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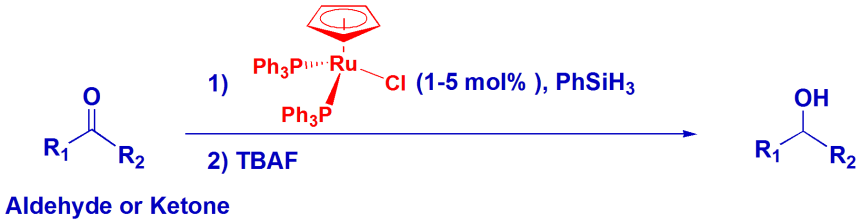
Graphical abstract



Cyclopentadienyl-Ruthenium(II) Complexes as Efficient Catalysts for the Reduction of Carbonyl Compounds

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Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal, Tel: 351 218419264; Fax: 351 218464455, anacristinafernandes@tecnico.ulisboa.pt

Abstract – This work reports the reduction of a large variety of aldehydes and ketones with the system $PhSiH_3$/$[CpRu(PPh_3)_2Cl]$ in good to excellent yields and high chemoselectivity. The catalyst $[CpRu(PPh_3)_2Cl]$ can be used in at least 12 catalytic cycles with excellent catalytic activity and several substrates were reduced under solvent free conditions.

Keywords: reduction, carbonyl compounds, alcohols, CpRu(II) complexes, silanes.

1.Introduction

Alcohols are important building blocks for the synthesis of a number of pharmaceuticals, agrochemicals and fine chemicals. The reduction of carbonyl compounds to yield primary and secondary alcohols is a very desirable reaction, since carbonyl compounds are among the most abundant starting materials for the synthetic chemist. Therefore, the development of new methodologies for the chemoselective reduction of carbonyl groups remains a challenge in organic synthesis.

Among the large variety of catalysts reported in the literature for the reduction of carbonyl compounds, the use of ruthenium complexes has received significant attention. For example, several ruthenium complexes have been employed as catalysts for the hydrogenation of carbonyl compounds, providing an efficient access to the corresponding alcohols.[1-4]

Transfer hydrogenation of carbonyl compounds catalyzed by ruthenium complexes with 2-propanol is convenient in large scale synthesis since there is no need to employ a high hydrogen pressure or to use hazardous reducing agents.[5-8]

The hydrosilylation is also an important methodology for the reduction of carbonyl compounds, producing initially a silyl ether which can easily be hydrolyzed to the corresponding alcohol. Due to its safety and operational simplicity, the catalytic hydrosilylation of carbonyl compounds has recently become an important alternative as a reduction strategy. In contrast to the other reduction methodologies, ruthenium complexes have not been widely used as catalysts in the hydrosilylation of carbonyl compounds.[9-12]

Cyclopentadienyl-ruthenium(II) complexes have been the subject of investigation by many research groups during past couple of decades not only because of their potential as catalysts[13-16] but also due to their strong anticancer activity.[17-20]

In continuation of our work about the hydrosilylation of carbonyl compounds catalyzed by molybdenum[21,22] and rhenium[23] complexes, here we report a novel methodology for the efficient reduction of aldehydes and ketones with silanes catalyzed by cyclopentadienyl ruthenium (II) complexes.

2.Results and discussion

The reduction of the test substrate 4-(methylthio)benzaldehyde was investigated with different CpRu(II) complexes, silanes and solvents. Initially, the reduction of 4-(methylthio)benzaldehyde was explored with different CpRu(II) complexes (1 mol%) (Figure 1) with phenylsilane at 80 ºC under solvent free conditions. All catalysts afforded the alcohol as the major product and the silyl ether as the minor one in 20-35% yields. After hydrolysis of the silyl ether with tetrabutylammonium fluoride (TBAF), 4-(methylthio)benzyl alcohol was obtained in excellent yields. The complex [CpRu(PPh_3)$_2$Cl] **1** (1 mol%) proved to be the best catalyst for this reduction, producing the corresponding benzyl alcohol in 98% yield after 40 min (Table 1, entry 1). Using only 0.5 mol% of [CpRu(PPh_3)$_2$Cl], the reaction also afforded the alcohol in excellent yield, but required 24 h (Table 1, entry 2). At room temperature, the product was isolated in 89% yield after 24 h (Table 1, entry 3). The ruthenium complex [CpRu(dppe)Cl] **2** required 24 h to reduce the aldehyde in 95% yield (Table 1, entry 4).

