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Synthesis and catalytic activity of heterodinuclear Ru–Ir and Ru–Rh Complexes. Crystal structure of $[H(CO)(PPh_3)_2Ru(\mu\text{-}Cl)(\mu\text{-}pz)Ir(TFB)]$ (pz = pyrazolate, TFB = tetrafluorobenzobarrelene)

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Abstract

Reactions of the ruthenium compounds $[RuHCl(CO)(PR_3)_n]$ (R = Ph, $n = 3$; R = ^{i}Pr, $n = 2$) with pyrazole $C_3H_4N_2$ (Hpz) give the complexes $[RuHCl(CO)(Hpz)(PR_3)_2]$. Treatment of these complexes with a hydrogen abstractor (methoxide ion or acetylacetonate (acac)), such as $[M(\mu\text{-}OMe)(diolefin)]_2$ (M = Ir, Rh; diolefin = cycloocta-1,5-diene (COD), tetrafluorobenzobarrelene (TFB)) or $[Pd(acac)(\eta^3\text{-}C_3H_5)]$ has given the heterobinuclear complexes $[H(CO)(PR_3)_2Ru(\mu\text{-}Cl)(\mu\text{-}pz)ML_2]$ (R = Ph; M = Ir or Rh, L_2 = COD or TFB; R = ^{i}Pr, M = Rh, L_2 = TFB; R = Ph, M = Pd, $L_2 = C_3H_5$). The structure of $[H(CO)(PPh_3)_2Ru(\mu\text{-}Cl)(\mu\text{-}pz)Ir(TFB)]$ has been established by an X-ray diffraction study. The species is binuclear, with a pyrazolate group and a chlorine atom as bridging ligands. The intermetallic separation is 3.8907(6) Å. The reduction of cyclohexanone by hydrogen transfer from isopropanol catalyzed by $[H(CO)(PPh_3)_2Ru(\mu\text{-}Cl)(\mu\text{-}pz)M(diolefin)]$ (M = Ir, Rh; diolefin = COD, TFB) is also reported.

Introduction

The chemistry of the heterobinuclear complexes has attracted considerable interest in recent years [1]. Much of this interest arises from their role in important catalytic reactions; in particular, attention has focused on the complexes containing electron-rich and electron-deficient metal centres [2].

We showed recently that the heterobinuclear complexes $[H(CO)(PPh_3)_2Ru(bim)M(COD)]$ (M = Rh, Ir; bim = 2,2′-biimidazolate; COD = cycloocta-1,5-diene) are more active catalysts than the mononuclear complexes $[RuH(CO)(Hbim)(PPh_3)_2]$

and [M(Hbim)(COD)] (M = Rh, Ir) for the reactions of hydrogenation of cyclohexene with molecular hydrogen and for hydrogen transfer from propan-2-ol to cyclohexanone, styrene or benzylideneacetophenone [3]. This enhancement of catalytic activity is most probably due to electronic communication between the non-adjacent metal centres through the biimidazolate ligand, and recent observations on iridium pyrazolate complexes provide clear evidence for such electronic communication between the iridium centres via orbital interaction with the bridging ligand [4].

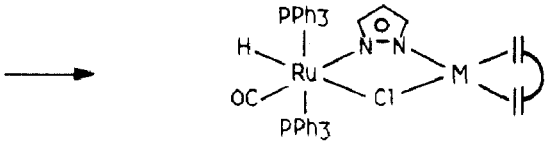
In order to gain more insight into the properties and catalytic activity of these heterobinuclear systems we decided to introduce two different bridges between the two metals and to examine the chemistry of these heterobridged species. The present study deals with the preparation of several complexes containing the "Ru(μ-Cl)(μ-pz)M" unit, the X-ray structure of one of them, and the catalytic activity of four of them in the reaction of hydrogen transfer from propan-2-ol to cyclohexanone.

Results and discussion

It has been reported that the complex [RuHCl(CO)(PPh_3)$_3$] reacts with 1-hydroxymethyl-3,5-dimethylpyrazole to give [RuHCl(CO)(Hdmpz)(PPh_3)$_2$] (Hdmpz = 3,5-dimethylpyrazole) [5]. Similarly, addition of a stoicheiometric amount of pyrazole (Hpz) to a suspension of [RuHCl(CO)(PPh_3)$_3$] in ethanol gives [RuHCl(CO)(Hpz)(PPh_3)$_2$] (**1**); the reaction has to be carried out at the reflux temperature and requires a few hours to reach completion. The ^{1}H NMR spectrum (in $CDCl_3$) of compound **1** exhibits, at high field, a hydride signal (−13.69 ppm, t, J(H–P) 19.3 Hz) and, downfield, a N–H signal (11.7 ppm). **1** reacts, in acetone, with [M(μ-OMe)(diolefin)]$_2$ (M = Ir, Rh; diolefin = COD, tetrafluorobenzobarrelene (TFB)) to give yellow solids, in 50–75% yield, identified as the heterobinuclear complexes [H(CO)(PPh_3)$_2$Ru(μ-Cl)(μ-pz)M(diolefin)] (eq. 1).

[RuHCl(CO)(Hpz)(PPh_3)$_2$] + 1/2 [M(μ-OMe)(Diolefin)]$_2$ ⟶

(1)



(**2**: diolefin = COD, M = Ir; **3**: diolefin = COD, M = Rh; **4**: diolefin = TFB, M = Ir; **5**: diolefin = TFB, M = Rh)

The crystal structure of **4** (see below) shows that the pyrazole ligand is *trans* to the CO ligand.

When carbon monoxide is bubbled through dichloromethane solutions of **2**–**5** the diolefin is displaced, and two new heterobimetallic complexes [H(CO)(PPh_3)$_2$-Ru(μ-Cl)(μ-pz)M(CO)$_2$] (**6**: M = Ir, **7**: M = Rh) are formed. The IR spectra of these compounds show three bands in the carbonyl region: the positions of two of them, at higher frequencies, are as expected for the two CO groups, in *cis*-disposition, attached to the Ir or Rh atoms, and the other one arises from the CO group joined to the Ru atom. The high field ^{1}H NMR spectra of these compounds show a triplet

Table 1

IR data for the complexes (Nujol mulls, ν in cm^{-1})

Compound	ν(N–H)	ν(Ru–H)	ν(CO) [a]
1	3215	2020	1930
2		2015	1927
3		2020	1925
4		2075	1930
5		2075	1925
6			2060, 1987, 1937
7			2070, 2000, 1930
8		2020	1950
9	3200	2025	1910
10		2070	1905

[a] In CH_2Cl_2.

