Dihydropentalenes from the Palladium(II)-induced Cyclotetramerisation of Acetylenes; *X*-Ray Crystal Structures of Two Dihydropentalenes

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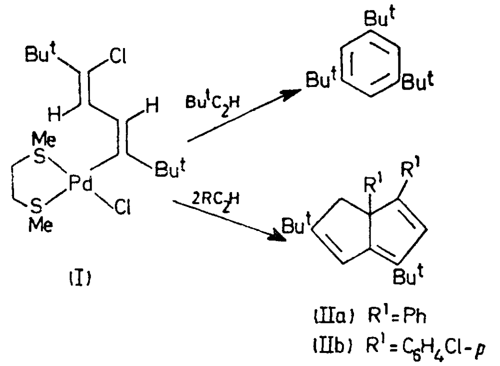
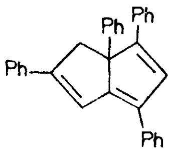
Summary Phenyl- or *p*-chlorophenyl-acetylene reacts with [PdL(Bu^{t}C=CHCH=CBu^{t}Cl)Cl] (L = 2,5-dithiahexane) to give the dihydropentalenes (IIa, R^1 = Ph) and (IIb, R^1 = C_6H_4Cl-*p*), which are isostructural with the orange tetramer ($Ph_4C_8H_4$) obtained from the reaction of phenylacetylene with $PdCl_2$; the structures of (IIb) and of the purple tetramer ($Ph_4C_8H_4$) also obtained from the latter reaction have been elucidated by *X*-ray crystallography.

WE recently reported the synthesis and the structure of complex (I) which is a derivative of an intermediate, containing a σ-butadienyl ligand, in the $PdCl_2$-induced cyclotrimerisation of t-butylacetylene.[1] The complex (I) also reacts with 1 equiv. of t-butylacetylene to give 1,3,5-tri-t-butyl-benzene.

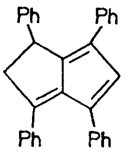


(I)

(IIa) R^1=Ph
(IIb) R^1=C_6H_4Cl-*p*



(III)



(IV)

When complex (I) was treated (C_6H_6, 80 °C, 2·5 h) with either phenylacetylene or *p*-chlorophenylacetylene two molecules of the acetylene were incorporated into the orange products isolated, (Bu$^t_2$$Ph_2C_8H_4$) (IIa) (m.p. 94—95 °C, 20%) and [Bu$^t_2$(*p*-$ClC_6H_4)_2C_8H_4$] (IIb) (m.p. 149—150 °C, 30%) respectively. Spectroscopic data indicated the compounds to be isostructural.

An *X*-ray structure determination of a crystal of (IIb) showed it to be the dihydropentalene, 2,7-di-t-butyl-4,5-di-*p*-chlorophenylbicyclo[3.3.0]octa-1,3,7-triene (Figure 1). *Crystal data*: $C_{28}H_{30}Cl_2$, *M* 437·46, monoclinic, a = 16·33(1), b = 17·67(1), c = 18·46(1) Å, β = 113·3(1)°, U = 4892, D_c = 1·188, Z = 8, space group $B2_1/c$. Three dimensional *X*-ray data were collected with the crystal mounted along the *a* axis, using Mo-K_α radiation (graphite monochromator) and a Stoe STADI 2 diffractometer. 2267 Independent reflections were collected with $I_{obs} \geqslant 3\sigma(I_{obs})$; the structure was solved using a symbolic addition procedure. Block diagonal least-squares refinement has reduced R to 0·050, allowing anisotropic thermal motion for the carbon and chlorine atoms.

