Triruthenium carbonyl clusters derived from chiral aminooxazolines: synthesis and catalytic activity

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Received 15th December 2005, Accepted 6th March 2006
First published as an Advance Article on the web 14th March 2006
DOI: 10.1039/b517758h

Treatment of $[Ru_3(CO)_{12}]$ with the chiral aminooxazolines (+)-2-amino-(4*R*)-phenyl-2-oxazoline (H_2amphox), (+)-2-amino-(4*R*,5*S*)-indanyl-2-oxazoline (H_2aminox) and (+)-2-(2′-anilinyl)-(4*R*,5*S*)-indanyl-2-oxazoline (H_2aninox) in THF at reflux temperature, affords the complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hox-}N,N)(CO)_9]$ (H_2ox = H_2amphox, **1**; H_2aminox, **2**) and $[Ru_3(\mu\text{-H})(\mu\text{-}\kappa^2\text{-Haninox-}N,N)(CO)_9]$ (**3**). In all cases, the activation of an N–H bond has occurred and the resulting amido fragment spans an edge of the metal triangle, while the N atom of the oxazoline ring is attached to the remaining metal atom (as in **1** and **2**), or to one of the metal atoms of the bridged edge (as in **3**). The use of **1–3** as catalyst precursors in the asymmetric hydrogen-transfer reduction of acetophenone and in the asymmetric cycloaddition of cyclopentadiene and acroleine is reported.

Introduction

A main focus of interest in current synthetic chemistry is the preparation of novel chiral metal catalysts for asymmetric processes.[1] In contrast with the vast amount of mono- and binuclear chiral complexes reported to date, transition metal clusters containing chiral ligands are scarce.[2–5] Apart from a triruthenium derivative of levamisole[6] and from a few triruthenium and triosmium clusters with the chiral atropisomeric ligand (+)-2,2′-diamino-1,1′-binaphthalene (H_2binam),[7] the remaining examples of chiral triruthenium clusters reported so far correspond to species containing mono- or bidentate chiral phosphane ligands. These latter complexes have been used as catalyst precursors in asymmetric isomerization,[4] hydroformylation[5] or hydrogenation[3] of unsaturated substrates. In most catalytic reactions, however, the catalyst precursors have been prepared *in situ* and their nature remains unknown.[3] No other cluster complexes containing chiral *N*-donor ligands have been reported to date.

During the last decade, our research group has thoroughly studied the synthesis and reactivity of carbonyl clusters derived from 2-aminopyridines.[8,9] Most of these clusters are trinuclear and contain a face-capping ligand that results from the activation of an N–H bond, to give an edge-bridging amido fragment and a hydride ligand, and from the coordination of the pyridine N atom to the remaining metal atom (Fig. 1). Some of these complexes have been recognized as catalytic precursors for the hydrogenation,[10,11] dimerization,[12] polymerization[12] and hydroformylation[13] of selected alkynes.

The considerable experience of our group in the preparation and study of the above mentioned derivatives, and the small number of cluster complexes containing *N*-donor chiral ligands known to date, prompted us to investigate the reactivity of $[Ru_3(CO)_{12}]$ with chiral aminooxazoline ligands. Chiral oxazolines and bis(oxazolines) are versatile ligands that are easily prepared and thus have been used in a wide range of asymmetric processes.[14,15] The ligands chosen for this study are (+)-2-amino-(4*R*)-phenyl-2-oxazoline (H_2amphox), (+)-2-amino-(4*R*,5*S*)-indanyl-2-oxazoline (H_2aminox) and (+)-2-(2′-anilinyl)-(4*R*,5*S*)-indanyl-2-oxazoline (H_2aninox) (Fig. 2). The first two contain an amino fragment in the oxazoline ring, while the amino fragment of H_2aninox is located on the phenyl ring.

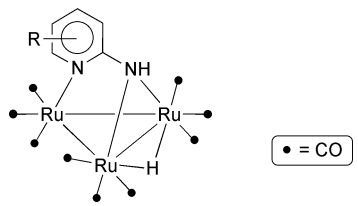

Fig. 1 Carbonyl clusters derived from 2-aminopyridines.

