

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

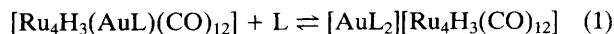
^a Reaction conditions: catalyst source 2.0 mM; pent-1-ene, 54 mM; solvent: CH₂Cl₂, 2.5 cm³; 1 atm H₂, 35.0 ± 0.2 °C, 24 h.

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.

We thank Mrs J. M. Street for n.m.r. spectra, Johnson Matthey for the loan of ruthenium chloride, and Dr. I. D. Salter for helpful communication. We are grateful to a referee for a helpful suggestion.

Received, 24th September 1984; Com. 1351

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