Synthesis and spectroscopic studies of new hydridoruthenium complexes: catalytic reactions of [RuHCl(bpzm)(cod)] (bpzm = bis(pyrazol-1-yl)methane, cod = cycloocta-1,5-diene)

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Abstract

The reaction of [RuHCl(bpzm)(cod)] (1) (bpzm = bis(pyrazol-1-yl)methane, cod = cycloocta-1,5-diene) with one equivalent of AgCF$_3$SO$_3$ afforded the triflate-containing [RuH(CF$_3$SO$_3$)(bpzm)(cod)] (2). The reaction of 2 with PMe$_2$Ph allowed the synthesis of *trans*-[RuH(PMe$_2$Ph)(bpzm)(cod)]CF$_3$SO$_3$ (3a), which isomerizes easily to *cis*-[RuH(PMe$_2$Ph)(bpzm)cod)]CF$_3$SO$_3$ (3b), while a similar reaction of 1, in the presence of AgCF$_3$SO$_3$, gave a series of phosphine-containing complexes such as [RuH(CF$_3$SO$_3$)(cod)(PMe$_2$Ph)$_2$] (4), the products of this process greatly depending on the reaction conditions. The complex *trans*-[RuH{P(OMe)$_3$}(bpzm)(cod)]CF$_3$SO$_3$ (5a), which also readily isomerizes to *cis*-[RuH{P(OMe)$_3$}(bpzm)(cod)]CF$_3$SO$_3$ (5b), was isolated from the reaction of 2 with P(OMe)$_3$, or alternatively from the reaction of 1 with P(OMe)$_3$ and AgCF$_3$SO$_3$. Finally, the reaction of 2 or 1 (in the presence of AgCF$_3$SO$_3$) with N-donors pyridine, 4-methylpyridine (4-picoline) or 3,5-dimethylpyridine (3,5-lutidine) yielded a mixture of products which we believe to contain both *cis*- and *trans*-[RuHL(bpzm)(cod)]CF$_3$SO$_3$ (L = pyridine, 4-picoline, or 3-5-lutidine). Spectroscopic data are provided for these compounds. Complex 1 catalyzes both the hydrogenation of the unsaturated substrates cyclohexene, cyclohexanone, acetone and propanal, with turn-over rates of up to 1506 h^{-1} for cyclohexanone in the presence of NaOH at 130°C, and the efficient transfer hydrogenation of cyclohexanone by propan-2-ol in the presence of NaOH at 80°C, with a turn-over rate of 880 h^{-1}.

*Keywords:* Ruthenium; BPZM; Cod; Hydride; Catalysis; Hydrogenation

1. Introduction

Although the chemistry of metal poly(pyrazol-1-yl)-borato complexes has been extensively studied in recent years [1], comparable development of the isosteric poly(pyrazol-1-yl)alkanes is unknown [2]. We have recently reported [3] a family of poly(pyrazol-1-yl)-alkaneruthenium complexes and one of them, [RuCl$_2$(bpzm)(cod)], was found to be a saturated species with a bpzm that could be replaced easily by phosphines and CO. This compound and Li[BEt$_3$H] gave [RuHCl-(bpzm)(cod)] [4] which was a good starting material in substitution processes with hydrogen and N-donors [5]. We subsequently became interested in the behaviour of this compound, and this paper focusses on the study of its reactivity towards some phosphorus donors as well as its catalytic activity in hydrogenation and transfer hydrogenation processes of several unsaturated substrates.

2. Results and discussion

The reaction of [RuHCl(bpzm)(cod)] (1) with AgCF$_3$SO$_3$ was investigated first. The standard procedure involved the addition of one equivalent of silver triflate to a suspension of 1 in acetone to give, after appropriate work-up, the complex [RuH(CF$_3$SO$_3$)-(bpzm)(cod)] (2):

$$[RuHCl(bpzm)(cod)] + AgCF_3SO_3$$
$$\rightarrow [RuH(CF_3SO_3)(bpzm)(cod)] + AgCl \qquad (1)$$
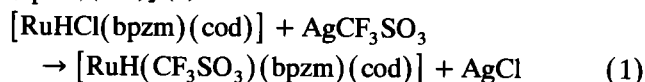
Complex 2 was isolated as a white crystalline air-stable solid, which was stable for several hours, although solutions in polar solvents such as acetone and tetrahydrofuran (THF) are air sensitive. In halogenated sol-

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Fig. 1. Proposed structure for 2.
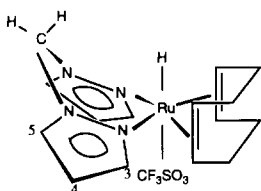
vents, for example chloroform, a quantitative transformation of 2 to the known [RuCl$_2$(bpzm)(cod)] was observed.

