Reactions of Acetylenes with Noble-Metal Halides. VIII.[1] The Palladium Chloride Catalyzed Trimerization of 2-Butyne and 1-Phenyl-1-propyne

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Abstract: Reaction of methylphenylacetylene with bis(benzonitrile)palladium chloride (**1**) in chloroform gave 1,2,4-trimethyl-3,5,6-triphenylbenzene (**2**, 58%), 1,3,5-trimethyl-2,4,6-triphenylbenzene (**3**, 39%), and 1,2,3-trimethyl-4,5,6-triphenylbenzene (**4**, 3%). In benzene, a complex $[(PhC_2Me)_3PdCl_2]_2$ was isolated which readily decomposed to palladium chloride, **2**, and **3**. 2-Butyne reacted with **1** in benzene to give a complex $[Cl(MeC_2Me)_3PdCl]_2$ (**6**) and in chloroform to give $[Cl(MeC_2Me)_3PdClPdCl_2]_n$ (**7**) and some complex **6**. On spectroscopic evidence, both **6** and **7** are assigned structures involving a 2-chloro-3,4,5,6-tetramethyl-2-*trans*,4-*cis*,6-*trans*-octa-2,4,6-triene σ-bonded at C_7 and π-bonded at $C_{2,3}$ to palladium(II). The ligand can take up two positions with respect to the metal, with the coordinated double bond parallel or perpendicular to the coordination plane. Both complexes **6** and **7** decomposed readily to palladium chloride and hexamethylbenzene. A new mechanism for the trimerization of acetylenes is proposed.

In 1962 one of us reported[3] a reinvestigation of the reaction, originally described by Malatesta, *et al.*,[4] in which diphenylacetylene was dimerized to an ethoxytetraphenylcyclobutenylpalladium chloride complex in the presence of palladium chloride in ethanol. Under slightly different conditions (aprotic solvents) from those used by Malatesta, *et al.*, we observed that diphenylacetylene could also be catalytically trimerized to hexaphenylbenzene. In addition, a tetraphenylcyclobutadienepalladium chloride complex ($[Ph_4C_4(PdCl_2)_n]_x$) was formed which eventually deactivated the catalyst.[5] These results have been confirmed by a number of workers.[6–8]

These reactions of diphenylacetylene and closely related acetylenes did not readily lend themselves to a more detailed investigation and, since the generality of the reaction was of considerable interest particularly as a very easy route to cyclobutadiene–metal complexes, we began an investigation of the reactions of some other acetylenes with palladium chloride.

Our first attempts, using acetylene, propyne, and monophenylacetylene, did not lead to characterizable products. Reactions always proceeded very easily to give mixtures of metal complexes. However, the latter were polymeric and nonstoichiometric in nature and not easily handled. It is probable that the ligands in these complexes are linear polyenes; however, hydrogen-transfer and cyclization reactions are by no means excluded.[9]

We then turned our attention to 1-phenyl-1-propyne (methylphenylacetylene, MPA) and 2-butyne (dimethylacetylene). This paper describes these reactions[11,12] and gives evidence for a trimerization mechanism different from those previously considered. The following paper describes in detail some reactions of a complex isolated from the latter reactions.

Results and Discussion

Reactions of Methylphenylacetylene (MPA) with Bis(benzonitrile)palladium Chloride. In a halogenated solvent (chloroform, methylene chloride), MPA was catalytically trimerized to trimethyltriphenylbenzenes by bis(benzonitrile)palladium chloride (**1**).[13] The products included a small amount of an uncharacterized brown metal complex and the benzenoid trimers **2**, **3**, and **4**. The trimethyltriphenylbenzene isomers **2**, **3**, and **4** were

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[1] Part VII: S. McVey and P. M. Maitlis, *J. Organometal. Chem.*, 19, 169 (1969).

[2] Fellow of the Alfred P. Sloan Foundation and author to whom any correspondence should be addressed.

[3] A. T. Blomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, **84**, 2329 (1962).

[4] L. Malatesta, G. Santarella, L. M. Vallarino, and F. Zingales. *Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis. Mat. Nat.*, 27, 230 (1959); *Angew. Chem.*, 72, 34 (1960).

[5] P. M. Maitlis, D. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, 43, 470 (1965).

[6] L. M. Vallarino and G. Santarella, *Gazz. Chim. Ital.*, 94, 252 (1964).

[7] R. Hüttel and H. J. Neugebauer, *Tetrahedron Lett.*, 354 (1964).

[8] R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965).

[9] One product, isolated in only low yield from the reaction of phenylacetylene, proved to be 2,4,6-triphenylfulvene.[10]

[10] J. Bloodworth and P. M. Maitlis, unpublished.

[11] Preliminary communications on part of this work have appeared: (a) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 481 (1968); (b) H. Reinheimer, H. Dietl, J. Moffat, D. Wolff, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 90, 5321 (1968).

[12] P. M. Maitlis, H. Reinheimer, H. Dietl, and J. Moffat, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**, B156 (1969).

[13] Bis(benzonitrile)palladium chloride, prepared by the method of Kharasch, *et al.*,[14] was used because of its solubility and ease of preparation. We also observed that the benzonitrile ligands coordinated only very weakly to the metal. In a Nujol mull the complex showed a sharp ν_{CN} at 2290 cm^{-1}, but when the complex was in solution two bands, ascribed to ν_{CN} (at 2230 and 2290 cm^{-1}), of about equal intensity were always observed, irrespective of solvent. The latter is due to coordinated PhCN, while the position of the former band is identical with that of free benzonitrile itself. Since bands of approximately equal intensity were observed, it suggests that an equilibrium such as

$$n(PhCN)_2PdCl_2 \rightleftharpoons nPhCN + (PhCNPdCl_2)_n$$

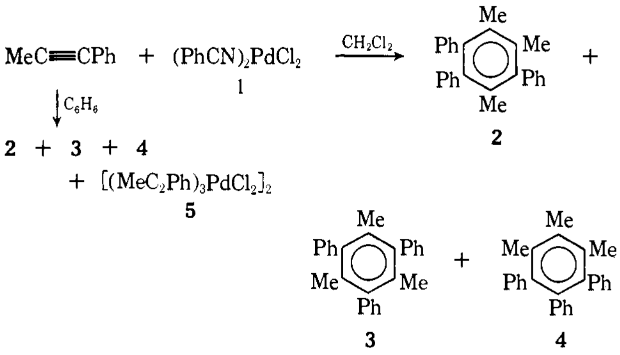
lies well over to the right-hand side. In fact when such solutions were allowed to stand, palladium chloride slowly crystallized out, indicating that the equilibrium

$$(PhCNPdCl_2)_n \rightleftharpoons nPhCN + (PdCl_2)_n$$

also lies over to the right. As far as we have been able to tell, benzonitrile, in the concentrations present, plays no significant role in these reactions, and therefore the complex $(PhCN)_2PdCl_2$ may for practical purposes be regarded simply as weakly solvated $PdCl_2$. A similar conclusion has been arrived at by Kitching and Moore.[15]

[14] M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, 60, 882 (1938).

[15] W. Kitching and C. J. Moore, *Inorg. Nucl. Chem. Lett.*, 4, 691 (1968).



separated by fractional crystallization and their relative amounts estimated by a combination of crystallization and quantitative pmr analysis as 58:39:3. Isomers **2** and **3** have previously been prepared by trimerization of MPA with $Hg(Co(CO)_4)_2$ by Hübel and Hoogzand.[16] Our spectroscopic data were in agreement with these structures.

The isolation of the 1,2,3-trimethyl-4,5,6-triphenylbenzene (**4**) was unexpected, and this compound had not been reported previously. The identification as **4** followed from its analysis and molecular weight (both mass spectroscopic and osmometric) and particularly from its pmr spectrum. The latter showed, apart from phenyl resonances, two singlets due to the two different types of methyls, in the ratio 1:2.[17] The infrared spectra of all three isomers were very similar, and they all showed a maximum at 2820 Å in the ultraviolet.

Although the full extent of the catalytic trimerization was not investigated, we were able to trimerize at least 63 mol of the acetylene, MPA, per mol of **1**.

In benzene some of the trimers **2**, **3**, and **4** were also obtained, but the major product (*ca.* 90%) was a yellow complex $[(MeC_2Ph)_3PdCl_2]_2$ (**5**). This material was very labile. Attempts to purify it led to materials having a higher palladium and chlorine content and some trimers. This was presumably due to a reaction such as

$$n[(MeC_2Ph)_3PdCl_2]_2 \longrightarrow n(MeC_2Ph)_3 + n[(MeC_2Ph)_3(PdCl_2)_2]$$

The complex was reasonably stable in the solid. In benzene solution the pmr spectrum showed a very complex pattern in the methyl region which was not analyzable. This did not change noticeably with time, despite the occurrence of the above decomposition.

