Dalton Communications

Synthesis and Structural Characterisation of $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t_3)_4]$: A Tetrahedral Palladium Cluster with a μ_3-Methylidyne Ligand

Andrew D. Burrows, D. Michael P. Mingos,* Stephan Menzer, Ramón Vilar and David J. Williams
Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

The compound $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t_3)_4]$ has been synthesised from $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone), PBu^t_3 and $CHCl_3$ and characterised spectroscopically and by single-crystal X-ray analysis; it undergoes substitution reactions with Br^- and tertiary phosphines and is a catalyst for the polymerisation of ethyne.

Alkylidyne carbonyl cluster compounds which have the CR (R = H, alkyl or aryl) group capping a triangular face of metal atoms (μ_3-CR) are well documented for the Group 8 and 9 metals.[1,2] The ethylidyne ligand has also been identified spectroscopically on clean Pt(111) crystal surfaces[3,4] and has been implicated as an intermediate in heterogeneous catalytic processes involving the hydrogenation of CO and C_2H_2.[5,6] However, there have been no previous reports of alkylidyne cluster compounds of the Ni, Pd, Pt group of metals. Here we describe the synthesis and structural characterisation of $[Pd_4(\mu_3\text{-}CH)\ (\mu\text{-}Cl)_3(PBu^t_3)_4]$ **1** which provides the first example of such a compound.

When $[Pd_2(dba)_3]\cdot C_6H_6$ (dba = dibenzylideneacetone) in toluene was treated with 2 mol equivalents of PBu^t_3 the solution changed to dark orange after 1 h. On addition of 0.5 mol equivalent of $CHCl_3$ the solution became dark green after 5 h. After the solvent had been removed crystals of $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t_3)_4]$ were obtained from acetone after cooling at 4 °C overnight (30% yield). A single-crystal X-ray analysis† of compound **1** has confirmed that it is a tetrahedral cluster with a face-capping methylidyne ligand. The molecular structure (Fig. 1) demonstrates that besides the μ_3-methylidyne ligand the chlorine atoms of the $CHCl_3$ molecule are retained within the cluster and bridge three edges, giving an effective C_{3v} symmetry to the metal cluster skeleton. The resulting cluster is sterically strained by the presence of the bridging groups and the bulky PBu^t_3 ligands and consequently the Pd–Pd bonds cover a wide range of lengths from 2.6683(11) to 3.1431(11) Å. In contrast the related tetrahedral gold cluster $[Au_4(PBu^t_3)_4]^{2+}$, which has no bridging ligands, has Au–Au bonds which vary from 2.7031(9) to 2.7302(7) Å.[8] The Pd–Pd bonds bridged by Cl ligands are all longer than 2.947 Å and the three bonds in the triangle capped by CH are shorter than 2.744 Å. The steric strain is also reflected in the presence of a long Pd(2)–Cl(7) bond [2.939(3) Å] which is much longer than the remaining Pd–Cl bonds which lie between 2.391(2) and 2.430(2) Å. The Pd–P distances vary in length from 2.359(2) to 2.374(2) Å. The Pd–C bond lengths to the methylidyne ligand average 1.955(8) Å, which is close to that reported for the ethylidyne ligand on a Pt(111) surface.[3]

The $^{31}P\text{-}\{^1H\}$ NMR spectrum‡ shows a quartet and a doublet which is consistent with a C_{3v} structure in solution. The methylidyne ^1H NMR resonance is observed as a doublet of quartets at δ 11.6 which is in the range previously reported for μ_3-methylidyne complexes.[9] The CH stretching frequency is obscured by ligand vibrations, but ν(C–D) for the corresponding compound prepared from $CDCl_3$ is observed at 2162 cm^{-1}.

Although μ_3-methylidyne cluster compounds have previously been synthesised from $CHCl_3$,[2] this cluster is unique in retaining all the atoms of the $CHCl_3$ molecule within the cluster. The final product appears structurally to document the effective chemisorption of a $CHCl_3$ molecule by a tetrahedral metal cluster with simultaneous breaking of three C–Cl bonds, but this is unlikely to be an accurate reflection of the actual mechanism.

In the reaction of $[Pd_2(dba)_3]\cdot C_6H_6$ with PBu^t_3 and $CHCl_3$ cyclometallated binuclear compounds similar to those previously reported[10] are also formed in a competing reaction which limits the yield of **1**. With $CHBr_3$ and CHI_3 no corresponding cluster compounds were formed, only cyclometallated products and $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ (X = Br or I).[11]

