

(ca. 1.7–1.8 eV). Thus any triplets produced by the reaction would end up as  $^3\text{DPA}^*$  which could undergo triplet–triplet annihilation, producing  $^1\text{DPA}^*$ . This cannot be the sole route, because of the absence of a significant magnetic field effect, but it could account for perhaps 35% of the intensity.

The results obtained with PPD and PPO are less clear as we do not know anything about the triplets in these systems but they may well lie below TH and (3) may apply. The reduction of phenanthrene is close to the solvent–electrolyte background level and the anion is not stable.

To sum up, the author has presented a hypothesis which is unsubstantiated by the data selected to support it. The basic phenomenon of a wavelength effect in fluorescence quantum yields is not discussed correctly in terms of existing knowledge and our experiment indicates that it is not a significant factor.

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Received October 18, 1974

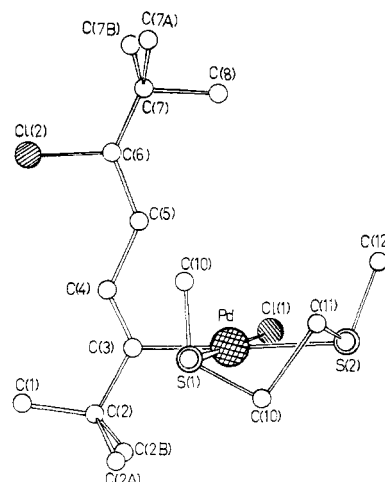
## A Definitive Example of Cis Chloropalladation. The Structure of Chloro(2,5-dithiahexane)-{1-(1,4-di-*tert*-butyl-4-chloro)butadienyl}palladium

Sir:

We report the preparation and structure of a complex derived from the  $\text{PdCl}_2$  induced dimerization of *tert*-butylacetylene, which has several novel features and which also shows that a cis chloropalladation of the acetylene occurs in the first step.

The stereochemistry and mechanism of the addition of  $\text{PdCl}$  to mono- and diolefins and acetylenes are the subject of considerable controversy. For monoolefins Henry<sup>1</sup> has shown that the  $\text{Pd}_2\text{Cl}_6^{2-}$  catalyzed exchange of chloride between vinylic chlorides and  $\text{LiCl}$  in acetic acid occurs non-stereospecifically and has suggested that cis chloropalladation is more important than trans chloropalladation in the initial step. Both stereospecific cis<sup>2</sup> and stereospecific trans<sup>3</sup> chloropalladation of diolefins in aprotic solvents have been reported, and Yukawa and Tsutsumi<sup>4</sup> have described the trans addition of  $\text{Pd-Cl}$  to the acetylenes  $\text{PhC}\equiv\text{CCH}_2\text{NMe}_2$  and  $\text{HC}\equiv\text{CCMe}_2\text{NMe}_2$  in methanol in the presence of  $\text{LiCl}$ .

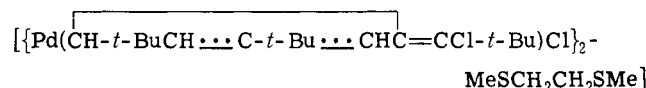
It has been proposed that the oligomerization of acetylenes with  $\text{PdCl}_2(\text{PhCN})_2$  in aprotic solvents (typically benzene or dichloromethane) occurs in a stepwise manner, the first, rate determining, step of which is a cis chloropalladation of the coordinated acetylene.<sup>5</sup> In order to study the mechanism further, the reaction of the hindered *tert*-butylacetylene (**1**) was examined in detail.  $\text{PdCl}_2(\text{PhCN})_2$ , in solvents such as  $\text{C}_6\text{H}_6$ ,  $\text{CH}_2\text{Cl}_2$ , or  $\text{CHCl}_3$  at  $20^\circ$ , has recently been shown to react with **1** to give the interconverting isomers **2a** and **2b**.<sup>6</sup> A kinetic study of the formation reaction by NMR at  $-20^\circ$  in  $\text{CDCl}_3$ <sup>7</sup> showed complicated behavior owing to the existence of a preequilibrium involving a metal  $\pi$ -acetylene complex,<sup>8</sup> but a plot of  $\log [1]$  vs. time gave a straight line up to the point where 3 equiv of **1** per  $\text{Pd}$  had been consumed; thereafter the rate slowed down