(**6**: δ −13.91 ppm, J(H–P) 20.2 Hz; **7**: δ −13.80 ppm, J(H–P) 20.1 Hz) for the hydride ligand.

As expected, complex **1** reacts with [Pd(acac)(η^3-C_3H_5)] to give [H(CO)(PPh_3)$_2$-Ru(μ-Cl)(μ-pz)Pd(η^3-C_3H_5)] (**8**).

A compound similar to **1** can be made from [RuHCl(CO)(P^iPr_3)$_2$] [6], which reacts with Hpz in methanol at room temperature to give [RuHCl(CO)(Hpz)(P^iPr_3)$_2$] (**9**) in ca. 70% yield. Treatment of **9** with [Rh(μ-OMe)(TFB)]$_2$ in acetone at the reflux temperature gives, [H(CO)(P^iPr_3)$_2$Ru(μ-Cl)(μ-pz)Rh(TFB)] (**10**) in a reaction similar to that shown in eq. 1. The IR and NMR spectroscopic data for the isolated complexes are summarized in Tables 1 and 2, respectively.

In order to obtain further information about the nature of these compounds, the crystal structure of the representative complex [H(CO)(PPh_3)$_2$Ru(μ-Cl)(μ-pz)Ir(TFB)] (**4**) was determined. Table 3 lists selected bond distances and angles for this species. As expected, the species proved to be binuclear (Fig. 1), with a pyrazolate group and a chlorine atom acting as bridging ligands.

In **4** the Ru atom exhibits a slightly distorted octahedral environment, probably because of the unequal steric requirements of the coordinated ligands (PPh_3 compared with H, for instance). The iridium centre shows a distorted square-planar coordination involving the chloride, the N(1) atom from the pyrazolate ligand, and a tetrafluorobenzobarrelene molecule bonded through both olefinic double bonds.

The separation between the two metals is 3.8907(6) Å, longer than the separations reported for the related complexes [(*p*-cymene)Ru(μ-Cl)$_2$(μ-pz)Rh(TFB)] (3.514(1) Å) [7], [(*p*-cymene)ClRu(μ-Cl)(μ-pz)Pd(C_8H_{11})] (3.516(1) Å) [8], or [Cp*$ClRh^{III}$(μ-Cl)(μ-pz)Rh^{I}(TFB)] (3.715(2) Å) [9], in which a chlorine and a pyrazolate ligand also act as bridging groups between the metal atoms; this distance clearly excludes any direct intermetallic interaction. The planarity observed for the Ru–Cl–Ir–N(1)–N(2) ring (no atom deviates more than 0.148(4) Å from the least-square plane through them), which additionally is roughly coplanar (dihedral angles $< 6.5(1)°$) with the Ir square-planar coordination plane and with the equatorial plane of the octahedral environment of the Ru atom, is remarkable. As far as we know, a similar planar conformation has been reported in complexes containing simultaneously Cl and pz bridges only for the complex [(C_2H_4)ClPt(μ-Cl)(μ-pz)PtCl(C_2H_4)] [10]. All the other complexes [7–9] mentioned above exhibit

Table 2

^{1}H and ^{31}P NMR data for the complexes (in $CDCl_3$, δ in ppm, J and N in Hz)

Complex	^{1}H							^{31}P
	Ru–H	diolefin			pyrazole		others	
		COD:	$-CH_2$	=CH	H(4)	H(3), H(5)		
		TFB:	=CH	–CH				
1	−13.69 (t,19.3)				5.60 (s)	6.70 (s)	N–H: 11.7	45.06
2	−13.05 (t,19.8)	1.29 (4H)	1.92 (4H)	3.36 (4H)	5.41 (s)	6.72 (s), 6.95 (s)		45.61
3	−13.03 (t,19.9)	1.60 (4H)	2.10 (4H)	3.72 (4H)	5.43 (t)	6.45 (d), 6.88 (d)		44.85
4	−13.04 (t,19.8)	2.02 (2H)	2.40 (2H)	5.06 (2H)	5.54 (s)	6.07 (s), 7.30 (s)		44.58
5	−13.08 (t,19.0)	2.83 (2H)	3.14 (2H)	5.05 (2H)	5.58 (s)	5.90 (s), 7.17 (s)		44.58
6	−13.91 (t,20.2)				5.46 (t)	6.83 (d), 7.23 (d)		44.13
7	−13.80 (t,20.1)				5.51 (s)	6.88 (s), 7.12 (s)		43.40
8	−13.52 (t,20.0)				5.55 (s)	6.96 (s)	allyl: H^{anti}: 2.21 (d, 12.2), 2.40 (d, 11.7); H^{syn}: 3.26 (d, 7.3), 3.42 (d, 6.3); H^{2}: 4.83(m)	43.86
9 [a]	−15.22 (t,21.1)				6.42 (s)	7.50 (s), 7.88 (s)		48.11
10	−15.17 (t,21.1)	3.45 (2H)	3.73 (2H)	5.40 (2H)	5.94 (s)	6.4 (s), 7.54 (s)	^{i}Pr: CH_3: 1.25, 1.38 (dvt, J(HH) 6.8, N 13); CH: 2.00(m)	45.72

[a] In C_3D_6O.

