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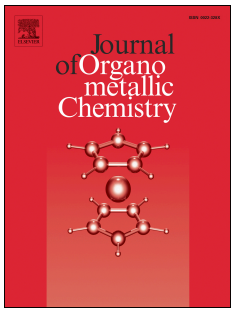

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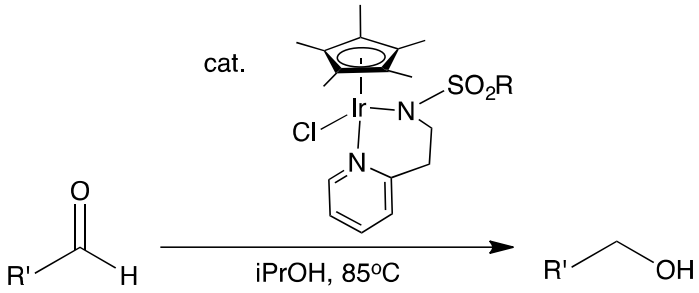

Transfer Hydrogenation of Aromatic and Linear Aldehydes Catalyzed Using Cp*Ir(pyridinesulfonamide)Cl Complexes Under Base-Free Conditions

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Abstract
Cp*Ir(pyridinesulfonamide)Cl (Cp* = pentamethylcyclopentadienyl) precatalysts **1-7** are active for the transfer hydrogenation of aryl, alkyl, and heterocyclic aldehydes. Catalysis is conducted under base-free conditions in air without dried or degassed substrates and solvents. These reductions occur rapidly in moderate to high conversion (39-100%). Benzaldehyde derivatives are reduced to alcohols within 30 min at 85 °C using 1 mol% iridium precatalyst; reduction also occurs at lower temperatures and loadings (60 °C, 0.50 mol% precatalyst). Benzaldehyde derivatives that possess electron-rich and electron-poor substituents in the *para* position, including base-sensitive 4-hydroxybenzaldehyde, are readily reduced. Aryl aldehydes containing electron-poor groups are reduced faster than substrates possessing electron-rich moieties. Reduction of the positional isomers of methoxybenzaldehyde and isopropylbenzaldehyde shows highest reduction for the *ortho* isomer, followed by the *meta* isomer. Heterocyclic substrates, including biomass derived 5-hydroxymethylfurfural and 2-furfural, were reduced selectively to the alcohol. Decyl aldehyde was reduced to the linear alcohol; importantly self-condensation was not observed. Competition studies demonstrated selective reduction of aldehydes over ketones and a mercury poisoning experiment supports a homogeneous catalyzed pathway.

Key Words
Iridium, transfer hydrogenation, aldehydes, base-free, catalysis

1. Introduction

Hydrogenation is a well-utilized step in the synthesis of pharmaceuticals, flavors, and fragrances and although a multitude of catalysts and precatalysts for this reaction exist, challenges include chemoselectivity and high-pressures of hydrogen.[1] A safer, cheaper, and greener alternative to hydrogenation is transfer hydrogenation. Common hydrogen donors used in transfer hydrogenation include formic acid, aqueous sodium formate, azeoptropic mixtures of formic acid/triethylamine, and 2-propanol.[2] Some substrates reduced under transfer hydrogenation conditions include alkenes, alkynes, imines, ketones, and aldehydes.[2–6] A limited number of complexes exist for the transfer hydrogenation of aldehydes. A major constraint in many transfer hydrogenation systems is the addition of base, which can cause side

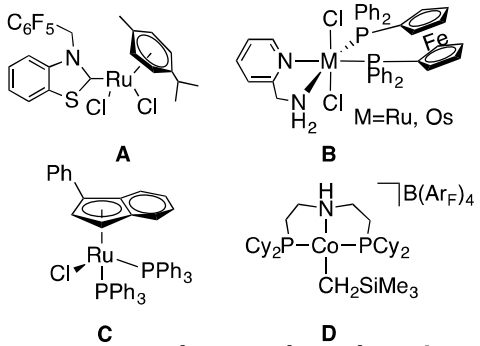


Figure 1. Recently reported complexes **A-D** for transfer hydrogenation of aldehydes.

reactions including the aldol condensation of aliphatic aldehydes; thus limiting the substrate scope.