IR and especially NMR spectroscopy have proved useful tools for the characterization of 2 and the remaining complexes. The IR spectrum of 2 shows the characteristic bands for the bpzm, cod and triflate as well as a band at 2051 cm^{-1} which corresponds to ν(Ru–H) of a terminal hydride [6]. However, more extensive structural information was obtained from NMR spectroscopy. The ^{1}H NMR spectrum of 2 is in accordance with the presence of a symmetrical bpzm ligand with two equivalent pyrazolyl rings, and a cyclooca-1,5-diene with C_s symmetry. Two additional ligands, hydride and triflate, complete the coordination sphere for ruthenium(II) in an octahedral geometry (Fig. 1). Selective irradiations of certain ancillary ligand signals in a series of nuclear Overhauser enhancement (NOE) experiments were carried out in order to assign the resonances of different protons in 2 and in other complexes (see below). This method has previously been successfully employed by us in other ruthenium complexes [3,4]. The application of this method allowed the assignment of the pyrazole H^3 and H^5 resonances by irradiation of the CH$_2$ group [7] and it is in accordance with the usual criterion for pyrazoles where $^3J_{45} > {^3}J_{34}$ [8].
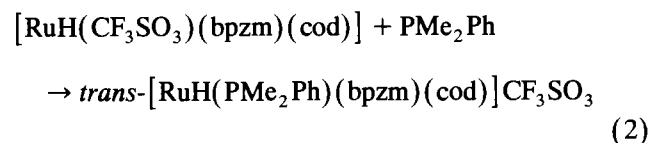
A complete assignment of the six resonances (see Section 3) for the olefinic (two) and aliphatic (four) protons of the cod was performed by two consecutive irradiations. The first, at the hydride proton whose resonance appears at −8.77 ppm, led to enhancement of the signals of the closer olefinic and *exo* aliphatic protons at 3.62 and 2.33 ppm respectively. A second selective irradiation of the latter gave an obvious enhancement of the signal at 3.62 ppm, and of that of the geminal aliphatic *endo* proton at 1.99 ppm. The ^{13}C NMR spectrum is in accordance with the proposed structure and shows (see Section 3) four signals for the bpzm and also four signals for the cod (two for the methylene and two for the olefinic carbon atoms).

Reactivity studies on 1 and 2 with N and P donors were then carried out.

2.1. Reactivity of 1 and 2 with PMe$_2$Ph

This reactivity was found to be highly dependent on molar ratio, temperature and reaction time. Thus the

reaction of 2 with PMe$_2$Ph in a 1:1 molar ratio for 15 min at room temperature in acetone gives *trans*-[RuH(PMe$_2$Ph)(bpzm)(cod)]CF$_3$SO$_3$ (3a) as the only product:

$$[\text{RuH}(\text{CF}_3\text{SO}_3)(\text{bpzm})(\text{cod})] + \text{PMe}_2\text{Ph}$$

$$\rightarrow \textit{trans-}[\text{RuH}(\text{PMe}_2\text{Ph})(\text{bpzm})(\text{cod})]\text{CF}_3\text{SO}_3$$

(2)

