Octahedral ruthenium(II) complexes cis,cis-[RuX$_2$(CNR)(CO)(P^P)] and cis,cis,cis-[RuX$_2$(CO)$_2$(P^P)] (X = Cl, Br; P^P = 1,1′-bis(diphenylphosphino)ferrocene, 1,1′-bis(diisopropylphosphino)ferrocene): Synthesis and catalytic applications in transfer hydrogenation of acetophenone and cycloisomerization of (Z)-3-methylpent-2-en-4-yn-1-ol

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In memoriam of our friend and colleague Prof. Lorenzo Pueyo.

Abstract

Carbonyl–isocyanide-ruthenium(II) complexes cis,cis-[RuX$_2$(CNR)(CO)(P^P)] (P^P = dppf, dippf; X = Cl, Br; R = Bn, Cy, ^{t}Bu, 2,6-C$_6$H$_3$Me$_2$, (S)-(−)-C(H)MePh) (**3–6a–e**) have been prepared in high yields by treatment of the dimeric derivatives [{RuX-(μ-X)(CO)(P^P)}$_2$] (P^P = dppf, dippf; X = Cl, Br) (**1–2a–b**) with isocyanides. Dimers **1–2a–b** also react with carbon monoxide to afford the dicarbonyl species cis,cis,cis-[RuX$_2$(CO)$_2$(P^P)] (**7–8a–b**). The catalytic activity of these compounds in transfer hydrogenation of acetophenone by propan-2-ol as well as in cycloisomerization of (Z)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran has been studied.
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Keywords: Carbonyl complexes; Isocyanide complexes; Ruthenium; Transfer hydrogenation; Cycloisomerization

1. Introduction

Over the last decades the interest in ruthenium-catalyzed reactions directed to organic synthesis has spectacularly increased and a large number of highly efficient synthetic approaches are nowadays well documented [1–3]. In particular, the transfer hydrogenation (TH) of ketones by H$_2$-donor solvents, such as propan-2-ol, using ruthenium(II) catalysts is currently one of the most appealing routes to alcohols and constitutes a good alternative to the widely used catalytic hydrogenation [4]. Despite the fact that the later route has a much greater potential for industrial applications [5], there has been a continuous interest in catalytic TH reactions, since alcohols can be obtained in high yields, under relatively mild conditions, avoiding the use of H$_2$ gas [4]. In this context, we have recently reported that octahedral bis(isocyanide)–ruthenium(II) complexes $trans,cis,cis$-[RuX$_2$(CNR)$_2$(dppf)] (X = Cl, Br; dppf = 1,1′-bis(diphenylphosphino)ferrocene; R = alkyl or aryl group) (**I** in Fig. 1) are valuable precursors of active catalytic species for TH of ketones (TOF values up to 1500 h^{-1}) [6].

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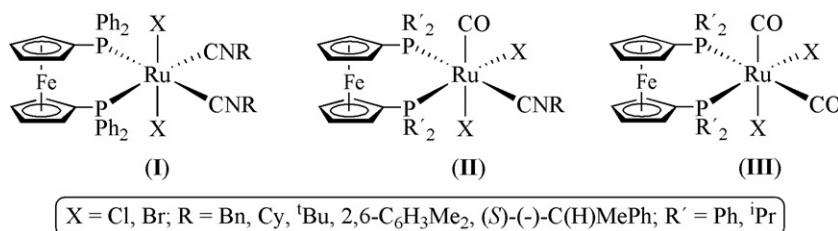*E-mail addresses:* vcm@uniovi.es (V. Cadierno), jgh@uniovi.es (J. Gimeno).

Fig. 1. Structure of the octahedral ruthenium(II) complexes **I**, **II** and **III**.

The efficiency shown by the bis(isocyanide)–Ru(II) complexes **I** is remarkable since precatalysts featuring a Ru–NH$_2$R linkage commonly offer the highest level of activity in TH of ketones [4,7]. This "NH effect" has been rationalized in terms of an outer-sphere mechanism in which the concerted transfer of H$_2$ from an hydride intermediate [H–Ru–NH$_2$R] to the ketone, via a six-membered metallacyclic transition state, takes place [8]. As a consequence, much effort has been devoted to the design of new ligands containing NH donor units during the last years [4]. Simultaneously, in order to overcome such a structural prerequisite, the development of alternative classes of efficient Ru-based TH catalysts has also gained a considerable interest, becoming an important and highly rewarding target [9].

With these precedents in mind and encouraged by the effectiveness shown by complexes *trans,cis,cis*-[RuX$_2$-(CNR)$_2$(dppf)] (**I**), we believed it of interest to explore the ability of related ferrocenyl-diphosphine-based octahedral ruthenium(II) complex to promote the catalytic transfer hydrogenation of ketones [10]. Thus, in this paper we report the high yield preparation of the novel carbonyl–isocyanide and dicarbonyl complexes *cis,cis*-[RuX$_2$(CNR)-(CO)(P^P)] (**II** in Fig. 1) and *cis,cis,cis*-[RuX$_2$(CO)$_2$(P^P)] (**III** in Fig. 1), respectively, and their behaviour in TH catalysis. In addition, the application of these compounds in the catalytic synthesis of 2,3-dimethylfuran, via cycloisomerization of (*Z*)-3-methylpent-2-en-4-yn-1-ol, will be also presented.

2. Results and discussion

2.1. Synthesis and characterization of complexes cis,cis-[RuX$_2$(CNR)(CO)(P^P)] and cis,cis,cis-[RuX$_2$-(CO)$_2$(P^P)]
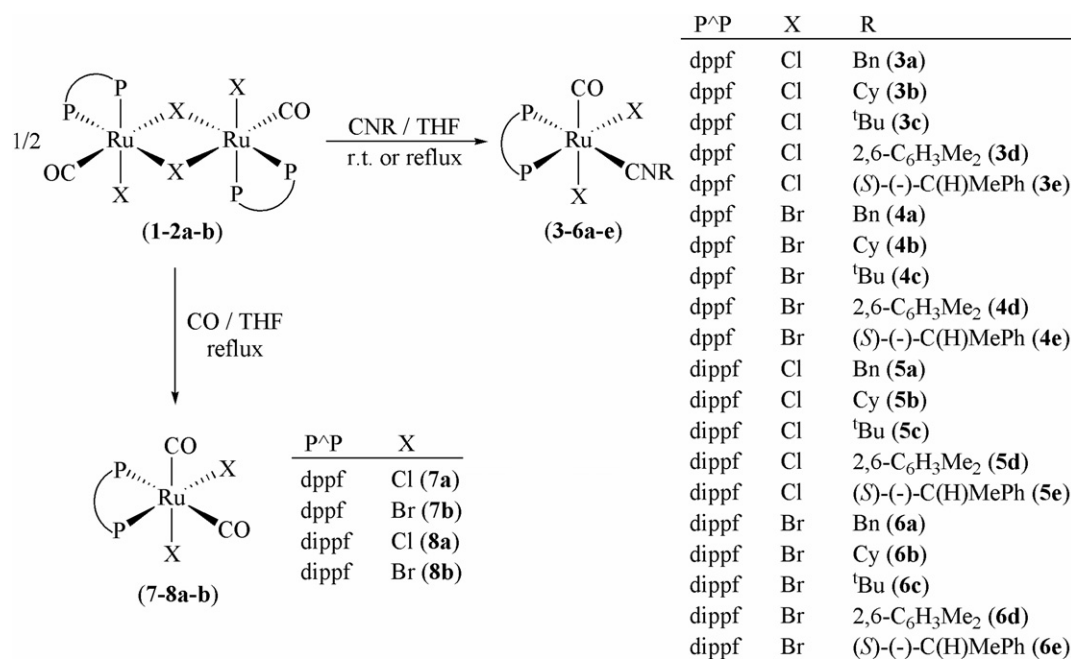
We have recently shown that, upon treatment with two-electron donor ligands L, the carbonyl-halide dimers [{RuX(μ-X)(CO)(P^P)}$_2$] (P^P = dppf, X = Cl (**1a**), Br (**1b**); P^P = dippf, X = Cl (**2a**), Br (**2b**)) are useful precursors for the preparation of octahedral mononuclear ruthenium(II) derivatives *cis,cis*-[RuX$_2$(L)(CO)(P^P)], via the expected cleavage of the halide bridges [11]. Following this synthetic methodology, the carbonyl–isocyanide complexes *cis,cis*-[RuX$_2$(CNR)(CO)(P^P)] (**3–6a–e**) have been synthesized in excellent yields (75–99%) by reacting a tetrahydro-

furan solution of dimers **1–2a–b** with a twofold excess of the appropriate isocyanide (Scheme 1).

