

Preliminary communication

INSERTION OF ACETYLENES IN THE Pd—Pd BOND OF $\text{Pd}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Cl}_2$

ALAN L. BALCH, CHUNG-LI LEE, CATHERINE H. LINDSAY and MARILYN M. OLMSTEAD

Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)

(Received April 30th, 1979)

Summary

Dimethylacetylene dicarboxylate and hexafluoro-2-butyne add to $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ ($\text{dpm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) to give crystalline adducts $\text{Pd}_2(\text{dpm})_2(\mu\text{-acetylene})\text{Cl}_2$. An X-ray crystal structure of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_4\text{F}_6)\text{Cl}_2$ reveals that the acetylene has inserted into the metal—metal bond and has been transformed into a *cis*-dimetalated olefin. The central C—C bond length of the bridging olefin is 1.338(16) Å. The coordination about each of the two similar palladium ions is planar and involves two *trans*-phosphines (one from each of the bridging dpm ligands), a terminal chloride, and one carbon of the bridging olefin. Both $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ and $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$ catalyze the cyclotrimerization of dimethylacetylene dicarboxylate.

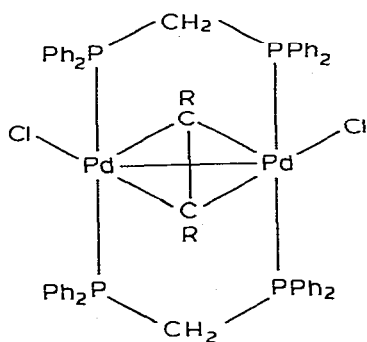
The formation of a dimetalated olefin from an acetylene is still an unusual transformation in organometallic chemistry. Structurally characterized dimetalated olefins have been formed from the reactions of acetylenes with mononuclear complexes [1—4]. Although the reactions of acetylenes with a variety of polynuclear metal complexes have been investigated [5, 6], the direct insertion of an acetylene into a metal—metal bond has been infrequently observed [7—10] and the structural characterization of the products of insertion is extremely limited [11].

We now report on the insertion of acetylene into the highly reactive metal—metal bond of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ (I, $\text{dpm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$), the structural characterization of the products and the ability of I to catalyze acetylene cyclotrimerization. The ability of I to undergo insertion reactions with carbon monoxide [12, 13], isocyanides [12, 13] and sulfur dioxide [14] has been reported previously.

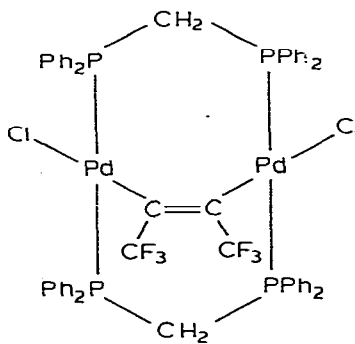
Addition of dimethylacetylene dicarboxylate to a dichloromethane solution of I at room temperature results in the gradual precipitation of yellow crystals of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$ (II) over a period of 2 to 4 days. $\text{Pd}_2(\text{dam})_2(\mu\text{-C}_2\{\text{CO}_2\text{CH}_3\}_2)\text{Cl}_2$ (III, $\text{dam} = \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$) is formed in a similar fashion from $\text{Pd}_2(\text{dam})_2\text{Cl}_2$. Exposure of a saturated dichloromethane solution of I to

one atmosphere of hexafluoro-2-butyne causes the gradual precipitation of $\text{Pd}_2(\text{dpm})_2(\mu\text{-C}_4\text{F}_6)\text{Cl}_2$ (IV) over several days. The infrared spectra of II, III and IV show no evidence of a perturbed acetylene stretching vibration in the region $2300\text{--}1600\text{ cm}^{-1}$. The spectrum of IV is featureless throughout this region. The spectra of II and III contain bands due to the carbonyl groups at 1705 and 1690 cm^{-1} for II and 1705 , 1693 cm^{-1} for III in this region. As is typical for insertion reactions of I, the Pd—Cl stretching vibrations occur at higher energies in the adducts: 275 cm^{-1} for II, 275 cm^{-1} for III and 278 cm^{-1} for IV vs. 249 cm^{-1} for I [13].

The most characteristic mode of interaction of an acetylene with two metal centers involves the formation of a tetrahedral $\mu_2\text{-}\eta^2$ unit. In the present case this would result in structure A for the geometry of the adducts II, III and IV. Such a structure would be analogous to the architecture found for the palladium (I) dimer $(\mu\text{-PhC}\equiv\text{CPh})(\eta^5\text{-C}_5\text{Ph}_5\text{Pd})_2$ which possesses a short Pd—Pd distance (2.64 \AA) and a direct Pd—Pd bond [15]. In order to distinguish between structure A and B, the true structure, an X-ray crystallographic investigation of IV, which was believed to be representative of the group, was undertaken.