Complex 3a was isolated as a white crystalline air-sensitive solid, which is soluble in polar solvents and insoluble in non-polar solvents. When solutions of 3a were kept, both at room temperature for a long time or at 45°C for 15 h, *cis*-[RuH(PMe$_2$Ph)(bpzm)(cod)]-CF$_3$SO$_3$ (3b) was formed as the main product, although it was always contaminated with non-hydride-containing byproducts and all attempts to isolate a pure sample of 3b were unsuccessful. It was also impossible to collect variable-temperature NMR data to establish the kinetics of the isomerization process. Surprisingly, neither 3a nor 3b was isolated from the reaction of 1 with AgCF$_3$SO$_3$ and PMe$_2$Ph in acetone in an 1:1:1 molar ratio at room temperature, but rather an unresolved mixture of phosphine containing complexes was observed (monitored by ^{1}H NMR). This suggests that several substitutions of both bpzm and cod by PMe$_2$Ph had taken place. This behaviour was also observed when the reactions were carried out in 1:1:2 and 1:1:3 molar ratios. Attempts to isolate pure samples of the complexes from the reaction mixtures were unsuccessful. However, when the reaction in 1:1:1 molar ratio was carried out at −80°C and the solution was allowed to warm to room temperature, [RuH(CF$_3$SO$_3$)-(cod)(PMe$_2$Ph)$_2$] (4) was isolated after appropriate work-up as a light-green solid, although always contaminated with byproducts. As previously pointed out, the reaction of 1 with AgCF$_3$SO$_3$ in the presence of PMe$_2$Ph is not very selective and, under various conditions, mixtures of products resulting from chloride abstraction were obtained, leading to the formation of AgCl and the substitution of bpzm and cod by PMe$_2$Ph.

Some of these phosphine complexes have been fully characterized spectroscopically. Complex 3a shows in its IR spectrum a terminal hydride band at 1981 cm^{-1}. The ^{1}H NMR spectrum displays three sets of low field signals for the aromatic protons of two equivalent pyrazol-1-yl groups and two signals of an AB system for the diastereotopic CH$_2$ group of the bpzm. Four signals for the aliphatic protons and two signals for the olefinic protons of the cod are also present, consistent with C_s symmetry. The assignment of proton signals was again facilitated by NOE experiments.

Both the hydride and the methyl phosphine resonances are doublets because of coupling with ^{31}P. The
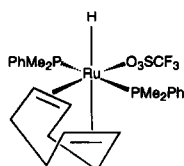
Fig. 2. Proposed structure for 4.

value of $J_{PH} = 96.9$ Hz for the hydride resonance at -0.68 ppm indicates a trans disposition arrangement of the H and PMe_2Ph [9]. This value is higher than the value of 23.7 Hz found in the cis-isomer 3b where the hydride signal appears at -7.43 ppm (see Section 3). The ^{31}P NMR spectrum shows a resonance at -1.63 ppm ($J_{PH} = 96.9$ Hz). The data are in accordance with an octahedral geometry for 3a similar to that previously found for 2 (see Fig. 1) where both H and PMe_2Ph are apical.

The ^{13}C NMR spectrum of 3a shows resonances for the carbon atoms of the bpzm and the cod (see Section 3). The phosphine resonances are a set of four signals for the phenyl groups and one signal for the methyl groups. In order to assign some of the resonances, a two-dimensional heteronuclear chemical shift correlation (^{1}H–^{13}C COSY) experiment was carried out and some J_{PC} values in the $^{13}C\{^{1}H\}$ NMR spectrum were determined. The J_{PC} values for the olefinic and carbon atoms close to the phosphine are larger than those of the more distant atoms. The IR spectrum of 4 shows ν(Ru–H) at 1992 cm^{-1} and the ^{1}H NMR spectrum displays six resonances for the cod, in accordance with C_s symmetry, while the hydride signal appears as a triplet at -11.31 ppm ($J_{PH} = 24.0$ Hz). This relatively small coupling constant value suggests a cis-disposition of the hydride and two equivalent phosphines. The phosphine resonances appear as two sets of signals for the phenyl groups and two pseudotriplets for the methyl groups which is the standard pattern observed for two mutually trans-phosphines [10]. The data are in accordance with the octahedral structure depicted in Fig. 2. The lack of solubility of 4 has prevented the recording of the ^{13}C NMR spectrum.

