Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 667 (2003) 197–208
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Ruthenium complexes with 1,1′-biisoquinoline as ligands. Synthesis and hydrogenation activity

Piero Frediani [a,*], Carlo Giannelli [a], Antonella Salvini [a], Sandra Ianelli [b]

[a] Department of Organic Chemistry, University of Florence, Via della Lastruccia, 13, 50019 Sesto Fiorentino, Florence, Italy
[b] Department of General, Inorganic, Analytical and Physical Chemistry, University of Parma, Parco Area delle Scienze 17/a, 43100 Parma, Italy

Received 28 October 2002; received in revised form 11 December 2002; accepted 18 December 2002

Abstract

The reaction of 1,1′-biisoquinoline (biisoq) with $[Ru_2(CO)_4(CH_3COO)_2]_n$ gives the binuclear complex $[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)$. The same reaction in acetic acid gives the mononuclear $[Ru(biisoq)_3](CH_3COO)_2$ complex instead of the expected $[Ru(biisoq)(CO)_2(CH_3COO)_2]$ compound. Starting from different precursors the following complexes containing the biisoq ligand $[Ru(biisoq)_3](PF_6)_2$, $[Ru_2(biisoq)_2(Cl)_4 \cdot NEt_3]$ and [Ru(η^6-*p*-cymene)(Cl)(biisoq)]X [X: Cl, BPh_4] were synthesized and characterized. The X-ray structure of [Ru(η^6-*p*-cymene)(Cl)(biisoq)][BPh_4] was also determined. Some of these complexes are catalytically active in the homogeneous hydrogenation of alkenes, alkynes and acetone in hydroalcoholic solvents. The better catalytic activity is shown in the hydrogenation of terminal and *trans*-olefins. Hex-1-ene is hydrogenated at 15 °C, using [Ru(η^6-*p*-cymene)(Cl)-(biisoq)]Cl even if a reaction temperature of 40 °C is required to obtain a high yield in 6 h.

Keywords: Homogeneous catalysis; Nitrogen ligands; Hydrogenation; Ruthenium; Complexes

1. Introduction

Catalytic hydrogenations are widely used in many processes of raw and fine chemical industry. One of the main challenges would be to find new catalytic systems achieving higher selectivity and low environmental impact. The latter problem may be overcome using water containing mixture as solvent [1,2]. Numerous examples of homogeneous hydrogenation of C=C and C=O double bonds in the presence of mono- and binuclear ruthenium carbonyl carboxylato complexes modified by nitrogen containing ligands like bipyridines and phenantrolines have been reported in literature [3–5]. Such complexes show a good catalytic activity in the chemoselective hydrogenation of C=C double bonds even in the presence of C=O double bonds The present work deals with the synthesis of new complexes containing a 1,1′-biisoquinoline (biisoq) and provides an account of their hydrogenation activity.

* Corresponding author. Tel.: +39-055-457-3522; fax: +39-055-457-3531.
E-mail address: piero.frediani@unifi.it (P. Frediani).

0022-328X/02/$ - see front matter © 2003 Published by Elsevier Science B.V.
doi:10.1016/S0022-328X(02)02193-9

2. Result and discussion

The biisoq ligand was obtained following the procedure reported by Ashby et al. [6] with small modifications. The spectroscopic characterization (IR, ^{1}H-NMR, ^{13}C-NMR, MS) and the elemental analysis of the ligand biisoq and the complexes synthesized are reported in Tables 1–5.

2.1. Ruthenium complexes

Using the methodologies reported for ruthenium carbonyl carboxylato complexes with bipyridines and phenantrolines [4,5,7] the binuclear complex $[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)_2$ (**1**) was obtained while the mononuclear $[Ru(biisoq)(CO)_2(CH_3COO)_2]$ was not synthesized.

2.1.1. $[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)$ (*1*)

The reaction of $[Ru_2(CO)_4(CH_3COO)_2]_n$ [8] with (**1**), in ethanol at the reflux temperature gave very small yellow needles of $[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3$-

Table 1
IR spectra of the synthesized compound [a]

Compound	Code	Absorptions (cm^{-1})
Biisoq		3043 (m, aromatic C–H stretching), 1619 (m, C=N stretching), 1581 (m), 1579 (s, C=C ring stretch), 1556 (s, C=C ring stretch), 1491 (m), 1373 (m), 1317 (s), 1136 (m)
$[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)$	(**1**)	3119 (w, aromatic C–H stretching), 3080 (w, aromatic C–H stretching), 3066 (w, aromatic C–H stretching), 2936 (vw, methyl C–H stretching), 2028 (s, C≡O stretching), 1975 (m, C≡O stretching), 1945 (sh, C≡O stretching), 1940 (s, C≡O stretching), 1911 (w, C≡O stretching), 1623 (m, C=O stretching of the carboxylato anion), 1570 (s, C=O asymmetric stretching), 1438 (s, C=O symmetric stretching)
$[Ru(biisoq)_3](CH_3COO)_2$	(**2a**)	3001 (m, aromatic C–H stretching), 2927 (m, methyl C–H stretching), 2857 (w, methyl C–H stretching), 1695 (m, C=C ring stretch), 1602 (m, C=O stretching of the carboxylato anion)
$[Ru(biisoq)_3](PF_6)_2$	(**2b**)	3066 (m, aromatic C–H stretching), 1618 (w C=C ring stretch), 1587 (m, C=C ring stretch), 1550 (w, C=C ring stretch), 1536 (w, C=C ring stretch), 1500 (w, C=C ring stretch), 843 (vs, P–F vibrations), 557 (s, P–F vibrations)
$Ru_2(biisoq)_2(Cl)_4 \cdot NEt_3$	(**3a**)	3053 (m, aromatic C–H stretching), 2955 (m, aliphatic C–H stretching), 2930 (m, aliphatic C–H stretching), 1916 (s), 1586 (s C=C ring stretch), 1529 (s, C=C ring stretch), 1441 (m, C=C ring stretch), 1404 (m C=C ring stretch), 1345 (s, C–N stretching), 283 (w, Ru–Cl vibrations), 228 (w, Ru–Cl vibrations)
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl) \cdot 0.5Et_2O$	(**4a**)	3045 (m, aromatic C–H stretching), 2962 (m, aliphatic C–H stretching), 2928 (w, aliphatic C–H stretching), 2879 (w, aliphatic C–H stretching), 1617 (m, C=C ring stretch), 1586 (m, C=C ring stretch), 1426 (m, C–H asymmetric bending), 1349 (m, C–H symmetric bending), 1156 (m, diethyl ether C–O stretching)
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$	(**4b**)	3054 (s, aromatic C–H stretching), 2975 (m, aliphatic C–H stretching), 2925 (m, aliphatic C–H stretching), 2868 (vw, aliphatic C–H stretching), 1598 (s, C=C ring stretch), 1578 (s, C=C ring stretch), 1476 (m, C=C ring stretch), 1423 (s, C–H asymmetric bending), 1348 (s, C–H symmetric bending), 1260 (w), 1155 (w), 1030 (w)

[a] All spectra were performed in KBr pellet.

COO) (**1**) with a 56.5% yield. The complex is insoluble in hexane, benzene, acetone, methanol, and slowly dissolves in DMSO, tetrahydrofuran (THF) and DMF. The carbonyl stretchings in the IR spectrum of (**1**), according to those reported for $Ru_2(CO)_4(CH_3COO)_2(PBu_3)_2$ [8] are an indication that each carbonyl group is terminal. The mass spectrum in DMF performed immediately after the dissolution of the complex suggests the formulation proposed. However, it reacts with coordinating solvents after a few hours at room temperature as shown by the ^{1}H-NMR spectra in DMSO-d_6 or DMF-d_7 revealing the resonances of the free ligand. The IR and MS data suggest the structure reported in Fig. 1.