The decomposition of **5** to a mixture of trimers and palladium chloride was fast in chloroform or methylene chloride. Only the two isomers **2** and **3** (in the ratio of 3:2) were detected in the product. An analogous reaction occurred when a benzene solution was treated with various ligands (L = triphenylphosphine, acetonitrile, or benzonitrile). In each case the appropriate palladium complex, L_2PdCl_2, and the trimers **2** and **3** were obtained.

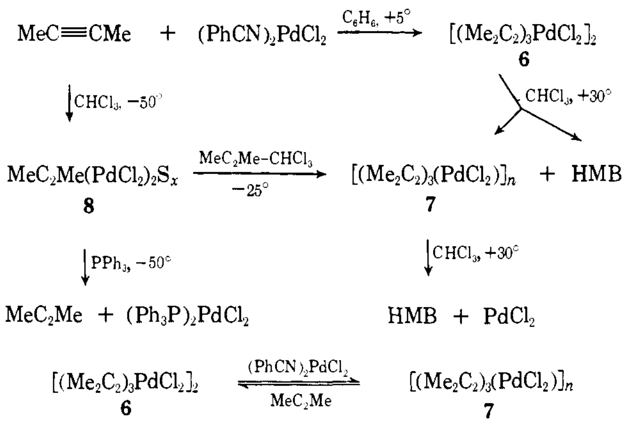
$$\mathbf{5} + 4L \longrightarrow \mathbf{2} + \mathbf{3} + 2L_2PdCl_2$$

The solid complex **5** also decomposed, beginning at 100°, to give a sublimate of white crystals (**2** and **3**) and a residue of palladium chloride. Unfortunately, any metal complex which gives rise to the trimers **2** and **3** (and possibly **4**) is bound to be a mixture of isomers (as indicated by its nmr spectrum). This severely limits the structural and mechanistic information which can be obtained. By analogy, however, we suggest that this complex is a mixture of isomers, each of which has the same basic skeleton as that of $[(MeC_2Me)_3PdCl_2]_2$ (**6**) discussed below.

Reactions of 2-Butyne with Bis(benzonitrile)palladium Chloride. When the reaction of 2-butyne with $(PhCN)_2PdCl_2$ was carried out under very carefully controlled conditions in benzene at 5°, we obtained in 50% yield a yellow crystalline complex $[(Me_2C_2)_3PdCl_2]_2$ (**6**). This complex appeared to behave similarly to $[(PhC_2Me)_3PdCl_2]_2$ (**5**) described above. It readily gave hexamethylbenzene (HMB) and $PdCl_2$ in chloroform or methylene chloride solution, or on heating. An intermediate in the decomposition was shown by nmr to be another complex, $[(Me_2C_2)_3(PdCl_2)_2]_x$ (**7**).

The reaction of 2-butyne with $(PhCN)_2PdCl_2$ in chloroform was followed by nmr. Below −40° a complex, identified as the solvated π-acetylene complex **8**, was formed. In the presence of excess 2-butyne at *ca.* −25°, the complex **7** was formed, and at higher temperatures, in the presence of 2-butyne, this was transformed into complex **6**. These reactions are summarized in Scheme I.

Scheme I



Complex 6, $[(Me_2C_2)_3PdCl_2]_2$. Although this complex is crystalline, the crystals obtained were too small for X-ray analysis, and we have been forced to rely on spectroscopic and chemical evidence in order to formulate a structure for it. This evidence is summarized.

(a) The complex **6** decomposed either on heating the solid to over 100°, or in halogenated solvents ($CHCl_3$, CH_2Cl_2) at 30° (Figure 1), or in solution on reaction with halogens (Br_2, I_2) at −15°, to HMB. The other product was palladium chloride in the first two cases.[18] This implied that three (rather than two or four) acetylenes were associated with each metal atom in the complex, which was therefore probably a chlorine-bridged dimer.

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[16] W. Hübel and C. Hoogzand, *Chem. Ber.*, **93**, 103 (1960).

[17] The methyl resonances observed were at δ 2.19 (1) and 2.28 (2) for **2**, δ 2.18 for **3**, and δ 2.30 (2) and 2.37 (1) for **4** in benzene. In CH_2Cl_2 these were shifted to 1.67 (1) and 2.00 (2) for **2**, 1.62 for **3**, and 2.06 (2) and 2.33 (1) for **4**. The resonances to lowest field are those of methyls most shielded by phenyls (*e.g.*, in **3**). The differences in chemical shift between the two solvents are also revealing and are largest (0.52, 0.56 ppm) for a methyl situated between two phenyls. A methyl between a methyl and a phenyl experiences a solvent shift of 0.24 (or 0.28) ppm, while one between the two methyls, *i.e.*, the 2-methyl in the 1,2,3-trimethyl isomer, **4**, is hardly moved at all (0.04 ppm). This provides useful confirmatory evidence for the structure of **4**.

[18] Under some conditions, for example, when **6** was allowed to stand undisturbed in chloroform for several days, a brown precipitate with composition agreeing with $[(Me_2C_2)_3(PdCl_2)_5]_n$ was obtained in addition to hexamethylbenzene.

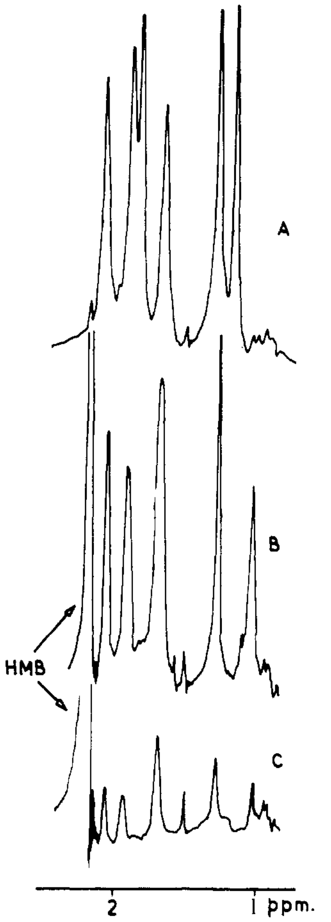
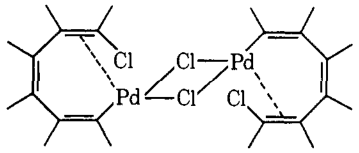


Figure 1. Nmr spectra (60 MHz) of the decomposition of complex **6** in $CDCl_3$ at 34°: (A) complex **6**; (B) HMB and complex **7**; (C) HMB and traces of complex **7**.

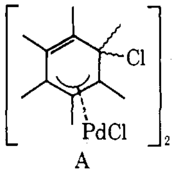
(b) The pmr spectrum of the complex in chloroform at 20° showed six singlets with equal intensities due to six inequivalent methyl groups.[19] This indicated a considerable asymmetry in the organic ligand and ruled out simple complexes involving dimethylacetylene, tetramethylcyclobutadiene, hexamethyl(Dewar benzene), or HMB as ligands.

(c) The ir spectrum of **6** was examined in several media. The most significant bands in Nujol and their proposed assignments are: 242 (m) and 273 (m) (ν_{Pd-Cl}, bridging),[20] 395 (m) ($\nu_{Pd-olefin}$),[22,26,27] 487 (w) or 530 (m) (ν_{Pd-C}),[28] 665 or 723 (vs) (ν_{C-Cl}),[29] 1512 (m) ($\nu_{C=C}$ coordinated[21,26,30]), and 1624 cm^{-1} (m) ($\nu_{C=C}$, uncoordinated). In addition, in CS_2 or CCl_4 solution, bands arising from C–C and C–H vibrations and deformations were seen at 953 (w), 1025 (s), 1029 (s); 1056 (m), 1072 (m), 1322 (w), 1361 (m), 1377 (m), 1384 (sh), 1411 (sh), 1423 (sh), 1431 (m), 1442 (m), 1450 (sh), 2872 (m), 2902 (m), 2929 (m), and 2966 cm^{-1} (m). Of particular interest is the absence of bands in the region (>3000 cm^{-1}) where vinylic ν_{C-H}'s are usually found.[31] This agrees with the pmr spectrum. The electronic spectrum of **6** has been recorded but does not appear to be of help in assigning a structure.[32]

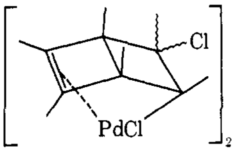
These results indicate the presence of three acetylenes linked to each other and to each metal atom, an asymmetric Pd_2Cl_2 bridge linking the two halves of the dimer, and an organic ligand containing a C–Cl and a coordinated and an uncoordinated double bond. The six



6



A



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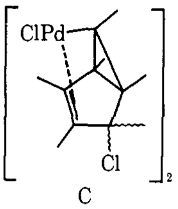

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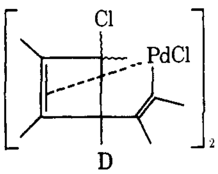

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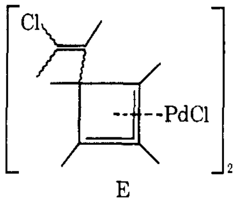

E

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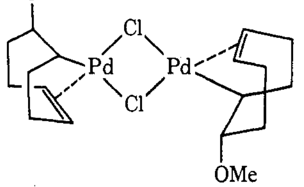
(19) The same result was obtained in CCl_4 and CS_2 solutions; however, in benzene the lowest field peak was split into a doublet (δ 2.04, 2.12).

