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Synthesis, crystal structure and catalytic properties of (*p*-cymene)ruthenium(II) azophenol complexes: azophenyl to azophenol conversion by oxygen insertion to a ruthenium–carbon bond

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Abstract

Azophenol complexes of formulation [(η^6-*p*-cymene)RuCl(L^n)] (**1**–**6**, $n = 1$–6) were prepared by two synthetic methods involving either an oxygen insertion to the Ru–C bond in cycloruthenated precursors forming complexes **1** and **2** or from the reaction of [{(η^6-*p*-cymene)RuCl}$_2$(μ-Cl)$_2$] with azophenol ligands (HL^3–HL^6) in the presence of sodium carbonate in CH_2Cl_2. The molecular structure of the 1-(phenylazo)-2-naphthol complex has been determined by X-ray crystallography. The complex has a η^6-*p*-cymene group, a chloride and a bidentate N,O-donor azophenol ligand. The complexes have been characterized from NMR spectral data. The catalytic activity of the complexes has been studied for the conversion of acetophenone to the corresponding alcohol in the presence of KOH and isopropanol. Complexes **4** and **6** having a methoxy group attached to the *ortho*-position of the phenylazo moiety and **2** with a methyl group in the *meta*-position of the phenolic moiety show high percentage conversion ($> 84\%$). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Arene ruthenium; Crystal structure; Oxygen insertion; Azophenol ligands; Transfer hydrogenation; Catalysis

1. Introduction

Current interest in the chemistry of half-sandwich (η^6-arene)ruthenium(II) complexes lies in the development of new catalytic systems for a variety of organic transformation reactions and in the enantioselective asymmetric induction studies [1–5]. Ruthenium-based catalytic systems are found to be effective in the hydrogenation of ketones for the synthesis of chiral alcohols [6–10]. Studies by Noyori and coworkers have shown that the transfer hydrogenation of prochiral ketones can be achieved by high enantiomeric excess by tailoring the chiral ruthenium catalysts [1b,6]. The N,N- and N,O-donor ancillary ligands play an important role in the catalytic reactions. The present work stems from our interest in studying the reactivity of (*p*-cymene)-ruthenium(II) azophenol complexes as new hydrogenation catalysts.

We have recently reported two cycloruthenated complexes [(η^6-*p*-cymene)Ru(L′)Cl], where L′ is a chelating C,N-donor (phenylazo)phenyl (pap) and (4,4′-dimethylphenylazo)phenyl (dmpap) ligands [11]. Herein, we report the two azophenol complexes (**1** and **2**) obtained from a regiospecific oxygenation of the ruthenium–carbon bond of the azophenyl moiety to form the corresponding azophenol ligand (HL^1, HL^2). We have also prepared a series of analogous complexes (**3**–**6**) by reacting [{(η^6-*p*-cymene)RuCl}$_2$(μ-Cl)$_2$] with the azophenol ligands, HL^3–HL^6. The synthesis, structure and properties of [(η^6-*p*-cymene)RuCl(L^n)] (**1**–**6**) ($n =$ 1–6) are presented here (Scheme 1). Complex **5** has been characterized by X-ray crystallography.

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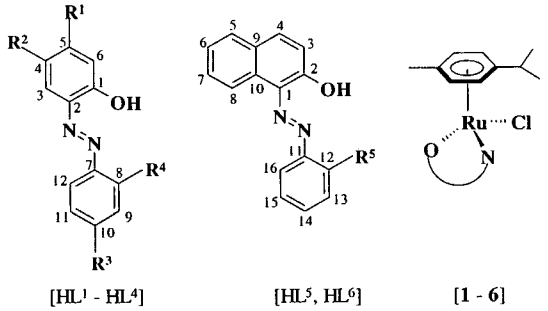
2. Results and discussion

2.1. Synthetic aspects

Complexes **1** and **2** were prepared by the insertion of oxygen into the ruthenium–carbon bond of the precursor complexes of formulation [(η^6-*p*-cymene)Ru(L′)Cl], where L′ is a bidentate, chelating, C,N-donor azophenyl ligand, using *m*-chloroperbenzoic acid in a chloroform–methanol solvent (Eq. (1)). The product yield from such a reaction is low ($\sim$20%), possibly because of the instability of the precursor complex under high thermal reaction conditions. While the insertion of oxygen to a palladium–carbon bond is quite common, a similar regiospecific oxygenation of a ruthenium–carbon bond is relatively rare [12]. Incidentally, it is difficult to prepare the ligand systems HL^1 and HL^2, obtained from the oxygenation reaction using the conventional methods employed in the synthesis of HL^3–HL^6. Complexes **3**–**6** were synthesized in $\sim$90% yield from a reaction of [{(η^6-*p*-cymene)RuCl}$_2$(μ-Cl)$_2$] with the azophenol ligand (HL^3–HL^6) in dichloromethane in the presence of sodium carbonate. All the complexes were found to be air stable in the solid state and moderately stable in the liquid state.



