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Ruthenium Phenylindenyl Complex as an Efficient Transfer Hydrogenation Catalyst

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Abstract: An efficient and green protocol for the transfer hydrogenation of carbonyl and imine compounds is presented. The transformations are catalysed by the inexpensive and easily synthesised complex [RuCl(PPh_3)(3-phenylindenyl)]. Its catalytic activity was compared to that of the most commonly encountered ruthenium complexes in transfer hydrogenation reactions involving several protypical substrates.

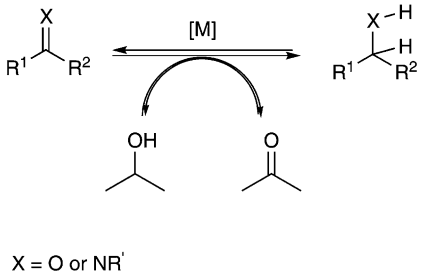
Keywords: alcohols; green chemistry; homogeneous catalysis; ruthenium; transfer hydrogenation

Introduction

The increasing demand for evermore-selective chemical transformations that avoid or reduce the amount of waste produced has made it important to develop new environmentally friendly synthetic assembly tools and protocols.[1] One of these "greener" processes is the transfer hydrogenation reaction. This eco-friendly methodology permits the reduction of ketones and imines to the corresponding alcohols and amines through the transfer of two hydrogen atoms from a sacrificial alcohol, usually isopropyl alcohol (Scheme 1).[2]

Numerous transfer hydrogenation systems have been reported in the literature, but most of them use expensive metals (Ir/Rh complexes)[2e,3] or poorly active and very unstable complexes (Fe complexes).[3d,4] Despite a recent report by Morris on highly active iron-based transfer hydrogenation catalysts,[5] ruthenium complexes remain to date the best compromise between price and reactivity.[3d,6]

Amongst the numerous ruthenium complexes reported[3c,7] for hydrogenation, one of the first very efficient catalysts was the complex [$Ru_2(CO)_4(\mu\text{-}H)(C_4Ph_4COHOCC_4Ph_4)$] (**1**), synthesised in 1984 by Shvo. This complex is also known as Shvo's catalyst.[8] Many applications have been reported with **1** in hydrogen transfer reactions.[9] In 2007, Frost reported an interesting variation, **3**, of [Ru(Cl)-(PPh_3)$_2$(indenyl)] (**2**),[10] first reported by Oro.[11] Complex **3** is remarkably active in transfer hydroge-



Scheme 1. Transfer hydrogenation system.

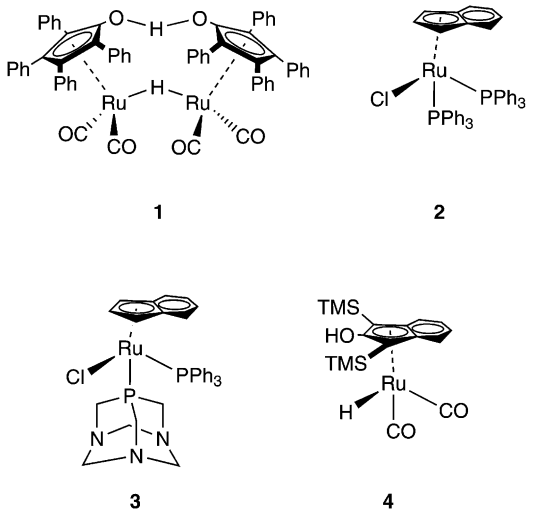
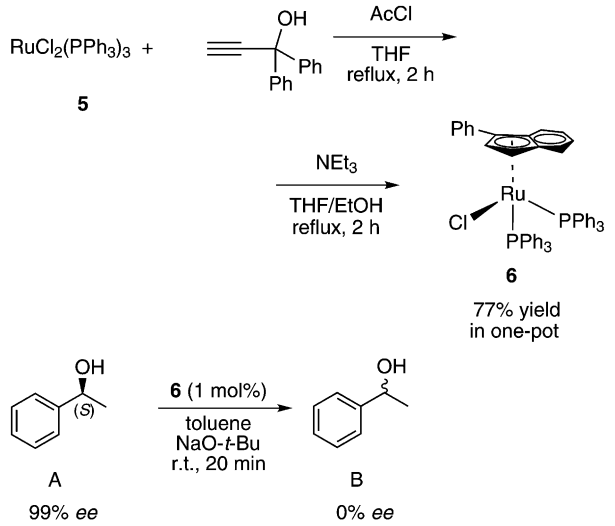


Figure 1. Ruthenium complexes for transfer hydrogenation.