2.1.2. *$[Ru(biisoq)_3](CH_3COO)_2$ (**2a**) and $[Ru(biisoq)_3](PF_6)_2$ (**2b**)*

Attempts to prepare $Ru(biisoq)(CO)_2(CH_3COO)_2$ were carried out following the procedure reported by Frediani et al. [4] for mononuclear ruthenium carbonyl carboxylato complexes with phenantroline or bipyridine. A suspension of biisoq and $[Ru_2(CO)_4(CH_3COO)_2]_n$ (1:1 ligand–ruthenium atoms) in acetic acid

Table 2
MS spectra of the synthesized compound

Compound	Code	Peak (m/z) [c]
Biisoq [a]		256 (55%, $[M]^+$); 255 (100%, $[M-1]^+$); 227 (10%); 128 (80%, $[C_9H_6N]^+$); 114 (40%); 100 (30%); 75 (20%); 51 (20%)
$[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)$ [b]	(**1**)	886.9 (100%, $[Ru_2(biisoq)_2(CO)_4(CH_3COO)]^+$), 701.0 (12%), 615.1 (23%), 473.0 (24%, $[Ru(biisoq)(CO)_2(CH_3COO)]^+$), 359.0 (18%), 322.0 (23%)
$[Ru(biisoq)_3](PF_6)_2$ [a]	(**2b**)	1015.1 (10%, $\{[Ru(biisoq)_3](PF_6)\}^+$), 901.1 (6%), 892.1 (6%), 435.1 (100%, $\{[Ru(biisoq)_3]\}^{2+}$)
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$ [a]	(**4b**)	527.0 (100%, $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)]^+$)

[a] Performed from acetone solution.
[b] Performed from DMF solution.
[c] The center of the isotopic peaks is reported; the simulated patterns are perfectly superimposable to those experimentally detected.

Table 3
^{1}H-NMR spectra

Compound	Code	Chemical shift (ppm)
Biisoq [a]		7.55 [ddd, $^3J_{7,8} = {}^3J_{7',8'} = 8.5$, $^3J_{7,6} = {}^3J_{7',6'} = 6.8$, $^4J_{7,5} = {}^4J_{7',5'} = 1.2$ Hz, 2H, C(7)–H, C(7′)–H]; 7.74 [dd, $^3J_{8,7} = {}^3J_{8',7'} = 8.5$, $^4J_{8,6} = J_{8',6'} = 1.1$ Hz, 2H, C(8)–H, C(8′)–H]; 7.79 [ddd, $^3J_{6,5} = {}^3J_{6',5'} = 8.3$, $^3J_{6,7} = {}^3J_{6',7'} = 6.8$, $^4J_{6,8} = {}^4J_{6',8'} = 1.1$ Hz, 2H, C(6)–H, C(6′)–H]; 7.97 [d, $^3J_{4,3} = {}^3J_{4',3'} = 5.6$ Hz, 2H, C(4)–H, C(4′)–H]; 8.09 [d, $^3J_{5,6} = {}^3J_{5',6'} = 8.3$ Hz, 2H, C(5)–H, C(5′)–H]; 8.68 [d, $^3J_{3,4} = {}^3J_{3',4'} = 5.6$ Hz, 2H, C(3)–H, C(3′)–H]
$[Ru(biisoq)_3](CH_3COO)_2$ [b]	(**2a**)	1.26 (s, 6H, CH_3COO); 6.5–6.8 (m, 2H); 7.3–8.8 (m, 34H)
$[Ru(biisoq)_3](PF_6)_2$ [a]	(**2b**)	6.8–7.2 (m, 2H); 7.6–8.8 (m, 34H)
$Ru_2(biisoq)_2(Cl)_4 \cdot NEt_3$ [b]	(**3a**)	0.9 (t, $^3J = 6.8$ Hz, 9H, N–CH_2–CH_3); 1.25 (m, 6H, N–CH_2–CH_3); 6.90 (d, $J = 6.3$ Hz, 1H); 6.98 (d, $J = 6.3$ Hz, 1H); 7.06 (d, $J = 6.3$ Hz, 1H); 7.09 (d, $J = 6.3$ Hz, 1H); 7.30–8.20 (m, 16H); 10.20 [d, $J = 6.0$ Hz, 1H, C(3)–H]; 10.30 [d, $J = 6.0$ Hz, 1H, C(3)–H]; 10.40 [d, $J = 6.0$ Hz, 1H, C(3)–H]; 10.50 [d, $J = 6.0$ Hz, 1H, C(3)–H]
[Ru(η^6-*p*-cymene)(Cl)(biisoq)](Cl)·0.5Et_2O [b]	(4a)	0.89 (d, $^3J = 7.0$ Hz, 3H, CH–CH_3'); 0.94 (d, $^3J = 7.0$ Hz, 3H, CH–CH_3); 1.18 [t, $^3J = 7.0$ Hz, 3H, O(CH_2–CH_3)$_2$]; 1.95 (s, 3H, CH_3–C_6H_4–); 2.62 [qq, $^3J = 7.0$, $^3J = 7.0$ Hz, 1H, –CH(CH_3)$_2$]; 3.46 [q, $^3J = 7.0$ Hz, 2H, O(CH_2–CH_3)$_2$]; 6.10–6.54 (m, CH_3–C_6H_4–, ABCD spin system, 4H); 7.45 [dd, $^3J_{7',6'} = 8.3$, $^3J_{7',8'} = 8.3$ Hz, 1H, C(7′)–H]; 7.60 [dd, $^3J_{7,6} = 8.3$, $^3J_{7,8} = 8.3$ Hz, 1H, C(7)–H]; 7.68 [d, $^3J_{8',7'} = 8.3$ Hz, 1H, C(8′)–H]; 7.72 [dd, $^3J_{6',7'} = 8.3$, $^3J_{6',5'} = 8.3$ Hz 1H, C(6′)–H]; 7.87 [dd, $^3J_{6,7} = 8.3$, $^3J_{6,5} = 8.3$ Hz, 1H, C(6)–H]; 7.88 [d, $^3J_{8,7} = 8.3$ Hz, 1H, C(8)–H]; 7.99 [d, $^3J_{5',6'} = 8.3$ Hz, 1H, C(5′)–H]; 8.15 [d, $^3J_{5,6} = 8.3$ Hz, 1H, C(5)–H]; 8.19 [d, $^3J_{4',3'} = 6.0$ Hz, 1H, C(4′)–H]; 8.31 [d, $^3J_{4,3} = 6.0$ Hz, 1H, C(4)–H]; 9.74 [d, $^3J_{3',4'} = 6.0$ Hz, 1H, C(3′)–H]; 9.75 [d, $^3J_{3,4} = 6.0$ Hz, 1H, C(3)–H]
[Ru(η^6-*p*-cymene)(Cl)(biisoq)][$B(C_6H_5)_4$] [a]	(**4b**)	0.94 (d, $^3J = 7.0$ Hz, 3H, CH–CH_3'); 1.01 (d, $^3J = 6.8$ Hz, 3H, CH–CH_3); 2.69 [qq, $^3J = 6.8$, $^3J = 6.8$ Hz, 1H, –CH(CH_3)$_2$]; 5.85–6.40 (m, 4H, CH_3–C_6H_4–, ABCD spin system); 6.76 [m, 4H, B(C_6H_5)$_4$: C(*p*)–H]; 6.93 [m, 8H, B(C_6H_5)$_4$: C(*m*)–H]; 7.34 [m, 8H, B(C_6H_5)$_4$: C(*o*)–H]; 7.66 [ddd, $^3J_{7',8'} = 8.7$, $^3J_{7',6'} = 6.8$, $^4J_{7',5'} = 1.2$ Hz, 1H, C(7′)–H]; 7.77 [ddd, $^3J_{7,8} = 8.7$, $^3J_{7,6} = 7.0$, $^4J_{7,5} = 1.2$ Hz, 1H, C(7)–H]; 7.89 [d, $^3J_{8',7'} = 8.7$ Hz, 1H, C(8′)–H]; 7.95 [ddd, $^3J_{6',5'} = 7.6$, $^3J_{6',7'} = 6.8$, $^4J_{6',8'} = 1.0$ Hz, 1H, C(6′)–H]; 8.03 [ddd, $^3J_{6,5} = 7.6$, $^3J_{6,7} = 7.0$, $^4J_{6,8} = 1.0$ Hz, 1H, C(6)–H]; 8.11 [d, $^3J_{8,7} = 8.7$ Hz, 1H, C(8)–H]; 8.25 [d, $^3J_{4',3'} = 6.5$ Hz, 1H, C(4′)–H]; 8.28 [d, $^3J_{4,3} = 6.5$ Hz, 1H, C(4)–H]; 8.35 [d, $^3J_{5,6} = {}^3J_{5',6'} = 7.6$ Hz, 2H, C(5)–H, C(5′)–H]; 9.41 [d, $^3J_{3',4'} = 6.5$ Hz, 1H, C(3′)–H]; 9.51 [d, $^3J_{3,4} = 6.5$ Hz, 1H, C(3)–H]

