Selective Hydrogenation of Lignin-derived Aromatics to Give Cyclohexanes with a Rhodium-Pincer Precatalyst

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Abstract

Catalytic hydrogenation of aromatic rings represents an essential industrial chemical process for the synthesis of commodity chemicals and intermediates in pharmaceuticals, polymers, and fine chemicals. Herein, we report an air-stable rhodium complex bearing a pincer bis(oxazolinyl)phenyl ligand that shows good catalytic activity for the hydrogenation of lignin-derived acetophenones, benzoic acids as well as other functionalised aromatics to the corresponding alicyclic products by reducing the aryl groups. The rhodium complex is a precatalyst, offering easy access to active rhodium species, which appears to be heterogeneous in the hydrogenation.

KEYWORDS: lignin, arene hydrogenation, cyclohexanes, rhodium catalysis, pincer complexes

Highlights:

- A pincer Rh complex catalyzes the selective hydrogenation of lignin-derived aromatics
- The Rh complex is air-stable and shows good catalytic activity in reducing the aryl groups at low temperature
- The rhodium complex is a precursor to active rhodium species
- The structure and electronic properties of the ligand affects the formation of active catalyst

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Introduction

Catalytic hydrogenation of arenes is one of the most powerful and useful reactions to convert two-dimensional aromatic compounds into three-dimensional alicyclic compounds.[1-6] The reaction has synthetic significance in the generation of pharmaceuticals, resins, dyes, polymers, and fundamental feedstock chemicals.[7-16] An notable example is seen in the industrial large-scale synthesis of cyclohexane and cyclohexene from benzene hydrogenation.[17-19] The easy availability of substrates, low price of the reductant and high atom efficiency makes arene hydrogenation appealing to the pharmaceutical industry, as the product can easily expand the chemical space of "non-flat" molecules.

Over the last several decades, the scope of arene hydrogenation has seen constant expansion and growth toward the stereo and chemoselective hydrogenation of aromatic compounds has been significant,[5] allowing for the synthesis of saturated carbocycles without the reduction of reactive functional groups that are attached to the arene.[20-26] However, the challenge of hydrodefunctionalization encountered in the hydrogenation of halogenated,[23-25] borylated[26, 27] or silylated[22] arenes largely remains to be addressed. Further, diastereomers are formed in the hydrogenation of multisubstituted aromatic compounds, although *cis* products usually dominate.[1-6, 20-27]

