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Ruthenium Containing Phosphinesulfonate Chelate for Hydrogenation of Arylketones

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Abstract: Various ruthenium(II) complexes containing phosphine sulfonate chelate have been synthesized. Arene free complexes were found to be efficient during the base free hydrogenation of various arylketones whereas the arene containing precatalysts required the presence of amine as additive. The seminal asymmetric hydrogenation by using the new Sulfo-Binepine ligand was also investigated as well as the possible intervention of a dihydride species. **Introduction**

The development of new complexes, catalytic systems operating through different catalytic pathways is an appealing area of research in order to discover new selective transformations, improve established methodologies and overcome patented processes.^[1] Among the important target field, hydrogenation and transfer hydrogenation have attracted considerable interest for their applications to access various fine chemicals and pharmaceuticals from unsaturated raw materials.^[2] In this regard, transition metal complexes catalyzed hydrogenation of aromatic ketones has become the method of choice to produce optically pure secondary alcohols at industrial scale.^[3]

Shvo's catalyst was one of the first ruthenium complex to efficiently hydrogenate ketones to alcohols.^[4] The breakthrough came from Noyori with the use of ruthenium complex containing diphosphine diamine ligands affording excellent enantioselectivities for the asymmetric hydrogenation of unfunctionalized aromatic ketones.^[5] [Cp*Ru]-based catalysts featuring diamines or aminoalcohols were also efficiently used in asymmetric ketone hydrogenation.^[6] Similarities arise from these catalytic systems where an acidic proton is held by the ligand through the formation of a hydroxyl or a N-H functionality and the hydride bound to the ruthenium allowing the ionic hydrogenation of the carbonyl group through a concerted outer sphere mechanism.^[7,8] Therefore efforts have been devoted to the development of a plethora of bifunctional catalysts featuring nitrogen ligands to play with the famous "N-H effect".^[9-16] Surprisingly, few reports deal with the use of non nitrogen based catalysts operating through different pathways for the hydrogenation of arylketones.^[17-18] Phosphine oxazolines have emerged as an excellent alternative to the bifunctional catalyst.^[18c-d,h,j] Nishiyama reported a cyclometallated ruthenium complex, which afforded promising enantioselectivities for the hydrogenation of aromatic ketones.^[18c,g] Recently, we demonstrated that well-defined ruthenium(II) and iridium(III) containing phosphine sulfonate as chelating ligand allowed the C(3)-H functionalization of amines with alcohols or aldehydes via oxidant free hydrogen autotransfer processes.^[19] Phosphinesulfonate chelates featuring either aryl, alkyl,^[20] ferrocenyl^[21] phosphines and more recently diazaphospholidine- and NHC-sulfonates^[22,23] have attracted considerable interest in polymerization.^[20-26] These bidentate ligand-containing complexes exhibit unique behaviour due to the different electronic properties of the phosphine and the sulfonate but more importantly sulfonate moiety can adopt different coordination mode depending on the interaction with other ligands and Lewis or Brønsted acids (Figure 1).^[24-26] Interestingly, they have also found application in hydroformylation,^[27] Heck coupling,^[28] allylation,^[29]

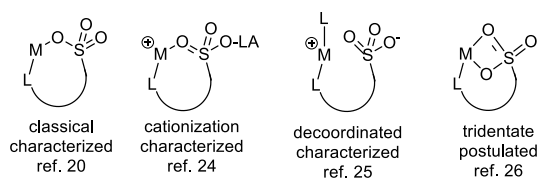


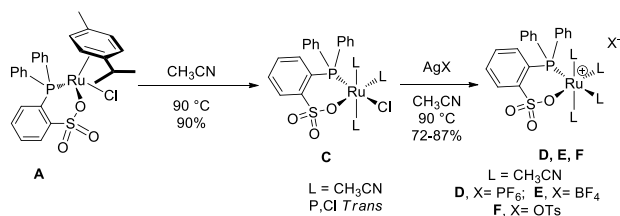
Figure 1. Different modes of coordination of the 6-membered sulfonate chelates.

conjugate additions^[30] and attractive Suzuki-Miyaura reactions in water.^[31] However, nothing is known about these ligands and on the effect of the sulfonate functionality in hydrogenation of polar bonds.

Herein we present our preliminary investigations on ruthenium(II) catalysts containing a phosphinesulfonate chelating ligand to hydrogenate arylketones.

Results and Discussion

The arene free ruthenium(II) complex **C** was prepared upon heating our previously described (*p*-cymene)ruthenium(II) complex **A**^[19a] in acetonitrile (Scheme 1). Complete characterization by room temperature NMR spectroscopy and further X-ray analysis of **C** revealed the formation of one complex and shows that the ruthenium centre is coordinated by three acetonitrile ligands in an octahedral environment (Figure 2). The structure also showed a *trans*



Scheme 1. Preparation of arene free ruthenium(II) complexes featuring phosphinesulfonate ligand from complex **A**.

relationship between the phosphorus and the chloride atoms. In the presence of silver salts such as AgOTs, AgPF₆, and AgBF₄, cationization of **C** occurred in acetonitrile solution to afford complexes **D-F** in up to 87% isolated yield (Scheme 1). The structure of the tetrakis(acetonitrile) complex **F** featuring a tosylate counteranion was confirmed by X-ray single crystal analysis (Figure 2). **B** the analog of **A** but featuring hexamethylbenzene was easily obtained from the treatment of the deprotonated diphenylphosphinosulfonate with [Ru(η^6 -C₆Me₆)Cl₂]₂.^[19a]

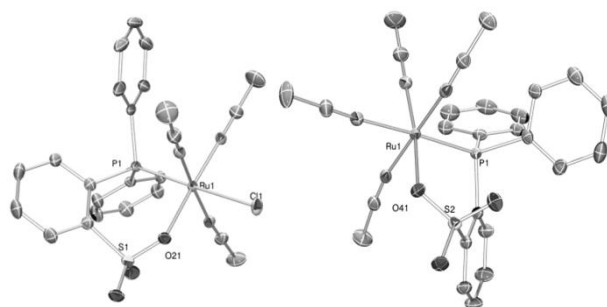


Figure 2. Molecular structures of arene free **C** (CCDC 927216) and **F** (CCDC 927217).