Several Ru complexes catalyze transfer hydrogenation of aldehydes (Figure 1). Ru-based complex **A**, which is utilized in refluxing 2-propanol/KOH, catalyzes the reduction of benzaldehyde.[7] Another Ru complex containing a sulfonated phosphine ligand catalyzes transfer hydrogenation of benzaldehyde derivatives in aqueous sodium formate and 2-propanol solutions.[8] Nolan's complex **C** also catalyzes the transfer hydrogenation of benzaldehyde in 2-propanol using 2.5 mol% of potassium hexamethylsilazane.[9] Complex **B**, possessing either a Ru or Os metal center, is active for transfer hydrogenation with 1 mol% sodium isopropoxide in refluxing 2-propanol; aliphatic aldehydes are reduced in under 30 min.[10,11] Building upon this work, Barrata more recently demonstrated that Ru complexes containing CNN pincer ligands catalyze transfer hydrogenation of a variety of aldehydes in 2-propanol with potassium carbonate as the base.[11] Additionally, Singh reported that $[Ru(p\text{-cymene})Cl_2]_2$ catalyzes the transfer hydrogenation of aromatic and heteroaromatic aldehydes in an 2-propanol/potassium acetate solution in air.[12]

Non-noble metal complexes for transfer hydrogenation of aldehydes are also known and include Fe-based pincer complexes. Iron PONOP (PONOP = 2,6-bis(phosphinito)pyridine) complexes catalyze the transfer hydrogenation of aromatic and aliphatic aldehydes with sodium formate in methanol[6] and iron PNNP (PNNP = (*R*,*R*)-{$PPh_2(o\text{-}C_6H_4)CH{=}NC_6H_{10}N{=}CH(o\text{-}C_6H_4)PPh_2$}) complexes catalyze reduction of benzaldehyde to benzyl alcohol (94%) with 4 mol% potassium *tert*-butoxide in 2-propanol.[13] Hanson's Co-based complex **D** (Figure 1) catalyzes the transfer hydrogenation of aromatic and α,β-unsaturated aldehydes in 3:1 2-propanol:THF.[14]

Of the aforementioned complexes, only **A** and $[Ru(p\text{-cymene})Cl_2]_2$ performed transfer hydrogenation in air; all of the other complexes catalyze transfer hydrogenation under inert atmosphere. Additionally, **D** was the only complex capable of transfer hydrogenation without base. Most substrate scopes are limited to aryl aldehydes, which cannot undergo self-condensation in the presence of base.

Several iridium complexes catalyze transfer hydrogenation of aldehydes (Figure 2). Complex **E** catalyzes the transfer hydrogenation of benzaldehyde in 98% conversion in 7 h in neat glycerol; however, a molar equivalent of KOH is required.[15] Sarkar's complex **F** catalyzes transfer hydrogenation of benzaldehyde and acetophenone; nearly complete conversion of benzaldehyde is observed in 3 h with 2-propanol and 20 mol% KOH.[16] In addition to requiring KOH as an additive, transfer hydrogenation using complexes **E** and **F** requires air-free conditions. One example of an Ir catalyst utilized in air is Xiao's complex **G**, which also catalyzes reductive amination of aromatic and aliphatic ketones and aldehydes, and transfer hydrogenation of imines, ketones, aldehydes, β-keto ethers, α- and β-keto esters.[17–21] Crabtree's Ir complex **H**, in refluxing 2-propanol and K_2CO_3, reduces *p*-nitrobenzaldehyde in 98% conversion of substrate.[22] Transfer hydrogenation of benzaldehyde derivatives and

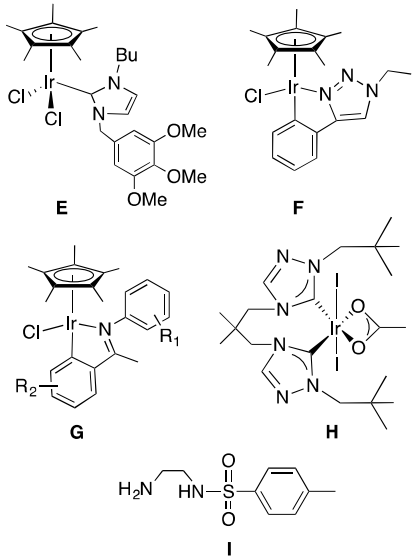


Figure 2. Recently reported Ir complexes **E-I** for transfer hydrogenation.