HL^1 : R^1 - R^4 =H
HL^2 : R^1 = R^3 = Me, R^2 = R^4 = H
HL^3 : R^1 = R^3 = R^4 = H, R^2 = Me
HL^4 : R^1 = R^3 = H, R^2 =Me, R^4 = OMe
HL^5 : R^5 = H
HL^6 : R^5 = OMe

Scheme 1.

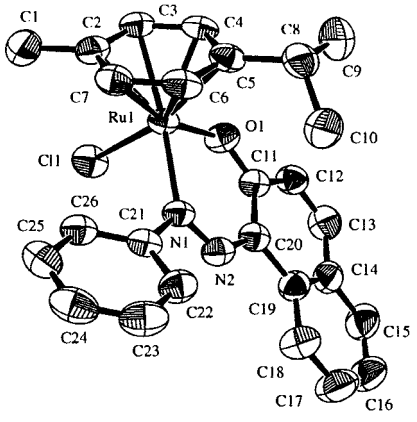
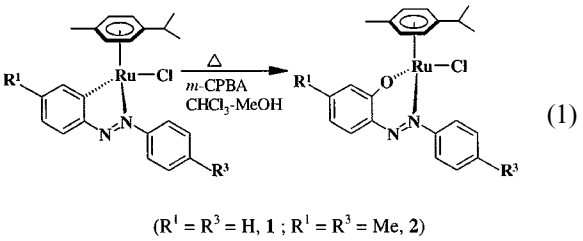


Fig. 1. ORTEP drawing of the complex showing 50% probability thermal ellipsoids and the atom numbering scheme for [(η^6-*p*-cymene)RuCl(L^5)]·MeCN (**5**·MeCN).



(1)

(R^1 = R^3 = H, **1** ; R^1 = R^3 = Me, **2**)

2.2. Spectral studies

The visible and near-UV electronic spectra of the complexes **1**–**6** in MeCN show three intense charge transfer bands in the following ranges: 525–562, 397–431 and 315–322 nm. Complex **5** exhibits an additional band at 360 nm. The azophenol complexes display lower energy bands in the visible region compared with the azonaphthol analogues. The complexes were characterized by ^{1}H-NMR and ^{13}C-{^{1}H}-NMR data.

The NMR spectral data suggest a 1:1 molar ratio of the *p*-cymene and azophenol ligands in **1**–**6**. The methyl (singlet) and the isopropyl protons (two doublets) of the *p*-cymene ligand appear in the ranges of 2.1–2.3 and 0.7–1.2 ppm, respectively. The isopropyl CH proton appears as a septet in the range of 2.2–2.7 ppm. The *p*-cymene ring protons are observed in the range of 3.7–5.7 ppm as either four doublets (4H) or two doublets (2H) and a singlet (2H). In ^{13}C–{^{1}H}-NMR, the *p*-cymene resonances are observed in four distinctive ranges of 22.2–21.8, 79.8–110.8, 30.5–31.3 and 18.7–21.9 ppm. The methyl and methoxy protons of the N,O-donor ligands appear in the range of 2.1–2.5 and at $\sim$4.0 ppm, respectively. The other spectral features are as expected. The formation of the oxygenated product **1** and **2** is evidenced from the ^{13}C–{^{1}H}-NMR studies. The disappearance of the carbon peak at $\sim$188 ppm for the Ru–C σ bond of the precursors and the appearance of a new peak at $\sim$170 ppm suggest the formation of a Ru–O–C moiety. Complexes **3**–**6** show a similar peak in the range of 160–178 ppm assignable to the phenolato–naphtholato carbon.