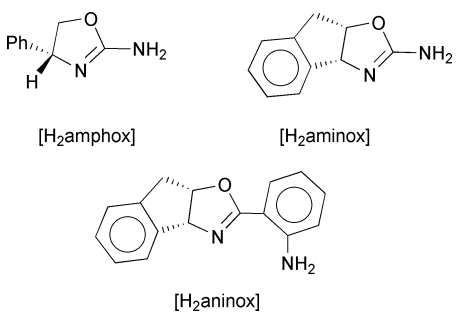

Fig. 2 The ligands H_2amphox, H_2aminox and H_2aninox.

We describe herein the synthesis of trinuclear derivatives of the types $[Ru_3(\mu\text{-H})(\mu_2,\kappa^2\text{-Hox-}N,N)(CO)_9]$ and $[Ru_3(\mu\text{-H})(\mu_3,\kappa^2\text{-Hox-}N,N)(CO)_9]$ (H_2ox = a generic aminooxazoline ligand). These compounds represent the first examples of triruthenium clusters containing oxazoline ligands. These complexes have been

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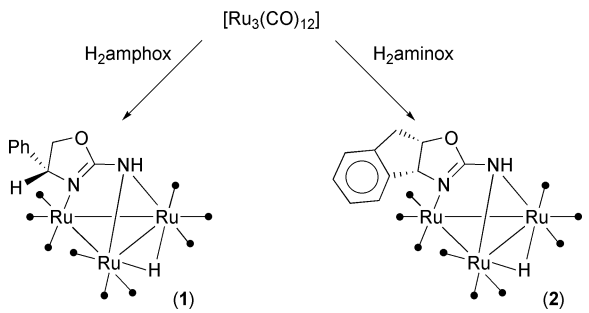
tested as catalyst precursors in asymmetric transfer hydrogenation and in a Diels–Alder reaction. The coordination chemistry of aminooxazolines has not been studied previously, although related amidooxazoline derivatives have been described.[16]

Results and discussion

Syntheses of compounds 1–3

Treatment of $[Ru_3(CO)_{12}]$ with 1.2 equiv. of H_2amphox or H_2aminox in THF at reflux temperature afforded, after chromatographic work-up, the trinuclear derivatives $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Hamphox-}N,N)(CO)_9]$ (**1**) and $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-Haminox-}N,N)(CO)_9]$ (**2**), respectively (Scheme 1). Their trinuclear nature and the presence of one equiv. of the ligand were clearly evidenced from their elemental analyses and mass spectra, which showed peaks corresponding to the molecular ions. The IR spectra of both complexes in the carbonyl stretching region are identical, and reflect only the presence of terminal CO ligands. These IR spectra resemble that of $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-ampy-}N,N)(CO)_9]$ (H_2ampy = 2-amino-6-methylpyridine),[17] suggesting an analogous ligand arrangement.



Scheme 1 Synthesis of compounds **1** and **2**.

The activation of an N–H bond of the amino fragment was clearly pointed out by the ^{1}H NMR spectra of both complexes, which showed a singlet resonance in the high field region (−11.10 ppm for **1** and −11.09 ppm for **2**), indicating the presence of a hydride ligand, and a broad signal at 5.62 ppm for **1** and 5.57 ppm for **2**, which correspond to the N–H proton. The $^{13}C\{^1H\}$ NMR spectra of both complexes showed the presence of nine terminal CO ligands and indicated the absence of *C*-metalation.

The absolute configurations of **1** and **2** were unambiguously determined by X-ray diffraction methods. A selection of bond lengths for both complexes is given in Table 1. For comparison purposes, the same labelling scheme is used where possible. Fig. 3 shows a view of complex **1**. The structure of **1** consists of a Ru_3 triangle face-capped by the Hamphox ligand in such a way that it

Table 1 Selected interatomic distances (Å) in compounds **1–3**

	1	**2**	**3**
Ru(1)–Ru(2)	2.7528(11)	2.7684(6)	2.7819(9)
Ru(1)–Ru(3)	2.7773(9)	2.7633(5)	2.7950(12)
Ru(2)–Ru(3)	2.7600(9)	2.7753(5)	2.8238(12)
Ru(1)–N(1)	2.173(5)	2.142(3)	2.120(4)
Ru(1)–N(2)	—	—	2.123(3)
Ru(2)–N(1)	2.159(5)	2.133(3)	2.169(4)
Ru(3)–N(2)	2.137(4)	2.170(3)	—