α,β-unsaturated aldehydes has also been achieved using $(Cp^*IrCl_2)_2$ in conjunction with monotosylated ethylenediamine ligand (**I**) in a sodium formate and water solution.[23] Aliphatic aldehydes are not reduced, likely due to competing aldol condensation. The basic or acidic reaction conditions of these systems can limit the substrate scope to aldehydes that do not contain acidic protons or pH sensitive functional groups.

An attractive reaction is the selective reduction of biomass-derived aldehydes to alcohols to form monomers for polymerization applications.[24–26] Glucose derived 5-hydroxymethylfurfural (HMF) can be reduced using heterogeneous catalysts and H_2 to either 2,5-bis(hydroxymethyl)furan (BHMF)[27] or 2,5-dimethylfuran (DMF)[28] (Figure 3). Of the few catalysts that have been reported for transfer hydrogenation of HMF, most are heterogeneous.[29,30] No examples of this reduction under base-free transfer hydrogenation conditions using homogeneous complexes are known based upon our searches.

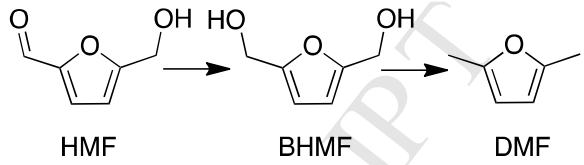


Figure 3. Reduction of HMF to BHMF or DMF.

Herein we describe the application of previously reported Cp*Ir(pyridinesulfonamide)Cl precatalysts[31] for transfer hydrogenation of aromatic, aliphatic, and heterocyclic aldehydes in air without additives or rigorously dried or degassed solvents and reagents. The electronics of the precatalysts were varied from electron-donating to withdrawing groups on the ligand. The electron rich precatalysts reduced aldehydes to alcohols in higher conversion than electron poor precatalysts. The substrate scope includes a number of *para* substituted aryl aldehyde derivatives, as well as positional isomers of methoxybenzaldehyde and isopropylbenzaldehyde, and 2-chloro-5-nitrobenzaldehyde. Other substrates include furfural derivatives, linear aldehydes, and 4-acetylbenzaldehyde. Under these base-free conditions, aryl aldehydes, 2-furfural, and HMF do not undergo aldol condensation with acetone and self-condensation of decanal is also not observed. Competition studies demonstrate selective and faster reduction of aldehydes in the presence of ketones. In contrast to our previous findings on reduction of α,β-unsaturated ketones, α,β-unsaturated aldehydes are not reduced. Only a minimal amount of aldehyde reduction is observed and the alkene is not reduced.

3. Results and Discussion

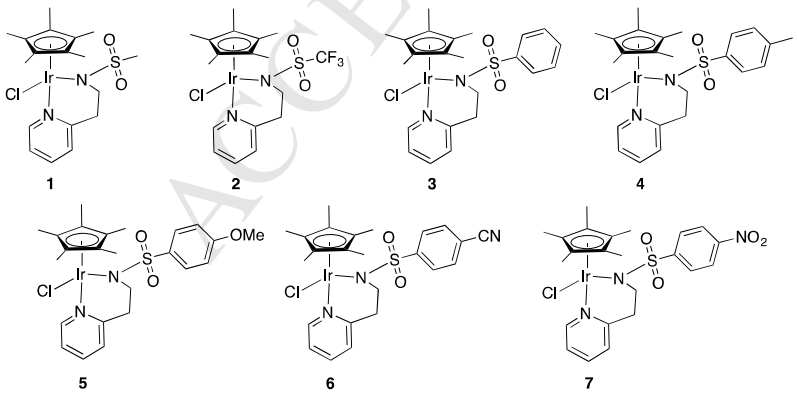
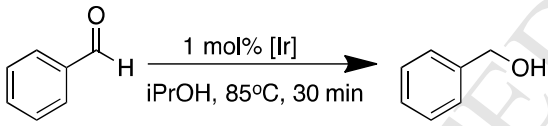


Figure 4. Precatalysts screened in base-free transfer hydrogenation of aldehydes.