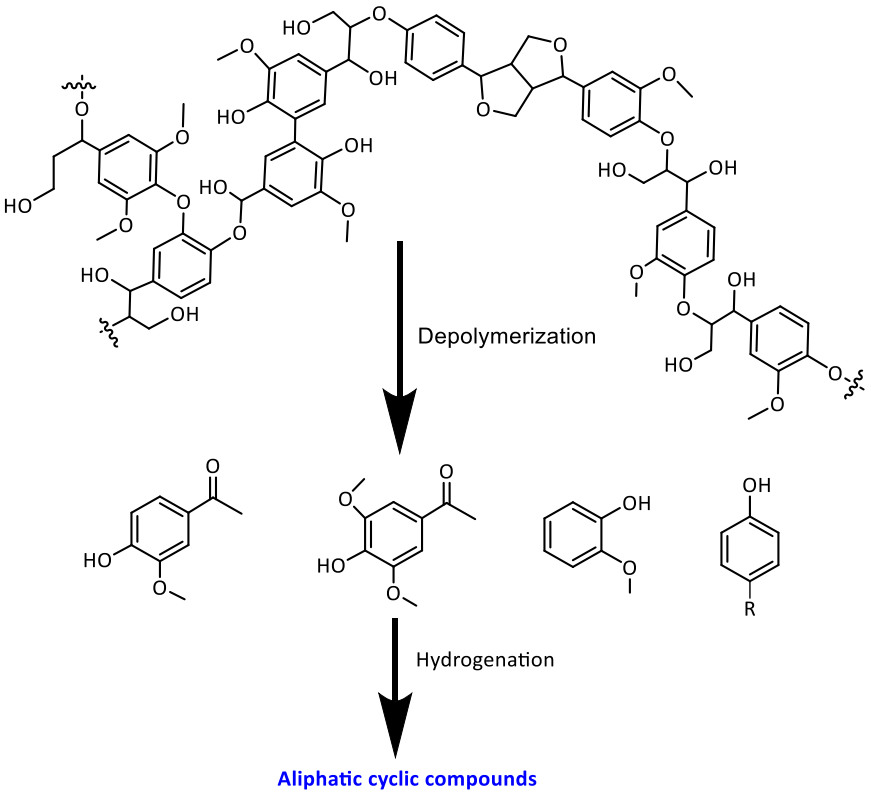


Figure 1. Valorisation of lignin and lignin oil via hydrogenation.

Arene hydrogenation could also play an important role in the valorisation of biomass-derived platform chemicals, particularly those from lignin, the most abundant aromatic biomass on earth.[28-35] Lignin depolymerisation has been extensively studied, leading to the development of various approaches that can be exploited to produce highly oxygenated aromatic monomers via C-O bond cleavage (Figure 1). This mixture of monomers, or bio-oils, comprises mainly phenol and derivatives, such as guaiacol, acetosyringone and acetovanillone, and is of limited practical use.[36-47] Hence, a great deal of effort has recently gone into upgrading the bio-oils, including the use of various catalytic methods, such as hydrolysis and hydrodeoxygenation. Selective hydrogenation is appealing, as the resulting functionalized cyclohexanes can serve as high-value building blocks or feedstock in fine and commodity organic synthesis. In the last a few years, a number of supported catalysts have been reported which allow for the hydrogenation of lignin-derived phenols and aryl ethers under relatively mild conditions, without hydrodeoxygenation.[48-51] For instance, the Beller group developed well-dispersed Ru nanoparticles supported on a nitrogen-doped carbon material, which catalyze selective hydrogenation of phenyl ether derivatives and substituted arenes.[52] Slightly later, Singh et al reported hydrogenation of a wide range of arenes and lignin derivatives catalyzed by Ru nanoparticles generated by reduction of $[(\eta^6\text{-benzene})Ru(en)Cl]^+$ with formic acid.[53] Rh nanoparticles immobilized within N-doped hollow carbon spheres were shown by Laurenczy, Dyson and coworkers to be highly active and selective for the hydrogenation of phenols and aryl ethers at 30-60 °C.[54] More recently, Cao *et al* reported a Ru/α-Al_2O_3 catalyst, which promotes selective hydrogenation of lignin-derived aromatic compounds at room temperature.[55] Low temperature is an attractive feature, as it is more likely to avoid hydrodeoxygenation. An electrocatalytic hydrogenation method has also been developed recently.[56] The ternary PtRhAu alloy electrocatalyst allows for selective reduction of lignin monomers to methoxylated cyclohexanes.

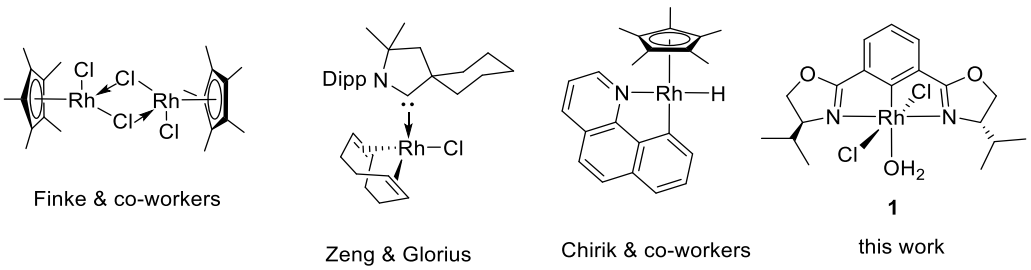


Figure 2. Known homogenous rhodium catalysts for arene hydrogenation.

