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SYNTHESIS AND APPLICATION OF PHOSPHINITE LIGAND-CONTAINING RUTHENIUM CATALYSTS IN TRANSFER HYDROGENATION

Abstract: *Transfer hydrogenation (TH) is a highly significant reaction in organic chemistry, especially in the synthesis of pharmaceuticals, agrochemicals, and fine chemicals. This method involves the transfer of hydrogen from a donor molecule to an unsaturated substrate, offering a safer and more convenient alternative to direct hydrogenation, which typically requires high-pressure hydrogen gas. TH stands out for its ability to selectively reduce multiple functional groups under milder conditions, thereby reducing the risk of over-reduction or damage to sensitive functional groups. This technique is particularly valuable in asymmetric synthesis (AS), where chiral catalysts enable the production of enantiomerically pure compounds, crucial for drug development.*

Ruthenium complexes are particularly noteworthy for their effectiveness in asymmetric TH. Their stability and adaptability to different reaction environments make them ideal for both laboratory-scale and industrial applications. Phosphinite ligands ($P(OR)R'_2$) *are used in synthesis of complexes to improve their properties. These ligands are known for their ability to finely tune the electronic and steric properties of metal centers. The electron-donating nature of the phosphorus atom, combined with the variability in the R and R' groups, allows for significant customization of the catalyst's properties.*

The purpose of the work is to review up-to-date discoveries in the field of TH.

The integration of phosphinite ligands into ruthenium catalysts marks a significant advancement in the field of TH. These catalysts exhibit enhanced efficiency, selectivity, and stability, proving crucial in AS. The study's exploration of various hydrogen sources, bases, and mechanisms has provided deeper insight into the process of TH.

Key words: *transfer hydrogenation, ruthenium catalyst, phosphinite ligand, asymmetric synthesis, enantioselectivity, catalytic efficiency, steric and electronic properties.*

Introduction

Transfer hydrogenation (TH) is a highly significant reaction in organic chemistry, especially in the synthesis of pharmaceuticals, agrochemicals, and fine chemicals. This method involves the transfer of hydrogen from a donor molecule to an unsaturated substrate, offering a safer and more convenient alternative to direct hydrogenation, which typically requires high-pressure hydrogen gas, upgraded from 2018 to 2023 [1-6]. TH stands out for its ability to selectively reduce multiple functional groups under milder conditions, thereby reducing the risk of over-reduction or damage to sensitive functional groups [3]. This technique is particularly valuable in asymmetric synthesis, where chiral catalysts enable the production of enantiomerically pure compounds, crucial for drug development [4].

Ruthenium catalysts have gained prominence in transfer hydrogenation due to their excellent catalytic activity by 2018. These catalysts are versatile and can be used in the reduction of various functional groups, including ketones, aldehydes, imines, and even nitriles [5, 6].

Ruthenium complexes are particularly noteworthy for their effectiveness in asymmetric transfer hydrogenation, providing high enantioselectivity in the reduction of prochiral substrates [7]. Their stability and adaptability to different reaction environments make them ideal for both laboratory-scale and industrial applications.

Phosphinite ligands, typically characterized by their $P(OR)R'_2$ structure (where R and R' represent alkyl or aryl groups), are a class of ligands that have attracted considerable interest in catalysis. These ligands are known for their ability to finely tune the electronic and steric properties of metal centers [8-12]. The electron-donating nature of the phosphorus atom, combined with the variability in the R and R' groups, allows for significant customization of the catalyst's properties. This customization can influence the catalyst's activity, selectivity, and stability, making phosphinite ligands highly valuable in the design of advanced catalytic systems [13].

The incorporation of phosphinite ligands into ruthenium catalysts has revolutionized their application in transfer hydrogenation. These ligands enhance the efficiency and selectivity of ruthenium catalysts, enabling more precise control over the reaction process. In asymmetric transfer hydrogenation, phosphinite ligands have been instrumental in achieving high levels of enantioselectivity, crucial for the production of chiral molecules. Additionally, the steric and electronic modulation provided by these ligands has been found to improve the turnover frequency and operational stability of ruthenium catalysts, making them more effective and durable for various synthetic applications. The development of ruthenium-phosphinite catalysts represents a significant advancement in catalysis, offering new possibilities for efficient, selective, and sustainable chemical synthesis [14-16].

Phosphinite Ligands: Structure, Properties, and Synthesis

Due to the distinctive properties of phosphorus derivatives in metal coordination, trivalent phosphorus ligands have consistently been significant in asymmetric homogeneous organometallic catalysis as metal binders. These compounds provide the ability to tailor the steric and electronic attributes of the ligands. From an electronic perspective, the π-acceptor characteristics of the phosphorus group can be significantly altered by substituting P-C bonds with P-O, resulting in the formation of phosphinites, phosphonites, or phosphites (refer to Figure 1a). Generally, ligands, and particularly phosphorus-based derivatives, vary based on their coordination style, including monodentate, bidentate, or polydentate modes, as illustrated inFigure 1b [17].