Compounds **3–6a–e**, isolated as air-stable yellow-orange solids, have been characterized by means of standard spectroscopic techniques (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) as well as elemental analysis, being all data fully consistent with the proposed formulations and stereochemistry (details are given in Section 4 and Table 1). Relevant spectroscopic features are the following: (i) (IR) The presence of two absorption bands in the ranges 1950–1979 cm^{-1} and 2156–2221 cm^{-1} (see Table 1), characteristic for metal-coordinated carbonyl and isocyanide ligands, respectively. (ii) (^{31}P{^{1}H} NMR) The appearance of two doublet resonances (δ_P 12.7–53.3 ppm; $^2J_{PP}$ = 17.4–25.7 Hz) as a typical sign of unequivalent phosphorus nuclei of the ferrocenyl-diphosphine ligand (see Table 1). (iii) (^{13}C{^{1}H} NMR) A characteristic downfield signal (δ_C 197.4–200.2 ppm) for the carbonyl group which appears as a doublet of doublets with $^2J_{CP}$ values of 12.1–14.0 Hz, indicating that the carbonyl group is located in a *cis* disposition with respect to both phosphorus nuclei of the diphosphine. And, (iv) in the case of complexes **5–6a–e**, containing the ferrocenyl-diphosphine dippf, the appearance in the ^{13}C{^{1}H} NMR spectra of a doublet of doublets resonance at δ_C 138.2–156.0 ppm assigned to the isocyanide ligand (for the dppf-containing compounds **3–4a–e** this signal falls within the aromatic carbon region). The $^2J_{PP}$ values observed, in the ranges 119.3–122.6 and 21.6–24.1 Hz, are in complete accord with the proposed stereochemistry, i.e. the isocyanide group is located in a *trans* and *cis* disposition with respect to the phosphorous nuclei of the dippf ligand.

It is also worth to note that the chiral complexes **3–6e**, containing the optically active (*S*)-(−)-α-methylbenzyl isocyanide, are formed as a non-separable mixture of two diastereoisomers (ca. 1:1 ratio) arising as a consequence of the stereogenic character of the ruthenium atom in this family of compounds (Fig. 2).

The dicarbonyl complexes *cis,cis,cis*-[RuX$_2$(CO)$_2$(P^P)] (P^P = dppf, X = Cl (**7a**), Br (**7b**); P^P = dippf, X = Cl (**8a**), Br (**8b**)) have been prepared (79–87% isolated yield) by bubbling carbon monoxide at atmospheric pressure through a refluxing THF solution of the corresponding dimeric species [{RuX(μ-X)(CO)(P^P)}$_2$] (**1–2a–b**) (Scheme 1). They have been characterized by IR and NMR spectroscopy, which support the mutually *cis* arrangement of both the carbonyl and halide ligands, and elemental analyses

P^P	X	R
dppf	Cl	Bn (**3a**)
dppf	Cl	Cy (**3b**)
dppf	Cl	^{t}Bu (**3c**)
dppf	Cl	2,6-C$_6$H$_3$Me$_2$ (**3d**)
dppf	Cl	(S)-(-)-C(H)MePh (**3e**)
dppf	Br	Bn (**4a**)
dppf	Br	Cy (**4b**)
dppf	Br	^{t}Bu (**4c**)
dppf	Br	2,6-C$_6$H$_3$Me$_2$ (**4d**)
dppf	Br	(S)-(-)-C(H)MePh (**4e**)
dippf	Cl	Bn (**5a**)
dippf	Cl	Cy (**5b**)
dippf	Cl	^{t}Bu (**5c**)
dippf	Cl	2,6-C$_6$H$_3$Me$_2$ (**5d**)
dippf	Cl	(S)-(-)-C(H)MePh (**5e**)
dippf	Br	Bn (**6a**)
dippf	Br	Cy (**6b**)
dippf	Br	^{t}Bu (**6c**)
dippf	Br	2,6-C$_6$H$_3$Me$_2$ (**6d**)
dippf	Br	(S)-(-)-C(H)MePh (**6e**)

P^P	X
dppf	Cl (**7a**)
dppf	Br (**7b**)
dippf	Cl (**8a**)
dippf	Br (**8b**)

Scheme 1. Synthesis of the mononuclear ruthenium(II) complexes **3–6a–e** and **7–8a–b** (dippf = 1,1′-bis(diisopropylphosphino)ferrocene).

Table 1
IR and ^{31}P{^{1}H} NMR data for the carbonyl–isocyanide complexes *cis,cis*-[RuX$_2$(CNR)(CO)(P^P)] (**3–6a–e**)

Complex	IR[a]		^{31}P{^{1}H} NMR[b]	
	v(CO)	v(CN)	δ_P	$^2J_{PP}$
3a[c]	1977	2221	17.3 (d), 42.8 (d)	25.7
3b	1975	2207	17.0 (d), 43.2 (d)	25.3
3c	1976	2191	17.4 (d), 43.3 (d)	25.3
3d	1977	2172	16.6 (d), 42.9 (d)	25.7
3e[d]	1974	2200	17.1 (d), 42.6 (d)	25.7
			17.6 (d), 43.3 (d)	25.7
4a	1978	2208	14.4 (d), 42.7 (d)	25.3
4b	1979	2203	14.3 (d), 43.3 (d)	23.5
4c	1979	2186	14.7 (d), 43.5 (d)	23.8
4d	1974	2170	12.7 (d), 41.6 (d)	25.3
4e[d]	1978	2198	14.3 (d), 42.7 (d)	24.4
			14.7 (d), 43.3 (d)	24.4
5a	1955	2197	26.9 (d), 52.8 (d)	18.5
5b	1952	2189	27.0 (d), 52.9 (d)	18.9
5c	1951	2186	27.1 (d), 53.1 (d)	18.5
5d	1956	2156	27.0 (d), 53.3 (d)	18.5
5e[d]	1956	2187	26.9 (d), 52.9 (d)	17.9
			27.1 (d), 53.0 (d)	17.9
6a	1951	2195	21.9 (d), 52.4 (d)	18.1
6b	1950	2191	22.1 (d), 52.4 (d)	17.8
6c	1952	2182	22.3 (d), 52.6 (d)	17.4
6d	1958	2158	22.3 (d), 53.1 (d)	17.8
6e[d]	1956	2183	22.1 (d), 52.5 (d)	18.9
			22.3 (d), 52.6 (d)	18.9

[a] Spectra recorded in KBr; v in cm^{-1}.
[b] Spectra recorded in CD$_2$Cl$_2$; δ in ppm and J in Hz.
[c] Data taken from Ref. [11].
[d] Obtained as a non-separable mixture of two diastereoisomers in ca. 1:1 ratio.
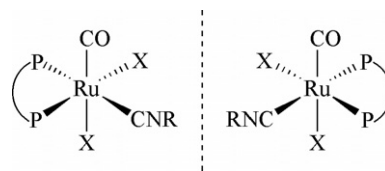
Fig. 2. The two enantiomeric forms of the carbonyl–isocyanide complexes **3–6a–e**.

(details are given in Section 4 and Table 2). Key spectroscopic data are the following: (i) The two strong v(CO) absorption bands that appear within the range 1978–2077 cm^{-1} in the IR spectra (see Table 2). (ii) The typical AB pattern of the phosphorus resonances (δ_P 11.8–26.2 and 38.6–53.9 ppm; $^2J_{PP}$ = 16.6–24.6 Hz; see Table 2). And, (iii) the two doublet of doublets carbonyl resonances in the ^{13}C{^{1}H} NMR spectra at 189.7–192.5 ($^2J_{CP}$ = 110.3–120.5 and 9.8–12.8 Hz) and 195.1–196.5 ($^2J_{CP}$ =

Table 2
IR and ^{31}P{^{1}H} NMR data for the dicarbonyl complexes *cis,cis,cis*-[RuX$_2$(CO)$_2$(P^P)] (**7–8a–b**)

Complex	IR[a]	^{31}P{^{1}H} NMR[b]	
	v(CO)	δ_P	$^2J_{PP}$
7a[c]	2009, 2070	15.3 (d), 38.8 (d)	25.3
7b	2000, 2077	11.8 (d), 38.6 (d)	24.6
8a	1978, 2048	26.2 (d), 53.5 (d)	17.4
8b	1982, 2047	21.5 (d), 53.9 (d)	16.6

[a] Spectra recorded in KBr; v in cm^{-1}.
[b] Spectra recorded in CD$_2$Cl$_2$; δ in ppm and J in Hz.
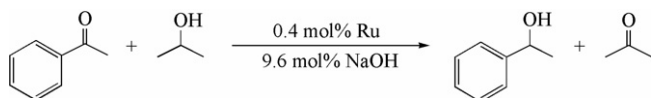[c] Data taken from Ref. [11].

13.6–14.4 and 11.3–12.1 Hz) ppm, which reveal a *trans,cis* and a *cis,cis* arrangement, respectively, of the carbonyl groups with respect the phosphorus nuclei of the diphosphine ligand.