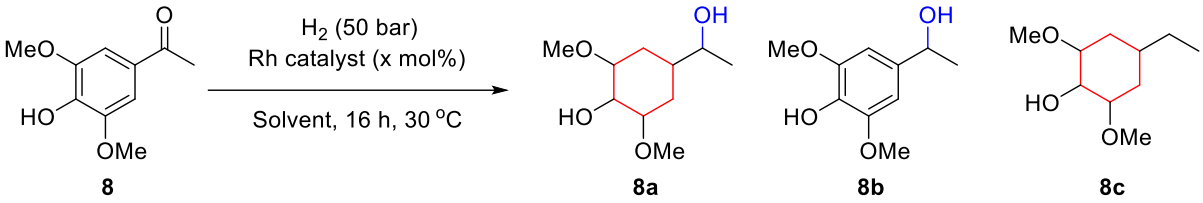
Historically, heterogeneous rhodium catalysts are the most active in arene hydrogenation.[57] Such catalysts are usually prepared by impregnation of a solid support with a metal salt followed by oxidation and reduction. However, over the last several decades, a range of well-defined organometallic rhodium complexes, represented by those shown in Figure 2, have been reported to

catalyse hydrogenation of arenes and heteroarenes,[25, 26, 58-65] which appear to undergo in-situ transformation into rhodium clusters and/or heterogeneous nanoparticles that drive the catalysis.[66-71] In particular, the complexes bearing tailored *N*-heterocyclic carbenes (NHCs) show high activities in the reduction of phenols and aryl ketones under relatively mild conditions.[21] Herein we report that the Rh(III) complex **1**, which contains an easily accessible bis(oxazolinyl)phenyl (Phebox) ligand,[72-78] catalyzes the hydrogenation of a variety of arenes including those that are lignin-related at a low temperature of 30 °C. Complex **1** is a precatalyst, being decomposed into heterogeneous rhodium particles under the reaction conditions.

Result and Discussion

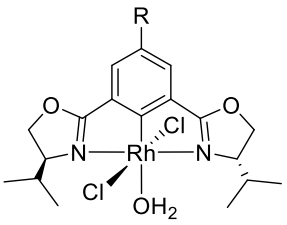
Recently, we reported lignin depolymerisation via a rhodium-catalyzed hydrogen autotransfer process in water.[34, 35] The resulting phenolic mixtures prompted us to seek catalysts for their hydrogenation to cyclohexanes derivatives. To this end, we found that the Phebox-coordinated pincer Rh(III) complex **1** is an efficient precatalyst for the hydrogenation of lignin-derived phenol derivatives, lignin β-O-4 model compounds, and benzoic acid derivatives. The initial conditions employed 0.1 mmol of 3,5-dimethoxy-4-hydroxyacetophenone **8**, a common compound founded in lignin bio-oils, hexafluoroisopropanol (HFIP) with 50 bar of H_2 at 30 °C with 3.0 mol% of a rhodium complex as the precatalyst (Table 1). Screening a range of rhodium complexes revealed **1** to be the most active, affording the desired product **8a** in 75% yield (Table 1, entry 2). In comparison, the closely related complexes **2** and **3** with an electron-donating group at the 5-position resulted in lower conversions (Table 1, entries 6 and 7), and **4** with an electron-withdrawing nitro group showed no activity (Table 1, entry 8). In the case of Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$ and $[Rh(Cp^*)Cl_2]_2$, negligible reactivity was observed (Table 1, entry 10 and 11), while with $RhCl_3{\cdot}H_2O$ and $[Rh(COD)Cl]_2$, a small amount of the product **7a** was detected (Table 1, entry 9 and 12). The other synthesised metal complexes **5**-**7** showed no reactivity under these conditions. We also examined a Ru-Phebox and a Ru-MACHO complex; they showed no activity either. It was observed that the hydrogenation using **1** led to the formation of rhodium black (see the Supporting Information), whereas in the case of the analogous **4** no decomposition of the complex was visible, suggesting that it is the in-situ generated rhodium particles from **1** that catalyzes the hydrogenation. Clearly the ligands play a critical role in the generation of active rhodium species, as is observed before.[60,68-70] In comparison with other common rhodium precatalysts, e.g. those in Figure 2, **1** is either more active (Table 1) or easier to access and more stable to handle.