**Figure 1.** The structure of chloro(2,5-dithiahexane){1-(1,4-di-*tert*-butyl-4-chloro)butadienyl}palladium (**3**). Bond lengths (esd's in parentheses) are:  $\text{Pd-Cl}(1)$ , 2.333 (7);  $\text{Pd-S}(1)$ , 2.268 (7);  $\text{Pd-S}(2)$ , 2.400 (7);  $\text{Pd-C}(3)$ , 2.06 (2);  $\text{C}(3)\text{-C}(4)$ , 1.31 (3);  $\text{C}(4)\text{-C}(5)$ , 1.46 (3);  $\text{C}(5)\text{-C}(6)$ , 1.36 (3) Å. Bond angles are:  $\text{S}(1)\text{PdS}(2)$ ,  $88^\circ$ ;  $\text{S}(1)\text{PdC}(3)$ ,  $90^\circ$ ;  $\text{S}(2)\text{PdCl}(1)$ ,  $90^\circ$ ;  $\text{Cl}(1)\text{PdC}(3)$ ,  $91^\circ$ ;  $\text{PdC}(3)\text{C}(4)$ ,  $118^\circ$ ;  $\text{C}(3)\text{C}(4)\text{C}(5)$ ,  $125^\circ$ ;  $\text{C}(4)\text{C}(5)\text{C}(6)$ ,  $127^\circ$ ;  $\text{C}(2)\text{C}(3)\text{Pd}$ ,  $118^\circ$ ;  $\text{C}(2)\text{C}(3)\text{C}(4)$ ,  $125^\circ$ ;  $\text{C}(5)\text{C}(6)\text{Cl}(2)$ ,  $117^\circ$ ;  $\text{Cl}(2)\text{C}(6)\text{C}(7)$ ,  $116^\circ$ ;  $\text{C}(5)\text{C}(6)\text{C}(7)$ ,  $127^\circ$ .

by a factor of ca. 10 and the formation of **2** began to be detected.

The reaction was repeated on a preparative scale in toluene at  $-10^\circ$ . After 30 min, the solution was divided into two equal portions. The one was allowed to stand for 6 hr at  $20^\circ$ ; after addition of 2,5-dithiahexane an 86% isolated yield of the dithiahexane adduct of **2b**