(20) Bands due to terminal Pd–Cl bonds are usually higher than this, in the region 339–366 cm^{-1}.[21,22] Two bands due to bridging Pd–Cl bonds in the Pd_2Cl_2 unit are usually observed, in the regions 255–280 and 294–308 cm^{-1}. However, the position of the lower of these bands is markedly influenced by the nature of the *trans* ligand. In complexes such as $[(allyl)PdCl]_2$, where the bridge is symmetrical, two bands close together, in the range 244–262 cm^{-1}, are observed.[23] Powell and Shaw however, noted that when an asymmetric M_2Cl_2 bridge is present, as in $[(allyl)_2RhCl]_2$, and where the M–Cl bond lengths are quite different, the two bridging ν_{M-Cl} bands also differ considerably.[24] We have shown,[11b] and this has been confirmed by Crociani, *et al.*,[25] that in complexes such as where a very asymmetric bridge is expected, owing to the very high *trans* influence of the Pd–C σ bond, ν_{PdCl} bands at 222 and 272 cm^{-1} are present. Our observation of bands at 242 and 273 cm^{-1} for ν_{PdCl} in **6** is consistent with the presence of an asymmetric Pd_2Cl_2 unit, but one not as asymmetric as in the cyclooctenyl complex (above). This can be rationalized in terms of a smaller *trans* influence exerted by a sp^2 carbon than by a sp^3 carbon. Our spectra also indicate the absence of terminal Pd–Cl bonds.



(21) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967.

(22) D. M. Adams and P. J. Chandler, *J. Chem. Soc., A*, 588 (1969).

(23) M. S. Lupin, J. Powell, and B. L. Shaw, *ibid.*, 1410 (1966).

(24) J. Powell and B. L. Shaw, *ibid.*, 583 (1968).

(25) B. Crociani, P. Uguagliati, J. Boschi, and U. Belluco, *ibid.*, 2869 (1968).

(26) M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, **88**, 5454 (1966); 90, 918 (1968).

(27) H. P. Fritz, *Chem. Ber.*, **94**, 1217 (1961).

(28) G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).

(29) T. Yukawa and S. Tsutsumi, *Inorg. Chem.*, 7, 1458 (1968).

(30) H. P. Fritz and C. G. Kreiter, *Chem. Ber.*, 96, 1672 (1963).

(31) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Methuen, London, 1962.

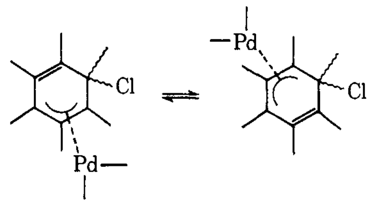
(32) Owing to solubility problems, the uv–visible spectrum could only be taken in methylene chloride or dioxane. In the former, a maximum was observed at 2780 Å (ε 4200) and points of inflection at *ca.* 3500 and 4000 Å. The maximum in dioxane was at 2890 Å. Although the datum is incomplete, it would appear inconsistent with reported spectra of π-allylic complexes, particularly of cyclic systems.[33,34]

(33) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963); 5003 (1964).

(34) B. F. Hegarty and W. Kitching, *J. Organometal. Chem.*, 6, 578 (1966).

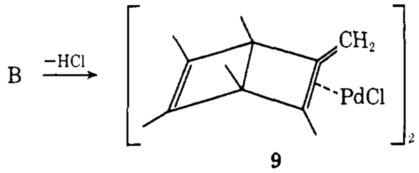
methyl resonances in the pmr spectrum suggest that no reaction involving movement of hydrogen has occurred.

A number of structures including **6** and A–D show the required asymmetry of organic ligand and can be formulated as bridged dimers. Models indicate that of these, C and D are unlikely, assuming normal bond angles and bond lengths, since there can be little effective coordination between the metal and the double bond. In these cases the distance from palladium to each double bond carbon is at least 3.0 Å. This compares with values of between 2.1 and 2.25 Å for palladium–carbon distances in π-bonded olefinic or allylic complexes.[35] This objection does not apply to structure A, though it is hard to see why the infrared spectrum should indicate a Pd_2Cl_2 bridge of high asymmetry here. A more pertinent objection to this structure is that a model indicates all the ring sp^2 carbons to be nearly coplanar. It is therefore difficult to see why the π-allylic group should be localized as shown. A structure of this type would be expected to exhibit fluxional behavior with a low-energy barrier between the forms



with consequent simplification of the pmr spectrum at ambient temperatures.

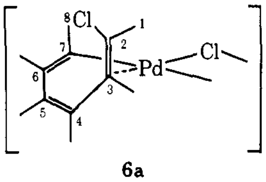
Structure B does not allow an uncoordinated double bond, and a complex of this type should lose HCl very readily to give complex **9**, already described by Shaw



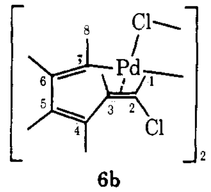
9

and Shaw.[36] Structure E is attractive from some viewpoints, but does not exhibit the asymmetry required by the pmr or the ir spectrum.

None of these objections applies to structure **6**, which is the structure which we favor. Although as written, the carbon skeleton, a 7-σ-bonded and 2,3-π-bonded 2-chloro-3,4,5,6-tetramethyl-2-*trans*,4-*cis*,6-*trans*-octatriene, appears cumbersome, models indicate this to be a strain-free molecule. Each half of the dimer can exist in two forms, one (**6a**) with the double bond perpendicular to the coordination plane of the metal, and the other (**6b**) with the double bond nearly coplanar to it. The first form is the more usual for olefin–metal complexes, but there is considerable evidence that the energy barrier in rotating the olefin from the perpendicular to the coplanar form is not high.[37,38] The two conformers **6a** and **6b** are interchanged by an operation involving twisting about the C_3C_4 bond and rotation of the C_2C_3 bond about its axis to the metal. No bonds need to be broken.

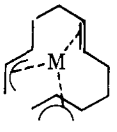


6a

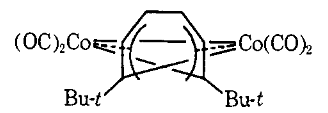


6b

The structure proposed leads to a rational understanding of the formation of **6** and suggests paths to its decomposition both to hexamethylbenzene and vinylpentamethylcyclopentadiene as discussed in the following paper. Although the structure is somewhat unusual, the trimerization of butadiene has been shown to occur *via* an acyclic bis-π-allylic complex of nickel (**10a**),[39] and a crystal structure determination of a ruthenium analog (**10b**) has been reported.[40]



10a, M = Ni
b, M = $RuCl_2$



11

An acyclic trimeric ligand has also been shown to occur in **11** (formed from 1 mol of acetylene and 2 mol of *t*-butylacetylene and dicobalt octacarbonyl).[41] Although the pmr spectrum of $[Cl(Me_2C_2)_3PdCl]_2$ (**6**) usually only showed six singlets (Figure 1),[19] on cooling a solution in $CHCl_3$ below −55° a very complex spectrum containing 16 or more lines of varying intensities was obtained (Figure 2). This may be attributed to the freezing of the equilibrium **6a** $\rightleftharpoons$ **6b** at these temperatures. The splittings can be assigned on the basis of the presence of three conformers (each half of the dimer can exist as either **6a** or **6b**). The different line shapes observed at ambient temperatures are also accounted for by the existence of these rapidly interconverting conformers. An alternative explanation for the low-temperature splitting involves restricted rotation of methyl groups, but our models of **6a** and **6b** indicate that this is probably a minor effect.

Complex 7, $[(Me_2C_2)_3(PdCl_2)_2]_n$. When the decomposition of **6** to HMB and palladium chloride in chloroform was followed by nmr, it became apparent that the reaction proceeded *via* another material, **7** (Figure 1). The concentration of this species reached a maximum when about half of complex **6** had decomposed. Although we have not been able to isolate **7**, we have established its stoichiometry as $[(Me_2C_2)_3PdCl_2 \cdot PdCl_2]_n$. Spectra identical with that shown in Figure 1B were obtained when palladium chloride (as the bis(benzonitrile) complex **1**) was added to **6**. In order to get **7** at least 2 mol of $PdCl_2$ per mol of **6** (dimer) had to be added. Excess palladium chloride had no detectable effect, and lower ratios gave spectra

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[35] Some representative values have been determined by A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965); J. N. Dempsey and N. C. Baenzinger, *J. Amer. Chem. Soc.*, **77**, 4984 (1955); I. A. Zakharova, G. A. Kukina, T. S. Kuli-Zade, I. I. Moiseev, G. Yu. Pek, and M. A. Porai-Koshits, *Russ. J. Inorg. Chem.*, **11**, 1364 (1966); C. J. Hamburger, *Diss. Abstr.*, **28**, 625B (1967).