Table 1. Influence of rhodium complexes on the hydrogenation of **7**[a]

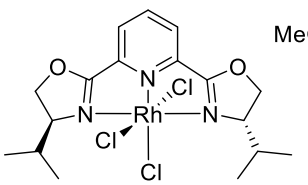


8 **8a** **8b** **8c**

Entry	Rh-catalyst (mol%)	Solvent	Conversion (%)[b]	Yield (%)[c], **8a**	Yield (%), **8b**	Yield (%), **8c**
1	none	HFIP	nd[d]	nd	nd	nd
2	**1** (3)	HFIP	100	75	trace	20
3	**1** (1)	HFIP	nd	nd	nd	nd
4	**1** (3)	TFE	100	40	5	55
5[e]	**1** (3)	HFIP	nd	nd	nd	nd
6	**2** (3)	HFIP	60	35	10	15
7	**3** (3)	HFIP	45	20	5	20
8	**4**-**7** (3)	HFIP	nd	nd	nd	nd
9	$RhCl_3.xH_2O$ (3)	HFIP	25	20	nd	nd
10	$Rh(PPh_3)_3Cl$ (3)	HFIP	nd	nd	nd	nd
11	$[Rh(Cp^*)Cl_2]_2$ (3)	HFIP	10	8	nd	nd
12	$[Rh(COD)Cl]_2$ (3)	HFIP	40	30	5	5



1, R = H
2, R = OMe
3, R = *i*Pr
4, R = NO_2



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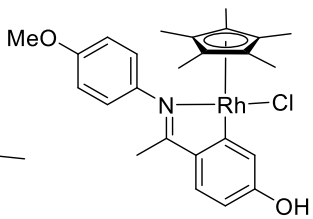

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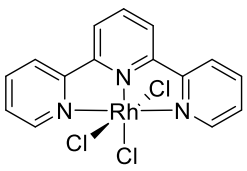


7

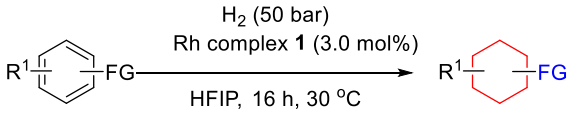
[a]**Reaction conditions**: **8** (0.1 mmol), Rh complex (0.003 mmol), HFIP (1.0 mL), and H_2 (50 bar) at 30 °C for 16 h. [b]Conversions determined by ^{1}H NMR analysis. [c]Isolated Yield. [d] Not detected. [e]30 bar H_2.

We performed the optimization of reaction conditions using the precatalyst **1** for the hydrogenation. First, the influence of the solvent was examined, and various organic solvents were tested. In solvents such as water, tetrahydrofuran, methanol, ethanol, 1,4-dioxane, toluene, dichloromethane, dichloroethane, acetone, and isopropanol, negligible reactivities were observed (Table S1 entries 1-10). The desired product **8a** was obtained in good yields only in TFE (trifluoroethanol) and HFIP (Table 1, entry 2 and 4). This may be due to the enhanced acidity, high hydrogen-bonding donor ability, and high ionizing power of fluorinated alkanols.[79-81] Lowering the catalyst loading from 3.0 to 0.05 mol% (Table 1, entry 2 and 3; Table S2) resulted in no formation of **8a**. Similar results were obtained by decreasing the H_2 pressure from 50 to 10 bar (Table 1, entry 2 and 5; Table S3). Further, a shorter reaction time (6 h) led to a decrease in conversion (Table S2, entry 5). The subsequent studies were therefore conducted under the conditions of 3.0 mol% of **1** at 30 °C and 50 bar hydrogen pressure in HFIP for 16 h, without the addition of any additives such as bases or acids.