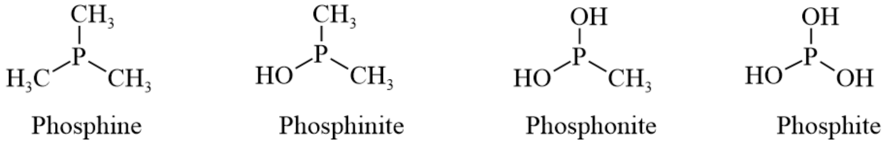


Figure 1a – Various trivalent phosphorus ligand families

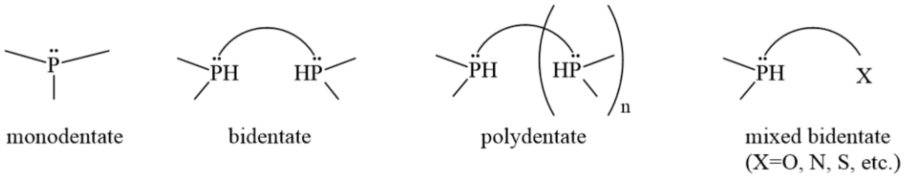


Figure 1b – Modes of coordination for the trivalent phosphorus ligands

The P-O bond in phosphinites is polar due to the higher electronegativity of oxygen compared to phosphorus, resulting in a partial negative charge on oxygen and a partial positive charge on phosphorus. This polarity significantly influences the ligand's electronic characteristics, affecting its coordination behavior with metals. Moreover, the steric properties of phosphinite ligands, dictated by the size and shape of the R and R' groups, are crucial in determining their utility in catalysis, particularly in controlling the spatial environment around the metal center [18, 19].

Synthesizing phosphinite ligands typically involves a reaction between a secondary phosphine and an alcohol. The general reaction can be represented as follows (1) [20]:

$$R\text{-}OH + R'_2PH \rightarrow R\text{-}OPR'_2 + H_2 \quad \mathbf{(1)}$$

The choice of R and R' groups offers a plethora of possibilities for the resultant phosphinite ligand. Key factors in this synthesis include the selection of appropriate secondary phosphine and alcohol, reaction conditions such as temperature and duration, and the potential use of catalysts or dehydrogenating agents to drive the reaction to completion [21-26].

A prototypical example is the synthesis of diphenylphosphinite ($H_2NC_6H_4$-$OPPh_2$) from diphenylphosphine (Ph_2PH) and an alcohol such as 2-aminophenol ($H_2NC_6H_4OH$) (Figure 2). The process generally yields high-purity phosphinite ligands, with typical yields exceeding 85% [27].

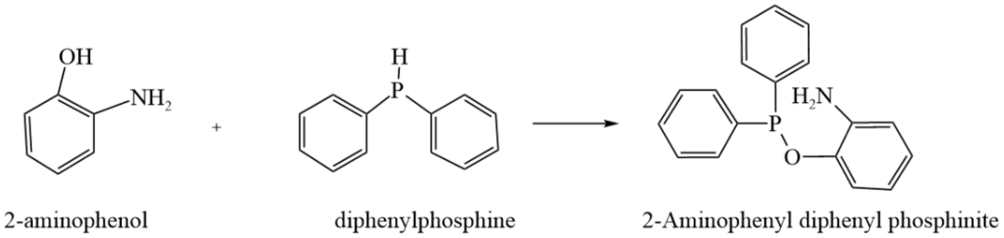


Figure 2 – Synthesis of 2-Aminophenyl diphenyl phosphinite

Another example of the preparation of phosphinite ligands is shown below in Figure 3

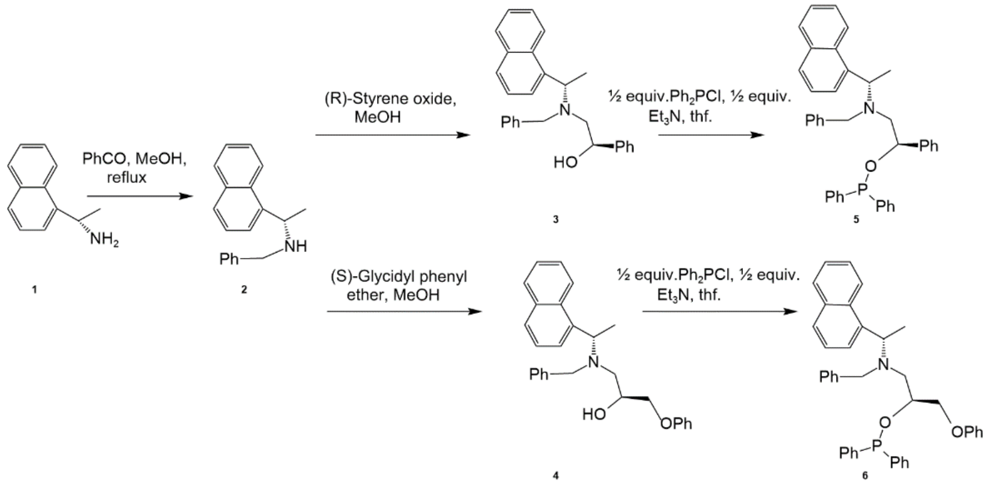


Figure 3 – Synthesis of phosphinite ligands [5].

Aydemir and Tribo groups [5, 28] describe the synthesis of chiral monodentate C_1-symmetric phosphinite ligands. This process involves hydrogen abstraction from specific chiral amino alcohols, using triethylamine (Et_3N) and reacting with phenyldichlorophosphine (Ph_2PCl) in anhydrous methylene chloride (CH_2Cl_2), all under an inert argon atmosphere [29]. The phosphinite ligands, known to gradually decompose into oxide and diphenylphosphinous acid ($Ph_2P(O)H$)[30], were characterized by ^{31}P-{^1H} NMR spectroscopy. This spectroscopy revealed the formation of PPh_2PPh_2 and $P(O)Ph_2PPh_2$, with distinctive NMR signals [31].

The advancement of the ligand preparation reactions was effectively tracked using ^{31}P-{^1H} NMR spectroscopy. The initial PPh_2Cl material, exhibiting signals at $\delta = 81.0$ ppm, vanished, and new singlets emerged at lower fields, indicating the formation of phosphinite ligands (3,4,5,6 in Figure 3). Moreover, the ^{31}P-{^1H} NMR spectra of the isolated ligands matched the values, $\delta=15.4$ ppm, 35.0 ppm, 21.6 ppm previously reported for similar compounds [5, 32, 33].

