetylene with $PdCl_2$. Two compounds resulted from this reaction, one purple (**22**), the other orange (**23**). At first I had thought them to be metal complexes because of their intense colours; however analytical and spectroscopic data immediately proved them both to be hydrocarbons and tetramers of phenylacetylene. The colours and the presence of three double bonds in each suggested the presence of highly conjugated, possibly fulvenoid groups and a dihydropentalene structure was an obvious choice. Although the compounds were nicely crystalline, they defied the efforts of several crystallographers over a number of years until Pam Bailey managed to disentangle one of

them in late 1975, some 14 years after it had been made, and then also successfully solved the crystal structure of an analogue of the other (24) made by Brian Mann from 21.



SCHEME 6

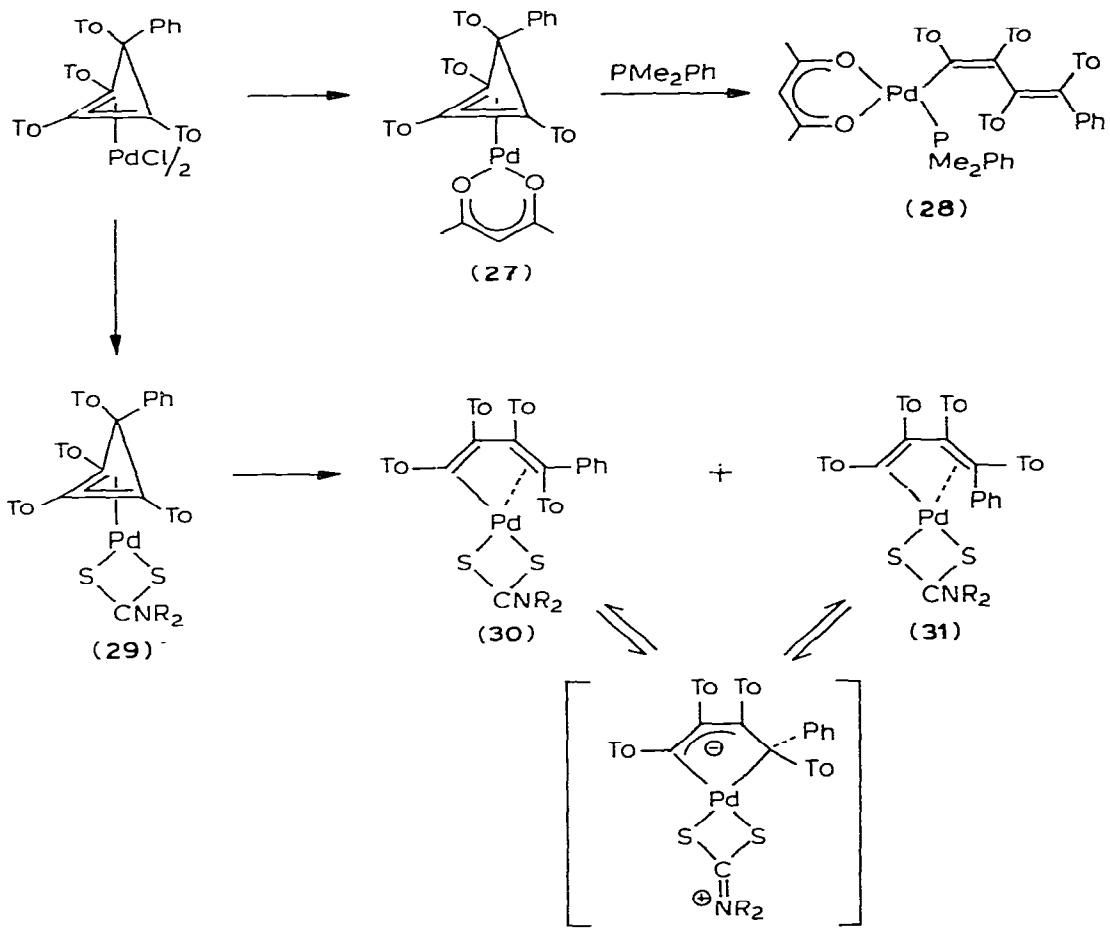


The structures gave new insight into the $PdCl_2$-mediated reactions of acetylenes; in particular the reaction giving 24 indicated that the stepwise principles we had suggested previously could also explain very nicely the stereochemistry of the cyclotetramerised products.

