A cluster model for the catalytic hydrogenation of CFCs and the synthesis and structural characterisation (when X = Br) of $[Pd_4(\mu_3\text{-CF})(\mu\text{-X})_3(PBu^t{}_3)_4]$ (X = Cl, Br)

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The syntheses, characterisation and crystal structure (when X = Br) of $[Pd_4(\mu_3\text{-CF})(\mu\text{-X})_3(PBu^t{}_3)_4]$ (X = Cl, Br) are reported; the μ_3-CF moiety is hydrogenated to CFH_3 under mild conditions and serves as a model for the heterogeneous hydrogenation of CFCs to HCFCs.

The cluster–surface analogy has a long history which can be traced back to Muetterties pioneering work.[1] Molecular clusters with coordinated organic fragments have proved to be invaluable for providing definitive spectroscopic data which have been used to identify analogous species on metal surfaces.[2] The study of such systems on clean and well defined metal surfaces has implications for understanding the heterogeneous catalysed transformations of organic feedstocks. The lack of reactivity of molecular clusters, specifically catalytic reactivity, has, however, limited the development of the cluster–surface analogy.

Alkylidyne ligands have been extensively studied when coordinated to group 8 and 9 metals.[3,4] However, fluoromethylidyne cluster compounds have been structurally characterised only for iron[5–7] and molybdenum.[8] Recently, $[Pd_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(PBu^t{}_3)_4]$, the first example of a palladium methylidyne cluster, has been described and structurally characterised.[9] Herein we report the syntheses of $[Pd_4(\mu_3\text{-CF})(\mu\text{-X})_3(PBu^t{}_3)_4]$ (X = Cl **1**, Br **2**) and the first structural characterisation of a palladium μ_3-CF cluster. Interestingly the CF group of $[Pd_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(PBu^t{}_3)_4]$ is readily cleaved when the cluster is reacted with H_2 under mild conditions.

When 1 mol equiv. of $[Pd_2(dba)_3]\cdot C_6H_6$, 2 mol equiv. of $PBu^t{}_3$ and 0.5 mol equiv. of $CFCl_3$ were reacted in toluene for 6 h the reaction mixture turned dark brown. The solvent was removed under reduced pressure and the crude product was recrystallised from toluene–acetone at 4 °C to give $[Pd_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(PBu^t{}_3)_4]$ **1** as dark green crystals. The formulation of this product was confirmed on the basis of IR, $^{31}P\{^1H\}$ NMR, ^{19}F NMR, FABMS and elemental analyses.†

A solution of $[Pd_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(PBu^t{}_3)_4]$ in toluene was treated with 3 mol equiv. of LiBr in acetone for 4 h and $[Pd_4(\mu_3\text{-CF})(\mu\text{-Br})_3(PBu^t{}_3)_4]$ **2** was obtained. After removing the solvents under reduced pressure the remaining dark green solid was extracted with benzene and crystals of $[Pd_4(\mu_3\text{-CF})(\mu\text{-Br})_3(PBu^t{}_3)_4]$ were obtained from benzene–acetone after cooling to 4 °C overnight. The formulation was confirmed by the IR, $^{31}P\{^1H\}$ NMR, ^{19}F NMR, FABMS and analytical data.‡ A single-crystal X-ray analysis§ of compound **2** has confirmed that the cluster has a structure similar to that previously reported for $[Pd_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(PBu^t{}_3)_4]$.[9] It consists of a tetrahedral cluster with a face-capping fluoromethylidyne ligand. The molecular structure (Fig. 1) demonstrates that the chlorine atoms of the starting material have been substituted by three bromine atoms, whilst retaining the effective C_{3v} symmetry of the metal cluster skeleton. The Pd–Pd bonds in the cluster are in the range 2.727(2)–3.123(2) Å compared with 2.668(1)–3.143(1) Å in the analogous $[Pd_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(PBu^t{}_3)_4]$ cluster compound.

The presence of the μ_3-CF capping ligand in these clusters is interesting in terms of the cluster–surface analogy. It is known that palladium black and palladium supported in alumina may be used as heterogeneous catalysts for the hydrogenation of chloroflurocarbons (CFCs) to hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs).[11] Recently these reactions have taken on considerable industrial importance because of the need for HFCs as possible substitutes for the ozone-damaging CFCs. However, to our knowledge only heterogeneous catalytic processes for converting CFCs to HCFCs have been reported.[12] $[Pd_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(PBu^t{}_3)_4]$ derived from $CFCl_3$ may be converted to CFH_3 homogeneously under mild conditions and therefore provides an effective model for such a process.