The Cp*Ir(pyridinesulfonamide)Cl precatalysts **1**-**7** (Figure 4) were prepared using a literature method.[31] Catalytic screening was conducted to evaluate Cp*Ir(pyridinesulfonamide)Cl precatalysts for transfer hydrogenation of aldehydes in 2-propanol under base-free conditions. All reactions, unless noted, were performed in air without base or dried and degassed reagents at 85 °C. In all cases, only the alcohol product and unreacted starting material (in some cases) were observed, as confirmed by GCMS and ^{1}H NMR spectroscopy.

Precatalysts **1**-**7** catalyze the reduction of benzaldehyde to benzyl alcohol in 30 min at 85 °C (Table 1). The conversion of substrate is directly correlated to the electronics of the precatalyst. Precatalysts **7**, **6**, and **2**, possessing electron-withdrawing substituents on the sulfonamide moiety, exhibit lower conversion, 87, 81, and 72%, respectively (entries 5-7). Precatalysts containing electron-donating substituents on the sulfonamide exhibit higher conversions to benzyl alcohol because electron-rich precatalysts are expected to more easily reduce the substrates. This trend was also observed for the reduction of 4-nitroacetophenone using these precatalysts.[31] This ligand effect is indicative of a reaction pathway that cooperatively involves both the metal and ligand. Control experiments were conducted to determine if 1 mol% $(Cp^*IrCl_2)_2$ dimer or 2 mol% ligand catalyze transfer hydrogenation of benzaldehyde (entries 9 and 10). Only 12% conversion to benzyl alcohol was observed with the $(Cp^*IrCl_2)_2$ dimer; no reduction was observed with ligand. A 15% conversion to benzyl alcohol was observed with $(Cp^*IrCl_2)_2$ dimer in conjunction with the ligand (entry 8). These results support that the precatalyst is responsible for the high reactivity observed and *in situ* formation of the precatalyst does not readily occur from dimer and ligand. No reduction was observed in trials without iridium (entry 11).

Table 1. Transfer hydrogenation of benzaldehyde[a]



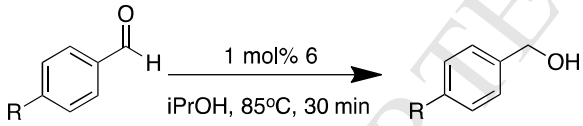
Entry	Precatalyst	% Conversion
1	**1**	100±1
2	**5**	100±1
3	**4**	100±1
4	**3**	100±1
5	**7**	87±2
6	**6**	81±1
7	**2**	72±3
8	$(Cp^*IrCl_2)_2$/2L	15±3
9	$(Cp^*IrCl_2)_2$	12
10	2 equiv L	0
11	No Catalyst	0
12[b]	**3**	100±1
13[c]	**1**	10±1
14[d]	**1**	98±2
15[e]	**1**	66±1
16[f]	**1**	92±1

[a] ^{1}H NMR used to determine conversion. Reported as an average of 3 trials, with error measured between the three trials. 1,4-Dimethoxybenzene used as internal standard. A 1.0 M solution of substrate in 2-propanol. **L**= *N*-(2-(pyridin-2-yl)ethyl)benzenesulfonamide. [b]Elemental Hg added. [c]Reaction run at 60 °C, 30 min. [d] Reaction run at 60 °C, 6 h. [e] 0.50 mol% precatalyst. [f] Reaction run for 1 h, 0.50 mol% precatalyst.

In all trials, decarbonylation of benzaldehyde to benzene was not observed, which has been reported for other iridium and rhodium precatalysts.[22,32,33] A mercury poisoning experiment was performed using precatalyst **3** and benzaldehyde (entry 12). Full reduction occurred in 30 min, supporting that the active catalyst is homogeneous, and likely not a heterogeneous or colloidal iridium species. Transfer hydrogenation is also catalyzed at lower temperatures; nearly complete conversion is observed after 6 h (entries 13 and 14). Lower loadings for reduction of benzaldehyde can be used, 66% conversion with 0.50 mol% of precatalyst **1** after 30 min and 92% conversion after 1 h (entries 15 and 16) are observed.