[36] B. L. Shaw and G. Shaw, *J. Chem. Soc., A*, 602 (1969).

[37] R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964); **89**, 5377 (1967); R. Cramer, J. B. Kline, and J. D. Roberts, *ibid.*, **91**, 2519 (1969).

[38] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., A*, 53 (1969).

[39] G. Wilke, M. Kröner, and B. Bogdanovic, *Angew. Chem.*, **73**, 755 (1961); G. Wilke, *Angew. Chem. Int. Ed. Engl.*, **2**, 105 (1962).

[40] J. E. Lydon and M. R. Truter, *J. Chem. Soc., A*, 362 (1968).

[41] W. Hübel, "Organic Syntheses via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1968, p 310; O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 187 (1964).

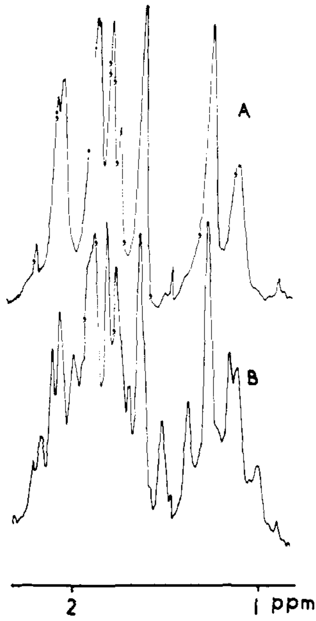

Figure 2. Nmr spectra (100 MHz) of complex **6** in $CHCl_3$: (A) at −55°; (B) at −70°.

characteristic of mixtures of **6** and **7**. Benzonitrile had no effect by itself.

Since we have only been able to obtain **7** in solution, we do not have complete evidence on which to base a structure assignment. The infrared spectrum of **7** in CCl_4 solution in the range 500–4000 cm^{-1} was very similar to that of **6**. In particular the bands at 1538 (s) ($\nu_{C=C}$ coordinated) and 1635 (w) cm^{-1} ($\nu_{C=C}$ uncoordinated) which were observed for **6** were also present in **7**. This and the fact that the differences between the nmr spectra of **6** and **7** were less than the differences for each of them observed in changing solvents (from chloroform to benzene, for example) leads us to the view that the basic structure of **7** is very like that of **6**. In particular, our observation of an uncoordinated double bond in **7** implies that the extra $PdCl_2$ is not π-complexed. Many examples of chloro-palladium complexes adding $PdCl_2$, especially in the absence of Cl^- and in weakly polar solvents, are known.[42–45] The mode of bonding in **7** is not clear;[44,45] one possibility is $Cl(MeC_2Me)_3PdCl \cdot PdCl_2 \cdot PdCl_2 \cdot ClPd(MeC_2Me)_3Cl$, but other formulations, perhaps involving triply bridging chlorines,[45] cannot be ruled out. The molecular size of **7** is not known, but its solubility suggests that it cannot be very large.

The formation of complex **7** from **6** was reversible at ambient temperatures in the presence of an excess of 2-butyne. This reaction occurred most easily in benzene; in chloroform decomposition to HMB competed with the formation of **6**. As a result spectra largely of HMB and complex **7**, but showing the presence of some 30% of complex **6**, were usually seen. However, a clean spectrum (Figure 3) corresponding to complex **6** and HMB could be obtained from solutions of complex **7** in chloroform under very carefully controlled conditions at +20°.

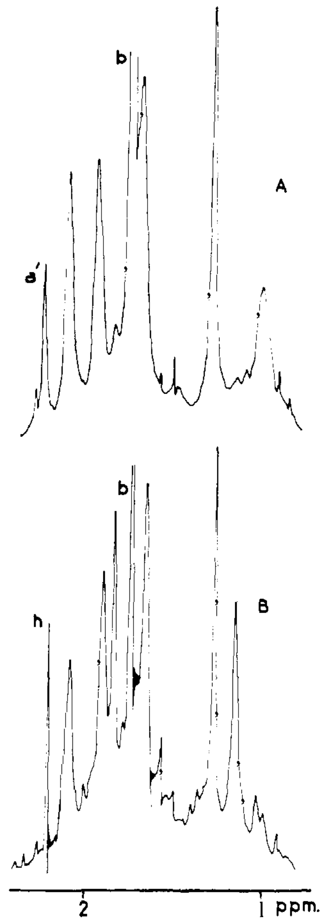

Figure 3. Nmr spectra (100 MHz) of the formation of complex **6** from **7** and 2-butyne in $CHCl_3$: (A) at 0°; (B) at +20° (a', π-complexed 2-butyne; b, free butyne; h, HMB, remaining peaks due to **7** for A, and **6** for B).

Since the decomposition of **7** was much slower in benzene, more satisfactory results were obtained in this solvent. Addition of 2 mol (or more) of $PdCl_2$ (as its bis(benzonitrile) complex) to a solution of **6** in benzene gave a somewhat different spectrum, which corresponded to **7**. On addition of 2-butyne to this at 30°, the spectrum of **6** was regenerated cleanly. Both complexes **6** and **7** in both chloroform and benzene acted as "catalysts" for the trimerization of 2-butyne to HMB.

Complex 8, $MeC_2Me(PdCl_2)_2 \cdot Solv_x$. At temperatures below −40° 2-butyne reacted immediately with $(PhCN)_2PdCl_2$ in chloroform, as shown by nmr studies (Figure 4A). The major peak at δ 1.81 was due to the butyne and that at δ 2.33 arose from a complex, **8**, formed with the metal. That this was an acetylene complex was established by adding triphenylphosphine at −50°. The lower field peak disappeared and the 2-butyne peak increased by a corresponding amount.

The stoichiometry of the acetylene complex **8** was found by varying the amounts of 2-butyne and $(PhCN)_2PdCl_2$ and integrating the areas of the two peaks.[46] The relative concentrations of $(PhCN)_2PdCl_2$ to 2-butyne were varied from 4.1:1 to 0.16:1. In no case did the complex:total palladium ratio exceed 0.45 (Table I), and we therefore believe that in the presence of an excess

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(42) P. M. Maitlis, D. F. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, 43, 470 (1965).

(43) R. Hüttel and H. J. Neugebauer, *Tetrahedron Lett.*, 3541 (1964).

(44) I. Moiseev, M. N. Varagaftik, and Ya. K. Syrkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 775 (1964).

(45) M. Donati and F. Conti, *Inorg. Nucl. Chem. Lett.*, 2, 343 (1966).

(46) The integrations were carried out both using the integrator on the spectrometer and by cutting out and weighing the peaks as recorded on the chart paper. This latter method was preferable in cases where poorly resolved specta were obtained.

Table I. Composition of the 2-Butyne Complex **8** at −40°

Pd(II), mmol/ml	2-Butyne, mmol/ml	Molar ratio $(PhCN)_2PdCl_2$/ MeC_2Me	Molar ratio [**8**]/[total Pd in system]
0.062	0.015	4.1	0.32
0.057	0.030	1.9	0.29
0.050	0.050	1.0	0.32
0.040	0.120	0.33	0.45
0.027	0.092	0.26	0.43
0.012	0.133	0.16	0.40

of 2-butyne, the stoichiometry of this complex is $Me_2C_2(PdCl_2)_2$. We have no evidence on the mode of bonding of the acetylene; it may involve the complexing of the acetylene to two metal atoms. However, in view of the fact that platinum(II) forms a number of monoacetylene complexes of general formula (acetylene)$PtCl_2L$ (L = Cl^- or amine),[47] the alternative possibility must be considered that here too the acetylene is bonded to only one metal atom, the other being linked to the first *via* chloride bridges. A 1:1 acetylene:palladium(II) complex, $[t\text{-}BuC_2\text{-}t\text{-}BuPdCl_2]_2$, has also very recently been reported by Moritani and coworkers.[48]

The molecular size of the complex **8** is also unknown; for simplicity we consider it to be a solvated monomer, $(Me_2C_2(PdCl_2)_2S_x)$ (S = solvent or benzonitrile).

From the values given in Table I we estimate the equilibrium constant for

$$Me_2C_2 + 2PdCl_2 \rightleftharpoons Me_2C_2(PdCl_2)_2$$

to be 1.5 ± 0.3 × 10^2. The equilibrium is established immediately at temperatures as low as −60°.

