

The Reaction of Di-iodoacetylene with $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$: Formation of $[\text{Pd}_2\text{Cl}_2(\mu\text{-}\sigma\text{-C=CCl}_2)(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ and $[\text{PdI}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$

Julian A. Davies,* A. Alan Pinkerton, Rashid Syed, and Mark Vilmer

Departments of Chemistry and Medicinal Chemistry, University of Toledo, Toledo, Ohio 43606, U.S.A.

The complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ reacts with di-iodoacetylene to yield $[\text{PdI}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ and $[\text{Pd}_2\text{Cl}_2(\mu\text{-}\sigma\text{-C=CCl}_2)(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$, which have been characterized by spectroscopic methods and by X-ray crystallography; formation of the bridged dichlorovinylidene complex involves a formal 1,2-halide shift accompanied by C–I/Pd–Cl bond metathesis.

It has been known for some years that the metal–metal bonded dipalladium complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ (**1**)¹ reacts with acetylenes bearing either one or two electron withdrawing groups to form bridged complexes of type (**2**).² Recently it has been demonstrated that this class of reaction may be extended to unactivated acetylenes through acid catalysis of the addition process.³ Here we report that the reaction of (**1**) with di-iodoacetylene yields not a bridged acetylene complex of type (**2**) but rather a bridged vinylidene complex (**3**) as a major product.

Thus, reaction of di-iodoacetylene (1 equiv.) with (**1**) in refluxing benzene, followed by removal of the solvent *in vacuo*, leads to formation of an orange solid. The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum (CDCl_3) of this material revealed a singlet at -63.1 p.p.m. (with respect to external 85% phosphoric acid) and a complex multiplet (Figure 1) centred at 10.1 p.p.m. Extraction of the orange solid with tetrahydrofuran (thf) allowed separation of these components. Thus, crystallization of the solid residue resulting from thf extraction using CHCl_3 /heptane led to isolation of the components responsible for the complex multiplet at 10.1 p.p.m., while cooling of the thf solution led to crystallization of the material exhibiting a singlet at -63.1 p.p.m.

The complex multiplet (Figure 1) consists of two singlets (indicated as 3A and 3B) superimposed upon a more complex pattern. Addition of excess of chloride ion (Bu_4NCl) caused

collapse of the complex multiplet into the singlet **3A** while addition of an excess of iodide ion caused collapse of the multiplet into the singlet **3B**. These data are consistent with the presence of chloro-(**3A**), iodo-(**3B**), and mixed chloro-iodo (**3C**) complexes in solution. Careful crystallization from CHCl_3 /heptane led to the formation of needle and plate-like yellow crystals of which only the plate-like crystals were of X-ray quality. A single crystal X-ray structure determination† revealed that this product is the dinuclear vinylidene complex

† *Crystal data* for $\text{C}_{52}\text{H}_{44}\text{Cl}_4\text{P}_4\text{Pd}_2$ (**3A**): $a = 21.174(2)$, $c = 14.327(2)$ Å; $Z = 4$; $D_c = 1.19$ g cm⁻³; space group $P4_1$; 7096 unique reflections collected using Mo- K_α radiation; $2\theta_{\text{max}} = 52^\circ$; 4492 reflections with $F_o^2 > 3\sigma(F_o)^2$ used in the full-matrix least-squares refinement; $R = 7.0\%$; $R_w = 9.5\%$. One phenyl group of one of the diphosphine ligands is disordered and at present a satisfactory model for this disorder has not been obtained. At the current stage of refinement we are unable to distinguish between space groups $P4_1$ and $P4_3$. The deposited atomic co-ordinates are thus arbitrarily for $P4_1$.

Crystal data for $\text{C}_{25}\text{H}_{22}\text{I}_2\text{P}_2\text{Pd}$ (**4**): $a = 9.011(1)$, $b = 14.327(2)$, $c = 19.892(3)$ Å; $\beta = 92.86(1)^\circ$; $Z = 4$; $D_c = 1.93$ g cm⁻³; space group $P2_1/n$; 5245 unique reflections collected using Mo- K_α radiation; $2\theta_{\text{max}} = 52^\circ$; 4135 reflections with $F_o^2 > 3\sigma(F_o)^2$ used in the full-matrix least-squares refinement; $R = 2.5\%$; $R_w = 3.9\%$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

