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Ruthenium-Containing Phosphinesulfonate Chelate for the Hydrogenation of Aryl Ketones

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Dedicated to Professor Irina Petrovna Beletskaya for her outstanding contribution to organometallic catalysis

Abstract: Various ruthenium(II) complexes that contain phosphinesulfonate chelate have been synthesized. Arene-free complexes were found to be efficient in the base-free hydrogenation of various aryl ketones, whereas the arene-containing precatalysts required the presence of an amine as an additive. The seminal asymmetric hydrogenation reaction by using the new Sulfo-Binepine ligand was also investigated for the possible intervention of a dihydride species.

Keywords: chelates · hydrogenation · ketones · ruthenium · sulfonates

Introduction

The development of new complexes and catalytic systems that operate through different catalytic pathways is an appealing area of research for discovering new selective transformations, for improving established methods, and for overcoming patented processes.[1] Among the important target fields, hydrogenation and transfer hydrogenation reactions have attracted considerable interest for their applications in the synthesis of various fine chemicals and pharmaceuticals from unsaturated raw materials.[2] In this regard, the hydrogenation of aromatic ketones catalyzed by transition-metal complexes has become the method of choice for producing optically pure secondary alcohols on an industrial scale.[3]

Shvo's catalyst was one of the first ruthenium complexes to efficiently hydrogenate ketones into alcohols.[4] The breakthrough came from Noyori, who used a ruthenium complex that contained diphosphinediamine ligands to afford excellent enantioselectivities for the asymmetric hydrogenation of unfunctionalized aromatic ketones.[5] [Cp′Ru]-based catalysts that featured diamine or amino alcohol ligands were also efficiently used in asymmetric ketone-hydrogenation reactions.[6] In these catalytic systems, an acidic proton is held by the ligand through a hydroxy or N–H functionality and through the hydride that is bound to the ruthenium center, thus allowing the ionic hydrogenation of the carbonyl group through a concerted outer-sphere mechanism.[7,8] Therefore, various efforts have been devoted to the development of a plethora of bifunctional catalysts that feature nitrogen ligands to play with the famous "N–H effect".[9–16] Surprisingly, few reports have dealt with the use of non-nitrogen-based catalysts that operate through different pathways for the hydrogenation of aryl ketones.[17,18] Phosphineoxazolines have emerged as an excellent alternative to bifunctional catalysts.[18c,d,h–j] Nishiyama and co-workers reported a cyclometalated ruthenium complex, which afforded promising enantioselectivities for the hydrogenation of aromatic ketones.[18e,g] Recently, we demonstrated that the use of well-defined ruthenium(II)- and iridium(III) complexes containing a phosphinesulfonates as chelating ligands allowed the C3–H functionalization of amines with alcohols or aldehydes through oxidant-free hydrogen autotransfer processes.[19] Phosphinesulfonate chelates that feature either aryl, alkyl,[20] ferrocenyl,[21] phosphines, or, more recently, diazaphospholidine- and NHC-sulfonates (NHC = N-heterocyclic carbene),[22,23] have attracted considerable interest in polymerization reactions.[20–26] These bidentate-ligand-containing complexes exhibit unique behaviors, owing to the different electronic properties of the phosphine and sulfonate moieties but, more importantly, the sulfonate group can adopt different coordination modes depending on the interactions with other ligands and Lewis or Brønsted acids (Figure 1).[23,24,26] Interestingly, they have also found applications in hydroformylation,[27] Heck coupling,[28] allylation,[29] conjuguate addition,[30] and attractive Suzuki–Miyaura reac-

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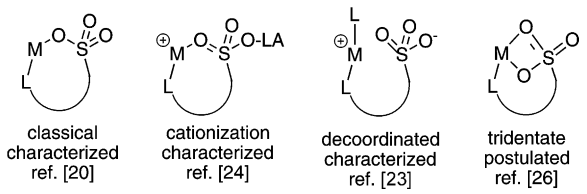


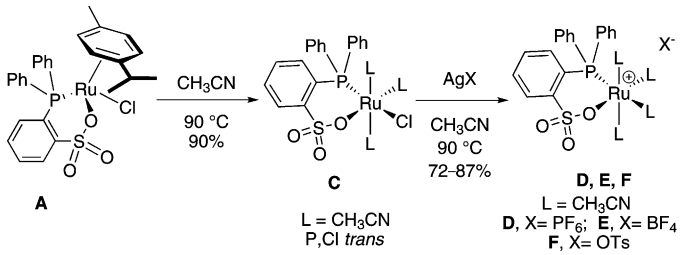
Figure 1. Different modes of coordination of the sulfonate chelates.

tions in water.[31] However, nothing is known about these ligands or on the effect of the sulfonate functionality in the hydrogenation of polar bonds.

Herein, we report our preliminary investigations on ruthenium(II) catalysts that contain a phosphinesulfonate chelating ligand to hydrogenate aryl ketones.

Results and Discussion

Arene-free ruthenium(II) complex **C** was prepared by heating our previously described (*p*-cymene)ruthenium(II) complex (**A**)[19a] in MeCN (Scheme 1). The complete characterization of complex **C** by room temperature NMR spectroscopy and further X-ray analysis revealed the formation of a single complex and showed that the ruthenium center was coordinated by three MeCN ligands in an octahedral environment (Figure 2). The structure also showed a *trans* relationship between the phosphorus and chloride atoms. In the presence of silver salts, such as AgOTs (Ts = tosyl), $AgPF_6$, and $AgBF_4$, cationization of complex **C** occurred in MeCN solution to afford the isolated complexes **D**–**F** in up to 87% yield (Scheme 1). The structure of tetrakis(MeCN) complex **F**, which featured a tosylate couteranion, was confirmed by single-crystal X-ray analysis (Figure 2). Complex **B**, an analogue of **A** that featured a hexamethylbenzene group, was easily obtained from the treatment of the deprotonated diphenylphoshinosulfonate with $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$.[19a]



Scheme 1. Preparation of arene-free ruthenium(II) complexes that feature the phosphinesulfonate ligand from complex **A**.

