

Activation of a Ruthenium Cluster by a Gold Centre

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Substitution of Au(PPh₃) for hydrogen in [Ru₄H₄(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 clusters² 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 [Ru₂Co₂(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 '[Ru₂Rh(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 [Ru₄H₄(CO)₁₂] by the introduction of M(PPh₃), M = Cu and Au, units.

The complexes [Ru₄H₃{M(PPh₃)}(CO)₁₂], M = Au (**1**) and Cu (**2**), and [Ru₄H₂{M(PPh₃)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 H₂ at 35 °C are presented in Table 1; comparisons with [Ru₄H₄(CO)₁₂] (**5**), [(Ph₃P)₂N][Ru₄H₃(CO)₁₂] (**6**) and [Au(PPh₃)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 [Ru₄H₄(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 [Ru₄H₃{Au(PPh₃)}(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 [Ru₄H₄(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 PPh₃ also retarded isomerisation catalysis, but in this case the spectroscopic results indicated an essentially stoichiometric reaction to form (**6**)⁹ and [Au(PPh₃)₂]⁺,¹⁰ according to equation (1) (L = PPh₃). The inhibition by added ligands suggests that the initial step is CO dissociation, as reported for the [Ru₄H₄(CO)₁₂]-catalysed isomerisation of pent-1-ene¹¹ and the hydrogenation of ethylene.¹² Indeed plots of (conversion)⁻¹ against P_{CO} and [PPh₃] 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

Catalyst source	Conversion (%)	Product proportions (%) of total C ₅ organics		
		Pentane	<i>trans</i> -Pent-2-ene	<i>cis</i> -Pent-2-ene
[Au(PPh ₃)Cl]	0	—	—	—
[H ₄ Ru ₄ (CO) ₁₂] (5)	32.9	1.7	19.8	11.0
[(Ph ₃ P) ₂ N][H ₃ Ru ₄ (CO) ₁₂] (6)	7.9	—	4.5	3.4
[H ₃ Ru ₄ {Au(PPh ₃)}(CO) ₁₂] (1)	71.0	1.4	51.4	18.2
[H ₂ Ru ₄ {Au(PPh ₃) ₂ }(CO) ₁₂] (3)	49.6	1.1	33.1	15.3
[H ₃ Ru ₄ {Cu(PPh ₃)}(CO) ₁₂] (2)	29.4	0.3	18.5	10.7
[H ₂ Ru ₄ {Cu(PPh ₃) ₂ }(CO) ₂] (4)	7.7	—	4.4	3.3

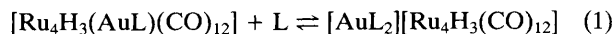
^a Reaction conditions: catalyst source 2.0 mM; pent-1-ene, 54 mM; solvent: CH₂Cl₂, 2.5 cm³; 1 atm H₂, 35.0 ± 0.2 °C, 24 h.

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

Conditions ^a	Conversion (%)	Product proportions (%) of total C ₅ organics		
		Pentane	<i>trans</i> -Pent-2-ene	<i>cis</i> -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
<i>P</i> _{H₂} 350 Torr	20.9	0.5	12.4	8.0
<i>P</i> _{H₂} 0 Torr	14.5	—	8.0	6.5
<i>P</i> _{CO} 0.5 Torr	3.1	—	1.8	1.3
<i>P</i> _{CO} 1.0 Torr	1.7	—	0.9	0.8
<i>P</i> _{CO} 5.0 Torr	0	—	—	—

^a Conditions as in Table 1 with *P*_{H₂} = (760 - *P*_{CO}) Torr, unless otherwise stated.

can also allow the removal of the unsaturated cluster by co-ordination of PPh₃. The reduction in rate by added PPh₃ 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 H₂ 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



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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