The tetrahedral palladium cluster has a polyhedral electron

---

† Crystal data: $C_{49}H_{109}Cl_3P_4Pd_4\cdot 0.5(CH_3)_2CO$, $M = 1383.23$, crystal dimensions 0.50 × 0.30 × 0.28 mm, monoclinic, space group $P2_1/n$, $a = 22.654(6)$, $b = 13.351(7)$, $c = 23.474(7)$ Å, $\beta = 113.31(1)°$, $U = 6520$ Å^3, $Z = 4$, $D_c = 1.409$ Mg m^{-3}, μ(Mo-Kα) = 1.336 mm^{-1}, $F(000) = 2856$. Data were measured at 293(2) K on a Siemens P4/PC diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using ω scans. The structure was solved by direct methods and refined anisotropically to give $R1 = 0.0496$, $wR2 = 0.1331$ (SHELXTL, SHELXL 93 for SGI-Iris)[7] for 8401 unique observed reflections ($|F| \geqslant 4\sigma|F_o|$), $2\theta \leqslant 50°$, $w = 1/[\sigma^2(F_o^2) + (0.0914\ P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Most of the hydrogens were located from a ΔF map, the others by using default bond lengths and angles. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

‡ Selected data for compound **1**: yield 30% (Found: C, 43.8; H, 7.9. $C_{49}H_{109}Cl_3P_4Pd_4$ requires C, 43.5; H, 8.1%); NMR ([$^2H_6$]acetone) $\delta(^1H)$ 11.6 [dq, ^4J(PP) 9.9, ^3J(HP) 2.1]; $\delta(^{31}P\text{-}\{^1H\})$ 100.2 (q) and 74.0 [d, ^3J(PP) 132.2 Hz].

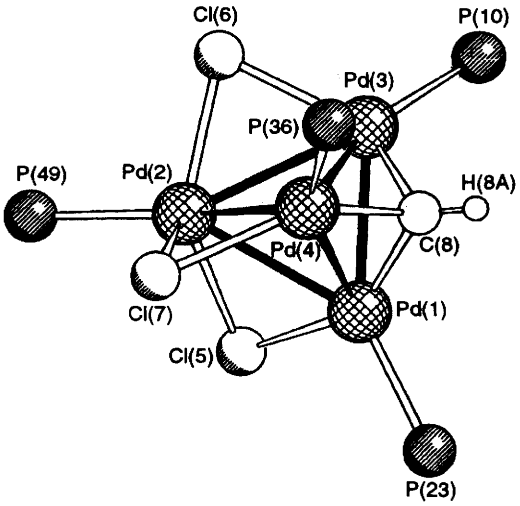
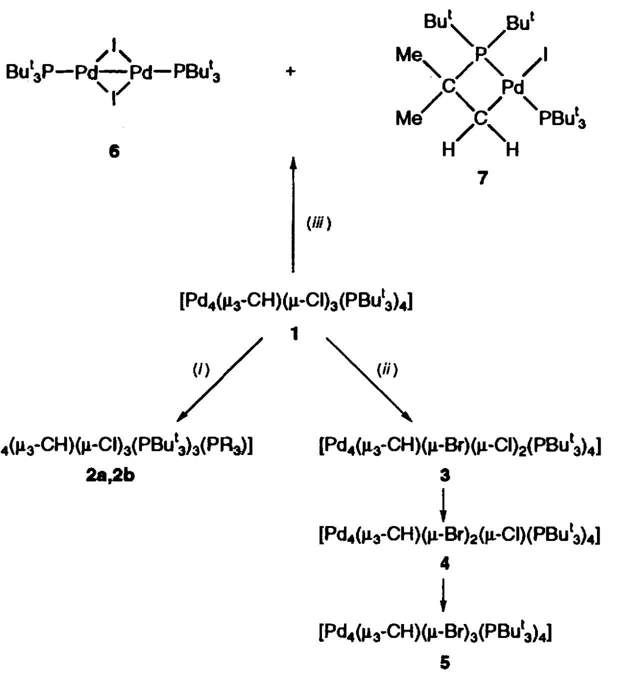


Fig. 1 Molecular structure of the cluster $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4]$ showing the atom numbering used. For clarity, the phosphine substituents have been omitted. Important bond lengths (Å) include: Pd(1)–C(8) 1.964(7), Pd(3)–C(8) 1.959(8), Pd(4)–C(8) 1.941(7), Pd(1)–Cl(5) 2.395(2), Pd(2)–Cl(5) 2.430(2), Pd(2)–Cl(6) 2.391(2), Pd(2)–Cl(7) 2.939(3), Pd(3)–Cl(6) 2.421(2), Pd(4)–Cl(7) 2.424(2), Pd(1)–P(23) 2.359(2), Pd(2)–P(49) 2.374(2), Pd(3)–P(10) 2.373(2), Pd(4)–P(36) 2.360(2), Pd(1)–Pd(2) 2.9886(10), Pd(1)–Pd(3) 2.7425(9), Pd(1)–Pd(4) 2.6683(11), Pd(2)–Pd(3) 2.9480(11), Pd(2)–Pd(4) 3.1431(11) and Pd(3)–Pd(4) 2.7444(12)

count of 60, which is the closed-shell requirement for a tetrahedral cluster which conforms to the polyhedral skeletal electron-pair theory.[12] Palladium is on the borderline of those elements which conform to this structural generalisation.[13,14]