2.2. Catalytic transfer hydrogenation of acetophenone

Following our interest in ruthenium-catalyzed transfer hydrogenation reactions [6,9e,9f,11,12], the catalytic activity in TH of acetophenone by propan-2-ol of the carbonyl–isocyanide and dicarbonyl complexes **3–6a–e** and **7–8a–b**, respectively, has been explored (Scheme 2). Thus, in a typical experiment, the ruthenium catalyst precursor (0.4 mol%) and NaOH (9.6 mol%) were added to a 0.1 M solution of acetophenone in ^{i}PrOH at 82 °C, the reaction being monitored by gas chromatography. Selected results are shown in Table 3.

Concerning the carbonyl–isocyanide complexes **3–6a–e**, all of them have proven to be efficient catalysts, leading to nearly quantitative conversions (yield $\geqslant 92\%$) of acetophenone into 1-phenylethanol within 3–24 h (Table 3). From the results depicted in Table 3, the following features deserve to be commented: (i) The catalytic performances shown by complexes containing the bulkier and more basic dippf ligands **5–6a–e** are in general higher than those of their corresponding dppf counterparts **3–4a–e** (final TOF = 10–82 versus 11–41 h^{-1}). (ii) There is a strong influence of the isocyanide substituents on the catalytic activity, increasing in the order Bn > C(H)MePh $\approx$ Cy > ^{t}Bu $\gg$ 2,6-C$_6$H$_3$Me$_2$. This indicates clearly that the steric requirements of the isocyanide ligands play a crucial role in the reaction. (iii) The chloride complexes **3**, **5a–e** are, in all cases, more efficient than their bromide counterparts **4**, **6a–e**. This behaviour stems from the higher ability of the Ru–Cl versus Ru–Br bonds to undergo metathesis reactions, favouring therefore the formation of the corresponding hydride-ruthenium(II) intermediates which are the real catalytically active species [13].

All the observations mentioned above are in complete accord with the behaviour shown previously by the bis(isocyanide) precatalysts *trans,cis,cis*-[RuX$_2$(CNR)$_2$(dppf)] (**I** in Fig. 1) [6]. Nevertheless, it is important to note that the catalytic performances of the carbonyl–isocyanide species **3–6a–e** are lower than those of the bis(isocyanide) complexes **I**. This difference could be associated to the lower stability of the active hydride species derived from **3–6a–e** versus **I** under the strong basic reaction conditions employed [13]. In order to investigate this behaviour in more detail, the activity of complex *cis,cis*-[RuCl$_2$(CNBn)(CO)(dippf)] (**5a**) was tested under different conditions

Table 3
Catalytic transfer hydrogenation of acetophenone by complexes **3–6a–e**[a]

Entry	Catalyst	Time (h)	Yield (%)[b]	TOF (h^{-1})[c]
1	**3a**	6	98	41 (480)
2	**3b**	7	98	35 (390)
3	**3c**	8	98	31 (450)
4	**3d**	24	98	11 (360)
5	**3e**[d]	7	96	34 (390)
6	**4a**	24	98	11 (150)
7	**4b**	24	99	11 (360)
8	**4c**	24	99	11 (210)
9	**4d**	24	97	11 (210)
10	**4e**[d]	8	92	29 (240)
11	**5a**	3	98	82 (750)
12	**5b**	6	97	40 (600)
13	**5c**	7	94	34 (630)
14	**5d**	10	98	24 (1200)
15	**5e**[d]	5	98	49 (900)
16	**6a**	6	98	41 (1080)
17	**6b**	7	96	34 (810)
18	**6c**	8	97	30 (660)
19	**6d**	24	98	10 (660)
20	**6e**[d]	7	97	35 (1110)

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of acetophenone (0.1 M in ^{i}PrOH). Ketone/Ru/NaOH ratio: 250/1/24.
[b] Yield of 1-phenylethanol determined by GC.
[c] Turnover frequencies ((mol product/mol catalyst)/time) were calculated at the time indicated in each case (TOF values after 5 min in parentheses).
[d] No chiral induction (0% *ee*) was observed when the optically active derivatives **3–6e** were used as catalysts. All the values given in the table are the average of two runs.

confirming the crucial role of the quantity of NaOH used on the performance of this catalyst. Thus, as it can be observed in Fig. 3, when a ketone/Ru/NaOH ratio of 250/1/5 versus 250/1/24 is used the activity of **5a** was visibly increased (the TOF value after 10 min increased from 476 to 636 h^{-1}).

The catalytic activity of the dicarbonyl complexes *cis,cis,cis*-[RuX$_2$(CO)$_2$(P^P)] (**7–8a–b**) was also tested (Fig. 4). The

Scheme 2. Ru-catalyzed transfer hydrogenation of acetophenone.
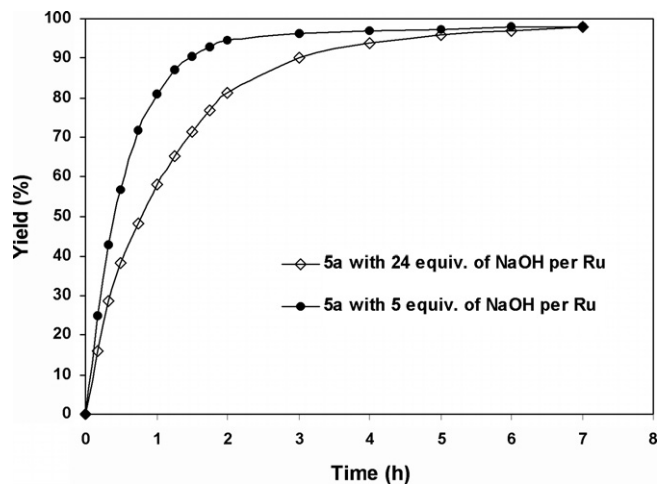
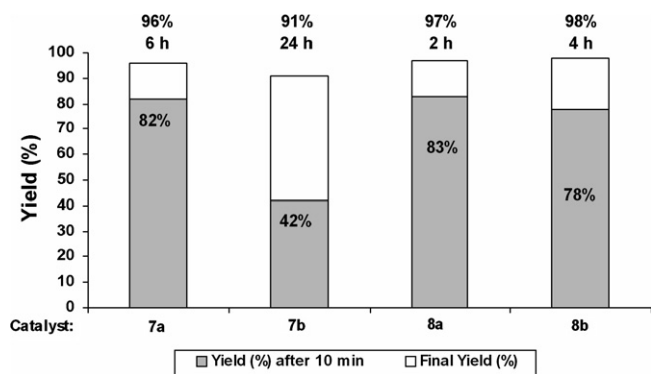Fig. 3. Influence of the quantity of NaOH used on the catalytic activity of **5a**.

Fig. 4. Catalytic activity of complexes **7**–**8a**–**b** in TH of acetophenone.

reactions were carried out at 82 °C using 5 mmol of aceto-phenone (0.1 M in ^{i}PrOH) and an acetophenone/Ru/NaOH ratio of 250/1/5. Under these conditions the four complexes efficiently reduced acetophenone into 1-phenylethanol ($\geqslant 91\%$ yield within 2–24 h; final TOF = 9–121 h^{-1}), the dichloride derivative *cis,cis,cis*-[RuCl$_2$(CO)$_2$(dippf)] (**8a**) showing the best performance. Thus, this complex was able to reduce acetophenone in 97% yield after only 2 h (TOF after 10 min = 1245 h^{-1}; final TOF = 121 h^{-1}). As it was observed for complexes **2**–**6a**–**e**, when 24 instead of 5 equivalents of NaOH were used the rate of the catalytic reaction decreased probably due to the same reasons explained above.

2.3. Catalytic cycloisomerization of (Z)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran

The synthesis of furans is of particular interest since they can be found in many naturally occurring compounds being also key structural units in several important pharmaceuticals, as well as in flavour and fragrance compounds [14]. Furthermore, furans are useful and versatile building blocks in organic synthesis [15]. Among the plethora of alternatives [14], the most direct synthetic strategies presently available for the construction of furan rings involve metal-mediated cycloisomerization of appropriate acyclic precursors. Among them, (Z)-2-en-4-yn-1-ols are particularly appealing since they are readily available starting materials [14]. In this context, several palladium [16], copper [17], silver [18], gold [19], rhodium [20], iridium [20b], and specially ruthenium [16a,20b,21] catalysts have been successfully used to promote the cycloisomerization of (Z)-2-en-4-yn-1-ol substrates into the corresponding furans. Owing to these facts, we decided to explore the catalytic activity of our carbonyl–isocyanide and dicarbonyl complexes **3**–**6a**–**e** and **7**–**8a**–**b**, respectively, in the cyclization of the commercially available (Z)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran (Scheme 3).