2.3. Crystal structure

The azonaphthol complex [(η^6-*p*-cymene)Ru(L^5)Cl]·(5·MeCN) has been structurally characterized by X-ray crystallography. An ORTEP [13] view is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1. The complex has an essentially octahedral coordination geometry comprising the η^6-*p*-cymene ring carbons occupying one face of the octahedron leaving the other three sites to be coordinated by a

Table 1
Bond lengths (Å) and bond angles (°) for **5**·MeCN with estimated SDs in parentheses

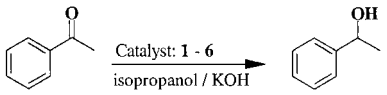
Bond lengths			
Ru(1)–O(1)	2.049(3)	Ru(1)–C(4)	2.194(4)
Ru(1)–N(1)	2.080(3)	Ru(1)–C(5)	2.205(4)
Ru(1)–Cl(1)	2.426(2)	Ru(1)–C(6)	2.168(4)
Ru(1)–C(2)	2.216(4)	Ru(1)–C(7)	2.206(4)
Ru(1)–C(3)	2.207(4)	Ru(1)–C^0	1.694(4)
Bond angles			
O(1)–Ru(1)–Cl(1)	84.47(10)	C^0–Ru(1)–Cl(1)	127.89(15)
O(1)–Ru(1)–N(1)	86.30(13)	C^0–Ru(1)–O(1)	125.53(18)
N(1)–Ru(1)–Cl(1)	85.57(10)	C^0–Ru(1)–N(1)	131.65(17)

C^0, the centroid of the η^6-arene ring.

chloride and the bidentate chelating N,O-donor azonaphthol ligand. The Ru–C(arene) distances vary considerably from 2.168 to 2.215 Å [14,15]. The structural features correspond well with the reported Schiff-base (*p*-cymene)–ruthenium(II) complexes [14–16].

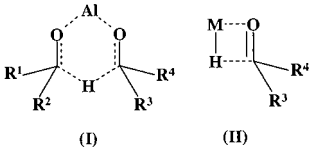
2.4. Catalytic activity

The catalytic hydrogenation of acetophenone in the presence of **1**–**6** has been studied in an isopropanol–KOH medium using a mole ratio of 1:2.5:100 for the catalyst, KOH and ketone in 5 ml isopropanol (Eq. (2)). The percentage conversions obtained using the complexes as promoters are given in Table 2. Complexes **2**, **4** and **6** gave conversions in the range of 84–96%. The higher activity in complexes **4** and **6** could be related to the presence of the *ortho*-methoxy group of the phenylazo moiety.



(2)

The activity of the present complexes is compared with those of other achiral catalysts including aluminum isopropoxide which is known as a promoter in Meerwein–Ponndorf–Verley (MPV) reduction of ketones (Table 2) [8b,c,17]. While the MPV reduction involves a direct transfer of a hydride through the formation of a non-hydridic intermediate (**I**), the half-sandwich ruthenium(II) complexes mediates through the formation of a hydride species (**II**) generated by KOH from the chloro precursor [6a,10b]. The present work is of significance towards developing the chemistry of chiral azophenol complexes as promoters in transfer hydrogenation reactions.



3. Conclusions

We have prepared a series of (arene)ruthenium(II) azophenol complexes that are catalytically active in the hydrogenation of acetophenone to 1-phenylethanol. The complexes **2**, **4** and **6** having *meta*-methyl and *ortho*-methoxy group are found to be moderately active in the catalytic reaction showing a percentage conversion of $>84\%$. Two complexes have been prepared by a novel oxygen-insertion reaction to the Ru–C bond of the azophenyl precursors.

4. Experimental

All reactions were carried out under a dry dinitrogen atmosphere following conventional Schlenk techniques. The solvents were distilled from the appropriate drying agents and deoxygenated prior to use. Acetophenone was distilled under vacuum. *m*-Chloroperbenzoic acid was purified before each use. Cycloruthenated precursors [11], $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ [18] and the ligands HL^3–HL^6 [19] were prepared by procedures outlined earlier. All other chemicals were of reagent grade and

Table 2
A comparison of the activity of achiral promoters in transfer hydrogenation of acetophenone in refluxing isopropanol

