Activation of a Ruthenium Cluster by a Gold Centre

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Substitution of Au(PPh_3) for hydrogen in [$Ru_4H_4(CO)_{12}$] increases the rate of catalytic pent-1-ene isomerisation.

Modification of catalytic activity by heterogeneous alloy catalysts is well documented.[1] Recent interest in the synthesis of heteronuclear transition metal clusters[2] has provided examples of related series of clusters to probe such modifications at a molecular level in homogeneous systems. An example of differentiated heterosite activity in [$Ru_2Co_2(CO)_{13}$] indicates that catalytic activity may be modified in heterometallic clusters,[3] and mixed metal homogeneous catalytic systems have been reported.[4—6] However in none of these systems has a particular heterometallic cluster been implicated in the catalysis, although '[$Ru_2Rh(CO)_{12}$]' has been identified as one component in an ethylene glycol synthesis.[5] In this communication we report on the modification of catalytic activity of [$Ru_4H_4(CO)_{12}$] by the introduction of M(PPh_3), M = Cu and Au, units.

The complexes [$Ru_4H_3\{M(PPh_3)\}(CO)_{12}$], M = Au (**1**) and Cu (**2**), and [$Ru_4H_2\{M(PPh_3)\}_2(CO)_{12}$], M = Au (**3**) and Cu (**4**), were prepared by procedures similar to those already described.[7,8] Results from catalytic experiments for these four complexes involving pent-1-ene under H_2 at 35 °C are presented in Table 1; comparisons with [$Ru_4H_4(CO)_{12}$] (**5**), [$(Ph_3P)_2N$][$Ru_4H_3(CO)_{12}$] (**6**) and [Au(PPh_3)Cl] are also included. All the cluster complexes excepting (**4**) were recovered unchanged after this reaction period. The two ruthenium–gold complexes clearly provide more active catalysts for pent-1-ene isomerisation than the parent [$Ru_4H_4(CO)_{12}$], in marked contrast to the behaviour of the copper-ruthenium analogues. The *trans*:*cis* ratios also increase with overall activity. At 60 °C, both [Ru_4H_3-$\{Au(PPh_3)\}(CO)_{12}$] (**1**) and the copper-containing analogue (**2**) are effective catalysts for the hydrogenation and isomerisation of pent-1-ene and display essentially identical activity to complex (**5**). Indeed the i.r. spectra of the recovered solutions indicated partial decomposition of the heterometallic clusters to complex (**5**).

These results indicate that, while a common species is probably responsible for the catalytic activity of (**1**) (**2**), and (**5**) at 60 °C, at 35 °C the gold centres in complexes (**1**) and (**3**) increase the catalytic activity towards isomerisation over that of [$Ru_4H_4(CO)_{12}$]. The effects of changes in conditions on the activity of (**1**) are given in Table 2. Addition of a small partial pressure of CO strongly inhibited isomerisation [this effect was also noted for complexes (**2**) and (**3**)], as did the reduction of the pressure of hydrogen. In all those runs, i.r. and n.m.r. spectroscopic measurements detected complex (**1**) as the sole inorganic species. The presence of PPh_3 also retarded isomerisation catalysis, but in this case the spectroscopic results indicated an essentially stoicheiometric reaction to form (**6**)[9] and [$Au(PPh_3)_2$]$^+$,[10] according to equation (1) (L = PPh_3). The inhibition by added ligands suggests that the initial step is CO dissociation, as reported for the [$Ru_4H_4(CO)_{12}$]-catalysed isomerisation of pent-1-ene[11] and the hydrogenation of ethylene.[12] Indeed plots of (conversion)$^{-1}$ against P_{CO} and [PPh_3] as employed in ref. 12 are fully consistent with that. Since the catalytic rates in the presence of complex (**1**) are faster than those of the two homonuclear clusters (**5**) and (**6**), we propose the initial step is in accord with equation (2). The equilibrium in equation (1) is presumably dynamic, as reported for gold–phosphine cluster transformations,[13] and

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Table 1. Isomerisation and hydrogenation of pent-1-ene.[a]

		Product proportions (%) of total C_5 organics		
Catalyst source	Conversion (%)	Pentane	*trans*-Pent-2-ene	*cis*-Pent-2-ene
$[Au(PPh_3)Cl]$	0	—	—	—
$[H_4Ru_4(CO)_{12}]$ (**5**)	32.9	1.7	19.8	11.0
$[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$ (**6**)	7.9	—	4.5	3.4
$[H_3Ru_4\{Au(PPh_3)\}(CO)_{12}]$ (**1**)	71.0	1.4	51.4	18.2
$[H_2Ru_4\{Au(PPh_3)\}_2(CO)_{12}]$ (**3**)	49.6	1.1	33.1	15.3
$[H_3Ru_4\{Cu(PPh_3)\}(CO)_{12}]$(**2**)	29.4	0.3	18.5	10.7
$[H_2Ru_4\{Cu(PPh_3)\}_2(CO)_2]$ (**4**)	7.7	—	4.4	3.3

[a] Reaction conditions: catalyst source 2.0 mM; pent-1-ene, 54 mM; solvent: CH_2Cl_2, 2.5 cm^3; 1 atm H_2, 35.0 ± 0.2 °C, 24 h.

Table 2. Isomerisation and hydrogenation of pent-1-ene catalysed by complex (**1**) at 35 °C.

		Product proportions (%) of total C_5 organics		
Conditions[a]	Conversion (%)	Pentane	*trans*-Pent-2-ene	*cis*-Pent-2-ene
	71.0	1.4	51.4	18.2
0.01 mM PPh_3	19.7	1.2	13.1	5.3
0.05 mM PPh_3	15.7	0.5	9.5	5.7
0.1 mM PPh_3	9.2	—	5.1	3.1
0.5 mM PPh_3	2.7	—	1.7	1.1
P_{H_2} 350 Torr	20.9	0.5	12.4	8.0
P_{H_2} 0 Torr	14.5	—	8.0	6.5
P_{CO} 0.5 Torr	3.1	—	1.8	1.3
P_{CO} 1.0 Torr	1.7	—	0.9	0.8
P_{CO} 5.0 Torr	0	—	—	—

[a] Conditions as in Table 1 with $P_{H_2} = (760 - P_{CO})$ Torr, unless otherwise stated.

can also allow the removal of the unsaturated cluster by co-ordination of PPh_3. The reduction in rate by added PPh_3 is too great to be accounted for solely by the reduction in the concentration of (**1**). Finally, we note the *trans*:*cis* ratio for catalysis by complex (**1**) at 35 °C under H_2 was 1.6(1) during the first 2—4 h of the reaction, rising to 2.8 after 24 h. This is indicative of some steric congestion at the active site.[14]

$$[Ru_4H_3(AuL)(CO)_{12}] + L \rightleftharpoons [AuL_2][Ru_4H_3(CO)_{12}] \quad (1)$$

$$[Ru_4H_3(AuL)(CO)_{12}] \rightleftharpoons [Ru_4H_3(AuL)(CO)_{11}] + CO \quad (2)$$

It is interesting to note that the most active complex, (**1**), is considered to be the only one with an open structure involving an edge bridging gold atom.[7,8] Nevertheless the triangulated structure of (**3**) also increases activity, albeit to a lesser extent. The precise reason for the preferential activation by gold rather than copper is also in question.

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