The mineral base free hydrogenation of acetophenone was selected as benchmark reaction for optimization and screening of the ruthenium phosphinesulfonate based catalysts (Table 1). We first examined the additive free catalytic activity of the well-defined prepared complexes in various solvents. In all cases, very low conversions and low selectivities were obtained with the neutral complex **A** containing an η^6 -arene ligand (entry 1). These

Table 1. Catalytic hydrogenation of acetophenone **1a**.

Entry ^[a]	Catalyst	Solvent	Pressure (bar)	Additives (mol%)	Yield ^[b] (%)
1	A	MeOH	30	None	6
2	A	MeOH	10	Et ₃ N (2)	9
3	A	MeOH	10	Et ₃ N (10)	86
4	A	MeOH	30	Et ₃ N (10)	98
5	A	THF	30	Et ₃ N (10)	2
6	A	CH ₂ Cl ₂	30	Et ₃ N (10)	1

7	A	Toluene	30	Et ₃ N (10)	1
8	A	MeOH	30	Pyridine (10)	99
9	A	MeOH	30	EtMe ₂ N (10)	93
10	A	MeOH	30	PPh ₃ (2)	35
11	A	MeOH	30	PPh ₃ (4)	15
12	A	MeOH	30	PPh ₃ (6)	0
13	B	MeOH	30	Et ₃ N (10)	13
14	B	MeOH	30	Pyridine (10)	97
15	C	MeOH	30	None	95
16	C	MeOH	30	Et ₃ N (10)	99
17	C	MeOH	30	PPh ₃ (2)	33
18	D	MeOH	30	None	99

[a] All reactions were carried with 1/**A-D** in 1/0.02 molar ratio for 16 h under the indicated hydrogen pressure using a thermostated oil bath at 60 °C. [b] Yield determined by ¹H NMR and GC.

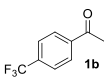


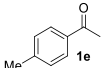

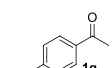
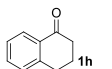

results might be explained by the stability of the P,O-chelate under hydrogen pressure and the difficult generation of cationic intermediates arising from the dissociation of the Ru-Cl bond, which further allows the formation of hydride species. In contrast, arene free neutral or cationic complexes such as **C** and **D** containing labile acetonitrile ligands which might allow ketone coordination afforded almost complete conversions and exclusive formation of 1-phenylethanol without any additives (entries 15 and 18). To overcome the initially supposed difficult dissociation of the Ru-Cl in **A**, we then evaluated the effect of external amine as additive.^[32] The latter would assist the formation of cationic species by ligand exchange after dissociation of the Ru-Cl bond. Indeed, substantial improvements were obtained by increasing the amount of triethylamine from 2 to 10 mol% reaching 86% yield of 1-phenylethanol at 10 bar H₂ pressure (entries 2 and 3). Increasing the hydrogen pressure up to 30 bar allowed complete conversion with 98% of alcohol **2a** (entry 4). Using triethylamine as additive, the nature of the solvent was found to be crucial; solvents with low dielectric constant and non protic solvents were unsuitable preventing the hydrogenation of acetophenone (entries 5-7). Other amines were also evaluated and Me₂EtN and an aromatic amine such as pyridine were also successfully used and gave phenylethanol in 93 and 99% yield, respectively (entries 8 and 9). Conversions were found to be strongly dependent on the nature of the η⁶-arene ligand and lower conversion in the presence of triethylamine was obtained by replacing *p*-cymene by hexamethylbenzene in catalyst **B**. However the replacement of triethylamine by pyridine as additive led to complete formation of 1-phenylethanol suggesting two distinct reaction pathways as a function of the nature of the amine (entries 13 and 14). Finally, the use of 2 mol% of triphenylphosphine as additive in the absence of amine afforded 35% yield whereas higher loading prevented hydrogenation (entries 10-12). Similar yield was obtained during the addition of 2 mol% of PPh₃ with **C** (entry 17). In contrast, under similar temperature and pressure conditions as entry 3, the use of water as solvent resulted in the formation of a dark brown solution highlighting the formation of ruthenium nanoparticles and led to the exclusive formation of cyclohexylethanol.^[33]

Having established the two best reaction conditions with our set of catalysts, we next turned out our attention on the substrate diversity during hydrogenation of aromatic ketones (Table 2). We observed that hydrogenation of electron deficient ketones containing trifluoromethyl groups such as **1b** and **1c**, led to the corresponding secondary alcohols by the amine free protocol with catalyst **C** and in the presence of triethylamine when **A** was employed in 87-99% yields under 30 bar of H₂ and a temperature of 60 °C (entries 1 and 2). Similar reaction conditions led to up to 99% yield with the *o*- and *p*-methylacetophenones **1d** and **1e** (entries 3 and 4). On the other hand, electron-rich functionalized ketones featuring a methoxy moiety at *o*- and *p*-positions required higher pressure and temperature (50 bar, 70 °C) to reach complete conversions (entries 5 and 6). Finally the hydrogenation of dimethylpropiofenone **1i** and cyclic ketones such as tetralone **1h** was more difficult with catalyst **A** and high conversions were only obtained at 70-80 °C (entries 7 and 8).