Entry	Catalyst	Base	*t* (H)	Conversion (%)	Reference
1	$Al(O^iPr)_3$	–	12	93	[17a]
2	$[(\eta^6\text{-}p\text{-Cymene})Ru(C_{16}H_{15}NOP)Cl]$	NaO^iPr	6	94	[8c]
3	$[(\eta^6\text{-}p\text{-Cymene})Ru(C_{16}H_{16}NOP)Cl]Cl$	Na^iOPr	6	94	[8c]
4	$[(\eta^6\text{-Benzene})Ru(C_{14}H_{17}N_2O_2P)Cl](O_3SCF_3)$	NaO^iPr	1	54	[8b]
5	$RuCl_2(PPh_3)_3$	NaO^iPr	6	75	[17b]
6	Complexes **1**, **5**	KOH	6	~46	This work
7	Complex **2**	KOH	6	87	This work
8	Complex **3**	KOH	6	59	This work
9	Complex **4**	KOH	6	84	This work
10	Complex **6**	KOH	6	96	This work

used as such. Elemental analysis was performed on a Perkin–Elmer 2400 CHN analyzer. The ^{1}H- and ^{13}C–{^{1}H}-NMR spectra were recorded on Bruker 200 MHz and Bruker AMX 400 (carbon channel 100.6 MHz) spectrometers using Me_4Si as the standard. Visible electronic spectra were obtained from a Hitachi U-3400 spectrophotometer.

4.1. Synthesis of [(η^6-*p*-cymene)Ru(L^n)Cl] ($n = 1$, 2) from oxygen-insertion reactions (**1**, **2**)

The complexes **1** and **2** were prepared by reacting 0.21 mmol of [(η^6-*p*-cymene)Ru(L′)Cl], where L′ is monoanionic, C,N-donor (phenylazo)-phenyl or 4,4′-dimethyl(phenylazo)phenyl, with 0.31 mmol (54 mg) of *m*-chloroperbenzoic acid under refluxing condition in a 10 ml solution of $CHCl_3$ and MeOH (1:1, v/v) for 6 h. After cooling the reaction mixture to an ambient temperature, it was filtered through celite, reduced to a volume of ~3 ml and subjected to column chromatography using neutral alumina, deactivated with MeOH prior to use. Elution with a mixture of MeOH and $CHCl_3$ (1:20, v/v) gave the product as a reddish band, which was separated and dried under vacuum (yield: ~20%).

Anal. Found: C, 57.20; H, 4.85; N, 6.21. Calc. for $C_{22}H_{23}N_2OClRu$ (**1**): C, 56.46; H, 4.90; N, 5.99%. Visible spectral data: λ_{max} (nm) (ε, l mol^{-1} cm^{-1}) (MeCN): 330 (23 990), 456 (12 760), 551 (6040). ^{1}H-NMR ($CDCl_3$, 200 MHz, δ ppm): 0.68, 0.86 (2d, 2 × 3H, [$^3J_{HH} = 8$ Hz], CH*Me*$_2$), 2.18 (s, 3H, Me), 2.21 (sp, [$^3J_{HH} = 7$ Hz], *CH*Me$_2$), 5.09, 5.38, 5.69, 5.77 (4d, 4 × 1H, [$^3J_{HH} = 6$ Hz], four ring H) (*p*-cymene), 7.3 (m, $H_{4,5}$), 7.53 (m, H_{9-11}), 8.12 (m, $H_{8,12}$), 8.30 (m, H_3), 8.50 (m, H_6) (L^1 ligand) (H_n, the hydrogen atom number corresponding to the C_n given in Scheme 1, s, singlet; d, doublet; m, multiplet; sp, septet). ^{13}C-NMR (CH_2Cl_2, 200 MHz, δ ppm): 18.87 (*C*HMe$_2$), 21.12, 22.21 (CH*Me*$_2$), 30.84 (Me), 85.9, 87.03, 92.59, 96.58, 102.2, 108.0 (ring C_6H_4) (*p*-cymene), 122.96, 124.60, 128.47, 129.92, 130.30, 130.50, 130.96, 133.58, 140.17 ($C_{3-6,8-12}$), 157.0, 163.50 ($C_{2,7}$), 168.85 (C_1) (L^1 ligand).