The mineral-base-free hydrogenation of acetophenone was selected as a benchmark reaction for the optimization and screening of ruthenium-phosphinesulfonate-based catalysts (Table 1). First, we examined the additive-free catalytic activity of the well-defined as-prepared complexes in various solvents. In all cases, very low conversions and low selectivities were obtained with neutral complex **A**, which contained an η^6-arene ligand (Table 1, entry 1). These results might be explained by the stability of the P,O chelate under hydrogen pressure and by the difficult generation of cationic intermediates that arises from the dissociation of the Ru–Cl bond, which further allows the formation of hydride species. In contrast, arene-free neutral or cationic complexes that contained labile MeCN ligands, such as **C** and **D**, which might allow ketone coordination, afforded almost complete

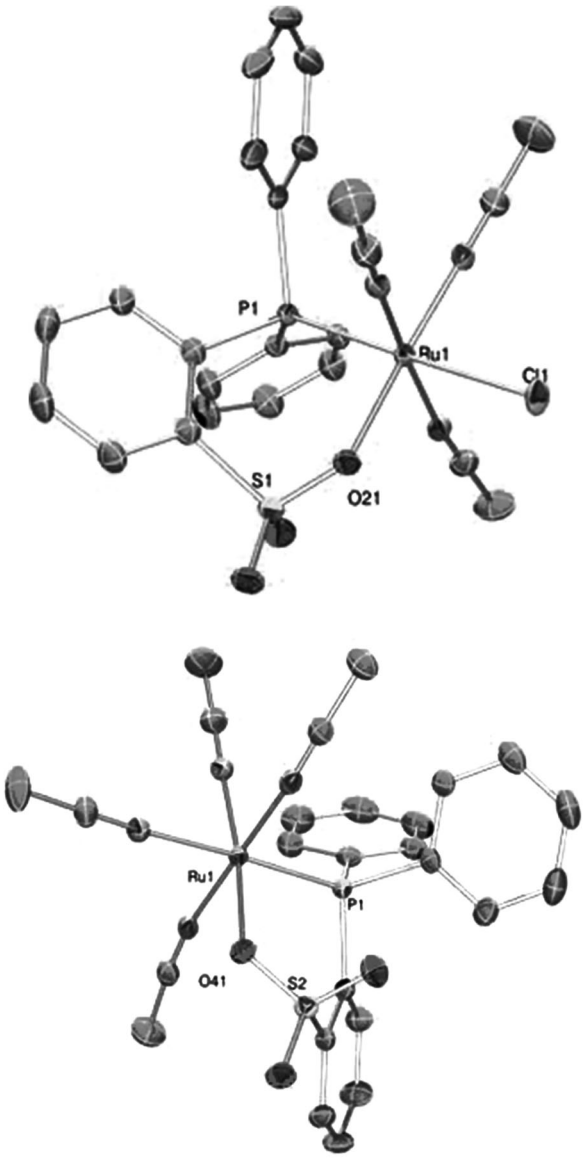
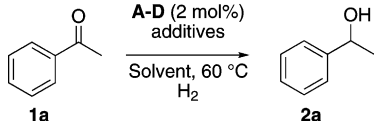


Figure 2. Molecular structures of arene-free complexes **C** (top) and **F** (bottom); CCDC-927216 (**C**) and CCDC-927217 (**F**).

conversions and the exclusive formation of 1-phenylethanol without the need for any additives (Table 1, entries 15 and 18). To overcome the initially supposed difficult dissociation of the Ru–Cl bond in complex **A**, we evaluated the effect of an external amine as an additive,[32] which would assist the formation of the cationic species by ligand exchange after the dissociation of the Ru–Cl bond. Indeed, substantial improvements were obtained by increasing the amount of triethylamine from 2–10 mol%, reaching 86% yield of 1-phenylethanol at 10 bar H_2 pressure (Table 1, entries 2 and 3). Increasing the hydrogen pressure up to 30 bar afforded complete conversion with 98% of alcohol **2a** (Table 1, entry 4). By using triethylamine as an additive, the nature of the solvent was found to be crucial; solvents with low dielectric constants and non-protic solvents were unsuitable, thus preventing the hydrogenation of acetophenone (Table 1, en-

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



1a **2a**

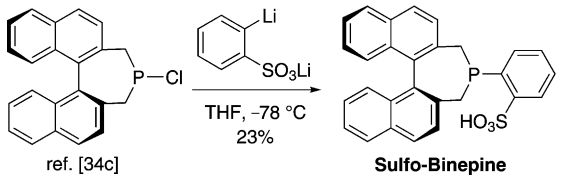
Entry[a]	Catalyst	Solvent	Pressure [bar]	Additive [mol%]	Yield[b] [%]
1	**A**	MeOH	30	none	6
2	**A**	MeOH	10	Et_3N (2)	9
3	**A**	MeOH	10	Et_3N (10)	86
4	**A**	MeOH	30	Et_3N (10)	98
5	**A**	THF	30	Et_3N (10)	2
6	**A**	CH_2Cl_2	30	Et_3N (10)	1
7	**A**	toluene	30	Et_3N (10)	1
8	**A**	MeOH	30	pyridine (10)	99
9	**A**	MeOH	30	$EtMe_2N$ (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_3N (10)	13
14	**B**	MeOH	30	pyridine (10)	97
15	**C**	MeOH	30	none	95
16	**C**	MeOH	30	Et_3N (10)	99
17	**C**	MeOH	30	PPh_3 (2)	33
18	**D**	MeOH	30	none	99

[a] All reactions were carried out with compound **1a** and catalyst **A**–**D** (1:0.02 molar ratio) for 16 h under the indicated hydrogen pressure by using a thermostated oil bath at 60 °C. [b] Yield determined by ^{1}H NMR spectroscopy and GC.