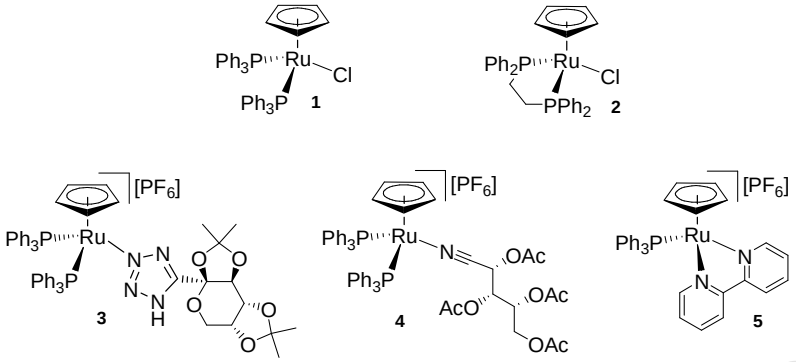
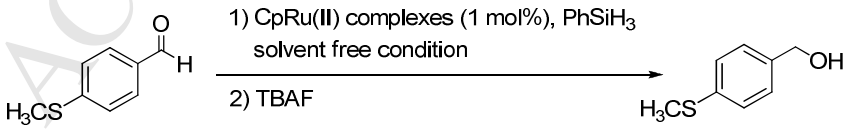


Figure 1 – Structures of the CpRu (II)

In our previous works,[17,18] we have demonstrated the excellent biological activity of cyclopentadienyl ruthenium (II) complexes **3** and **4**, containing fructose and xylose carbohydrate derivative moieties, respectively. In this work we explored the catalytic activity of these monocationic, *N*-bonded complexes in the reduction of carbonyl compounds, to study the influence of these structural changes on their catalytic activity when compared with the parent complex [CpRu(PPh_3)$_2$Cl].The reactions catalyzed by complexes **3** and **4**, were very fast (20 min-1h), producing the alcohol in good to excellent yields (Table 1, entries 5-6). The complex [RuCp(PPh_3)(2,2′-bipy][PF_6] **5** was also efficient in the reduction of the aldehyde with 84% yield after 3 h (Table 1, entry 7). Finally, in absence of catalyst was observed the formation of the alcohol in only 30% yield after 24 h (Table 1, entry 8). Complex [CpRu(PPh_3)$_2$Cl] proved to be the most efficient catalyst for the conversion of 4-(methylthio) benzaldehyde in 4-(methylthio)benzyl alcohol,within the CpRu(II) compounds tested.

Table 1

Reduction of 4-(methylthio)benzaldehyde catalyzed by different CpRu(II) complexes[a]



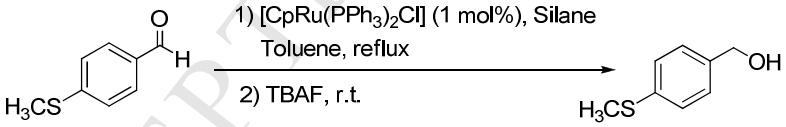
Entry	Catalyst	Catalyst (mol%)	Temp. (°C)	Time	Yield (%)[b]
1	[CpRu(PPh_3)$_2$Cl] **1**	1.0	80	40 min	98
2	[CpRu(PPh_3)$_2$Cl] **1**	0.5	80	24 h	93
3	[CpRu(PPh_3)$_2$Cl] **1**	1.0	r.t.	24 h	89

4	[CpRu(dppe)Cl] **2**	1.0	80	24 h	95
5	[RuCp(PPh_3)$_2$(TFru)][PF_6] **3**	1.0	80	1 h	98
6	[RuCp(PPh_3)$_2$NCXylAc][PF_6] **4**	1.0	80	20 min	72
7	[RuCp(PPh_3)(2,2'-bipy)][PF_6] **5**	1.0	80	3 h	84
8	Without catalyst	–	80	24 h	30

[a] The reactions were carried out with 1.0 mmol of 4-(methylthio)benzaldehyde, 1.2 mmol of $PhSiH_3$ and 1.0 mmol TBAF.
[b] Isolated yields.