Table 3

Selected bond distances (Å) and angles (°) in $[H(CO)(PPh_3)_2Ru(\mu\text{-}Cl)(\mu\text{-}pz)Ir(TFB)]$ (**4**), with e.s.d.'s in parentheses

Ru...Ir	3.8907(6)		
Ru–P(1)	2.354(1)	Ir–Cl	2.334(1)
Ru–P(2)	2.351(1)	Ir–N(1)	2.065(4)
Ru–Cl	2.503(2)	Ir–C(41)	2.112(4)
Ru–N(2)	2.153(3)	Ir–C(42)	2.134(4)
Ru–C(1)	1.845(5)	Ir–C(44)	2.101(5)
Ru–H(1)	1.46(4)	Ir–C(45)	2.113(6)
N(1)–N(2)	1.372(5)	C(2)–C(3)	1.374(7)
N(1)–C(2)	1.333(6)	C(3)–C(4)	1.378(7)
N(2)–C(4)	1.345(5)	C(1)–O(1)	1.136(6)
C(41)–C(42)	1.406(8)	C(44)–C(45)	1.408(8)
C(41)–C(46)	1.546(8)	C(45)–C(46)	1.531(6)
C(42)–C(43)	1.540(7)	C(46)–C(47)	1.528(8)
C(43)–C(44)	1.546(8)	mean C–F	1.33(1)
C(43)–C(52)	1.528(9)		
P(1)–Ru–P(2)	174.7(1)	P(2)–Ru–H(1)	84.6(15)
P(1)–Ru–Cl	93.1(1)	Cl–Ru–N(2)	86.8(1)
P(1)–Ru–N(2)	90.1(1)	Cl–Ru–C(1)	98.0(1)
P(1)–Ru–C(1)	89.4(2)	Cl–Ru–H(1)	174.4(15)
P(1)–Ru–H(1)	90.3(15)	N(2)–Ru–C(1)	175.2(2)
P(2)–Ru–Cl	92.2(1)	N(2)–Ru–H(1)	97.8(15)
P(2)–Ru–N(2)	89.1(1)	C(1)–Ru–H(1)	77.5(15)
P(2)–Ru–C(1)	91.0(2)		
Cl–Ir–N(1)	92.5(1)	N(1)–Ir–M(1) [a]	171.7(2)
Cl–Ir–M(1) [a]	95.8(1)	N(1)–Ir–M(2) [a]	100.4(1)
Cl–Ir–M(2) [a]	167.0(1)	M(1)–Ir–M(2) [a]	71.3(1)

[a] M(1) and M(2) represent the midpoints of the C(41)–C(42) and C(44)–C(45) olefin double bonds.

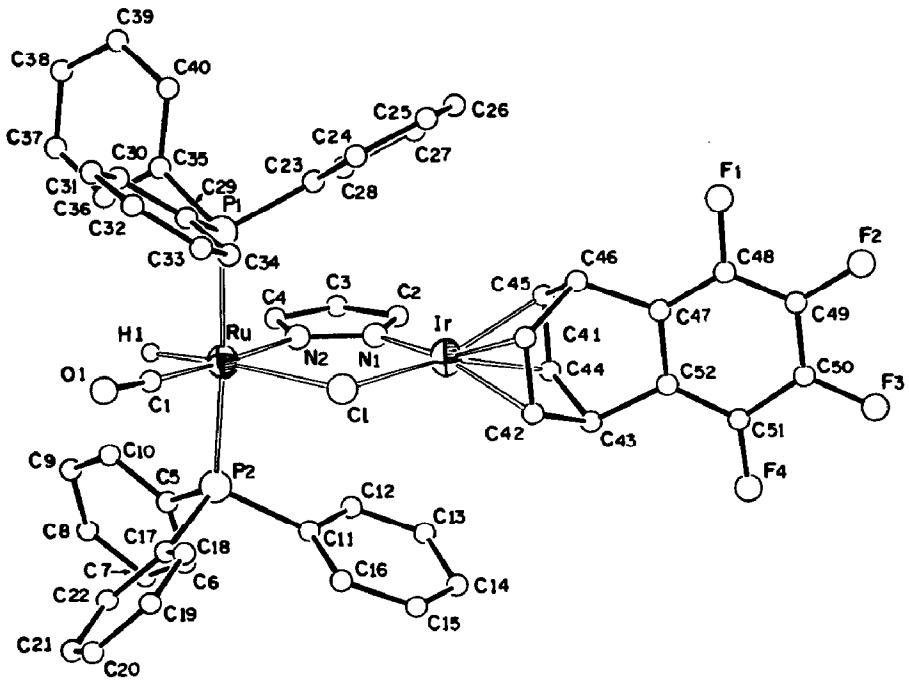


Fig. 1. View of the structure of complex **4**.

Table 4

Reduction of cyclohexanone by hydrogen transfer from propan-2-ol (Reaction conditions: [catalyst] = 1.25×10^{-3} mol l^{-1}; activation period 60 min; reaction temperature 83° C. [cyclohexanone]/[catalyst] = 200)

Catalyst	mol cyclohexanol/(mol catalyst · min)
1	0.14
2	0.58
3	0.36
4	0.36
5	0.13
11–14	$< 1.0 \times 10^{-4}$

twist or envelope conformations for this ring, allowing shorter intermetallic separations. An analogous planar disposition of the bridge and coordination spheres around the metals has been reported for the closely related, and catalytically active, complex $[H(CO)(PPh_3)_2Ru(\mu\text{-bim})Rh(COD)]$ [3].

Comparison of the structure of **4** with that of the mononuclear complex $[RuHCl(CO)(Hdmpz)(PPh_3)_2]$ [5] reveals no relevant modifications of the molecular parameters arising from idealized bonding of the 'Ir(TFB)' moiety to the Ru complex, except for the significant shortening of the Ru–Cl bond distance *trans* to the hydride ligand, from a value of 2.568(3) Å in the mononuclear species to 2.503(2) Å in **4**. This is anomalous, since bond distances for terminal chlorides in related Ru^{II} or Rh^{I} complexes are usually shorter than those for bridging ones [8,9].

The TFB group has similar features to those reported for related Rh or Ir complexes [9,11].

Reduction of cyclohexanone by hydrogen transfer from isopropanol

The heterobinuclear complexes **2–5** catalyze the hydrogen transfer from isopropanol to cyclohexanone. The results of the catalytic experiments are summarized in Table 4; to provide a comparison, the activities of the mononuclear compounds **1**, and [MCl(Hpz)(diolefin)] (diolefin = COD, M = Ir (**11**), Rh (**12**); diolefin = TFB, M = Ir (**13**), Rh (**14**)) are also included. Table 4 shows that for this reaction the heterobinuclear complexes **2–4** are more active catalysts than the mononuclear compounds **11–14** and **1**. However, the activity of complex **1** is similar to that of **5**.