Encouraged by the fact that ruthenium(II) complexes featuring a phosphinesulfonate were able to efficiently hydrogenate aromatic ketones we wanted to investigate the possibility to develop an enantioselective version. However, examples of enantiopure phosphinesulfonate chelate are scarce in the literature. Last year, Nozaki and co-workers reported the application of P-chiral phosphinesulfonate in palladium-catalyzed copolymerization but the access to these phosphines required preparative chiral HPLC.^[20e] On the other hand, binaphthophosphine^[34-35] arising from binaphthol have shown interesting activities in enantioselective hydrogenation of functionalized β-ketoesters.^[34d] We then decided to prepare the new chiral phosphinesulfonic

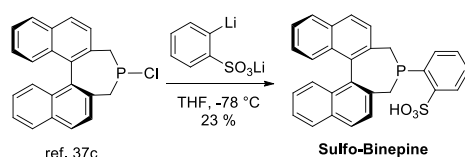
acid based on binaphthophosphine. Thus, after preparation of the enantiopure atropoisomeric chlorophosphine based on reported methodology,^[34c] treatment of the latter with the dilithiated salt of benzenesulfonic acid resulted in the formation of the expected phosphine (Scheme 2). From this ligand, deprotonation by reacting potassium tert-butoxide with the sulfonic acid in methanolic solution followed by the addition of [Ru(η^6 -*p*-cymene)Cl₂]₂ afforded the expected chiral ruthenium complex **I** (Scheme 3). The ³¹P NMR data of the fully characterized complex gave one singlet at 42 ppm and ¹H and ¹³C

Table 2. Substrate diversity for ketone hydrogenation.

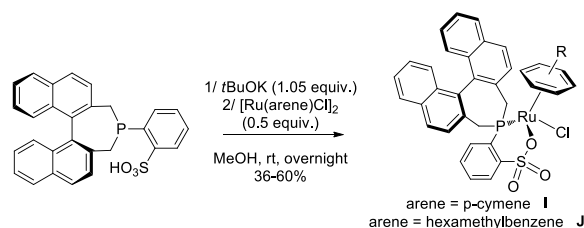
$ \begin{array}{c} \text{R}_1-\text{C}(=\text{O})-\text{R}_2 \\ \text{1b-i} \end{array} \xrightarrow[\text{MeOH, } T, ^\circ\text{C}]{\text{A or C (2 mol\%)} \atop \text{additives} \atop \text{H}_2} \begin{array}{c} \text{R}_1-\text{CH}(\text{OH})-\text{R}_2 \\ \text{2b-i} \end{array} $						
Entry ^[a]	Substrate	Catalyst	Pressure (bar)	T (°C)	Additives (mol%)	Yield ^[b,c] (%)
1		C	30	60	None	99(80)
		A	30	60	Et ₃ N (10)	87
2		C	30	60	None	99 (93)
		A	30	60	Et ₃ N (10)	99
3		C	30	60	None	99 (80)
		A	50	70	Et ₃ N (10)	99
4		C	30	60	None	99 (85)
		A	50	60	Et ₃ N (10)	99
5		C	50	70	None	99(85)
		A	50	70	Et ₃ N (10)	92
6		C	50	70	None	99 (81)
		A	50	70	Et ₃ N (10)	85
7		C	50	80	None	94 (90)
		A	50	80	Et ₃ N (10)	99
8		C	30	60	None	99 (94)
		A	50	70	Et ₃ N (10)	62

[a] All reactions were carried with **1/A-C** in 1/0.02 molar ratio for 15 h under the indicated hydrogen pressure using a thermostated oil bath. [b] Conversion determined by ¹H NMR and GC. [c] number in parenthesis is isolated yield after column chromatography.

analyses suggested that complex **I** was formed as only one diastereoisomer. Structure confirmation was obtained by recrystallization of **I** by layering dichloromethane and hexane in the presence of a small amount of methanol (Figure 3). Similar procedure by treatment with [Ru(η^6 -Me₆C₆)Cl₂]₂ afforded complex **J**. With these enantiopure chiral complexes in hand, the enantioselective hydrogenation of acetophenone with a S:C ratio of 100 was investigated (Table 3). When **1a** was hydrogenated at 60 °C in the presence of complex **I** along with 10 mol% of the acyclic



Scheme 2. Chiral phosphine sulfonate from enantiopur atropoisomeric chlorophosphine



Scheme 3. Preparation of chiral ruthenium complexes **I** and **J**

tertiary triethylamine ($pK_a = 10.8$) under 10 bar of H_2 , 90% of phenylethanol was formed and the enantiomeric excess reached 32% in (*R*)-**2** demonstrating a promising enantioselectivity (Table 3, entry 1). The pressure exerted a strong influence on enantio-discrimination whereas temperature ranging from 60 to 80 °C had less impact and a 88:12 enantiomeric ratio was obtained at 80 °C under 50 bar of H_2 (entries 2-4). It is important to note that temperature below 50 °C led to low conversion whereas temperature over 80 °C afforded lower enantioselectivities (not presented in the Table). However, other attempts to improve this result with triethylamine were unsuccessful.

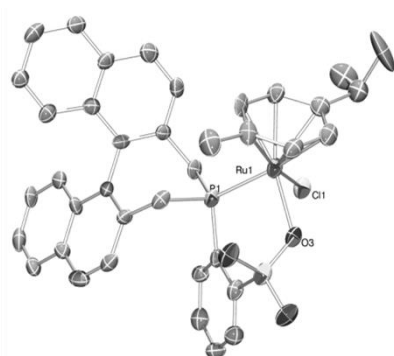
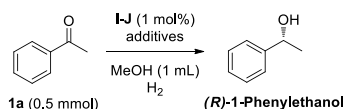


Figure 3. Molecular structure of complex **I** (CCDC 927220)