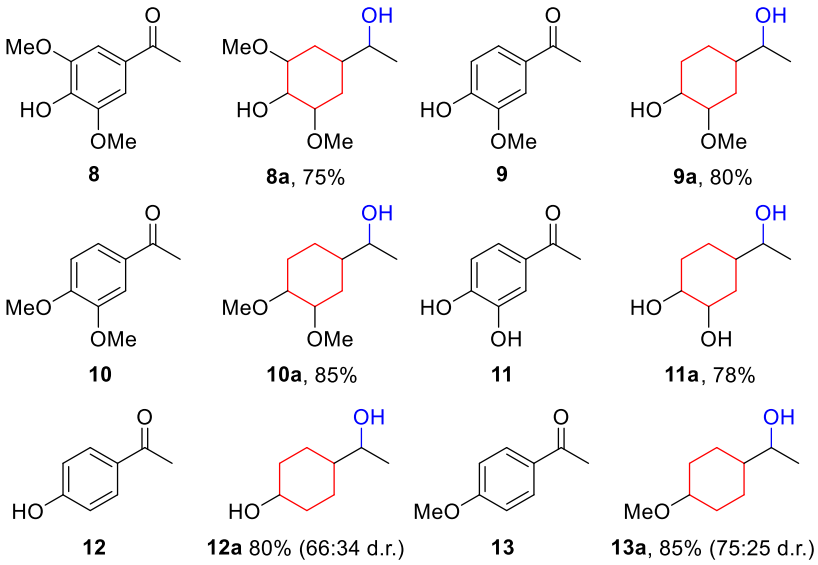
With the optimised reaction condition in hand, we expanded the scope of the substrates of arene hydrogenation reaction. As shown in Scheme 1, **1** was able to convert a variety of lignin-derived acetophenones (**8** - **13**)[34, 35] and phenols (**14** - **17**) into their corresponding hydrogenated cyclohexane products. It was observed that the di- and tri-substituted acetophenone derivatives were well accommodated, affording the corresponding hydrogenated products (**8a** -**13a**) with good isolated yields. It is noted that the complete reduction of both benzene ring and carbonyl group was observed and the major products are the *cis* isomers in the reaction of the acetophenone substrates (Scheme 1). Thus, the hydrogenation of **8** and **9** gave the corresponding cyclohexane product in >70% yields and 3,4-dimethoxy acetophenone **10** was hydrogenated to the corresponding *cis* product **10a** with 85% yield. However, the d.r. values of compound **8**-**10** could hardly be determined by ^{1}H NMR because these hydrogenated compounds were always formed as mixtures of a few diastereomers which were difficult to distinguish. Hydrogenation of 4-hydroxyacetophenone **12** and 4-methoxyacetohenone **13** resulted in good isolated yields, and good diastereoselectivities (60:40 d.r. **12a**; 75:25 d.r. **13a**) were observed through ^{1}H NMR. Interestingly, whilst the hydroxy and methoxy-containing acetophenone substrates (Scheme 1, **8** - **13**) gave the desired products in good isolated yields, no reactivity could be detected for substrates containing strongly electron-withdrawing group, e.g. -CF_3, -NO_2 and –CN, presumably due to some weakened interaction with the catalyst surface and/or poisoning of the catalyst by amines resulting from the reduction of the nitro group. The latter view finds support in the

observation that upon the addition of 10 mol% aniline into the reaction mixture of substrate **8**, the loss of catalytic activity was observed.

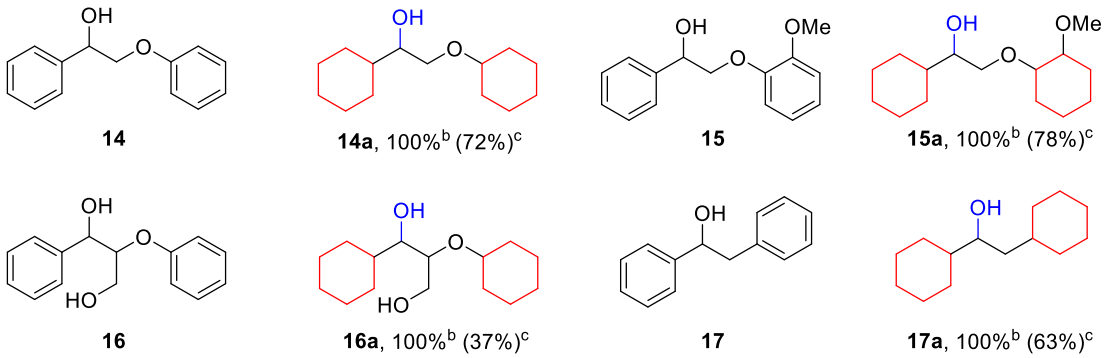
Scheme 1. Substrate scope for aryl hydrogenation using **1**[a]