[a] Solvent acetone-d_6.
[b] Solvent $CDCl_3$.

Table 4
^{13}C-NMR spectra

Compound	Code	Chemical shift (ppm)
Biisoq [a]		121.0 [s, 2C, C(4), C(4′)]; 127.18 [s, 2C, C(8), C(8′)]; 127.24 [s, 2C, C(5), C(5′)]; 127.6 [s, 2C, C(7), C(7′)]; 128.0 [s, 2C, C(8a), C(8a′)]; 130.5 [s, 2C, C(6), C(6′)]; 137.0 [s, 2C, C(4a), C(4a′)]; 142.0 [s, 2C, C(3), C(3′)]; 158.5 [s, 2C, C(1), C(1′)]
$[Ru(biisoq)_3](PF_6)_2$ [a]	(**2b**)	126.2; 126.5; 126.6; 127.5; 127.9; 128.2; 128.4; 128.4; 128.9; 129.7; 129.8; 129.9; 130.0; 130.2; 132.9; 133.2; 133.3; 137.5; 137.7; 137.9; 143.6; 144.7; 145.1; 145.4; 160.9; 161.8
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$ [b]	(**4a**)	19.0 [s, 1C, $O(CH_2{-}CH_3)_2$]; 19.2 (s, 1C, $CH_3{-}C_6H_4{-}$); 22.0 (s, 1C, CH–CH_3); 22.3 (s, 1C, CH–CH_3); 31.1 [s, 1C, –$CH(CH_3)_2$]; 65.8 [s, 1C, $O(CH_2{-}CH_3)_2$]; 83.8 (s, 1C, $CH_3{-}C_6H_4{-}$); 84.8 (s, 1C, $CH_3{-}C_6H_4{-}$); 87.4 (s, 1C, $CH_3{-}C_6H_4{-}$); 87.9 (s, 1C, $CH_3{-}C_6H_4{-}$); 105.2 [s, 1C, $CH_3{-}C_6H_4{-}$: C(*ipso*)]; 105.3 [s, 1C, $CH_3{-}C_6H_4{-}$: C(*ipso*)]; 126.1 [s, 1C, C(4′)]; 126.2 [s, 1C, C(4)]; 127.1 [s, 1C, C(8′)]; 127.2 [s, 1C, C(8)]; 127.7 [s, 2C, C(5), C(5′)]; 128.0 [s, 1C, C(7′)]; 128.1 [s, 1C, C(7)]; 128.4 [s, 1C, C(8a′)]; 128.8 [s, 1C, C(8a)]; 132.4 [s, 1C, C(6′)]; 132.5 [s, 1C, C(6)]; 137.1 [s, 1C, C(4a′)]; 137.8 [s, 1C, C(4a)]; 148.6 [s, 1C, C(3′)]; 149.0 [s, 1C, C(3)]; 154.8 [s, 1C, C(1′)]; 156.7 [s, 1C, C(1)]
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$ [a]	(**4b**)	18.9 (s, 1C, $CH_3{-}C_6H_4{-}$); 22.1 (s, 1C, CH–CH_3); 22.2 (s, 1C, CH–CH_3); 31.8 [s, 1C, –$CH(CH_3)_2$]; 84.3 (s, 1C, $CH_3{-}C_6H_4{-}$); 85.1 (s, 1C, $CH_3{-}C_6H_4{-}$); 87.3 (s, 1C, $CH_3{-}C_6H_4{-}$); 87.7 (s, 1C, $CH_3{-}C_6H_4{-}$); 105.5 [s, 1C, $CH_3{-}C_6H_4{-}$: C(*ipso*)]; 106.3 [s, 1C, $CH_3{-}C_6H_4{-}$: C(*ipso*)]; 122.1 [s, 8C, $B(C_6H_5)_4$: C(*o*)]; 125.9 [m, 4C, $B(C_6H_5)_4$: C(*p*)]; 126.2 [s, 1C, C(4′)]; 126.4 [s, 1C, C(4)]; 128.1 [s, 1C, C(8′)]; 128.4 [s, 1C, C(8)]; 128.5 [s, 2C, C(5), C(5′)]; 128.9 [s, 1C, C(8a′)]; 129.1 [s, 1C, C(8a)]; 129.7 [s, 1C, C(7′)]; 130.0 [s, 1C, C(7)]; 133.6 [(s, 1C, C(6′)]; 133.8 [s, 1C, C(6)]; 137.0 [s, 8C, $B(C_6H_5)_4$: C(*m*)]; 138.2 [s, 1C, C(4a′)]; 138.7 [s, 1C, C(4a)]; 147.9 [s, 1C, C(3′)]; 148.1 [s, 1C, C(3)]; 156.3 [s, 1C, C(1′)]; 157.9 [s, 1C, C(1)]; 164.9 [q, $^1J_{CB} = 47.7$ Hz, 4C, $B(C_6H_5)_4$: C(*ipso*)]

[a] Solvent acetone-d_6.
[b] Solvent $CDCl_3$.

was kept at the reflux temperature for 4 days avoiding direct exposure to sunlight.

A mixture of different complexes was obtained instead of the expected $Ru(biisoq)(CO)_2(CH_3COO)_2$. By using preparative TLC on aluminium oxide we were able to isolate a purple fraction containing the complex $[Ru(biisoq)_3](CH_3COO)_2$ (**2a**).

By a methatesis reaction of (**2a**) with NH_4PF_6 (1:2 molar ratio) in water, $[Ru(biisoq)_3](PF_6)_2$ (**2b**) was obtained as small purple needles.

2.1.3. $Ru_2(biisoq)_2(Cl)_4\cdot NEt_3$ (**3a**) and $Ru(biisoq)(\mu^2\text{-}CH_3COO)_2$ (**3b**)

Using the procedure reported for $Ru(BINAP)(\mu^2\text{-}CH_3COO)_2$ [9] a mixture of $[Ru(Cl)_2(\eta^4\text{-}1,5\text{-}COD)]_n$ [10] and **1** (molar ratio 1:1) in the presence of an excess of triethylamine was heated in toluene at 140 °C. The binuclear complex $Ru_2(biisoq)_2(Cl)_4\cdot NEt_3$ (**3a**) was obtained.