Aryl aldehyde substrates were screened to evaluate the substrate scope. Electron-poor precatalyst **6** was used in order to show appreciable changes in turnover number within 30 min trials (Table 2). Substrates that possess electron-withdrawing substituents in the *para* position, such as nitro or trifluoromethyl, exhibited the highest conversion: 97% and 96%, respectively (entries 1 and 2). Substrates containing electron-donating groups in the *para* position, such as hydroxy and methoxy, exhibited lower conversions in the same reaction time: 40% and 39%, respectively (entries 6 and 8). In addition, reduction of the nitro group of *p*-nitrobenzaldehyde is not observed. Electron-withdrawing groups in the *para* position remove electron density from the ring and weaken the carbonyl bond, making it more susceptible to reduction. Furthermore, a base sensitive substrate, 4-hydroxybenzaldehyde, was completely reduced to the alcohol product in 20 h (entry 7). Base-sensitive substrates are often not reduced under previously reported transfer hydrogenation conditions due to basic additives.[23]

Table 2. Reduction of Aromatic Aldehydes[a]



Entry	R	% Conversion
1	NO_2	97±2
2	CF_3	96±4
3	Cl	96±1
4	H	81±1
5	CH_3	76±1
6	OH	40±1
7[b]	OH	98±1
8	OMe	39±1

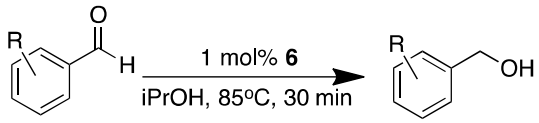
[a] ^{1}H NMR spectroscopy used to determine conversion. Reported as an average of 3 trials, with error measured between the three trials. 1,4-Dimethoxybenzene used as an internal standard. A 1.0 M solution of substrate in 2-propanol. [b] Reaction for 20 h.

The *ortho*, *meta*, and *para* isomers of methoxybenzaldehyde were screened for transfer hydrogenation using precatalyst **2** to examine substituent positional effects on conversion. The

ortho isomer exhibited complete conversion after 30 min, while the *meta* and *para* isomers were only partially converted to product (45%) in the same time (Table 3, entries 1-3). This indicates that inductive effects are more significant than resonance effects in these reductions. A similar trend was also observed for methoxyacetophenone reductions using these precatalysts.[31] Another series of isomers was evaluated. *Ortho*, *meta*, and *para* isopropylbenzaldehyde were screened for transfer hydrogenation (entries 4-6). This substrate contains a bulkier substituent, and displayed the same trend as methoxybenzaldehyde; the *ortho* isomer had the highest conversion while *para* had the lowest conversion: 97 vs. 83%, respectively. These results indicate the most sterically hindered isomer results in the highest conversion to alcohol product and inductive effects are less significant for isopropylbenzaldehyde.

Chemoselectivity was examined using precatalyst **7** with *p*-nitroacetophenone and *p*-nitrobenzaldehyde as substrates in the same reaction vessel for 1 h (Scheme 1). *p*-Nitrobenzaldehyde was selectively reduced in the presence of *p*-nitroacetophenone (100% vs. 5%, respectively), which is consistent with the reduction times necessary for equivalent conversions of the aldehydes and ketones to the respective alcohol products. 4-Acetylbenzaldehyde also showed selective reduction of the aldehyde before the ketone moiety, with full reduction of the aldehyde moiety within 30 min (Table 4).

Table 3. Reduction of *ortho*, *meta*, and *para* methoxybenzaldehyde and isopropylbenzaldehyde[a]

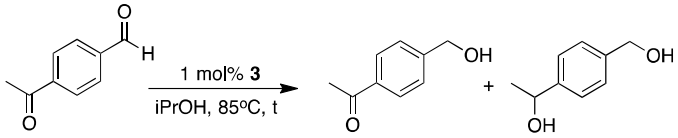


Entry	R	% Conversion
1	2-OMe	100±1
2	3-OMe	46±1
3	4-OMe	44±1
4	2-*i*Pr	97±1
5	3-*i*Pr	91±1
6	4-*i*Pr	83±1

[a] ^{1}H NMR spectroscopy used to determine conversion. Reported as an average of 3 trials, with error measured between the three trials. 1,4-Dimethoxybenzene used as an internal standard. A 1.0 M solution of substrate in 2-propanol.