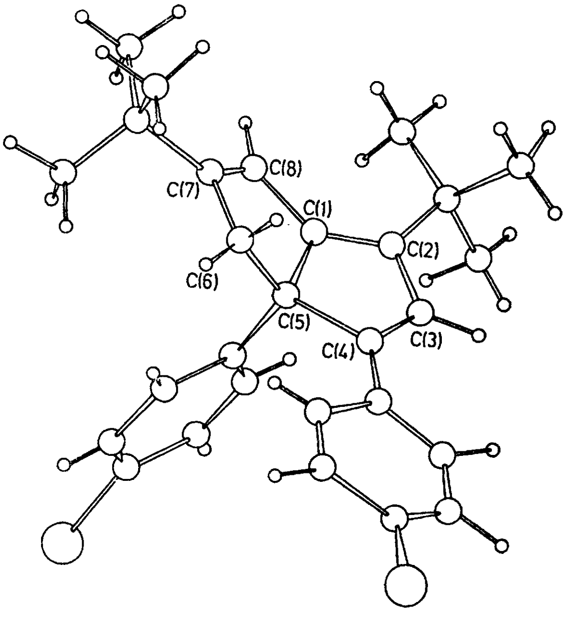


FIGURE 1. The structure of (IIb); bond lengths (in Å, e.s.d.'s in parentheses): C(1)–C(2), 1·352(6); C(1)–C(5), 1·523(5); C(1)–C(8), 1·448(6); C(2)–C(3), 1·465(6); C(3)–C(4), 1·356(6); C(4)–C(5), 1·522(5); C(5)–C(6), 1·558(5); C(6)–C(7), 1·522(5); and C(7)–C(8), 1·348(6).

This result is of particular interest since two related organic tetramers (III) and (IV), together with as yet uncharacterised organopalladium compounds, are obtained directly from the $PdCl_2$-induced oligomerisation of phenylacetylene ($PdCl_2$,HCl, tetrahydrofuran–H_2O, 20 °C).‡ Spectroscopic studies, in particular the ^1H n.m.r. spectrum (Table), indicated that the orange-red tetramer (III) (m.p. 209 °C) was isostructural with (IIa) and (IIb).

The structure of the red-purple tetramer (IV), m.p. 176 °C, was after considerable difficulty finally elucidated from *X*-ray diffraction measurements and was shown to be the dihydropentalene, 2,4,6,8-tetraphenylbicyclo[3.3.0]octa-1,3,5-triene (Figure 2). *Crystal data*: $C_{32}H_{24}$, *M* 408·55, monoclinic, a = 17·54, b = 5·760, c = 22·54 Å, β = 90·8°, U = 2276, D_c = 1·192, Z = 4, space group *Ic*. Three-dimen-

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‡ These compounds were first isolated by one of us (P.M.M.) in 1962 in the laboratories of Professor F. G. A. Stone at Harvard.

TABLE. ^{1}H N.m.r. spectra in CDCl$_3$ (δ), couplings in parentheses (in Hz).

Compound	CH$_2$		–CH=		Others
(IIa)	2·45(dd,1H) (2·5, 15)	3·38(d,1H) (15)	6·10(d,1H) (2·5)	6·99(s,1H)	1·17(s,9H)[d] 1·28(s,9H)[d] 7·2(m,10H)[e]
(IIb)	2·42(dd,1H) (2·5, 15)	3·31(d,1H) (15)	6·12(d,1H) (2·5)	6·98(s,1H)	7·18(s,8H)[e]
(III)	2·94(dd,1H) (2·5, 14·5)	3·97(d,1H) (14·5)	7·05[a](d,1H) (2·5)	[b]	7·3(m,21H)[e]
(IV)	3·38(dd,1H) (1·5, 19)	4·07(dd,1H) (6·5, 19)	4·45(dd,1H)[c] (1·5, 6·5)	[b]	7·2(m,21H)[e]

[a] Detected using INDOR. [b] Obscured by aromatic resonances. [c] Assigned to benzylic –CH<. [d] t-Butyl resonance. [e] Aromatic resonances.

sional *X*-ray data were collected using a Syntex $P\bar{1}$ diffractometer with Mo–K_α radiation. 481 Independent reflections were collected with $I_{\text{obs}} \geqslant 2\sigma(I_{\text{obs}})$; the structure was solved using the tangent formula with multiple starting points.[2] Block diagonal least-squares refinement, with the phenyls treated as groups, has reduced *R* to 0·097.

