

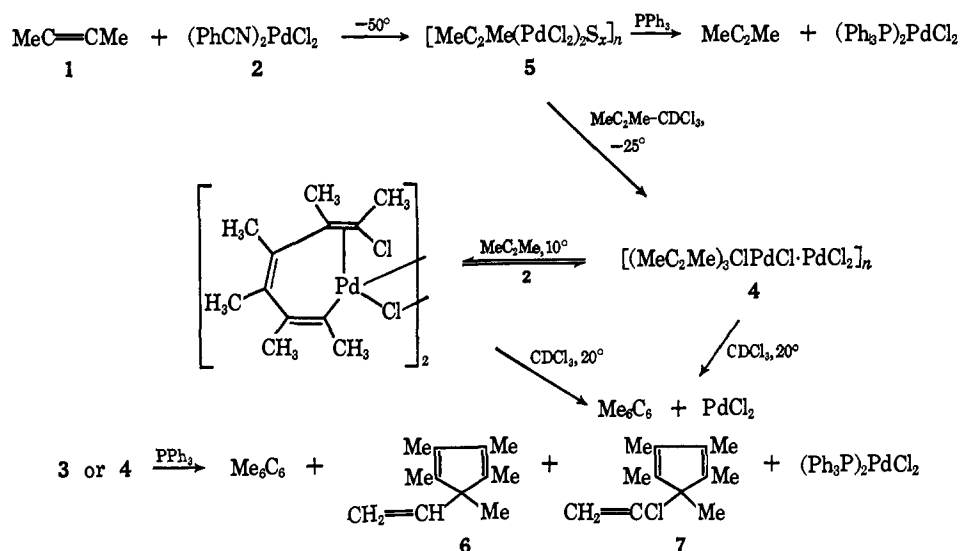
The Reaction of 2-Butyne with Palladium Chloride¹

Sir:

We have examined the trimerization of 2-butyne (1) with dichlorobis(benzonitrile)palladium (2) and have evidence for intermediates and a reaction mechanism quite different from those hitherto considered for metal-catalyzed trimerizations of acetylenes.² At -50° a π complex was formed which reacted at -25° with more 2-butyne to give an intermediate, the organic ligand of which we propose to be a 2-chloro-3,4,5,6-tetramethyl-2-trans,4-cis,6-trans-octatriene σ bonded to a PdCl at the 7 position and π bonded to the PdCl at the other end. At higher temperatures this decomposed to hexamethylbenzene and PdCl₂. Two metal atoms are involved in these reactions.

The palladium complex 2 reacted with an excess of 1 in benzene at $\sim 10^\circ$ to give a product from which could be isolated a little hexamethylbenzene and a palladium complex (3) which analyzed correctly for [(Me₂C₂)₃PdCl₂]₂.³ The 60-Mc pmr spectrum of 3 in

Scheme I



CDCl₃ showed the presence of six singlets of equal intensity⁴ due to six inequivalent methyl groups. After some minutes at 34° the spectrum began to change; this was marked by the appearance of a sharp singlet at τ 7.78 (hexamethylbenzene). When this reaction was followed at $10-20^\circ$, a new six-line spectrum was also observed⁵ when about half the complex had decomposed to

hexamethylbenzene. The species 4 which gave rise to this new six-line pmr spectrum decomposed even more readily than 3 to hexamethylbenzene and PdCl₂ without giving rise to any other detectable intermediates. On adding 2 moles of 2 to a solution of 1 mole of 3 in either CDCl₃ or benzene solution, a pmr spectrum identical with that of 4 was obtained. The complex (4) was too labile to be isolable; however, the above evidence implies a molecular formula [(Me₂C₂)₃(PdCl₂)₂]_n for it.