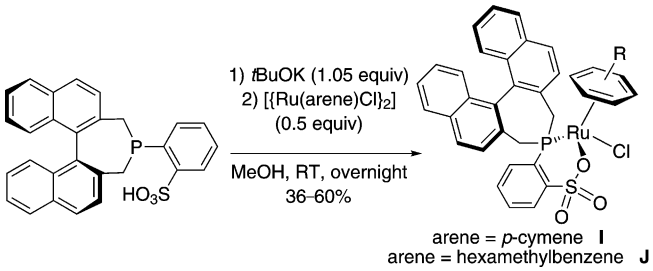
tries 5–7). Other amines were also evaluated and Me_2EtN and an aromatic amine, such as pyridine, also successfully gave phenylethanol in 93 and 99% yield, respectively (Table 1, entries 8 and 9). The conversions were found to be strongly dependent on the nature of the η^6-arene ligand and a lower conversion in the presence of triethylamine was obtained by replacing *p*-cymene by hexamethylbenzene in catalyst **B**. However, the replacement of triethylamine by pyridine as an additive led to the complete formation of 1-phenylethanol, thus suggesting the operation of two distinct reaction pathways as a function of the nature of the amine (Table 1, entries 13 and 14). Finally, the use of 2 mol% triphenylphosphine as an additive in the absence of an amine afforded the product in 35% yield, whereas higher loading prevented hydrogenation (Table 1, entries 10–12). A similar yield was obtained during the addition of 2 mol% PPh_3 with complex **C** (Table 1, entry 17). In contrast, under similar reaction conditions (temperature and pressure) as those in Table 1, entry 3, the use of water as a solvent resulted in the formation of a dark-brown solution, thus highlighting the formation of ruthenium nanoparticles, and led to the exclusive formation of cyclohexylethanol.[33]

Having established the two optimal reaction conditions with our set of catalysts, we next turned out our attention on the substrate scope in the hydrogenation of aromatic ketones (Table 2). We observed that the hydrogenation of electron-deficient ketones that contained trifluoromethyl groups, such as compounds **1b** and **1c**, led to their corresponding secondary alcohols by using an amine-free procedure with catalyst **C** or with catalyst **A** in the presence of triethylamine in 87–99% yields under 30 bar of H_2 pressure at a temperature of 60 °C (Table 2, entries 1 and 2). Similar reaction conditions led to up to 99% yield with *o*- and *p*-methylacetophenones **1d** and **1e** (Table 2, entries 3 and 4). On the other hand, electron-rich functionalized ketones that featured a methoxy moiety at the *o*- and *p*-positions required higher pressures and temperatures (50 bar, 70 °C) to reach complete conversions (Table 2, entries 5 and 6). Finally the hydrogenation of dimethylpropiophenone (**1i**) and cyclic ketones, such as tetralone **1h**, were more difficult with catalyst **A** and high conversions were only obtained at 70–80 °C (Table 2, entries 7 and 8).

Encouraged by the fact that ruthenium(II) complexes that featured a phosphinesulfonate moiety were able to efficiently hydrogenate aromatic ketones, we wanted to investigate the possibility of developing an enantioselective version of this hydrogenation. However, examples of enantiopure phosphinesulfonate chelates are scarce in the literature. Last year, Nozaki and co-workers reported the application of P-chiral phosphinesulfonates in palladium-catalyzed copolymerization reactions, but the access to these phosphines required preparative chiral HPLC.[20e] On the other hand, binaphthophosphepine,[34,35] which was synthesized from binaphthol, has shown interesting activities in the enantioselective hydrogenation of functionalized β-ketoesters.[34d] Then, we decided to prepare a new chiral phosphinesulfonic acid based on binaphthophosphepine. Thus, after the preparation of enantiopure atropoisomeric chlorophosphine according to a literature procedure,[34c] the treatment of the latter compound with the dilithiated salt of benzenesulfonic acid resulted in the formation of the expected phosphine (Scheme 2). From this ligand, deprotonation by treating potassium *tert*-butoxide with the sulfonic acid in methanolic solution, followed by the addition of [{Ru(η^6-*p*-cymene)Cl_2}$_2$], afforded the expected chiral ruthenium complex (**I**, Scheme 3). The ^{31}P NMR data of the fully characterized

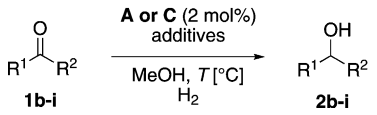


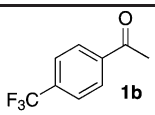
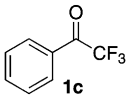
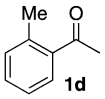
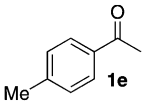
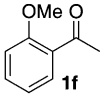
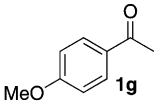
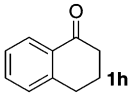
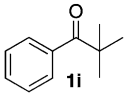
Scheme 2. Synthesis of a chiral phosphinesulfonate from an enantiopure atropoisomeric chlorophosphine.



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

Table 2. Substrate scope in the ketone-hydrogenation reaction.