For hydrogenation reactions of cyclohexene catalyzed by binuclear complexes containing homobridges of azolate type, the kinetic studies suggest that the nuclearity of the catalyst precursors is constant during the catalysed reaction [12]; however, in heterobridged compounds cleavage of the bridge or redistribution reactions may occur because the stability of the heterobridged "$M(\mu\text{-pz})(\mu\text{-Cl})M$" framework is lower than that of the homobridged "$M(\mu\text{-pz})_2M$" one [9]. Thus under the conditions of the hydrogen transfer, the following equilibrium may be present:

$$2\left[H(CO)(PPh_3)_2Ru(\mu\text{-Cl})(\mu\text{-pz})M(\text{diolefin})\right] \rightleftharpoons 2\left[RuHCl(CO)(PPh_3)_2\right] + \left[M(\mu\text{-pz})(\text{diolefin})\right]_2 \quad (2)$$

($[M(\mu\text{-pz})(\text{diolefin})]_2$: diolefin = COD, M = Ir (**15**), Rh (**16**); diolefin = TFB, M = Ir (**17**), Rh (**18**))

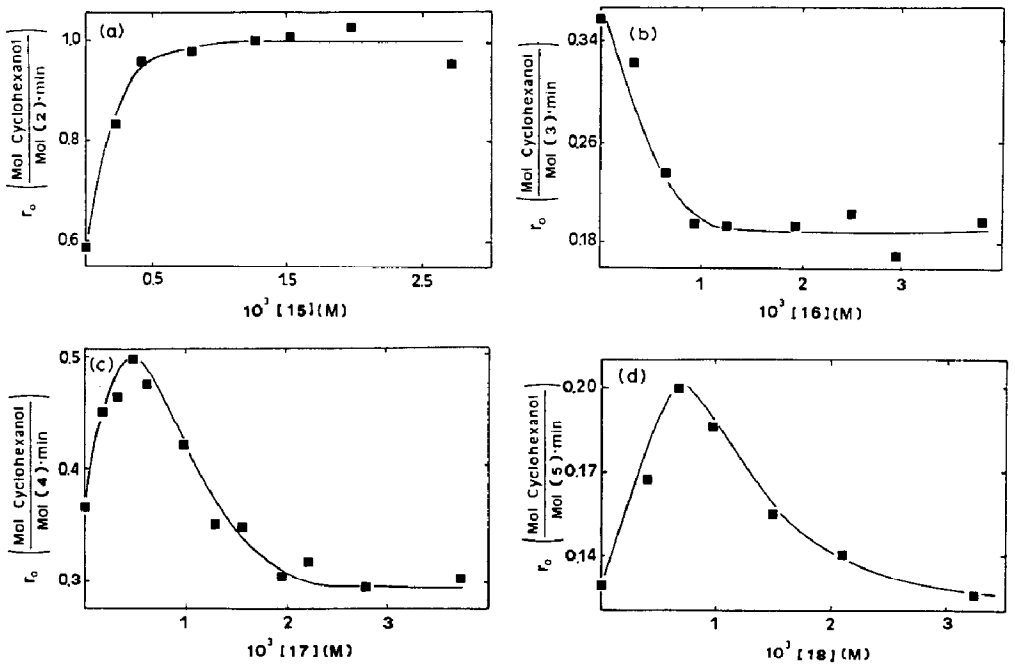


Fig. 2. Initial rate for the reduction of cyclohexanone as a function of $[M(\mu\text{-pz})(\text{diolefin})]_2$ concentration; (a) **2** = $[H(CO)(PPh_3)_2Ru(\mu\text{-Cl})(\mu\text{-pz})Ir(COD)]$, **15** = $[Ir(\mu\text{-pz})(COD)]_2$; (b) **3** = $[H(CO)(PPh_3)_2Ru(\mu\text{-Cl})(\mu\text{-pz})Rh(COD)]$, **16** = $[Rh(\mu\text{-pz})(COD)]_2$; (c) **4** = $[H(CO)(PPh_3)_2Ru(\mu\text{-Cl})(\mu\text{-pz})Ir(TFB)]$, **17** = $[Ir(\mu\text{-pz})(TFB)]_2$; (d) **5** = $[H(CO)(PPh_3)_2Ru(\mu\text{-Cl})(\mu\text{-pz})Rh(TFB)]$, **18** = $[Rh(\mu\text{-pz})(TFB)]_2$.

If this equilibrium exists the addition of these non active homobinuclear complexes to the catalytic solutions obtained from **2–5** should modify the initial rate of reduction in the catalytic process. This consideration prompted us to study the catalytic activity of **2–5** in the presence of the inactive complexes **15–18**. The results are illustrated in Fig. 2. For complex **2** in the presence of **15**, the initial rate of the catalytic proceeding rises for low concentrations of **15** as the concentration of **15** increases. However, for complex **3** in the presence of **16** the initial rate decreases. At high concentrations of **15** ($> 7.5 \times 10^{-4}$ *M*) the initial rate is constant at about 1.0 mol cyclohexanol (mol Ru)$^{-1}$ min^{-1} (Fig. 2a). Similarly, at concentrations of **16** above 9.3×10^{-4} *M* the initial rate is constant, with a value ca. 0.2 mol cyclohexanol (mol Ru)$^{-1}$ min^{-1} (Fig. 2b). The pattern in Fig. 2a and 2b suggests that for complexes **2** and **3**, under catalytic conditions the equilibrium shown in eq. 2 does exist.