Anal. Found: C, 58.25; H, 5.40; N, 5.83. Calc for $C_{24}H_{27}N_2ORuCl$ (**2**): C, 58.11; H, 5.45; N, 5.65%. Visible spectral data: λ_{max} (nm) (ε, l mol^{-1} cm^{-1}) (MeCN): 349 (21 570), 443 (13 010), 547 (6620). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 0.73, 0.88 (2d, 2 × 3H, [$^3J_{HH} = 7$ Hz], CH*Me*$_2$), 2.10 (s, 3H, Me), 2.24 (sp, [$^3J_{HH} = 7$ Hz], *CH*Me$_2$), 5.06, 5.14, 5.54, 5.64 (4d, 4 × 1H, [$^3J_{HH} = 6$ Hz], four ring H) (*p*-cymene), 2.46 (s, 6H, C_5–*Me*, C_{10}–*Me*), 6.97 (d, [$^3J_{HH} = 7$ Hz], H_4), 7.27 (d, [$^3J_{HH} = 8$ Hz], $H_{8,12}$), 8.05 (m, $H_{3,6,9,11}$) (L^2 ligand). ^{13}C-NMR ($CDCl_3$, 400 MHz, δ ppm): 19.70 (*C*HMe$_2$), 21.12, 22.65 (CH*Me*$_2$), 31.31 (Me), 85.76, 87.77, 92.36, 96.73, 103.42, 107.52 (ring C_6H_4) (*p*-cymene), 22.97, 24.49 (C_5–*Me*, C_{10}–*Me*), 123.35, 126.76, 129.47, 131.90, 140.93, 142.28 ($C_{3-6,8-12}$), 156.09, 162.91 ($C_{2,7}$), 170.74 (C_1) (L^2 ligand).

4.2. Synthesis of [(η^6-*p*-cymene)Ru(L^n)Cl] (**3**–**6**) ($n = 3$–6)

Complexes **3**–**6** were synthesized by a general procedure in which a 0.33 mmol (200 mg) of [(η^6-*p*-cymene)$RuCl_2$]$_2$ was treated with 0.70 mmol of the ligand HL^n in the presence of 0.83 mmol (90 mg) of Na_2CO_3 under continuous stirring for 4 h in 15 ml CH_2Cl_2 at 25 °C. The solid product thus obtained was thoroughly washed with *n*-hexane and dried under vacuum (yield: ~90%). Dark-red crystals of **5**·MeCN were obtained on cooling a solution of the complex in a mixture of Me_2CO, petroleum ether and MeCN at −10 °C.

Anal. Found: C, 57.51; H, 4.94; N, 5.89. Calc. for $C_{23}H_{25}N_2OClRu$ (**3**): C, 57.32; H, 5.19; N, 5.82%. Visible spectral data: λ_{max} (nm) (ε, l mol^{-1} cm^{-1}) (MeCN): 316 (19 700), 398 (11 320), 562 (7980). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 1.07, 1.14 (2d, 2 × 3H, [$^3J_{HH} = 7$ Hz], CH*Me*$_2$), 2.19 (s, 3H, Me), 2.55 (sp, [$^3J_{HH} = 7$ Hz], *CH*Me$_2$), 4.47, 4.93 (2d, 2 × 1H, [$^3J_{HH} =$ 6 Hz], ring H), 5.35 (s, 2H, ring H) (*p*-cymene), 2.21 (s, 3H, Me), 6.95, 7.09 (2d, 2 × 1H, [$^3J_{HH} = 9$ Hz], $H_{5,6}$), 7.37–7.48 (m, $H_{5,9-11}$), 7.88 (m, $H_{8,12}$) (L^3 ligand). ^{13}C-NMR ($CDCl_3$, 400 MHz; δ ppm): 19.21 (*C*HMe$_2$), 20.34, 22.53 (CH*Me*$_2$), 31.51 (Me), 81.34, 83.21, 86.14, 95.57, 99.97 (ring C_6H_4) (*p*-cymene), 30.95 (Me), 117.63, 121.53, 123.51, 124.34, 127.29, 128.27, 129.36, 136.32, 151.69 ($C_{3-6,8-12}$), 156.73 ($C_{2,7}$), 161.98 (C_1) (L^3 ligand).