2.2. Reactivity of 1 and 2 towards P(OMe)₃

The reaction of 2 with one equivalent of $P(OMe)_3$ was carried out in a similar way to that previously

described for PMe_2Ph (see above) and gave trans-$[RuH\{P(OMe)_3\}(bpzm)(cod)]CF_3SO_3$ (5a). This was prepared alternatively from the reaction of 1 with $AgCF_3SO_3$ and $P(OMe)_3$ in a 1:1:1 molar ratio at $-80°C$ in acetone. In both procedures, 5a was isolated as an air-stable white crystalline solid, although solutions in polar solvents such as acetone or THF, in which it is moderately soluble, are very air sensitive. Complex 5a reacts with halogenated solvents to give $[RuCl_2$-$(bpzm)(cod)]$. The IR spectrum of 5a shows ν(Ru–H) at 1976 cm^{-1}, and ^{1}H and ^{13}C NMR data support the structure depicted in Fig. 1 for 2, with the hydride and phosphite trans. The assignment of proton and carbon signals was also carried out by NOE and ^{1}H–^{13}C COSY experiments, which also allowed the assignment of some of J_{PC} values in the $^{13}C\{^{1}H\}$ NMR spectrum. Complex 5a isomerizes to cis-$[RuH\{P(OMe)_3\}(bpzm)(cod)]CF_3$-$SO_3$ (5b) after heating a solution of the former for 40 h (monitored by ^{1}H NMR spectroscopy), although other byproducts were detected which were not afterwards identified. It was again impossible to determine the kinetics of the isomerization process. The hydride resonance for 5b appears as a doublet at -8.0 ppm, $J_{PH} = 24$ Hz, in contrast with the values of -0.31 ppm, $J_{PH} = 48.5$ Hz, found for 5a.

The behaviour of 1 with $AgCF_3SO_3$ and $P(OMe)_3$, in a molar ratio 1:1:1, is clearly different from that previously described for PMe_2Ph, where substitution of the bpzm by the phosphine was observed.

2.3. Reactivity of 1 and 2 towards pyridine and related donors

The reaction of 1 with $AgCF_3SO_3$ and pyridine, 4-methylpyridine (4-picoline) or 3,5-dimethylpyridine (3,5-lutidine) or 2 with the N-donors in molar ratios 1:1:1 and 1:1 respectively, at room temperature or at $-80°C$, affords a mixture of two products which are tentatively identified as isomers $[RuHL(bpzm)(cod)]$-CF_3SO_3 (L = py, 4-picoline or 3,5-lutidine) judged by spectroscopic and analytical data. The mixture of products was isolated as yellow solids, which were soluble in common polar solvents. Attempts to resolve the mixtures were unsuccessful because of similar solubilities. We cannot explain the isolation of the mixture of the isomers under these conditions and we have not

Table 1
^{1}H NMR data for the cis and trans isomers[RuH(4-picoline)(bpzm)(cod)]CF₃SO₃

Isomer	^{1}H NMR, δ (ppm)						
	Bis(pyrazolyl)methane				Picoline		Hydride
	CH₂	H³	H⁴	H⁵	Aromatic	Methyl	
trans	7.02 (s)	8.85 (d, $^{3}J_{34}$ = 2.0 Hz)	6.84 (pt)	8.39 (d, $^{3}J_{45}$ = 2.5 Hz)	8.21 (d), 7.29 (d, ^{3}J = 5.4 Hz)	2.35 (s)	−5.61 (s)
cis	6.03 (J_{AX} = 14.5 Hz)	8.21 (d, $^{3}J_{34}$ = 1.7 Hz), 8.13 (d, $^{3}J_{34}$ = 2.0 Hz)	6.47 (pt)	8.27 (d, $^{3}J_{45}$ = 2.7 Hz), 8.13 (d, $^{3}J_{45}$ = 2.6 Hz)	7.98 (d, ^{3}J = 6.1 Hz), 7.14 (d, ^{3}J = 5.9 Hz)	2.28 (s)	−4.50 (s)

observed an interconversion of isomers when the temperature was raised. The ^{1}H NMR spectra show two hydride resonances. However, the assignment of the remaining signals is very difficult. In order to obtain additional structural data an exhaustive ^{1}H NMR study on the mixture derived from 4-picoline was carried out. Double-resonance experiments, J_{HH} values and relative intensities of the signals resulted in the assignments depicted in Table 1.

We conclude that the reactions of 1 and 2 with N-donors are not selective and we believe that a mixture of products, corresponding to cis and trans isomers form.