Scheme 2. One-pot synthesis of complex **6** and its activity in chiral alcohol racemisation catalysis.

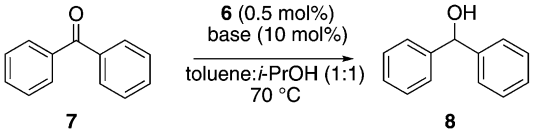
nation in formic acid. Casey has reported a novel complex (**4**) bearing an OTMS-substituted indenyl ligand, showing activity in transfer hydrogenation reactions (Figure 1).[12]

In order to achieve an efficient hydrogenation system using a relatively inexpensive metal complex, we proceeded to evaluate the catalytic activity of the complex [$RuCl(PPh_3)_2$(3-phenylindenyl)] complex (**6**) recently reported. Complex **6** can be synthesised in a straightforward manner, starting from a propargylic alcohol and [$RuCl_2(PPh_3)_3$] (**5**).[13] Complex **6** is extremely active in the alcohol racemisation reaction, which is formally a tandem hydrogenation/dehydrogenation process. Additionally, as shown before, Ru-indenyl systems have been extensively studied, displaying interesting activity in hydrogen transfer. For these reasons, we hypothesized that complex **6** could be a very active catalyst in transfer hydrogenation reactions (Scheme 2).[14]

Results and Discussion

Using the reduction of benzophenone as a benchmark reaction, the hydrogenation conditions were optimised by first screening various bases needed to assist (or not) in the activation steps leading to catalytic activity. As shown in Table 1, a base is necessary to activate the catalyst and the catalytic activity depends considerably on the base used (Table 1, entry 1). A detailed analysis allows the nature of the various tested bases to be rationalised. Stronger bases are significantly more efficient in the catalysis; for example, NaOAc is not basic enough to activate the catalyst (Table 1, entry 7), but stronger bases, such as alkoxides, show improved catalytic efficiency (Table 1, entries 8, 9, 10 and 11). The solubility of the base in the reaction medium appears to play an important role; there is a difference in activity when using NaOH, KOH or CsOH even though they have similar basicity (Table 1, entries 4, 5 and 6). Potassium hexamethylsilazane (KHMDS) was found to be the best base for the system examined (Table 1, entry 12). However, even with less expensive bases such as NaOH, the catalytic activity remains remarkably high (Table 1, entry 4).

Table 1. Base optimisation.[a]



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Entry	Base	Conv. after 1 h [%][b]	Conv. after 5 h [%][b]
1	None	0	0
2	K_3PO_4	30	45
3	Cs_2CO_3	16	25
4	NaOH	58	85
5	CsOH	25	55
6	KOH	23	30
7	NaOAc	0	6
8	NaOMe	67	78
9	NaO-*t*-Bu	71	83
10	KO-*t*-Bu	48	79
11	KO-*t*-Am	66	72
12	**KHMDS**	**75**	**91**

[a] *Reaction conditions:* benzophenone (0.25 mmol), **6** (0.5 mol%) and base (10 mol%) dissolved in 1:1 toluene/isopropyl alcohol (1 mL).

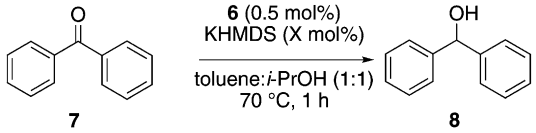
[b] Conversion determined by ^{1}H NMR from an average of at least two runs.

The loading of the base also plays an important role in terms of catalytic activity (Table 2).

KHMDS alone cannot promote transfer hydrogenation, even if used in stoichiometric amounts (Table 2, entries 1 and 2). However, varying the base loading can significantly influence the catalytic activity. In fact, high and low loadings of base led to low conversions. The best catalytic activity was achieved using 2.5 mol% of base in the reaction (Table 2, entry 6). The unusual reactivity at low loadings can be explained by the decrease of the rate of the bimolecular reaction necessary to generate the active species. On the other hand, at high loading of base, the desired alcohols react with the base forming an alkoxide that can be oxidised back to the ketone by the catalyst, as most of the newly formed alcohols are more acidic than isopropyl alcohol.