Development of Ruthenium-Phosphinite Catalysts

Ru complexes in Figure 4 were synthesized using specific phosphinite ligands and ruthenium precursors [34]. Notably, the use of $[Ru(\eta^6\text{-p-cymene})(\mu\text{-Cl})Cl]_2$ and $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ as precursors is outlined, with the formation of mono- or binuclear complexes [35]. In the synthesis of ruthenium(II) complexes, the initial material used was $[Ru(\eta^6\text{-p-cymene})(\mu\text{-Cl})Cl]_2$. This precursor was synthesized through a reaction involving a commercially available compound, α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene), and $RuCl_3$ [36]. The ligand p-cymene is especially revealing in understanding the symmetry of the tri-legged fragment in the molecular structure [37].

In ruthenium chemistry, p-cymene is a common arene ligand, and its NMR signal is sensitive to the symmetry of organometallic compounds [38]. When coupled to a ML$_2$L' metal fragment (C$_s$ symmetry), the ^{1}H and ^{13}C NMR peaks are significantly different from those associated with h^6-coordinated to a ML$_1$L$_2$L$_3$ fragment (C$_1$ symmetry) [39]. In this case, the free rotation of p-cymene ligand around the axis of Ru-arene prevented by the steric hindrance of amino alcohol phosphinite ligands [40]. The authors discuss the sensitivity of NMR signals of p-cymene to the symmetry in ruthenium complexes and analyzes the nuclear Overhauser effect interaction to deduce stereochemistry. The synthesis and characterization of complexes are described in detail, with a focus on their NMR spectra and the influences of solubility on the target product's yields. The study concludes with the confirmation of the structures of these complexes using IR spectroscopy and microanalysis [5].

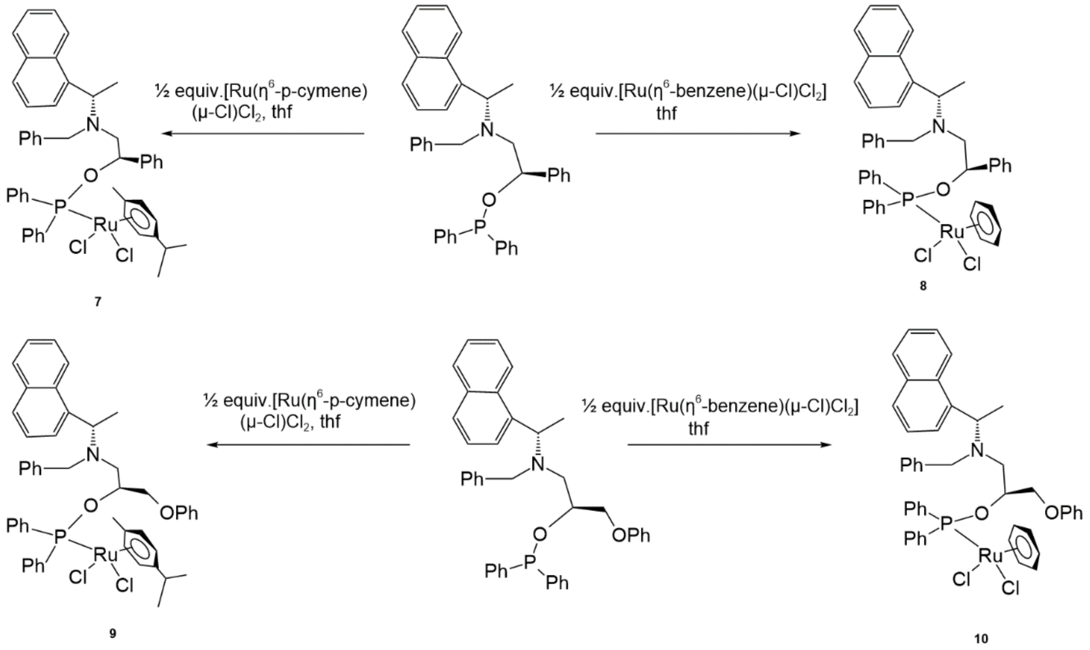


Figure 4 – Synthesis of Ru catalysts [5].

The Ru-arene complexes shows singlets in their ^{31}P-{^{1}H} NMR spectra at approximately δ 106-110 ppm [41]. The successful formation of Ru-phosphinite complexes in 2020 is often validated by a combination of spectroscopic and crystallographic techniques [41]. These complexes are significant due to their enhanced catalytic properties, particularly in transfer hydrogenation reactions, where they exhibit improved reactivity and selectivity [42-47].

Catalytic Applications in Transfer Hydrogenation

The authors [5] discuss the development of new Ru(II) complexes with carefully crafted ligands, driven by the impressive catalytic capabilities and structural flexibility of phosphinite-based transition metal complexes in 2018 [48, 49]. Special emphasis was placed on arene ligands [50] due to their unique properties: they occupy three adjacent sites in ruthenium's octahedral coordination environment, offer distinct reactivity due to their relatively weak electron-donating nature, and allow for flexible substitution patterns. The study tested these complexes as catalysts in the transfer hydrogenation of aromatic ketones using iPrOH solution, with compounds in Figure 4 serving as precatalysts alongside iPrOH/KOH as the reducing system and acetophenone as the model substrate, Figure 5.