We next turned our attention on the effect of the amine toward enantioselectivity. Diamines such as TMEDA ($pK_{a1} = 4$, $pK_{a2} = 10.7$) inhibited the hydrogenation (entry 5) and similar low conversions were obtained with enantiopure cyclohexanediamine and *N*-tosyl-1,2-diphenylethylenediamine presumably due to the formation of a stable chelate. Hünig's base ($pK_a = 11.4$) as a hindered tertiary amine under similar reaction conditions gave lower enantioselectivity as compared to triethylamine (entries 2 compared to 6) whereas cyclic *N*-methylpiperidine ($pK_a = 10.1$) afforded better result (entries 2 compared to 7). Primary and secondary amines such as diisopropylamine and cyclohexylamine led to the formation of racemic phenylethanol (entries 9 and 10). Similarly, the use of pyridine led to the formation of a racemic alcohol (entry 8). As expected, the in situ generated corresponding tris-acetonitrile complex obtained by treatment of **I** in the presence of acetonitrile followed by precipitation afforded almost complete conversion without additives but with a low 31% ee (entry 11). These seminal results demonstrated that the tertiary cyclic amines led to better results and we thus decided to investigate the influence of the more rigid bicyclic DABCO ($pK_{a1} = 3.0$, $pK_{a2} = 8.8$). Thus, treatment of acetophenone using conditions described in entry 2 by simply replacing Et_3N by DABCO afforded 80% ee (entries 12 compared to 2). As we previously observed, temperatures ranging

Table 3. Influence of amines towards asymmetric ionic hydrogenation of acetophenone.



Entry ^[a]	Cat.	<i>P</i> (bar)	<i>T</i> (°C)	<i>t</i> (h)	Additives (mol%)	Yield ^[b] (%)	e.r. ^[c]
1	I	10	60	15	Et_3N (10)	90	66:34
2	I	30	60	15	Et_3N (10)	90	72:28
3	I	50	60	15	Et_3N (10)	91	86:14

4	I	50	80	15	Et ₃ N (10)	91	88:12
5	I	30	60	15	TMEDA (10)	6	n.d.
6	I	30	60	15	DIPEA (10)	79	66:34
7	I	30	60	15	MeN(CH ₂) ₅ (10)	95	82.5:17.5
8	I	50	60	15	Pyridine (10)	49	51:49
9	I	50	60	15	<i>i</i> Pr ₂ NH (10)	48	55.5:44.5
10	I	50	60	15	C ₆ H ₁₁ NH ₂ (10)	89	50:50
11 ^[d]	in situ	50	60	15	None	93	65.5:34.5
12	I	30	60	15	DABCO (5)	98	90:10
13	I	30	70	15	DABCO (5)	98	89:11
14	I	30	80	15	DABCO (5)	94	88.5:11.5
15 ^[e]	I	30	60	15	DABCO (5)	90	80:20
16 ^[f]	I	30	60	15	DABCO (5)	0	n.d.
17	I	30	60	15	DABCO (8)	98	91:9
18	I	30	60	15	DABCO (10)	99	89:11
19	I	30	60	15	DABCO (15)	98	89:11
20	I	40	60	15	DABCO (8)	95	92:8
21	I	60	60	15	DABCO (8)	99	92.5:7.5
22	I	50	60	5	DABCO (8)	99	92:8
23	I	50	60	24	DABCO (8)	99	92.5:7.5
24 ^[g]	I	50	60	15	DABCO (8)	94	91:9
25 ^[h]	in situ	50	60	15	DABCO (8)	98	91.5:9.5
26	I	40	50	15	<i>t</i> BuOK (1)	63	45.5:55.5
27 ^[i]	I	40	50	15	DABCO (10)	99	58:42
28	J	50	70	21	DABCO (10)	95	82.5:17.5
29	J	30	60	15	Pyridine (10)	3	n.d.

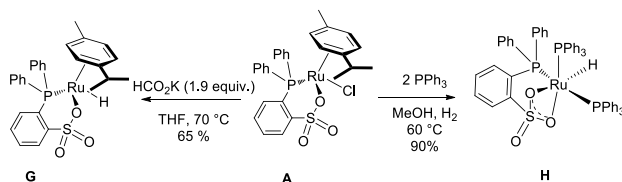
[a] All reactions were carried with **1**/**I** or **J** in 1/0.01 molar ratio under the indicated hydrogen pressure using a thermostated oil bath. [b] conversion determined by ¹H NMR and GC. [c] e.r. determined by chiral GC. [d] arene free ruthenium species generated by treatment of **I** with acetonitrile followed by precipitation. [e] Solvent ethanol. [f] Solvent *i*PrOH. [g] **1**/**I** in 1/0.005 molar ratio. [h] **1**/[Ru(*p*-cymene)Cl₂]₂/Sulpho-Binapine in 1/0.005/0.011 molar ratio. [i] 1 mol% of *t*BuOK was added.

from 60 to 80 °C had little influence on enantioselectivity (entries 12-14). Other alcoholic solvents such as ethanol afforded lower yield and ee, and the reaction was inhibited in isopropanol (entries 15-16). Variation of the amount of DABCO in the range 5-15 mol% showed that the pH did not affect the enantioselectivity (entries 12, 17-19). Finally, ee reached 85% by increasing the pressure up to 50 bar (entry 21). It is important to note that a similar result was obtained with the *in situ* generated catalyst (entries 21 as compared to 25). Lowering the amount of catalyst did not affect enantioselectivity (entry 24) whereas higher catalyst loading had a negative influence on the ee presumably due to the side formation of dimeric organometallic species. As observed in entries 22 and 23 no racemisation and no DKR occurred by varying the reaction time leading to the same ee as entry 21. The reaction of **J** gave lower ee, thus demonstrating the strong influence of the arene motif toward conversion and enantio-discrimination (entry 28). The presence of an alkoxide base such as *t*BuOK (1 mol%) with or without DABCO dramatically lowered the ee with (entries 26 and 27). From this table, the results demonstrated that secondary amines and aromatic amines led to mainly racemic phenylethanol whereas the use of tertiary amines allowed enantiodiscrimination. It is also important to note that

the nature of the tertiary amine had a strong impact during asymmetric hydrogenation. Indeed, under similar pressure and temperature, the use of distinct tertiary amines afforded product **2a** in 32–78% ee (entries 2, 6, 7 and 18).