The methatesis reaction of **3a** with sodium acetate gave the corresponding $Ru(biisoq)(\mu^2\text{-}CH_3COO)_2$ complex **3b**, subsequently seen to decompose during the purification. The presence of **3b** was deduced from an ^{1}H-NMR by the characteristic signals of C(3)–H and C(3′)–H of the coordinated biisoq and the signals of the acetate ligands in a 1:3 ratio.

2.1.4. $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$ (**4a**) and $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$ (**4b**)

Mononuclear arene ruthenium complexes $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq]X$ (X: Cl^-, $B(C_6H_5)_4^-$) were successfully synthesized from the commercial $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)_2]_2$.

Following the procedure reported by Mashima et al. [11] (Scheme 1) a solution of $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)_2]_2$ and biisoq (ligand–Ru = 1 molar ratio) in ethanol–benzene was heated at 55 °C giving the complex $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$ (**4a**) with a 98% conversion evaluated by ^{1}H-NMR.

The complex was purified by flash chromatography and the solution was slowly dropped in diethyl ether under vigorous stirring. The expected complex was obtained in the form of very small light orange needles, soluble and stable in water.

The ^{1}H-NMR spectrum showed signals attributable to diethyl ether in a complex–ether ratio of 2:1 in agreement with the following formulation: $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$ (**4a**). The chemical shifts of diethyl ether suggested that it was present as inclusion in the crystals of **4a** and not directly coordinated to the metal.

By reaction of a solution of **4a** with $NaB(C_6H_5)_4$ (molar ratio 1:1.5) at reflux temperature the product $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$ (**4b**) was synthesized as very small orange needles (75% yield).

Table 5
Elemental analysis, decomposition or melting temperature

Compound	Code	M.p. (°C)	Elemental analysis (%) [a]		
			C	H	N
Biisoq		158–160	84.10 (84.35)	4.72 (4.72)	10.69 (10.93)
$[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)$	(**1**)		55.42 (55.81)	2.83 (3.20)	5.58 (5.92)
$[Ru(biisoq)_3](CH_3COO)_2$	(**2a**)		70.10 (70.50)	4.30 (4.28)	8.52 (8.51)
$[Ru(biisoq)_3](PF_6)_2$	(**2b**)		55.46 (55.92)	3.42 (3.13)	7.55 (7.25)
$Ru_2(biisoq)_2(Cl)_4 \cdot NEt_3$	(**3a**)		52.20 (52.67)	4.31 (4.10)	7.12 (7.31)
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl) \cdot 0.5Et_2O$	(**4a**)	150–155 [b]	59.70 (60.10)	4.99 (5.21)	4.44 (4.67)
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$	(**4b**)	215–220 [b]	73.32 (73.80)	5.33 (5.48)	3.23 (3.31)

[a] Calculated values in parenthesis.
[b] Decompose.

Table 6
X-ray data of $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$ (**4b**): summary of crystal data collection parameters

Formula	$C_{52}H_{36}BClN_2Ru$
Fw	836.16
Space group	$P2_1/n$
a (Å)	11.843(9)
b (Å)	19.827(16)
c (Å)	18.370(9)
β (°)	100.75(1)
V (Å^3)	4238(21)
Z	4
ρ (g cm^{-3})	1.296
μ (mm^{-1})	0.470
Crystal size (mm^3)	$0.20 \times 0.32 \times 0.39$
Number of independent reflections	7663 [$R_{int} = 0.0808$]
Number of reflections [$I > 2\sigma(I)$]	4656
θ Range (°)	1.90–25.29
Number of parameters	494
R [$I > 2\sigma(I)$]	0.0675
wR_{F2}	0.1681

Table 7
X-ray data of $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$ (**4b**): selected interatomic distances (Å), angles (°), and torsion angles (°)

Bond lengths	
Ru–Cl	2.387(3)
Ru–N	2.070(5)
Ru–N′	2.092(9)
Ru–G [a]	1.680(10)
Bond angles	
N–Ru–N′	75.8(2)
N′–Ru–Cl	84.0(2)
N–Ru–Cl	87.0(2)
N–Ru–G	131.2(1)
N′–Ru–G	133.1(2)
Cl–Ru–G	127.5(1)
Torsion angles	
N–C1–C1′–N′	−24.8(7)
C8a–C1–C1′–C8a′	−34.5(9)
C8″–C7″–C1″–C6″	157.08(7)
C9″–C7″–C1″–C6″	−75.6(8)

[a] G represents the centeroid of the η^6-p-cymene.

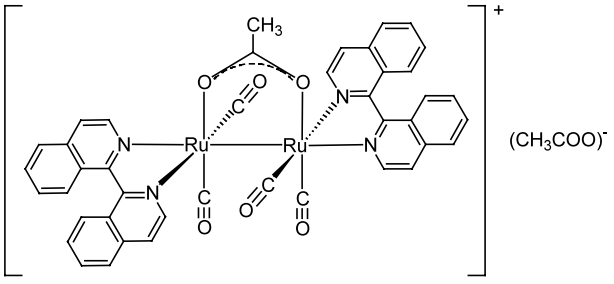


Fig. 1. Suggested structure of $[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)$.

The complex was pure enough to be used as a catalyst. However, it was possible to crystallize it through a slow evaporation of an acetone–ethanol or THF–ethanol or dichloromethane–ethanol solutions obtaining dark red micro crystals.

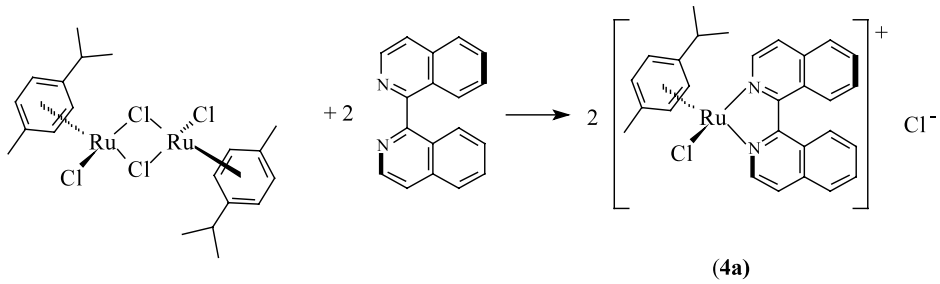
Crystals suitable for X-ray structure determination were obtained by slow diffusion of a methanol solution of $NaB(C_6H_5)_4$ in a methanol solution of **4a**.

The ^{1}H-NMR signals of the chelate biisoq present in both complexes showed a different pattern with respect to the free ligand because the two isoquinoline rings were not equivalent. These data confirm the presence of biisoq chelate to ruthenium in an atropisomeric form (see Fig. 2) with a low rate of interconversion. The coalescence of the C(3)–H, C(3′)–H signals was reached at 110 °C.

As shown for phenantrolines and bipyridines chelate to ruthenium complexes [5,7] the C(3)–H and C(3′)–H protons were shifted at higher field than in the free ligand.

The signals of the p-cymene protons of these complexes were interesting if compared with those of the starting $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)_2]_2$ [12].

- The two methyl protons of the isopropyl group of **4a** and **4b** were not chemically equivalent even if they showed the same chemical shift in the starting complex;



(4a)

Scheme 1.

- The aromatic proton shifts of **4a** and **4b** are at lower frequencies than in the free *p*-cymene [12] due to the η^6 coordination. They show a AA′XX′ spin system in the starting complex but in the biisoq containing complex they show an ABCD spin system.