2.4. Catalytic hydrogenation processes

Complex 1 was used as a catalyst in catalytic hydrogenations of the following substrates: cyclohexene, cyclohexanone, acetone and propanal, because of the well-known activity of several hydride ruthenium complexes in this kind of process [11]. In a typical procedure, solutions of the mixture of reagents, using as solvent either THF for the hydrogenation of cyclohexene or the corresponding carbonyl compound in the case of the remaining substrates, were placed in a steel reactor and H_2 was introduced at the pressure. The reaction conditions for the different experiments required, as well as the observed catalytic activity, are shown in Table 2.

The ability of ruthenium complex 1 to hydrogenate the substrates is greatest for cyclohexene and is especially low for cyclohexanone. This may be due to the higher coordination capacity of the olefin. The low activity towards cyclohexanone occurs in spite of its greater basicity than acetone. In addition, electronic and steric factors may be responsible for the greater catalytic activity for the hydrogenation of propanal than of acetone. The rates of hydrogenation clearly show a temperature dependence, and the highest turn-over rates were obtained at 130°C. With the aim of generating coordination sites, silver or thallium salts were added to the mixtures employing cyclohexene and acetone (see

Table 3
Catalytic activity in basic medium [a]

	Catalytic activity (turn-over per hour)		
Cyclohexene	965		
Cyclohexanone	174	1506 [b]	880 [c]
Acetone	1091		

[a] Reaction conditions: H_2 pressure, 30 bar; [substrate]/[precursor] = 2000:1; reaction time, 2 h without previous activation of the precursor; 80°C; NaOH–MeOH, 0.1 M.
[b] 130°C.
[c] Transfer hydrogenation from 2-propanol; 80°C; NaOH–/^{i}PrOH (0.05 M); reaction time, 3 h.

Table 2) but, surprisingly, in both cases a decrease in the catalytic activity was found.

Owing to the favourable effect on the rates of hydrogenation, especially for ketones, strong bases, such as NaOH or KOH, are frequently added as cocatalysts [12], although their function is not well understood [13]. We decided to study the effect of base in some of our hydrogenation processes. In a typical procedure a solution of NaOH in MeOH was used, and the reaction conditions and the observed values for the turn-over rates are shown in Table 3. The hydrogenation of propanal under these experimental conditions did not take place and the formation of condensation products was observed. A marked increase in activity in the presence of base was found and the turn-over rate for the hydrogenation of cyclohexanone at 130°C is, to the best of our knowledge, among the largest described.

The results prompted us to study the transfer hydrogenation of cyclohexanone, which showed a low hydrogenation activity (see Table 2). Ruthenium complexes are useful in the dehydrogenation of alcohols and in transferring hydrides to ketones in transfer hydrogenation catalytic processes [14]. When cyclohexanone was treated with the catalytic system [RuHCl(bpzm)(cod)]–NaOH] in propan-2-ol at 80°C, an efficient reduction of the ketone took place, and a dramatic improvement in the catalytic activity compared with previously described hydrogenations at the same temperature (174 turn-overs per hour) was found (Table 3). An apprecia-

Table 2
Catalytic activity [a]

	Catalytic activity (turn-over per hour)					
Cyclohexene	9 [b]	400 [c]	540 [d]	0.4 [b,e]	10 [c,e]	115 [d,e]
Cyclohexanone	0 [b]	0 [c]	14 [d]			
Acetone	4 [b]	80 [c]	200 [d]		16 [c,f]	16.4 [d,f]
Acetaldehyde	44 [b]	82 [c]	260 [d]			

[a] Reaction conditions: H_2 pressure, 30 bar; [substrate]/[precursor] = 2000:1; reaction time, 2 h without previous activation of the precursor.
[b] Room temperature.
[c] 80°C.
[d] 130°C.
[e] With addition of TlBF4.
[f] With addition of AgBF4.

ble enhancement in the rates of hydrogen transfer to many ketones when a small quantity of base was added to the system has previously observed [14c,d,15].