Entry[a]	Substrate	Catalyst	Pressure [bar]	T [°C]	Additive [mol%]	Yield[b,c] [%]
1	 1b	**C**	30	60	none	99 (80)
		A	30	60	Et_3N (10)	87
2	 1c	**C**	30	60	none	99 (93)
		A	30	60	Et_3N (10)	99
3	 1d	**C**	30	60	none	99 (80)
		A	50	70	Et_3N (10)	99
4	 1e	**C**	30	60	none	99 (85)
		A	50	60	Et_3N (10)	99
5	 1f	**C**	50	70	none	99 (85)
		A	50	70	Et_3N (10)	92
6	 1g	**C**	50	70	none	99 (81)
		A	50	70	Et_3N (10)	85
7	 1h	**C**	50	80	none	94 (90)
		A	50	80	Et_3N (10)	99
8	 1i	**C**	30	60	none	99 (94)
		A	50	70	Et_3N (10)	62

[a] All reactions were carried out with compound **1b–1i** and catalyst **A/C** (1:0.02 molar ratio) for 15 h under the indicated hydrogen pressure by using a thermostated oil bath. [b] Conversion determined by ^1H NMR spectroscopy and GC. [c] Numbers in parentheses are the yields of the isolated products after column chromatography on silica gel.

complex showed one singlet at $\delta = 42$ ppm, and ^1H and ^{13}C analyses suggested that complex **I** was formed as only one diastereoisomer. Structure confirmation was obtained by recrystallization of complex **I** by layering CH_2Cl_2 and *n*-hexane in the presence of a small amount of MeOH (Figure 3). A similar procedure, by treatment with [{Ru(η^6-Me_6C_6)Cl_2}$_2$], afforded complex **J**. With these enantiopure chiral complexes in hand, the enantioselective hydrogenation of acetophenone with a S/C ratio of 100:1 was investigated (Table 3). When compound **1a** was hydrogenated at 60 °C in the presence of complex **I**, along with 10 mol% of the acyclic tertiary triethylamine ($pK_a = 10.8$) under 10 bar of H_2, phenylethanol was formed in 90% yield and 32% enantiomeric excess for (*R*)-**2**, thus demonstrating promising enantioselectivity (Table 3, entry 1). The reaction pressure exerted a strong influence on the enantiodiscrimination in this reaction, whereas temperatures ranging from 60 to 80 °C had less of an impact and an 88:12 enantiomeric ratio was obtained at 80 °C under 50 bar of H_2 (Table 3, entries 2–4). It is important to note that temperatures below 50 °C led to low conversions, whereas temperatures above 80 °C afforded lower enantioselectivities (not shown). However, other attempts to improve this result with triethylamine were unsuccessful.

Next, we turned our attention to the effect of the amine on the enantioselectivity. Diamines, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, $pK_{a1} = 4$, $pK_{a2} = 10.7$), inhibited the hydrogenation reaction (Table 3, entry 5) and similar (low) conversions were obtained with enantiopure cyclohexanediamine and *N*-tosyl-1,2-diphenylethylenediamine, presumably owing to the formation of a stable chelate. Under similar reaction conditions, Hünig's base ($pK_a = 11.4$), as a hindered tertiary amine, gave lower enantioselectivity as compared to triethylamine (Table 3, entry 2 versus entry 6), whereas cyclic *N*-methylpiperidine ($pK_a = 10.1$) afforded a better result (Table 3, entry 2 versus entry 7). Primary and secondary amines, such as diisopropylamine and cyclohexylamine, led to the formation of racemic phenylethanol (Table 3, entries 9 and 10). Similarly, the use of pyridine led to the formation of a racemic alcohol (Table 3, entry 8). As expected, the corresponding in situ generated tris-MeCN complex, as obtained by the treatment of complex **I** in the presence of MeCN followed by precipitation, afforded almost complete conversion in the absence of additives, but with a low *ee* value (31%; Table 3, entry 11). These seminal results demonstrated that the tertiary cyclic amines led to better results and, thus, we decided to investigate the influence of the more rigid bicyclic 1,4-diazabicyclo[2.2.2]octane (DABCO, $pK_{a1} = 3.0$, $pK_{a2} = 8.8$). Thus, the treat-

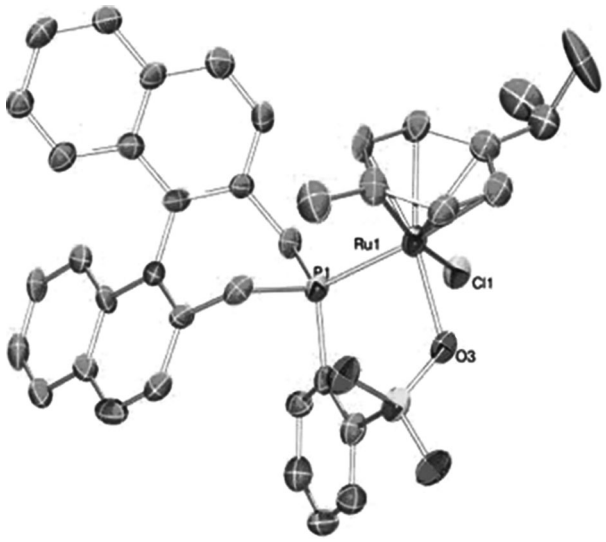
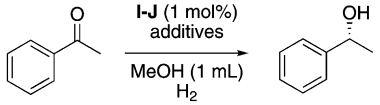


Figure 3. Molecular structure of complex **I**; CCDC 927220.

Table 3. Influence of the amine on the asymmetric ionic hydrogenation of acetophenone.



1a (0.5 mmol) **(*R*)-1-Phenylethanol**

Entry[a]	Cat.	*P* [bar]	*T* [°C]	*t* [h]	Additive [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_3N (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	iPr_2NH (10)	48	55.5:44.5
10	**I**	50	60	15	$C_6H_{11}NH_2$ (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	*t*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.