This effect is slowed down at low catalyst loadings due to high concentration of isopropyl alcohol compared to the alcohol.

Table 2. Base optimisation.[a]



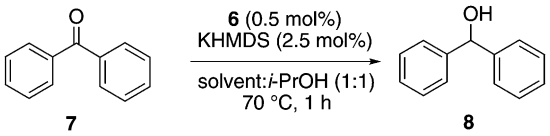
Entry	Catalyst	Base loading	Conv. [%][b]
1	none	100	0
2	none	10	0
3	**6**	100	25
4	**6**	10	70
5	**6**	5	86
6	**6**	**2.5**	**90**
7	**6**	1	0
8	**6**	0.5	0

[a] *Reaction conditions:* benzophenone (0.25 mmol), **6** (0.5 mol%), KHMDS (X mol%) dissolved in 1:1 toluene/isopropyl alcohol (1 mL).
[b] Conversion determined by ^{1}H NMR from an average of at least two runs.

The solvent choice also plays a role in defining the catalytic activity. Solvents with boiling points greater than or equal to 70 °C were considered (Table 3).

As shown above, catalyst **6** is efficient in polar and aprotic solvents, such as dimethoxyethane (DME) or 1,4-dioxane and in relatively non-polar solvents, for example cyclohexane (C_6H_{12}) or toluene (Table 3, entries 7, 8, 9 and 10.). Coordinating solvents, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and CH_3CN led to poor conversions (Table 3, entries 3, 4 and 5). Unfortunately transfer hydrogenation in water is not efficient (Table 3, entry 1). However, it is possible to use isopropyl alcohol in a green system where a relatively inexpensive and industrially acceptable[15] solvent performs also as a hydrogen source, reducing the amount of waste generated (Table 3, entry 2).

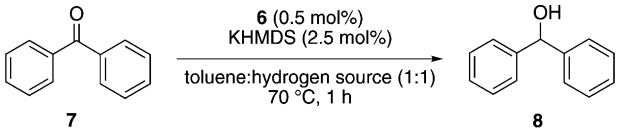
Table 3. Solvent optimisation.[a]



Entry	Solvent	Conv. [%][b]
1	H_2O	20
2	***i*-PrOH**	**93**
3	DMSO	0
4	CH_3CN	8
5	DMF	0
6	DCE	0
7	DME	79
8	toluene	90
9	dioxane	72
10	C_6H_{12}	89

[a] *Reaction conditions:* benzophenone (0.25 mmol), **6** (0.5 mol%), KHMDS (2.5 mol%) dissolved in 1:1 solvent/isopropyl alcohol (1 mL).
[b] Conversion determined by ^{1}H NMR from an average of at least two runs.

Table 4. Hydrogen source screening.[a]



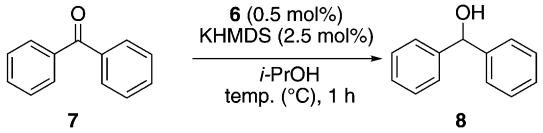
Entry	Hydrogen source	Conv. [%][b]
1	***i*-PrOH**	**90**
2	EtOH	15
3	HCOOH	0
4	H_2	0[c]

[a] *Reaction conditions:* benzophenone (0.25 mmol), complex **6** (0.5 mol%), KHMDS (2.5 mol%) dissolved in toluene (0.5 mL) and hydrogen source added.
[b] Conversion determined by ^{1}H NMR from an average of at least two runs.
[c] Reaction performed in autoclave with a continuous pressure of H_2 (2 bar).

Complex **6** was studied in the presence of different hydrogen sources, including H_2 gas (Table 4). As expected, primary alcohols are poorer hydrogen sources than secondary alcohols (Table 4, entries 1 and 2). Interestingly, complex **6** seems to be unreactive in the presence of gaseous H_2 (Table 4, entry 4). Catalyst **6** is also not active in the presence of formic acid (Table 4, entry 3).

The effect of temperature was also studied (Table 5). The results show that a minimum temperature of 40 °C is required to activate the catalyst (Table 5, entry 3). The best results were achieved

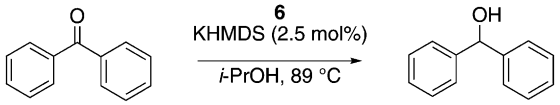
Table 5. Temperature optimisation.[a]



Entry	Temp. [°C]	Conv. [%][b]
1	**89 (reflux)**	**95**
2	70	93
3	40	52
4	rt	8

[a] *Reaction conditions:* benzophenone (0.25 mmol), **6** (0.5 mol%), KHMDS (2.5 mol%) dissolved in isopropyl alcohol (1 mL).
[b] Conversion determined by ^{1}H NMR from an average of at least two runs.