Scheme 1. Competition between aryl aldehyde and ketone.[a]

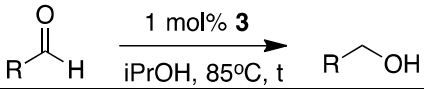
Table 4. Reduction of 4-acetylbenzaldehyde[a]

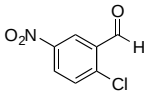
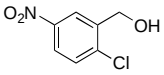
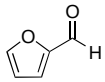
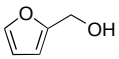
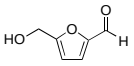
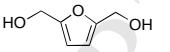
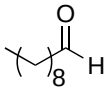
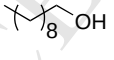


Entry	t (h)	% Conversion
1	0.5	81±1, 19±1
2	3	54±1, 46±1
3	6	42±1, 58±1
4	12	26±1, 74±1

[a] ^{1}H NMR spectroscopy used to determine conversion. Reported as an average of 3 trials, with error measured between the three trials. 1,4-Dimethoxybenzene used as an internal standard. A 1.0 M solution of substrate in 2-propanol.

Table 5. Substrate scope[a]



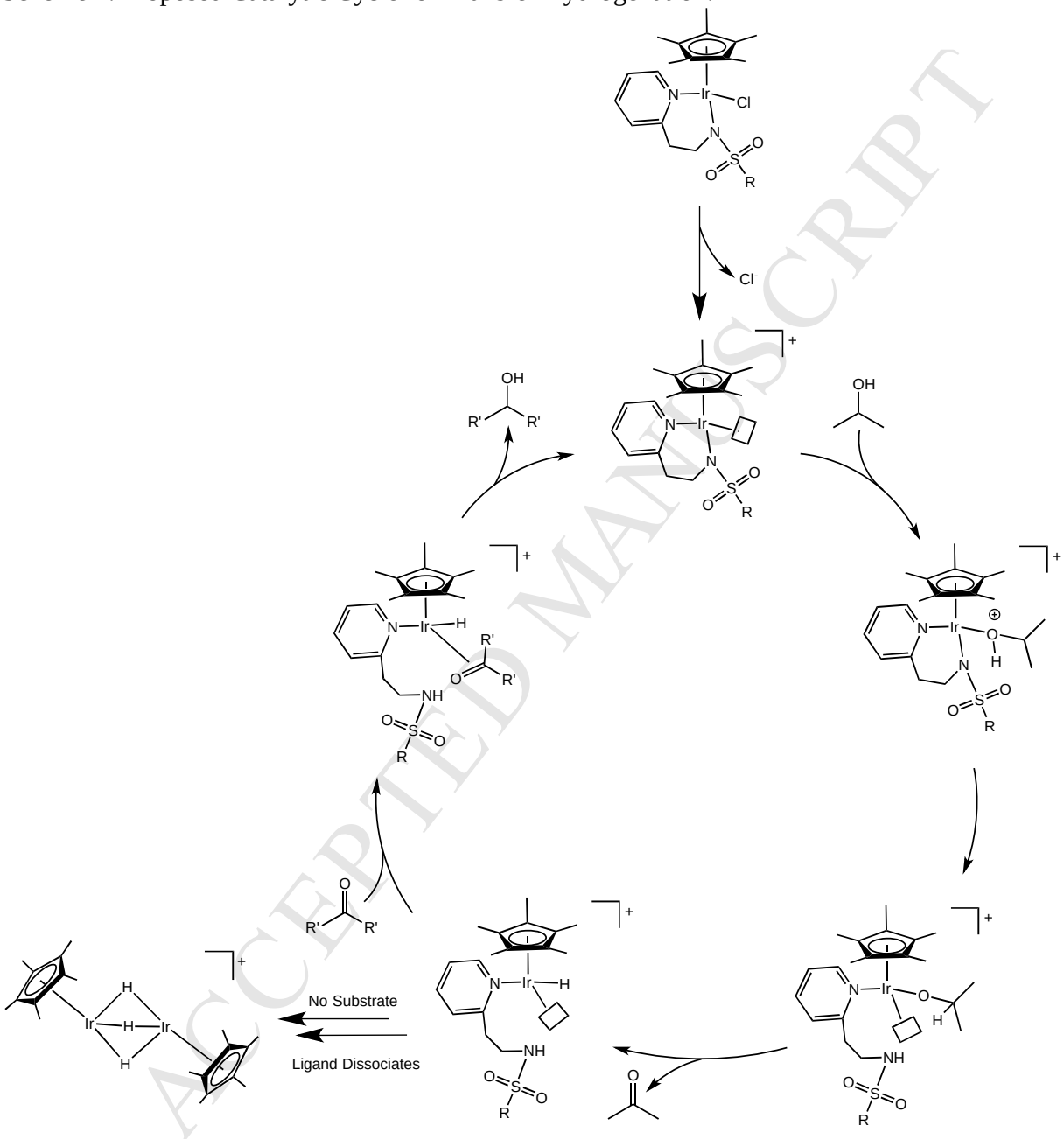
Entry	Reactant	Product	t (h)	% Conversion
1			0.5	100±1
2			0.5	95±1
3			0.5	100±1
4 5 6 7			0.5 3 6 12	53±1 78±1 84±1 100±1