The reactivity of different silanes was also evaluated in the reduction of the 4-(methylthio)benzaldehyde catalyzed by [CpRu(PPh_3)$_2$Cl] (1 mol%). The best result was obtained with $PhSiH_3$, affording the alcohol in 96% yield after 40 min (Table 2, entry 1). The silanes $PhMe_2SiH$, Ph_3SiH, Pr_3SiH, Et_3SiH and polymethylhydrosiloxane (PMHS) also produced good yields of 4-(methylthio)benzyl alcohol, but these reactions required 24 h (Table 2, entries 2-6). In absence of silane we did not observe the reduction of the aldehyde (Table 2, entry 7).

Table 2
Reduction of 4-(methylthio)benzaldehyde catalyzed by [CpRu(PPh_3)$_2$Cl] using different silanes[a]



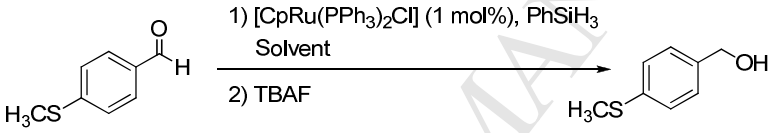
Entry	Silane	Time	(Yield)[b]
1	$PhSiH_3$	40 min	96
2	Me_2PhSiH	24 h	87
3	Ph_3SiH	24 h	83
4	PMHS	24 h	75
5	Pr_3SiH	24 h	70
6	Et_3SiH	24 h	66
7	Without silane	24 h	No reaction

[a] The reactions were carried out with 1.0 mmol of 4-(methylthio)benzaldehyde, 1.2 mmol of silane and TBAF (1.0 mmol).
[b] Isolated yields.

The reduction of 4-(methylthio)benzaldehyde catalyzed by [$CpRu(PPh_3)_2Cl$] (1 mol%) with $PhSiH_3$ was also investigated in different solvents (Table 3). The best result was obtained under solvent free conditions at 80 ºC, producing the benzyl alcohol in 98% yield after 40 min (Table 3, entry 1). The reduction performed at reflux of toluene gave the alcohol in 96% (Table 3, entry 2). At room temperature, this reaction afforded the alcohol in 89% yield, but the reaction took 24 h (Table 3, entry 3). THF was also a good solvent for this reaction, giving the benzyl alcohol in 92% yield after 2 h (Table 3, entry 4). Excellent yields of the product were also isolated in benzene, dichloromethane and chloroform (Table 3, entries 5-7). Finally, the reduction performed in acetonitrile produced the alcohol in only 21% yield (Table 3, entry 8).

Table 3

Reduction of 4-(methylthio)benzaldehyde catalyzed by [$CpRu(PPh_3)_2Cl$] in different solvents[a]



Entry	Solvent	Temp. (ºC)	Time	Yield (%)[b]
1	Neat	80	40 min	98%
2	Toluene	Reflux	40 min	96%
3	Toluene	r. t.	24 h	89%
4	THF	Reflux	2 h	92%
5	Benzene	Reflux	24 h	97%
6	CH_2Cl_2	Reflux	24 h	95%
7	$CHCl_3$	Reflux	24 h	94%
8	CH_3CN	Reflux	24 h	21%

[a] The reactions were carried out with 1.0 mmol of 4-(methylthio)benzaldehyde, 1.2 mmol of $PhSiH_3$ and TBAF (1.0 mmol).
[b] Isolated yields.