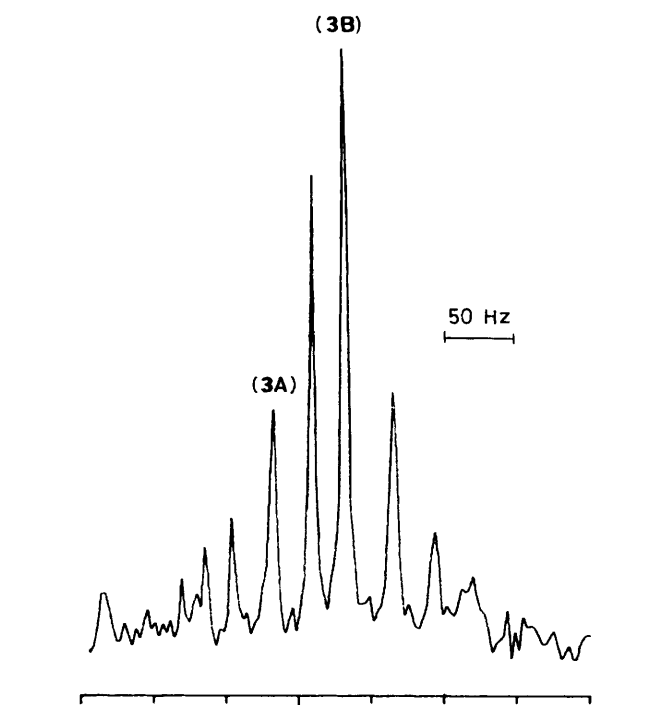
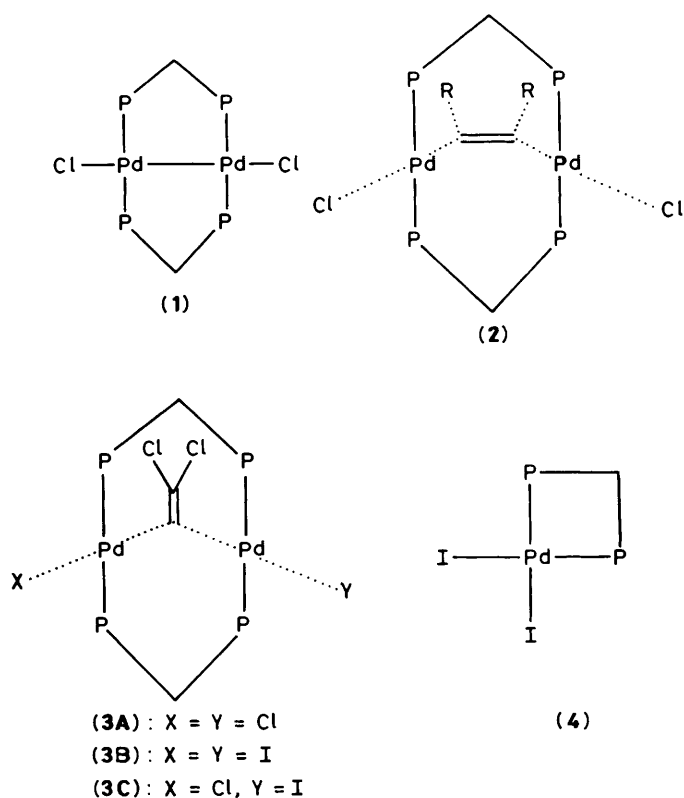


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum showing resonances due to (3A), (3B), and (3C).

(3A) (Figure 2). A single crystal X-ray structure determination† of the material exhibiting a singlet at -63.1 p.p.m. showed it to be the mononuclear di-iodide (4) (Figure 3).

The structural and spectroscopic data show that di-iodoacetylene reacts with (1) to produce the vinylidene bridged complexes (3A–3C) and the mononuclear iodide complex (4). The complexes (3A–3C) may be interconverted by simple halide metathesis. Formation of these products is unusual since they result from a formal 1,2-halide shift of the acetylene accompanied by C–I/Pd–Cl bond metathesis. The 1,2-hydride shift of acetylenes, leading to vinylidene formation, is well documented⁴ but only one example of a 1,2-halide shift has previously been described.⁵ We are aware of no other examples of 1,2-shifts accompanied by substitution.