When the reaction of 2 and an excess of 1 was followed in CDCl₃ at *ca.* -25° , only the spectrum of 4 was observed to appear. Furthermore, within the limits of accuracy of our measurements, the rate of formation of 4 was not found to be dependent on the concentration of the butyne.⁶

At -50° 1 and 2 reacted in CDCl₃ to give a complex, 5, characterized by a single peak at τ 7.67 to low field of 2-butyne (τ 8.19). On addition of Ph₃P to the solution this peak disappeared and a corresponding increase in the intensity of the 2-butyne peak was observed. We therefore formulate this species 5 as a π complex of

2-butyne and PdCl₂. The intensity of this peak did not increase, even at high butyne concentrations, beyond that required by a butyne: PdCl₂ ratio of 1:2 nor was the intensity materially affected by addition of excess benzonitrile. We therefore formulate 5 as [(Me₂C₂Me)(PdCl₂)₂S_x]_n, where S is solvent or benzonitrile, and envisage the reaction to proceed as shown in Scheme I.

The structure shown for 3 is proposed on the following evidence: (a) the pmr spectrum which indicates a high asymmetry of the organic ligand; (b) the infrared spectrum which indicates the presence of an asymmetric PdCl₂Pd bridge and no terminal PdCl bonds, a coordinated C=C, and a band which is assigned to vinylic Cl⁻; and (c) its reactions.

8.31, 8.77, and 9.01, intensities 1:1:2:1:1. At 100 Mc and at -30° in CDCl₃ the peak of relative intensity 2 was resolved into peaks at τ 8.24 and 8.30; however, other peaks also showed smaller splittings at this temperature. These effects are being studied. In benzene at 10° the 100-Mc spectrum was cleaner and showed six equal intensity singlets at τ 7.89, 8.25, 8.59, 8.61, 8.85, 9.07, and 9.13.

(6) Solutions with ratios of (PhCN)₂PdCl₂:MeC₂Me from 0.3 to 6.0 were examined. At temperatures above 10° 4 reacted slowly with the butyne to give 3. This reaction in CDCl₃ was, however, complicated by the decomposition of 4 at this temperature to hexamethylbenzene and PdCl₂.

(7) The infrared spectrum in Nujol shows bands, among others, at

(1) Part VIII of Reactions of Acetylenes with Noble-Metal Halides; part VII: H. Diel and P. M. Maitlis, *Chem. Commun.*, 481 (1968).

(2) This topic has been recently reviewed by (a) V. O. Reikhsfeld and K. L. Makovetskii, *Russ. Chem. Rev.*, 35, 510 (1966); (b) W. Hübel in "Organic Syntheses via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1967, p 273; (c) C. Hoogzand and W. Hübel, ref 2b, p 343. The mechanistic aspects of the oligomerization reactions are also extensively discussed by (d) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, 7, P22 (1967); (e) J. T. Mague and G. Wilkinson, *Inorg. Chem.*, 7, 542 (1968); (f) H. Singer and G. Wilkinson, *J. Chem. Soc., A*, 849 (1968); (g) G. M. Whitesides and W. J. Ehmann, *J. Am. Chem. Soc.*, 90, 804 (1968); (h) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

(3) This was obtained as small yellow crystals, dec pt $99-100^\circ$, in 45-50% yield. *Anal.* Calcd for C₂₄H₃₈Cl₄Pd₂: C 42.44; H, 5.34; Cl, 20.88; Pd, 31.3; mol wt, 679. Found: C, 42.20; H, 5.55; Cl, 20.68; Pd, 31.0; mol wt, 673, 678. On heating, either in the solid or in benzene solution, 3 decomposed cleanly to hexamethylbenzene and PdCl₂. When very pure, 3 was stable in the solid for a day or so at 25° ; the benzene solutions were also stable for some time at 25° .

(4) At τ 7.86, 8.05, 8.13, 8.31, 8.72, and 8.87.

(5) This appeared as a five-line spectrum at 60 Mc: τ 7.92, 8.05,

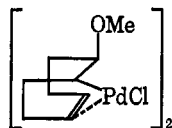
As already mentioned **3** decomposed readily under a variety of conditions to hexamethylbenzene and PdCl_2 ; this indicates that a ligand made up of only three acetylenes is coordinated to each palladium. In both CDCl_3 and C_6H_6 **3** reacted with Ph_3P to give a small amount of hexamethylbenzene and two organic compounds formulated as the vinylpentamethylcyclopentadienes **6** and **7** on the basis of their analyses and spectroscopic properties;⁹ in addition, $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ was also obtained quantitatively from the lower temperature reactions where **6** was the main product. The formation of **7** lends support to a structure for **3** which has a vinylic Cl in the organic ligand.¹⁰