Mode of Formation of $[Cl(MeC_2Me)_3PdCl]_2$ (6) and $[Cl(MeC_2Me)_3PdCl\cdot PdCl_2]_n$ (7). In a number of experiments, chloroform solutions containing the acetylene π complex $MeC_2Me(PdCl_2)_2S_x$ (**8**) were allowed to warm up in the presence of an excess of butyne, and the reaction was followed by nmr (Figure 4). Reaction was already detectable at −50° over longer periods of time and became significant above −30°. It was marked by the appearance of the spectrum of $[Cl(MeC_2Me)_3PdCl\cdot PdCl_2]_n$ (**7**) (Figure 4B). Above −30°, decomposition of **7** to HMB also began to occur.

No other intermediate species were detectable, but there was a change in the peak due to the π-acetylene complex concurrent with the formation of **7**. This peak, originally at δ 2.33, was replaced by one at δ 2.26 (Figure 4B). While an excess of 2-butyne was present, the intensity of this peak was approximately the same as that of a single methyl peak in the spectrum of **7**. When the 2-butyne concentration fell, the intensity of this peak also decreased rapidly. On addition of more 2-butyne to this solution the δ 2.26 peak was immediately reestablished, though at much greater intensity than had previously been observed. Both this peak and that due to the free 2-butyne again decayed with further reaction. We believe that this peak is also due to a π-acetylene complex, but in this case the acetylene is probably π-bonded to a metal atom of complex **7**.

Eventually, when the reaction mixture was allowed to warm up to *ca.* −14°, the δ 2.26 peak was replaced by the HMB peak at δ 2.23, and new peaks, particularly one at δ 1.13, characteristic of $[Cl(MeC_2Me)_3PdCl]_2$ (**6**), were seen.

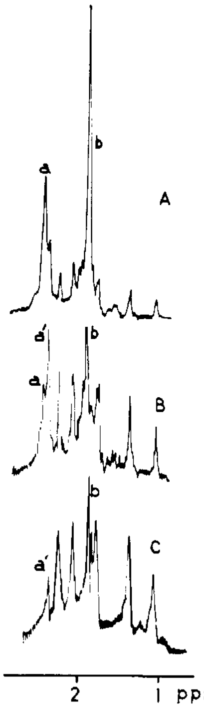

Figure 4. Nmr spectra (100 MHz) of the synthesis of complex **7** in $CHCl_3$: (A) $(PhCN)_2PdCl_2$ + MeC_2Me at −50° (a, π-complexed butyne, **8**; b, free butyne); (B) at −45° (a, π-complexed butyne, **8**; b, free butyne); (B) at −45° (a', new π-complexed butyne; b, free butyne, remaining peaks due to **7**; (C) at −30°.

Some experiments in which the rates of appearance of the peaks due to complex **7** were measured have been carried out. Technical problems severely limited the accuracy of this approach, especially in the region where only a little reaction had occurred. However, at −21° there appeared to be little difference in the rates of formation of $[Cl(MeC_2Me)_3PdCl\cdot PdCl_2]_n$ (**7**), using ratios of $(PhCN)_2PdCl_2$:2-butyne of 3:1 and 0.17:1. If anything, the latter appeared slightly slower. Similar results were obtained at −27°. More detailed work, currently in progress, is needed to completely establish this point, but it does appear that the rate of formation of the trimer complex **7** is not dependent on 2-butyne concentration.

This result is consistent with a mechanism for the formation of **7** from **8** (represented by F in Scheme II) in which the rate-determining step is a chlorine migration from palladium onto an acetylenic carbon giving a σ-vinyl intermediate, G (Scheme II). Further evidence that a process of this type does occur in provided by the structure proposed for **6** (and, by analogy, for **7**), in which a vinylic chlorine is present.

The addition of Pd–X to double and triple bonds is well established and has been shown to occur when X = Ph, Me,[49] OH,[50] OCOR,[51] as well as for Cl.[29,52] The

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[47] 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); G. R. Davies, W. Hewertson, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 423 (1967).

[48] T. Hosokawa, I. Moritani, and S. Nishioka, *Tetrahedron Lett.*, 3833 (1969).

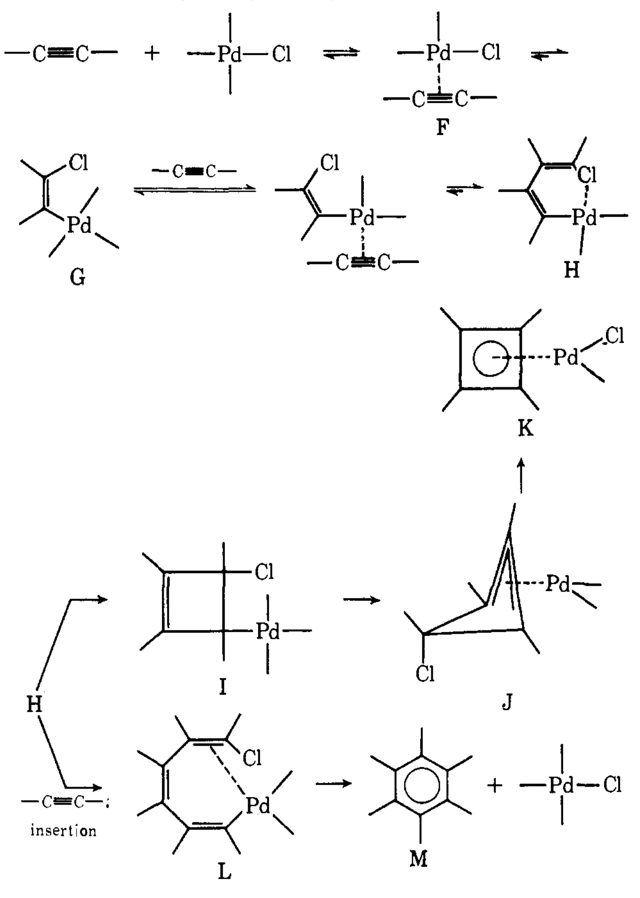
[49] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518, 5526, 5531, 5535, 5538, 5542 (1968); **91**, 6707 (1969).

[50] P. M. Henry, *ibid.*, **86**, 3246 (1964); **88**, 1595 (1966).

[51] P. M. Henry, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**, B15 (1969).

[52] B. L. Shaw, *Chem. Ind.* (London), 1190 (1962); M. Donati and F. Conti, *Tetrahedron Lett.*, 1219 (1966); M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc., A*, 1687 (1966).

Scheme II. Mechanism Proposed for the Reaction of Disubstituted Acetylenes (–C≡C–) with PdCl$_2$



evidence available also suggests that the addition to olefins of Pd–O and Pd–C occurs readily but is less favored for Pd–Cl. Activation, for example, the presence of a conjugated double bond, is normally required here. Acetylenes appear sufficiently activated not to require this.

The mode of addition is probably *cis* in our case[49,53] (nonpolar or weakly polar solvents) but could conceivably be *trans*.[29] This would lead to complexes analogous to **6** and **7** but with the opposite configuration at C$_2$.

Further reaction of the σ-vinyl complex, G, involving complexation with further acetylene and *cis* addition of Pd—C= to the acetylene is expected to be very fast, and all attempts to isolate or detect any further intermediates have failed.

It seems very probable that other disubstituted acetylenes react by a similar stepwise path. Malatesta, *et al.*,[4] one of us in previous papers,[3,5] and others[6–8] have shown that diphenylacetylene reacted with (PhCN)$_2$PdCl$_2$ in aprotic solvents to give hexaphenylbenzene and a tetraphenylcyclobutadiene complex, Ph$_4$C$_4$(PdCl$_2$)$_x$, and in alcohols to give *endo*-alkoxytetraphenylcyclobutenyl complexes, [ROPh$_4$C$_4$PdCl]$_2$.[54]

These facts can be accommodated by the reactions outlined in Scheme II, if it is postulated the extent to which the σ-vinyl intermediate H reacts further with acetylenes is governed by the size of the acetylenic substituents. Thus, for big substituents such as phenyl or *t*-butyl[55] further reaction ceases to an appreciable degree when two acetylenes have been allowed to react, whereas for smaller substituents such as methyl, units smaller than trimers have not been isolated.[56] In the former case a cyclization to an inactive cyclobutenyl or cyclobutadiene complex (J or K) occurs. We have previously shown that tetraphenylcyclobutadienepalladium complexes are not intermediates in the formation of hexaphenylbenzene.[3,57] Tetramethylcyclobutadienepalladium chloride is not known, but the low reactivity of cyclobutadiene–metal complexes toward reactions of this type is well documented.[58] We therefore prefer to regard the complexes containing acetylenic dimers as well as those containing acetylenic trimers as arising from a common intermediate, H.

