Evidence for Enhancement of Catalysis by a Second Metal in Heterobinuclear Complexes: X-Ray Structure of [H(CO)(PPh₃)₂Ru(bim)Rh(cod)] (bim = 2,2'-bi-imidazolato, cod = cyclo-octa-1,5-diene)

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The binuclear complexes [H(CO)(PPh₃)₂Ru(bim)M(cod)] (M = Rh or Ir, cod = cyclo-octa-1,5-diene) are more active as catalysts for the reduction of cyclohexanone, styrene, benzylideneacetophenone, and cyclohexene than the mononuclear parent (ruthenium, rhodium, or iridium) compounds.

Binuclear complexes of transition metals in which the metal atoms are constrained to be proximate have been studied because of their properties as catalysts.[1,2] In binuclear complexes in which non-adjacent platinum group atoms are held by bridging ligands, no clear enhancement of catalysis has been observed previously. However, recent data on iridium pyrazolate complexes[3] offer clear evidence for electronic communication between the iridium centres *via* orbital interaction with the bridging ligand.

In this communication we report the significant modification of catalytic activity of the mononuclear fragment (**1**) by bonding to M(cod) (cod = cyclo-octa-1,5-diene) units.

The binuclear complexes (**2**) and (**3**) were prepared by reaction in dichloromethane of [M(OMe)(cod)]₂ (M = Rh, Ir) with the complex (**1**) (obtained by reaction of [RuH-(CO)Cl(PPh₃)₃][4] with H₂bim (bim = 2,2'-bi-imidazolato) and a stoicheiometric amount of KOH in methanol).†

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† The reactions were carried out under oxygen-free nitrogen by Schlenk-tube techniques. All the new compounds were characterised by elemental analyses and i.r. and n.m.r. (¹H and ³¹P{¹H}) spectra. Selected data: (**1**) ν(CO) (CH₂Cl₂) 1915 cm⁻¹, ¹H n.m.r. (CDCl₃) δ −11.45 (1H, t, RuH, $J_{H-P(cis)}$ 20.5 Hz), ³¹P n.m.r. (CDCl₃) δ 47.98; (**2**) ν(CO) (CH₂Cl₂) 1920 cm⁻¹, ¹H n.m.r. (CDCl₃) δ −12.89 (1H, t, RuH, $J_{H-P(cis)}$ 19.5 Hz), ³¹P n.m.r. (CDCl₃) δ 48.50; (**3**) ν (CO) (CH₂Cl₂) 1930 cm⁻¹, ¹H n.m.r. (CDCl₃) δ −13.276 (1H, t, RuH, $J_{H-P(cis)}$ 19.5 Hz), ³¹P n.m.r. (CDCl₃) δ 48.33.

Table 1. Hydrogen transfer reactions from propan-2-ol.[a]

Catalyst	Substrate (S)	Time (h)	mol SH$_2$	
			mol M[b]	SH$_2$
(1)	cyclo-C$_6$H$_{10}$O	24	5.5	cyclo-C$_6$H$_{11}$OH
	PhCH=CH$_2$	9	0.0	PhCH$_2$Me
	PhCH=CHCOPh	8	4.5	PhCH$_2$CH$_2$COPh
(2)	cyclo-C$_6$H$_{10}$O	19	76.0	cyclo-C$_6$H$_{11}$OH
	PhCH=CH$_2$	9	2.5	PhCH$_2$Me
	PhCH=CHCOPh	8	92.5	PhCH$_2$CH$_2$COPh
			6.0	PhCH$_2$CH$_2$CH(OH)Ph
	cyclo-C$_6$H$_{10}$O:	23	13.5	cyclo-C$_6$H$_{11}$OH
	PhCH=CH$_2$ (1:1)		2.0	PhCH$_2$Me
(3)	cyclo-C$_6$H$_{10}$O	8	80.0	cyclo-C$_6$H$_{11}$OH
	PhCH=CH$_2$	9	1.0	PhCH$_2$Me
	PhCH=CHCOPh	8	57.0	PhCH$_2$CH$_2$COPh
			1.5	PhCH$_2$CH$_2$CH(OH)Ph
	cyclo-C$_6$H$_{10}$O:	23	13.5	cyclo-C$_6$H$_{11}$OH
	PhCH=CH$_2$ (1:1)		2.0	PhCH$_2$Me
(4)	cyclo-C$_6$H$_{10}$O	24	0.5	cyclo-C$_6$H$_{11}$OH
	PhCH=CH$_2$	9	0.0	PhCH$_2$Me
	PhCH=CHCOPh	8	2.0	PhCH$_2$CH$_2$COPh
(5)	cyclo-C$_6$H$_{10}$O	24	0.5	cyclo-C$_6$H$_{11}$OH
	PhCH=CH$_2$	9	0.5	PhCH$_2$Me
	PhCH=CHOPh	8	2.0	PhCH$_2$CH$_2$COPh

