

### Preliminary communication

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## A NOVEL PRODUCT DERIVED FROM REACTION OF 3,3-DIMETHYL-4-METHYLTHIO-1-BUTYNE WITH DICHLOROBIS(BENZONITRILE)-PALLADIUM; X-RAY CRYSTAL STRUCTURE OF CHLORO(2,4-BIS-(1',1'-DIMETHYL-2'-(METHYLTHIO)ETHYL)-3-FURYL-C,S,S)-PALLADIUM(II)

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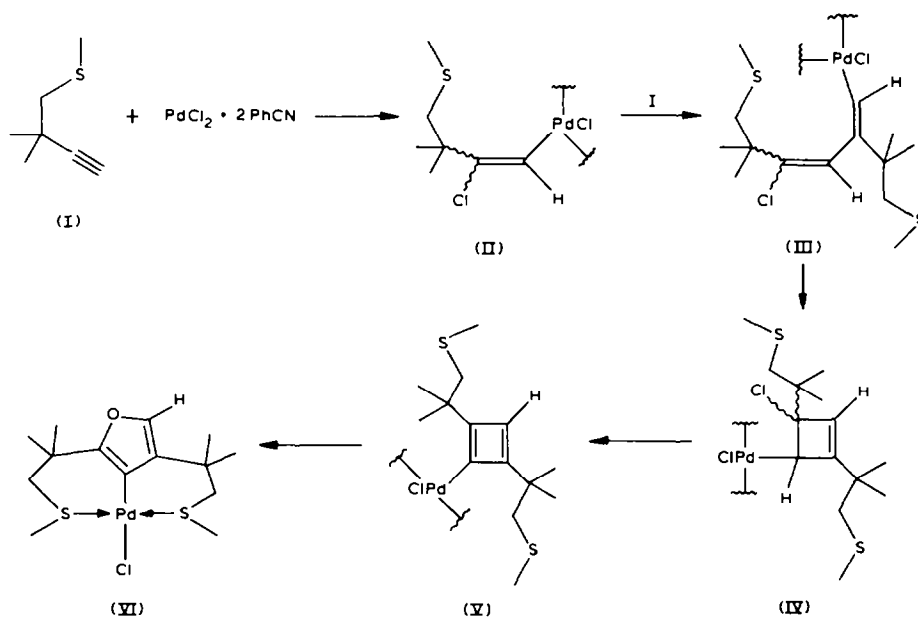
### Summary

One of the products isolated from the reaction of 3,3-dimethyl-4-methylthio-1-butyne with dichlorobis(benzonitrile)palladium is chloro(2,4-bis(1',1'-dimethyl-2'-(methylthio)ethyl)-3-furyl-C,S,S)palladium(II).

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The oligomerization of acetylenes in the presence of PdCl<sub>2</sub> has generated considerable interest and is now fairly well understood [1], particularly in the case of disubstituted acetylenes. However, studies in this area involving terminal acetylenes have had only limited success [2], the products being usually polymeric and not easily handled [3]. We have undertaken a study of the interaction of 3,3-dimethyl-4-methylthio-1-butyne (I) with dichlorobis(benzonitrile)palladium in the expectation that chelation might stabilise dimeric or trimeric intermediates and perhaps, in addition, force novel modes of reaction.

When a solution of I (0.916 mmol) in dry dichloromethane was treated with a solution of PdCl<sub>2</sub>·2PhCN (0.453 mmol) in the same solvent, an orange-brown precipitate formed within 30 min. At this stage, a further amount (0.458 mmol) of I was added and, upon stirring for 18 h, the precipitate redissolved. Evaporation of the solvent and preparative thin layer chromatography (Kieselgel G; dichloromethane/methanol, 99/1) of the oily residue gave 5 products in an overall yield of about 60% based on Pd, although the two least polar of these are not cleanly separable under these conditions. The two most polar products appear, on spectral evidence (see Table 1), to



SCHEME 1

TABLE 1

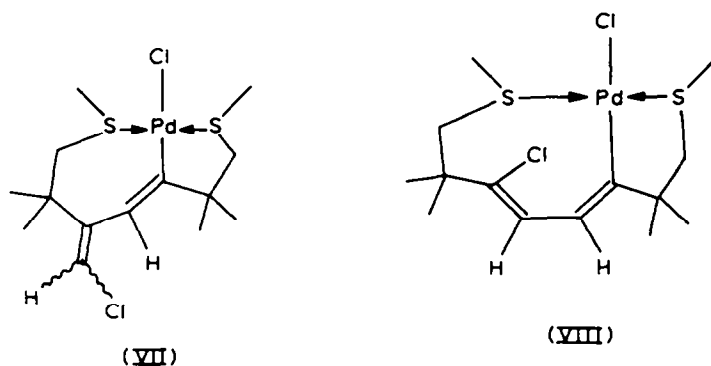
HYDROGEN-1 NMR (ppm)<sup>a</sup>, MELTING POINT (°C) AND ULTRAVIOLET SPECTRAL (nm)<sup>b</sup> DATA FOR THE COMPLEXES