The structure of (4) is not unusual and may be compared directly with the reported structures of the analogous chloro⁶ and bromo⁷ complexes. The significance of the structure is that it unambiguously confirms that C–I bond cleavage occurs and that Pd–I bond formation results. Conversely, the structure of (3A) is most interesting. Until very recently no structural determinations had been performed on bridged vinylidene complexes which are not supported by a metal–metal bond. The structure of (3A) shows that both palladium centres are approximately square planar, with the square planes intersecting at an angle of $109.9(8)^\circ$. Viewing the molecule along the Pd–Pd vector shows that the two P–Pd–P axes are not perfectly eclipsed and form an angle of 7° . Other structural data are similar to those of the related dinickel and nickel–palladium complexes recently described by Shaw and co-workers.⁸

We have found that di-iodoacetylene reacts with (1) by a formal 1,2-halide shift accompanied by C–I/Pd–Cl bond metathesis to yield complexes of type (3). Since it is known that acetylenes such as diphenylacetylene react to form

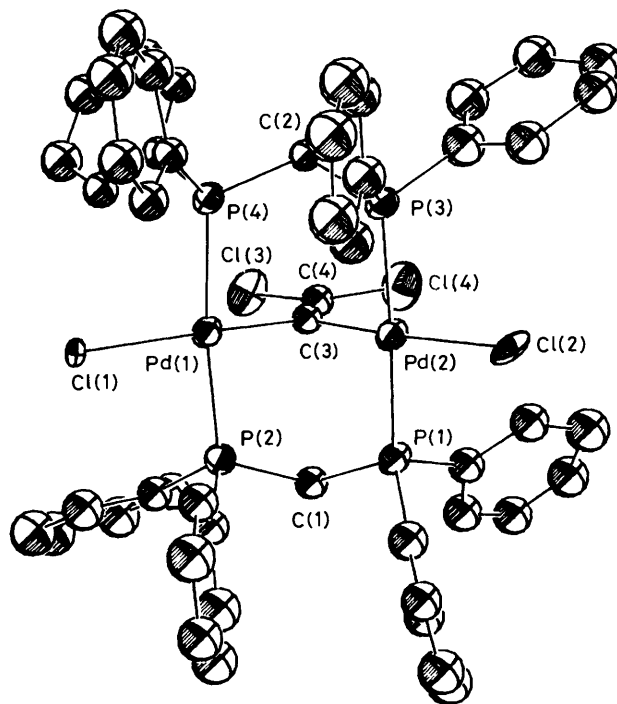


Figure 2. ORTEP diagram of $\text{C}_{52}\text{H}_{44}\text{Cl}_4\text{P}_4\text{Pd}_2$ (3A). The disordered phenyl group is represented by average atomic positions with isotropic thermal parameters. Selected bond distances (Å) and angles ($^\circ$): Pd(1)–Cl(1) 2.483(4); Pd(2)–Cl(2) 2.462(4); Pd(1)–P(2) 2.303(5); Pd(1)–P(4) 2.327(5); Pd(2)–P(1) 2.315(5); Pd(2)–P(3) 2.300(5); Pd(1)–C(3) 1.96(1); Pd(2)–C(3) 2.01(2); C(3)–C(4) 1.30(2); Cl(1)–Pd(1)–P(2) $91.8(1)$; Cl(1)–Pd(1)–P(4) $96.0(1)$; Cl(1)–Pd(1)–C(3) $178.1(5)$; P(2)–Pd(1)–P(4) $172.0(2)$; P(2)–Pd(1)–C(3) $86.6(5)$; P(4)–Pd(1)–C(3) $85.6(5)$; Cl(2)–Pd(2)–P(1) $95.7(2)$; Cl(2)–Pd(2)–P(3) $90.8(2)$; Cl(2)–Pd(2)–C(3) $174.5(4)$; P(1)–Pd(2)–P(3) $172.5(2)$; P(1)–Pd(2)–C(3) $85.8(5)$; P(3)–Pd(2)–C(3) $87.5(5)$; Pd(1)–C(3)–Pd(2) $109.9(8)$. The Pd(1)–Pd(2) separation is $3.248(2)$ Å.