The reactions were performed at 75 °C using 5 mmol of (Z)-3-methylpent-2-en-4-yn-1-ol and 1 mol% of the ruthenium catalyst precursor, the reaction being monitored by gas chromatography. It is worthy to note that no additional solvents are added to the reaction mixture [22].
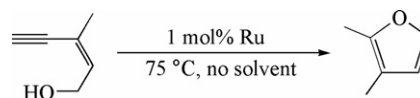
Scheme 3. Ru-catalyzed cycloisomerization of (Z)-3-methylpent-2-en-4-yn-1-ol.

As shown in Table 4, all the carbonyl–isocyanide complexes **3**–**6a**–**e** (entries 1–20), as well as the dicarbonyl complexes **7**–**8a**, **b** (entries 21–24), are able to convert the enynol into 2,3-dimethylfuran in good yields (78–99%) after 0.5–24 h. The results clearly evidence that, as it was observed for the catalytic transfer hydrogenation of acetophenone, there is a strong influence of the isocyanide substituents on the catalytic activity of complexes **3**–**6a**–**e**, increasing in almost the same order Bn > C(H)MePh > Cy > ^{t}Bu > 2,6-C$_6$H$_3$Me$_2$. Analogously, the catalytic performances shown by complexes containing the bulkier and more basic dippf ligands **5**–**6a**–**e** (TOF = 4–66 h^{-1}; entries 11–20) and **8a**–**b** (TOF = 20–198 h^{-1}; entries 23–24) are higher than those of their corresponding dppf counterparts **3**–**4a**–**e** (TOF = 3–7 h^{-1}; entries 1–10) and **7a**–**b** (TOF = 3 h^{-1}; entries 21–22), respectively. This increase in the catalytic activity is particularly remarkable in the case of dicarbonyl complexes (see entries 23–24 versus 21–22), with the derivative *cis,cis,cis*-[RuCl$_2$(CO)$_2$(dippf)] (**8a**) showing the

Table 4
Catalytic cycloisomerization of (Z)-3-methylpent-2-en-4-yn-1-ol by complexes **3**–**6a**–**e** and **7**–**8a**–**b**[a]

Entry	Catalyst	Time (h)	Yield (%)[b]	TOF (h^{-1})[c]
1	**3a**	14	99	7
2	**3b**	24	99	4
3	**3c**	24	99	4
4	**3d**	24	93	4
5	**3e**	15	99	7
6	**4a**	24	97	4
7	**4b**	24	93	4
8	**4c**	24	85	3
9	**4d**	24	78	3
10	**4e**	24	96	4
11	**5a**	1.5	99	66
12	**5b**	2	99	50
13	**5c**	2.5	99	40
14	**5d**	2.5	99	40
15	**5e**	1.5	99	66
16	**6a**	9	99	11
17	**6b**	15	99	7
18	**6c**	24	99	4
19	**6d**	24	99	4
20	**6e**	9.5	99	10
21	**7a**	24	85	3
22	**7b**	24	72	3
23	**8a**	0.5	99	198
24	**8b**	5	99	20

[a] Conditions: reactions were carried out at 75 °C using 5 mmol of (Z)-3-methylpent-2-en-4-yn-1-ol and 1 mol% of catalyst.
[b] Yield of 2,3-dimethylfuran determined by GC.
[c] Turnover frequencies ((mol product/mol catalyst)/time) were calculated at the time indicated in each case. The values given in the table are the average of two runs.
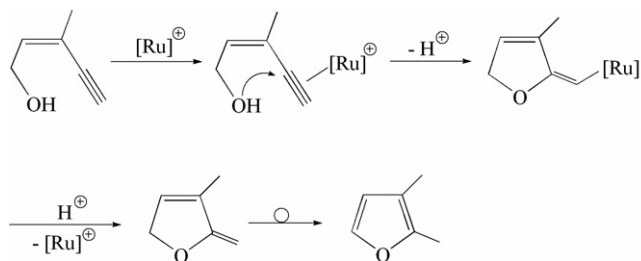
Scheme 4. Mechanism of the Ru-catalyzed cycloisomerization process.

highest activity (99% yield in only 0.5 h; TOF = 198 h^{-1}; entry 23). It should be noted that, although the efficiency shown by this complex is comparable to that shown by other Ru(II) catalysts previously described [23], it still remains less efficient than AuCl$_3$ (TOF = 999 h^{-1} at r.t.) which is the best catalyst reported to date for this cycloisomerization reaction [19].

Finally, it is also interesting to note that, as observed in the TH reactions, the catalytic performances shown by the chloride complexes **3**, **5a–e** and **7**, **8a** are, in all cases, better than those of their bromide counterparts **4**, **6a–e** and **7**, **8b**, respectively (entries 1–5 versus 6–10, 11–15 versus 16–20 and 21/23 versus 22/24). Assuming that this cycloisomerization reaction proceeds through the classical pathway, i.e. via initial π-coordination of the C≡C of the enynol on the metal and subsequent intramolecular *endo* nucleophilic attack of the pendant OH group on the coordinated alkyne unit (Scheme 4) [16], the higher catalytic activities shown by the chloride versus bromide complexes can be explained on the basis of greater tendency of the former to undergo dissociation, generating more easily the required vacant coordination site.

3. Conclusion

In summary, in this paper we have described an efficient and straightforward synthetic protocol for the stereoselective preparation of novel carbonyl–isocyanide and dicarbonyl–ruthenium(II) complexes, namely *cis,cis*-[RuX$_2$(CNR)(CO)(P^P)] (P^P = dppf, dippf; X = Cl, Br; R = Bn, Cy, ^{t}Bu, 2,6-C$_6$H$_3$Me$_2$, (S)-(−)-C(H)MePh; **3–6a–e**) and *cis,cis,cis*-[RuX$_2$(CO)$_2$(P^P)] (P^P = dppf, dippf; X = Cl, Br; **7–8a–b**), by the reaction of the readily available dimers [{RuX(μ-X)(CO)(P^P)}$_2$] (**1–2a–b**) [11] with an excess of the appropriate isocyanide or carbon monoxide, respectively. All the complexes tested have proven to be active catalysts for the transfer hydrogenation of acetophenone using 2-propanol as hydrogen source. Nevertheless, their catalytic performances are lower than those of the closely related bis(isocyanide) complexes *trans,cis,cis*-[RuX$_2$(CNR)$_2$(dppf)] (**I** in Fig. 1) previously reported by us [6], probably due to the instability of the corresponding catalytic active dihydride species in the strong basic media required for this transformation. In addition, both the carbonyl–isocyanide (**3–6a–e**) and dicarbonyl–ruthenium(II) (**7–8a**, **b**) derivatives have shown to be efficient catalysts

for the cycloisomerization of the commercially available (Z)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran, with the dicarbonyl species *cis,cis,cis*-[RuCl$_2$(CO)$_2$(dippf)] (**8a**) showing a remarkable activity.

4. Experimental

4.1. General information

All manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of the compounds [{RuX(μ-X)(CO)(P^P)}$_2$] (P^P = dppf, X = Cl (**1a**), Br (**1b**); P^P = dippf, X = Cl (**2a**), Br (**2b**)), *cis,cis*-[RuCl$_2$(CNBn)(CO)(dppf)] (**3a**) and *cis,cis,cis*-[RuCl$_2$(CO)$_2$(dppf)] (**7a**), which were prepared by following the methods reported in the literature [11]. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Gas chromatographic measurements were made on a Hewlett–Packard HP6890 equipment using a HP-INNOWAX cross-linked poly(ethyleneglycol) (30 m, 250 μm) or a Supelco Beta-Dex™ 120 (30 m, 250 μm) column. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using SiMe$_4$ or 85% H$_3$PO$_4$ as standards. DEPT experiments have been carried out for all the compounds reported. IR and ^{31}P{^{1}H} NMR data are collected in Tables 1 and 2.

4.2. Synthesis of carbonyl–isocyanide complexes cis,cis-[RuX$_2$(CNR)(CO)(P^P)] (P^P = dppf, X = Cl, R = Cy (3b), ^{t}Bu (3c), 2,6-C$_6$H$_3$Me$_2$ (3d), (S)-(−)-C(H)MePh (3e); P^P = dppf, X = Br, R = Bn (4a), Cy (4b), ^{t}Bu (4c), 2,6-C$_6$H$_3$Me$_2$ (4d), (S)-(−)-C(H)MePh (4e); P^P = dippf, X = Cl, R = Bn (5a), Cy (5b), ^{t}Bu (5c), 2,6-C$_6$H$_3$Me$_2$ (5d), (S)-(−)-C(H)MePh (5e); P^P = dippf, X = Br, R = Bn (6a), Cy (6b), ^{t}Bu (6c), 2,6-C$_6$H$_3$Me$_2$ (6d), (S)-(−)-C(H)MePh (6e))

A solution of the corresponding dimeric precursor [{RuX(μ-X)(CO)(P^P)}$_2$] (**1–2a–b**; 0.5 mmol) in 30 ml of THF was treated, at 70 °C (**3b–e** and **4a–e**) or at room temperature (**5–6a–e**), with the appropriate isocyanide (1.1 mmol) for 3 h. The solvent was then removed under reduced pressure and the resulting yellow-orange solid residue washed with hexanes (3 × 30 ml) and vacuum-dried. Compounds **3e**, **4e**, **5e**, and **6e** have obtained as a non-separable mixture of two diastereoisomers in ca. 1:1 ratio.