The main area where our knowledge was now still deficient concerned the mechanism of the formation of the dimer and of its cyclisation to the cyclobutadiene. We had recognised for some time the determining effect of the sizes of the acetylenic substituents on the degree of oligomerisation. t-Butyl(methyl)acetylene (4,4-dimethylpent-2-yne) seemed to offer the best possibility since it had an appropriate combination of bulky and less-bulky substituents and since their NMR properties were simple and useful.

Albert Wright, our genial synthetic genie, made us some of the acetylene and the reactions with palladium chloride were examined by Liz Kelley. Liz was a very welcome and attractive addition to our group since she also had patience and a remarkable ability to grow nice crystals out of quite unpromising material. She showed that t-butyl(methyl)acetylene first gave a σ-butadienylpalladium complex (25), the structure of which we established spectroscopically

SCHEME 7

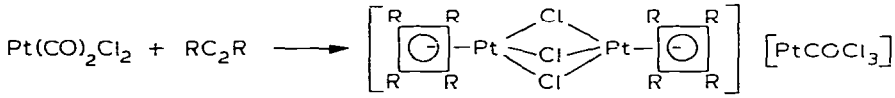


and with the aid of a crystal structure determination. This complex cyclised to the cyclobutadiene complex **26** [30] (Scheme 6). The regiochemistry of the σ-butadienyl complex brought into sharp focus once more the difference between the first and subsequent steps of the reaction. Liz Kelley's work also suggested that in order for reaction to occur, two acetylenes needed to be complexed to the metal in a cationic complex intermediate.

Another fine piece of work was done by Sue Taylor (Scheme 7), again with Pam Bailey's help. Following on from some work of John Powell in Toronto [31], she showed that the cyclobutenyl complex **27** readily ring opened to give a α-butadienyl complex (**28**), the stereochemistry of which was completely in agreement with that predicted for a conrotatory electrocyclic ring-opening [32].

The related reaction of complex **29**, gave a mixture, beautifully uncovered by Pam Bailey, of two isomers (**30** and **31**) [33]. We suggested that the unexpected isomer **31** arose from **30** by a metallocycle flip process [32].

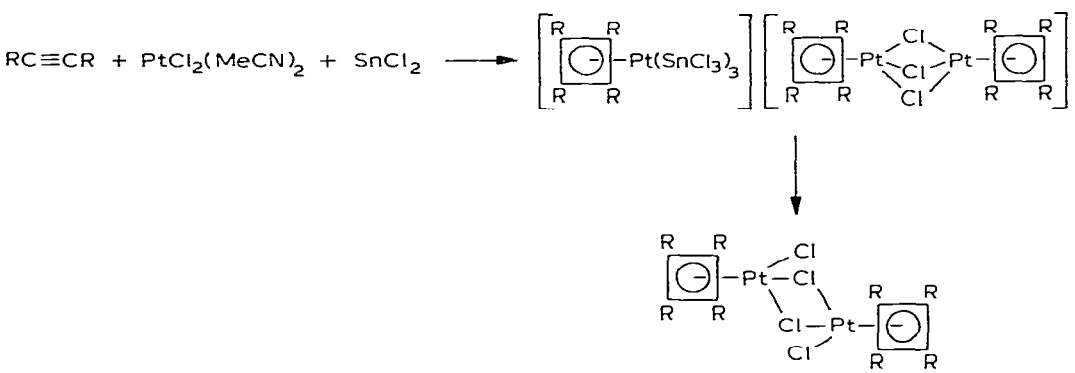
In the meantime, Canziani and his collaborators in Milan had shown that a number of di-substituted acetylenes reacted with Pt^{II} to give amongst other products, the cyclobutadienes **32** [34], in what was an apparently closely related type of reaction to those we had investigated with Pd^{II}.



(**32**, R = alkyl, Ph)

Two points were immediately clear. Platinum(II) was less labile than palladium(II) and needed activation (e.g. by CO), and even the dialkylacetylenes gave cyclobutadienes. In contrast to the palladium reactions, where acetylene trimers and their complexes were the major products, these were hardly in evidence for platinum. We wondered whether other activating ligands could also promote the Pt^{II}-induced reactions, and in 1977 Josep Moreto from Barcelona came to spend a couple of years with me, and showed that the $SnCl_3$ ligand was very effective and established the reaction shown in Scheme 8. A parallel to the

