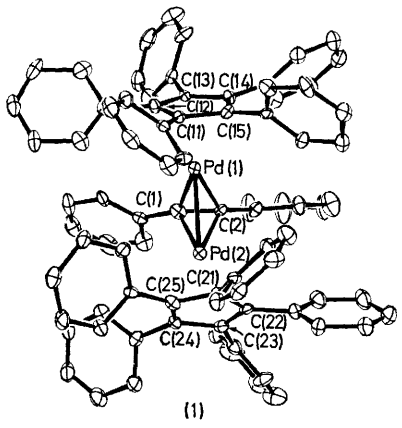
X-Ray Crystallographic Determination of the Structure of μ-Diphenylacetylene-bis-(π-pentaphenylcyclopentadienyl)dipalladium(I)

By EVA BAN, PEI-TAK CHENG, THOMAS JACK, STANLEY C. NYBURG, and JOHN POWELL*
(*Lash Miller Chemical Laboratories, University of Toronto, Toronto* M5S 1A1, *Ontario, Canada*)

Summary The structure of μ-diphenylacetylene-bis-(π-pentaphenylcyclopentadienyl)dipalladium(I), which is readily and quantitatively synthesised by the reaction of diphenylacetylene with palladium acetate in methanol, has been determined by *X*-ray crystallography.

THE reactions of acetylenes with compounds of palladium often result in the formation of organopalladium(II) complexes containing acetylene monomer, dimer, or trimer units co-ordinated to the palladium in a variety of ways.[1–3] We report the formation of a pentaphenylcyclopentadienyl

complex of palladium(I) obtained from the reaction of diphenylacetylene with palladium acetate.

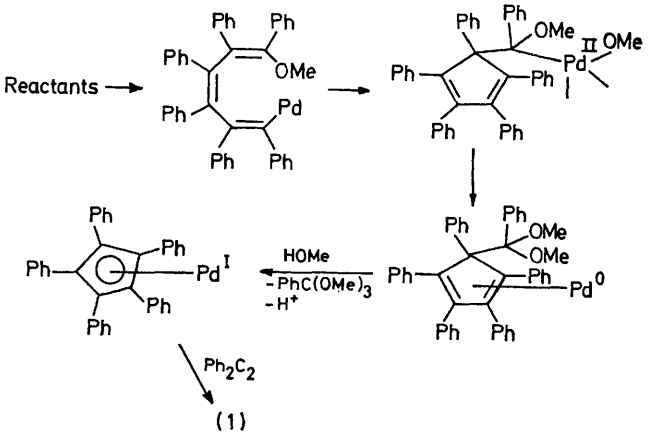


(1)

FIGURE. *Bond lengths*: Pd(1)–Pd(2) 2·639(1), Pd(1)–C(1) 1·98, Pd(1)–C(2) 2·06, Pd(2)–C(1) 2·06, Pd(2)–C(2) 2·09, Pd(1)–C(11) 2·46, Pd(1)–C(12) 2·37, Pd(1)–C(13) 2·32, Pd(1)–C(14) 2·45, Pd(1)–C(15) 2·45, Pd(2)–C(21) 2·30, Pd(2)–C(22) 2·37, Pd(2)–C(23) 2·35, Pd(2)–C(24) 2·27, Pd(2)–C(25) 2·27, C(1)–C(2) 1·33.

On stirring a methanolic solution of palladium acetate with 4 mol. equiv. of diphenylacetylene/Pd at room temperature, an intense dark green, diamagnetic compound (**1**) and elemental palladium are slowly precipitated (4—12 h). Microanalysis and molecular weight studies of (**1**) support a molecular formula of $Pd_2C_{12}Ph_{12}$. Its structure was determined by *X*-ray crystallography.

The complex (**1**) crystallised from benzene as green parallelpipeds. *Crystal data:* monoclinic, $a = 14{\cdot}93(2)$ $b = 22{\cdot}51(3)$, $c = 21{\cdot}88(2)$ Å, $\beta = 113{\cdot}04(1)°$, $D_m = 1{\cdot}36$ g cm^{-3} $Z = 4$, space group $Cc(C_s^4)$. Intensity data were collected by an automated diffractometer using Cu-K_α radiation in 2θ scan mode at 4° min^{-1} in the range $0 \leqslant \sin\theta \leqslant 0{\cdot}9$. The structure was determined by the heavy-atom method. Based on 5159 observed independent reflections, the structure was refined by least-squares to $R = 6{\cdot}2\%$. The structure of (**1**) (Figure) identifies this compound as $(\mu\text{-PhC}{\equiv}\text{CPh})(\pi\text{-}C_5Ph_5)_2Pd_2$. Complex (**1**), which is formally of palladium(I)[4] and the first example of an acetylene bridging palladium, is structurally analogous to $(\mu\text{-PhC}{\equiv}\text{CPh})(\pi\text{-}C_5H_5)_2Ni_2$.[5] It completes the Ni,Pd,Pt triad for structures of this type in that $(\mu\text{-}C_5H_5C_5H_5)(\pi\text{-}C_5H_5)_2Pt_2$ is structurally related, with cyclopentadienylcyclopentadiene replacing diphenylacetylene.[6]



SCHEME

The ready formation of a π-cyclopentadienyl ligand directly from an acetylene has not been previously observed. Two molecules of $PhC(OMe)_3$ per molecule of (**1**) are also formed during its preparation. The overall reaction [>90% yield of (**1**) based on diphenylacetylene] is shown in equation (1).The formation of (**1**) may be envisaged to

$$Pd_3(OAc)_6 + 7Ph_2C_2 + 6MeOH \rightarrow (\mathbf{1}) + 2PhC(OMe)_3 + 6HOAc + Pd\downarrow \quad (1)$$

proceed qualitatively as shown in the Scheme by analogy with previous studies of acetylene–palladium chemistry.[1,3]†

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† Hexaphenylbenzene was not observed in the reaction products. A small amount of methyl benzoate was usually obtained in the preparation of (**1**) and is presumably formed *via* hydrolysis of $PhC(OMe)_3$.

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