Lignin oil type sutstrates



Lignin model substrates



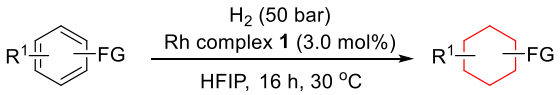
[a]**Reaction conditions**: Substrate (0.3 mmol), Rh complex (0.009 mmol), HFIP (1.0 mL), and H_2 (50 bar) at 30 °C for 16 h. Isolated yields were reported. d.r. was determined from NMR. [b]Conversions were determined from NMR. [c]Isolated yield.

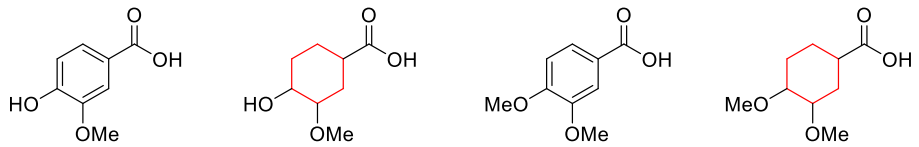
We next turned attention to the hydrogenation of phenoxy lignin model substrates. As shown in Scheme 1, precatalyst **1** also showed good activity in the hydrogenation of lignin β-O-4 model

compounds and gave the isolated products in good yields with the C-O bond largely retained. For example, 2-phenoxy-1-phenylethanol **14** was hydrogenated under the standard reaction condition, affording the corresponding alicyclic product **14a** with 72% isolated yield, although C-O bond cleavage also took place as indicated by GC analysis. Similarly, substrate **15** with methoxy substituents was well tolerated and gave a good yield (78% **15a**). The β-O-4 type of lignin model compound **16** was fully reduced, but with a lower yield, which might result from C-O bond cleavage. Moreover, 1,2-diphenylethanol **17** could also be hydrogenated to the desired product **17a** with 63% yield. These results reveal the preference of **1** for the hydrogenation of aromatic rings in the presence of the β-phenoxy C–O and α-hydroxyl C-O bonds.

The rhodium complex **1** is also shown to be a highly effective precatalyst for the hydrogenation of aromatic rings in aryl carboxylic acid derivatives, tolerating carboxyl, alkoxy carbonyl, hydroxyl and carbonyl amine groups. As shown in Scheme 2, the catalytic hydrogenation of mono- and di-substituted benzoic acids was complete at 30 °C within 16 h, showing *cis* diastereoselectivity, high yield and chemoselectivity. Thus, a range of acids having electron-donating and electron-withdrawing groups were reduced to arene-hydrogenated products in good to excellent yields (Scheme 2). Full conversions and high yields (87–99%) were achieved with substrates that bear methoxy ($-OCH_3$), trifluoromethyl ($-CF_3$), hydroxyl (-OH), *tert*-butyl ($-C(CH_3)_3$), and methyl ($-CH_3$) groups at the para position of the aromatic ring and afforded *cis* isomers as the main products (Scheme 2, **18** – **27**). Furthermore, benzoate esters with varied steric bulky substituents were hydrogenated in high yield with the functional group preserved (Scheme 2, **28**-**32**), as with the case of benzoic acid (**22**). The bulky *tert*-butyl moiety at the *para*-position of these substrates is well tolerated. Where possible, major isomers of products were shown to be *cis* according to the ^1H NMR spectra and literature data.[23, 82] It is noteworthy that benzamide **33** underwent the hydrogenation without the amide group affected. In this scenario, Rh nanoparticles stabilized by polyvinylpyrrolidone (PVP) were reported for hydrogenation of benzoic acid derivatives with 99 – 53% at 150 °C.[83] Based on the reported literature reports, no homogeneous catalysts have yet been employed for the arene hydrogenation of benzoic acid derivatives.