Compound	M.p. (°C)	$\lambda_{\text{max}}$	$\delta(\text{C-Me})$	$\delta(\text{S-Me})$	$\delta(\text{S-CH}_2)$	$\delta(\text{olefinic})$
VI	199–200	300 ( $\epsilon$ 2 200)	1.45(6H)	2.72(3H)	2.89(2H) <sup>c</sup>	7.05(1H:furyl)
		244 ( $\epsilon$ 15 000)	1.42(6H)	2.71(3H)	2.45(2H) <sup>c</sup>	
		228 ( $\epsilon$ 21 000)				
VII	195–196	300 ( $\epsilon$ 2 000)	1.46(3H)	2.65(3H)	2.73(1H) <sup>d</sup>	6.05(1H) <sup>e</sup>
		228 ( $\epsilon$ 17 000)	1.38(3H)	2.58(3H)	2.67(1H) <sup>c</sup>	5.57(1H) <sup>e</sup>
			1.26(3H)		2.50(1H) <sup>c</sup>	
			1.18(3H)		2.16(1H) <sup>d</sup>	
VIII	218–220	340 ( $\epsilon$ 2 100)	1.46(3H)	2.82(3H)	3.75(1H) <sup>d</sup>	5.59(1H) <sup>g</sup>
		294 ( $\epsilon$ 4 000)	1.45(3H)	2.60(3H)	3.72(1H) <sup>f</sup>	4.90(1H) <sup>g</sup>
		260 ( $\epsilon$ 6 800)	1.39(3H)		3.43(1H) <sup>d</sup>	
		228 ( $\epsilon$ 10 000)	1.34(3H)		2.59(1H) <sup>f</sup>	

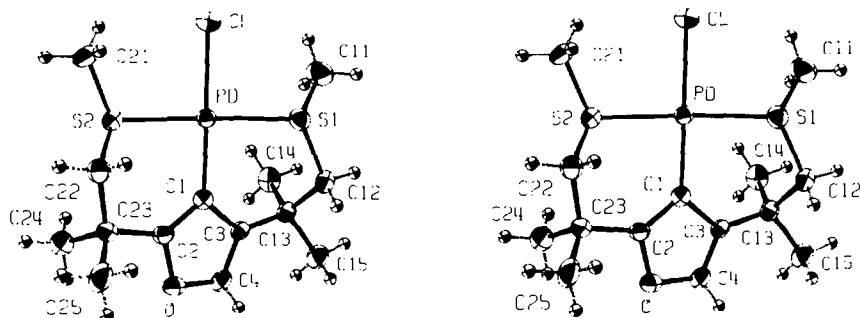
<sup>a</sup> In  $\text{CDCl}_3$ , on a Bruker WH-400 spectrometer at ambient temperature for VI and VIII and  $-10^\circ\text{C}$  for VII.

<sup>b</sup> In methanol. <sup>c</sup> br s. <sup>d</sup>  $J$  11.5 Hz. <sup>e</sup>  $J$  1.3 Hz. <sup>f</sup>  $J$  10.6 Hz. <sup>g</sup>  $J$  6.3 Hz.

be dienes (the less polar (24% yield) is probably VII, while the other (6% yield) may be VIII). The product of intermediate polarity (ca. 10% yield) also has a  $^1\text{H}$  NMR spectrum (see Table 1) attributable to a palladium complex derived from two molecules of the starting ligand. The spectrum indicates the presence of one aromatic proton and two magnetically non-equivalent  $\text{CMe}_2\text{CH}_2\text{SMe}$  moieties in which both sulfurs are coordinated to the metal. The structure VI of this complex was elucidated by X-ray crystallography [4] (see Fig. 1). This represents an entirely new type of product from oligomerization of an acetylene. Precedent [1] would suggest a route of the type



shown in the scheme for its formation. Two aspects of this pathway are unexpected [1]; the ligand insertion into II takes place in a Markownikow sense, and IV loses HCl rather than PdCl. There are precedents [5] for the oxidation, in air, of cyclobutadienes to furans, although none of these have contained metal atoms. Alternative mechanisms involving loss of PdCl from IV to give a cyclobutadienepalladium chloride complex and then cyclopalladation of the ring either before or after oxidation to a furan seem less likely in view of the stability [1,6] of such complexes.



**Fig. 1.** Stereoview of VI. The palladium atom has close to square planar geometry; main dimensions are: Pd—Cl 2.388(1), Pd—S(1) 2.307(1), Pd—S(2) 2.299(1), Pd—C(1) 2.007(2) Å, Cl—Pd—S(1) 89.61(3), Cl—Pd—S(2) 93.11(3), S(1)—Pd—C(1) 91.54(7), S(2)—Pd—C(1) 86.24(7)°. Deviations of the atoms from the PdS<sub>2</sub>ClC plane are: Pd 0.023, S(1) - 0.113, S(2) - 0.115, Cl 0.091, C(1) 0.114 Å.

**Crystal data:** C<sub>14</sub>H<sub>23</sub>ClOPdS<sub>2</sub>,  $M_r = 413.3$ , monoclinic, space group  $P2_1/n$ ,  $a$  10.332(3),  $b$  9.957(2),  $c$  16.189(5) Å,  $\beta$  103.16(2)°,  $Z = 4$ ,  $D_c$  1.69 g cm<sup>-3</sup>,  $F(000) = 840$ ; Mo radiation. Anisotropic refinement of non-hydrogen atoms, with hydrogen atoms included in geometrically idealised positions, converged at  $R = 0.0178$  ( $R_w = 0.0211$ ) for the 2589 reflexions with  $I > 3\sigma(I)$  measured with an Enraf-Nonius CAD-4 diffractometer.

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## References

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