Site-selective hydrogenolysis, hydrogenation and alcoholysis involving the homometallic cluster [$W_6H_5(CPr^i)(OPr^i)_{12}$]

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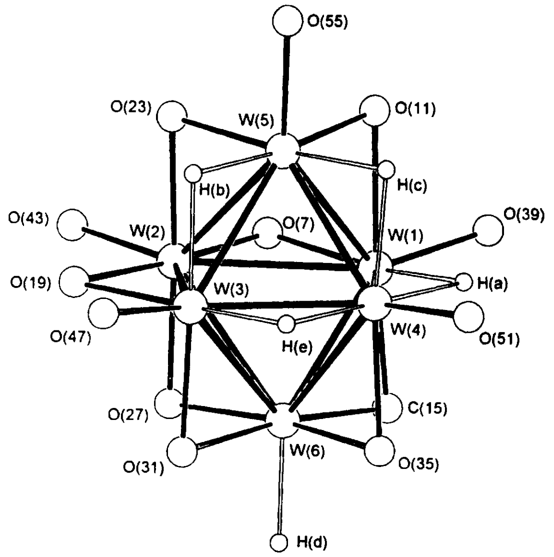
The octahedral W_6 cluster [$W_6(\mu$-$H)_4H(\mu$-$CPr^i(\mu$-$OPr^i)_7(OPr^i)_5$] 1 reacts with D_2 to give D for H exchange, reacts reversibly with ethene, and in the presence of H_2 yields ethane by exclusive use of the terminal W–H bond; 1 also reacts with $(CD_3)_2CDOD$ to give selective alcoholysis of one terminal OR group.

In a recent Feature Article in this Journal, Maitlis *et al.*[1] posed the question 'Can heterogeneous catalysis occur at a single site on a metal surface?' They also noted that while metal clusters and metal surfaces often reveal common modes of substrate binding, the greater reactivity of the latter can be attributed to the relative degrees of unsaturation of the two systems. Although high turnover rates and selectivity are always desirable in catalysis, the two rarely operate cooperatively. It is, therefore, in some of the slower reactions that most insight can be gained with respect to selectivity and, indeed, therein one might hope to address such questions as: do reactions occur at single metal centres?

We describe here some reactions of a homometallic cluster [$W_6H_5(CPr^i)(OPr^i)_{12}$] 1[2] which by virtue of its chemical *inertness* reveals site selective reactivity of the type not seen before in the chemistry of homometallic clusters. The $W_6H_5CO_{12}$ skeleton A of the cluster is shown below and the ^1H NMR spectrum of the five hydrides is shown in Fig. 1.



Assignment of the hydride signals to the hydride ligands H(a)–H(e) shown in A is possible by NOE difference spectroscopy (Fig. 2). The hydride W–H(d) is also indicated to be a terminal hydride from the intensity of the satellites due to coupling to ^{183}W ($I = \frac{1}{2}$, 14.5% natural abundance).

The methine signals of the twelve OPr^i ligands appear as 12 partially overlapping septets in the region δ 4.5–6.0 in C_6D_6 at 500 MHz, 23 °C. Having assigned the tungsten–hydride resonances, a partial assignment of the OR groups was possible by NOE difference spectroscopy. Of particular note is the assignment of the septet centred at δ 5.10 to the terminal OPr^i ligand bonded to W(4). Note this OR group is adjacent to three bridging hydrides, denoted by H(a), H(c) and H(e), to which it shows NOE.