These attributions were confirmed by selective decoupling and by ^{1}H-NMR COSY spectrum.

2.1.5. *X-ray molecular structure of [Ru(η^6-p-cymene)(Cl)(biisoq)][B(C_6H_5)$_4$] (**4b**)*

The molecular structure of the cationic complex is reported in Fig. 3. The cation displays a three-legged piano-stool geometry involving an η^6-*p*-cymene group, a Cl atom, and the N, N′ atoms of the biisoq chelate ligand. Assuming the arene occupies three facial sites, the coordination geometry can be also described as a distorted octahedral. The Ru atom, is π-bonded to the *p*-cymene ligand with a separation between the arene plane and the metal center of 1.680(10) Å. Due to restraints of the N–N′ chelate, the five-membered ring Ru–N–C1–C1′–N′ is not planar (C1 and C1′ atoms are displaced by −0.128(5) and 0.118(5) Å, respectively, from the mean plane through the other three atoms) with a bit angle of 75.8(2)°. The Ru–N 2.070(5) Å and Ru–N′ 2.090(9) Å distances are essentially equal and in agreement with those found in related structures [13]. The N–C1–C1′–N′ torsion angle of −24.8(7)° that describes the twist of the biisoq ligand is comparable with the −24.1(6)° value found in literature for the biisoq Ru-complexes [14] and the two halves of the ligand, which are not planar, form between them a dihedral angle of 39.5(1)°. In the η^6-arene ring the C–C bond distances fall in the range 1.348(8)–1.440(10) Å, the Ru–C arene ranging from 2.164(8) to 2.217(7) Å.

2.2. Catalytic activity of ruthenium complexes

The complexes **1**, **4a** and **4b** were tested in the catalytic hydrogenation of hex-1-ene (Table 8) using a hydro-alcoholic solvent. All the catalysts showed an high catalytic activity in the hydrogenation of hex-1-ene. Complex **4a** was catalytically active even at 15 °C with a TOF of 4.5 h^{-1}. However, increasing the reaction temperature up to 40 °C resulted in a significant enhancement of the activity of **4a** and **4b** giving TOF values of 63.9 and 118.2, respectively (Table 9).

The catalytic activity of **4a** and **4b**, was found to be dependent on the nature of the counterion, as previously reported in the literature [7] for other ruthenium complexes. In fact **4a** showed a better activity than **4b**, at temperatures higher than 40 °C while at lower temperatures the reverse is true.

An increase of the hydrogen pressure from 15 to 50 atm raised the TOF of hex-1-ene hydrogenation from 1.3 to 151.5 h^{-1} suggesting the formation of a ruthenium hydride complex was required in the first step of the process (Table 10).

The influence of substrate concentration was tested using **4a** in the range between 0.712 and 5.7 M. A surprising behavior was noted with the higher yield (98.8%) being obtained for a concentration of 1.07 M while at higher olefin concentration the yield decreased down to 7.5% hex-1-ene concentration of 5.7 M (Table 11). This behavior suggests the formation of a π-olefin ruthenium complex hindering the coordination of the hydrogen to the catalyst. As a consequence the rate of hydrogenation is reduced.

The catalyst having the higher activity at 60 °C, **4a**, was also tested in the hydrogenation of other substrates such as internal alkenes, alkynes and ketones (Table 12). This complex showed a good activity and an appreciable selectivity for the hydrogenation of C=C double bond. The *trans* alkenes were easier to hydrogenate than the *cis* isomers. Furthermore the catalytic activity in the hydrogenation of terminal olefin was higher than for internal ones. Aromatic olefin was more difficult to hydrogenate than aliphatic alkene.

The reluctance of this catalyst to hydrogenate the *cis* isomers was confirmed by the hydrogenation of cyclohexene. It was obtained with almost the same yield of *cis*-hex-3-ene.

The hydrogenation of phenylacetylene under the same conditions has been obtained with very low yield. In fact only 3.1% of styrene was formed together with a 1.6% of ethylbenzene.

A C=C double bond conjugated with a carbonyl or carboxylato group was hydrogenated with a low efficiency as indicated by the case of *trans*-4-phenylbut-3-

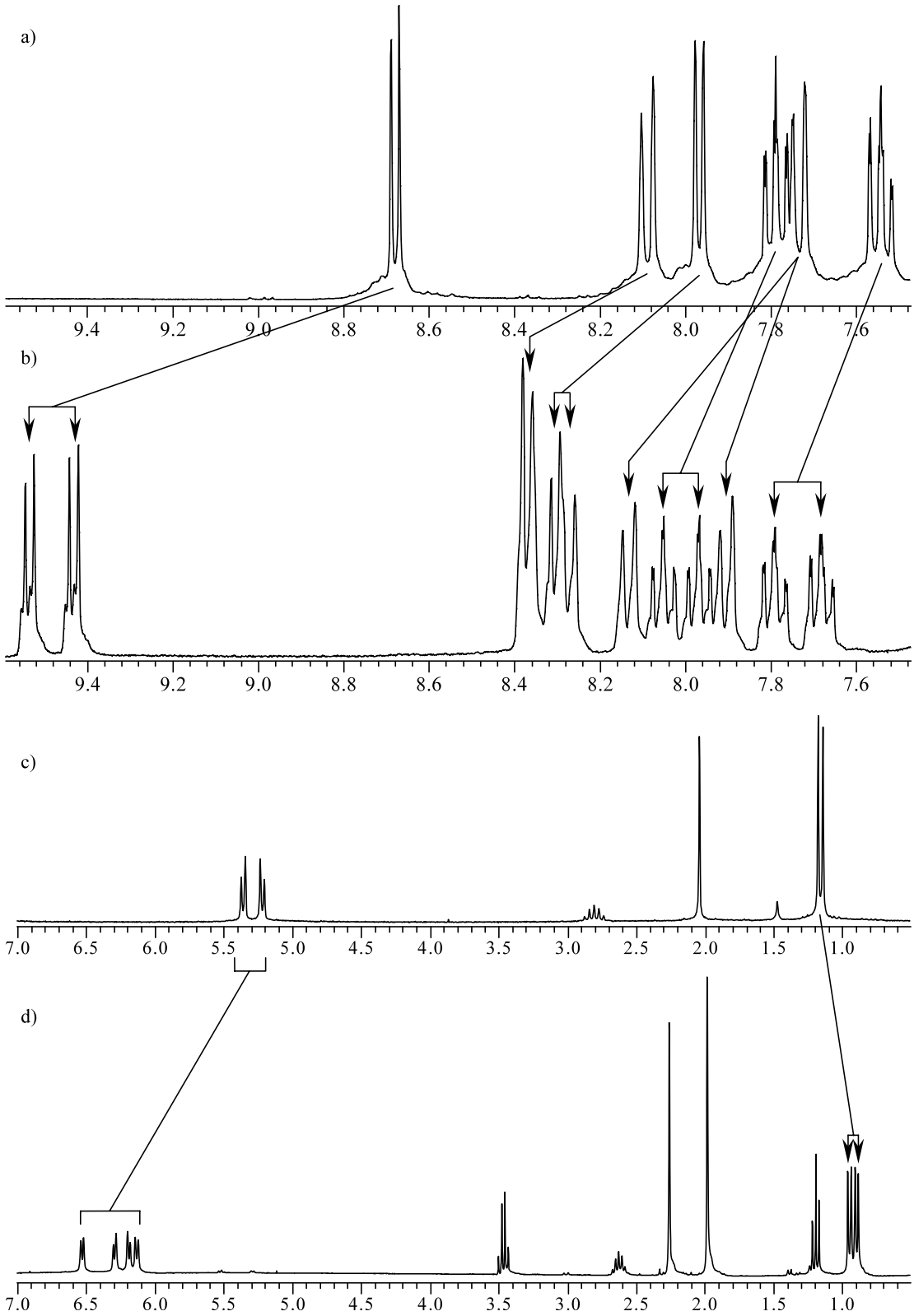


Fig. 2. ^{1}H-NMR of (a) biisoq (acetone-d_6, 9.6–7.5 ppm), (b) [Ru(η^6-*p*-cymene)(Cl)(biisoq)][$B(C_6H_5)_4$] (**4b**) (acetone-d_6, 9.6–7.5 ppm), (c) [Ru(η^6-*p*-cymene)$(Cl)_2]_2$ ($CDCl_3$, 7.0–0.5 ppm), (d) [Ru(η^6-*p*-cymene)(Cl)(biisoq)](Cl)·0.5Et_2O (**4a**) ($CDCl_3$, 7.0–0.5 ppm).