A different situation arises for the related tetrafluorobenzobarrelene compounds. Thus, the results of the addition of the complexes **17** and **18** to complexes **4** and **5**, respectively, are quite different as can be seen from Fig. 2c and 2d. The addition of **17** to a solution 1.25×10^{-3} *M* of **4** causes an increase of the initial reductive rate of cyclohexanone up to a maximum value of 0.5 mol cyclohexanol (mol Ru)$^{-1}$ min^{-1}, followed by a progressive fall (Fig. 2c). For the addition of **18** to **5**, the behaviour is similar (Fig. 2d), with a maximum value of the initial rate of 0.20 mol cyclohexanol (mol Ru)$^{-1}$ min^{-1} at a molar homobinuclear to heterobinuclear complex ratio of about 0.5. These results do not provide clear evidence for the involvement of

equilibrium 2. Unfortunately, attempts to identify the possible intermediates in the catalytic reaction were unsuccessful.

The special features of the "M(TFB)" unit merit further comment; the diolefin TFB has a high π-acceptor ability, as is shown in its high tendency to form pentacoordinated species [13]. On the other hand heterobinuclear complexes containing the unit "M(TFB)" bonded to other metal atom through chloride and pyrazolate bridges are more stable than those with the "M(COD)" unit [8]. We believe that this diolefin stabilizes the heterobridged "Ru(μ-pz)(μ-Cl)M" in **4** and **5**, inhibiting its complete cleavage. Thus, in the absence of **17**, the plot of log[mol cyclohexanol · min^{-1}] against log **[4]** gives a straight line of slope 1.07, showing that the reaction catalyzed by **4** is first order in terms of catalyst concentration; this dependence of the rate on the concentration of **4** eliminates the possibility that **4** breaks down to catalytically active species of lower nuclearity. This would favour the interaction of the heterobinuclear complex with the homodinuclear one to give species of higher nuclearity (possibly trinuclear species, since the maximum values of the reductive rate is produced when the homobinuclear/heterobinuclear ratio is ca. 0.5). These polynuclear intermediates would decompose to their redistribution products [14] at a homobinuclear/heterobinuclear ratio higher than 0.5. In this context, it is relevant to note that the trinuclear complex $[\{Rh(NBD)\}_3(tpt)](ClO_4)_3$ (NBD = bicyclo[2.2.1]heptadiene, tpt = 2,4,6-tris(2-pyridyl)-*s*-triazine) is 1.6 times more active than the dinuclear $[\{Rh(NBD)\}_2(bipym)](ClO)_4)_2$ (bypim = 2,2′-bipyrimidine) [15].

Experimental

Reactions were carried out under oxygen-free nitrogen by Schlenk-tube techniques. C, H and N analyses were carried out with a Perkin Elmer 240 B microanalyzer. Infrared spectra were recorded on a Perkin Elmer 783 spectrophotometer (range 4000–200 cm^{-1}) with Nujol mulls between polyethylene sheets or in dichloromethane solutions between NaCl plates. ^1H and ^{31}P NMR spectra were recorded on a Varian XL 200 spectrophotometer at 200.057 and 80.984 MHz, respectively; chemical shifts are reported relative to tetramethylsilane and phosphoric acid at 85% as external references.

The analysis of the catalytic reactions was carried out on a Perkin Elmer 8500 gas chromatograph with a packing of FFAP on Chromosorb GHP 80/100 mesh (3.68 × 1/8in) column, at 120 °C. Initial rate data were fitted by conventional linear regression methods.

The precursors $[RuHCl(CO)(PPh_3)_3]$ [16], $[RuHCl(CO)(P^iPR)_3]_2$ [6], $[M(OMe)(diolefin)]_2$ (diolefin = COD, M = Ir, Rh; diolefin = TFB, M = Rh) [17], $[IrCl(TFB)_2]$ [18], $[Ir(OMe)(TFB)]_2$ [11], [Ir(acac)(TFB)] [19], $[Pd(Cl)(C_3H_5)]_2$ [20], [MCl(Hpz)(diolefin)] and $[M(pz)(diolefin)]_2$ (diolefin = COD, M = Ir, Rh; diolefin = TFB, M = Rh) [21,22] were prepared by published methods. The complexes [IrCl(Hpz)(TFB)] and $[Ir(pz)(TFB)]_2$ were obtained as described below.

Preparation of [IrCl(Hpz)(TFB)]. A suspension of $[IrCl(TFB)_2]$ (136 mg, 0.2 mmol) in acetone (20 ml) was treated with an excess of pyrazole (40.8 mg, 0.6 mmol). After 30 min stirring at room temperature the yellow solution was concentrated in vacuo to ca. 2 ml. Addition of hexane gave a yellow precipitate, which was filtered off, repeatedly washed with hexane, and vacuum dried. Yield 70 mg

(67%). Found: C, 35.02; H, 2.00; N, 6.01. $C_{15}H_{10}ClF_4IrN_2$ calc.: C, 34.52; H, 1.93; N, 5.37%. ^{1}H NMR ($CDCl_3$): δ 12.55, NH; 7.60 (d), 6.70 (d), 6.42 (t), pyrazole; 5.53, CH, 3.08, =CH. IR (Nujol) ν(NH) 3300 cm^{-1}.

Preparation of [Ir(μ-pz)(TFB)]$_2$. A solution of [Ir(acac)(TFB)] (103.5 mg, 0.20 mmol) in acetone (15 ml) was treated with a stoicheiometric amount of pyrazole (13.6 mg, 0.20 mmol) and the mixture was stirred for 1 h at room temperature. The resulting suspension was reduced in volume and the orange solid was filtered off, washed with methanol and vacuum dried. Yield 81 mg (84%). Found: C, 36.87; H, 1.84; N, 5.67. $C_{30}H_{18}F_4Ir_2N_4$ calc.: C, 37.11; H, 1.87; N, 5.77%. ^{1}H NMR ($CDCl_3$): δ 7.02 (d), 6.15 (t), pyrazole; 5.69, CH, 3.00, =CH.

Preparation of [RuHCl(CO)(Hpz)(PPh$_3$)$_2$] (1). Pyrazole (20.4 mg, 0.30 mmol) was added to a suspension of [RuHCl(CO)(PPh_3)$_3$] (285.7 mg, 0.30 mmol) in ethanol (50 ml). The mixture was stirred for 5 h at the reflux temperature; the suspension was then cooled to room temperature, some of the solvent was evaporated, and the white microcrystalline solid was filtered off, washed with ethanol and diethyl ether, and dried under vacuum. Yield 218 mg (96%). Found: C, 63.54; H, 4.67; N, 3.63. $C_{40}H_{35}ClN_2OP_2Ru$ calc.: C, 63.37; H, 4.65; N, 3.69%.