Finally, the scope of the asymmetric hydrogenation was extended to various arylketones (Table 4). *o*-Substituted arylketones led to the best results and *o*-methylacetophenone gave complete conversion and 91% ee (entry 2). *o*-Methoxyacetophenone led to similar enantioselectivity 92% ee suggesting that no binding of the ether to the ruthenium centre took place during hydrogenation (entry 4). Confirmation was obtained during hydrogenation of **1j** affording 91% ee (entry 6). Electron-deficient ketones such as **1b** led to lower ee (entry 1). In contrast, *para*-substituted electron rich ketones were efficiently converted to the corresponding alcohols in up to 86% ee (entries 3 and 5). As expected, propiophenone **1k** afforded similar ee as acetophenone (entry 7).

Owing to the difference of reactivity and/or enantioselectivity of the acetonitrile containing precatalysts and the arene ruthenium complexes and assuming that it could result from the formation of different active species, we investigated the nature of the possibly formed hydride species in solution. Thus, treatment of complex **A** with 1.9 equivalent of potassium formate in THF solution at 70 °C overnight resulted in the complete disappearance of the ^{31}P NMR signal of **A** highlighting the formation of the monohydride **G**, a yellow complex isolated in 65% yield after purification (Scheme 4). The hydride was observed in ^1H NMR at δ – 6.95 ppm as a sharp doublet (J = 53 Hz) and the *p*-cymene ligand remained coordinated to the ruthenium centre with the arene protons located between 6.15 and 4.79 ppm as a set of four doublets. The $^{31}\text{P}\{^1\text{H}\}$ appeared as two singlets at 46.0 and 46.1 ppm indicating the presence of rotamers. In contrast, treatment of complex **A** with two



Scheme 4. Preparation of ruthenium(II) monohydride complexes

Table 4. Scope of the Asymmetric Hydrogenation of aromatic ketones.

Entry ^[a]	Substrate	Pressure (bar)	T (°C)	Yield ^[b] (%)	e.r. ^[c]
1		50	60	99	73:27(<i>R</i>)
2		50	60	98	95.5:4.5(<i>R</i>)
3		50	60	98	93:7
4		50	70	99	96:4(<i>R</i>)
5		60	60	99	90.5:9.5(<i>R</i>)
6		60	60	99	95.5:4.5(<i>R</i>)
7		60	60	98	92:8(<i>R</i>)

[a] All reactions were carried with **1**/**I** in 1/0.01 molar ratio for 15 h under the indicated hydrogen pressure using a thermostated oil bath. [b] Conversions determined by ^1H NMR and GC. [c]er determined by chiral GC and absolute configuration attributed according previous reports.

equivalents of triphenylphosphine under H_2 pressure in highly diluted methanolic solution resulted in the loss of the arene ligand and the precipitation of the sole light red monohydride ruthenium **H** featuring the phosphinesulfonate acting as a tridentate $\kappa^3\text{-P,O,O}$ ligand (Scheme 4).^[26] The X-ray analysis shows a distorted pseudo-octahedral environment in **H** where the hydride is in *cis* relationship with all the three phosphorus atoms indicating the additional π binding character of the sulfonate moiety (Figure 4). However, it was found to be unstable in solution but the

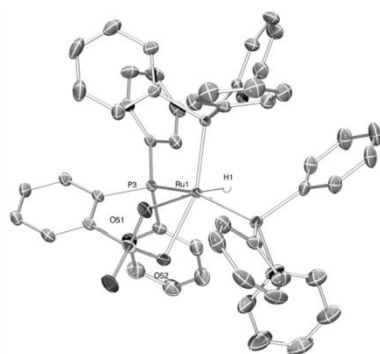
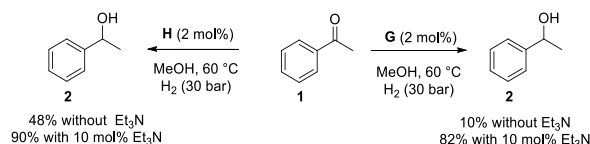


Figure 4. Molecular structure of the monohydride complex **H** (CCDC 927212); Ru1-H1 1.50(3) Å, Ru1-O51 2.3523(12) Å, Ru1-O52 2.3127(12) Å, Ru1-P1 2.2461(4) Å

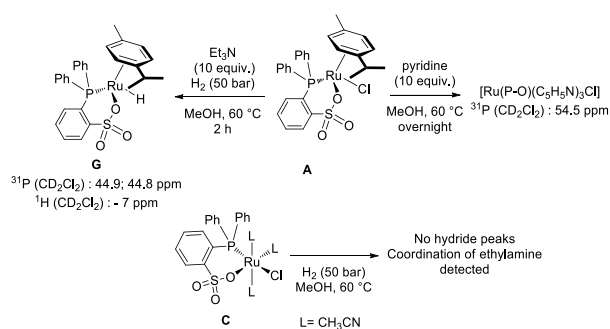
^1H NMR showed only one hydride located at -19.3 ppm as a quartet. ^{31}P NMR revealed the decoordination of one of the oxygen atoms resulting in the formation of two green 16 $\bar{\text{e}}$ monohydride isomers (see SI). Nevertheless, the comparison with the reported formato-hydrido-tris-triphenylphosphine ruthenium(II) supported the structure.^[36] With these well-defined monohydride complexes in hands, we then investigated the nature of the hydride species during hydrogenation of ketones.