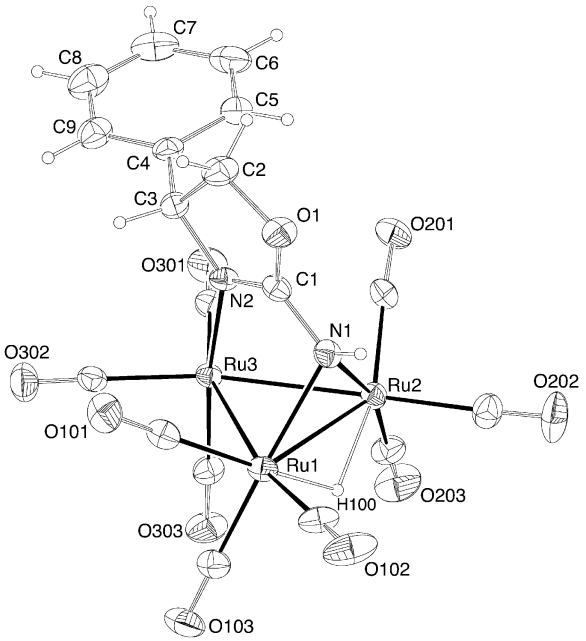


Fig. 3 Molecular view of **1**. Ellipsoids are drawn at the 30% probability level.

binds a Ru atom through the N atom of the oxazoline ring, while the amido fragment bridges the other two metal atoms. A hydride ligand spans the same metallic edge as the amido fragment. The cluster shell is completed with nine terminal CO ligands.

A molecular plot of compound **2** is displayed in Fig. 4. The ligand disposition in **2** is identical to that described above for **1**. In both cases, the stereochemistry of the original oxazoline ligand is maintained in the metal complex. The coordination of the oxygen atom in the oxazoline ring was not observed in either case. These two structures are analogous to that reported for

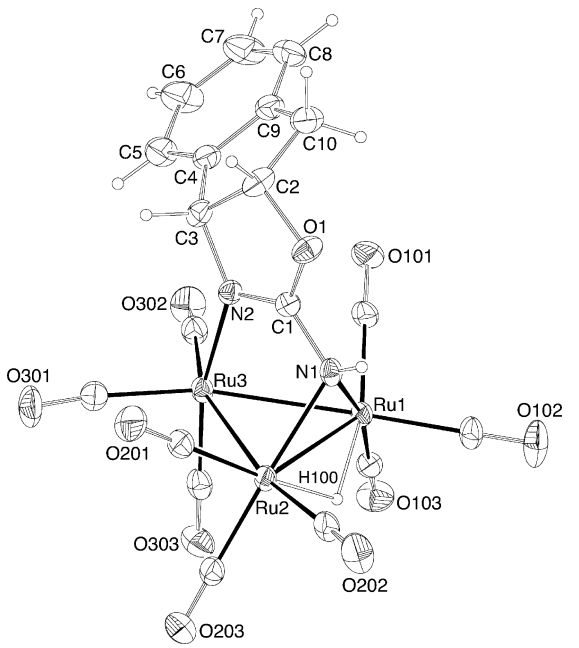
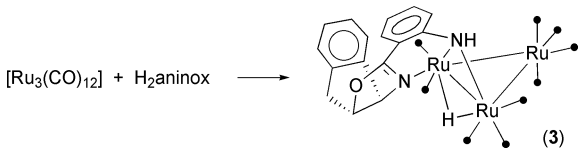


Fig. 4 Molecular view of **2**. Ellipsoids are drawn at the 30% probability level.

$[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-ampy-}N,N)(CO)_9]$,[17] in which an amido fragment and a hydride atom bridge the same edge of the cluster, while the third Ru atom is attached to the pyridine nitrogen atom.

When $[Ru_3(CO)_{12}]$ was treated with 1.2 equiv. of H_2aninox under the same conditions as those described above for **1** and **2**, the trinuclear derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-Haninox-}N,N)(CO)_9]$ (**3**, Scheme 2) was obtained. The IR spectrum of **3** in the carbonyl stretching region varies from that of **1** and **2**, pointing to a different ligand disposition. Its ^{1}H NMR spectrum again showed a singlet resonance at −12.03 ppm, indicating the presence of a hydride ligand, and a broad signal at 6.69 ppm, attributable to an NH fragment.