SCHEME 8



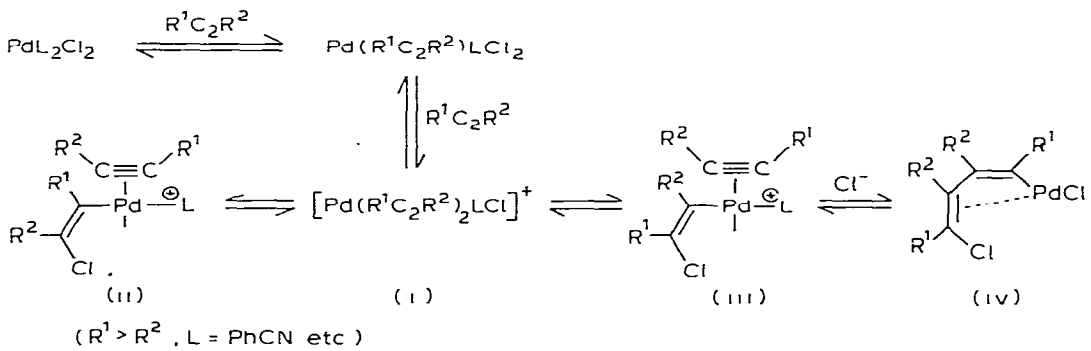
palladium reactions was again evident but it appeared, from our lack of success in isolating or detecting an intermediate and from the lack of trimers, that

here the σ-butadienyl complex was rather labile and readily underwent cyclisation in preference to insertion of a further acetylene [35].

The mechanism of acetylene oligomerisation with Pd^{II}

A summary of the routes by which acetylene trimer complexes and trimers are formed has recently been given [36]. The present account amplifies some aspects of this mechanism and also extends the discussions to the formation of cyclic tetramers and of dimers.

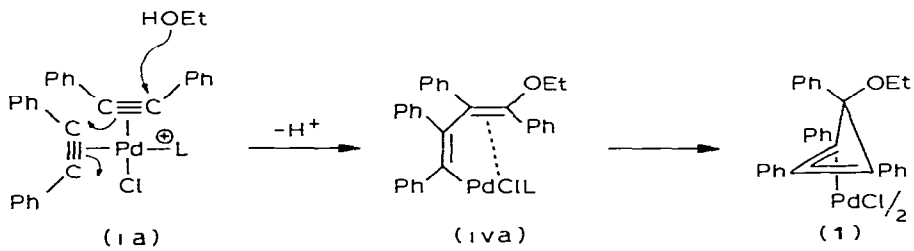
The very first step in the overall sequence is clearly the formation of a π-acetylene complex. One such, $[Pd_2Cl_4(t\text{-}BuC_2t\text{-}Bu)_2]$ is stable [19], and others have been detected at low temperature for cases where the acetylene bears less bulky substituents [14,30]. The next detectable species are the σ-butadienyl complexes where, for asymmetric acetylenes, the two acetylenes have linked tail-to-tail. No evidence for σ-alkenyl intermediates has been obtained for the Pd^{II} induced reactions, and we incline to the view that such intermediates are at best very transient and that no σ-bonds are formed until two acetylenes are attached to the metal centre in a, probably cationic, complex $[Pd(R^1C_2R^2)_2Cl]Y$, (i), (L = PhCN, Y = Cl, $\frac{1}{2}Pd_2Cl_6$, for example). We suggest that this intermediate is in a labile equilibrium with two σ-alkenyl isomers (ii and iii) and that (when R^1 is larger than R^2) the latter is favoured since the steric hindrance at Pd will be less when the carbon bearing the smaller substituent (R^2) is attached to the metal. The next step, insertion of the second coordinated acetylene into the Pd—alkenyl bond, then occurs quickly and is irreversible since a C—C bond is formed. (It is also possible that these two steps are concerted.) This gives the σ-butadienyl complex (iv) with the stereochemistry (acetylene moieties tail to tail and both *cis*) that is observed in the isolated complexes (**21**) and (**25**).



At this point, if R^1 is sufficiently large, further insertion into the Pd—C σ-bond becomes difficult and the molecule stabilises itself by conrotatory cyclisation to a cyclobutenyl complex which then loses Cl to give the cyclobutadiene (e.g. **25** → **26**). The stereospecificity and the reversibility of this step is shown by the sequence **27** → **28**, for example.

Further evidence is provided by the stereospecific formation of the *endo*-ethoxytetraphenylcyclobutenyl complex **1** in the Malatesta reaction. This can be satisfactorily explained by the reaction sequence ia → **1**, analogous to i → iv

above, but with *exo*-attack by ethanol (non-coordinating solvent) on a cationic bis-acetylene complex (ia). A conrotatory cyclisation of the intermediate σ-butadienyl complex (iva) yields the observed product (**1**) with the ethoxy group *endo*- to the metal.