First, we examined the behaviour of the arene free ruthenium hydride complexes. The latter might allow the coordination of the substrate due to the presence of the labile ligands resulting in an inner sphere hydrogenation pathway. Interestingly, the arene free monohydride **H** under H_2 (30 bar) afforded moderate conversions without base and high conversion in the presence of Et_3N (Scheme 5). The study of the acetonitrile containing complex **C**, which allowed efficient base free hydrogenation was surprising as the ^1H NMR study carried out at 60 °C in methanol under hydrogen pressure exhibited no hydride peaks (Scheme 6).^[37]



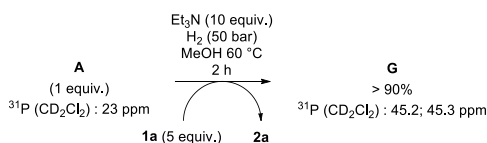
Scheme 5. Hydrogenation in the presence of the ruthenium monohydrides species

Next, we focused our attention on the arene ruthenium based precatalysts. Thus, the treatment of a methanolic solution of **A** under 50 bar H_2 in the presence of 10 equivalents of triethylamine followed by NMR study at atmospheric pressure demonstrated the quantitative formation of the monohydride species **G** in less than 3 hours, whereas no conversion was observed without triethylamine under similar pressure and temperature, showing that the phosphinesulfonate chelate and the arene coordination remained unchanged at this pressure both in the presence and absence of triethylamine (Scheme 6). In contrast, the treatment of **A** with pyridine resulted in the formation of an arene free metal species as confirmed by the disappearance of the arene motif by ^1H NMR, and explained the absence of asymmetric induction when pyridine was used as additive (Scheme 6). These experiments show that the choice of the amine plays an important role on the reaction pathway during hydrogenation and tend to demonstrate that the



Scheme 6. NMR studies of in situ generated complexes

arene remained bound in the presence of tertiary aliphatic amines such as Et₃N or DABCO allowing enantiodiscrimination in asymmetric hydrogenation. Confirmation was obtained during the substoichiometric hydrogenation of acetophenone in the presence of **A**, as NMR analyses revealed that the nature of the generated species **G** was recovered after hydrogenation (Scheme 7). Importantly, very low yield of phenylethanol was obtained with the hydride species **G** without external aliphatic amine, whereas good yields were obtained in the presence of triethylamine demonstrating that tertiary amine was not only useful to remove the chlorine atom but also might play the role of proton acceptor during the heterolytic cleavage of H₂ generating tertiary ammonium salts (Scheme 5).^[38]



Scheme 7. Effect of acetophenone towards the stability of the generated monohydride species **G**

Our previous results on allylation with ruthenium(IV) species containing phosphinesulfonate ligand showed that the sulfonic/sulfonate exchange favoured the release of water from allylic alcohols through hydrogen bonding.^[29] Following the same trend it is plausible to assume that the heterolytic cleavage of H₂ occurred via a concerted 6-membered transition state where the amine stabilizes the ruthenium hydride by H-bonding through tight ion pairing followed by deprotonation of the sulfonic group (Figure 5).

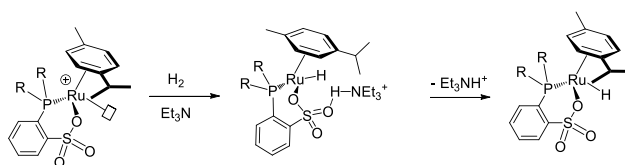


Figure 5. Proposed ionic heterolytic cleavage of H₂

At this point, even if monohydride species **G** were observed after hydrogenation, the real nature of the active species during the hydrogenation of ketones in the presence of aliphatic tertiary amines as additives remained unclear. Therefore, three key intermediates based on mono- or dihydride species can be considered to explain the mechanism (Figure 6).

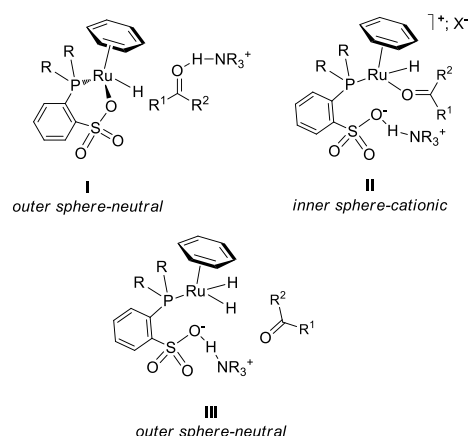
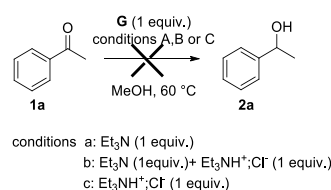


Figure 6. Possible key intermediates for ionic hydrogenation of arylketones with tertiary amines (arene substitution omitted for clarity)

Experiments from Table 1, 2, 3 and Scheme 7 demonstrated that the arene ligand remained bound to the metal centre in the presence of tertiary aliphatic amines. In the inner sphere mechanism, the hemilability of the sulfonate ($pK_a = -0.93$) moiety due to a possible H-bonding with a tertiary ammonium salt would result in the formation of an 16 e^- ruthenium(II) cationic monohydride species allowing the coordination of the ketone (species **II**). Recently, Jordan demonstrated that an excess of pyridine led to the reversible decoordination of a sulfonate chelate with palladium(II).^[25] Thus, an outer sphere ionic catalytic mechanism involving the formation of a tight ion pair between the sulfonate and the ammonium cannot be excluded. On the other hand, Bullock and Norton highlighted that the use of well defined [CpW-H] and [CpRu-H] diphosphine complexes allowed the hydrogenation of various ketones and iminiums.^[39-40] These interesting reports demonstrated that the ionic hydrogenation occurred through an outer sphere stepwise mechanism involving protonation followed by reduction with the resulting metal monohydride species. Based on these reports an outer sphere mechanism can also be postulated where the tertiary ammonium salt acts as a Brønsted acid to activate the carbonyl group leading to electrophilic intermediates (species **I**). It is noteworthy that during the stoichiometric treatment of acetophenone **1a** in the presence of the monohydride species **G** along with triethylammonium chloride and or triethylamine, the formation of phenylethanol was never detected in the absence of hydrogen (Scheme 8).