Scheme 2 Synthesis of compound **3**.

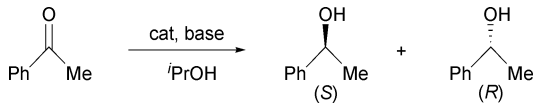
The atom connectivity in **3** was unambiguously determined by X-ray diffraction. A molecular plot of **3** is shown in Fig. 5. A selection of bond distances is given in Table 1. The structure consists of a metallic triangle in which two of the three Ru atoms are attached to the Haninox ligand, in such a way that the amido fragment spans the Ru(1)–Ru(2) edge, while the oxazoline ring coordinates to Ru(1) through the N(2) atom. A hydride ligand spans the same edge as the NH fragment. The cluster shell is completed with nine terminal carbonyl ligands.

The different coordination behaviour observed for the H_2aninox ligand, which bridges only two of the three metal atoms and chelates one of them through its two nitrogen atoms, is favoured by the formation of a six-membered ring in **3**. In contrast, the Hamphox and Haminox ligands would render highly constrained four-membered rings when acting as chelating agents; consequently, they prefer to adopt a face-capping disposition similar to that observed in compounds **1** and **2**.

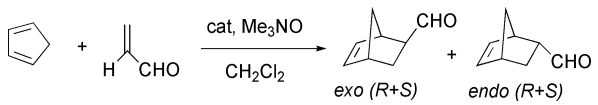
Complexes **1–3** are the first cluster complexes containing oxazoline ligands and they also represent rare examples of metal clusters containing *N*-donor chiral ligands. Their easy preparation and the high regio- and enantioselectivity observed in their synthesis allowed us to undertake a study of some catalytic applications.

Catalytic activity

For the study of the asymmetric catalytic properties of **1–3**, we chose two well-known processes, *i.e.*, the asymmetric hydrogen transfer hydrogenation of acetophenone (Scheme 3) and the [4 + 2]-cycloaddition reaction of cyclopentadiene and acroleine (Scheme 4).



Scheme 3 Asymmetric hydrogenation of acetophenone.



Scheme 4 Asymmetric Diels–Alder reaction.

Asymmetric hydrogenation of acetophenone. The catalysis results are summarized in Table 2. Reactions were carried out in refluxing isopropanol, using 0.025 mmol of catalyst and 5 mmol of acetophenone (0.5% of catalyst with respect to the ketone). Potassium hydroxide (0.34 M solution in isopropanol) was used as co-catalyst in a 4 : 1 ratio with respect to the catalyst.

No reaction was observed when the free aminooxazoline ligands were used as pre-catalysts (Table 2, entry 2). When $[Ru_3(CO)_{12}]$ was used as the pre-catalyst in the presence of the oxazoline ligands, the conversion was always lower than 5%, suggesting that these species do not catalyse this process in an effective way (entries 3–5). However, when compounds **1–3** were used as pre-catalysts, quantitative conversion was observed after 10 h, the most active catalyst being the H_2aninox derivative **3**, which afforded a TOF of 200 h^{-1} (entries 6–8). The ee values observed were similar in all cases, the highest being 20% for complex **1**.

In this process, the catalysis is assumed to follow the *hydride route* mechanism, in which the pre-catalyst would react with