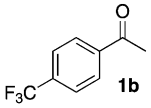
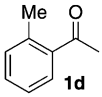
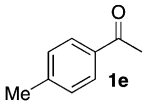
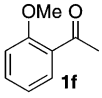
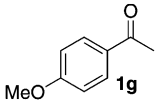
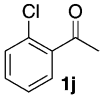
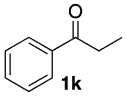
[a] All reactions were carried with compound **1a** and catalyst **I**/**J** (1:0.01 molar ratio) under the indicated hydrogen pressure by using a thermostated oil bath. [b] Conversion determined by ^1H NMR spectroscopy and GC. [c] Determined by chiral GC. [d] Arene-free ruthenium species that was generated by the treatment of catalyst **I** with MeCN, followed by precipitation. [e] In EtOH solvent. [f] In *i*PrOH solvent. [g] Compound **1** and catalyst **I** (1:0.005 molar ratio). [h] Compound **1**, $[\{Ru(p\text{-cymene})Cl_2\}_2]$, and Sulpho-Binepine (1:0.005:0.011 molar ratio). [i] *t*BuOK (1 mol %) was added.

ment of acetophenone under the conditions described in Table 3, entry 2, by simply replacing Et_3N by DABCO, afforded the product in 80% *ee* (Table 3, entry 12 versus entry 2). As we had previously observed, temperatures ranging from 60 to 80°C had little influence on the enantioselectivity (Table 3, entries 12–14). Other alcoholic solvents, such as EtOH, afforded lower yields and *ee* values and the reaction was inhibited in isopropanol (Table 3, entries 15–16). Variation of the amount of DABCO in the range 5–15 mol% showed that the pH value did not affect the enantioselectivity (Table 3, entries 12, 17–19). Finally, the *ee* value reached 85% by increasing the pressure up to 50 bar (Table 3, entry 21). It is important to note that a similar result was obtained with the in situ generated catalyst (Table 3, entry 21 vs. entry 25). Decreasing the amount of the catalyst did not affect the enantioselectivity (Table 3, entry 24), whereas higher catalyst loadings had a negative influence on the *ee* value, presumably owing to the side formation of dimeric organometallic species. As observed in Table 3, entries 22 and 23, no racemization and no dynamic kinetic resolution (DKR) occurred by varying the reaction time, thus leading to the same *ee* value as in Table 3, entry 21. The reaction of complex **J** gave a lower *ee* value, thus demonstrating the strong influence of the arene motif on the conversion and enantiodiscrimination of the reaction (Table 3, entry 28). The presence of an alkoxide base, such as *t*BuOK (1 mol%), with or without DABCO, dramatically lowered the *ee* value (Table 3, entries 26 and 27). From this table, the results demonstrated that secondary amines and aromatic amines mainly led to 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 on the asymmetric hydrogenation reaction. Indeed, under similar reaction conditions (pressure and temperature), the use of distinct tertiary amines afforded the product (**2a**) in 32–78% *ee* (Table 3, entries 2, 6, 7, and 18).

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

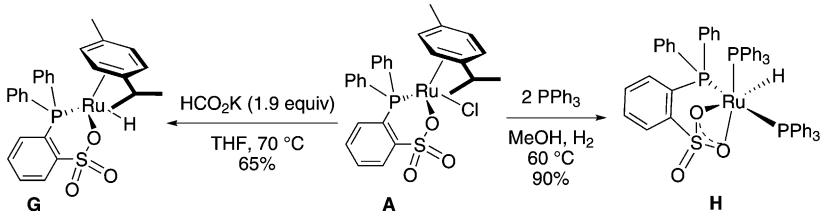
Owing to the differences in reactivities and/or enantioselectivities of the MeCN-containing precatalysts and the arene-ruthenium complexes and, assuming that it could result from the formation of different active species, we investigated the nature of the possibly formed hydride species in solution.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

Table 4. Scope of the asymmetric hydrogenation reaction of aromatic ketones.

Entry[a]	Substrate	Pressure [bar]	T [°C]	Yield[b] [%]	e.r.[c]
1	 1b	50	60	99	73:27 (*R*)
2	 1d	50	60	98	95.5:4.5 (*R*)
3	 1e	50	60	98	93:7
4	 1f	50	70	99	96:4 (*R*)
5	 1g	60	60	99	90.5:9.5 (*R*)
6	 1j	60	60	99	95.5:4.5 (*R*)
7	 1k	60	60	98	92:8 (*R*)

[a] All reactions were carried out with compound **1** and catalyst **I** (1:0.01 molar ratio) for 15 h under the indicated hydrogen pressure by using a thermostated oil bath. [b] Conversions were determined by ^{1}H NMR spectroscopy and GC. [c] Determined by chiral GC and the absolute configuration was determined by analogy to previous reports.

in highly dilute methanolic solution resulted in the loss of the arene ligand and the precipitation of the sole light-red monohydride ruthenium complex (**H**), which featured a phosphinesulfonate moiety, acting as a tridentate κ^3-P,O,O ligand (Scheme 4).[26] X-ray analysis shows a distorted pseudo-octahedral environment in complex **H**, in which the hydride is in a *cis* relationship with all three phosphorus atoms, thus indicating additional π-binding character of the sulfonate moiety (Figure 4). However, it was found to be unstable in solution, but the ^{1}H NMR spectrum only showed one hydride that was located at $\delta = -19.3$ ppm as a quartet.