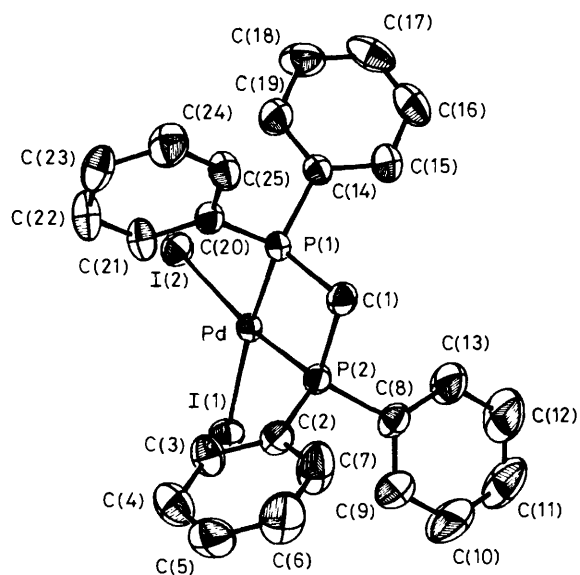


Figure 3. ORTEP diagram of $C_{25}H_{22}I_2P_2Pd$ (**4**). Selected bond distances (Å) and angles ($^\circ$): Pd–I(1) 2.6514(4); Pd–I(2) 2.6519(4); Pd–P(1) 2.241(1); Pd–P(2) 2.2525(9); I(1)–Pd–I(2) 96.22(1); I(1)–Pd–P(1) 169.06(3); I(1)–Pd–P(2) 95.77(3); I(2)–Pd–P(1) 94.44(3); I(2)–Pd–P(2) 167.99(3); P(1)–Pd–P(2) 73.56.

bridged complexes of type (**2**), it will be of interest to examine the reactions of unsymmetrically substituted acetylenes, such as phenyliodoacetylene, to determine their mode of reactivity.

Thanks are expressed to the Petroleum Research Fund administered by the American Chemical Society for financial

support, and Professor B. L. Shaw for communicating details of his work prior to publication.

Received, 29th May 1987; Com. 729

References

- 1 A. L. Balch and I. S. Benner, *Inorg. Synth.*, 1982, **21**, 47.
- 2 C.-L. Lee, C. T. Hunt, and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 249.
- 3 S. J. Higgins and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1986, 1629.
- 4 K. Foltling, J. C. Huffman, L. N. Lewis, and K. G. Caulton, *Inorg. Chem.*, 1979, **18**, 3483; R. M. Kirchner and J. A. Ibers, *J. Organomet. Chem.*, 1974, 243; M. H. Chisholm, *Platinum Met. Rev.*, 1975, **19**, 100; A. N. Nesmeyanov, G. G. Aleksandrov, A. B. Antonova, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1976, **110**, C36; A. N. Nesmeyanov, A. B. Antonova, K. N. Anisimov, and N. E. Kolobova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1974, 2873; A. B. Antonova, N. E. Kolobova, P. V. Petrovsky, B. V. Loshkin, and N. S. Oberyuk, *J. Organomet. Chem.*, 1977, **137**, 55; N. E. Kolobova, A. B. Antonova, O. M. Khitrova, M. Yu. Atipin, and Yu. T. Struchkov, *ibid.*, 1977, **137**, 69; M. I. Bruce and R. C. Wallis, *ibid.*, 1978, **161**, C1; S. Aime, G. Gervasio, L. Milone, E. Sappa, and M. Franchini-Angela, *Inorg. Chim. Acta*, 1978, **27**, 145; V. Raverdino, S. Aime, L. Milone, and E. Sappa, *ibid.*, 1978, **30**, 9; E. Sappa, A. M. Manotti-Lanfredi, A. Tiripicchio, *ibid.*, 1979, **36**, 197; E. Sappa, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc., Chem. Commun.*, 1979, 254; O. Gambino, E. Sappa, A. M. Manotti-Lanfredi, and A. Tiripicchio, *Inorg. Chim. Acta*, 1979, **36**, 189.
- 5 I. T. Horvath, G. Palyi, L. Marko, and G. J. Andreotti, *Inorg. Chem.*, 1983, **22**, 1049.
- 6 W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 2432.
- 7 K. Peters, E.-M. Peters, H. G. Von Schnering, and H.-P. Z. Abicht, *Z. Kristallogr.*, 1984, **168**, 149.
- 8 X. L. R. Fontaine, S. J. Higgins, B. L. Shaw, M. Thornton-Pett, and W. Yichang, *J. Chem. Soc., Dalton Trans.*, in the press.