Preparation of [[H(CO)(PPh$_3$)$_2$Ru(μ-Cl)(μ-pz)Ir(COD)] (2). A suspension of **1** (227.5 mg, 0.30 mmol) in acetone (30 ml) was treated with [Ir(μ-OMe)(COD)]$_2$ (99.5 mg, 0.15 mmol) and the mixture was stirred for 9 h at the reflux temperature. The suspension was cooled to room temperature, some of the solvent was evaporated, and the lemon yellow microcrystalline solid was filtered off, washed with acetone and hexane, and vacuum dried. Yield 152 mg (48%). Found: C, 53.97; H, 4.48; N, 2.53. $C_{48}H_{46}ClIrN_2OP_2Ru$ calc.: C, 54.51; H, 4.38; N, 2.65%.

Preparation of [H(CO)(PPh$_3$)$_2$Ru(μ-Cl)(μ-pz)Rh(COD)] (3). A stoicheiometric amount of [Rh(μ-OMe)(COD)]$_2$ (72.7 mg, 0.15 mmol) was added to a suspension of **1** (227.5 mg, 0.30 mmol) in acetone (30 ml) and the mixture was stirred for 24 h at room temperature. The pale yellow solid formed was filtered off, washed with acetone and hexane, and vacuum dried. Yield 197 mg (68%). Found: C, 59.04; H, 5.01; N, 2.91. $C_{48}H_{46}ClN_2OP_2RhRu$ calc.: C, 59.54; H, 4.79; N, 2.89%.

Preparation of [H(CO)(PPh$_3$)$_2$Ru(μ-Cl)(μ-pz)Ir(TFB)] (4). The procedure described for **2**, but starting from [Ir(μ-OMe)(TFB)]$_2$ (134.0 mg, 0.15 mmol), gave a lemon yellow microcrystalline solid. Yield 241 mg (68%). Found: C, 52.43; H, 3.65; N, 2.49. $C_{52}H_{40}ClF_4IrN_2OP_2Ru$ calc.: C, 53.13; H, 3.43; N, 2.38%. Suitable crystals for X-ray diffraction were obtained by slow diffusion of methanol into a dichloromethane solution of the complex at room temperature.

Preparation of [H(CO)(PPh$_3$)$_2$Ru(μ-Cl)(μ-pz)Rh(TFB)] (5). The procedure described for **3**, but starting with [Rh(μ-OMe)(TFB)]$_2$ (108.1 mg, 0.15 mmol), gave a yellow microcrystalline solid. Yield 242 mg (74%). Found: C, 57.11; H, 3.75; N, 2.57. $C_{52}H_{40}ClF_4N_2OP_2RhRu$ calc.: C, 57.50; H, 3.71; N, 2.58%.

Preparation of [H(CO)(PPh$_3$)$_2$Ru(μ-Cl)(μ-pz)Ir(CO)$_2$] (6). Carbon monoxide was bubbled through a solution of **2** (158.6 mg, 0.15 mmol) in dichloromethane (20 ml) for 15 min. The resulting pale yellow solution was concentrated in vacuo to ca. 1 ml, and methanol was added. The pale yellow solid formed was filtered off, washed with methanol, and vacuum dried. Yield 110 mg (73%). Found: C, 49.8; H, 3.38; N, 2.66. $C_{42}H_{34}ClIrN_2O_3P_2Ru$ calc.: C, 50.18; H, 3.41; N, 2.66%.

Preparation of [H(CO)(PPh$_3$)$_2$Ru(μ-Cl)(μ-pz)Rh(CO)$_2$] (7). Carbon monoxide was bubbled through a solution of **5** (162.9 mg, 0.15 mmol), in dichloromethane (20

Table 5

Final atomic coordinates ($\times 10^4$) for the non-hydrogen atoms for the complex [H(CO)(PPh_3)$_2$Ru(μ-Cl)(μ-pz)Ir(TFB)] (4)

Atom	x	y	z
Ru [a]	21048(3)	58389(3)	81734(2)
Ir [a]	47983(2)	54147(2)	70345(2)
H(1)	1645(34)	6101(32)	8865(20)
Cl	2753(1)	5492(1)	6934(1)
P(1)	1650(1)	3852(1)	8332(1)
P(2)	2542(1)	7858(1)	8130(1)
F(1)	6798(5)	2119(5)	5386(2)
F(2)	8544(5)	2770(7)	4474(2)
F(3)	9346(3)	5007(7)	4280(2)
F(4)	8411(4)	6630(6)	4997(2)
O	−546(3)	5597(3)	7824(2)
N(1)	4920(3)	5849(3)	8125(2)
N(2)	3978(3)	6007(3)	8531(2)
C(1)	471(4)	5708(4)	7946(2)
C(2)	5925(4)	6012(5)	8554(2)
C(3)	5670(5)	6295(5)	9245(3)
C(4)	4442(4)	6268(4)	9210(2)
C(5)	2904(4)	8785(4)	8978(2)
C(6)	3615(5)	9928(4)	9005(3)
C(7)	3826(6)	10663(5)	9643(3)
C(8)	3289(6)	10273(5)	10248(3)
C(9)	2603(7)	9143(6)	10225(3)
C(10)	2403(6)	8406(5)	9591(3)
C(11)	3848(4)	8408(3)	7601(2)
C(12)	5009(4)	8448(4)	7893(3)
C(13)	6035(5)	8766(5)	7495(4)
C(14)	5865(6)	9026(6)	6778(4)
C(15)	4726(6)	8955(5)	6501(3)
C(16)	3694(5)	8650(5)	6902(3)
C(17)	1306(4)	8373(4)	7723(2)
C(18)	731(4)	7812(4)	7076(3)
C(19)	−170(6)	8165(6)	6736(3)
C(20)	−560(6)	9109(6)	7056(4)
C(21)	−42(6)	9676(5)	7698(4)
C(22)	884(5)	9308(5)	8048(4)
C(23)	2757(4)	3037(4)	8039(3)
C(24)	2560(6)	2217(4)	7435(3)
C(25)	3454(7)	1643(6)	7240(4)
C(26)	4566(7)	1879(6)	7655(4)
C(27)	4802(5)	2710(6)	8247(4)
C(28)	3884(5)	3276(5)	8448(3)
C(29)	214(4)	3077(4)	7852(3)
C(30)	−813(4)	2543(5)	8183(3)
C(31)	−1896(5)	2020(6)	7786(4)
C(32)	−1984(5)	2012(5)	7065(4)
C(33)	−986(6)	2567(5)	6720(3)
C(34)	131(5)	3113(5)	7106(3)
C(35)	1427(4)	3438(4)	9238(2)
C(36)	1258(5)	4234(5)	9784(3)
C(37)	1040(6)	3908(6)	10475(3)
C(38)	949(5)	2774(6)	10599(3)
C(39)	1114(6)	1963(5)	10050(3)