[a] ^{1}H NMR spectroscopy used to determine conversion. Reported as an average of 3 trials, with error measured between the three trials. 1,4-Dimethoxybenzene used as an internal standard. A 1.0 M solution of substrate in 2-propanol.

The substrate scope was expanded to include polysubstituted aryl, aliphatic, and heterocyclic aldehydes. The complete reduction of 2-chloro-5-nitrobenzaldehyde was observed in 30 min with precatalyst **3** (Table 5, entry 1). Only aldehyde reduction was observed and reduction of the nitro group was not observed. 2-Furfural and 5-hydroxymethylfurfural (HMF) were reduced to 95% furfuryl alcohol and 100% 2,5-bis(hydroxymethyl)furan (BHMF), in 30 min respectively (entries 2 and 3). There have not been any previously reported homogeneous catalysts capable of selective transfer hydrogenation of HMF to BHMF without base or

formation of side products. Decyl aldehyde was reduced to the alcohol product in 12 h, without condensation products.

Scheme 2. Proposed Catalytic Cycle for Transfer Hydrogenation.



A proposed catalytic cycle is shown in Scheme 2. Preliminary mechanistic studies indicate the dissociation of the chloride from the precatalyst to generate the active catalyst for transfer hydrogenation. It is likely the mechanism is cooperative catalysis between the iridium center and the sulfonamide moiety of the ligand as supported by the catalysis data. Initial findings obtained by ^{1}H NMR spectroscopy confirm the presence of protonated ligand and a metal hydride intermediate, although the exact nature of this complex is still being investigated.

Without substrate, the hydride intermediate decomposes to the known cationic Cp* iridium trihydride dimer, which is not active for transfer hydrogenation catalysis under these conditions. Attempts to synthesize the proposed intermediates in Scheme 2 are currently underway, in addition to DFT calculations.

3. Conclusions

Transfer hydrogenation was catalyzed by precatalysts **1-7** for a variety of aryl, alkyl, and heterocyclic aldehydes in 2-propanol at 85 °C under base-free conditions. Electron-donating groups present on the ligand of the precatalysts and substrates possessing electron-withdrawing moieties were found to have the highest conversion to alcohol product. Reduction of the *ortho* isomers of both methoxybenzaldehyde and isopropylbenzaldehyde was observed in higher conversions than the *meta* and *para* isomers. Decyl aldehyde was fully reduced after 12 h, without self-condensation. Biomass-derived HMF was fully reduced to BHMF in 30 min, a conversion not previously achieved via homogeneous transfer hydrogenation. Competition studies with *p*-nitroacetophenone and *p*-nitrobenzaldehyde showed selective reduction of aldehydes over ketones. The reduction of 4-acetylbenzaldehyde also demonstrated full reduction of the aldehyde moiety before the ketone. Control experiments indicate that the iridium complex is responsible for catalysis and a mercury poisoning experiment supports a homogeneous mechanism. There is clearly a ligand effect observed for these catalysts, indicating both the ligand and metal play a cooperative role in the catalysis. Preliminary mechanistic studies support the dissociation of chloride to form a cationic iridium catalyst, which is active for transfer hydrogenation. Spectroscopic data supports cooperative catalysis involving an iridium hydride and protonated ligand. Current work is focused on isolating relevant intermediates in the proposed catalytic cycle along with kinetic studies and DFT calculations to support the proposed catalytic cycle.