To evaluate the applicability of the system $PhSiH_3$/[$CpRu(PPh_3)_2Cl$], we tested it in the reduction of aldehydes and ketones. The reactions of liquid aldehydes were carried out under solvent free conditions at 80 ºC and the reactions of solid aldehydes were performed in toluene at reflux temperature (Table 4). The results obtained demonstrated

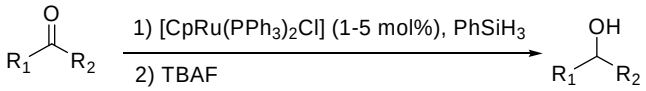
that this system was very efficient for the reduction of a large variety of aldehydes in good to excellent yields with high chemoselectivity, tolerating several of functional groups, such as -F, -Br, -CF_3, -OMe, -CN, -CO_2Me, heterocyclic ring and double bond. Other interesting results were also obtained in the reduction of hydrocinnamaldehyde in 85% (Table 4, entry 7) and in the reduction of ferrocenecarboxaldehyde in 68% yield (Table 4, entry 11).

The efficiency of the system $PhSiH_3$/[$CpRu(PPh_3)_2Cl$] was tested in the reduction of several ketones containing electron-donating and electron-withdrawing groups, producing the alcohols in good yields (Table 4). These reductions were carried out at reflux temperature of toluene and required a higher amount of [$CpRu(PPh_3)_2Cl$] (5 mol%). Curiously, this system was also appropriated for the reduction of the natural product flavanone, producing the corresponding alcohol in 77% yield after 4h 30min (Table 4, entry 15).

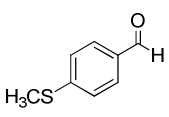
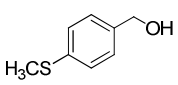
The reduction of 4-(methylthio)benzaldehyde was also carried out in the presence of 4′-(trifluoromethyl)acetophenone with the system $PhSiH_3$/[$CpRu(PPh_3)_2Cl$], affording 4-(methylthio)benzyl alcohol in 97% yield along with 5% yield of 1-(4-(trifluoromethyl)phenyl)ethanol after 4 h at 80ºC, demonstrating the selective reduction of aldehydes in the presence of ketones.

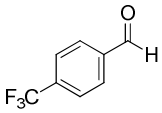
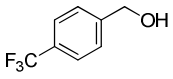
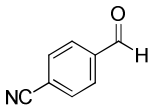
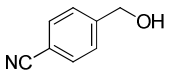
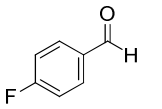
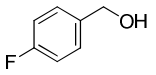
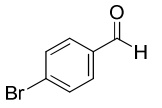
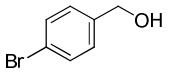
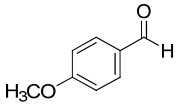
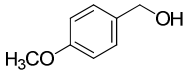
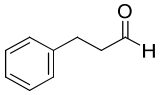
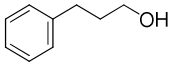
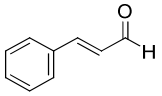
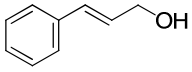
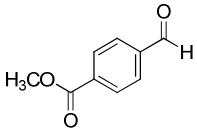
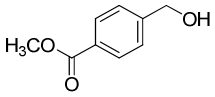
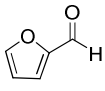
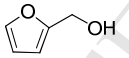
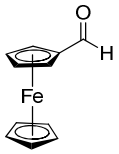
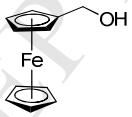
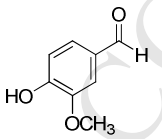
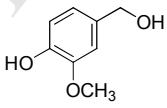
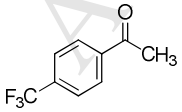
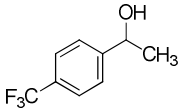
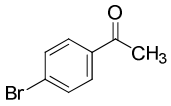
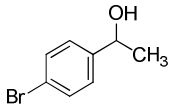
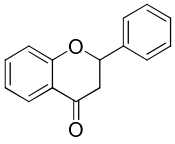
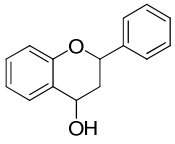
The catalytic system $PhSiH_3$/[$CpRu(PPh_3)_2Cl$] proved to be very efficient for the reduction of aldehydes and ketones with excellent chemoselectivity, however this method required higher reaction temperature than other methodologies reported in the literature.[9-12]