Table 6. Low catalyst loading screening.[a]



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Entry	Catalyst loading [mol%]	Time [h]	Conv. [%][b]
1	0.5	1	95
2	0.25	3	92
3	0.15	10	90
4	0.1	24	92
5	**0.05**	**48**	**96**
6	0.025	72	48

[a] *Reaction conditions:* benzophenone (0.25 mmol), **6** (X mol%), KHMDS (2.5 mol%) dissolved in isopropyl alcohol (1 mL).

[b] Conversion determined by ^{1}H NMR from an average of at least two runs.

when the reaction was heated to 89 °C (Table 5, entry 1).

With the aim of further improving the environmental impact of our process and hopefully attaining a more acceptable and greener level of catalyst use, the effect of further decreasing the catalyst loading was examined (Table 6).

This achievement would lower the process costs, not only those associated with the catalyst but also with the removal of residual ruthenium from the products. Complex **6** showed good activity, achieving almost complete hydrogenation of benzophenone (**7**) to benzhydrol (**8**) with loadings as low as 0.05 mol% in 48 h (Table 6, entry 5), reaching a maximum TON of 1920.

To place these results into context, the catalytic activity of **6** was compared with that of various ruthenium catalysts reported in the literature (Figure 2 and Table 7).

In comparison with all other ruthenium complexes examined, complex **6** was found to be the most active for the model transformation (Table 7, entry 1). Interestingly, when changing from the simple $RuCl_2(PPh_3)_3$ to complexes bearing a cyclopentadienyl or indenyl ligand (complexes **5**, **10** and **2**, respectively), the reactivity dramatically decreases (from 66% to 44% conversion), but with complex **6** that bears a 3-phenylindenyl ligand this trend is not followed. Indeed on performing this structural modification, there is an *increase* in the catalytic activity (95% conversion). This may very well be due to the electronic effect variation brought about by the presence of a phenyl substituent on the indenyl moiety, rendering the ruthenium centre slightly more electron rich. Of course, the steric mapping of the Ph-indenyl ligand being somewhat different than those of unsubstituted indenyl counterparts cannot be completely excluded as a cause for this improved catalyst activity. Various isoelectronic ruthenium complexes display low or no reactivity. Of the 16 e$^-$ species, only the

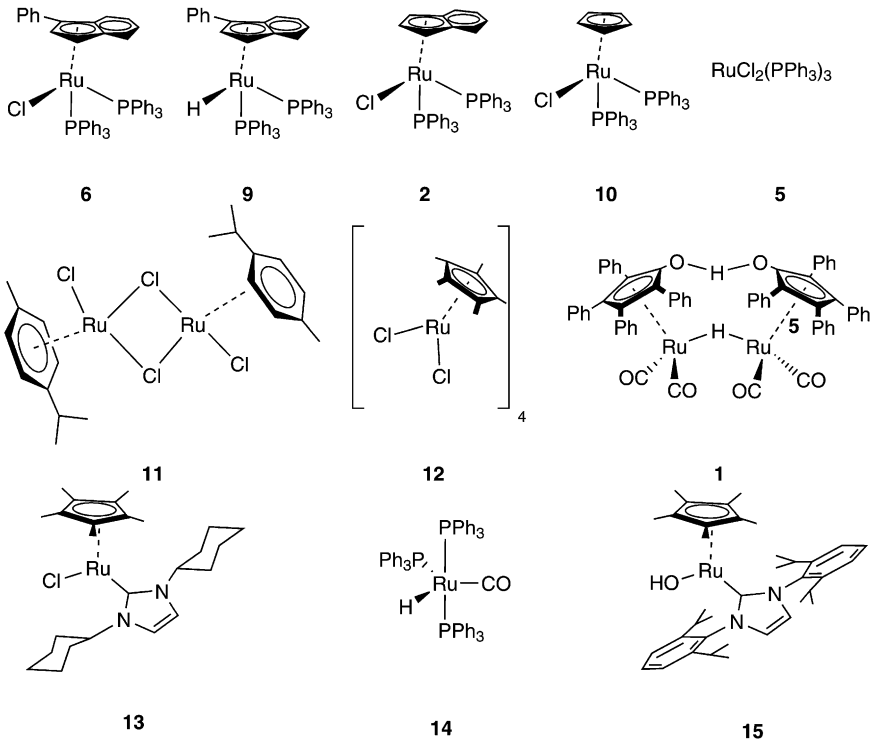


Figure 2. Ruthenium complexes used for catalyst comparison.