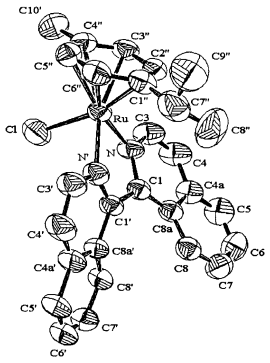


Fig. 3. Molecular structure of cation $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)]^+$. Hydrogen atoms and $B(C_6H_5)_4^-$ are omitted for clarity.

Table 8
Catalytic hydrogenation of hex-1-ene

Complex	Code	Yield (%)	TOF [a] (h^{-1})
$[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)$	(**1**)	87.3	142.2
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$	(**4a**)	99.1	161.2
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$	(**4b**)	78.7	128.1

Substrate 8.55 mmol; catalyst 8.755 μmol; solvent: methanol 4 ml + water 2 ml; pH_2 100 atm (at 20 °C); reaction time 6 h; T 60 °C.
[a] TOF: turn over frequency (mol substrate) (mol-Ru × h)$^{-1}$.

en-2-one (benzylidenacetone) and 2-methylbut-2-enoic acid (tiglic acid); the C=O double bond was not reduced. The reduction of a C=O double bond to secondary alcohol was obtained with low yield at 140 °C.

3. Conclusion

The free biisoq is not a chiral ligand like BINAP because the two atropisomeric forms freely convert through an *anti* 1,1′ rotation [6]. The ligand chelated to a metal may be able, without breaking bonds, to convert only through a *cis* 1,1′ rotation [6]: it may be hindered by the steric encumbrance of the 8,8′ hydrogen atoms.

Table 10
Catalytic hydrogenation of hex-1-ene to hexane in the presence of $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$ (**4a**)

pH_2	Hexane	
	Yield (%)	TOF [a] (h^{-1})
5	0.0	0.0
15	0.8	1.3
30	4.7	7.6
50	93.1	151.5

Influence of hydrogen pressure. Substrate 8.55 mmol; catalyst 8.755 μmol; solvent: methanol 4 ml + water 2 ml; reaction time 6 h, T 60 °C.
[a] TOF: turn over frequency (mol substrate) (mol-Ru × h)$^{-1}$.

In the complexes synthesized **4a** and **4b** for each hydrogens of the two isoquinoline rings we observe different resonances (see Fig. 2) in agreement with an asymmetric structure. These data confirm that the energy barrier for the *cis* rotation of the ligand is higher than in the free ligand and the kinetic of the interconversion at room temperature is low in the NMR time scale.

The X-ray structure of $[Ru(\eta^6\text{-benzene})(Cl)(biisoq)][PF_6]$ [13] was previously reported in the literature. The ^{1}H-NMR data of the benzene derivative are in agreement with those reported in this paper for the *p*-cymene

Table 11
Catalytic hydrogenation of hex-1-ene to hexane in the presence of $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$ (**4a**)

Hex-1-ene (M)	Hexane	
	Yield (%)	TOF [a] (h^{-1})
0.712	3.3	2.6
1.070	98.8	120.1
1.420	93.1	151.5
2.850	67.9	221.0
5.700	7.5	48.6

Influence of substrate concentration. Catalyst 8.755 μmol; solvent: methanol 4 ml + water 2 ml; pH_2 50 atm (at 20 °C); reaction time 6 h, T 60 °C.
[a] TOF: turn over frequency (mol substrate) (mol-Ru × h)$^{-1}$.

Table 9
Catalytic hydrogenation of hex-1-ene in the presence of $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$ (**4a**) or $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](BPh_4)$ (**4b**)

Catalyst	Code	T (°C)	Yield (%)	TOF [a] (h^{-1})
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl)\cdot 0.5Et_2O$	(**4a**)	15	2.8	4.5
	(**4a**)	40	39.3	63.9
	(**4a**)	60	99.1	161.2
	(**4a**)	80	100	162.8
$[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](BPh_4)$	(**4b**)	40	72.6	118.2
	(**4b**)	60	78.7	128.1
	(**4b**)	80	92.8	151.1

Substrate 8.55 mmol; catalyst 8.755 μmol; solvent: methanol 4 ml + water 2 ml; pH_2 100 atm (at 20 °C); reaction time 6 h.
[a] TOF: turn over frequency (mol substrate) (mol-Ru × h)$^{-1}$.

Table 12
Catalytic hydrogenations using [Ru(η^6-*p*-cymene)(Cl)(biisoq)](Cl)·0.5Et_2O (**4a**)

Substrate	Product	Hydrogenation yield (%)	TOF [a] (h^{-1})
Hex-1-ene	Hexane	99.1	161.2
cis-Hex-2-ene	Hexane	38.8	63.1
trans-Hex-2-ene	Hexane	98.5	160.3
cis-Hex-3-ene	Hexane	16.3	26.6
trans-Hex-3-ene	Hexane	94.2	153.2
Cyclohexene	Cyclohexane	12.0	19.5
trans-2-Methylbut-2-enoic acid	2-Methylbutanoic acid	1.2	2.0
trans-4-Phenyl-3-buten-2-one	4-Phenylbutan-2-one	9.9	16.3
Styrene	Ethylbenzene	52.3	85.1
Phenylacetylene	Styrene	3.1	7.6
	Ethylbenzene	1.6	
Acetone[b]	Isopropyl alcohol	10.5	77.1

Substrate 8.55 mmol; catalyst 8.755 μmol; solvent: methanol 4 ml+water 2 ml; pH_2 100 atm (at 20 °C); reaction time 6 h; *T* 60 °C.
[a] TOF: turn over frequency (mol substrate) (mol-Ru × h)$^{-1}$.
[b] *T* 140 °C

analog, confirming the asymmetric structure of the mononuclear complexes **4a** and **4b**.

These complexes are soluble and stable in hydroalcoholic solvents and they show a good catalytic activity in the hydrogenation of alkenes. They are able to selectively hydrogenate a C=C double bond in presence of a carbonyl or carboxylato double bond.

4. Experimental

IR spectra were recorded with a FTIR Perkin–Elmer 1760-X instrument, using a PC and the PE-SPECTRA V2000 program. KBr pellets were used for solid.

^{1}H-NMR and ^{1}H-NMR COSY spectra were recorded at 299.945 MHz on a Varian VXR 300 using tetramethylsilane as external standard. ^{13}C-NMR spectra were recorded at 75.429 MHz on a Varian VXR 300, using tetramethylsilane as external standard. All ^{13}C-NMR spectra were acquired using a broad band decoupler. ^{1}H, ^{13}C-NMR, HETCOR spectra were recorded using the pulse sequence reported by Varian.