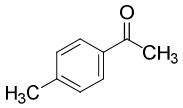
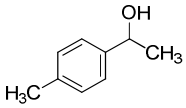
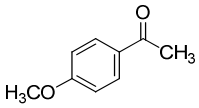
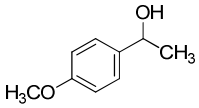
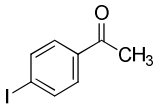
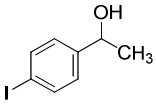
Table 4
Reduction of carbonyl compounds with the system $PhSiH_3$/[$CpRu(PPh_3)_2Cl$] [a]



Aldehyde or Ketone

Entry	Substrate	Alcohol	Solvent	Temp. (ºC)	Time	Yield (%)[b]
1			Neat	80	40 min	98

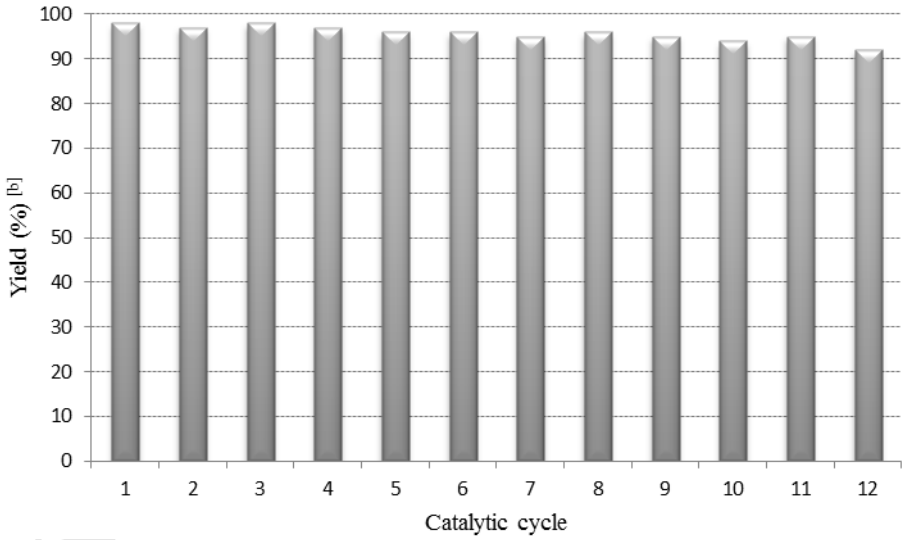
2			Toluene	Reflux	2 h 30min	97
3			Toluene	Reflux	20 h	96
4			Neat	80	1 h	93
5			Toluene	Reflux	30 min	92
6			Neat	80	1 h 30 min	88
7			Neat	80	7 h	85
8			Neat	80	40 min	82
9			Toluene	Reflux	2 h 30 min	74
10			Neat	80	1 h 30 min	71
11			Toluene	Reflux	30 min	68
12			Toluene	Reflux	24 h	63
13			Toluene	Reflux	4 h	78
14			Toluene	Reflux	3 h	77
15			Toluene	Reflux	4 h 30 min	77

16			Toluene	Reflux	2 h	75
17			Toluene	Reflux	3 h 30 min	71
18			Toluene	Reflux	2 h 30 min	61

[a] The reactions were carried out with 1.0 mmol of carbonyl compound, 1.2 mmol of $PhSiH_3$, TBAF (1.0 mmol) using 1 mol% of catalyst in the reaction of aldehydes and 5 mol% of catalyst in reduction of ketones.
[b] Isolated yields.

In order to study the possible use of the complex $[CpRu(PPh_3)_2Cl]$ (1 mol%) as catalyst in multiple cycles, we carried out successive reactions by sequential addition of fresh substrate 4-(methylthio)benzaldehyde and phenylsilane to the reaction mixture. The results obtained showed that $[CpRu(PPh_3)_2Cl]$ can be used in at least 12 catalytic cycles with excellent yields (Graphic 1).