Table 7. Comparison of catalysts.[a]

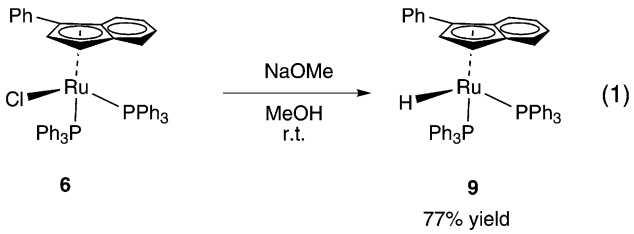
Entry	Base	Catalyst	Conv. [%][b]
1	KHMDS	**6**	95
2	none	**9**	3
3	KHMDS	**9**	53
4	KHMDS	**2**	44
5	KHMDS	**10**	62
6	KHMDS	**5**	66
7	KHMDS	**11**	15
8	KHMDS	**12**	1
9	KHMDS	**13**	53
10	none	**14**	0
11	KHMDS	**15**	0
12	KHMDS	**1**	27

[a] *Reaction conditions:* benzophenone (0.25 mmol), catalyst (0.5 mol%), KHMDS (2.5 mol%) dissolved in isopropyl alcohol (1 mL).

[b] Conversion determined by ^{1}H NMR from an average of at least two runs.

RuCl(ICy)(Cp*) (**13**)[16] complex gives comparable conversions, achieving 53% conversion to **3** in 1 h.

As a ruthenium hydride is oftentimes invoked as an active catalytic species in such hydrogenation transformations, the hydride derivative of **6**, namely **9**, was synthesised by reacting **6** with NaOMe in methanol [Eq. (1)].



6 **9**

77% yield

(1)

Unfortunately, complex **9** showed low catalytic activity with and without addition of base (Table 7, entries 2 and 3), suggesting that complex **9** is not the active species in this transformation but may very well be the catalyst resting state.[17] The active species is most likely a 16 e$^-$ hydride species bearing only one phosphine. A mechanistic study is presently ongoing to elucidate the exact nature of reaction intermediates in this transformation.

Pleasingly, catalyst **6** showed remarkable activity compared to Shvo's catalyst (**1**), one of the most often used complexes for hydrogen transfer reactions (Table 7, entries 1 and 9).[9a] Indeed, **6** reached almost complete conversion in 1 h for the model reaction, whereas **1** only achieved 30% in the same time, showing that **6** can be a viable alternative to traditional formic acid transfer hydrogenation with the Shvo catalyst.

The tolerance of the catalytic system to different substrates bearing various structural motifs was examined and these result are presented in Table 8.

Complex **6** shows very high activity in the hydrogenation of ketones, aromatic aldehydes and primary imines[18] (Table 8, entries 1–10). Remarkably, catalyst **6** surpasses the catalytic activity of Shvo's catalyst under optimized conditions in the hydrogenation of *N*-benzylideneaniline (**22**), achieving full conversion in only 1 h [TOF (**6**) = 200 h^{-1}, TOF (**1**) = 66 h^{-1}] (Table 8, entry 5).[19]

The catalytic hydrogenation system is very tolerant to substrate variations. Increasing the steric bulk of substrates causes the reaction to become more sluggish as expected, especially in the case of aliphatic substituents (Table 8, entries 12, 13 and 15). Considering electronic effects, substrates with electron-withdrawing substituents are less prone to hydrogenation, especially if the substituent is in the *para* position (Table 8, entries 16, 17, 18 and 19). Interestingly, the hydrogenation is faster for aliphatic than for aromatic ketones (Table 8, entries 1, 2, 8 and 9). In the case of aldehydes, complex **6** showed high activity with aromatic substrates.

Conclusions

In conclusion, we report here a novel system capable of mediating the hydrogenation of ketones and imines using isopropyl alcohol as a hydrogen source. This system shows high activity for the hydrogenation of aldehydes, ketones and imines, and good compatibility with various bases and substrate functional groups. To the best of our knowledge **6** represents one of the most efficient ruthenium arene transfer hydrogenation catalysts reported to date. Further studies are ongoing in our laboratory to evaluate the catalytic potential of **6** in related reactions.