Scheme 8. Stoichiometric attempts to convert **1a** with monohydride species **G**

These last results excluded intermediates **I**, **II** as active species and demonstrated that the monohydride intermediate **G** is the resting species of the catalytic system.

Importantly, the presence of methanol as mandatory solvent revealed that a charge separation occurred to allow intermolecular ionic interactions between the hydride species and the reagents, (Table 1). Therefore, from the results obtained in Scheme 8, a ruthenium dihydride species **III** or closely related species arising from the hemilability of the σ sulfonate ligand seems to be a plausible active species.^[41] Thus, if we assume that no slip of hapticity from η^6 to η^4 of the arene ligand occurred to allow the coordination of the substrate, an outer sphere mechanism can be rationalized to explain the hydrogenation mechanism (Figure 7).

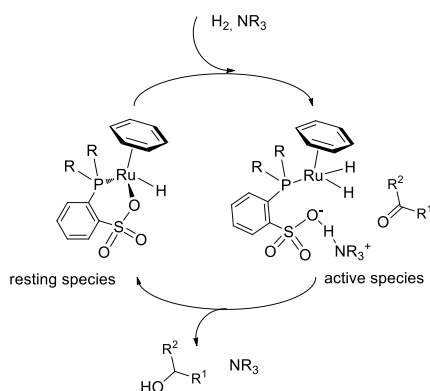


Figure 7. Proposed catalytic cycle

Conclusion

In conclusion we have developed two catalytic systems involving ruthenium(II) complexes featuring phosphinesulfonate chelate for the hydrogenation of arylketones. Acetonitrile based complexes allowed the base free hydrogenation of various ketones whereas ruthenium(arene) complexes required the presence of an external amine to make the reduction possible. We have shown the choice of the amine is crucial and that with tertiary amines the arene ligand remains bound to the metal centre. Stoichiometric investigations revealed that ruthenium monohydride species were the resting species of the hydrogenation process. Even if at this stage the seminal applications in asymmetric hydrogenation of the new Sulfo-binepine ligand are below the well-established reported hydrogenation catalysts, it demonstrated the potential of such ligands in hydrogenation. The modularity of tertiary amines combined with hemilabile L-O chelate diversity should afford interesting uses in enantioselective hydrogenation. Our current efforts are focused on the isolation of the dihydride species **III** and will be reported in due course.

Experimental Section

2-((11bS)-3H-dinaphtho[2,1-c:1',2'-e]phosphepin-4(5H)-yl)benzenesulfonic acid (Sulfo-Binepine):

To a solution of benzenesulfonic acid (0.58 g, 3.66 mmol, 1.0 equiv.) in THF (10 mL) was added *n*-BuLi (1.6 M solution in *n*-hexane, 5.0 mL, 8.04 mmol, 2.2 equiv.) drop wise at 0 °C over 10 min under an argon atmosphere. The mixture was stirring at 0 °C for 10 minutes, at room temperature for 10 minutes and at room temperature for 10 minutes. Then the resulted salt was cooled at -78 °C. Simultaneously, (11bS)-4-chloro-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphine (1.25 g, 3.66 mmol, 1.0 equiv.) was dissolved in 5 mL THF and cooled at -78 °C. Then the lithiated benzenesulfonic acid was transferred dropwise through a cannula to the phosphine precursor in THF at -78 °C. The reaction mixture was stirring for 1 h at -78 °C and allowed to warm at room temperature for another 24 h. Upon warming, the slurry became a red solution, which turned dark red and finally a dark orange clear solution. Evaporation of the solvent under vacuum was followed by dissolution of the residue with degassed deionized water (10 mL) at 0 °C. The aqueous layer was acidified with 1 N HCl aqueous solution to pH ~ 2 at 0 °C and extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over MgSO₄, followed by filtration and evaporation under vacuum to generate a yellow solid. The solid was washed with distilled THF followed by filtration, and washed with a minimum amount of THF to afford a white powder in (0.41 g) 23% yield.

$[\alpha]_D^{20} = -191$ (*c* 0.36, CH₂Cl₂);

¹H NMR (400 MHz, CD₂Cl₂): δ 8.17 (dd, 1H, *J* = 7.6, 4.4 Hz), 8.12 (d, 1H, *J* = 8.4 Hz), 8.04 (d, 1H, *J* = 8.2 Hz), 7.99 (d, 1H, *J* = 8.1 Hz), 7.95 (d, 1H, *J* = 8.5 Hz), 7.77 (m, 1H), 7.71 (d, 1H, *J* = 8.4 Hz), δ 7.57 (m, 2H), 7.45-7.41 (m, 1H), δ 7.36-7.31 (m, 3H), 7.26-7.16 (m, 3H), 4.26 (t, 1H), 3.80-3.71 (m, 2H), 3.59-3.51 (m, 1H);

³¹P (162 MHz, CD₂Cl₂): δ 15.98.

¹³C NMR (100 MHz, CD₂Cl₂): δ 151.19 (d, *J*_{P-C} = 7.2 Hz, C_{quat}), 135.69 (d, *J*_{P-C} = 3.2 Hz, CH), 135.11 (d, *J*_{P-C} = 4.0 Hz, C_{quat}), 134.93 (d, *J*_{P-C} = 4.8 Hz, C_{quat}), 134.29 (d, *J*_{P-C} = 3.2 Hz, C_{quat}), 134.22 (d, *J*_{P-C} = 3.2 Hz, C_{quat}), 132.91 (CH), 132.8 (CH), 132.48 (d, *J*_{P-C} = 2.4 Hz, C_{quat}), 132.31 (d, *J*_{P-C} = 3.2 Hz, C_{quat}), 130.79 (d, *J*_{P-C} = 2.4 Hz, CH), 130.30 (d, *J*_{P-C} = 2.38 Hz, CH), 130.21 (CH), 130.08 (CH), 128.98 (CH), 128.90 (CH), 128.22 (d, *J*_{P-C} = 4.0 Hz, CH), 127.52, 127.47, 127.41, 127.23, 127.17, 127.05 (signals from 127.52 to 127.05 are all tertiary carbons, but they were not fully characterized due to complex P-C couplings), 126.58 (d, *J*_{P-C} = 11.1 Hz, C_{quat}), 126.12 (d, *J*_{P-C} = 8.7 Hz, C_{quat}), 112.76 (d, *J*_{P-C} = 78.7 Hz, C_{quat}), 28.06 (d, *J*_{P-C} = 54.0 Hz, CH₂), 24.95 (d, *J*_{P-C} = 47.7 Hz, CH₂).