Compound 3b: Yield: 97% (0.837 g). Anal. Calc. for FeRuC$_{42}$H$_{39}$Cl$_2$P$_2$NO (863.53 g mol^{-1}): C, 58.42; H, 4.55; N, 1.62. Found: C, 58.76; H, 4.36; N, 1.57%; ^{1}H NMR (CD$_2$Cl$_2$): δ 1.26–1.81 (m, 10H, CH$_2$), 3.64 (m, 1H, NCH), 4.19, 4.25, 4.29 and 4.58 (br, 2H each, C$_5$H$_4$),

7.28–8.31 (m, 20H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 21.8$, 24.3 and 31.4 (s, CH$_2$), 54.1 (s, NCH), 70.9, 71.4, 71.6 and 76.3 (d, $^2J_{CP} = 5.5$ Hz, CH of C$_5$H$_4$), 74.1, 74.6, 76.9 and 77.7 (d, $^3J_{CP} = 8.6$ Hz, CH of C$_5$H$_4$), 78.5 and 79.1 (d, $^1J_{CP} = 52.8$ Hz, C of C$_5$H$_4$), 126.4–136.3 (m, Ph and RuCN), 197.4 (dd, $^2J_{CP} = 12.9$ and 12.9 Hz, CO) ppm.

Compound 3c: Yield: 93% (0.779 g). Anal. Calc. for FeRuC$_{40}$H$_{37}$Cl$_2$P$_2$NO (837.50 g mol^{-1}): C, 57.36; H, 4.45; N, 1.67. Found: C, 57.54; H, 4.21; N, 1.70%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 1.25$ (s, 9H, CH$_3$), 4.20, 4.26, 4.29 and 4.56 (br, 2H each, C$_5$H$_4$), 7.23–8.30 (m, 20H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 30.3$ (s, CH$_3$), 58.2 (s, C(CH$_3$)$_3$), 71.3, 71.7, 71.9 and 76.6 (d, $^2J_{CP} = 5.9$ Hz, CH of C$_5$H$_4$), 74.4, 74.7, 77.2 and 77.9 (d, $^3J_{CP} = 8.5$ Hz, CH of C$_5$H$_4$), 79.4 and 80.1 (d, $^1J_{CP} = 52.1$ Hz, C of C$_5$H$_4$), 127.3–137.5 (m, Ph and RuCN), 198.3 (dd, $^2J_{CP} = 13.2$ and 13.2 Hz, CO) ppm.

Compound 3d: Yield: 92% (0.815 g). Anal. Calc. for FeRuC$_{44}$H$_{37}$Cl$_2$P$_2$NO (885.54 g mol^{-1}): C, 59.68; H, 4.21; N, 1.58. Found: C, 59.93; H, 3.97; N, 1.62%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 2.13$ (s, 6H, CH$_3$), 4.16, 4.26, 4.31 and 4.63 (br, 2H each, C$_5$H$_4$), 6.99–8.42 (m, 23H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 18.7$ (s, CH$_3$), 71.2, 71.8, 72.1 and 76.8 (d, $^2J_{CP} = 5.4$ Hz, CH of C$_5$H$_4$), 74.5, 75.1, 77.2 and 78.2 (d, $^3J_{CP} = 8.7$ Hz, CH of C$_5$H$_4$), 79.4 and 79.6 (d, $^1J_{CP} = 53.6$ Hz, C of C$_5$H$_4$), 127.4–137.6 (m, Ph and RuCN), 198.1 (dd, $^2J_{CP} = 13.1$ and 13.1 Hz, CO) ppm.

Compound 3e: Yield: 94% (0.832 g). Anal. Calc. for FeRuC$_{44}$H$_{37}$Cl$_2$P$_2$NO (885.54 g mol^{-1}): C, 59.68; H, 4.21; N, 1.58. Found: C, 59.82; H, 4.48; N, 1.61%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 1.39$ and 1.52 (d, 3H each, $^3J_{HH} = 6.8$ Hz, CH$_3$), 4.18, 4.19, 4.21, 4.25, 4.29, 4.32, 4.56 and 4.58 (br, 2H each, C$_5$H$_4$), 4.59 and 4.73 (q, 1H each, $^3J_{HH} = 6.8$ Hz, NCH), 7.15–8.37 (m, 50H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 25.0$ and 25.4 (s, CH$_3$), 56.6 and 56.7 (s, NCH), 71.2, 71.3, 71.6, 71.7, 71.8, 72.0, 76.5 and 76.7 (d, $^2J_{CP} = 5.7$ Hz, CH of C$_5$H$_4$), 74.4, 74.5, 74.8, 74.9, 77.1, 77.2, 77.5 and 78.0 (d, $^3J_{CP} = 8.4$ Hz, CH of C$_5$H$_4$), 78.1, 78.7, 79.3 and 79.9 (d, $^1J_{CP} = 52.4$ Hz, C of C$_5$H$_4$), 126.0–139.0 (m, Ph and RuCN), 198.1 and 198.5 (dd, $^2J_{CP} = 12.4$ and 12.4 Hz, CO) ppm.

Compound 4a: Yield: 85% (0.816 g). Anal. Calc. for FeRuC$_{43}$H$_{35}$Br$_2$P$_2$NO (960.41 g mol^{-1}): C, 53.77; H, 3.67; N, 1.46. Found: C, 54.09; H, 3.41; N, 1.51%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 4.24$, 4.29, 4.41, 4.55 and 4.60 (br, 2H each, C$_5$H$_4$ and NCH$_2$), 7.24–8.37 (m, 25H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 48.4$ (s, NCH$_2$), 71.6, 71.9, 72.2 and 76.9 (d, $^2J_{CP} = 5.7$ Hz, CH of C$_5$H$_4$), 74.7, 74.9, 77.4 and 78.7 (d, $^3J_{CP} = 8.8$ Hz, CH of C$_5$H$_4$), 80.0 and 81.3 (d, $^1J_{CP} = 52.0$ Hz, C of C$_5$H$_4$), 127.3–136.9 (m, Ph and RuCN), 198.5 (d, $^2J_{CP} = 12.3$ and 12.3 Hz, CO) ppm.

Compound 4b: Yield: 89% (0.848 g). Anal. Calc. for FeRuC$_{42}$H$_{39}$Br$_2$P$_2$NO (952.44 g mol^{-1}): C, 52.96; H, 4.13; N, 1.47. Found: C, 53.18; H, 3.86; N, 1.49%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 1.34$–1.86 (m, 10H, CH$_2$), 3.68 (m, 1H, NCH), 4.25, 4.28, 4.41 and 4.55 (br, 2H each, C$_5$H$_4$),

7.34–8.27 (m, 20H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 23.3$, 25.6 and 33.2 (s, CH$_2$), 55.8 (s, NCH), 71.7, 71.8, 72.3 and 76.9 (d, $^2J_{CP} = 5.3$ Hz, CH of C$_5$H$_4$), 74.4, 74.7, 77.4 and 78.6 (d, $^3J_{CP} = 8.1$ Hz, CH of C$_5$H$_4$), 80.2 and 80.9 (d, $^1J_{CP} = 52.9$ Hz, C of C$_5$H$_4$), 127.4–137.2 (m, Ph and RuCN), 198.7 (dd, $^2J_{CP} = 12.1$ and 12.1 Hz, CO) ppm.

Compound 4c: Yield: 86% (0.797 g). Anal. Calc. for FeRuC$_{40}$H$_{37}$Br$_2$P$_2$NO (926.40 g mol^{-1}): C, 51.86; H, 4.03; N, 1.51. Found: C, 52.08; H, 3.77; N, 1.52%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 1.26$ (s, 9H, CH$_3$), 4.26, 4.29, 4.54 and 4.63 (br, 2H each, C$_5$H$_4$), 7.25–8.28 (m, 20H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 30.2$ (s, CH$_3$), 58.3 (s, C(CH$_3$)$_3$), 71.6, 71.7, 72.1 and 76.6 (d, $^2J_{CP} = 5.2$ Hz, CH of C$_5$H$_4$), 74.2, 74.4, 77.2 and 78.1 (d, $^3J_{CP} = 8.7$ Hz, CH of C$_5$H$_4$), 80.2 and 80.8 (d, $^1J_{CP} = 55.1$ Hz, C of C$_5$H$_4$), 127.1–137.0 (m, Ph and RuCN), 198.3 (dd, $^2J_{CP} = 12.1$ and 12.1 Hz, CO) ppm.