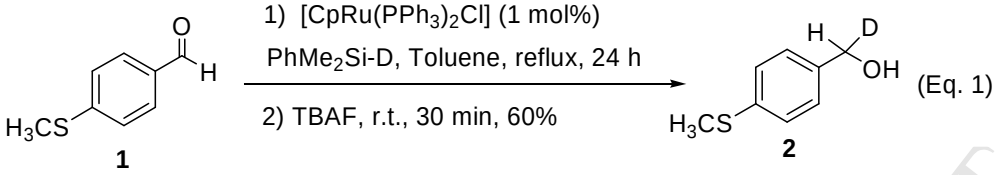
Graphic 1. Use of the catalyst $[CpRu(PPh_3)_2Cl]$ in multiple cycles[a]



[a]The reactions were carried out by successive addition of 0.5 mmol of 4-(methylthio)benzaldehyde and 0.6 mmol of $PhSiH_3$.
[b]Yields determined by ^1H NMR using mesitylene as internal standard.

We have also performed the reduction of 4-(methylthio)benzaldehyde with deuterated dimethylphenylsilane (Me_2PhSiD) catalyzed by $[CpRu(PPh_3)_2Cl]$ (Eq. 1). In the ^1H NMR spectrum of the deuterated alcohol **2**, the signal at δ 4.60 ppm integrates only one

proton, which is consistent with the reduction of the carbonyl to the corresponding methylene group and the incorporation of one deuterium atom in alcohol **2**.



(Eq. 1)

This result also suggests that the mechanism for the reduction of carbonyl compounds with silanes catalyzed by [CpRu(PPh_3)$_2$Cl] should involve the activation of the silane by the catalyst, with formation of a hydride that reduces the carbonyl group.

3. Conclusion

We report a novel procedure for the reduction of carbonyl compounds catalyzed by CpRu(II) complexes using a silane as reducing agent. The system $PhSiH_3$/[CpRu(PPh_3)$_2$Cl] proved to be very efficient for the reduction of a large variety of aldehydes and ketones in good to excellent yields with high chemoselectivity, tolerating a large range of functional groups such as -CO_2R, -CN, -CF_3, -F, -Br, -OMe, -SMe, heterocyclic ring and double bond. Furthermore, this procedure has the advantages that many of the substrates can be reduced under solvent free conditions and the catalyst can be used in at least 12 catalytic cycles with excellent catalytic activity. This work demonstrates that cyclopentadienyl-ruthenium(II) complexes activate the silanes and they are good catalysts for the reduction of carbonyl compounds.

Further studies to explore the catalytic activity of other CpRu(II) complexes as well to extend this methodology to the reduction of other substrates are now under investigation in our group.

4. Experimental section

4.1. General information

All the reactions were carried out under air atmosphere and without any dry solvents. Carbonyl compounds and silanes were obtained from commercial suppliers and were used without further purification. The catalysts [CpRu(PPh_3)$_2$Cl],[24] [CpRu(dppe)Cl],[24] [RuCp(PPh_3)(2,2′-bipy][PF_6],[25] [RuCp(PPh_3)$_2$(TFru)][PF_6],[18]

$[RuCp(PPh_3)_2NCXylAc][PF_6]$,[17] and $PhMe_2SiD$[26] were prepared according to literature procedures. Flash chromatography was performed on MN Kieselgel 60M 230-400 mesh. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance II^+ 400 MHz and 300 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard.

4.2 General procedure for the reduction of liquid aldehydes with the system $PhSiH_3/[CpRu(PPh_3)_2Cl]$

To a solution of $[CpRu(PPh_3)_2Cl]$ (1 mol%) and liquid aldehyde (1.0 mmol) was added $PhSiH_3$ (1.2 mmol). The reaction mixture was stirred at 80 ºC under an air atmosphere (the reaction times are indicated in Table 4). Then, TBAF (1.0 mmol) was added and the reaction mixture was stirred at room temperature during 30 minutes. After evaporation, the reaction mixture was purified by silica gel column chromatography with ethyl acetate:*n*-hexane (1:3) to afford the corresponding alcohols.