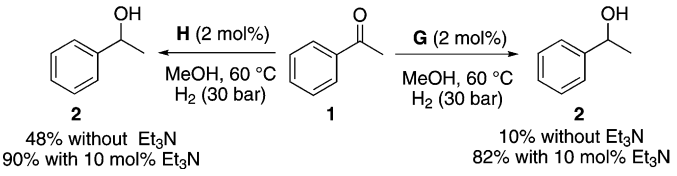


Scheme 4. Preparation of ruthenium(II)-monohydride complexes.

^{31}P NMR analysis revealed the decoordination of one of the oxygen atoms, thus resulting in the formation of two green 16*e* monohydride isomers (see the Supporting Information). Nevertheless, a comparison with the reported formato-hydrido-tris-triphenylphosphine ruthenium(II) complex supported the structural analysis.[36] With these well-defined monohydride complexes in hand, we investigated the nature of the hydride species during the hydrogenation of ketones.

First, we examined the behavior of arene-free ruthenium-hydride complexes. These complexes might allow the coordination of the substrate, owing to the presence of labile ligands, thus resulting in an inner-sphere hydrogenation pathway. Interestingly, the use of arene-free monohydride complex **H** under H_2 pressure (30 bar) afforded moderate conversions without base and high conversions in the presence of Et_3N (Scheme 5). The fact that MeCN-containing complex **C** promoted efficient base-free hydrogenation reactions was surprising because a ^{1}H NMR study at 60 °C in MeOH under hydrogen pressure exhibited no hydride peaks (Scheme 6).[37]

Next, we focused our attention on the arene-ruthenium-based precatalysts. Thus, the treatment of a methanolic solution of complex **A** under 50 bar H_2 pressure in the presence of 10 equiv triethylamine, as followed by NMR study at atmospheric pressure, demonstrated the quantitative formation of monohydride species **G** in less than 3 h, whereas no conversion was observed without triethylamine under similar pressures and temperatures, thus showing that the phosphinesulfonate chelate and the arene-coordination mode remained unchanged at this pressure, both in the presence and absence of triethylamine (Scheme 6). In contrast, the treatment of complex **A** with pyridine resulted in the formation of an arene-free metal species, as confirmed by the disappearance of the arene motif by ^{1}H NMR spectroscopy and explained the absence of asymmetric induction when pyridine



Scheme 5. Hydrogenation reactions in the presence of ruthenium-monohydride species **G** and **H**.

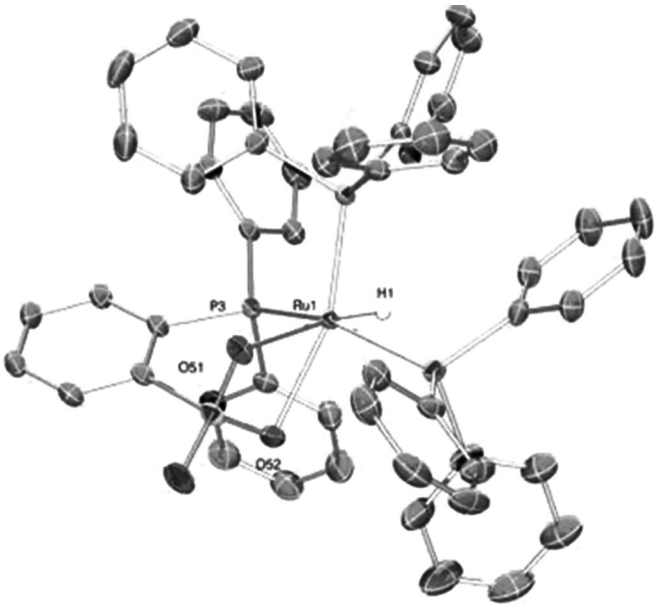
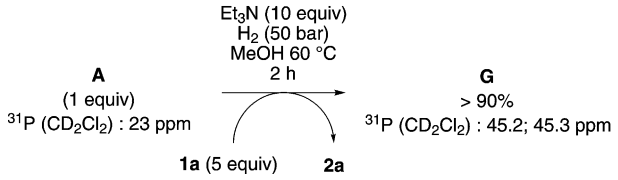
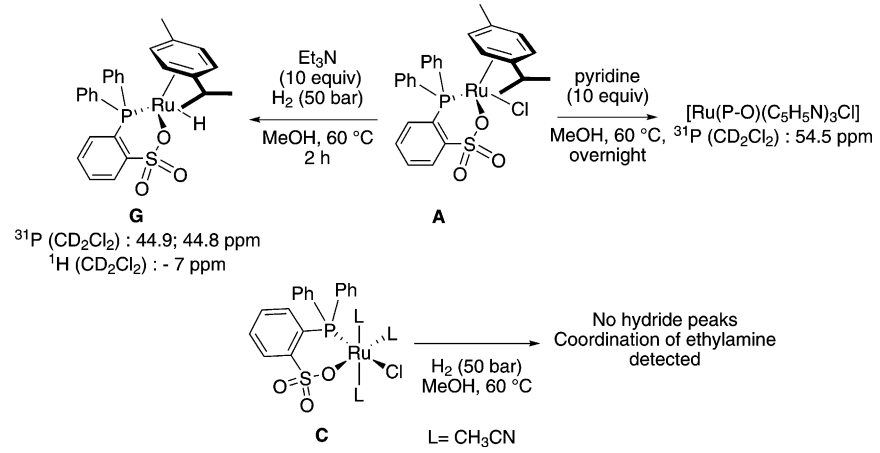


Figure 4. Molecular structure of monohydride complex **H**; CCDC 927212. Ru_1–H_1 1.50(3) Å, Ru_1–O_{51} 2.3523(12) Å, Ru_1–O_{52} 2.3127(12) Å, Ru_1–P_1 2.2461(4) Å.