Compound 4d: Yield: 84% (0.818 g). Anal. Calc. for FeRuC$_{44}$H$_{37}$Br$_2$P$_2$NO (974.44 g mol^{-1}): C, 54.23; H, 3.83; N, 1.44. Found: C, 54.56; H, 3.61; N, 1.46%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 2.15$ (s, 6H, CH$_3$), 4.24, 4.29, 4.36 and 4.59 (br, 2H each, C$_5$H$_4$), 6.99–8.33 (m, 23H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 18.8$ (s, CH$_3$), 71.3, 71.6, 72.0 and 76.8 (d, $^2J_{CP} = 5.5$ Hz, CH of C$_5$H$_4$), 74.4, 74.7, 77.2 and 78.6 (d, $^3J_{CP} = 8.2$ Hz, CH of C$_5$H$_4$), 79.8 and 80.9 (d, $^1J_{CP} = 52.9$ Hz, C of C$_5$H$_4$), 127.2–136.6 (m, Ph and RuCN), 198.1 (dd, $^2J_{CP} = 12.1$ and 12.1 Hz, CO) ppm.

Compound 4e: Yield: 90% (0.877 g). Anal. Calc. for FeRuC$_{44}$H$_{37}$Br$_2$P$_2$NO (974.44 g mol^{-1}): C, 54.23; H, 3.83; N, 1.44. Found: C, 54.45; H, 3.90; N, 1.40%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 1.41$ and 1.55 (d, 3H each, $^3J_{HH} = 6.7$ Hz, CH$_3$), 4.23, 4.26, 4.29, 4.42, 4.49, 4.53, 4.57 and 4.60 (br, 2H each, C$_5$H$_4$), 4.69 and 4.76 (q, 1H each, $^3J_{HH} = 6.7$ Hz, NCH), 7.16–8.36 (m, 50H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 25.4$ and 25.6 (s, CH$_3$), 57.0 and 57.2 (s, NCH), 71.6, 71.7, 71.9, 72.0, 72.2, 72.4, 76.8 and 77.0 (d, $^2J_{CP} = 5.2$ Hz, CH of C$_5$H$_4$), 74.6, 74.7, 74.8, 74.9, 77.4, 77.5, 77.6 and 77.7 (d, $^3J_{CP} = 8.8$ Hz, CH of C$_5$H$_4$), 78.5, 78.6, 79.3 and 80.1 (d, $^1J_{CP} = 53.6$ Hz, C of C$_5$H$_4$), 126.2–139.0 (m, Ph and RuCN), 197.9 and 198.6 (dd, $^2J_{CP} = 13.6$ and 13.6 Hz, CO) ppm.

Compound 5a: Yield: 85% (0.625 g). Anal. Calc. for FeRuC$_{31}$H$_{43}$Cl$_2$P$_2$NO (735.45 g mol^{-1}): C, 50.63; H, 5.89; N, 1.90. Found: C, 50.94; H, 5.53; N, 2.01%; ^{1}H NMR (CD$_2$Cl$_2$) $\delta = 1.27$ (m, 24H, CH(CH$_3$)$_2$), 2.36, 2.58, 2.92 and 3.11 (m, 1H each, CH(CH$_3$)$_2$), 4.36, 4.51, 4.69, 4.77 and 4.91 (br, 2H each, C$_5$H$_4$ and NCH$_2$), 7.36–7.52 (m, 5H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) $\delta = 19.2$, 19.6, 20.0, 20.2, 20.3, 20.4, 20.5 and 20.9 (s, CH(CH$_3$)$_2$), 25.9, 26.3, 30.2 and 31.6 (d, $^1J_{CP} = 23.4$ Hz, CH(CH$_3$)$_2$), 49.0 (s, NCH$_2$), 71.2, 71.7, 72.0 and 76.7 (d, $^2J_{CP} = 5.1$ Hz, CH of C$_5$H$_4$), 72.4, 75.0, 77.2 and 78.2 (d, $^3J_{CP} = 8.7$ Hz, CH of C$_5$H$_4$), 79.1 and 79.7 (d, $^1J_{CP} = 41.5$ Hz, C of C$_5$H$_4$), 127.2–132.3 (m, Ph), 147.2 (dd, $^2J_{CP} = 120.7$ and 21.8 Hz, RuCN), 199.9 (dd, $^2J_{CP} = 13.6$ and 13.6 Hz, CO) ppm.

Compound 5b: Yield: 82% (0.596 g). Anal. Calc. for FeRuC$_{30}$H$_{47}$Cl$_2$P$_2$NO (727.47 g mol^{-1}): C, 49.53; H, 6.51; N, 1.93. Found: C, 49.78; H, 6.32; N, 1.89%; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.65 (m, 34H, CH(CH_3)$_2$ and CH$_2$), 2.48, 2.71, 2.89 and 3.18 (m, 1H each, CH(CH$_3$)$_2$), 3.89 (m, 1H, NCH), 4.38, 4.47, 4.67 and 4.80 (br, 2H each, C$_5$H$_4$) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 19.0, 20.0, 20.3, 20.4, 20.5, 20.6, 21.3 and 22.7 (s, CH(CH$_3$)$_2$), 23.4, 25.3 and 32.4 (s, CH$_2$), 25.8, 26.3, 30.2 and 31.6 (d, $^1J_{CP}$ = 25.4 Hz, CH(CH$_3$)$_2$), 55.4 (s, NCH), 71.2, 71.5, 71.6 and 75.1 (d, $^2J_{CP}$ = 5.3 Hz, CH of C$_5$H$_4$), 71.9, 73.6, 75.6 and 75.8 (d, $^3J_{CP}$ = 8.4 Hz, CH of C$_5$H$_4$), 79.4 and 79.9 (d, $^1J_{CP}$ = 42.7 Hz, C of C$_5$H$_4$), 143.4 (dd, $^2J_{CP}$ = 119.3 and 22.4 Hz, RuCN), 200.1 (dd, $^2J_{CP}$ = 12.1 and 12.1 Hz, CO) ppm.

Compound 5c: Yield: 80% (0.561 g). Anal. Calc. for FeRuC$_{28}$H$_{45}$Cl$_2$P$_2$NO (701.43 g mol^{-1}): C, 47.94; H, 6.47; N, 2.00. Found: C, 47.95; H, 6.43; N, 2.11%; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.32 (m, 24H, CH(CH_3)$_2$), 1.54 (s, 9H, C(CH_3)), 2.49, 2.74, 2.91 and 3.19 (m, 1H each, CH(CH$_3$)$_2$), 4.39, 4.47, 4.69 and 4.81 (br, 2H each, C$_5$H$_4$) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 19.5, 19.6, 19.7, 19.7, 19.9, 20.2, 20.5 and 20.6 (s, CH(CH$_3$)$_2$), 25.8, 26.3, 30.2 and 31.8 (d, $^1J_{CP}$ = 23.1 Hz, CH(CH$_3$)$_2$), 30.5 (s, C(CH$_3$)$_3$), 58.3 (s, C(CH$_3$)$_3$), 71.2, 71.4, 72.1 and 76.6 (d, $^2J_{CP}$ = 5.9 Hz, CH of C$_5$H$_4$), 74.4, 75.2, 77.1 and 78.3 (d, $^3J_{CP}$ = 7.5 Hz, CH of C$_5$H$_4$), 79.5 and 80.1 (d, $^1J_{CP}$ = 40.9 Hz, C of C$_5$H$_4$), 142.6 (dd, $^2J_{CP}$ = 121.8 and 24.1 Hz, RuCN), 200.1 (dd, $^2J_{CP}$ = 14.0 and 14.0 Hz, CO) ppm.

Compound 5d: Yield: 81% (0.607 g). Anal. Calc. for FeRuC$_{32}$H$_{45}$Cl$_2$P$_2$NO (749.47 g mol^{-1}): C, 51.28; H, 6.05; N, 1.87. Found: C, 51.53; H, 5.84; N, 1.98%; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.38 (m, 24H, CH(CH_3)$_2$), 2.31, 2.79, 2.96 and 3.28 (m, 1H each, CH(CH$_3$)$_2$), 2.56 (s, 6H, CH$_3$), 4.42, 4.46, 4.75 and 4.85 (br, 2H each, C$_5$H$_4$), 7.03–7.36 (m, 3H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 18.9, 19.1, 19.6, 19.7, 20.0, 20.5, 20.7 and 21.1 (s, CH(CH$_3$)$_2$), 19.4 (s, CH$_3$), 26.3, 26.4, 30.4 and 31.7 (d, $^1J_{CP}$ = 25.7 Hz, CH(CH$_3$)$_2$), 71.4, 71.4, 71.8 and 73.9 (d, $^2J_{CP}$ = 5.2 Hz, CH of C$_5$H$_4$), 71.9, 75.2, 75.5 and 75.9 (d, $^3J_{CP}$ = 8.1 Hz, CH of C$_5$H$_4$), 78.8 and 79.4 (d, $^1J_{CP}$ = 41.8 Hz, C of C$_5$H$_4$), 128.4–136.6 (m, Ph), 147.2 (dd, $^2J_{CP}$ = 122.3 and 23.2 Hz, RuCN), 199.9 (dd, $^2J_{CP}$ = 13.6 and 13.6 Hz, CO) ppm.