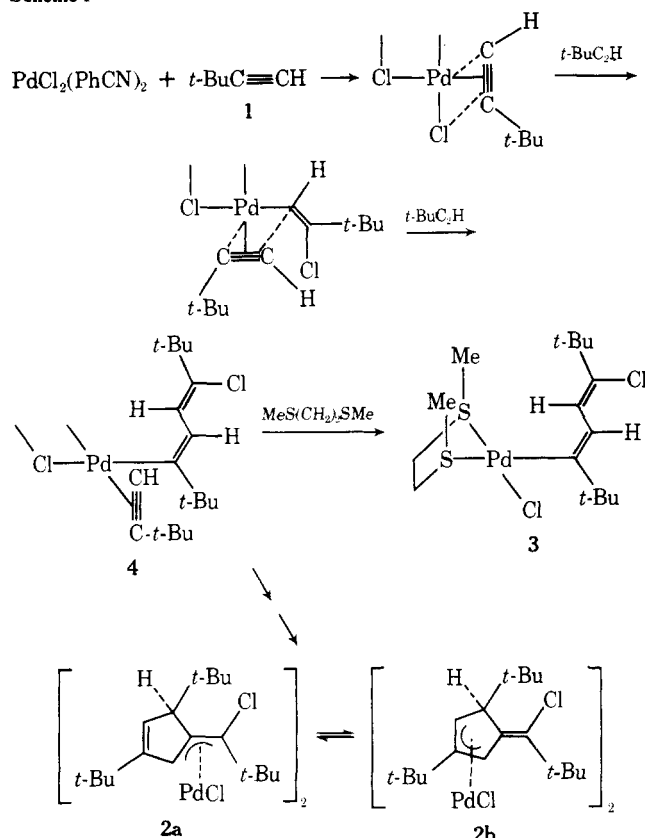


was obtained. The other portion was treated with 2,5-dithiahexane immediately and gave a 60% isolated yield of a complex (**3**) which was shown by analysis, molecular weight determination, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR and ir spectroscopy to be  $[\text{Pd}\{\text{C-}t\text{-Bu}=\text{CHCH}=\text{CCl-}t\text{-Bu}\}\text{Cl}\{\text{MeSCH}_2\text{CH}_2\text{SMe}\}]$ . This was confirmed by an X-ray crystal structure determination: crystal data,  $\text{C}_{16}\text{H}_{30}\text{Cl}_2\text{PdS}_2$ ; mol wt, 463.8; crystals are trigonal with  $a = 25.62$ ,  $c = 18.32$  Å (hexagonal setting); space group  $R\bar{3}$ ;  $Z = 18$ . The structural analysis was based on Fourier and least-squares analysis of 1306 reflections which were observed using a Stoe STADI 2 diffractometer (Mo  $K\alpha$  radiation) having  $F^2 \geq 3\sigma(F^2)$ .  $R$  has converged to 0.070.

The significant features of the structure are shown (Figure 1). The  $\text{Pd}$  is square planar, two (cis) coordination sites are occupied by the two S's of the dithiahexane, one by a terminal Cl, and the remaining one by the  $\sigma$ -butadienyl ligand. It is clear that two acetylenes have been linked tail-to-tail and that both have reacted in a cis manner.

Although this is the first case where a dienylnpalladium complex has been isolated, the intermediacy of such complexes has been predicted in previous discussions of the general mechanism of palladium(II) induced acetylene trimerization,<sup>5</sup> in which the first step was proposed to be a cis chloropalladation and the second a cis vinylpalladation of the coordinated acetylene. Scheme I shows the suggested mechanism for reaction of **1**. Since the kinetic data show that three molecules of **1** are consumed in the first stages, we presume that the intermediate (**4**) has the same  $\sigma$ -butadienyl ligand as **3** but that an additional acetylene is coordinated to the metal. Steric effects can be expected to slow

Scheme I



down the reaction of the Pd-butadienyl  $\sigma$ -bond with the coordinated acetylene in 4 thereby making it possible to isolate derivatives such as 3; however, 4 is clearly an intermediate in the formation of 2. The probable mechanism of this latter type of transformation has already been described in general terms<sup>5</sup> and will be further discussed in a full paper.

A noteworthy feature of the structure of 3 is an angle of  $89.5^\circ$  between the plane defined by the atoms Pd, S(1), S(2), Cl(1), and C(3) (rms deviation 0.031 Å) and the plane defined by C(3), C(4), C(5), and C(6) (rms deviation 0.026 Å). The distance of the hydrogen on C(5) (calculated assuming a trigonal geometry around C(5)) from the metal is 2.63 Å, and the angle H(5)–Pd–C(3) is  $68^\circ$ ; this, together with the observation that the NMR resonance of this hydrogen is at anomalously low field ( $\delta$  7.18), indicates the possibility of an interaction between the metal and this hydrogen both in the solid state and in solution.<sup>9,10</sup>

**Acknowledgment.** We thank the University of Sheffield for the award of a Junior Research Fellowship (to P.M.B.), the Science Research Council for support of this work, and I.C.I. Ltd. for a grant.