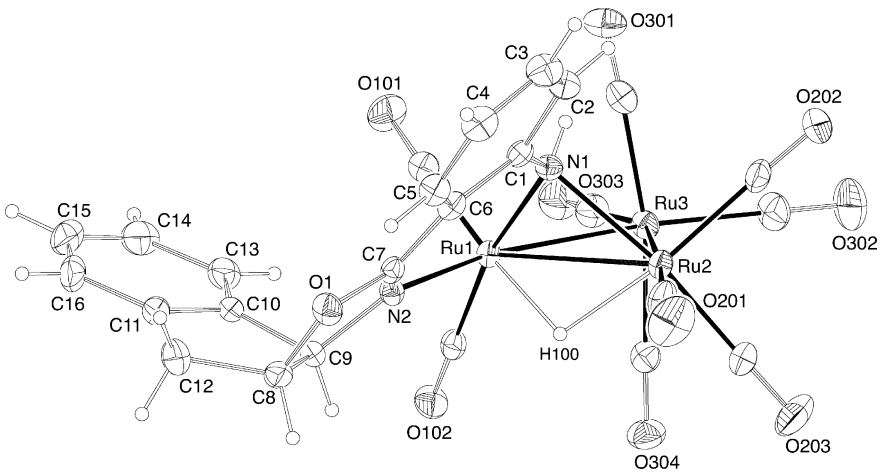


Fig. 5 Molecular view of **3**. Ellipsoids are drawn at the 30% probability level.

Table 2 Asymmetric hydrogenation of acetophenone

Entry	Pre-catalyst	t/h	TOF[a]/h^{-1}	Conv. (%)	ee (%)
1	—	24	—	—	—
2	H_2ox	24	—	—	—
3	$[Ru_3(CO)_{12}] + H_2$amphox	10	—	3	—
4	$[Ru_3(CO)_{12}] + H_2$aminox	10	—	4	—
5	$[Ru_3(CO)_{12}] + H_2$aninox	10	—	5	—
6	**1**	10	144	99	20(*S*)
7	**2**	10	160	99	19(*S*)
8	**3**	10	200	99	18(*S*)
9[b]	**1**	10	65	62	18(*S*)
10[b]	**2**	10	85	72	15(*S*)
11[b]	**3**	10	91	51	16(*S*)

[a] TOF at $t = 10$ min. [b] No KOH added.

the KOH to generate an active species which contains at least one hydride ligand. This hydride ligand would be subsequently transferred to the acetophenone.[18] Since compounds **1–3** already contain a hydride ligand, we performed the catalytic reactions under the same conditions but without KOH (Table 2, entries 9–11). In this case, however, the processes were slower, resulting in lower conversions and TOF, while the enantiomeric excesses observed were in the same range. This lower activity can be explained by assuming that the role played by the KOH is not only to generate a hydride ligand but also to create a vacant coordination site that facilitates the interaction of the incoming substrate with the active hydride species. The nucleophilic attack of a hydroxy group onto a coordinated carbonyl ligand to generate CO_2 and a hydride species is a well documented process.[19]

[4 + 2]-Cycloaddition of cyclopentadiene and acroleine. The results are collected in Table 3. Reactions were carried out in dichloromethane at room temperature, dissolving 0.025 mmol of metal complex (5% with respect to acroleine), 3 mmol of cyclopentadiene and 0.5 mmol of acroleine. Me_3NO (0.025 mmol) was used as the CO abstractor.

The reaction proceeded in the absence of catalyst to afford the final adduct with an *endo* to *exo* ratio of *ca.* 80 : 20 and a *ca.* 20% conversion after 2 h (Table 3, entry 1). No significant changes were observed in conversion nor in regioselectivity when the chiral ligands (entry 2) or when $[Ru_3(CO)_{12}]$ in the presence of the chiral oxazolines (entries 3–5) were used as catalyst precursors.

When compounds **1–3** were employed (entries 6–8), conversions went up to 80% after 2 h, with a TOF of 25 h^{-1} at a reaction time of 10 min. Unfortunately, no enantiomeric excesses were obtained in any case. It seems that the use of Me_3NO as the CO abstractor yields mixtures of products that result in moderate conversions and no enantiomeric excesses. The low activity observed for compounds **1–3** in this process prevented us from attempting to improve the ee by lowering the temperature.

It is well established that the use of ancillary ligands which bind the three metal atoms often prevents cluster fragmentation during catalytic reactions.[10,11,20] However, it has also been proven that some trinuclear complexes having edge-bridging ligands lead to mononuclear catalytic species.[21] Without kinetic data, the nuclearity of the real catalytic species involved in the reactions described in this contribution cannot be unequivocally assigned.

Conclusions

The first examples of trinuclear clusters containing oxazoline-type ligands are described. Compounds **1–3** represent three of the few examples of triruthenium carbonyl clusters containing chiral *N*-donor ligands known so far. These complexes catalyse efficiently the hydrogen-transfer asymmetric hydrogenation of acetophenone, although the ees obtained are low. However, these complexes present low activity when used as catalyst precursors in an asymmetric Diels–Alder reaction. No previous examples of the use of trinuclear species as catalyst precursors for these two processes have been reported.