4.3 General procedure for the reduction of solid aldehydes with the system $PhSiH_3/[CpRu(PPh_3)_2Cl]$

To a solution of $[CpRu(PPh_3)_2Cl]$ (1 mol%) and solid aldehyde (1.0 mmol) in toluene (3 ml) was added $PhSiH_3$ (1.2 mmol). The reaction mixture was stirred at reflux temperature under an air atmosphere (the reaction times are indicated in Table 4). Then, TBAF (1.0 mmol) was added and the reaction mixture was stirred at room temperature during 30 minutes. After evaporation, the reaction mixture was purified by silica gel column chromatography with ethyl acetate:*n*-hexane (1:3) to afford the corresponding alcohols.

4.4 General procedure for the reduction of ketones with the system $PhSiH_3/[CpRu(PPh_3)_2Cl]$

To a solution of $[CpRu(PPh_3)_2Cl]$ (5 mol%) and ketones (1.0 mmol) in toluene (3 ml) was added $PhSiH_3$ (1.2 mmol). The reaction mixture was stirred at reflux temperature under an air atmosphere (the reaction times are indicated in Table 4). Then, TBAF (1.0 mmol) was added and the reaction mixture was stirred at room temperature during 30 minutes. After evaporation, the reaction mixture was purified by silica gel column chromatography with ethyl acetate:*n*-hexane (1:3) to afford the corresponding alcohols.

4.5 NMR characterization of products

Table 4, entry 1: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.31-7.25 (m, 4H), 4.65 (s, 2H), 2.49 (s, 3H), 1.61 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 138.0, 137.9, 127.8, 127.0, 65.1, 16.1 ppm.

Table 4, entry 2: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.58 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 2H), 2.57 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 144.9, 132.4, 130.8, 130.0, 129.7, 128.9, 127.0, 126.9, 125.6, 125.5, 125.4, 125.3, 122.9, 116.2, 64.4 ppm.

Table 4, entry 3: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.59 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 4.71 (s, 2H), 2.88 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 146.7, 132.2, 127.0, 119.0, 110.8, 63.9 ppm.

Table 4, entry 4: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.33-7.30 (m, 2H), 7.03 (t, *J* = 8.8 Hz, 2H), 4.63 (s, 2H), 1.94 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 163.6, 161.2, 136.7, 136.7, 128.9, 128.8, 115.6, 115.4, 64.7 ppm.

Table 4, entry 5: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.49 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.66 (d, *J* = 4.8 Hz, 2H), 1.67 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 139.9, 131.8, 128.7, 121.6, 64.8 ppm.

Table 4, entry 6: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.29 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.61 (s, 2H), 3,82 (s, 3H), 2.08 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 159.3, 133.3, 1128.7, 114.0, 65.0, 55.4 ppm.

Table 4, entry 7: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.31-7.17 (m, 5H), 3.68 (t, *J* = 6.4 Hz, 2H), 2,71 (t, *J* = 7.2 Hz, 8.0 Hz, 2H), 1,93-1.87 (m, 2H), 1.43 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 141.9, 128.5, 128.4, 125.9, 62.2, 34.3, 32.1 ppm.

Table 4, entry 8: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.38 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 7.6 Hz, 2H), 7.26-7.24 (m, 1H), 6.60 (d, *J* = 16 Hz, 1H), 6.39-6.32 (m, 1H), 4.31 (dd, *J* = 1.2 Hz, 4.4 Hz, 2H), 1.78 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 136.8, 131.2, 128.7, 128.6, 128.5, 128.4, 127.8, 126.6, 63.8 ppm.

Table 4, entry 9: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.98 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 4.73 (s, 2H), 3.89 (s, 3H), 2.46 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 167.2, 146.2, 129.9, 129.3, 126.6, 64.7, 52.2 ppm.

Table 4, entry 10: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.39 (t, *J* = 0.8 Hz, 1H), 6.32-6.33 (m, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 4.56 (s, 2H), 2.61 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 154.2, 142.5, 110.4, 107.6, 56.9 ppm.

Table 4, entry 11: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 4.33 (s, 2H), 4.24 (s, 2H), 4.18 (s, 7H), 1,55 (brs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 88.6, 68.5, 68.4, 68.0, 60.9 ppm.