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- Containing 2.5% PhCN (v/v) to inhibit dissociation of  $\text{PdCl}_2(\text{PhCN})_2$ .
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(10) NOTE ADDED IN PROOF. We have recently shown that a sample of complex 3, made from  $(\text{CH}_3)_3\text{CC}\equiv\text{CD}$ , reacted with  $(\text{CH}_3)_3\text{C}\equiv\text{CH}$  in the presence of  $\text{Ag}^+$  (to remove  $\text{Cl}^-$ ) to give 1,3,5-tri-*tert*-butylbenzene containing  $\text{d}_2$  on the benzene ring. 1,3,5-Tri-*tert*-butylbenzene is the major product from the reaction of  $\text{PdCl}_2(\text{PhCN})_2$  and 1 in acetone [M. Avram, E. Avram, G. D. Mateescu, I. G. Dinulescu, F. Chiraleu, and C. D. Nenitzescu, *Chem. Ber.*, **102**, 3996 (1969)] and hence 4 is the likely intermediate both in its formation and that of 2.

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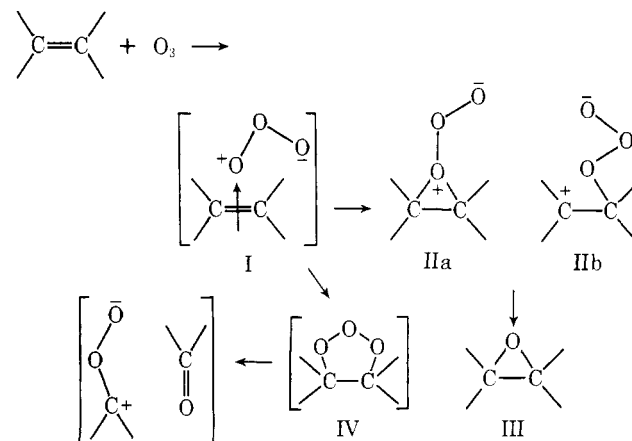
Received October 29, 1974

## Ozonolysis of *cis*- and *trans*-1,2-Difluoroethylene. Stereoselectivity in Epoxide Formation

Sir:

We have found that *cis*-1,2-difluoroethylene oxide and formyl fluoride are the major products from the ozonolysis of both *cis*- and *trans*-1,2-difluoroethylene in methyl chloride. Lesser amounts of *cis*- and *trans*-1,2-difluoroethylene ozonide are formed as well as a trace product from the *cis* olefin which is identified as *cis*-1,2,3-trifluorocyclopropane. In isobutane solvent, a striking solvent effect was observed. The ozonide isomers and formyl fluoride are the major products, and the *cis* epoxide is the minor product from both olefin isomers. No trace of *cis*-1,2,3-trifluorocyclopropane could be detected in the products from the *cis* olefin in isobutane. A *cis*/*trans* ozonide ratio of approximately 10/90 was determined by gas chromatography for the ozonolysis of both olefin isomers in either solvent.<sup>1</sup>

Epoxides have been reported as products in the ozonolysis of olefins,<sup>2-7</sup> but the mechanism of their formation is not well-understood. Bailey and Lane<sup>3</sup> proposed that for sterically hindered 1-olefins a competition exists between 1,3-dipolar cycloaddition to give normal ozonolysis products via IV and electrophilic attack of ozone to give epoxide III via a  $\pi$  complex (I)<sup>8</sup> and possibly a  $\sigma$  complex (IIa or IIb).<sup>9-11</sup> Murray and Suzui found that *cis*- and *trans*-1-(1-naphthyl)-1-phenyl-1-propene gave epoxides stereospecifically with retention of configuration.<sup>5</sup> They suggested IIa as the intermediate although IIb is consistent if ring closure is faster than C–C bond rotation.



Different mechanisms were proposed for epoxide formation in the ozonolysis of olefins with halogen substituents at the double bond.<sup>6,7</sup> Gozzo and Camaggi found perfluoroethylene oxide and carbonyl fluoride as the major ozonolysis products of tetrafluoroethylene in perhalogenated solvents.<sup>6</sup> Polytetrafluoroethylene was also observed as well as minor amounts of perfluorocyclopropane and a trace of per-