HRMS-ESI: C₂₈H₂₁O₃NaPS [M+Na]⁺, Calcd: 491.08467; Found: 491.0849 (0 ppm); C₂₈H₂₂O₃PS [M+H]⁺, Calcd: 469.10273; Found: 469.1033 (1 ppm).

Synthesis of complex I {Ru[η⁶-*p*-cymene][κ²-*o*-((11bS)-3H-dinaphtho[2,1-c:1',2'-e]phosphepin-4(5H)-yl)C₆H₄SO₃]Cl}:

2-((11bS)-3H-dinaphtho[2,1-c:1',2'-e]phosphepin-4(5H)-yl)benzenesulfonic acid (0.792 mmol, 1.0 equiv.) and *t*-BuOK (0.871 mmol, 1.2 equiv.) were added into a 25 mL Schlenk tube. The sealed Schlenk tube was evacuated and filled with argon three times. A minimum amount of MeOH (degassed by nitrogen purge for 30 min) was added and the solution was stirred at room temperature for 30 min. To this solution [Ru(η⁶-*p*-cymene)Cl₂]₂ (0.200 g, 0.396 mmol, 0.5 equiv.) was added. The red solution became to a slurry after 1 h. After stirring for 16 h at room temperature, the solution was concentrated, and cannulated to remove methanol, the solid was washed by 2 x 1 mL of methanol. Then the crude was dissolved into 2 x 8 mL of CH₂Cl₂. The solution was filtrated with distilled and degassed CH₂Cl₂ as eluent over dry celite to remove the inorganic salt. Then, the solvent was removed under vacuum to generate the orange solid. Complex **I** was synthesized according to this general procedure in (0.37 g) 36% yield.

CCDC 927220 (Complex **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

$[\alpha]_D^{20} = -127$ (c 0.1733, CH₂Cl₂);

¹H NMR (400 MHz, CD₂Cl₂): δ 8.11 (d, 1H, $J = 8.3$ Hz), 8.07 (d, 1H, $J = 8.3$ Hz), 7.98 (ddd, 1H, $J = 7.6, 3.9, 1.0$ Hz), 7.93 (d, 1H, $J = 8.0$ Hz), 7.70 (d, 1H, $J = 8.4$ Hz), 7.59–7.55 (m, 2H), 7.51–7.46 (m, 2H), 7.38–7.30 (m, 2H), 7.30–7.26 (m, 1H), 7.18–7.12 (m, 2H), 6.73 (d, 1H, $J = 8.2$ Hz), 6.63 (dd, 1H, $J = 7.9, 7.9$ Hz), 5.89 (d, 1H, $J = 5.9$ Hz), 5.54 (d, 1H, $J = 6.0$ Hz), 4.88 (d, 1H, $J = 5.8$ Hz), 4.71–4.68 (m, 1H), 4.17 (dd, 1H, $J = 13.8, 5.6$ Hz), 3.76 (dd, 1H, $J = 13.2, 4.1$ Hz), 3.66 (m, 2H), 3.03 (qq, 1H, $J = 6.9, 7.0$ Hz), 2.10 (s, 3H), 1.37 (d, 3H, $J = 7.0$ Hz), 1.36 (d, 3H, $J = 6.8$ Hz);

³¹P NMR (162 MHz, CD₂Cl₂): δ 42.34;

¹³C NMR (100 MHz, CD₂Cl₂): δ 147.53 (d, $J_{P-C} = 11.1$ Hz, C_{quat}), 135.76 (d, $J_{P-C} = 4.0$ Hz, C_{quat}), 133.84 (d, $J_{P-C} = 3.2$ Hz, C_{quat}), 133.53 (d, $J_{P-C} = 2.4$ Hz, C_{quat}), 133.37 (d, $J_{P-C} = 1.6$ Hz, C_{quat}), 132.88 (d, $J_{P-C} = 1.6$ Hz, C_{quat}), 132.70 (d, $J_{P-C} = 11.9$ Hz, C_{quat}), 132.33 (d, $J_{P-C} = 1.6$ Hz, C_{quat}), 132.09 (CH), 131.54 (d, $J_{P-C} = 4.8$ Hz, C_{quat}), 131.19, 131.18, 129.74, 129.68, 128.96, 128.87, 128.65, 128.62, 128.45, 128.43, 128.00, 127.93, 127.47, 127.19, 126.99, 126.76, 126.62, 126.12, signals from 131.19 to 126.12 were not fully characterized tertiary carbon due to complex P–C couplings, 96.53 (C_{quat}), 90.08 (CH), 86.41 (d, $J_{P-C} = 9.5$ Hz, CH), 84.35 (CH), 74.07 (CH), 33.88 (d, $J_{P-C} = 20.7$ Hz, CH₂), 31.51 (CH), 30.00 (d, $J_{P-C} = 33.4$ Hz, CH₂), 22.91 (CH₃), 20.84 (CH₃), 18.55 (CH₃);

HRMS-ESI: C₃₈H₃₄O₃PS102Ru [M–Cl]⁺, Calcd: 703.10043; Found: 703.1006 (0 ppm).

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