(A)



(B)

Yellow needles of $\text{Pd}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2(\mu\text{-C}_4\text{F}_6)\text{Cl}_2$, which were obtained by slow evaporation of a saturated dichloromethane solution of the complex, belong to the space group $P4_1$. Crystal data (140 K): $a\ 21.165(6)\text{ \AA}$, $c\ 14.328(3)\text{ \AA}$, $\rho_{\text{calc}}^{140} = 1.26$ for $Z = 4$; $\mu(\text{Mo-K}\alpha) 7.8\text{ cm}^{-1}$. Intensity data were collected on a Syntex P2₁ diffractometer which was equipped with a graphite monochromator, and the structure was solved by standard heavy atom methods using 4369 unique reflections with $I > 3\sigma(I)$. At the present stage of refinement with isotropic thermal parameters for all non-hydrogen atoms the conventional discrepancy index, R , is 0.050^* .

The asymmetric unit contains one molecule which has no crystallographically imposed symmetry. A perspective drawing of the entire molecule is shown in

*A Table of interatomic distances, bond angles, atomic positions and isotropic thermal parameters and structure factors has been deposited as NAPS Document No. 03488 (37 p.). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting \$ 9.25 for photocopies or \$ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

Fig. 1. The coordination about each of the two palladium ions is similar and involves bonding to the two *trans*-phosphine ligands, the terminal halide, and one carbon of the bridging olefin. The geometry of each PdP₂ClC unit is nearly planar. Figure 2 shows a projection of another nearly flat section of the molecule; this section contains the bridging olefin, the two palladium ions and the terminal chloride ligands. Important distances and angles are contained in Fig. 2. This compound represents the first case in which a two atom unit has been inserted into the palladium—palladium bond of Pd₂(dpm)₂Cl₂. The geometry of the inserted ligand is consistent with its formulation as a dimetallated olefin. The central carbon—carbon bond length has increased significantly from that of the parent acetylene, and the angular distribution of substituents about these two carbon atoms is indicative of sp² hybridization. The non-bonded palladium—palladium separation is the largest yet found for any binuclear complex involving dpm as a bridging ligand [16]. Since this compound contains a η²-bridge between the metal centers it is not surprising that wide palladium—palladium separation exists. This separation is a reflection of the steric requirements of the bridging olefin and at the same time demonstrates the remarkable flexibility of the dpm-bridging framework.

Pd₂(dpm)₂Cl₂ acts as a catalyst (or catalyst precursor) for the cyclotrimerization of dimethylacetylene dicarboxylate. Pd₂(dpm)₂(μ-C₂{CO₂CH₃})₂Cl₂ may be an intermediate in this process since it is formed under the conditions of the catalytic reaction and itself also serves to catalyze the cyclotrimerization reaction. At 398 ± 5 K with a reaction time of 1.6 h both complexes produce 40%

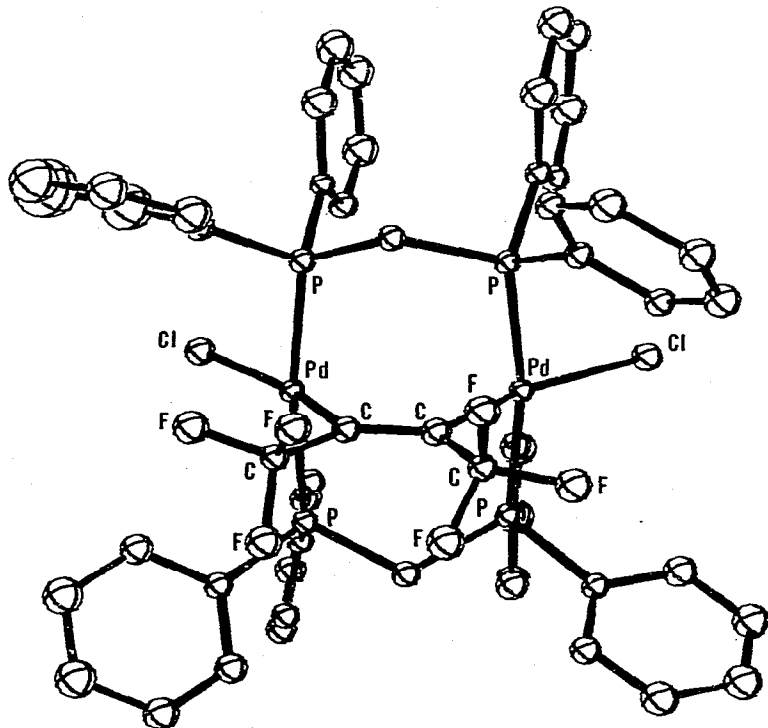


Fig. 1. An ORTEP drawing of Pd₂(Ph₂PCH₂PPh₂)₂(μ-C₄F₆)Cl₂ showing 50% thermal ellipsoids.