The reactions of $[Pd_4(\mu_3\text{-}CH)(\mu\text{-}Cl)_3(PBu^t{}_3)_4]$ **1** which have been investigated to date are summarised in Scheme 1. The $^{31}P\text{-}\{^1H\}$ NMR§ spectra showed that the reaction with phosphines resulted only in the monosubstituted products **2a** and **2b** even when an excess of phosphine was used. In contrast, with LiBr sequential substitution of all of the bridging chlorides by bromides was observed and compounds **3**–**5** have been characterised by $^{31}P\text{-}\{^1H\}$ NMR studies.¶ Full substitution required *ca.* 2 h at room temperature. With LiI cluster degradation results and among the products detected by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy are the binuclear metal–metal bonded palladium(I) compound **6**[11] and the palladium cyclometallated compound **7** which are formed in approximately equal yields.

The lability of complex **1** towards substitution reactions together with the μ_3-CH ligand suggested that it may have interesting catalytic chemistry. When ethyne was bubbled through a toluene solution (0.25 mmol dm^{-3}) of **1** poly(ethyne) was formed as a solid precipitate and was characterised by IR spectroscopy.[15]



Scheme 1 (*i*) PR_3 (R = Ph or C_6H_{11}); (*ii*) LiBr; (*iii*) LiI

Acknowledgements

We thank Consejo Nacional de Ciencia y Tecnologia for a Scholarship for R. V., EPSRC and BP for financial support.

References

1 J. B. Keistler, *Polyhedron*, 1988, **7**, 847.
2 D. Seyferth, J. E. Hallgreen and P. L. K. Hung, *J. Organomet. Chem.*, 1973, **50**, 265.
3 G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces*, Cornell University Press, Ithaca, 1978, p. 278.
4 N. R. Avery and N. Sheppard, *Surf. Sci.*, 1986, **169**, L367.
5 J. M. Moses, A. H. Weiss, K. Matusek and L. Guczi, *J. Catal.*, 1984, **86**, 417; M. Ichikawa, *Adv. Catal.*, 1992, **38**, 283.
6 E. L. Muetterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479.
7 G. M. Sheldrick, SHELXTL, Siemens Analytical Instruments, Madison, WI, 1990; SHELXL 93, University of Göttingen, 1993.
8 E. Zeller, H. Beruda and H. Schmidbaur, *Inorg. Chem.*, 1993, **32**, 3203.
9 M. Akita, K. Noda and Y. Moro-oka, *Organometallics*, 1994, **13**, 4145 and refs. therein.
10 R. G. Goel and R. G. Montemayor, *Inorg. Chem.*, 1977, **16**, 2183; H. C. Clark, A. L. Goel and W. O. Ogini, *J. Organomet. Chem.*, 1978, **157**, C16.
11 C. Cardin, R. Vilar and D. M. P. Mingos, unpublished work.
12 D. M. P. Mingos and D. J. Wales, *Introduction to Cluster Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1990.
13 E. G. Mednikov, N. K. Eremenko, S. P. Gubin, Yu L. Slovokhotov and Yu T. Struchkov, *J. Organomet. Chem.*, 1982, **239**, 401.
14 J. Dubrawski, J. C. Kriege-Simondsen and R. D. Feltham, *J. Am. Chem. Soc.*, 1980, **102**, 2080.
15 J. C. W. Chien, *Polyacetylene: Chemistry, Physics and Material Science*, Academic Press, Orlando, 1984.

Received 5*th April* 1995; *Communication* 5/02198G

---

§ $^{31}P\text{-}\{^1H\}$ NMR ([$^2H_6$]acetone): **2a**, δ 97.1 (P_x, dt), 75.9 (P_a, dd) and 26.7 [P_b, dt, $^3J(P_aP_x)$ 125.6, $^3J(P_bP_x)$ 139.0, $^3J(P_aP_b)$ 20.4]; **2b**, δ 98.5 (P_x, dt), 76.5 (P_a, dd) and −2.0 [P_b, dt, $^3J(P_aP_x)$ 125.5, $^3J(P_bP_x)$ 139.0, $^3J(P_aP_b)$ 17.0 Hz].

¶ $^{31}P\text{-}\{^1H\}$ NMR ([$^2H_6$]acetone): **3**, δ 101.6 (P_x, dt), 78.9 (P_a, dt) and 72.2 [P_b, dd, $^3J(P_aP_x)$ 149.2, $^3J(P_bP_x)$ 128.8, $^3J(P_aP_b)$ 23.7]; **4**, δ 105.5 (P_x, dt), 77.3 (P_a, dd) and 71.2 [P_b, dt, $^3J(P_aP_x)$ 139.0, $^3J(P_bP_x)$ 128.8, $^3J(P_aP_b)$ 23.7]; **5**, δ 108.3 (q) and 76.5 [d, $^3J(PP)$ 149.0 Hz].