Table 5 (continued)

Atom	x	y	z
C(40)	1365(5)	2282(5)	9359(3)
C(41)	4731(4)	4392(5)	6049(2)
C(42)	5134(4)	5567(5)	5939(2)
C(43)	6531(5)	6019(5)	6051(3)
C(44)	6663(4)	5792(5)	6839(3)
C(45)	6271(4)	4610(5)	6940(2)
C(46)	5776(5)	3825(5)	6250(2)
C(47)	6738(5)	4059(7)	5700(3)
C(48)	7194(6)	3257(8)	5307(3)
C(49)	8047(8)	3551(11)	4839(4)
C(50)	8469(6)	4687(11)	4734(4)
C(51)	8011(5)	5564(9)	5113(3)
C(52)	7142(4)	5215(7)	5595(3)

[a] Atom coordinates for Ru and Ir are expressed $\times 10^5$.

ml) for 1 h. The yellow solution was concentrated in vacuo. Addition of hexane gave a pale yellow precipitate, which was filtered off, washed with hexane and vacuum dried. Yield 79 mg (57%). Found: C, 55.43; H, 4.11; N, 3.06. $C_{42}H_{34}ClN_2O_3P_2RhRu$ calc.: C, 55.06; H, 3.74; N, 3.06%.

Preparation of [H(CO)(PPh$_3$)$_2$Ru(μ-Cl)(μ-pz)Pd(η^3-C$_3$H$_5$)] (8). A solution of **1** (151.6 mg, 0.20 mmol) in dichloromethane (20 ml) was treated with [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ (36.6 mg, 0.10 mmol) and Tl(acac) (60.7 mg, 0.20 mmol) and the mixture was stirred in the absence of light at room temperature for 30 min. The precipitated TlCl was removed by filtration through kieselghur and the pale yellow filtrate was stirred for 3 days. Then the red brown solution was concentrated in vacuo to ca. 1 ml, and 10 ml of methanol were added. The yellowish solid formed was filtered off, washed with methanol, and vacuum dried. Yield 64 mg (35%). Found: C, 57.63; H, 4.46; N, 3.14. $C_{43}H_{39}ClN_2OP_2PdRu$ calc.: C, 57.09; H, 4.35; N, 3.10%.

Preparation of [RuHCl(CO)(Hpz)(P^{i}Pr$_3$)$_2$] (9). Pyrazole (14.1 mg, 0.21 mmol) was added to a suspension of [RuHCl(CO)(P^{i}Pr$_3$)$_2$] (100.5 mg, 0.21 mmol) in methanol (10 ml) and the mixture was stirred for 2 h at room temperature. The resulting white precipitate was filtered off, washed with methanol and diethyl ether, and vacuum-dried. Yield 77.5 mg (68%). Found: C, 47.58; H, 8.80; N, 5.06. $C_{22}H_{47}ClN_2OP_2Ru$ calc.: C, 47.69; H, 8.55; N, 5.06%.

Preparation of [H(CO)(P^{i}Pr$_3$)$_2$Ru(μ-Cl)(μ-pz)Rh(TFB)] (10). The procedure described for **2**, but starting from **9** (166.2 mg, 0.30 mmol) and [Rh(μ-OMe)(TFB)]$_2$ (108.1 mg, 0.15 mmol), gave a yellow solid. Yield 122 mg (46%). Found: C, 46.41; H, 6.12; N, 3.27. $C_{34}H_{52}ClF_4N_2OP_2RhRu$ calc.: C, 46.30; H, 5.94; N, 3.17%.

X-Ray structure determination of [H(CO)(PPh$_3$)$_2$Ru(μ-Cl)(μ-pz)Ir(TFB)] (4)

A prismatic yellow block of dimensions ca. $0.15 \times 0.17 \times 0.41$ mm was used for data collection. Unit cell parameters were obtained by least-squares refinement of the values of 66 carefully centred reflections ($20 \leqslant 2\theta \leqslant 30°$). A total of 9118 reflections were measured on a Stoe–Siemens AED-2 four circles diffractometer within the angular range $3 \leqslant 2\theta \leqslant 50°$ ($\omega/2\theta$ scan) using monochromated Mo-K_α radiation. From the 8402 unique reflections collected, 7509 having $F \geqslant 6\sigma(F)$ were

used for the calculations. Three standard reflections were measured every hour as a check on crystal and instrument stability; no variation was observed. A numerical absorption correction was applied based on indexed faces of the crystal; min. and maximum transmission factors were 0.5433 and 0.6267.

Crystal data. $C_{52}H_{40}ClF_4IrN_2OP_2Ru$, $M = 1175.59$, triclinic, space group $P\bar{1}$, a 11.2907(4), b 11.9296(4), c 18.8764(8) Å, α 95.578(3), β 92.154(3), γ 103.740(3)°, U 2453.2(2) Å^3, $Z = 2$, μ(Mo-K_α) 31.17 cm^{-1}, $D_c = 1.544$ g · cm^{-3}, $F(000) = 1312$.