3. Experimental details

All reactions were performed using standard Schlenk-tube techniques in dry dinitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Ruthenium materials [{RuCl$_2$(cod)}$_n$] [16] and [RuHCl(cod)(bpzm)] [4] were prepared as previously reported. Microanalyses were performed with a Perkin–Elmer 2400 CHN analyser. IR spectra were obtained in the region 4000–200 cm^{-1} using a Perkin–Elmer 883 spectrophotometer. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR and NOE difference spectra were recorded at 19°C on a Unity Varian FT300 spectrometer and referenced to the residual deuteriated solvents. NOE difference spectra were recorded with the following acquisition parameters: spectral width, 5000 Hz; acquisition time, 3.27 s; pulse width, 90°; relaxation delay, 4 s; irradiation power, 5–10 L; number of scans, 120. The two-dimensional NMR spectra were acquired using standard Varian FT sofware, and processed using an IPC-Sun computer. The gas chromatograph (GC) analyses for the reaction products in the catalytic experiments were carried out on a Hewlett–Packard 5890 chromatograph with a flame ionization detector connected to a Hewlett–Packard 3395 integrator, and using a HP-FFAP (12 m × 0.2 mm × 0.33 pm) glass capillary column at 70°C. The hydrogenation reactions were carried out in an autoclave under H$_2$ at 30 bar and in a thermostatic bath with magnetic stirring.

3.1. Preparations

3.1.1. [RuH(CF$_3$SO$_3$)(bpzm)(cod)] EtOH (2).

AgCF$_3$SO$_3$ (65 mg, 0.25 mmol) was added to an acetone (20 ml) suspension of [RuHCl(bpzm)(cod)] (100 mg, 0.25 mmol) at −80°C in a darkened Schlenk tube. The mixture was stirred and allowed to warm to room temperature. The yellowish solution was filtered and evaporated to dryness. Complex **2** was obtained as a white microcrystalline solid from ethanol diethyl ether (yield, 98.2 mg (71%)).

Anal. Found: C, 39.61; H, 5.00; N, 10.44. C$_{18}$H$_{27}$F$_3$N$_4$O$_4$RuS calc.: C, 39.02; H, 4,88; N, 10.12%. IR (KBr cm^{-1}): ν(Ru–H) 2051 cm^{-1}. ^{1}H NMR ([^{2}H$_6$]-acetone, tetramethylsilane (TMS)) δ 8.27 (d, 2H, $^3J_{45}$ = 2.5 Hz, H^5); 7.58 (d, 2H, $^3J_{34}$ = 1.7 Hz, H^3); 7.19 (s, 2H, CH$_2$bpzm); 6.50 (pt, 2H, H^4); 3.70 (bs, 2H, H^{olef}cod); 3.62 (bs, 2H, H^{olef}cod); 2.72 (m, 2H, H^{exo}cod); 2.33 (m, 2H, H^{exo}cod); 1.99 (d, 2H, J_{gem} = 7.5 Hz, H^{endo}cod); 1.93 (d, 2H, J_{gem} = 8.1 Hz, H^{endo}cod); −8.77 (s, 1H, hydride) ppm. ^{13}C NMR ([^{2}H$_4$]-

methanol, TMS): δ 143.78 ($^1J_{CH}$ = 187.5 Hz, C^3); 134.66 ($^1J_{CH}$ = 195.9 Hz, C^5); 108.6 ($^1J_{CH}$ = 181.9 Hz, C^4); 76.4 ($^1J_{CH}$ = 159.7 Hz, C^{sp2}cod); 73.7 ($^1J_{CH}$ = 153.7 Hz, C^{sp2}cod); 64.92 ($^1J_{CH}$ = 151.7 Hz, CH$_2$bpzm); 34.18 ($^1J_{CH}$ = 125.2 Hz, C^{sp3}cod); 29.05 ($^1J_{CH}$ = 126.0 Hz, C^{sp3}cod) ppm.

3.1.2. trans-[RuH(PMe$_2$Ph)(bpzm)(cod)]CF$_3$SO$_3$ (3a).

PMe$_2$Ph (35.22 μl, 0.25 mmol) was added to an acetone solution (20 ml) of [RuH(CF$_3$SO$_3$)(bpzm)(cod)] (126 mg, 0.25 mmol) and the solution was stirred for 15 min. The initial yellow solution turned pale and was evaporated to 2 ml. Complex **3a** crystallized as a white solid when diethyl ether was slowly added (yield, 119.4 mg (74%)).