Experimental

General Data

Solvents were dried over sodium diphenyl ketyl (hydrocarbons, THF) or CaH_2 (dichloromethane, isopropanol) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and spot TLC. (+)-2-Amino-(4*R*)-phenyl-2-oxazoline (H_2amphox),[22] (+)-indanyl-2-amino-(4*R*,5*S*)-2-oxazoline (H_2aminox)[23] and (+)-indanyl-2-(2′-anilinyl)-(4*R*,5*S*)-2-oxazoline (H_2aninox)[23] were prepared as previously reported. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^{1}H NMR spectra were run on a Bruker DPX-300 instrument, at room temperature, using the dichloromethane solvent resonance as internal standard ($\delta = 5.30$). Microanalyses were obtained from the University of Oviedo Analytical Service. FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

Table 3 Asymmetric cycloaddition of cyclopentadiene and acroleine

Entry	Pre-catalyst	TOF[a]/h^{-1}	Conv.[b] (%)	Endo : exo	ee (%)
1	—	—	19	79 : 21	—
2	H_2ox	—	19	80 : 20	—
3	$[Ru_3(CO)_{12}] + H_2$amphox	—	18	81 : 19	—
4	$[Ru_3(CO)_{12}] + H_2$aminox	—	18	80 : 20	—
5	$[Ru_3(CO)_{12}] + H_2$aninox	—	20	79 : 21	—
6	**1**	20	77	86 : 14	—
7	**2**	22	74	88 : 12	—
8	**3**	25	80	90 : 10	—

[a] TOF at $t = 10$ min. [b] $t = 2$ h.

Syntheses

[Ru_3(μ-H)(μ$_3$-κ^2-Hamphox-*N*,*N*)(CO)$_9$] (1). A solution of [$Ru_3(CO)_{12}$] (100 mg, 0.156 mmol) and (+)-2-amino-(4*R*)-phenyl-2-oxazoline (30.5 mg, 0.187 mmol) in THF (30 mL) was stirred at reflux temperature for 20 min. The colour changed from yellow to orange. The solution was concentrated under reduced pressure to *ca.* 3 mL and the residue was set onto a silica gel column (2 × 15 cm) packed in hexane. Elution with hexane afforded a small amount of unreacted [$Ru_3(CO)_{12}$]. Elution with hexane–dichloromethane (8 : 1) afforded an orange band from which compound **1** was obtained as an orange solid after solvent removal (70 mg, 63%). Calcd for $C_{18}H_{10}N_2O_{10}Ru_3$ (717.48): C, 30.13; H, 1.40; N, 3.90. Found: C, 30.62; H, 1.46; N, 3.83. FAB-MS (*m*/*z*): 719 [M^+]. IR (CH_2Cl_2): ν_{CO} = 2082 (m), 2051 (s), 2030 (vs), 1996 (s, br), 1960 (w, sh) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.50–7.35 (m, 5 H; C*H*), 5.62 (s, br, 1 H, N*H*), 5.06 (t, *J* = 9.5 Hz, 1 H; C*H*), 4.59 (t, *J* = 9.5 Hz, 1 H; *C*H), 4.54 (t, *J* = 9.5 Hz, 1 H; *C*H), −11.10 (s, 1 H; *μ-H*). ^{13}C{^{1}H} NMR (DEPT, CD_2Cl_2): δ 206.4, 205.1, 204.1, 202.9, 202.0, 200.5, 198.7, 197.3, 195.4 (9 *C*O); 181.3, 136.4 (2 *C*); 128.4, 128.2 (×2), 127.3 (×2), 68.7 (6 *C*H); 77.4 (*C*H$_2$).