The mode by which cyclization H → I or L → M (for example, [Cl(MeC$_2$Me)$_3$PdCl]$_2$ to HMB) occurs is not known, but one route for the latter is discussed in the following paper.[60] The role which the extra PdCl$_2$ plays in the reactions **8** → **7** → **6** is not clear. The isolation of cyclobutadiene complexes R$_4$C$_4$(PdCl$_2$)$_x$ (x = 2, 3, etc.)[5,7] from the reactions of diphenylacetylenes (RC$_2$R) with (PhCN)$_2$PdCl$_2$ suggests this effect to be widespread. In the absence of evidence to the contrary, however, we are tempted not to ascribe any profound mechanistic significance to it, but merely to regard the complexes MeC$_2$Me(PdCl$_2$)$_2$S$_x$ (**8**) and [Cl(MeC$_2$Me)$_3$PdCl·PdCl$_2$]$_2$ (**7**) (rather than [MeC$_2$MePdCl$_2$]$_2$ or [Cl(MeC$_2$Me)$_3$PdCl]$_2$ (**6**), respectively) as arising because of some solvation effect.

Formation of the "Abnormal" Hexasubstituted Benzenes. As mentioned above, a minor product from the (PhCN)$_2$PdCl$_2$-catalyzed trimerization of methylphenylacetylene was 1,2,3-trimethyl-4,5,6-triphenylbenzene (**4**). Furthermore, the elegant work of Whitesides and Ehmann has shown that isomer **10** is formed to the extent of *ca.* 10% in the (PhCN)$_2$PdCl$_2$-catalyzed trimerization of CD$_3$C≡CCH$_3$ in benzene at 80°.[61] In some cooperative experiments, Whitesides and Ehmann obtained very similar results on three samples of C$_6$(CH$_3$)$_3$(CD$_3$)$_3$ which we had prepared from CD$_3$C≡CCH$_3$ at lower temperatures under different conditions.[62]

The formation of these abnormal isomers, **4** and **10**, cannot be explained by the mechanism proposed (Scheme II), unless the decomposition L → M is a complex reaction during which scrambling occurs. There

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[53] P. Cossee, *Rec. Trav. Chim.*, **85**, 1151 (1966); B. L. Shaw, *Chem. Commun.*, 464 (1968).

[54] (a) L. F. Dahl and W. E. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965). (b) Scheme II can also very easily explain the formation of the alkoxycyclobutenyl complexes [ROPh$_4$C$_4$PdCl]$_2$, if the reactive palladium complex is now RO–Pd< ($>$PdCl + ROH → $>$PdOR + HCl). In this case reaction ceases at a complex equivalent to J (OR in place of Cl).

[55] T. Hosokawa and I. Moritani (*Tetrahedron Lett.*, 3021 (1969)) have obtained the 1,2-di-*t*-butyl-3,4-diphenylcyclobutadienepalladium chloride complex from PhC≡CBu-*t* and (PhCN)$_2$PdCl$_2$ in benzene.

[56] The nature of the substituents, whether electron releasing or withdrawing, must also be important. We have too little evidence on which to comment on this at present, but we feel that this may prove to be of secondary importance to the size factor.

[57] D. Pollock and P. M. Maitlis, *Can. J. Chem.*, 44, 2673 (1966).

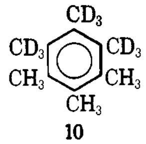
[58] For example, Reeves, *et al.*,[59] have recently prepared π-maleate and π-fumarate complexes of dicarbonylcyclobutadieneiron, and there appears to be no reaction between the dienophile and the diene until the complex is decomposed by an external reagent, *e.g.*, Ce(IV).

[59] P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969).

[60] H. Reinheimer, J. Moffat, and P. M. Maitlis, *ibid.*, **92**, 2285 (1970).

[61] G. M. Whitesides and W. J. Ehmann, *ibid.*, **91**, 3800 (1969).

[62] Although we were unable to find any of the isomer **4** in the products of the decomposition of [Cl(MeC$_2$Ph)$_3$PdCl]$_2$ (**5**), the amount of it expected and the difficulties involved in isolating or detecting it do not justify the conclusion that it is not formed from **5**. Furthermore, a sample of [Cl(CD$_3$C$_2$CH$_3$)$_3$PdCl]$_2$ from CD$_3$C≡CCH$_3$ was shown to give C$_6$(CH$_3$)$_3$(CD$_3$)$_3$ containing 10.2 ± 0.5% of the isomer **10**.



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is some evidence in support of this; we observed that on heating a solution of $[Cl(MeC_2Me)_3PdCl]_2$ (**6**) in benzene in an nmr tube to 60° some coalescence of the peaks did occur (Figure 5). This was reversible, on cooling, but unfortunately decomposition to complex **7** and to HMB was fast under these conditions and prevented our observation of a limiting high-temperature spectrum. Evidence presented in the following paper, in which it is shown that an averaging process occurs when **6** is treated with PPh_3 or $AsPh_3$, also lends support to this idea.[60]

Formation of Tetramers in the Reactions of Acetylenes with $(PhCN)_2PdCl_2$. In the reaction of 2-butyne with $(PhCN)_2PdCl_2$ in benzene, complex **6** accounted for rather more than 50% of the metal used. Other products, including some HMB and other metal complexes, were also formed. After removal of complex **6** by crystallization from the reaction, the mother liquors were treated with hydrazine to destroy the remaining complexes. The metal was removed and the organic compounds were analyzed by vpc. The first component, 10%, was vinylpentamethylcyclopentadiene, which arose from **6**.[60] Three other materials were formed in large enough amounts for identification and included two of composition $C_{16}H_{23}Cl$ (7 and 55%, respectively) and one of composition $C_{16}H_{22}$ (25%). The structures of these materials are not known, but their isolation shows that tetramers can be formed in this reaction under some conditions. No tetramers were obtained in the reactions of diphenylacetylene or phenylmethylacetylene with $(PhCN)_2PdCl_2$. However, Zingales has reported the isolation of complexes containing tetramers from reaction of ethylphenylacetylene and $PdCl_4^{2-}$ in methanol.[63] The structures of these complexes are far from clear.

Interestingly, we obtained no evidence for the formation of tetramers from the reaction of 2-butyne with $(PhCN)_2PdCl_2$ in chloroform or with complexes **6** or **7**.

Mechanism of the Trimerization of Acetylenes with $PdCl_2$. A number of different mechanisms have been advanced to account for the cyclotrimerization of acetylenes on metal complex catalysts. The main ones are, in brief, (i) a concerted process whereby three acetylenes come together at a metal atom and then combine,[64] (ii) a reaction *via* a metalacyclopentadiene,[1,65–67] (iii) a reaction *via* cyclobutadiene and Dewar benzene complexes,[68,69] or (iv) a stepwise reaction *via* a metal hydride intermediate.[70]

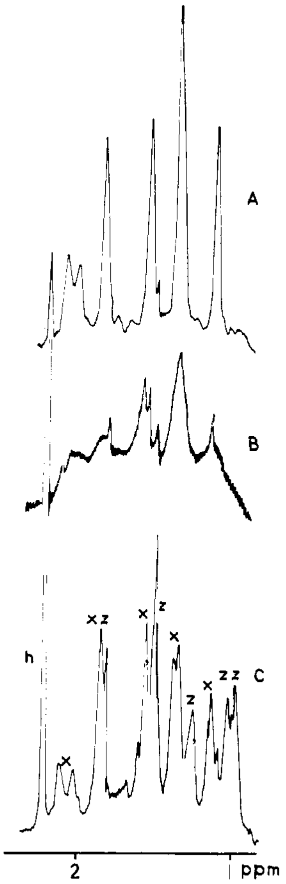

Figure 5. Nmr spectra (100 MHz) of complex **6** in benzene: (A) at +34°; (B) at + 60°; (C) after cooling to +34° again (h, HMB; x, complex **6**; z, complex **7**).

The mechanism proposed here is a novel variant of the last of these originally proposed by Meriwether, *et al.*, for nickel-catalyzed oligomerization of monosubstituted acetylenes.[70] Although a Pd–H intermediate does not appear to be implicated in the reactions discussed here, it may well be of importance in other reactions, for example, of RC≡CH.

It is clear that no single mechanism will serve to explain all cyclotrimerization reactions. For a number of reasons, reactions of this type are very difficult to unravel. Until now reaction mechanism proposals have been based on the structures of complexes isolated from such reactions and presumed to be intermediates. We anticipate that the reactions described here will prove simpler to disentangle than many others and feel that we have arrived at the point where meaningful kinetic studies can be initiated.[71]

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(63) F. Zingales, *Ann. Chim.* (Rome), **52**, 1174 (1962).

(64) G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem. Int. Ed. Engl.*, **3**, 185 (1964); G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 550 (1962).

(65) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **7**, P22 (1967).

(66) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968).

(67) L. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 7292 (1969).

(68) P. M. Maitlis, *Advan. Organomental. Chem.*, **4**, 138 (1966).

(69) A. N. Nesmeyanov, A. I. Gusev., A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 739 (1969).