Figure 5 – Transfer hydrogenation of acetophenone

Table 1 – Transfer hydrogenation of acetophenone with 2-propanol catalyzed by (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen 1-yl)ethyl] amino} – 1-phenylethyl diphenylphosphinito [dichloro(η^6-*p*-cymene)ruthenium(II)] (7), (1*R*)-2{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito [dichloro(η^6-benzene) ruthenium (II)] (8), (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinito[dichloro(η^6-*p*-cymene)ruthenium (II)] (9) and (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino} – 3 phenoxypropan–2-yl diphenylphosphinito [dichloro(η^6-benzene) ruthenium (II)] (10), (catalysts 7, 8, 9, 10 are shown in picture 4)

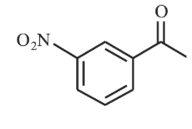
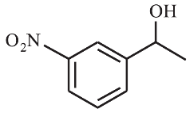
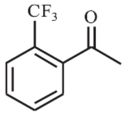
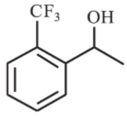
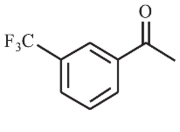
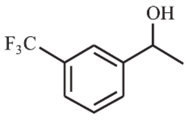
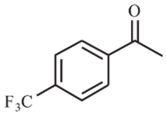
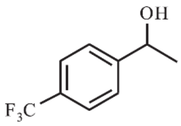
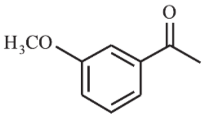
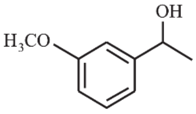
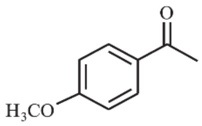
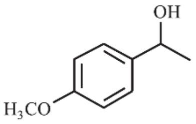
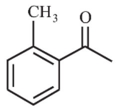
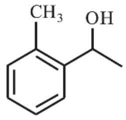
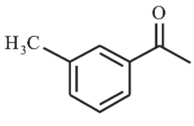
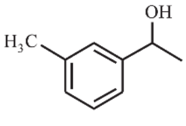
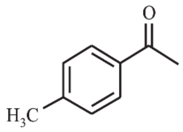
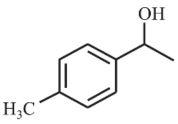
Entry	Complex	S/C/KOH	Time	Conversion (%)[f]	% ee[g]	Conf.[h]	TOF(h^{-1})[j]
1	7[a]	100:1:5	96h	12 (22) d	72 (65) d	S	<5
2	8[a]	100:1:5	96h	16 (28) d	81 (77) d	S	<5
3	9[a]	100:1:5	96h	21 (34) d	86 (81) d	R	<5
4	10[a]	100:1:5	96h	28 (53) d	91 (87) d	R	<5
5	7[b]	100:1	1h	trace	…	…	…
6	8[b]	100:1	1h	trace	…	…	…
7	9[b]	100:1	1h	trace	…	…	…
8	10[b]	100:1	1h	trace	…	…	…
9	7[c]	100:1:5	2h	97 (91) e	78 (70) e	S	48
10	8[c]	100:1:5	1h	98 (93) e	87 (79) e	S	98
11	9[c]	100:1:5	1h	99 (93) e	91 (86) e	R	99
12	10[c]	100:1:5	1/2h	98 (92) e	96 (91) e	R	196
13	10	100:1:3[k]	1/2h	94	89	S	188
14	10	100:1:5[k]	1/2h	98	96	S	196
15	10	100:1:7[k]	1/2h	90	90	R	180
16	10	100:1:9[k]	1/2h	87	91	R	174

Reaction conditions: [a] At room temperature; acetophenone/Cat./KOH, 100:1:5; [b] Refluxing in 2-propanol; acetophenone/Cat., 100:1, in the absence of base; [c] Refluxing in 2-propanol; acetophenone/Cat./KOH, 100:1:5; [d] At room temperature; acetophenone/Cat./KOH, 100:1:5, (120 h); [e] Refluxing in 2-propanol; acetophenone/Cat./NaOH, 100:1:5; [f] Determined by GC (three independent catalytic experiments); [g] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m x 0.32 mm I.D. x 0.25 μm film thickness); [h] Determined by comparison of the retention times of the enantiomers on the GC traces with the literature values, (S) or (R) configuration was obtained in all experiments; [i] TOF = (mol product/mol Cat.) x h-1; [k] Refluxing in 2-propanol; acetophenone/Cat.,100:1.