Experimental Section

General Considerations

All ketones, **22** and solvents were purchased from commercial suppliers and used as received. Complexes **6, 10, 12, 13, 14** and **15** were synthesised according to previously described procedures.[14,16b,20] Aldehydes **18** and **20** were purified according to the reported procedure.[21] Imines **24** and **26** were synthesised according to the procedure reported in the literature.[22] Complexes **1** and **11** were purchased from commercial suppliers and used as received. Flash column chromatography was performed on silica gel 60 (230–400 mesh). ^{1}H, ^{13}C, and ^{31}P NMR spectra were acquired on an Avance II 400 MHz spectrometer. All solvents except for water were purchased from commercial suppliers as anhy-

Table 8. Scope of the transfer hydrogenation reactions.[a]

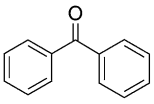
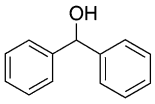
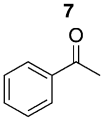
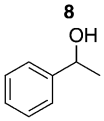
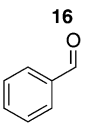
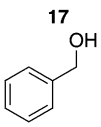
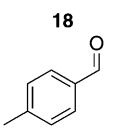
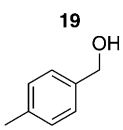
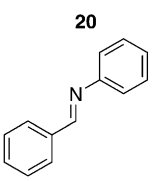
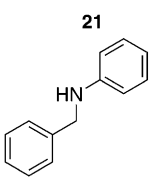
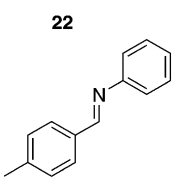
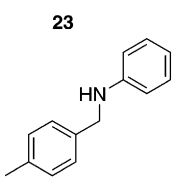
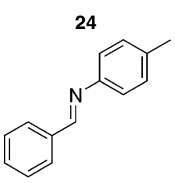
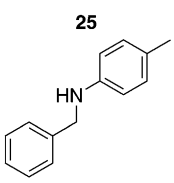
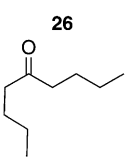
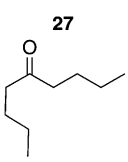
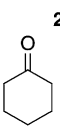
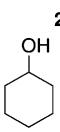
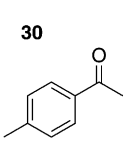
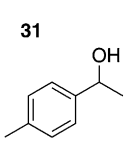
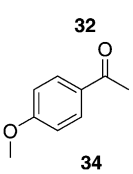
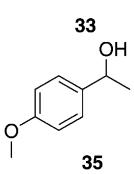
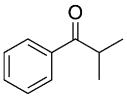
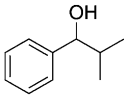
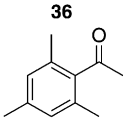
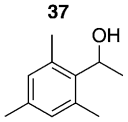
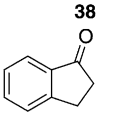
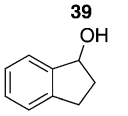
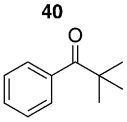
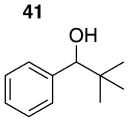
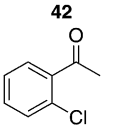
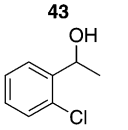
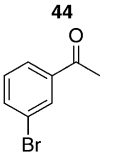
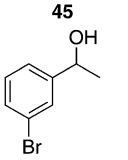
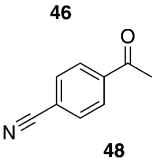
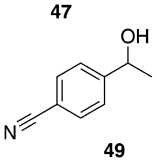
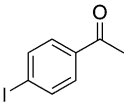
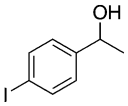
Entry	Time [h]	Substrate	Product	Conv. [%][b]	Yield [%][c]
1	1			95	93
2	1	**7** 	**8** 	94	88
3	1	**16** 	**17** 	92	85
4	1	**18** 	**19** 	>99	98
5	1	**20** 	**21** 	95	86
6	1	**22** 	**23** 	88	83
7	1	**24** 	**25** 	80	75
8	1	**26** 	**27** 	>99	81
9	1	**28** 	**28** 	>99	78
10	1	**30** 	**31** 	90	87
11	1	**32**  **34**	**33**  **35**	73	66