A solution of $[Pd_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(PBu^t{}_3)_4]$ in toluene was reacted with H_2–NEt_3 and 4 mol equiv. of $PBu^t{}_3$ under mild conditions (at STP). The products formed in this reaction were $[Pd(PBu^t{}_3)_2]$, $[HNEt_3]Cl$ and CFH_3 (in > 50% yield after 2 h as detected by gas chromatography).¶ No other volatile fluorocarbon compounds were detected by gas chromatography. $[Pd(PBu^t{}_3)_2]$ was detected using $^{31}P\{^1H\}$ NMR, by its characteristic resonance at δ 85.5[13] and monitoring its signal indicated that the reaction was complete after 4 h. This confirms that a μ_3-CF moiety, derived by an oxidative-addition process from $CFCl_3$, may be hydrogenated to CFH_3 under mild conditions.

When the hydrogenation reaction was repeated using the mononuclear compound $[Pd(PBu^t{}_3)_2]$, generated *in situ* from $[Pd_2(dba)_3]$ and $PBu^t{}_3$, with an excess of $CFCl_3$ {50 : 1 relative

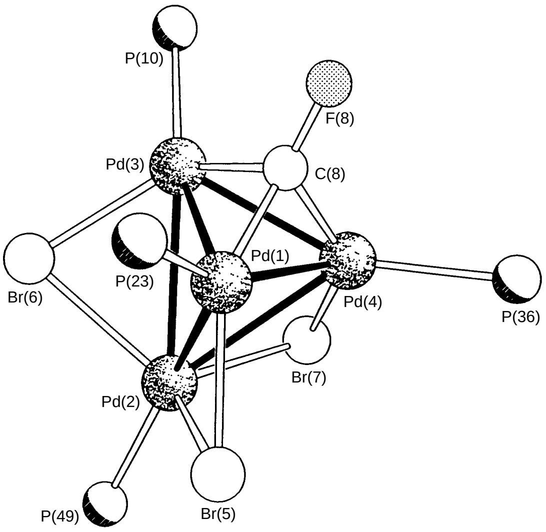


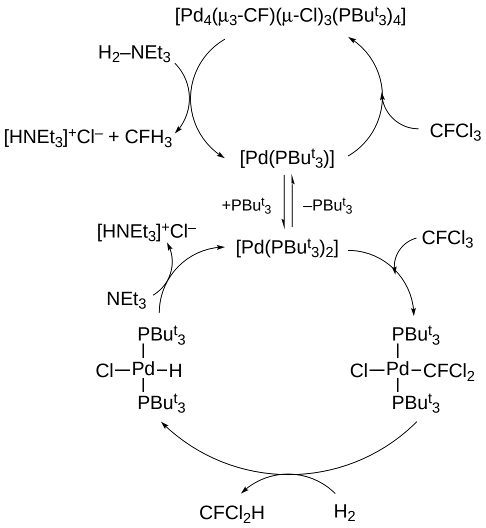
Fig. 1 The molecular structure of the cluster $[Pd_4(\mu_3\text{-CF})(\mu\text{-Br})_3(PBu^t{}_3)_4]$ showing the numbering used (the phosphine substituents are omitted for clarity). Important bond lengths (Å): Pd(1)–C(8) 1.94(2), Pd(3)–C(8) 1.96(2), Pd(4)–C(8) 1.96(2), Pd(1)–Br(5) 2.524(3), Pd(2)–Br(5) 2.668(3), Pd(2)–Br(6) 2.666(3), Pd(2)–Br(7) 2.639(3), Pd(3)–Br(6) 2.531(3), Pd(4)–Br(7) 2.529(2), Pd(1)–P(23) 2.397(5), Pd(2)–P(49) 2.361(5), Pd(3)–P(10) 2.403(6), Pd(4)–P(36) 2.392(5), Pd(1)–Pd(2) 3.112(2), Pd(1)–Pd(3) 2.727(2), Pd(1)–Pd(4) 2.729(2), Pd(2)–Pd(3) 3.097(2), Pd(2)–Pd(4) 3.123(2), Pd(3)–Pd(4) 2.731(2), C(8)–F(8) 1.36(2).

to $[Pd_2(dba)_3]$}, the only hydrogenation product observed was $CFCl_2H$. Complete conversion of the $CFCl_3$ to $CFCl_2H$ required 24 h. No traces of CFH_3 or any other gas were detected, suggesting that the cluster $[Pd_4(\mu_3\text{-}CF)(\mu\text{-}Cl)_3(PBu^t_3)_4]$ plays an essential role in the hydrogenation of $CFCl_3$ to CFH_3.