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

(71) NOTE ADDED IN PROOF. A recent paper by Avram, *et al.*,[72] reported the isolation of $[(t\text{-}BuC_2H)_3PdCl_2]$ from reaction of *t*-BuC≡CH and $(PhCN)_2PdCl_2$ in benzene. These authors formulated the complex as a *monomeric* tri-*t*-butyl(Dewar benzene)palladium chloride complex largely on the basis of the pmr spectrum. A reinvestigation of this complex, currently being carried out by Dr. K. L. Kaiser of this laboratory, however, shows it to be *dimeric*, and to have properties quite different from those associated with known (Dewar benzene)palladium chloride complexes.[73,74] It should also be pointed out that hexamethyl(Dewar benzene)palladium chloride has been prepared by us[73] and is quite different from 6.

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

(73) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967).

(74) E. E. van Tamelen and D. Carty, *J. Amer. Chem. Soc.*, **89**, 3922 (1967).

Experimental Section

All reactions were carried out under nitrogen using pure, dry, degassed solvents. Chloroform was purified from ethanol by distilling from phosphorus pentoxide. Methylphenylacetylene (Columbia) was redistilled and checked for purity by vpc. Pure 2-butyne was purchased from Farchan. In some of the experiments, a crude 2-butyne, obtained from Air Reduction, was used. This material was carefully fractionated before use, that fraction boiling between 27 and 29° being collected. A persistent and objectionable impurity here was dimethyl sulfide which was removed by shaking the 2-butyne with solid palladium chloride for a while. The material obtained after redistillation was pure by nmr and vpc analysis.

Nmr spectra were recorded on Varian T-60, A-60, and HA-100 instruments. The spectra were originally calibrated against internal TMS, but in the more accurate work calibration was against internal hexamethylbenzene, the chemical shift of which also appeared relatively insensitive to solvent changes. Infrared spectra were recorded on Beckman IR-5, Perkin-Elmer 337G, and also, in the region 200–600 cm^{-1}, on a Perkin-Elmer IR-12. Vpc analysis was carried out on a Varian A90-P3 gas chromatograph using columns of SE30 or Carbowax 20M on 60–80 Chromosorb W for both analytical and preparative purposes.

Reaction of Methylphenylacetylene with Bis(benzonitrile)palladium Chloride in Methylene Chloride. Methylphenylacetylene (1.25 g, 12 mmol) in 5 ml of methylene chloride was added to a solution of 0.93 g (2.4 mmol) of **1** in 30 ml of methylene chloride at +20°. The solution was stirred at 20° for 4 hr. At the end of this time the solution was dark brown but contained no precipitate. It was poured into 300 ml of light petroleum (bp 30–60°) to give a brown precipitate (0.72 g) which contained chlorine and some 90% of the total palladium used. *Anal.* Found: Pd, 31.5. The filtrate was evaporated to dryness to leave a pale brown solid. This was dissolved in a 20 ml of hot methylene chloride to which 0.5 g of charcoal was added (to remove the remaining complex). The mixture was filtered and allowed to crystallize at −15°. Colorless needles (0.31 g) were obtained of a material with mp 320°, identified as 1,3,5-trimethyl-2,4,6-triphenylbenzene (**2**)[16] by its pmr[17] and mass spectrum. *Anal.* Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94; mol wt, 348. Found: C, 93.17; H, 6.73; mol wt, 348.

The mother liquors were evaporated to dryness, leaving an oily crystalline residue which was washed with 20 ml of light petroleum at −15°. The solid obtained (0.53 g) was largely **3**, as determined from its pmr spectrum, but contained about 8% of isomer **2**. This was recrystallized from a large volume of methanol to give needles of 1,2,4-trimethyl-3,5,6-triphenylbenzene (**3**), mp 223°.[16,17] *Anal.* Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94; mol wt, 348. Found: C, 91.59; H, 6.66; mol wt, 348 (mass spectroscopic).

The light petroleum washings from **3** were taken to dryness to leave an oil containing some benzonitrile. A few drops of ethanol were added and the solution left at −15° for 18 hr. Colorless needles (35 mg), largely of **4** but still containing *ca.* 15% of **3** (by nmr), were obtained. This was recrystallized from ethanol to give 1,2,3-trimethyl-4,5,6-triphenylbenzene (**4**), mp 155°, identified by analysis and mass and pmr spectra. *Anal.* Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94; mol wt, 348. Found: C, 92.49; H, 7.40; mol wt, 348 (mass spectroscopic), 354 (osmometric, in chloroform).

The catalytic trimerization was also carried out using **1** as catalyst in refluxing methylene chloride for 3 hr (63 mol trimerized) and in refluxing benzene for 2.5 hr (66 mol trimerized), and using **5** as catalyst in refluxing methylene chloride for 2 hr (72 mol trimerized) or in benzene at 20° (2 days, 16 mol trimerized).

Reaction of Methylphenylacetylene with Bis(benzonitrile)palladium Chloride in Benzene. It is essential to use bis(benzonitrile)-palladium chloride (**1**) prepared from AR reagents in order to obtain good yields of **5** and **6** in these reactions. Complex **1** must also be washed several times with hexane and air-dried for 5 min immediately before use.

Bis(benzonitrile)palladium chloride (6.05 g, 16 mmol) was dissolved in 150 ml of benzene and filtered. To this solution was then added, with stirring, a solution of 7.0 g (60 mmol) of methylphenylacetylene in 30 ml of benzene. The solution was stirred for 5 hr and then filtered and the volume reduced to 50 ml on a rotary evaporator. Light petroleum (300 ml) was added, with stirring, to the benzene solution to give 5.1 g (9.7 mmol, 61%) of a yellow solid. The freshly precipitated solid was shown to be $[(MeC_2Ph)_3PdCl_2]_2$ (**5**). *Anal.* Calcd for $C_{54}H_{48}Cl_4Pd_2$: C, 61.68; H, 4.60; Cl, 13.49; Pd, 20.24; mol wt, 1052. Found: C, 62.16; H, 4.76; Cl, 12.95; Pd, 20.4; mol wt, 1020 (osmometric, in benzene).

Samples reprecipitated from benzene solution by light petroleum gave significantly worse analyses. *Anal.* Found: C, 58.84; H, 4.57; Cl, 14.35; and, on another sample, C, 50.06; H, 4.18; Cl, 18.26; Pd, 27.60.

The light petroleum mother liquors from **5** were taken to dryness and dissolved in a small volume of benzene. On addition of light petroleum, more (2.4 g) of complex **5**, but of poorer quality and darker in color, was obtained. When all the complex had been precipitated and removed, the mother liquors were examined as described above. All three trimethyltriphenylbenzene isomers, in approximately the same ratios, were present.

Decomposition of the Complex $[(MeC_2Ph)_3PdCl_2]_2$ (5). In the solid, complex **5** turned brown at around 100° and decomposition was complete at 140°. In methylene chloride or chloroform decomposition occurred rapidly at 20° and could be followed in an nmr tube. The products, in each case, were palladium chloride, identified by analysis, and 1,2,4-trimethyl-3,5,6-triphenylbenzene (**2**), and 1,3,5-trimethyl-2,4,6-triphenylbenzene (**3**) in a 3:2 ratio.

Analogous results were obtained on treatment of **5** in benzene with triphenylphosphine, benzonitrile, or acetonitrile. In each case **2** and **3**, together with the appropriate palladium chloride complex, were isolated.

Formation of the Complex $[Cl(Me_2C_2)_3PdCl]_2$ (6) in Benzene. Bis(benzonitrile)palladium chloride (**1**) (10 g, 26.8 mmol) was washed by stirring it in 100 ml of light petroleum (bp 30–60°) for 15 min, then collected on a filter, washed with three more portions of light petroleum, and air dried for 5 min.

Benzene (400 ml) was saturated with nitrogen at 20°,[75] 2-butyne (13.5 ml, 170 mmol) was added, and the solution was cooled to 5° in an ice bath. The solid complex **1** was now added in small portions over 15 min. This was accompanied by a rise in temperature, which did not exceed 15°. When the temperature had again dropped to 5°, the solution was filtered from a small amount of insoluble material.

The benzene was then removed on a rotary evaporator at 30° to leave an oil. To this was added 150 ml of light petroleum containing 5 ml of 2-butyne. The solution was shaken and filtered to remove some pale yellow solid. It was then resaturated with nitrogen and left to stand, with occasional shaking, at −10 to −15°. After 5 hr a bright yellow microcrystalline powder, $[Cl(MeC_2Me)_3PdCl]_2$ (**6**), was collected on a filter.

The solvent was again removed from the mother liquors and 50 ml of a light petroleum–2-butyne mixture (25:1) was added. This solution was cooled to −75° to precipitate a solid. This product was the same as the above, **6**, but of somewhat lower purity, total yield 4.4 g (49%). The solid decomposed at 100° in capillary to give hexamethylbenzene (sublimate) and left a residue of palladium chloride. *Anal.* Calcd for $C_{24}H_{36}Cl_4Pd_2$: C, 42.44; H, 5.34; Cl, 20.88; Pd, 31.33; mol wt, 679. Found: C, 42.20; H, 5.55; Cl, 20.68; Pd, 31.0; mol wt, 673, 678 (osmometric in benzene).