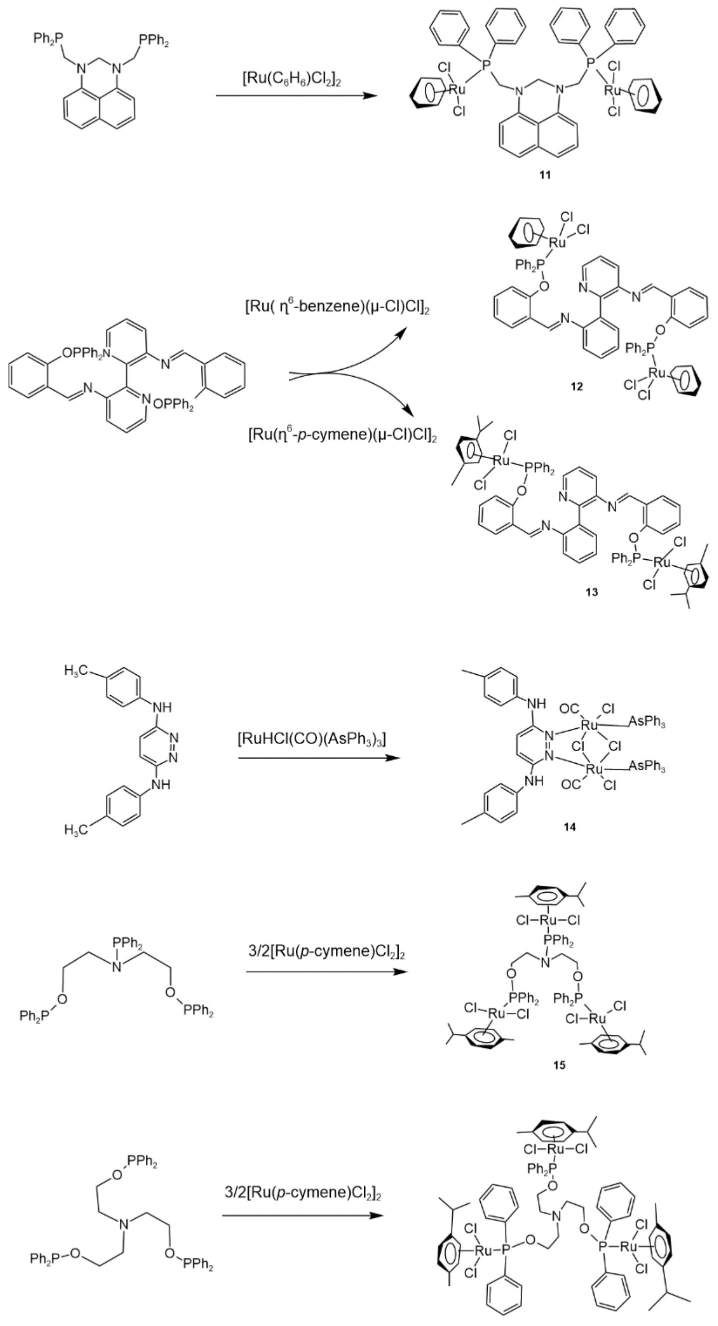
Also, outlines the efficiency evaluation of Ru(II) complexes in the asymmetric transfer hydrogenation of ketones, using acetophenone as a standard test reaction. The experiments, conducted under argon using Schlenk-line techniques, involved adding acetophenone and KOH/iPrOH solution to an iPrOH solution of each complex at room temperature. The reactions yielded (R) or (S)-1-phenyl ethanol with varying conversions and enantiomeric excesses. Temperature was found to play a crucial role in catalytic activity and enantioselectivity. The study also notes that the Ru(II) complexes were highly active, leading to quantitative conversions with varying catalyst/base ratios. A control experiment without a base showed no significant conversion. Also, replacing KOH with NaOH resulted in a minor reduction of both the reaction speed and the enantioselectivity, Table 1. The research further revealed that complexes with -CH_2OPh in the phosphinite skeleton showed higher activity than those with -Ph moiety. The electronic characteristics, including both the type and the location of substituents on the phenyl ring of the ketone, influenced the rate of reduction and the enantioselectivity. Notably, adding electron-withdrawing groups to the aryl ring of the ketone reduced the electron density on the C=O bond, thereby enhancing the activity and facilitating easier hydrogenation, Table 2. [51-53].

Binuclear and trinuclear ruthenium complexes have emerged as an important class of catalysts for TH. Both the Li and Aydemir research groups synthesized stable phosphinite-bridged dinuclear ruthenium arene complexes [54,55], labeled 12 and 13, through the metalation of phosphinite-containing Schiff base ligands with [Ru(η^6-arene)-(μ-Cl)Cl]$_2$. These complexes demonstrated high catalytic efficiency in TH of aromatic ketones, with 12 and 13 achieving turnover frequency (TOF) values up to 530 h^{-1} [55]. Additionally, a binuclear ruthenium(II) pyridazine complex, 14, proved effective for similar reactions [56]. Innovative tridentate aminophosphine−phosphinite and phosphinite ligands were also developed, leading to trinuclear ruthenium(II) dichloro complexes. When applied in TH of ketones in 2-PrOH solution, particularly with 4-fluoro acetophenone, these complexes, especially catalyst 15, achieved a TOF of 1176 h^{-1} [57], Figure 6.

Table 2 – Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito [dichloro(h^6-*p*-cymene)ruthenium(II)] (7), (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito [dichloro(h^6-benzene)ruthenium(II)] (8), (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yldiphenyl-phosphinito [dichloro-(h^6-*p*-cymene) ruthenium(II)] (9) and (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinito [dichloro(h^6-benzene)ruthenium(II)](10)[a], (catalysts 7, 8, 9, 10 are shown in picture 4)

Entry	Cat.	Substrate	Product	Time	Conv.(%)[b]	% ee[c]	Config.[d]
1	7			45 min	98	77	S
2	8			20 min	97	85	S
3	9			20 min	99	90	R
4	10			10 min	99	94	R
5	7			1 h	97	79	S
6	8			30 min	98	87	S
7	9			20 min	98	92	R
8	10			20 min	97	96	R
9	7			45 min	99	76	R
10	8			20 min	98	85	R
11	9			20 min	98	90	R
12	10			10 min	99	94	R
13	7			30 min	99	74	S
14	8			15 min	99	84	S
15	9			15 min	97	86	R
16	10			5 min	98	90	R
17	7			13 h	97	81	S
18	8			8 h	99	89	S
19	9			8 h	98	92	R
20	10			5 h	98	98	R
21	7			8 h	99	66	S
22	8			5 h	99	73	S
23	9			5 h	97	81	R
24	10			3 h	99	87	R
25	7			12 h	97	70	S
26	8			7 h	99	74	S
27	9			7 h	98	85	R
28	10			4 h	99	93	R
29	7			9 h	97	67	S
30	8			5 h	98	71	S
31	9			5 h	98	81	R
32	10			3 h	99	90	R
33	7			6 h	98	64	S
34	8			3 h	99	68	S
35	9			3 h	97	79	R
36	10			2 h	99	84	R

Reaction conditions: [a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), KOH (0.025 mmol%), 82ºC, the concentration of acetophenone derivatives are 0.1M; [b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone; [c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m 0.32 mmI.D. x 0.25 mm film thickness);[d] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, (S) or (R) configuration was obtained in all experiments.