Anal. Found: C, 44.36; H, 4.84; N, 8.93. C$_{24}$H$_{32}$F$_3$N$_4$O$_3$PRuS calc.: C, 44.65; H, 4.99; N, 8.68%. IR (KBr): ν(Ru–H) 1981 cm^{-1} ^{1}H NMR ([^{2}H$_6$]-acetone, TMS): δ 8.19 (d, 2H, $^3J_{45}$ = 2.7 Hz, H^5); 7.27 (d, 2H, $^3J_{34}$ = 1.2 Hz, H^3); 7.27 (m, 2H, H^{2}Ph); 6.98 (m, 3H, H^{3,4} Ph); 6.88 (AX system, 2H, J_{AX} = 13.9 Hz, CH$_2$bpzm); 6.49 (pt, 2H, H^4); 3.17 (bs, 2H, H^{olef}cod); 2.92 (bs, 2H, H^{olef}cod); 2.56 (m, 2H, H^{exo}cod); 2.41 (m, 2H, H^{exo}cod); 1.86 (m, 2H, H^{endo}cod); 1.80 (m, 2H, H^{endo}cod); 1.51 (d, 6H, $^2J_{PH}$ = 6.9 Hz, Me); −0.68 (d, 1H, $^2J_{PH}$ = 96.9 Hz, hydride) ppm. ^{31}P NMR ([^{2}H$_6$]-acetone, H$_3$PO$_4$): δ −1.63 (d, J_{PH} = 96.9 Hz) ppm. ^{13}C NMR ([^{2}H$_6$]-acetone, TMS): δ 144.09 ($^1J_{CH}$ = 189.0 Hz, $^3J_{PC}$ = 2.55 Hz, C^3); 136.90 (C^{1}Ph); 135.60 ($^1J_{CH}$ = 194.3 Hz, C^5); 130.10 (C^{2}Ph); 129.5 (C^{4}Ph); 128.50 (C^{3}Ph); 108.66 ($^1J_{CH}$ = 182.2 Hz, C^4); 72.90 (^1J = 161.3 Hz, $^3J_{PC}$ = 2.02 Hz, C^{sp2}cod); 64.90 ($^1J_{CH}$ = 160.7 Hz, $^3J_{PC}$ = 3.75 Hz, C^{sp2}cod); 64.29 ($^1J_{CHA}$ = 150.6 Hz, $^1J_{CHX}$ = 151.27 Hz, CH$_2$bpzm); 32.25 ($^1J_{CH}$ = 125.4 Hz, C^{sp3}cod); 29.37 ($^1J_{CH}$ = 125.4 Hz, $^4J_{PC}$ = 3.0 Hz, C^{sp3}cod); 11.84 ($^1J_{PC}$ = 19.05 Hz, Me) ppm.

3.1.3. [RuH(CF$_3$SO$_3$)(cod)(PMe$_2$Ph)$_2$] (4).

PMe$_2$Ph (71.57 μl, 0.51 mmol) was added to an acetone (20 ml) suspension of [RuHCl(bpzm)(cod)] (100 mg, 0.25 mmol). The mixture was stirred for 10 min, and a light-green solution was obtained. AgCF$_3$SO$_3$ (97.6 mg, 0.38 mmol) was added to this solution at −80°C in a light-protected Schlenk tube and the mixture was stirred and allowed to warm to room temperature. The solution was filtered and evaporated to dryness to give a white solid which corresponds to **4** (yield, 63.5 mg (40%)). No satisfactory analytical data were observed.

IR (KBr): ν(Ru–H) 1992 cm^{-1}. ^{1}H NMR ([^{2}H$_6$]-acetone, TMS): δ 7.69 (bs, 4H, H^{2}Ph); 7.32 (bs, 6H, H^{3,4} Ph); 3.73 (bs, 2H, H^{olef}cod); 3.27 (bs, 2H, H^{olef}cod); 2.57 (m, 2H, H^{exo}cod); 2.17 (m, 2H, H^{exo}cod); 2.03 (bs, 2H, H^{endo}cod); 1.85 (bs, 2H, H^{endo}cod); 1.51 (pt, 6H, Me); 1.36 (pt, 6H, Me); −11.53 (t, ^{1}H, $^2J_{PH}$ = 24.0 Hz, hydride) ppm.