Flash chromatographic columns were filled with neutral or basic aluminium oxide Merck 35–70 mesh or silica gel Merck 35–70 mesh.

GC analyses were performed using a Shimadzu GC14 instrument for packed columns or a Perkin–Elmer 8320 apparatus for capillary columns. All instruments were equipped with FID detectors. The following packed columns (2 m length, 1/8 in.) were employed: SQ (Squalane supported on Chromosorb P-AW 10% 60–80 mesh), FFAP column ('Free Fatty Acids Phase' supported on Chromosorb G AW-DMCS 5%), PORAPAK (Porapak Q polymer, 100–120 mesh).

GC–MS analyses were carried out using a Shimadzu GC–MS-QP5050A mass instrument with a capillary column SP^{TM}-1 (30 m length, 0.25 mm diameter, 0.1 μm film layer) using a PC and the Shimadzu CLASS 5000 v 2.20 program.

MS analyses of the ruthenium complexes were carried out using a PE Biosystems' Mariner ESI/time-of-flight mass spectrometer.

Elemental analyses were carried out using a Perkin–Elmer Series II CHNS/O analyzer.

4.1. Materials

All preparations and manipulations were routinely performed under a dry nitrogen atmosphere using Schlenk tube techniques.

Acetone, methanol, THF, diethyl ether, toluene, ethanol, benzene and chloroform were purified and stored using the method reported in literature [17]. Diisopropylamine (Aldrich, 99.5%) was refluxed for 3 h on CaH_2, than distilled (boiling point (b.p.) 84 °C) and stored under nitrogen. Isoquinoline (Aldrich 97%) (melting point (m.p.) 26 °C) was kept on activated 4 Å molecular sieves for 3 h than distilled (b.p. 86 °C/3 mmHg) and stored under nitrogen. Hexamethylphosphoramide (HMPA) (Merk, 99%) was dried for 2 days on CaO than distilled (b.p. 100–105 °C/6 mmHg) and stored under nitrogen.

Hex-1-ene and cyclohexene were purified by elution through a neutral Al_2O_3 (70–230 mesh) chromatographic column, then distilled and stored under nitrogen.

Styrene and phenylacetylene were distilled under vacuum (12 mmHg) and stored under nitrogen.

$[Ru_2(CO)_4(CH_3COO)_2]_n$ [8] and $[Ru(Cl)_2(\eta^4$-1,5-COD)$]_n$ [10] were synthesized according to the procedure reported.

The other substrates and products were employed as purchased without further purification.

4.2. Syntheses of the biisoq (**1**)

4.2.1. Lithium diisopropylamide (LDA)

Butyllithium 1.6 M solution in hexanes (14 ml, 22.4 mmol) was introduced under nitrogen in a 100 ml Schlenk tube and concentrated by bubbling nitrogen up to 1/3 of the starting volume. The solution was cooled to −78 °C, with vigorous stirring under nitrogen, THF (15 ml) and than diisopropylamine (3 ml, 21.4 mmol) were added. The stirred solution was heated to 0 °C and kept at this temperature for 10 min. The LDA solution was immediately employed.

4.2.2. 1,1′-Biisoquinoline

Isoquinoline (5 ml, 42.5 mmol), HMPA (7.4 ml, 42.3 mmol) and diethyl ether (75 ml) were introduced under nitrogen in a 250 ml round bottom flask; the solution was cooled to −78 °C and under vigorous stirring, the LDA solution previously prepared was slowly added in 10 min. The solution was stirred for 1 h at −78 °C and 1 h at 25 °C under nitrogen then another 12 h in the presence of air. The solution became purple red after the first 2 h, and orange at the end. Twenty ml of water were added to the solution under stirring, than the aqueous layer was separated. The organic layer was washed three times with water (50 ml each) and the washing water combined with the initial water layer was extracted with diethyl ether three times (50 ml each). All organic layers were combined and dried with sodium sulfate. The solvent was distilled under reduced pressure and the oily residue purified from HMPA through a basic aluminium oxide column (2 cm length) eluted with a methanol–toluene (5/95) mixture. The fractions containing the product were combined and the solvent distilled under reduced pressure. The oily residue was purified by flash chromatography using a silica gel column (20 cm length, eluted with a MTBE–PE 4:1 mixture). The first fraction contains isoquinoline and the second biisoq. The solvent of the biisoq fraction was distilled under reduced pressure and the residue was collected as yellow crystals (1.89 g, yield 34.4%).

4.3. Syntheses of the ruthenium complexes

4.3.1. $[Ru_2(biisoq)_2(CO)_4(CH_3COO)](CH_3COO)$ (**1**)

In a 50 ml round bottom flask equipped with a reflux condenser $[Ru_2(CO)_4(CH_3COO)_2]_n$ (154.5 mg, 0.715 mmol of ruthenium), biisoq (182.3 mg, 0.712 mmol) and ethanol (30 ml) were introduced and kept for 3 h at the reflux temperature. The yellow solid was filtered, washed with ethanol (3 × 5 ml) and dried under vacuum (191 mg, 56.5% yield).

4.3.2. $[Ru(biisoq)_3](CH_3COO)_2$ (**2a**)

In a 50 ml round bottom flask equipped with a reflux condenser $[Ru_2(CO)_4(CH_3COO)_2]_n$ (108.4 mg, 0.50 mmol of ruthenium), **1** (138 mg, 0.53 mmol) and acetic acid (15 ml) were introduced and kept 4 days at the reflux temperature avoiding the exposure to sun light. The solvent was distilled under reduced pressure and the residue **2a** was purified using a preparative thin layer chromatography (Al_2O_3 eluted with methanol): the second fraction (purple) was recovered. The complex (yield 10%) was crystallized from a methylene chloride–heptane solution.

4.3.3. $[Ru(biisoq)_3](PF_6)_2$ (**2b**)

In a sample tube **2a** (60 mg, 0.06 mmol) was dissolved in 10 ml of deionized water, than NH_4PF_6 (20 mg, 0.12 mmol) was introduced. The complex was found to crystallize readily (yield 96%) as very small purple needles that were centrifuged, washed with water (3 × 2 ml) and dried under vacuum.

4.3.4. $Ru_2(biisoq)_2(Cl)_4 \cdot NEt_3$ (**3a**)

Biisoq **1** (205 mg, 0.8 mmol), $[Ru(Cl)_2(\eta^4\text{-}1,5\text{-}COD)]_n$ (0.73 mmol of Ru), triethylamine (1.8 ml, 12.8 mmol) and 25 ml of toluene were introduced in an autoclave under nitrogen and kept for 3 h at 140 °C under stirring. The solvent was distilled under vacuum, the solid residue dissolved in methylene chloride and filtered through celite 545. The complex (286.5 mg, yield 82%) was crystallized as very small green needles by addition of diethyl ether.

4.3.5. $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)](Cl) \cdot 0.5Et_2O$ (**4a**)

In a 100 ml round bottom flask equipped with a reflux condenser, biisoq (347 mg, 1.36 mmol), $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)_2]_2$ (411 mg, 1.34 mmol of Ru), ethanol (35 ml) and benzene (5 ml) were introduced under nitrogen. The solution was heated and stirred at 55 °C for 40 min. The solvent was distilled under reduced pressure and the red oily residue purified with a flash chromatography using a neutral aluminium oxide as support and methanol as eluent. The product was collected in the first fraction, the solvent distilled under reduced pressure and the oily residue dissolved in chloroform. The solution was slowly dropped in diethyl ether under vigorously stirring: the free ligand remains in ether and very small light orange needles were collected. The complex (766 mg, yield 95.6%) was washed with ether and dried under high vacuum on potassium hydroxide.