ligand - 1,3-Bis[(diphenylphosphanyl)methyl]-2,3-dihydro-1H-perimidine
substrate: ketones
ee > 70%
[54]

ligand - N_3,N_3-di-2 (diphenylphosphino)benzylidene-[2,2]bipyridinyl-3,3-diamine,
substrate: acetophenone and its derivatives,
ee > 92%
[55]

ligand -N_3,N_3-di-2 (diphenylphosphino)benzylidene-[2,2]bipyridinyl-3,3-diamine,
substrate: acetophenone and its derivatives,
ee > 92%
[55]

ligand - N,N'-*Di*-*p*-tolyl-pyridazine-3,6-diamine
substrate: ketones
ee >67%
[56]

ligand - 2-[(diphenylphosphanyl)({2-[(diphenylphosphanyl)oxy]ethyl})amino]ethyldiphenylphosphinite
substrate: acetophenone and its derivatives
ee> 94%
[57]

ligand - 2-[bis({2-[(diphenyl phosphanyl)oxy]ethyl})amino]ethyldiphenylphosphinite
substrate: acetophenone and its derivatives
ee> 93%
[57]

Figure 6 – Binuclear and Trinuclear Ru TH Catalysts and their ligands [54-57]

Hydrogen sources and bases in TH

In the realm of TH powered by transition-metal catalysts, a diverse array of "sacrificial" hydrogen sources has been employed, including cyclohexene, cyclohexadiene, various alcohols (2-PrOH, MeOH, EtOH, glycerol), formic acid, Hantzsch esters [58], hydrazine, benzothiazoles, and more. The prevalent use of 2-PrOH and formate as reducing agents is largely attributed to their affordability and sustainability. Certain instances saw the use of an alkane as the hydrogen donor and an olefin as the acceptor, to optimize the thermodynamics of the TH reaction. A pioneering example by Crabtree's group [59] in 1979 demonstrated the efficient catalysis of hydrogen transfer from cyclones to t-butylethylene using an iridium complex, yielding the corresponding cycloolefins and 2,2-dimethylbutane. Subsequent studies revealed the activity of other complexes as $[IrH_2(O_2CCF_3)(PAr_3)_2]$ and $[ReH_7(PPh_3)_2]$ in similar dehydrogenation processes [60,61].

In 2003, Goldman's research identified the "pincer"-ligated transition-metal complex $[Ir(^{t\text{-}Bu}PCP)H_2]$ as a robust catalyst for TH reactions [62,63], producing enamines and cyclooctenes with good yields. The solvent medium for TH has varied from organic, ionic liquid [64-67], and aqueous states [68]. Enzyme-catalyzed TH in aqueous media, a longstanding natural process, has guided recent advances in metal-catalyzed TH in water [69-74]. These advancements underline the economic and environmental advantages of water as a solvent, its compatibility with commonly used hydrogen sources, and the breakthroughs in synthesizing water-soluble catalysts or ligands [75-77]. The performance of transition metals in aqueous media is particularly influenced by the pH of the reaction mixtures, enhancing selectivity and minimizing side reactions [78-80]. In particular, reactions in water have been observed to proceed faster than in organic solvents, marking a significant stride in the field of catalysis [81,82].

In TH, a variety of organic and inorganic bases, including Et_3N, KOH, NaOH, and others, have been utilized. The catalytic efficiency of transition-metal catalysts in TH is influenced by the base's pKa value and whether it's cationic or anionic [83]. Interestingly, TH has been successfully conducted in some instances without any base [84-87]. A wide range of unsaturated compounds, such as ketones and aldehydes, have been reduced through TH, facilitated by either homogeneous or heterogeneous transition-metal catalysts. This process has even been extended to the industrial-scale synthesis of asymmetric products [88].

Proposed transfer hydrogenation reaction pathways

The transfer of hydrogen to ketones or aldehydes generally follows three distinct pathways. The first, known as "direct hydrogen transfer," is associated with main group elements and does not involve a metal hydride intermediate. The second pathway, the "hydridic route," is common for most transition metal catalysts and includes a metal hydride intermediate in the hydrogen transfer. Metal-ligand bifunctional catalysts, which have both a hydridic hydrogen on the metal and an acidic hydrogen on the ligand, also function via this hydridic route. Additionally, an "ionic mechanism" has been suggested for some transition-metal-catalyzed hydrogenations [89, 90].

For catalysts that are monohydride complexes and follow the "hydridic route" in hydrogen transfer to ketones, two distinct pathways, "inner-sphere" and "outer-sphere" mechanisms, have been proposed. In both cases, the hydride moves to the carbonyl carbon. However, the inner-sphere mechanism involves the formation of a metal alkoxide intermediate, requiring the substrate's coordination with the catalyst. In contrast, the outer-sphere mechanism suggests a concerted hydrogen transfer that occurs without substrate coordination to the catalyst [89].

A prominent example in hydrogen-transfer catalysts is the Shvo catalyst, identified as $\{[Ph_4(\eta^5\text{-}C_4CO)]_2H\}\text{-}Ru_2(CO)_4H$ [90, 101], Figure 7, 8.