3.1.4. trans-[RuH{P(OMe)$_3$}(bpzm)(cod)]CF$_3$SO$_3$ (5a).

P(OMe)$_3$ (22.40 μl, 0.19 mmol) was added to an acetone solution (20 ml) of [RuH(CF$_3$SO$_3$)(bpzm)(cod)] (100 mg, 0.19 mmol). After stirring at room temperature for 15 min, the solution was evaporated down to 2 ml and, following cooling at $-180°C$, 7a as a white solid was isolated (yield, 62.5 mg (52%)).

Anal. Found: C, 36.38; H, 4.85; N, 8.58. C$_{19}$H$_{31}$F$_3$N$_4$O$_6$PRuS calc.: C, 36.11; H, 4.75; N, 8.87%. IR (KBr): ν(Ru–H) 1976 cm^{-1}. ^{1}H NMR ([^{2}H$_6$]-acetone, TMS): δ 8.32 (d, 2H, $^3J_{45}$ = 2.1 Hz, H^5); 7.43 (d, 2H, $^3J_{34}$ = 1.5 Hz, H^3); 7.19 (AB system, 2H, J_{AB} = 12.0 Hz, CH$_2$); 6.52 (pt, 2H, H^4); 3.36 (d, 11H, $^2J_{PH}$ = 9.9 Hz, H^{olef}cod, Me); 3.18 (bs, 2H, H^{olef}cod); 2.57 (bs, 4H, H^{exo}cod); 1.84 (m, 2H, H^{endo}cod); 1.78 (m, 2H, H^{endo}cod); -0.31 (d, 1H, $^2J_{PH}$ = 148.5 Hz, hydride) ppm. ^{31}P NMR ([^{2}H$_6$]-acetone, H$_3$PO$_4$): 5.00 (d, J_{PH} = 148.5 Hz) ppm. ^{13}C NMR ([^{2}H$_6$]-acetone, TMS): δ 145.33 (^1J = 190.8 Hz, $^3J_{PC}$ = 2.5 Hz, C^3); 135.29 ($^1J_{CH}$ = 200.0 Hz, C^5); 108.28 ($^1J_{CH}$ = 181.8 Hz, C^4); 71.46 ($^1J_{CH}$ = 150.73 Hz, C^{sp2}cod); 66.00 ($^1J_{CH}$ = 123.9 Hz, $^2J_{PC}$ = 7.0 Hz, C^{sp2}cod); 64.50 ($^1J_{CH}$ = 157.7 Hz, $^3J_{PC}$ = 2.03 Hz, CH$_2$bpzm); 52.38 ($^1J_{CH}$ = 146.2 Hz, $^2J_{PC}$ = 8.03 Hz, Me); 34.58 ($^1J_{CH}$ = 121.9 Hz, C^{sp3}cod); 30.33 ($^1J_{CH}$ = 123.9 Hz, $^4J_{PC}$ = 3.0 Hz, C^{sp3}cod) ppm.

3.2. Catalytic hydrogenation processes

In a typical experiment, a solution of [RuHCl(bpzm)(cod)] (6 mg, 0.015 mmol) in 10 ml of THF to which 3 ml(30 mmol) of cyclohexene had been added was introduced under dinitrogen into the reactor and the reaction vessel was pressurized at 30 bar. After heating at the appropriate temperature and stirring the reaction for 2 h, the autoclave was cooled, and the products analysed by GC.

The hydrogenation procedures for the carbonyl-containing products were carried out in a similar way.

In the experiments with the cocatalyst NaOH, the precursor [RuHCl(bpzm)(cod)] was dissolved in methanol solutions containing base. For example 1 (6 mg, 0.015 mmol) was dissolved in 10 ml of NaOH–MeOH (0.1 M) and 3 ml of cyclohexene were subsequently added. The remaining operations were similar to those described above.

3.3. Catalytic transfer hydrogenation of cyclohexanone

A solution of [RuHCl(bpzm)(cod)] (6 mg, 0.015 mmol) in 10 ml of propan-2-ol and 5 ml of NaOH Pr^{i}OH (0.05 M) was heated at 80°C. Cyclohexanone (3

ml) was added, the mixture was heated under reflux at 80°C for 3 h, and then the reaction products were analysed by GC.

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