The infrared spectrum of **4** is very similar to that of **3** in the region $500\text{--}4000\text{ cm}^{-1}$ and suggests that a very similar organic ligand is present and that the extra PdCl_2 is not coordinated to a double bond but rather to the PdCl in **3**.¹¹

Our observation that the rate of synthesis of **4** is not dependent on the butyne concentration suggests that the rate-determining step is probably a rearrangement. One reasonable such rearrangement would be "cis insertion" of the acetylene in **5** into a $\text{Pd}\text{--}\text{Cl}$ bond, which would then be followed by two further very fast "cis insertions" of coordinated acetylenes into the $\text{Pd}\text{--}\text{C}$

242 and 273 (m) (asymmetric $\text{PdCl}_2\text{Pd}^{\delta}$), 487 (w) and 530 (m) ($\nu_{\text{Pd}\text{--}\text{C}}$), 772 (s) ($\nu_{\text{C}\text{--}\text{Cl}}$), 1512 (m) (coordinated $\text{C}\text{=}\text{C}$), and 1624 cm^{-1} (mw) (uncoordinated $\text{C}\text{=}\text{C}$).

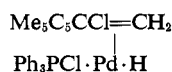
(8) J. Powell and B. L. Shaw, *J. Chem. Soc., A*, 583 (1968), found that in $[(\text{allyl})_2\text{RhCl}]_2$ complexes, where the bridging $\text{Rh}\text{--}\text{Cl}$ bonds have been shown to have very different lengths, the two predicted $\nu_{\text{Rh}\text{--}\text{Cl}}$ bands were quite widely different, whereas in $[(\text{allyl})\text{PdCl}]_2$ where the bridging $\text{Pd}\text{--}\text{Cl}$ bond lengths are equal, the two $\nu_{\text{Pd}\text{--}\text{Cl}}$'s are very close together. For comparison we have examined the low-frequency infrared spectrum of



and find again two very different ν_{PdCl} 's at 222 and 272 cm^{-1} . This is to be expected in both this complex and in **3** since in both cases one $\text{Pd}\text{--}\text{Cl}$ is *trans* to a $\text{Pd}\text{--}\text{C}$ σ bond and hence is expected to be very long, whereas the other, *trans* to a $\text{Pd}\text{--}\text{olefin}$ bond, will be nearly normal.

(9) The mass spectra show molecular ion peaks at 162.139930 (for **6**) and 196.10326 and 198.100317 (for **7**). Calcd for $\text{C}_{12}\text{H}_{18}$ (**6**): 162.140844; calcd for $\text{C}_{12}\text{H}_{17}^{35}\text{Cl}$: 196.101872; calcd for $\text{C}_{12}\text{H}_{17}^{37}\text{Cl}$: 198.098922 (**7**). The mass spectroscopic cracking patterns also support the assigned structures. The pmr spectra show the following resonances: for **6** at τ 9.00 (singlet, bridgehead methyl), 8.34 (doublet at 100 Mc, separation 0.9 cps, diene methyls), 8.22 (doublet at 100 Mc, separation 0.8 cps, diene methyls), and 4.96 (multiplet, vinyl protons) with intensity ratios 3:6:6:3. For **7**, resonances appear at τ 8.90 (singlet), 8.33 (doublet at 100 Mc; $J = 1.0$ cps), 8.22 (doublet at 100 Mc; $J = 0.85$ cps), and 4.75 (double doublet, $J = 4$ cps, vinyl protons) with intensity ratio 3:6:6:2. The infrared spectra of **6** and **7** also agree well with the proposed structures and show, apart from bands due to vibrations associated with the methyls, bands at 3080 (m), 3050 (w) (vinylic CH), 1655 (w), 1625 (s), and 906 (s) cm^{-1} for **6** and at 3110 (w), 1660 (m), 1625 (s), 1620 (sh), 882 (vs), and 708 (s) ($\text{C}\text{--}\text{Cl}$) cm^{-1} for **7**.