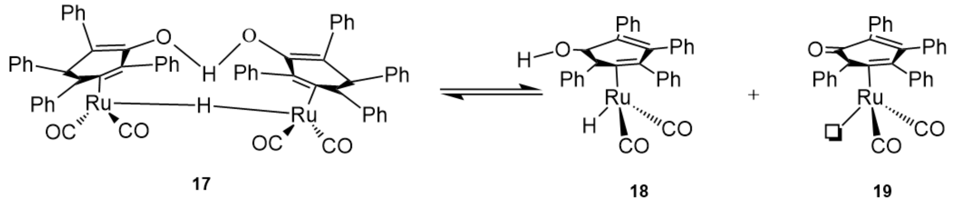


Figure 7 – Equilibrium between Precursor and Active Species of the Shvo Catalyst

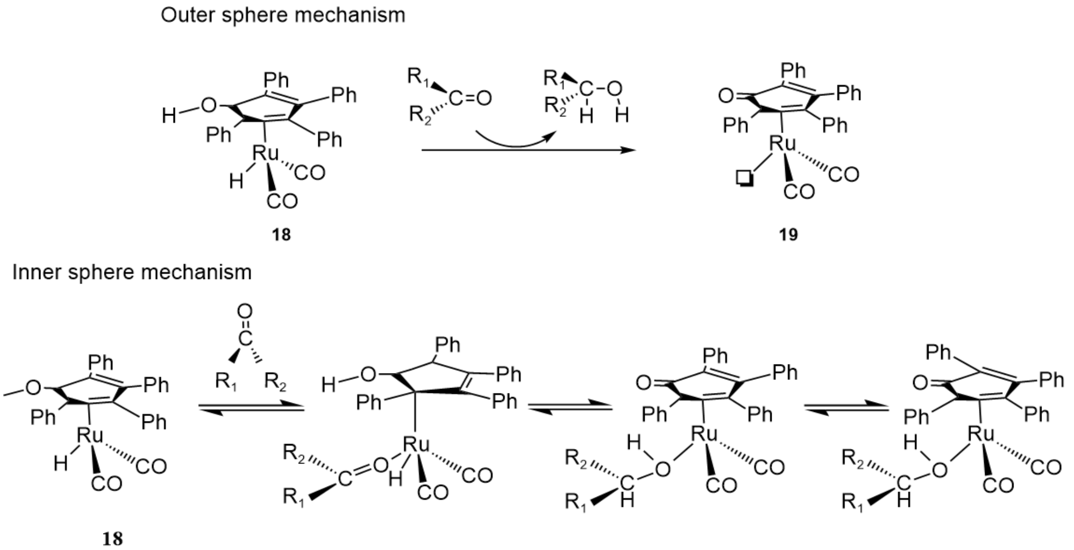


Figure 8 – Proposed mechanisms for the carbonyl hydrogenation by means of the Shvo catalyst

Catalyst (17) in Figure 7 has been effectively utilized in various hydrogen-transfer [90,91] reactions, including the hydrogenation of alkynes [92], carbonyls [93], and imines [94], as well as the oxidation of alcohols [95] and amines [96]. It's also used in the dynamic kinetic resolution of secondary alcohols [97] and primary amines [98] alongside lipases. Introduced about two decades ago, the Shvo catalyst was among the earliest metal-ligand bifunctional catalysts. Since its development, numerous such catalysts based on Ru [99], including Noyori's Ru(diamine)(BINAP) and Ru(η^6-arene)-TsDPEN, as well as others involving Rh, Ir, and Os, have been synthesized [100].

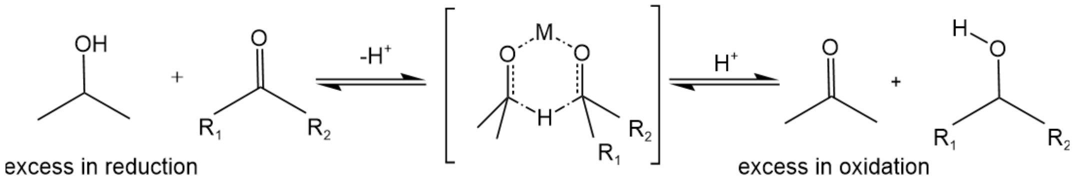


Figure 9 – MPV reduction and Oppenauer oxidation [102].

The pathway through a «direct hydrogen transfer» was proposed for the Meerwein–Ponndorf–Verley (MPV) reduction in Figure 9 [102].

Conclusion

In conclusion, the exploration of phosphinite ligand-containing ruthenium catalysts in transfer hydrogenation has demonstrated significant potential to transform organic synthesis. The unique properties of these ligands, combined with the versatility and efficiency of ruthenium complexes, suggest that future research will likely focus on innovative ligand design and synthesis to enhance catalytic performance. Advancements in mechanistic understanding, driven by advanced spectroscopic techniques and computational modeling, will provide deeper insights into reaction pathways, enabling the rational design of more efficient catalysts. Additionally, there is a growing emphasis on sustainable catalysis, with future efforts prioritizing the use of environmentally benign hydrogen donors and solvent systems, improved catalyst recyclability, and the expansion of substrate scope to include more challenging and diverse functional groups. Interdisciplinary approaches, involving collaborations across materials science, computational chemistry, and chemical engineering, will be essential for developing more robust catalytic systems and integrating them into industrial applications. By addressing these areas, researchers can unlock new potentials, making these catalysts indispensable tools in organic synthesis and paving the way for innovative applications in various industries.

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ҚҰРАМЫНДА ФОСФИНИТ ЛИГАНДЫ БАР РУТЕНИЙ КАТАЛИЗАТОРЛАРЫНЫҢ СИНТЕЗІ ЖӘНЕ ТРАНСФЕРЛІК ГИДРЛЕУДЕ ҚОЛДАНУ

Трансферлік гидрлеу (ТГ) органикалық химиядағы, әсіресе фармацевтикалық препараттарды, агрохимиялық заттарды және жұқа химиялық заттарды синтездеудегі өте маңызды реакция болып табылады. Бұл әдіс сутегінің донорлықмолекуладан қанықпаған субстратқа ауысуын қамтиды, әдетте жоғары қысымды сутегі газын қажет ететін тікелей гидрлеуге қауіпсіз және ыңғайлы балама болады. ТГ жұмсақ жағдайларда бірнеше функционалдық топтарды таңдамалы түрде азайту қабілетімен ерекшеленеді, осылайша сезімтал функционалдық топтардың шамадан тыс азаю немесе зақымдалу қаупін азайтады. Бұл әдіс әсіресе асимметриялық синтезде құнды, мұнда хиральды катализаторлар дәрілік заттардың дамуы үшін маңызды болып табылатын энантиомерлік таза қосылыстарды алуға мүмкіндік береді.