Table 4, entry 12: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 6.92-6.85 (m, 3H), 5.62 (brs, 1H), 4.60 (s, 2H), 3.90 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 146.8, 145.3, 133.1, 120.4, 114.4, 110.1, 65.6, 56.1 ppm.

Table 4, entry 13: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.55 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 4.83 (q, *J* = 8.0 Hz, 1H), 3.11 (brs, 1H), 1.42 (d, *J* = 8.0Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 149.8, 125.8, 125.6, 125.5, 125.4, 125.3, 69.8, 25.3 ppm.

Table 4, entry 14: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.41 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.74 (q, *J* = 8.0 Hz, 1H), 2,79 (brs, 1H), 1.38 (d, *J* = 8.0 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 144.8, 131.5, 127.2, 121.1, 69.6, 25.2 ppm.

Table 4, entry 15: ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ: 7.50 (d, *J* = 8.0 Hz, 1H), 7.45-7.36 (m, 4H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H) , 6.89 (d, *J* = 6.0 Hz, 1H), 5.19-5.10 (m, 2H), 2.52 (dd, *J* = 4.0 Hz, 1H), 2.15 (q, *J* = 12.0 Hz, 1H), 1.72 (t, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 154.5, 140.5, 129.2, 128.7, 128.2, 127.0, 126.1, 125.7, 121.0, 116.7, 76.8, 65.8, 40.0 ppm.

Table 4, entry 16: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.23 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.82 (q, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 2.07 (brs, 1H), 1.45 (d, *J* = 8.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 137.2,129.2, 125.5, 70.3, 25.2, 21.2 ppm.

Table 4, entry 17: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.25 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 4.79 (q, *J* = 4.0 Hz, 1H), 3.76 (s, 3H), 2.30 (brs, 1H), 1.43 (d, *J* = 8.0 Hz,

3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 138.1, 126.7, 113.9, 69.9, 55.3, 25.1 ppm.

Table 4, entry 18: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.62 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.75 (q, *J* = 4.0 Hz, 1H), 2.60 (brs, 1H), 1.39 (d, *J* = 4.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3, 137.5, 127.5, 125.4, 69.7, 25.3 ppm.

4.6 Use of the catalyst [CpRu(PPh$_3$)$_2$Cl] in several catalytic cycles

To a solution of [$CpRu(PPh_3)_2Cl$] (1 mol%) and 4-(methylthio)benzaldehyde (0.5 mmol) was added $PhSiH_3$ (0.6 mmol). The reaction mixture was stirred at 80 ºC under an air atmosphere. The reaction mixture was cooled and the yield was determined by ^{1}H NMR spectroscopy using mesitylene (0.5 mmol) as the internal standard. In the next catalytic cycles, the aldehyde (0.5 mmol), phenylsilane (0.6 mmol) and mesitylene (0.5 mmol) were added to the reaction mixture and stirred at 80 ºC. The yields were determined by ^{1}H NMR spectroscopy.

4.7 Synthesis of deuterated alcohol 2

To a solution of [$CpRu(PPh_3)_2Cl$] (1 mol%) and 4-(methylthio)benzaldehyde (1.0 mmol) was added $PhMe_2SiD$ (1.2 mmol). The reaction mixture was stirred at 80 ºC during 24 h under an air atmosphere. Then, TBAF (1.0 mmol) was added and the reaction mixture was stirred at room temperature during 30 minutes. After evaporation, the reaction mixture was purified by silica gel column chromatography with ethyl acetate:*n*-hexane (1:3), giving the deuterated alcohol **2** in 60% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.28-7.23 (m, 4H), 4.60 (s, 1H), 2.47 (s, 3H), 1.89 (brs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.9, 137.8, 127.8, 127.0, 64.8, 16.1 ppm.

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Highlights

- $CpRu(PPh_3)_2Cl$ is highly efficient catalyst for the reduction of carbonyl compounds
- The reductions can be performed under solvent free conditions
- The catalyst $CpRu(PPh_3)_2Cl$ can be use in 12 catalytic cycles with excellent activity