Anal. Found: C, 56.80; H, 5.31; N, 5.49. Calc. for $C_{24}H_{27}N_2O_2ClRu$ (**4**): C, 56.30; H, 5.28; N, 5.47%. Visible spectral data: λ_{max} (nm) (ε, l mol^{-1} cm^{-1}) (MeCN): 317 (17 310), 431 (13 440), 557 (6490). ^{1}H-NMR ($CDCl_3$, 200 MHz, δ ppm): 1.05, 1.11 (2d, 2 × 3H, [$^3J_{HH} = 8$ Hz], CH*Me*$_2$), 2.10 (s, 3H, Me), 2.63 (sp, [$^3J_{HH} = 7$ Hz], *CH*Me$_2$), 3.76, 4.91, 5.13, 5.53 (4d, 4 × 1H, [$^3J_{HH} = 6$ Hz], four ring H) (*p*-cymene), 2.17 (s, 3H, Me), 4.03 (s, 3H, OMe), 6.86–7.17 (m, $H_{5,9-11}$), 7.36–7.61 (m, $H_{3,6,12}$) (L^4 ligand). ^{13}C-NMR ($CDCl_3$, 400 MHz; δ ppm): 18.92 (*C*HMe$_2$), 20.19, 21.81 (CH*Me*$_2$), 30.75 (Me), 80.77, 81.35, 82.50, 101.43, 103.07, 110.78 (ring C_6H_4) (*p*-cymene), 22.67 (Me), 56.02 (OMe), 117.72, 120.11, 121.09, 122.67, 125.64, 128.79, 136.03, 145.54 ($C_{3-6,8-12}$), 147.54, 152.23 ($C_{2,7}$), 172.23 (C_1) (L^4 ligand).

Anal. Found: C, 59.65; H, 4.91; N, 5.37. Calc. for $C_{26}H_{25}N_2OClRu$ (**5**): C, 60.29; H, 4.83; N, 5.41%. Visible spectral data: λ_{max} (nm) (ε, l mol^{-1} cm^{-1}) (MeCN): 322 (15 400), 360 (15 010), 397 (11 820), 529 (10 200). ^{1}H-NMR ($CDCl_3$, 200 MHz, δ ppm): 1.05, 1.12 (2d, 2 × 3H, [$^3J_{HH} = 7$ Hz], CH*Me*$_2$), 2.25 (s, 3H, Me), 2.51 (sp, [$^3J_{HH} = 7$ Hz], *CH*Me$_2$), 4.58, 4.96 (2d, 2 × 1H,

[$^3J_{HH} = 6$ Hz], ring H), 5.40 (s, 2H, ring H) (*p*-cymene), 7.14–7.56 (m, $H_{3,4,12-16}$), 7.67 (d, [$^3J_{HH} = 9$ Hz], H_5), 7.98 (d, [$^3J_{HH} = 7$ Hz], $H_{6,7}$), 8.28 (d, [$^3J_{HH} = 8$ Hz], H_8) (L^5 ligand). ^{13}C-NMR ($CDCl_3$, 400 MHz, δ ppm): 18.79 (*CH*Me_2), 21.89, 22.72 (CH*Me*$_2$), 30.50 (Me), 83.41, 83.72, 85.83, 88.08, 101.14, 101.80 (ring C_6H_4) (*p*-cymene), 121.95, 123.44, 124.50, 124.82, 127.19, 127.71, 128.27, 130.13, 134.91, 137.23, 153.18 ($C_{1,3-16}$), 162.29 (C_2) (L^5 ligand).

Anal. Found: C, 59.31; H, 5.11; N, 4.98. Calc. for $C_{28}H_{27}N_2O_2ClRu$ (**6**): C, 59.18; H, 4.93; N, 5.11%. Visible spectral data: λ_{max} (nm) (ε, l mol^{-1} cm^{-1}) (MeCN): 315 (24 500), 418 (22 870), 525 (13 600). ^{1}H-NMR ($CDCl_3$, 200 MHz, δ ppm): 1.03, 1.11 (2d, 2×3H, [$^3J_{HH} = 7$ Hz], CH*Me*$_2$), 2.12 (s, 3H, Me), 2.58 (sp, *CH*Me_2), 3.63, 5.13, 5.18, 5.59 (4d, 4×1H, [$^3J_{HH} = 6$ Hz], four ring H) (*p*-cymene), 4.06 (s, 3H, OMe), 7.06–7.64 (m, $H_{4,5-8,13-16}$), 9.38 (d, [$^3J_{HH} = 9$ Hz], H_3) (L^6 ligand). ^{13}C-NMR ($CDCl_3$, 400 MHz, δ ppm): 18.90 (*CH*Me_2), 21.74, 22.63 (CH*Me*$_2$), 30.69 (Me), 79.80, 81.25, 82.10, 89.55, 100.34, 103.44 (ring C_6H_4) (*p*-cymene), 56.12 (OMe), 110.71, 121.11, 122.58, 123.39, 123.69, 123.87, 127.85, 127.94, 128.08, 128.44, 130.03, 135.95, 147.91, 152.05 ($C_{1,3-16}$), 177.90 (C_2) (L^6 ligand).