(10) Formation of **6** and **7** from **3** can be rationalized in terms of an insertion of the coordinated $\text{C}\text{=}\text{C}$ bond in **3** into the $\text{Pd}\text{--}\text{C}$ bond to give $\text{Me}_5\text{C}_5\text{CCl}(\text{PdCl}(\text{PPh}_3))\text{Me}$. This is converted to another π complex by H abstraction from the terminal methyl)



which can then either lose $\text{HPdCl}(\text{PPh}_3)_2$ to give **7**, or add $\text{Pd}\text{--}\text{H}$ to the double bond to give $\text{Me}_5\text{C}_5\text{CClH}\cdot\text{CH}_2\text{PdCl}(\text{PPh}_3)_2$ which on elimination of $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ gives **6**.

(11) There are many examples of chloropalladium complexes adding extra PdCl_2 molecules (e.g., R. Hüttel and H. J. Neugebauer, *Tetrahedron Letters*, 3541 (1964); P. M. Maitlis, D. F. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, **43**, 470 (1965); M. Donati and F. Conti, *Inorg. Nucl. Chem. Letters.*, **2**, 343 (1966)), but the mode of bonding is not clear.

(vinyl) bond, eventually yielding **4**.¹² The extra PdCl_2 present must assist these processes in some way not yet clear, either by coordinating another acetylene or by activating the one present in **5**. We have previously shown that PdCl_2 will catalyze the decomposition of dewar hexamethylbenzenepalladium chloride to hexamethylbenzene and PdCl_2 ;¹³ it also appears to catalyze the decomposition of **3** in CDCl_3 , and this seems to be a general phenomenon.¹⁴

The evidence presented here makes it clear that the reactions which occur between **1** and **2** are of a type quite different to those which have previously been considered to account for metal-catalyzed trimerization reactions.¹⁵ Further details of these processes are under investigation and will be reported in detail shortly.

Acknowledgment. We thank the National Research Council of Canada for supporting this work and Johnson, Matthey and Mallory for the loan of PdCl_2 .

(12) R. Heck (private communication) has shown that compounds in which $\text{Pd}\text{--}\text{C}$ bonds are present react very rapidly with olefins. We feel that the reaction studied here largely finishes after 3 moles of acetylene has been added for steric reasons. Molecular models show that the structure represented by **3** is very favorable and strain free; further, the coordinated olefin has the alternative of either lying in the coordination plane of the metal or perpendicular to it. The former arrangement would obviously facilitate the further intramolecular *cis* insertion postulated above.¹⁰

(13) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967); however, we have no evidence which indicates that either a dewar benzene- or a cyclobutadiene-metal complex is an intermediate in the reactions described here.

(14) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **147**, 399 (1962), have observed that in the absence of excess chloride ion, the PdCl_2 -catalyzed oxidation of ethylene to acetaldehyde is second order in $\text{Pd}(\text{II})$.

(15) These mechanisms have been of two broad types, those involving "concerted" reactions^{2a,16} and those in which five-membered metallo-cycles have been isolated as intermediates.^{2d,e,h} Stepwise reactions involving insertion of acetylenes into $\text{M}\text{--}\text{C}\equiv\text{CR}$ bonds have been postulated to occur for reactions involving monosubstituted acetylenes.^{2i,17} A trimerization reaction which appears to proceed *via* a binuclear complex is that which occurs between acetylenes and $\text{Co}_2(\text{CO})_8$, but the probable intermediate, $(\text{acetylene})_2\text{Co}_2(\text{CO})_4$,^{2b} is of quite a different type to the one postulated here and is also much more stable.

(16) G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem.*, **76**, 28 (1964).

(17) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962).

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Novel Reactions of Benzyne with Acetylenic Ethers

Sir:

The reaction of benzyne with ethoxyacetylene (Ia) to form 2-ethoxyphenylacetylene, reported earlier by Stiles,¹ represents an unusual rearrangement in benzyne-acetylene chemistry.^{2,3} We now wish to report further novel transformations in this series arising from the reaction of benzyne with ethoxypropyne (Ib) and with the thioacetylenes IIa-d.

(1) M. Stiles, U. Burckhardt, and A. Haag, *J. Org. Chem.*, **27**, 4715 (1962).

(2) V. Franzen and H. I. Joschek, *Ann.*, **703**, 90 (1967).

(3) S. F. Dyke, A. R. Marshall, and J. P. Watson, *Tetrahedron*, **22**, 2515 (1966).