Compound 5e: Yield: 75% (0.562 g). Anal. Calc. for FeRuC$_{32}$H$_{45}$Cl$_2$P$_2$NO (749.47 g mol^{-1}): C, 51.28; H, 6.05; N, 1.87. Found: C, 51.41; H, 6.34; N, 1.94%; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.36 (m, 48H, CH(CH_3)$_2$), 1.47 and 1.81 (d, 3H each, $^3J_{HH}$ = 6.9 Hz, CH$_3$), 2.37, 2.51, 2.69, 2.72, 2.82, 2.85, 3.23 and 3.34 (m, 1H each, CH(CH$_3$)$_2$), 4.27, 4.32, 4.39, 4.48, 4.61, 4.67, 4.73 and 4.81 (br, 2H each, C$_5$H$_4$), 4.95 and 5.23 (q, 1H each, $^3J_{HH}$ = 6.9 Hz, NCH), 7.27–7.61 (m, 10H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 18.9, 19.1, 19.3, 19.5, 19.8, 19.9, 20.0, 20.2, 20.3, 20.4, 20.5, 20.7, 20.8, 20.9, 21.1 and 21.3 (s, CH(CH$_3$)$_2$), 24.3 and 25.4 (s, CH$_3$), 24.6, 24.8, 26.5, 26.7, 30.2, 30.3, 32.2 and 32.8 (d, $^1J_{CP}$ = 23.9 Hz, CH(CH$_3$)$_2$), 57.4 and

57.9 (s, NCH), 71.2, 71.5, 71.6, 71.7, 71.8, 71.9, 75.4 and 75.5 (d, $^2J_{CP}$ = 5.6 Hz, CH of C$_5$H$_4$), 72.0, 72.1, 73.9, 74.1, 75.6, 75.8, 76.0 and 76.1 (d, $^3J_{CP}$ = 7.7 Hz, CH of C$_5$H$_4$), 78.9, 79.1, 80.2 and 80.4 (d, $^1J_{CP}$ = 43.3 Hz, C of C$_5$H$_4$), 126.2–132.1 (m, Ph), 139.2 and 140.1 (dd, $^2J_{CP}$ = 119.8 and 21.6 Hz, RuCN), 199.5 and 200.2 (dd, $^2J_{CP}$ = 12.4 and 12.4 Hz, CO) ppm.

Compound 6a: Yield: 87% (0.717 g). Anal. Calc. for FeRuC$_{31}$H$_{43}$Br$_2$P$_2$NO (824.35 g mol^{-1}): C, 45.17; H, 5.26; N, 1.70. Found: C, 45.32; H, 5.06; N, 1.81%; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.36 (m, 24H, CH(CH_3)$_2$), 2.44, 2.71, 2.78 and 3.23 (m, 1H each, CH(CH$_3$)$_2$), 4.35, 4.38, 4.42, 4.70 and 4.97 (br, 2H each, C$_5$H$_4$ and NCH$_2$), 7.28–7.54 (m, 5H, Ph) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 19.5, 19.8, 20.2, 20.3, 20.6, 20.7, 20.8 and 21.2 (s, CH(CH$_3$)$_2$), 26.8, 27.9, 30.9 and 33.8 (d, $^1J_{CP}$ = 21.8 Hz, CH(CH$_3$)$_2$), 49.1 (s, NCH$_2$), 70.9, 71.3, 71.6 and 75.5 (d, $^2J_{CP}$ = 5.8 Hz, CH of C$_5$H$_4$), 72.3, 74.0, 75.9 and 76.0 (d, $^3J_{CP}$ = 8.3 Hz, CH of C$_5$H$_4$), 79.6 and 80.2 (d, $^1J_{CP}$ = 42.7 Hz, C of C$_5$H$_4$), 127.8–138.8 (m, Ph), 145.4 (dd, $^2J_{CP}$ = 121.5 and 23.1 Hz, RuCN), 199.6 (dd, $^2J_{CP}$ = 12.8 and 12.8 Hz, CO) ppm.

Compound 6b: Yield: 88% (0.718 g). Anal. Calc. for FeRuC$_{30}$H$_{47}$Br$_2$P$_2$NO (816.37 g mol^{-1}): C, 44.14; H, 5.80; N, 1.72. Found: C, 44.31; H, 5.53; N, 1.80%; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.57 (m, 34H, CH(CH_3)$_2$ and CH$_2$), 2.57, 2.87, 2.94 and 3.24 (m, 1H each, CH(CH$_3$)$_2$), 4.01 (m, 1H, NCH), 4.39, 4.51, 4.70 and 4.98 (br, 2H each, C$_5$H$_4$) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 18.9, 19.3, 19.9, 20.5, 20.6, 20.7, 20.8 and 21.3 (s, CH(CH$_3$)$_2$), 23.0, 24.9 and 32.4 (s, CH$_2$), 26.3, 27.5, 30.4 and 33.6 (d, $^1J_{CP}$ = 22.7 Hz, CH(CH$_3$)$_2$), 55.4 (s, NCH), 70.5, 70.8, 71.0 and 74.7 (d, $^2J_{CP}$ = 5.9 Hz, CH of C$_5$H$_4$), 71.9, 73.6, 75.5 and 75.7 (d, $^3J_{CP}$ = 8.9 Hz, CH of C$_5$H$_4$), 78.5 and 80.2 (d, $^1J_{CP}$ = 43.4 Hz, C of C$_5$H$_4$), 138.2 (dd, $^2J_{CP}$ = 122.5 and 25.1 Hz, RuCN), 199.7 (dd, $^2J_{CP}$ = 13.4 and 13.4 Hz, CO) ppm.

Compound 6c: Yield: 93% (0.735 g). Anal. Calc. for FeRuC$_{28}$H$_{45}$Br$_2$P$_2$NO (790.33 g mol^{-1}): C, 42.55; H, 5.74; N, 1.77. Found: C, 42.81; H, 5.63; N, 1.92%; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.29 (m, 24H, CH(CH_3)$_2$), 1.57 (s, 9H, C(CH_3)), 2.58, 2.85, 2.98 and 3.24 (m, 1H each, CH(CH$_3$)$_2$), 4.35, 4.39, 4.68 and 4.98 (br, 2H each, C$_5$H$_4$) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 19.7, 20.1, 20.2, 20.3, 20.7, 20.8, 20.9 and 21.8 (s, CH(CH$_3$)$_2$), 26.7, 27.9, 31.2 and 34.2 (d, $^1J_{CP}$ = 25.6 Hz, CH(CH$_3$)$_2$), 30.4 (s, C(CH$_3$)$_3$), 58.6 (s, C(CH$_3$)$_3$), 70.9, 71.4, 71.6 and 74.0 (d, $^2J_{CP}$ = 5.3 Hz, CH of C$_5$H$_4$), 72.3, 75.4, 75.9 and 76.1 (d, $^3J_{CP}$ = 9.0 Hz, CH of C$_5$H$_4$), 79.9 and 80.4 (d, $^1J_{CP}$ = 40.5 Hz, C of C$_5$H$_4$), 141.6 (dd, $^2J_{CP}$ = 122.6 and 22.7 Hz, RuCN), 199.8 (dd, $^2J_{CP}$ = 12.8 and 12.8 Hz, CO) ppm.

Compound 6d: Yield: 96% (0.805 g). Anal. Calc. for FeRuC$_{32}$H$_{45}$Br$_2$P$_2$NO (838.38 g mol^{-1}): C, 45.84; H, 5.41; N, 1.67. Found: C, 46.08; H, 5.23; N, 1.68%; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.26 (m, 24H, CH(CH_3)$_2$), 2.54, 2.87, 2.95 and 3.27 (m, 1H each, CH(CH$_3$)$_2$), 2.59 (s, 6H, CH$_3$),

4.41, 4.46, 4.78 and 5.07 (br, 2H each, C_5H_4), 7.11–7.21 (m, 3H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 19.1$, 19.7, 20.3, 20.4, 20.5, 20.9, 21.0 and 21.5 (s, $CH(CH_3)_2$), 19.5 (s, CH_3), 26.8, 27.9, 31.3 and 33.9 (d, $^1J_{CP} = 22.8$ Hz, $CH(CH_3)_2$), 70.9, 71.0, 71.6 and 74.1 (d, $^2J_{CP} = 5.9$ Hz, CH of C_5H_4), 72.4, 75.6, 75.7 and 76.1 (d, $^3J_{CP} = 8.7$ Hz, CH of C_5H_4), 79.6 and 80.2 (d, $^1J_{CP} = 42.2$ Hz, C of C_5H_4), 128.0–136.1 (m, Ph), 156.0 (dd, $^2J_{CP} = 119.9$ and 21.9 Hz, RuCN), 199.6 (dd, $^2J_{CP} = 12.8$ and 12.8 Hz, CO) ppm.