Scheme 7. Effect of acetophenone on the stability of as-generated monohydride species **G**.



Scheme 6. NMR studies of in situ generated complexes.

was used as an additive (Scheme 6). These experiments show that the choice of the amine plays an important role on determining the reaction pathway during the hydrogenation reaction and they tend to demonstrate that the arene remains bound in the presence of tertiary aliphatic amines, such as Et_3N or DABCO, thus allowing enantiodiscrimination in asymmetric hydrogenation reactions. Confirmation was obtained during the substoichiometric hydrogenation of acetophenone in the presence of complex **A**, because NMR analyses revealed that the nature of the generated species (**G**) was recovered after hydrogenation (Scheme 7). Importantly, a very low yield of phenylethanol was obtained with hydride species **G** without an external aliphatic amine, whereas good yields were obtained in the presence of triethylamine, thus demonstrating that tertiary amine was not only useful for removing the chlorine atom, but also that is might play the role of proton acceptor during the heterolytic cleavage of H_2, thus generating tertiary ammonium salts (Scheme 5).[38]

Our previous results on allylation reactions with ruthenium(IV) species that contained phosphinesulfonate ligands showed that the sulfonic/sulfonate exchange favored the release of water from allylic alcohols through hydrogen-bonding interactions.[29] Following the same trend, it is plausible to assume that the heterolytic cleavage of H_2 occurs through a concerted six-membered transition state in which the amine stabilizes the ruthenium-hydride moiety through hydrogen-bonding interactions with tight ion-pairing, followed by deprotonation of the sulfonic group (Figure 5).

At this point, even if monohydride species **G** was 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 this mechanism (Figure 6).

Experiments shown in Table 1, Table 2, Table 3, and Scheme 7 demonstrated that the arene ligand remained bound to the metal center in the presence of tertiary aliphatic amines. In the inner-sphere mechanism, the hemilability of the sulfonate ($pK_a = -0.93$) moiety, owing to possible hydrogen bonding with a tertiary ammonium salt, would result in the formation of a cationic

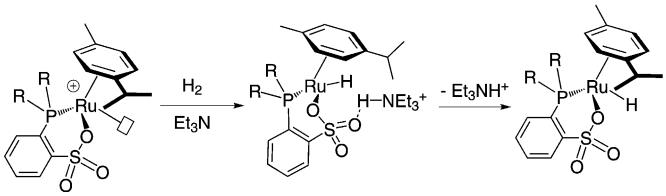


Figure 5. Proposed ionic heterolytic cleavage of H_2.

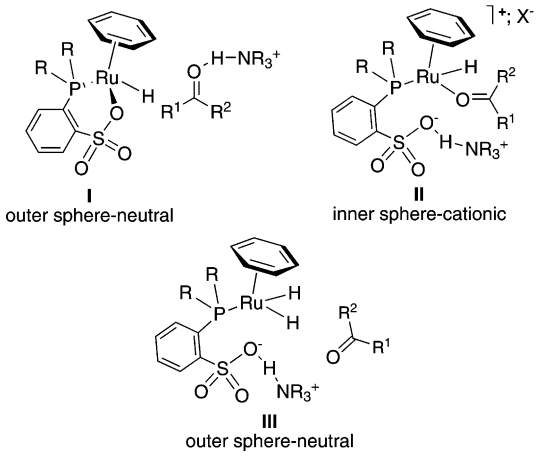


Figure 6. Possible key intermediates in the ionic hydrogenation of aryl ketones with tertiary amines; arene substituents are omitted for clarity.

16*e* ruthenium(II)-monohydride species, thus allowing the coordination of the ketone (species **II**). Recently, Jordan and co-workers 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 that involves the formation of a tight ion-pair between the sulfonate and the ammonium cannot be excluded. On the other hand, the groups of Bullock and Norton highlighted that the use of well-defined [CpW-H] and [CpRu-H] diphosphine complexes promoted the hydrogenation reactions of various ketones and iminium species.[39,40] These interesting reports demonstrated that the ionic hydrogenation reaction occurred through a stepwise outer-sphere mechanism that involved protonation followed by reduction with the resulting metal monohydride species. Based on these reports, an outer-sphere mechanism can also be postulated in which the tertiary ammonium salt acts as a Brønsted acid to activate the carbonyl group, thus leading to electrophilic intermediates (species **I**). It is noteworthy that, during the stoichiometric treatment of acetophenone **1a** in the presence of monohydride species **G**, along with triethylammonium chloride and/or triethylamine, the formation of phenylethanol was never detected in the absence of hydrogen (Scheme 8).

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

Importantly, the presence of MeOH as the 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 that were obtained in Scheme 8, a ruthenium-dihydride species (**III**), or closely related species that arose 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 occurs to allow the coordination of the substrate, an outer-sphere mechanism can be rationalized to explain the mechanism of this hydrogenation reaction (Figure 7).

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

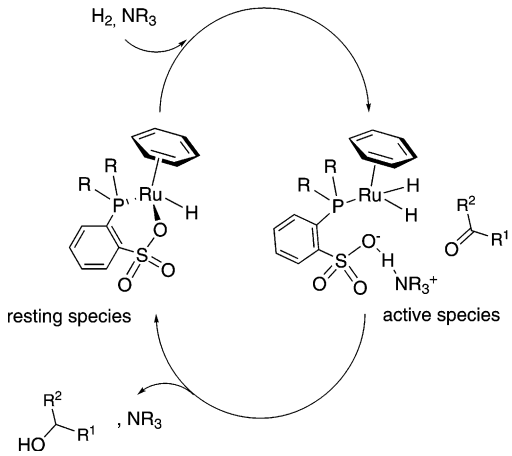


Figure 7. Proposed catalytic cycle.