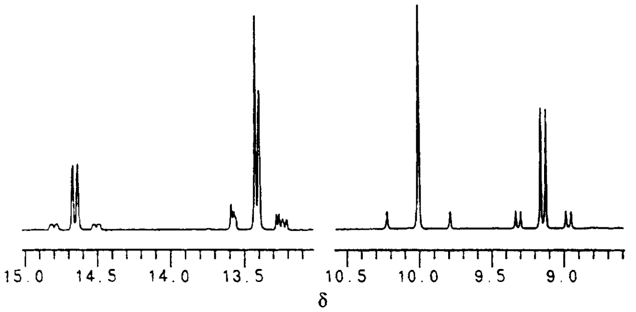


Fig. 1 Hydride region of the ^1H NMR spectrum of [$W_6H(\mu$-$H)_4$ $(\mu$-$CPr^i)(OPri^i)_5(\mu$-$OPr^i)_7$] **1**

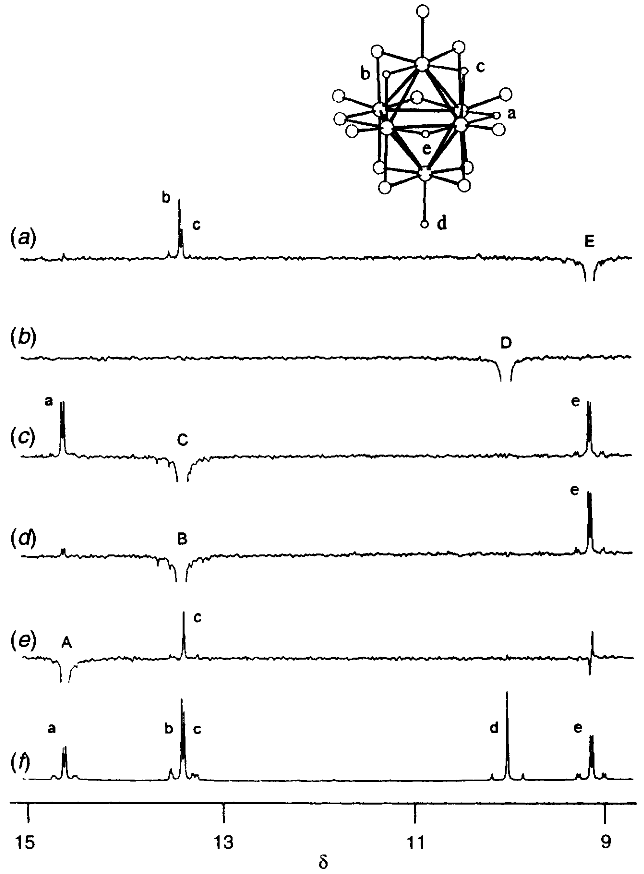


Fig. 2 Assignment of the hydride ligands (a)–(e) in compound **1** to the hydride resonances in the ^1H NMR spectrum (*f*) based on the NOE difference spectra [(*a*)–(*e*)] obtained by selective irradiation

When the protio cluster **1** is dissolved in C_6D_6 and placed in an NMR tube under an atmosphere of D_2 gas the formation of $[^2H_1]$**1** is observed by the slow disappearance of the ^1H signal associated with H(d). When the converse experiment is carried out wherein $[W_6D_5(CPr^i)(OPr^i)_{12}]$ is allowed to react with H_2, then the formation of W–H(d) is observed. It should be emphasized that these reactions are slow with $t_{1/2} \approx 2$ days at 22 °C. Over a period of several days (> 7 days) a much slower but also selective H/D exchange reaction is detected involving H(a). When **1** is allowed to react with $CD_2{=}CD_2$ (in excess) in C_6D_6 at 22 °C and the reaction is monitored by ^1H NMR spectroscopy the loss of the ^1H signal associated with H(d) is observed and the formation of $CHD{=}CD_2$ is seen. Conversely, deuteriated cluster $[W_6D_5(CPr^i)(OPr^i)_{12}]$ reacts with $CH_2{=}CH_2$ to yield $[W_6H(D)_4(CPr^i)(OPr^i)_{12}]$ and C_2H_3D. Only the H(d) site is involved.

The reaction between **1**, $CH_2{=}CH_2$ and H_2 (3 atm.) in C_6D_6 yields ethane with a turnover rate of *ca.* 2 molecules of ethene per molecule of **1** per day. Labelling experiments show that this process involves exclusively the reactivity of the terminal W–H(d) site.