Compound 6e: Yield: 86% (0.721 g). Anal. Calc. for $FeRuC_{32}H_{45}Br_2P_2NO$ (838.38 g mol^{-1}): C, 45.84; H, 5.41; N, 1.67. Found: C, 46.11; H, 5.27; N, 1.85%; ^1H NMR (CD_2Cl_2) $\delta = 1.28$ (m, 48H, $CH(CH_3)_2$), 1.44 and 1.80 (d, 3H each, $^3J_{HH} = 6.2$ Hz, CH_3), 2.48, 2.50, 2.83, 2.86, 2.90, 2.94, 3.21 and 3.30 (m, 1H each, $CH(CH_3)_2$), 4.34, 4.36, 4.39, 4.42, 4.63, 4.69, 4.94 and 4.98 (br, 2H each, C_5H_4), 5.20 and 5.24 (q, 1H each, $^3J_{HH} = 6.2$ Hz, NCH), 7.32–7.54 (m, 10H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 19.8$ (2C), 19.9 (2C), 20.0, 20.1, 20.2, 20.3 (2C), 20.4, 20.5, 20.7, 20.8 (2C), 21.4 and 21.4 (s, $CH(CH_3)_2$), 24.5 and 24.7 (s, CH_3), 26.7, 26.8, 27.9, 28.0, 31.0, 31.1, 33.7 and 34.1 (d, $^1J_{CP} = 22.3$ Hz, $CH(CH_3)_2$), 57.2 and 57.3 (s, NCH), 71.0, 71.1, 71.3 (2C), 71.6 (2C) and 74.0 (2C) (d, $^2J_{CP} = 5.3$ Hz, CH of C_5H_4), 72.3 (2C), 75.5 (2C), 75.8 (2C) and 76.0 (2C) (d, $^3J_{CP} = 8.2$ Hz, CH of C_5H_4), 79.7, 79.8, 80.2 and 80.3 (d, $^1J_{CP} = 42.7$ Hz, C of C_5H_4), 125.7–138.7 (m, Ph), 144.1 and 144.4 (dd, $^2J_{CP} = 121.3$ and 23.1 Hz, RuCN), 199.6 and 199.9 (dd, $^2J_{CP} = 13.0$ and 13.0 Hz, CO) ppm.

4.3. Synthesis of dicarbonyl complexes cis,cis,cis-[RuX$_2$(CO)$_2$(P^P)] (P^P = dppf, X = Br (7b); P^P = dippf, X = Cl (8a), Br (8b))

Carbon monoxide was bubbled at 65 °C through a solution of the corresponding dimeric species [{RuX-(μ-X)(CO)(P^P)}$_2$] (1–2a–b; 0.5 mmol) in 70 ml of THF for 5 h (7b) or 15 min (8a–b). After removing the solvent under reduced pressure, diethyl ether (50 ml) was added to the residue, yielding the precipitation of a yellow solid, which was filtered off, washed with diethyl ether (2 × 50 ml), and vacuum-dried.

Compound 7b: Yield: 84% (0.732 g). Anal. Calc. for $FeRuC_{36}H_{28}Br_2O_2P_2$ (871.28 g mol^{-1}): C, 49.63; H, 3.24. Found: C, 49.87; H, 3.13%; ^1H NMR (CD_2Cl_2) $\delta = 4.28$, 4.40, 4.63 and 4.66 (br, 2H each, C_5H_4), 7.29–8.30 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 71.7$, 72.4, 72.5 and 77.2 (d, $^2J_{CP} = 5.3$ Hz, CH of C_5H_4), 74.4, 75.4, 77.3 and 78.4 (d, $^3J_{CP} = 8.3$ Hz, CH of C_5H_4), 77.9 and 79.1 (d, $^1J_{CP} = 45.3$ Hz, C of C_5H_4), 127.3–136.5 (m, Ph), 189.7 (dd, $^2J_{CP} = 120.5$ and 9.8 Hz, CO), 195.1 (dd, $^2J_{CP} = 13.6$ and 11.3 Hz, CO) ppm.

Compound 8a: Yield: 79% (0.510 g). Anal. Calc. for $FeRuC_{24}H_{36}Cl_2O_2P_2$ (646.31 g mol^{-1}): C, 44.60; H, 5.61. Found: C, 44.42; H, 5.87%; ^1H NMR (CD_2Cl_2) $\delta = 1.24$ (m, 24H, $CH(CH_3)_2$), 2.41, 2.73, 2.91 and 3.12 (m, 1H each,

$CH(CH_3)_2$), 4.28, 4.34, 4.56 and 4.82 (br, 2H each, C_5H_4) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 18.4$, 18.5, 18.6, 18.7, 19.3, 19.4, 19.8 and 20.2 (s, $CH(CH_3)_2$), 24.7, 25.4, 29.9 and 31.6 (d, $^1J_{CP} = 25.7$ Hz, $CH(CH_3)_2$), 70.7, 71.2, 71.3 and 73.1 (d, $^2J_{CP} = 5.5$ Hz, CH of C_5H_4), 71.8, 74.3, 75.2 and 75.3 (d, $^3J_{CP} = 8.6$ Hz, CH of C_5H_4), 76.8 and 77.4 (d, $^1J_{CP} = 43.5$ Hz, C of C_5H_4), 191.3 (dd, $^2J_{CP} = 113.3$ and 12.8 Hz, CO), 196.0 (dd, $^2J_{CP} = 14.4$ and 12.1 Hz, CO) ppm.

Compound 8b: Yield: 87% (0.639 g). Anal. Calc. for $FeRuC_{24}H_{36}Br_2O_2P_2$ (735.21 g mol^{-1}): C, 39.21; H, 4.94. Found: C, 39.07; H, 5.13%; ^1H NMR (CD_2Cl_2) $\delta = 1.32$ (m, 24H, $CH(CH_3)_2$), 2.61, 2.89, 2.97 and 3.30 (m, 1H each, $CH(CH_3)_2$), 4.39, 4.43, 4.47 and 4.70 (br, 2H each, C_5H_4) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) $\delta = 19.4$, 19.5, 20.5, 20.6, 20.9, 21.2, 21.4 and 21.9 (s, $CH(CH_3)_2$), 26.6, 28.1, 32.2 and 34.9 (d, $^1J_{CP} = 26.4$ Hz, $CH(CH_3)_2$), 71.9, 72.2, 72.4 and 74.8 (d, $^2J_{CP} = 5.3$ Hz, CH of C_5H_4), 73.5, 75.8, 76.6 and 76.7 (d, $^3J_{CP} = 8.3$ Hz, CH of C_5H_4), 78.5 and 79.0 (d, $^1J_{CP} = 44.7$ Hz, C of C_5H_4), 192.5 (dd, $^2J_{CP} = 110.3$ and 12.1 Hz, CO), 196.5 (dd, $^2J_{CP} = 14.3$ and 11.3 Hz, CO) ppm.

4.4. General procedure for the catalytic transfer hydrogenation of acetophenone

Under inert atmosphere, acetophenone (5 mmol), the ruthenium catalyst precursor (0.02 mmol; 0.4 mol% of Ru), and 45 ml of propan-2-ol were introduced into a Schlenk tube fitted with a condenser and heated at 82 °C for 10 min. NaOH was then added (5 ml of a 0.096 M solution in propan-2-ol; 9.6 mol%). The course of the reaction was monitored by regular sampling and analysis by gas chromatography. 1-Phenylethanol and acetophenone were the only products detected in all cases. The identity of the resulting 1-phenylethanol was assessed by comparison with commercially available pure sample.

4.5. General procedure for the catalytic cycloisomerization of (Z)-3-methyl-2-penten-4-yn-1-ol

(Z)-3-Methylpent-2-en-4-yn-1-ol (5 mmol) and the corresponding ruthenium catalyst precursor (0.05 mmol; 1.0 mol% of Ru) were introduced into a sealed tube under inert atmosphere. The reaction mixture was then heated at 75 °C for the indicated time (see Table 4). The course of the reaction was monitored by regular sampling and analysis by gas chromatography. 2,3-Dimethylfuran and (Z)-3-methylpent-2-en-4-yn-1-ol were the only products detected in all cases. The identity of the resulting 2,3-dimethylfuran was assessed by comparison with a commercially available pure sample.

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