Conclusion

In conclusion, we have developed two catalytic systems that contained ruthenium(II) complexes with phosphinesulfonate chelates for the hydrogenation of aryl ketones. MeCN-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 that the choice of amine is crucial and that, with tertiary amines, the arene ligand remains bound to the metal center. Stoichiometric investigations revealed that ruthenium-monohydride species were the resting species in the hydrogenation process. Even if, at this stage, the seminal applications in asymmetric hydrogenation of the new Sulfo-binepine ligand are less effective than the well-established hydrogenation catalysts, these results demonstrate the potential use of such ligands in hydrogenation reactions. The modularity of tertiary amines, combined with the diversity in hemilabile L–O chelates, should afford interesting uses in enantioselective hydrogenation reactions. Our current efforts are focused on the isolation of dihydride species **III**.

Experimental Section

Synthesis of 2, (11b*S*)-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepin-4(5*H*)-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) dropwise at 0 °C over 10 min under an argon atmosphere. The mixture was stirred at 0 °C for 10 min, at RT for 10 min, at 50 °C for 10 min, and at RT for 10 min. Then the resulted salt was cooled at −78 °C. Simultaneously, (11b*S*)-4-chloro-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine (1.25 g, 3.66 mmol, 1.0 equiv) was dissolved in THF (5 mL) and cooled to −78 °C. Then, the lithiated benzenesulfonic acid was transferred dropwise through a cannula into the solution of the phosphine precursor in THF at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and allowed to warm at RT for a further 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 M HCl aqueous solution to pH ≈ 2 at 0 °C and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under vacuum to generate a yellow solid. The solid was washed with distilled THF, filtered, and washed with a minimum amount of THF to afford a white powder (0.41 g, 23 %). $[\alpha]_D^{20} = -191$ ($c = 0.36$, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.17$ (dd, $J = 7.6$, 4.4 Hz, 1H), 8.12 (d, $J = 8.4$ Hz, 1H), 8.04 (d, $J = 8.2$ Hz, 1H), 7.99 (d, $J = 8.1$ Hz, 1H), 7.95 (d, $J = 8.5$ Hz, 1H), 7.77 (m, 1H), 7.71 ppm (d, $J = 8.4$ Hz, 1H), $\delta = 7.57$ (m, 2H), 7.45–7.41 ppm (m, 1H), $\delta = 7.36$–7.31 (m, 3H), 7.26–7.16 (m, 3H), 4.26 (t, 1H), 3.80–3.71 (m, 2H), 3.59–3.51 ppm (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta =$ 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 127.52–127.05 all corresponded to tertiary carbon atoms, but they were not fully characterized owing to complex P,C coupling), 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; CH_2), 24.95 ppm (d, J(P,C) = 47.7 Hz; CH_2); ^{31}P (162 MHz, CD_2Cl_2): $\delta = 15.98$ ppm; HRMS (ESI): m/z calcd for $C_{28}H_{21}O_3NaPS$: 491.08467 $[M+Na]^+$; found: 491.0849; m/z calcd for $C_{28}H_{22}O_3PS$: 469.10273 $[M+H]^+$; found: 469.1033.

Synthesis of complex I, [Ru(η⁶-*p*-cymene)(κ²-*o*-{(11b*S*)-3*H*-dinaphtho(2,1-*c*:1′,2′-*e*)phosphepin-4(5*H*)-yl}C₆H₄SO₃)Cl]: 2-((11b*S*)-3*H*-Dinaphtho[2,1-*c*:1′,2′-*e*]phosphepin-4(5*H*)-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 RT for 30 min. To this solution was added $[\{Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$ (0.200 g, 0.396 mmol, 0.5 equiv). The red solution became a slurry after 1 h. After stirring for 16 h at RT, the solution was concentrated, the MeOH was removed by cannula, and the solid was washed with MeOH (2 × 1 mL). Then, the crude was washed with CH_2Cl_2 (2 × 8 mL). The solution was filtered through dry celite (distilled and degassed CH_2Cl_2) to remove the inorganic salts. Then, the solvent was removed under vacuum to generate complex **I** as an orange solid (0.37 g, 36 %). $[\alpha]_D^{20} = -127$ ($c = 0.1733$, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.11$ (d, $J = 8.3$ Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 1H), 7.98 (ddd, $J = 7.6$, 3.9, 1.0 Hz, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 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, $J =$ 8.2 Hz, 1H), 6.63 (dd, $J = 7.9$, 7.9 Hz, 1H), 5.89 (d, $J = 5.9$ Hz, 1H), 5.54 (d, $J = 6.0$ Hz, 1H), 4.88 (d, $J = 5.8$ Hz, 1H), 4.71–4.68 (m, 1H), 4.17 (dd, $J = 13.8$, 5.6 Hz, 1H), 3.76 (dd, $J = 13.2$, 4.1 Hz, 1H), 3.66 (m, 2H), 3.03 (qq, $J = 6.9$, 7.0 Hz, 1H), 2.10 (s, 3H), 1.37 (d, $J = 7.0$ Hz, 3H), 1.36 ppm (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 147.53$ (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 131.19–126.12 all corresponded to tertiary carbon atoms, but they were not fully characterized owing to complex P,C coupling), 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; CH_2), 31.51(CH), 30.00 (d, J(P,C) = 33.4 Hz; CH_2), 22.91(CH_3), 20.84(CH_3), 18.55 ppm (CH_3); ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 42.34$ ppm; HRMS (ESI): m/z calcd for $C_{38}H_{34}O_3PSRu$: 703.10043 $[M-Cl]^+$; found: 703.1006.

CCDC 927220 (**I**) 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.

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