[a] Reaction conditions: [M] = 2.5 × 10^{-3} mol l^{-1}; [S]/[M] = 100; activation period 60 min; activation temp. 83 °C; solvent propan-2-ol; atmosphere N$_2$. [b] M = Ru (1), Rh (4), Ir (5), Ru + Rh (2), or Ru + Ir (3).
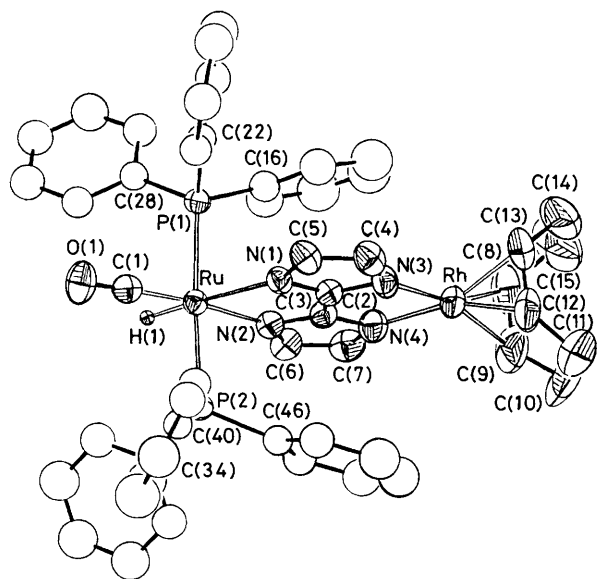
Figure 1. Structure of the complex (2); selected bond distances (Å) and angles (°): Ru–P(1) 2.367(2), Ru–P(2) 2.358(2), Ru–N(1) 2.283(5), Ru–N(2) 2.180(5), Ru–C(1) 1.829(6), Ru–H(1) 1.51(5), Rh–N(3) 2.127(5), Rh–N(4) 2.134(5), Rh–C(8) 2.103(8), Rh–C(9) 2.102(10), Rh–C(12) 2.110(8), Rh–C(13) 2.118(8); P(1)–Ru–P(2) 175.7(1), N(2)–Ru–C(1) 174.2(2), N(1)–Ru–H(1) 172(2), N(1)–Ru–N(2) 79.2(2), N(3)–Rh–N(4) 82.2(2).

Results from catalytic experiments with these binuclear complexes, involving hydrogen transfer from propan-2-ol to cyclohexanone, styrene, or benzylideneacetophenone are summarized in Table 1. The results of hydrogenation of cyclohexene with molecular hydrogen are listed in Table 2. For comparison, the activities of the mononuclear complexes (1), (4), and (5)[5] are also included.
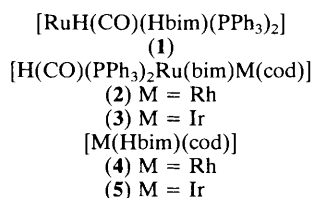
Table 2. Reduction of cyclohexene.[a]

Catalyst	Time (h)	mol cyclohexane
		mol M[b]
(1)	8	1.5
(2)	10	52.5
(3)	10	68.0
(4)	8	2.5
(5)	8	2.0

[a] Reaction conditions: [M] = 2.5 × 10^{-3} mol l^{-1}; [cyclohexane]/[M] = 100; activation period 30 min; reaction temp. 60 °C; solvent propan-2-ol; atmosphere H$_2$, P_{H_2} 1 atm. [b] M = Ru (1), Rh (4), Ir (5), Ru + Rh (2), or Ru + Ir (3).

The binuclear complexes (2) and (3) are clearly more active catalysts for this type of reaction than the mononuclear complexes (1), (4), and (5). This significant enhancement of catalytic activity is most probably due to electronic communication between the non-adjacent metal centres through the bi-imidazolato ligand.

As expected, the X-ray crystal structure of (2)‡ (Figure 1) shows the two different metal centres bridged through a bi-imidazolate anion, bonded as a chelate ligand to both Ru

[RuH(CO)(Hbim)(PPh₃)₂]
(1)
[H(CO)(PPh₃)₂Ru(bim)M(cod)]
(2) M = Rh
(3) M = Ir
[M(Hbim)(cod)]
(4) M = Rh
(5) M = Ir

and Rh atoms, which are separated by 5.579(2) Å. The n.m.r. spectra show that for (2) and (3) the hydridic hydrogen signals are displaced towards higher field and in the i.r. spectra v(CO) is shifted towards higher frequencies. These data reflect significant modifications at the ruthenium atom.

The binuclear complexes were recovered unchanged after the catalytic reactions, indicating that the co-ordinated cyclo-octa-1,5-diene ligand is not altered. Because the Ru is co-ordinatively saturated, the creation of a co-ordination vacancy could well be necessary for catalysis. In this context the relatively long Ru–N(1) distance [2.283(5) Å] [N(1) is *trans* to the hydride ligand] suggests that this bond may be broken during the catalytic cycle.

Competitive catalytic experiments on hydrogen transfer reduction of mixtures of cyclohexanone and styrene show preferential reduction of the carbon–oxygen double bond (Table 1). However, the α,β-unsaturated ketone benzylideneacetophenone is preferentially reduced at the carbon–carbon double bond.

References

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