Рутений кешендері асимметриялық ТГ кезіндегі тиімділігімен ерекше назар аудартады, олардың тұрақтылығы мен әртүрлі реакциялық орталарға бейімделуі оларды зертханалық масштабта да, өнеркәсіптік қолдану үшін де өте қолайлы етеді. Фосфинитті лигандтар ($P(OR)R'_2$) олардың қасиеттерін жақсарту үшін комплекс синтезінде қолданылады. Бұл лигандтар металл орталықтарының электрондық және стерикалық қасиеттерін дәл баптай алатын қабілетімен танымал. Фосфор атомының электрон беретін табиғаты R және R' топтарындағы өзгергіштікпен үйлесіп, катализатордың қасиеттерін айтарлықтай реттеуге мүмкіндік береді. Бұл өзгеріс катализатордың белсенділігіне, селективтілігіне және тұрақтылығына әсер ете алады, сондай-ақ фосфинитті лигандтарды жетілдірілген каталитикалық жүйелерді жобалауда өте құнды етеді, сонымен қатар, осы лигандтармен қамтамасыз етілген стерикалық және электрондық модуляция рутений катализаторларының айналым жиілігін және жұмыс тұрақтылығын жақсартады, бұл оларды әртүрлі синтетикалық қолданбалар үшін тиімдірек және берік етеді.

Жұмыстың мақсаты – трансферлік гидрлеу саласындағы заманауи жаңалықтарды қарастыру.

Фосфинитті лигандтардың рутений катализаторларына интеграциялануы трансферлік гидрлеу саласындағы елеулі ілгерілеушілікті көрсетеді. Бұл катализаторлар жоғары тиімділікті, селективтілікті және тұрақтылықты көрсетеді, яғни асимметриялық синтезде өте маңызды.

Зерттеудің әртүрлі сутегі көздерін, негіздерін және механизмдерін зерттеу ТГ процесін тереңірек түсінуге мүмкіндік берді.

Түйін сөздер: *трансфертті гидрлеу, рутений катализаторы, фосфинитті лиганд, ассиметриялық синтез, энантиоселективтілік, каталитикалық тиімділік, стерикалық және электронды қасиеттер.*

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СИНТЕЗ И ПРИМЕНЕНИЕ ФОСФИНИТОВЫХ РУТЕНИЙ СОДЕРЖАЩИХ КАТАЛИЗАТОРОВ В ТРАНСФЕРНОМ ГИДРИРОВАНИИ

Трансферное гидрирование (ТГ) является весьма важной реакцией в органической химии, особенно при синтезе фармацевтических препаратов, агрохимикатов и продуктов тонкой химии. Этот метод включает перенос водорода от донорной молекулы к ненасыщенному субстрату, предлагая более безопасную и удобную альтернативу прямому гидрированию, для которого обычно требуется газообразный водород под высоким давлением, что является небезопасным. ТГ выделяется своей способностью избирательно восстанавливать несколько функциональных групп в более мягких условиях, тем самым снижая риск чрезмерного восстановления или повреждения чувствительных функциональных групп. Этот метод особенно ценен в асимметричном способе получения веществ, где хиральные катализаторы позволяют получать энантиомерно чистые соединения, имеющие решающее значение для разработки фармацевтических лекарств.

Рутениевые комплексы особенно примечательны своей эффективностью при асимметричном трансферном гидрировании. Их стабильность и адаптируемость к различным реакционным средам делают рутениевых комплексов идеальными как для лабораторного, так и для промышленного применения, они универсальны и могут использоваться для восстановления кетонов, альдегидов, иминов и нитрилов. Фосфинитовые лиганды (P(OR)R'2) используются в синтезе комплексов для улучшения их свойств. Эти лиганды очень известны своей способностью тонко настраивать электронные и стерические свойства металлоцентров. Электронодонорная природа атома фосфора в сочетании с изменчивостью функциональных групп R и R' позволяет существенно настраивать свойства катализатора.

Цель работы – обзор современных открытий в области трансферного гидрирования и исторических предпосылок ТГ.

Интеграция фосфинитных лигандов с рутениевыми катализаторами знаменует собой значительный прогресс в области трансферного гидрирования. Эти катализаторы демонстрируют повышенную эффективность, селективность и стабильность, что имеет решающее значение в асимметричном синтезе, который важен для получения фармакологических препаратов и агрохимикатов. Изучение в ходе исследования различных источников, оснований и механизмов водорода позволило глубже понять процесс ТГ.

Ключевые слова: *трансферное гидрирование, рутениевый катализатор, фосфинитовый лиганд, асимметрический синтез, энантиоселективность, каталитическая активность, стерические и электронные свойства.*

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РАЗЛИЧНЫЕ СПОСОБЫ ИЗВЛЕЧЕНИЯ ЛИТИЯ ИЗ СПОДУМЕНА

Аннотация: *Эта статья представляет собой обширный обзор современных достижений в области извлечения лития из сподуменовых концентратов, что является ключевым аспектом в разработке этого важного ресурса. Статья начинается с детального описания химических и физических свойств β-сподумена, особенно акцентируя внимание на его значимости для процесса извлечения лития. Основное внимание уделяется разнообразным методам обработки сподумена, включая техники, такие как термическая обработка, кислотное и алкалийное выщелачивание, а также более инновационные подходы, вроде использования растворителей и ионного обмена.*

В статье освещаются не только технические аспекты каждого метода, но и их экономическая и экологическая устойчивость. Особое внимание уделяется экологическим и экономическим проблемам, связанным с извлечением лития, в том числе стремлению к минимизации отходов и повышению общей эффективности. Авторы также критически анализируют существующие ограничения, такие как высокие затраты и сложности масштабирования процессов.

Важной частью статьи является обзор и сравнение различных исследований и экспериментальных работ в этой области, с акцентом на те, которые успешно перешли от лабораторных исследований к реальному применению. Обсуждается текущее состояние исследований в области извлечения лития и выделяют потенциальные направления для будущих