Table 8. (Continued)

Entry	Time [h]	Substrate	Product	Conv. [%][b]	Yield [%][c]
12	3			90	67
13	5	**36** 	**37** 	89	69
14	5	**38** 	**39** 	80	77
15	14	**40** 	**41** 	75	62
16[d]	14	**42** 	**43** 	89	87
17[d]	14	**44** 	**45** 	64	41
18[d]	14	**46** 	**47** 	34	n.d.
19[d]	14	**48** 	**49** 	11	n.d.
		50	**51**		

[a] *Reaction conditions:* substrate (1 mmol), **6** (0.5 mol%), KHMDS (2.5 mol%) dissolved in isopropyl alcohol (2 mL).
[b] Conversion determined by ^{1}H NMR from an average of at least two runs.
[c] Isolated yield.
[d] Catalyst loading increased to 1 mol%.

drous and used as received. Distilled water was degassed prior to use.

General Procedure for the Hydrogenation of Ketones, Imines and Aldehydes

In a vial fitted with a screw cap, the substrate (1 mmol), catalyst **1** (0.005 mmol, 4.4 mg) and KHMDS (0.025 mmol, 4.8 mg) were charged inside the glovebox and dissolved in isopropyl alcohol (2 mL). The solution was stirred at 89 °C for the period of time indicated in Table 8. The reaction was monitored by ^{1}H NMR analysis of aliquots. The solvent was removed under vacuum, and the product was purified by silica gel chromatography (pentane/ethyl acetate from 98:2 to 50:50).

General Procedure for Optimisation of Reactions and Catalyst Comparison

In a vial fitted with a screw cap, benzophenone (**7**) (0.25 mmol), catalyst (0.00125 mmol) and the proper amount of base were charged inside the glovebox and dissolved in organic solvent (0.5 mL). To this mixture the hydrogen source was added (0.5 mL). The solution was stirred at the given temperature for 1 h hour (in the case of Table 1 the reactions are analysed for 1 h and 5 h). The solvent was

removed under vacuum and the crude reaction mixture was analysed by ^{1}H NMR.

Low Catalyst Loading Procedure

In a vial fitted with a screw cap, inside the glovebox, an aliquot of **6**, from a stock solution of catalyst **6** in dichloromethane (2.6 mg in 5 mL) was added. The solvent was removed under vacuum and the benzophenone (0.25 mmol), KHMDS (0.0625 mmol, 1.2 mg) were added and dissolved in isopropyl alcohol (1 mL). The solution was stirred at 89 °C for a period of time indicated in Table 6. The solvent was removed under vacuum and the crude reaction mixture was analysed by ^{1}H NMR.

Synthesis of [RuH(PPh$_3$)$_2$(3-phenylindenyl)] (9)

In a round-bottomed flask, inside an argon-filled glovebox, complex **6** (0.47 mmol, 400 mg) and NaOMe (0.47 mmol, 25 mg) were added and dissolved in methanol (23.5 mL). The reaction mixture was stirred at room temperature for 3 h. The suspension was filtered and the solid collected was washed with methanol (2×5 mL) and then with pentane (5 mL). The solid was collected and dried under vacuum, affording **9** as yellow solid; yield: 277 mg (77%). ^{1}H NMR (300 MHz, C_6D_6): $\delta = -14.33$ (t, $J = 31.2$ Hz, 1H) 4.58–4.66 (m, 1H) 6.03 (s, 1H) 6.23 (dd, $J = 8.2$, 3.6 Hz, 2H) 6.74–6.82 (m, 7H) 6.83–6.96 (m, 15H) 6.97–7.12 (m, 12H) 7.31 (ddd, $J = 9.8$, 7.1, 2.2 Hz, 6H) 7.81 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 74.24$–75.14 86.79–87.69 88.72–89.49 106.63–107.08 110.88 119.87 125.27 125.46 125.82 126.97 127.08 127.35 127.47 127.90 128.55 129.52 139.19 139.43 139.94 140.85 141.37; ^{31}P NMR (121 MHz, C_6D_6): $\delta = 62.78$ (d $J = 25.5$ Hz) 65.65 (d $J = 25.5$ Hz); anal. calcd. for $C_{51}H_{41}P_2Ru$: C 74.99, H 5.06; found: C 74.83, H 4.95;

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