[Ru_3(μ-H)(μ$_3$-κ^2-Haminox-*N*,*N*)(CO)$_9$] (2). A solution of [$Ru_3(CO)_{12}$] (100 mg, 0.156 mmol) and (+)-indanyl-2-amino-(4*R*,5*S*)-2-oxazoline (32.6 mg, 0.187 mmol) in THF (30 mL) was stirred at reflux temperature for 30 min, whereupon the colour changed from yellow to orange. The solvent was removed under reduced pressure to *ca.* 3 mL and the residue was set onto a silica gel column (2 × 15 cm) packed in hexane. Elution with hexane afforded a small amount of unreacted [$Ru_3(CO)_{12}$]. Elution with hexane–dichloromethane (7 : 1) afforded a yellow band from which compound **2** was obtained as a bright yellow solid after solvent removal (65 mg, 58%). Calcd for $C_{19}H_{10}N_2O_{10}Ru_3$ (729.50): C, 31.28; H, 1.38; N, 3.84. Found: C, 31.40; H, 1.39; N, 3.72. FAB-MS (*m*/*z*): 731 [M^+]. IR (CH_2Cl_2): ν_{CO} = 2082 (m), 2051 (s), 2030 (vs), 1996 (s, br), 1960 (w, sh) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.64 (d, *J* = 6.0 Hz, 1 H; C*H*), 7.40–7.32 (m, 3 H; C*H*), 5.80 (td, *J* = 7.9, 3.5 Hz, 1 H; *C*H), 5.57 (s, br, 1 H, *NH*), 4.95 (d, *J* = 7.9 Hz, 1 H; C*H*), 3.53 (dd, *J* = 17.8, 7.9 Hz, 1 H; *C*H), 3.12 (dd, *J* = 17.8, 3.5 Hz, 1 H; *C*H) −11.09 (s, 1 H; *μ-H*). ^{13}C{^{1}H} NMR (DEPT, CD_2Cl_2): δ 207.8, 205.7, 204.1, 203.2, 201.8, 200.5, 197.4, 195.5, 194.7 (9 *C*O); 181.3, 139.8, 137.4 (3 *C*); 130.3, 127.8, 126.9, 125.5, 87.8, 74.6 (6 *C*H); 39.7 (*C*H$_2$).

[Ru_3(μ-H)(μ-κ^2-Haninox-*N*,*N*)(CO)$_9$] (3). A solution of [$Ru_3(CO)_{12}$] (100 mg, 0.156 mmol) and (+)-indanyl-2-(2′-anilinyl)-(4*R*,5*S*)-2-oxazoline (47 mg, 0.187 mmol) in THF (30 mL) was stirred at reflux temperature for 2.5 h, whereupon the colour changed from yellow to orange. The solution was concentrated under reduced pressure to *ca.* 3 mL and the residue was set onto a silica gel column (2 × 15 cm) packed in hexane. Elution with hexane afforded a small amount of unreacted [$Ru_3(CO)_{12}$]. Elution with hexane–dichloromethane (4 : 1) afforded a yellow band from which compound **3** was obtained as a yellow solid after solvent removal (85 mg, 67%). Calcd for $C_{25}H_{14}N_2O_{10}Ru_3$ (805.59): C, 37.27; H, 1.75; N, 3.47. Found: C, 37.90; H, 1.86; N, 3.27. FAB-MS (*m*/*z*): 807 [M^+]. IR (CH_2Cl_2): ν_{CO} = 2086 (m), 2048 (vs), 2004 (s, br), 1986 (m, sh), 1972 (w, sh), 1933 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.21 (t, *J* = 5.5 Hz, 1 H; C*H*), 7.90 (d, *J* = 6.6 Hz, 1 H; C*H*), 7.47–7.36 (m, 5 H; C*H*), 7.05 (t, *J* = 6.6 Hz, 1 H; C*H*), 6.69 (s, br, 1 H, N*H*), 6.08 (d, *J* = 7.4 Hz, 1 H; C*H*), 5.52 (ddd, *J* = 7.4, 7.2, 3.6 Hz, 1 H; *C*H), 3.79 (dd, *J* = 17.9, 3.6 Hz, 1 H; *C*H), −12.03 (s, 1 H; *μ-H*). ^{13}C{^{1}H} NMR (DEPT, CD_2Cl_2): δ 207.0, 206.1, 205.5, 202.9, 200.9, 198.9, 198.0, 192.3, 184.0 (9 *C*O); 161.9,