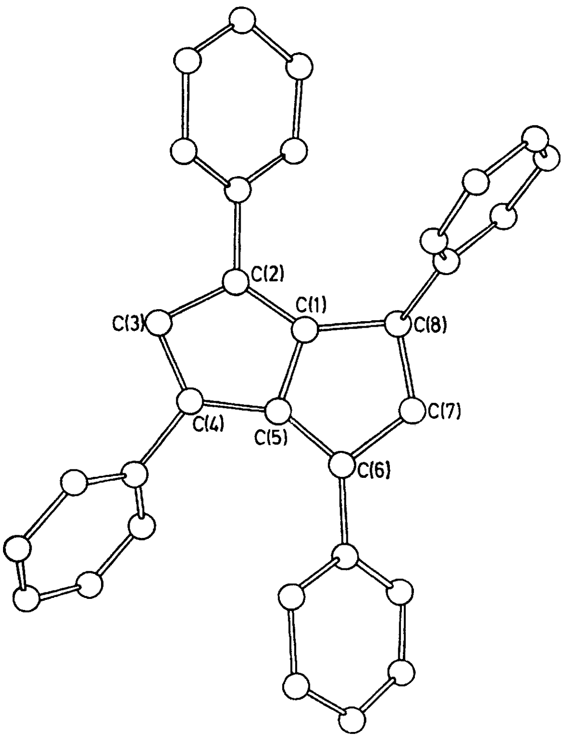
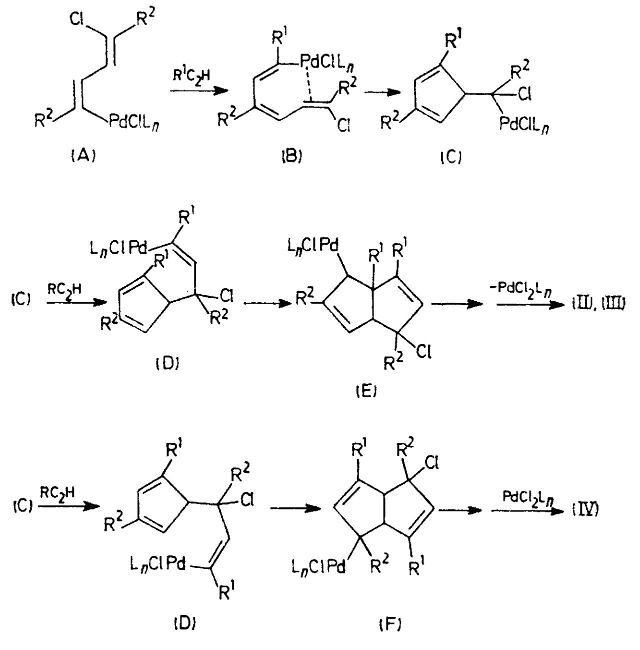


FIGURE 2. The structure of (IV); bond lengths (in Å, e.s.d.'s in parentheses): C(1)–C(2), 1·35(4); C(1)–C(5), 1·44(4); C(1)–C(8), 1·71(4); C(2)–C(3), 1·55(4); C(3)–C(4), 1·42(3); C(4)–C(5), 1·54(4); C(5)–C(6), 1·39(4); C(6)–C(7), 1·58(3); and C(7)–C(8), 1·50(4).

These structures for the dihydropentalenes (II), (III), and (IV) fit in well with our picture of the di- and tri-merisation reactions of acetylenes induced by PdCl$_2$[3] and also allow us to extend our concepts in a consistent manner to the formation of tetramers (Scheme). All four tetramers can be built up from a 1,4-disubstituted-butadienylpalladium (A),[1] which then undergoes *cis*-insertion of a further acetylene followed by cyclisation of the resultant 1,3,6-trisubstituted-hexatrienylpalladium (B) to the cyclopentadienylmethylpalladium (C). This intermediate (C) can then *cis*-insert a further acetylene to give a new σ-alkenylpalladium species (*D*) which can cyclise in two ways, giving either (E) (R^1 = Ph or C$_6$H$_4$Cl-*p*, R^2 = Bu^t), or (E) and (F) (for R^1 = R^2 = Ph). Clearly the manner in which this last cyclisation occurs will depend on the sizes of the cyclopentadienyl substituents R^1 and R^2. Loss of Pd–Cl accompanied by migration of H then leads to the observed products.



SCHEME. R^1 = Ph or C$_6$H$_4$Cl-*p*, R^2 = Bu^t or Ph.

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[1] B. E. Mann, P. M. Bailey, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1975, **97**, 1275.

[2] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, A**27**, 368.

[3] P. M. Maitlis, *Accounts Chem. Res.*, in the press; see also P. M. Maitlis, 'The Organic Chemistry of Palladium,' vol. II, Academic Press, New York, 1971, pp. 47—58 and P. M. Maitlis, *Pure Appl. Chem.*, 1973, **33**, 489.