Although the formation of $[Pd_4(\mu_3\text{-}CF)(\mu\text{-}Cl)_3(PBu^t_3)_4]$ from $CFCl_3$ and its subsequent hydrogenation provides an illustration of how $CFCl_3$ may be hydrogenated to CFH_3 on a metal surface, the cluster compound itself is not an effective homogeneous catalyst. When H_2 was bubbled through a solution of $[Pd_4(\mu_3\text{-}CF)(\mu\text{-}Cl)_3(PBu^t_3)_4]$ in toluene in the presence of NEt_3 and with a 50-fold excess of $CFCl_3$, the gases produced were identified as CFH_3 and $CFCl_2H$ with a ratio of $CFCl_3H/CFH_3$ of *ca.* 2.3. $^{31}P\{^1H\}$ NMR data confirmed that the cluster had fragmented during this reaction.

Scheme 1 summarises plausible mechanistic cycles involving the reactions for the mono- and tetra-nuclear palladium compounds. Although in the absence of hydrogen the formation of the tetranuclear cluster with the μ_3-CF group proceeds at a sufficient rate to compete with the formation of the simple oxidative-addition products, the hydrogenation step proceeds more quickly for the mononuclear product than for the tetranuclear compound leading to the formation of $CFCl_2H$ in addition to CFH_3. Attempts are currently being made to use variations in the ligands to change the relative rates of the competing cycles and thereby improve the selectivity of the catalytic hydrogenation process.

We thank CONACYT and ORS for scholarships to R. V., EPSRC for financial support to S. E. L., BP plc for endowing D. M. P. M.'s chair and ICI for providing reference samples of $CFCl_2H$ and CFH_3.



Scheme 1 Reactions involved in the palladium-assisted hydrogenation of $CFCl_3$

Footnotes

† *Selected data* for **1**: yield 18%. (Found C, 42.4; H, 7.4. $C_{49}H_{108}Cl_3FP_4Pd_4$ requires C, 42.9; H, 7.9%). $^{31}P\{^1H\}$ NMR ($[^2H_6]$benzene) δ 103.4 (q), 68.6 (dd); ^{19}F NMR ($[^2H_6]$benzene) δ 111.0 [dq, ^3J(PP) 132.2, ^3J(PF) 39.7, ^4J(PF) 8.5 Hz]. IR ν(C–F) 1052 cm^{-1}.

‡ *Selected data* for **2**: yield 61%. (Found C, 40.9; H, 6.8 $C_{49}H_{108}Br_3FP_4Pd_4\cdot 0.75C_6H_6\cdot 0.75Me_2CO$ requires C, 41.0; H, 7.1%). $^{31}P\{^1H\}$ NMR ($[^2H_6]$benzene) δ 117.0 (q), 70.5 (dd); ^{19}F NMR ($[^2H_6]$benzene) δ 116.0 [dq, ^3J(PP) 173.0, ^3J(PF) 40.1, ^4J(PF) 11.0 Hz]. The metathesis reaction of **1** to **2** was monitored at different reaction times by $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopy. The asymmetric mixed-halogen clusters $[Pd_4(\mu_3\text{-}CF)(\mu\text{-}Br)(\mu\text{-}Cl)_2(PBu^t_3)_4]$ **3** and $[Pd_4(\mu_3\text{-}CF)(\mu\text{-}Br)_2(\mu\text{-}Cl)(PBu^t_3)_4]$ **4** were identified as intermediates, suggesting that the substitution reaction takes place sequentially.

§ *Crystal data* for **1**: $C_{49}H_{108}Br_3FP_4Pd_4\cdot 0.75Me_2CO\cdot 0.75C_6H_6$, $M = 1607.7$, monoclinic, space group $C2/c$; $a = 25.989(4)$, $b = 25.529(4)$, $c = 24.216(4)$ Å, $\beta = 118.77(1)°$; $U = 14083(4)$ Å^3, $Z = 8$, $D_c = 1.517$ g cm^{-3}; μ(Mo-Kα) = 2.833 mm^{-1}; $F(000) = 6524$. Data were measured on a Siemens P4/PC diffractometer with graphite-monochromated Mo-Kα radiation using ω scans. The structure was solved by direct methods and the non-hydrogen atoms of the cluster refined anisotropically by full-matrix least-squares based on F^2 to give $R_1 = 0.0783$, $wR_2 = 0.1446$ (SHELXTL)[10] for 3824 unique observed reflections ($|F| > 4\sigma|F_o|$, $2\theta \leqslant 50°$) and 609 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/330.

¶ *Selected data for chromatographic studies*: the chromatographic studies were performed in a Perkin Elmer 8500-GC with an FID detector and a Carbopack B/5% Fluorocol column special to detect fluorinated compounds. The oven temperature was set to 60 °C, the detector to 250 °C and the injection temperature to 200 °C. The carrier gas (N_2) flow rate was adjusted to 25 ml min^{-1}. Samples: 200 μl of sample (gases produced in the reaction) was injected using a gas-tide syringe. The assignment of the peaks was made by comparison with standards of CFH_3, $CFCl_2H$ and $CFCl_3$ at the same temperature and flow rate conditions.

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Received, 16th October 1996; Com. 6/07048E