The pmr spectrum (100 MHz) showed resonances (of equal intensity except where stated) at δ 1.13, 1.28, 1.69, 1.87, 1.95, 2.18 (in $CDCl_3$ at 34°); 1.14, 1.27, 1.66, 1.83, 1.92, 2.10 (in $CDCl_3$ at 0°). On cooling this solution further, irregular splittings of these peaks occurred until, at *ca.* −70°, resonances of unequal intensities at δ 1.11, 1.16, 1.27, 1.38, 1.54, 1.66, 1.79, 1.80, 1.85, 1.92, 1.94, 2.04, 2.12, and 2.16 were observed (Figure 2). Attempts to go still lower failed owing to crystallization of the complex. In the range −60 to +34° considerable sharpening of the peaks with increase in temperature was observed. In benzene at 34° resonances at δ 1.14, 1.37, 1.39, 1.58, 1.87, 2.04, and 2.12 were observed in the ratios 2:2:2:2:2:1:1. On warming this solution to 60°, the two lowest field peaks coalesced, and the others broadened considerably.

On holding a solution of **6** in chloroform at 34°, a change in the nmr spectrum was observed. This led to the growth of a singlet at δ 2.23 due to hexamethylbenzene and a slow change in the spectrum of the complex. After approximately half of complex **6** had decomposed, a spectrum (corresponding to **7**) with equal intensity resonances (100 MHz) at δ 0.99, 1.25, 1.67, 1.69, 1.92, and 2.06 was observed. An identical spectrum could be produced by adding 2 mol of bis(benzonitrile)palladium chloride to **6**. This reaction also occurred in benzene to give resonances (equal intensity at 10°, 100 MHz) at δ 0.99, 1.04, 1.27, 1.50, 1.52, and 1.87. At +34° the resonances at 1.50 and 1.52 were not resolved.

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(75) It was found that passage of a slow stream of dry HCl gas through the benzene for 1 min before addition of the butyne frequently led to a cleaner and more easily isolable product. It did not appear to affect the yield of 6.

On heating a benzene solution of **6** to 60°, considerable broadening and coalescence and the formation of HMB was observed (Figure 5). When this was cooled to 34°, the resonances of **6** at δ 1.13, 1.36, 1.39, 1.57, 1.86, 2.03, and 2.14 and those of **7** at δ 0.98, 1.03, 1.26 (overlap with **6** resonances at 1.57, 1.86) and that of HMB (2.23) were distinguished.

Reduction of the Mother Liquors from the Precipitation of 6. The solvent was removed from the mother liquors, the oil remaining (*ca.* 13 ml) was stirred with 15 ml of benzene, and an excess of anhydrous hydrazine was added. Metallic palladium precipitated and was removed by filtration. The solvent was removed and the oil remaining was chromatographed over alumina using light petroleum as solvent to remove impurities and HMB. A pale yellow oil (2.0 g) was obtained and was shown to consist of four fractions by vpc. Samples of each of these fractions were collected by preparative vpc using a 5-ft column (0.25 in.) of 20% SE30 at 185°.

Fraction i (*ca.* 10%, 3 min) was identified by its nmr spectrum as vinylpentamethylcyclopentadiene, the product obtained by hydrazine reduction of **6** (see following paper).

Fraction ii (*ca.* 7%, 4.5 min) was obtained in too small amount for complete characterization. From its mass spectrum, it appeared to be an isomer of fraction iv below.

Fraction iii (*ca.* 25%, 13 min) was an oil with analysis corresponding to $C_{16}H_{22}$. *Anal.* Calcd for $C_{16}H_{22}$: C, 89.75; H, 10.25; mol wt, 214. Found: C, 89.27; H, 10.55; mol wt, 214 (mass spectroscopic).

Fraction iv (*ca.* 55%, 19 min) was a yellow oil with molecular formula corresponding to $C_{16}H_{25}Cl$. *Anal.* Calcd for $C_{16}H_{25}Cl$: C, 76.01; H, 9.97; Cl, 14.02; mol wt, 252. Found: C, 75.91; H, 9.99; Cl, 14.26; mol wt, 252 (mass spectroscopic), 258 (osmometric in benzene).

The pmr spectra of iii and iv were recorded but were very complex, showing a large number of resonances in the methyl region.

Formation of $[Cl(MeC_2Me)_3PdCl\cdot PdCl_2]_n$ (7) from 2-Butyne and $(PhCN)_2PdCl_2$ in $CDCl_3$. Solutions were made up containing 228 mg (0.6 mmol) of $(PhCN)_2PdCl_2$ in 10 ml of $CDCl_3$ and 108 mg (2.0 mmol) of 2-butyne in 10 ml of $CDCl_3$. The solutions were cooled to −78° and four mixtures were made up in nmr tubes each containing 0.3 ml of the solution of $(PhCN)_2PdCl_2$ and (A) 0.03 ml, (B) 0.1 ml, (C) 0.3 ml, and (D) of 0.6 ml of the 2-butyne solution. The tubes were shaken at −78° to ensure mixing and then allowed to come to equilibrium in the probe of the 60-MHz nmr spectrometer. Spectra were drawn out at regular intervals, and after completion of the runs the peaks corresponding to $[Cl(MeC_2Me)_3PdCl\cdot PdCl_2]_n$ (**7**) were cut out and weighed. In this case this method was preferable to integration since the peaks were rather small and broad, particularly at the beginning of the run. Mixtures A and D were allowed to react at −21° and the peak weights (mg) obtained were (time in minutes in parentheses): (A) 9.8 (3), 13.1 (6), 17.8 (9), 14.5 (12), 18.2 (15), 18.9 (18), 18.2 (27), 19.4 (39); (D) 10.8 (6), 14.0 (10), 14.8 (14), 15.7 (20), 15.9 (30), 16.9 (50), and 17.3 (60). Similar results but rather slower rates were observed for B and C at −27°.

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Reactions of Acetylenes with Noble-Metal Halides. IX.[1] The Decomposition of the Complex $[Cl(Me_2C_2)_3PdCl]_2$, Particularly to Vinylpentamethylcyclopentadiene

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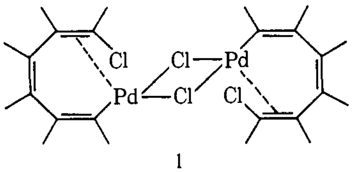
Abstract: The reaction of the previously reported complex $[Cl(MeC_2Me)_3PdCl]_2$ (**1**) with triphenylphosphine, -arsine, and -stibine gave hexamethylbenzene (HMB), vinylpentamethylcyclopentadiene (VCP), and 1-chlorovinylpentamethylcyclopentadiene (CVCP). The CVCP was formed at higher temperatures; below 0°, VCP, together with a small amount of HMB, was the only organic product. The reaction of **1** with triphenylphosphine was studied by nmr from −60 to +30°. Two reaction paths were found. One, at a phosphine:palladium ratio of 2, involved (i) cyclization to a five-membered ring, (ii) an averaging of five methyl groups by a "cyclopropane merry-go-round" process, and (iii) decomposition of this to VCP and HMB. The second path predominated at phosphine:palladium ratios of 4 and over. Step i is the same as above, but no averaging process occurred on raising the temperature. Instead, a new species stable to −10° was detected in step ii. This species, identified as 1-[chloro-*cis*-bis(triphenylphosphine)palladium]vinyl-1,2,3,4,5-pentamethylcyclopentadiene (**4**), arose from the five-membered ring intermediate in (i) by loss of a proton. In step iii at higher temperatures, **4** reacted with the proton to give VCP and HMB again. The reaction with triphenylarsine (and probably that with triphenylstibine) proceeded in a similar fashion to the first reaction path. *o*-Phenanthroline reacted with **1** to give a stable complex identified as 1-[chloro(*o*-phenanthroline)palladium]vinyl-1,2,3,4,5-pentamethylcyclopentadiene. Complex **1** was decomposed by halogens to HMB; hydrazine gave VCP; lithium aluminum hydride gave largely ethylpentamethylcyclopentadiene; and ethanol or dimethyl sulfoxide gave acetylpentamethylcyclopentadiene. The mechanisms of some of these reactions are discussed.

In the preceding paper[1] we reported on the synthesis of a novel type of complex, $[Cl(Me_2C_2)_3PdCl]_2$ (**1**), from the trimerization of 2-butyne by palladium chloride (as its bis(benzonitrile) complex) in benzene. From its mode of formation, analysis, and spectroscopic properties, as well as its ready decomposition to hexamethylbenzene (HMB) in halogenated solvents, we concluded that its structure was best formulated as



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[1] Part VIII: H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **92**, 2276 (1970).

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