The protio cluster **1** reacts with $(CD_3)_2CDOD$ in C_6D_6 to form $[W_6H_5(CPr^i)(OPr^i)_{11}\{OCD(CD_3)_2\}]$ at 22 °C. Formation of the latter compound is indicated by the disappearance of the methine septet at δ 5.10. If the solvent and excess propan-2-ol are removed, the selectively deuteriated cluster is chemically persistent with respect to OR group site exchange in C_6D_6 for weeks under a dry inert atmosphere. The deuteriated cluster $[W_6D_5(CPr^i)\{OCD(CD_3)_2\}_{12}]$ also was shown to react with Pr^iOH in C_6D_6 to yield $[W_6D_5(CPr^i)\{OCD(CD_3)_2\}_{11}(OPr^i)]$. The exchange of the single terminal OR site by alcoholysis occurs within a few hours in the presence of *ca.* 6 equiv. of added free alcohol. If a large excess of Pr^iOH (*ca.* 100 equiv.), is allowed to react with the cluster then further but slow OPr^i group exchange can be observed. It must be emphasized, however, that the latter proceeds *via* different alcohol–alkoxide site exchange since the cluster **1** with the isotopomer having a labelled OPr^i ligand at site O(51) (that with the methine septet at δ 5.10) is indefinitely persistent with respect to intramolecular (and intermolecular) group scrambling at 22 °C.

Finally we have examined the reactivity of **1** in C_6D_6 with $Me_2{}^{13}C{=}O$ and $(CD_3)_2CDOD$. By ^1H NMR spectroscopy the Meerwein–Ponndorf–Verley (MPV) equilibrium[3] shown in eqn. (1) is quickly established and ^{13}C labelled (along with deuteriated) Pr^iO is incorporated at the site denoted by O(51) in **A**.

$$(CH_3)_2{}^{13}C{=}O + (CD_3)_2CDOD \rightleftharpoons (CH_3)_2{}^{13}CDOD + (CD_3)_2C{=}O \quad (1)$$

The equilibrium (1) is established more rapidly than that involving **1** and exchange with $(CD_3)_2CDOD$ and $(CH_3)_2{}^{13}CDOH$. From this we must conclude that the cluster is not the catalyst for eqn. (1) but rather that some species present in solution, quite probably arising from trace decomposition of **1** by adventitious water, is the active catalyst for the MPV reaction, and it is by subsequent alcohol–alkoxide exchange that the ^{13}C labelled OPr^i ligands are incorporated at site O(51) in **A**.

In conclusion, the chemical inertness of **1** has allowed a rare insight into the different reactivities of specific ligands which differ because of their local environments. The terminal W–H bond is labile to exchange with D_2, reversible insertion with ethene and participates exclusively as the site for ethene hydrogenation. The terminal OPr^i ligand at site O(51) is chemically labile toward alcohol exchange, quite probably because it is the least sterically encumbered site being adjacent to three bridging hydrides. Our ability to monitor these site-selective processes is due to the lack of intramolecular site exchange. Typically intramolecular ligand site exchange is facile in cluster chemistry as ligands roam freely from one metal site to another.[4] In reactions involving metal surfaces this movement of surface bound groups, such as hydride, renders high reactivity but masks the ability to address the question raised by Maitlis and his coworkers. However, from the work of those involving ultra-high vacuum conditions it is now well recognized that specific modes of reactivity may be associated with specific sites on a surface such as steps and edges.[5] Moreover the ensemble effect of several metal atoms overcomes the difficulties of multistep bimolecular reactions which must occur, for example, in the cleavage of CO by reaction with a mononuclear metal complex such as $Ta(OSiBu^t_3)_3$.[6] It is, however, from the study of the reactivity of a chemically inert cluster such as **1** that we can actually monitor site-specific reactivity and, discern, for the first time, the different reactivity of bridging *vs.* terminal metal–hydride ligands.

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