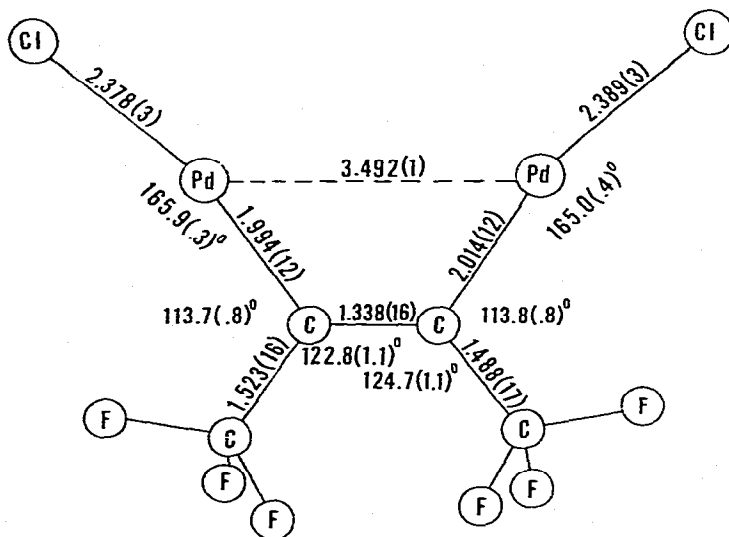


Fig. 2. A planar projection of the $\text{Pd}_2\text{C}_4\text{Cl}_2$ portion of the molecule showing some important distances and angles. The unlabeled PdCC angles are $123.5(9)^\circ$ (left) and $121.5(9)^\circ$ (right).

conversion of dimethylacetylene dicarboxylate into hexamethyl mellitate with at least 15–20 moles of product formed per mole of palladium complex used. A plausible mechanism involves insertion of the acetylene into the Pd–Pd bond of I to give II followed by two successive insertions of the acetylene into the Pd–C bond of II and reductive elimination (with coupling to form C–C and Pd–Pd bonds) to give I, and hexamethyl mellitate. However the initial insertion could be incidental to a mechanism (established for palladium(II) catalysis of acetylene oligomerization [17]), which involves successive insertion of acetylenes into the Pd–Cl bond. Further investigations of the catalytic activity are in progress.

It appears that other unsaturated organic substrates may insert in a similar fashion into the palladium–palladium bond of I. Adducts of I with tetracyanoethylene, phenylisothiocyanate, methylisothiocyanate, and carbonyl sulfide have been isolated as crystalline complexes and the details of their structures are currently under investigation.

Acknowledgement

We thank National Science Foundation for support. Acquisition of the X-ray diffractometer used in this study was made possible through an NSF instrument grant.

References

- 1 M.E. Kimball, J.P. Martella and W.C. Kaska, *Inorg. Chem.*, **6** (1967) 414.
- 2 C.J. Gilmore and P. Woodward, *J. Chem. Soc., Chem. Commun.*, (1971) 1233.
- 3 J. Clemens, N. Green, M.-C. Kuo, C.J. Fritchie, Jr., J.T. Mague and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1972) 53.
- 4 L.E. Smart, J. Browning, M. Green, A. Laguna, J.I. Spender and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1977) 1777.

- 5 W. Hübel in I. Wender and P. Pino (Eds.), *Organic Synthesis via Metal Carbonyls*, 1 (1968) 273.
- 6 E.L. Muetterties, *Bull. Soc. Chim. Belg.*, 85 (1976) 451.
- 7 K. Yasufuku and H. Yamazaki, *J. Organometal. Chem.*, 35 (1972) 367.
- 8 H. Ogoshi, J. Setsune and Z. Yoshida, *J. Amer. Chem. Soc.*, 99 (1977) 3869.
- 9 J.L. Davidson and D.W.A. Sharp, *J. Chem. Soc., Dalton*, (1975) 2284.
- 10 R. Mathiew and R. Poilblanc, *J. Organometal. Chem.*, 142 (1977) 351.
- 11 J.L. Davidson, W. Harrison, D.W.A. Sharp and G.A. Sim, *J. Organometal. Chem.*, 46 (1972) C47.
- 12 M.M. Olmstead, H. Hope, L.S. Benner and A.L. Balch, *J. Amer. Chem. Soc.*, 99 (1977) 5502.
- 13 L.S. Benner and A.L. Balch, *J. Amer. Chem. Soc.*, 100 (1978) 6099.
- 14 L.S. Benner, M.M. Olmstead, H. Hope and A.L. Balch, *J. Organometal. Chem.*, 153 (1978) C31.
- 15 E. Ban, P.-T. Cheng, T. Jack, S.C. Nyburg and J. Powell, *J. Chem. Soc., Chem. Commun.*, (1973) 368.
- 16 M.M. Olmstead, C.H. Lindsay, L.S. Benner and A.L. Balch, submitted for publication.
- 17 P.M. Maitlis, *Accounts Chem. Res.*, 9 (1976) 93.