4.3.6. $[Ru(\eta^6\text{-}p\text{-cymene})(Cl)(biisoq)][B(C_6H_5)_4]$ (**4b**)

In a 250 ml round bottom flask equipped with a reflux condenser **4a** (678.7 mg, 1.13 mmol), $NaB(C_6H_5)_4$ (621 mg, 1.82 mmol) and ethanol (90 ml) were introduced

under nitrogen and the mixture heated and stirred for 3 h at the reflux temperature. The orange solid product was filtered, washed with cold methanol and dried under vacuum (716.4 mg, yield 75%).

4.4. Crystal structure determination of [Ru(η^6-p-cymene)(Cl)(biisoq)][B(C_6H_5)$_4$] (**4b**)

The crystal data and experimental details are given in Tables 6 and 7. X-ray data were collected on a Bruker Smart 1000 area detector diffractometer using a graphite monochromated Mo–K_α radiation. Absorption was applied using SADABS, Bruker software. The structure was solved by direct methods and different Fourier techniques. Full-matrix least-squares refinement on F^2 was used with anisotropic thermal parameters for all non-hydrogen atoms with exception for the methyl C9″ atom and some of the carbon atoms of $B(C_6H_5)_4^-$ counteranion, which had a very large thermal motion, and therefore, refined isotropically. The hydrogen atoms of the cation complex were refined isotropically in their calculated riding position, the hydrogen atoms of $B(C_6H_5)_4^-$ were ignored. Calculations were carried out using SHELXS97 [15] and SHELXL97 [16] programs. Selected interatomic distances, angles and torsion angles are given in Table 7. Final positional parameters are available as Supporting Information.

4.5. Hydrogenation reactions and analysis of the products

The reactions were carried out in a 150 ml stainless steel rocking autoclave. The air was evacuated prior to the introduction of the solution containing solvent, catalyst and substrate. Hydrogen was then added up to 100 atm. The autoclave was heated in an oil bath thermostated at the prefixed temperature (±1 °C) and rocked for the prefixed time. After rapid cooling at room temperature, the hydrogen was vented and the solution collected and analyzed by gas chromatography.

A GC capillary column Al_2O_3–Na_2SO_4 PLOT (Chrompack, length: 50 m, diameter: 0.45 mm) was used to analyze hexane and the residual hexenes: the oven was kept at 130 °C for 25 min, then heated at a rate of 30 °C min^{-1} up to 200 °C and kept at this temperature for 50 min; the sample before analysis was added with THF to unify the two layers present at the end of the reaction.

Cyclohexene: hydrogenation products were analyzed using a SQ column: the oven was kept at 40 °C for 20 min, then heated a rate of 10 °C min^{-1} up to 130 °C and kept at this temperature for 20 min; the sample before analysis was added with THF to unify the two layer present at the end of the reaction.

trans-2-Methylbut-2-enoic acid: hydrogenation products were analyzed using a FFAP column kept at 150 °C for 60 min.

trans-4-Phenyl-3-buten-2-one: hydrogenation products were analyzed using a FFAP column kept at 50 °C for 2 min, then heated a rate of 10 °C min^{-1} up to 180 °C and kept at this temperature for 20 min.

Styrene: hydrogenation product was analyzed using a FFAP column kept at 80 °C for 40 min.

Phenylacetylene: hydrogenation products were analyzed using a FFAP column kept at 80 °C for 40 min, then heated at a rate of 10 °C min^{-1} up to 200 °C and kept at this temperature for 30 min.

Acetone: hydrogenation product was analyzed using a PORAPAK column kept at 100 °C for 10 min, then heated at a rate of 2 °C min^{-1} up to 150 °C and kept at this temperature for 10 min.

5. Supplementary material

Crystallographic data (crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters) for **4b** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 192845. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We wish to thank the University of Florence and the "Ministero dell'Istruzione, dell'Università e della Ricerca (M.I.U.R.), Programmi di Ricerca di Notevole Interesse Nazionale, Cofinanziamento M.I.U.R. 2000–2001" for financial support. We would like to thank Brunella Innocenti of the University of Florence for the elemental analysis; Mara Camaiti of the C.N.R.-C.S.C.O.A. of Florence for the help given in the registration of the IR spectrum in the 'far IR' region; Gloriano Moneti of the University of Florence for the ESI/time-of-flight mass spectra; Fabrizio Zanobini of the C.N.R.-I.C.C.O.M. of Florence and Elisabetta Berti for the help given in the crystallization technique.

References

[1] B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, 2002.
[2] (a) U. Matteoli, P. Frediani, M. Bianchi, S. Gladiali, C. Botteghi, J. Mol. Catal. 12 (1981) 265;
(b) U. Matteoli, M. Bianchi, G. Menchi, P. Frediani, F. Piacenti, J. Mol. Catal. 29 (1985) 269;

(c) U. Matteoli, G. Menchi, P. Frediani, M. Bianchi, F. Piacenti, J. Organomet. Chem. 285 (1985) 281;
(d) U. Matteoli, G. Menchi, M. Bianchi, P. Frediani, F. Piacenti, F. Gazz. Chim. Ital. 115 (1985) 603;
(e) M. Bianchi, G. Menchi, P. Frediani, F. Piacenti, A. Scrivanti, U. Matteoli, J. Mol. Catal. 50 (1989) 277;
(f) U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti, J. Mol. Catal. 64 (1991) 257.

[3] P. Frediani, M. Bianchi, A. Salvini, R. Guarducci, L.C. Carluccio, F. Piacenti, J. Organomet. Chem. 463 (1993) 187.

[4] P. Frediani, M. Bianchi, A. Salvini, R. Guarducci, L.C. Carluccio, F. Piacenti, J. Organomet. Chem. 476 (1994) 7.

[5] E. Rivalta, University of Florence, personal communication.

[6] M.T. Ashby, G.N. Govindan, A.K. Grafton, J. Am. Chem. Soc. 116 (1994) 4801.

[7] P. Frediani, M. Bianchi, A. Salvini, R. Guarducci, L.C. Carluccio, F. Piacenti, J. Organomet. Chem. 498 (1995) 187.

[8] G.R. Crooks, B.F.G. Johnson, J. Lewis, I.G. Williams, G.J. Gamlen, Chem. Soc. A (1969) 2761.

[9] T. Otha, H. Takaya, R. Noyori, Inorg. Chem. 27 (1988) 566.

[10] M.O. Albers, T.V. Ashworth, H.E. Oosthuizen, E. Singleton, Inorganic Synthesis, vol. 26, Wiley, Weinheim, 1989, p. 68.

[11] K. Mashima, K. Kusano, T. Otha, R. Noyori, H. Takaya, J. Chem. Soc. Chem. Commun. (1989) 1208.

[12] C.J. Pouchert, J. Behnke, The Aldrich Library of ^{13}C and ^{1}H FT-NMR spectra, first ed, Aldrich Chemical, Milwaukee, 1993.

[13] M.T. Ashby, S.S. Alguindigue, M.A. Kahn, Organometallics 19 (2000) 547.

[14] M.T. Ashby, J. Am. Chem. Soc. 117 (1995) 2000.

[15] G.M. Sheldrick, SHELXS-97, a Program for Automatic Solution of Crystal Structures, University of Göttingen (pre-release version 1997-2).

[16] G.M. Sheldrick, SHELXL-97, a Program for Refining Crystal Structures, University of Göttingen (pre-release version 1997-2).

[17] A.I. Vogel, Vogel's Textbook of Pratical Organic Chemistry, Longman, London, 1978.