Scheme 2. Aryl hydrogenation of benzoic acid derivatives using **1**[a]



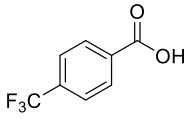


18

18a, 99%

19

19a, 93%



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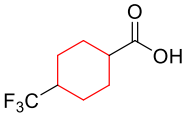
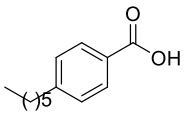


20a, 97% (d.r.= 76:24)



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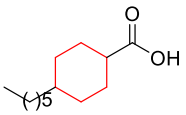
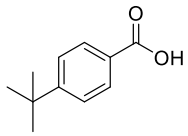


21a, 75% (d.r.= 79:21)



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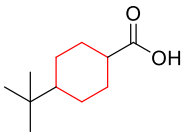
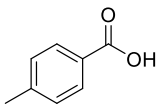


22a, 93% (d.r.= 75:25)



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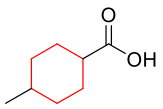
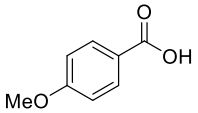


23a, 89% (d.r.= 75:25)



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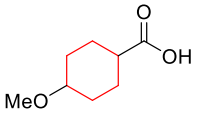
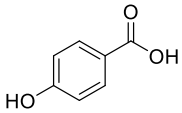


24a, 87% (d.r.= 85:15)



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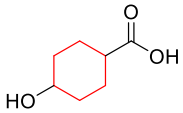
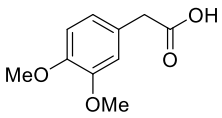


25a, 90% (d.r.= 71:29)



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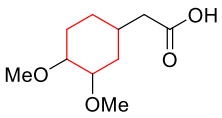
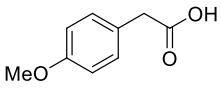
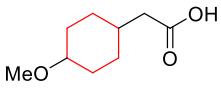


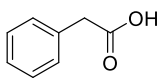
26a, 83%



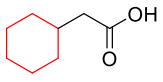
27



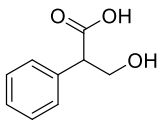
27a, 75% (d.r.= 88:12)



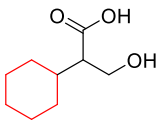
28



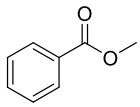
28a, 94%



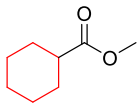
29



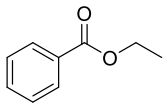
29a, 81%



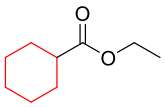
30



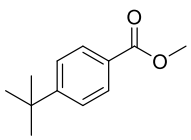
30a, 99%[b]



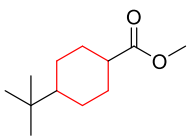
31



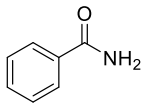
31a 99%[b]



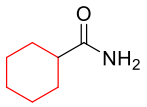
32



32a, 93% (d.r.=75:25)



33



33a, 93%

[a] **Reaction conditions**: Substrate (0.3 mmol), Rh complex **1** (0.009 mmol), HFIP (1.0 mL), and H_2 (50 bar) at 30 ^oC for 16 h. Isolated yields are reported. d.r. was determined from NMR. [b] Yields were determined by ^1H NMR using 1,3,5-trimeoxylbenzene as the internal standard.

Conclusion

In summary, we have found a new, easily accessible catalytic system for the hydrogenation of arenes to cyclohexanes. The pincer Rh complex **1** exhibits good-to-excellent activity in the hydrogenation of acetophenones, simple lignin model compounds, and aromatic acids, esters, and amides affording predominantly *cis*-configurated alicyclic compounds under mild reaction conditions. The complex acts as a precatalyst in the hydrogenation, decomposing into rhodium black which catalyses the reaction, and it is easily accessible and easy to handle. Interestingly, the structure and electronic properties of the ligand play an important role in the in-situ formation of the active catalyst. This opens up a new opportunity for further improving the activity and selectivity of the catalyst and points to the possibility for discovering other active heterogeneous catalysts from well-defined molecular metal complexes.

Author Contributions

‡ These authors contributed equally.

Notes

The authors declare no competing financial interest.

Data availability

The data supporting the findings of this study are available within this article and its Supporting Information or from the authors on reasonable request.

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Graphic Abstract