(ia) (iva) (1)

No cyclobutadiene is formed directly in this reaction nor are significant amounts of the acetylene trimer, hexaphenylbenzene, observed. This is consistent with a high nucleophilicity of HOEt towards carbon; attack by EtOH competes successfully with intramolecular attack by coordinated Cl and the rate of cyclisation of the σ-butadienyl (iva) must be considerably faster than any further acetylene insertion reactions.

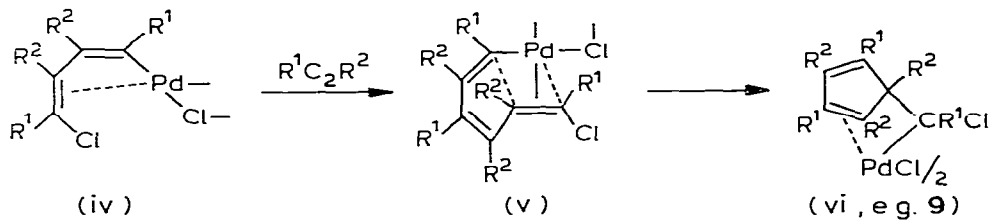
This is not the case when this reaction is carried out in aprotic solvents, when hexaphenylbenzene is formed catalytically and the terminating step is the formation of the cyclobutadiene salt $[Pd_2Cl_3(Ph_4C_4)_2]\frac{1}{2}[Pd_2Cl_6]$ (equation 2), analogous to **26**. The formation of such ionic complexes was unexpected but may reflect the importance of ionic intermediates such as i, ii and iii in the initial steps.

Once the basic σ-butadienyl unit has been established, the course of the further reactions becomes clear. We suggest that the next step (when R^1 is reasonably small) is anti-Markowinkow *cis*-insertion of another acetylene into the Pd—butadienyl σ-bond to give a σ-hexatrienyl complex. Models show that a stable conformer for this exists such that the terminal double bond comfortably coordinates to the metal (v) in such a way that internal cyclisation is facilitated and the palladiamethylcyclopentadiene skeleton (vi) is achieved (Scheme 9).

In order to stabilise itself the metal in vi should coordinate a cyclopentadiene double bond. This is sterically unfavourable, though it does happen in the very labile complex (**9**) from dimethylacetylene, and other forms of stabilisation are preferred. When $R^1 = R^2 = CO_2Me$ internal coordination to an ester carbonyl can occur in preference and this gives **14**. In other cases 1,2-hydrogen shifts occur to give, for example, **19** (R^1 = t-Bu, R^2 = H) or **13**.

Thirdly, vi can decompose to give benzenoid trimers and regenerate $PdCl_2$ which can then cyclise more acetylenes to the corresponding benzenes in a catalytic cycle. The course of this reaction is complex as may be judged from the isolation of only 1,3,5-tri-t-butylbenzene from the tail-to-tail σ-butadienyl complex (**21**), and from the isolation of isomer **8** from the methyl(phenyl)-acetylene reaction. Based upon our understanding of the mode of decomposition of **9** to trimer products (equation 3) we suggested that these reactions all proceeded via a cyclisation to a bicyclo[3.1.0]hexenyl system (vii) which can undergo dynamic behaviour as indicated (vii ⇌ viii), and then decompose to