The structure was solved by Patterson and Fourier methods. Refinement was carried out by full-matrix least squares by use of the SHELX system [23] with initially isotropic and subsequently anisotropic thermal parameters for all non hydrogen atoms. The hydride ligand was clearly located from a difference Fourier map and was refined isotropically. The other hydrogens were not included. The function minimized in the least-squares calculations was $\Sigma\omega|\Delta F|^2$; the final weighting scheme used was $\omega = k/[\sigma^2(F_o) + gF_o^2]$ with $k = 1.000$ and $g = 0.00214$. Final R and R_w values were 0.033 and 0.038. The maximum residual electron density was 1.16 e/Å^3, close to the Ir atom. Scattering factors, corrected for the anomalous dispersion of Ru, Ir, P and Cl atoms, were taken from ref. [24]. Atom coordinates for the non-hydrogen atoms are given in Table 5.

Complete lists of structure amplitudes, anisotropic thermal parameters, and bond lengths and angles are available from F.J.L.

Hydrogen transfer reactions

The reactions were carried out under nitrogen in a refluxing mixture of propan-2-ol and toluene, with magnetic stirring, in a 50 ml round bottomed flask fitted with a condenser and provided with a serum cap. In a typical procedure, a solution of the catalyst (0.01 mmol) in 1 ml of toluene and 4 ml of propan-2-ol was refluxed for 1 h and 2 mmol of cyclohexanone in 3 ml of propan-2-ol was injected.

For the reactions involving the catalysts $[H(CO)(PPh_3)_2Ru(\mu\text{-}Cl)(\mu\text{-}pz)M(diolefin)]$ in the presence of the corresponding dimers $[M(\mu\text{-}pz)(diolefin)]_2$ the procedure was as follows: A solution containing the catalyst (0.01 mmol) and the appropriate amount of the homobinuclear complex in 1 ml of toluene and 4 ml of propan-2-ol was refluxed for 1 h, and 2 mmol of the substrate in 3 ml of propan-2-ol was then injected.

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References

1 A few recent examples include: (a) M.J. Chetcuti and K.A. Green, Organometallics, 7 (1988) 2450; (b) R.T. Baker, J.C. Calabrese and T.E. Glassman, Organometallics, 7 (1988) 1889; (c) R. Zoet, G. van Koten, F. Muller, K. Vrieze, M. van Wijnkoop, K. Goubitz, C.J.G. van Halen and C.H. Stam, Inorg. Chim. Acta, 149 (1988) 193; (d) L.W. Arndt, B.T. Bancroft, M.Y. Darensbourg, C.P. Janzen, C.M. Kim, J. Reibenspies, K.E. Varner and K.A. Youngdahl, Organometallics, 7 (1988) 1302.

2 A few recent examples include: (a) L. Gelmini and D.W. Stephan, Organometallics, 7 (1988) 849; (b) J. Jenck, P. Kalck, E. Pinelli, M. Siani and A. Thorez, J. Chem. Soc., Chem. Commun., (1988) 1428; (c) I. Ojima, M. Okabe, K. Kato, H.B. Kwon and I.T. Horváth, J. Am. Chem. Soc., 110 (1988) 150;

(d) M.O. Okoroafor, L.-H. Shen, R.V. Honeychuck and C.H. Brubaker, Jr., Organometallics, 7 (1988) 1297.
3 M.P. Garcia, A.M. López, M.A. Esteruelas, F.J. Lahoz and L.A. Oro, J. Chem. Soc., Chem. Commun., (1988) 793.
4 G.W. Bushnell, D.O.K. Fjeldsted, S.R. Stobart, M.J. Zaworotko, S.A.R. Knox and K.A. Macpherson, Organometallics, 4 (1985) 1107.
5 A. Romero, A. Vegas, A. Santos and A.M. Cuadro, J. Chem. Soc., Dalton Trans., (1987) 183.
6 M.A. Esteruelas and H. Werner, J. Organomet. Chem., 303 (1986) 221.
7 L.A. Oro, D. Carmona, M.P. Garcia, F.J. Lahoz, J. Reyes, C. Foces-Foces, and F.H. Cano, J. Organomet. Chem., 296 (1985) C43.
8 M.P. García, A. Portilla, L.A. Oro, C. Foces-Foces and F.H. Cano, J. Organomet. Chem., 322 (1987) 111.
9 L.A. Oro, D. Carmona, J. Reyes, C. Foces-Foces and F.H. Cano, J. Chem. Soc., Dalton Trans., (1986) 31; and ref. therein.
10 W.C. Deese, D.A. Johnson, and A.W. Cordes, Inorg. Chem., 20 (1981) 1519.
11 R. Usón, L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces, F.H. Cano, S. García-Blanco and A. Vázquez de Miguel, J. Organomet. Chem., 273 (1984) 111.
12 L.A. Oro, M.A. Esteruelas, European Conference on Homogeneus Catalysis, Arles, 1989.
13 L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces and F.H. Cano, J. Organomet. Chem., 307 (1986) 83.
14 P.E. Garrou, Adv. Organomet. Chem., 23 (1984) 95.
15 M.P. García, J.L. Millan, M.A. Esteruelas and L.A. Oro, Polyhedron, 6 (1987) 1427.
16 N. Ahmed, J.J. Levison, S.D. Robinson and M.F. Yttley, Inorg. Synth., 15 (1974) 48.
17 R. Usón, L.A. Oro, J. Cabeza, Inorg. Synth., 23 (1985) 126.
18 R. Usón, L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces, F.H. Cano and S. García-Blanco, J. Organometal. Chem., 254 (1983) 249.
19 R. Usón, L.A. Oro, D. Carmona, M.A. Esteruelas, J. Organomet. Chem., 263 (1984) 109.
20 Y. Tatsuno, T. Yoshida and Seitsuka, Inorg. Synth., 19 (1979) 220.
21 F.H. Cano, C. Foces-Foces, L.A. Oro, M.T. Pinillos and C. Tejel, Inorg. Chim. Acta, 128 (1987) 75.
22 A.W. Coleman, D.T. Eadie, R.S. Stobart, M.J. Zaworotko, J.L. Atwood, J. Am. Chem. Soc., 104 (1982) 922.
23 G.M. Sheldrich, SHELX System of Computing Programs, University of Cambridge, 1976.
24 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.