4.3. General procedure for the catalytic hydrogenation of acetophenone

In a typical reaction, a mixture containing 0.05 mmol of the catalyst (**1**–**6**), 0.125 mmol (7 mg) of KOH and 5 mmol (0.6 ml) of acetophenone was heated to reflux in 5 ml of isopropanol for 6 h. The reaction mixture was cooled to room temperature (r.t.). The catalyst was removed by the addition of 15 ml of petroleum ether (b.p., 40–60 °C) followed by filtration and subsequent neutralization with dilute HCl. The petroleum ether layer was extracted and dried over anhydrous Na_2SO_4. The solvent was distilled off to obtain a crude mixture containing acetophenone and its hydrogenated product, 1-phenylethanol. Percentage conversion was calculated by comparing the methyl proton signals of acetophenone (s, $\delta = 2.62$ ppm) and 1-phenylethanol (d, $\delta =$ 1.50 ppm, $^3J_{HH} = 6.8$ Hz) in the ^{1}H-NMR spectra of the crude mixture.

4.4. X-ray structure determination of *5*·MeCN

A crystal of approximate dimensions $0.2 \times 0.18 \times 0.56$ mm^3 was mounted on a glass fiber with epoxy cement. Unit cell dimensions were obtained using 24 reflections on an Enraf–Nonius CAD-4 diffractometer, equipped with graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The intensity data were collected ($0 \le h \le 9$; $0 \le k \le 20$; $-22 \le l \le 22$) within the $2° \le 2\theta \le 50°$ range using a ω-scan mode. Out of 4335 unique reflections, 3355 with $F_o \ge 4\sigma(F_o)$ were used for the structure solution and refinement. Data were corrected for Lorentz, polarization and absorption effects. Crystal data: $C_{28}H_{28}N_3OClRu$, $M_r = 558.6$, monoclinic, $P2_1/a$, $a = 7.759(4)$, $b = 17.135(3)$, $c = 18.594(3)$ Å, $\beta = 92.61(2)°$, $V = 2469.5(13)$ Å^3, $D_{calc} = 1.496$ g cm^{-3}, $Z = 4$, $F(000) = 1132$, μ(Mo–K_α) = 7.69 cm^{-1}, $T = 293(2)$ K.

The structure was solved by Patterson's heavy atom method using the program SHELXS-86 [20], which revealed the position of the ruthenium atom in the crystallographic asymmetric unit. The positions of the remaining atoms were determined by successive ΔF synthesis using the program SHELXL-97 [21]. All non-hydrogen atoms except the nitrogen of the solvent molecule were refined anisotropically. The hydrogen atom positions were generated and isotropic thermal parameters were assigned, riding to the atoms they were bonded with. After the assignment of the core structure, four peaks with an electron density of ~ 2.3 e Å^{-3} were observed in the ΔF map. The peaks were assigned for a disordered acetonitrile molecule. While two peaks having the site occupancy factor (SOF) of 1.0 are assigned to carbon atoms, the remaining two terminal peaks were assigned for the two nitrogen atoms with a SOF value of 0.5. The model is based on the fact that the peaks are arranged in an essentially linear fashion and the distance between the peaks fits well for a disordered MeCN lattice molecule. An empirical absorption correction [22] was made to the data after obtaining the complete structural model. The transmission coefficients were in the range of 0.67–0.87. The final refinement was converged to $R_1 = 0.0401$ and $wR_2 = \{\Sigma w[(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]\}^{1/2} = 0.1010$ with a weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 2.6228P]$, where $P = (F_o^2 + 2F_c^2)/3$ [R indices (all data): $R = 0.0596$, $wR = 0.1131$] using 306 parameters for 4335 reflections. Final ΔF map showed the largest peak and hole as 0.79 and -0.38 e Å^{-3}. The goodness-of-fit on F^2 was 1.035.

5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 160046. 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).

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