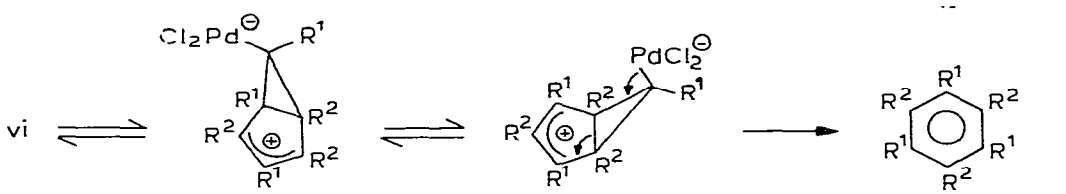
SCHEME 9



(vi, $R^1 = R^2 = CO_2Me$) ⟶ 14

(vi, R^1 = t-Bu; R^2 = H) —1,2-H shift→ 19

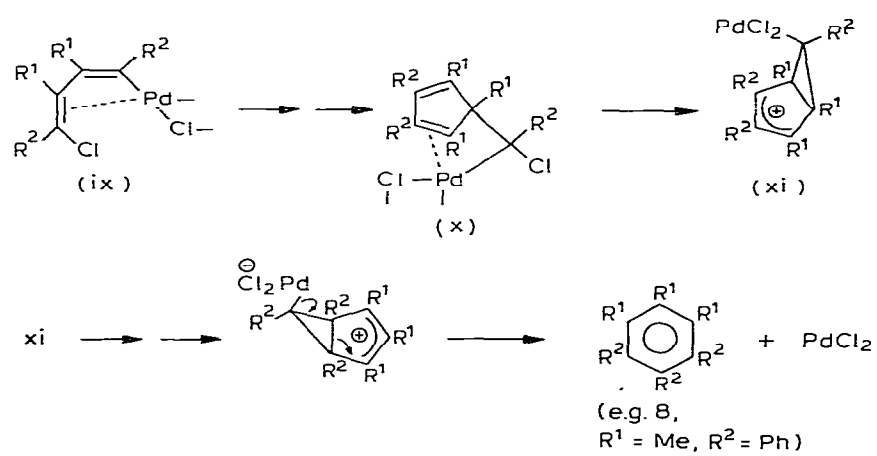
(vi, $R^1 = R^2$ = Me; Ph in place of Cl) —1,2-H shift→ 13



give the appropriate benzenoid isomer.

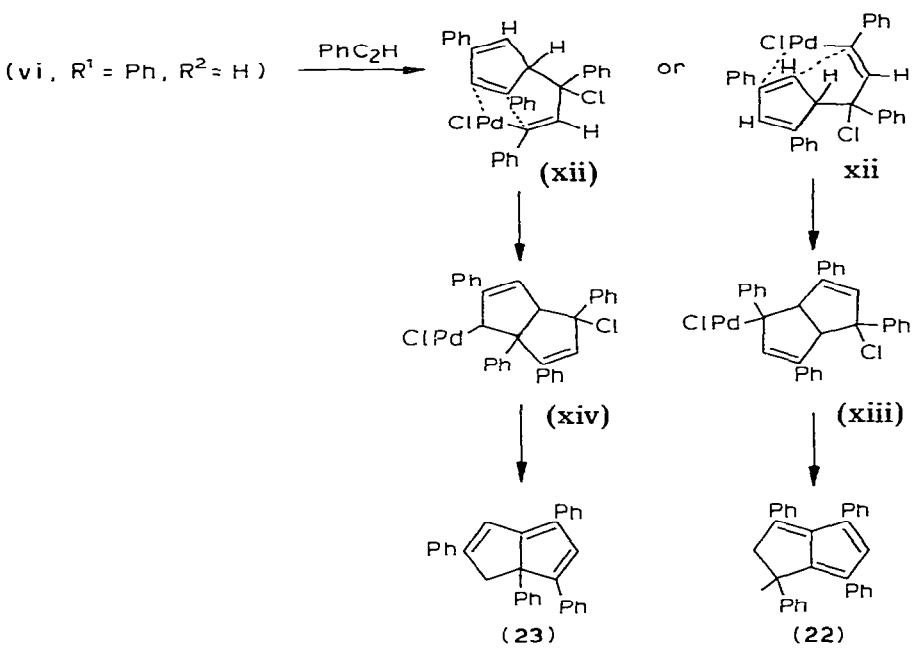
It will be evident that isomer 8 cannot arise from vi bearing R^1 (= Ph) and R^2 (= Me) as indicated. However we suggest that the effective sizes of methyl and phenyl (in so far as the metal is concerned) are very similar; this is clear, for example, from the similarity of the reactions involving dimethyl- or phenyl (methyl)-acetylene. In that case isomer ix is formed in addition to iv and this sequence then leads, via x and xi to the observed product 8 (Scheme 10).

SCHEME 10



The last mode of reaction that has been observed is the one giving rise to the bicyclic dihydropentalene tetramers **22** and **23** (or **24**) from phenylacetylene. This again fits well into the general scheme. The first steps are the formation of intermediates corresponding to iv, v and vi; since the substituent R^1 (= Ph) is relatively small and R^2 (= H) is very small this last intermediate here is then able to insert a further acetylene into the Pd—C σ-bond. The product xii can again cyclise, in two alternative ways giving xiii and xiv, which then undergo hydrogen shifts and loss of $PdCl_2$ to yield the observed products **22** and **23** (Scheme 11). The formation of **24** can be explained similarly.

SCHEME 11



I dedicate this article to my teachers, especially Michael Dewar, who practised and taught lateral thinking long before it became popular, and Gordon Stone from whom I learnt inorganic chemistry and much else, and to all my collaborators who worked so hard and well to uncover how nature, this time in the guise of a metal, organises chemistry around itself.

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