Table 4 Selected crystal, measurement and refinement data for compounds **1–3**

	1	**2**	**3**
Formula	$C_{18}H_{10}N_2O_{10}Ru_3$	$C_{19}H_{10}N_2O_{10}Ru_3$	$C_{25}H_{14}N_2O_{10}Ru_3$
Formula weight	717.49	729.50	805.59
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	8.579(3)	7.466(1)	7.758(3)
b/Å	13.436(6)	15.525(3)	17.703(7)
c/Å	19.870(8)	19.898(4)	19.581(8)
V/Å^3	2290.5(16)	2306.4(7)	2689(2)
Z	4	4	4
F(000)	1376	1400	1560
D_c/g cm^{-3}	2.081	2.101	1.990
Radiation (λ/Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ/mm^{-1}	2.008	1.996	1.722
Crystal size/mm	0.22 × 0.21 × 0.10	0.30 × 0.24 × 0.23	0.34 × 0.10 × 0.07
Temperature/K	296(2)	296(2)	293(2)
θ limits/°	1.83 to 23.31	1.66 to 23.27	1.55 to 23.25
Min/max *h*, *k*, *l*	−9/9, −14/14, −22/22	−8/8, −17/17, −22/22	−8/8, −19/19, −21/21
Collected reflections	14753	15461	17278
Unique reflections	3303	3316	3872
Reflections with $I > 2\sigma(I)$	3177	3278	3683
Absorption correction	SADABS	SADABS	SADABS
Max/min transmission	0.818/0.687	0.819/0.629	0.886/0.713
Parameters/restraints	306/0	316/0	359/0
GOF on F^2	1.086	1.030	1.047
R_1 (on F, $I > 2\sigma(I)$)	0.0228	0.0147	0.0212
wR_2 (on F^2, all data)	0.0525	0.0367	0.0495
Max/min Δρ/e Å^{-3}	0.303/−0.375	0.224/−0.215	0.488/v0.352
Absolute structure parameter	−0.05(4)	−0.04(3)	−0.03(4)

161.7, 140.2, 139.2, 113.4 (5 *C*); 133.5, 130.7, 129.7, 127.7, 126.2, 125.6, 124.7, 122.6, 81.8, 81.7 (10 *C*H); 38.6 (CH_2).

Hydrogen transfer reactions

All reactions were carried out in Schlenk tubes under nitrogen, using magnetic stirrers and thermostated oil baths. Isopropanol was used as solvent. Acetophenone was distilled under nitrogen prior to use. In a typical experiment, the metal complex (0.025 mmol), KOH (0.1 mmol, solution 0.34 M in isopropanol) and 20 mL of isopropanol were introduced in a Schlenk tube and the mixture was heated to reflux temperature. After 10 min, acetophenone (5 mmol) was added. Conversions and enantiomeric excesses were determined by GC, using a chiral GAMMA-DEX fused-silica capillary column (0.25 mm id) and *p*-xylene as the internal standard.

Asymmetric Diels–Alder reactions

Reactions were carried out using dichloromethane as solvent. Cyclopentadiene was freshly obtained from its dimer by distillation. Acroleine was distilled under nitrogen prior to use. In a typical experiment, the metal complex (0.025 mmol), cyclopentadiene (3 mmol, dissolved in 2 mL of dichloromethane), acroleine (0.5 mmol, dissolved in 2 mL of dichloromethane), Me_3NO (0.025 mmol) and 10 mL of dichloromethane were placed into a Schlenk tube and the mixture was stirred in a thermostated bath. Conversion data, the *endo* : *exo* ratio and the enantiomeric excesses were determined by GC using a chiral GAMMA-DEX fused-silica capillary column (0.25 mm id) and *p*-xylene as the internal standard.

X-Ray crystallography

A selection of crystal, measurement and refinement data for compounds **1–3** is collected in Table 4. Diffraction data were measured at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromated Mo Kα radiation. Semi-empirical absorption corrections were applied with SADABS.[24] Structures were solved by direct methods and refined by full matrix least-squares against F^2 with SHELXTL.[25] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plots were made with the PLATON program package.[26] The WINGX program system[27] was used throughout the structure determinations.

CCDC reference numbers 293020–293022.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517758h

Acknowledgements

This work was supported by the Spanish MEC-MCyT research projects BQU2002-2623 (to J.A.C.) and BQU2002-3414 (to D.M.) and by the Natural Sciences and Engineering Research Council of Canada (NSERC, research project to R.A.G.).

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