4. Experimental Procedure

4.1. Materials

Solvents and materials involved in the synthesis of the ligands and all substrates were purchased from Aldrich or Alfa Aesar and used as received. $IrCl_3*H_2O$ was purchased from Pressure Chemical. The $(Cp*IrCl_2)_2$ dimer was prepared according to a literature procedure[34] and stored at room temperature in air. The products were examined using NMR spectroscopic methods. A Bruker Biospin Ascend 400 MHz Nuclear Magnetic Resonance Spectrometer and a Bruker Biospin Ultra Shield 400 MHz Nuclear Magnetic Resonance Spectrometer were used to collect $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and ^1H NMR spectra. Chemical shifts are referenced to residual $CHCl_3$ (δ 7.24 for 1H), $CH(D)Cl_2$ (δ 5.32 for ^1H), $^{13}CDCl_3$ (δ 77.0 for ^{13}C), and $^{13}CD_2Cl_2$ (δ 54.0 for ^{13}C). All NMR spectra were collected at 27°C. GCMS was carried out using an Agilent 6890 gas chromatograph/5873 quadropole mass spectrometer system with a 7683B autoinjector. All glassware was dried for at least 1 h at 150 ºC before use.

4.2. General Procedure to synthesize pyridinesulfonamide ligands

A literature procedure was used to prepare the ligands.[31,35,36]

4.3. General Procedure to synthesize iridium precatalysts 1-7

A literature procedure was used to prepare the precatalysts.[31]

4.4. Catalytic Transfer Hydrogenation

The precatalyst (0.005 mmol) was weighed into three different 1 dram vials. If the substrate was liquid, a standard solution containing the substrate (0.500 mmol), and the internal standard 1,4-dimethoxybenzene (0.050 mmol) was prepared using 2-propanol as the solvent. If the substrate was solid it was weighed directly into the vial with the precatalyst and the standard solution was prepared from 1,4-dimethoxybenzene (0.050 mmol) using 2-propanol as the solvent. A 500 μL aliquot of the standard solution was added via syringe to each of the vials containing precatalyst. The vials were then heated to 85 °C in an OptiMag-ST aluminum heating plate containing wells fit for the vials for the time indicated. The product yield was determined using ^{1}H NMR spectroscopy (sample spectra in Supporting Information). Each run was conducted in triplicate and the values are reported as an average with standard deviation in the tree trials.

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Appendix A. Supplementary data: Representative NMR spectra for conversion determination.

References

[1] H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, Selective Hydrogenation for Fine Chemicals: Recent Trends and New Developments, Adv. Synth. Catal. 345 (2003) 103–151. doi:10.1002/adsc.200390000.

[2] D. Wang, D. Astruc, The Golden Age of Transfer Hydrogenation, Chem. Rev. 115 (2015) 6621–6686. doi:10.1021/acs.chemrev.5b00203.

[3] S. Guo, P. Yang, J. (Steve) Zhou, Nickel-catalyzed asymmetric transfer hydrogenation of conjugated olefins, Chem Commun. 51 (2015) 12115–12117. doi:10.1039/C5CC01632K.

[4] E. Richmond, J. Moran, Ligand Control of E/Z Selectivity in Nickel-Catalyzed Transfer Hydrogenative Alkyne Semireduction, J. Org. Chem. 80 (2015) 6922–6929. doi:10.1021/acs.joc.5b01047.

[5] N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, Asymmetric Transfer Hydrogenation of Imines, J. Am. Chem. Soc. 118 (1996) 4916–4917. doi:10.1021/ja960364k.

[6] S. Mazza, R. Scopelliti, X. Hu, Chemoselective Hydrogenation and Transfer Hydrogenation of Aldehydes Catalyzed by Iron(II) PONOP Pincer Complexes, Organometallics 34 (2015) 1538–1545. doi:10.1021/acs.organomet.5b00105.

[7] Z.İ. Oruç, L. Gök, H. Türkmen, O. Şahin, O. Büyükgüngör, B. Çetinkaya, Piano-stool benzothiazol-2-ylidene Ru(II) complexes for effective transfer hydrogenation of carbonyls, J. Organomet. Chem. 807 (2016) 36–44. doi:10.1016/j.jorganchem.2016.02.003.

[8] I. Szatmári, G. Papp, F. Joó, Á. Kathó, Unexpectedly fast catalytic transfer hydrogenation of aldehydes by formate in 2-propanol–water mixtures under mild conditions, Catal. Today. 247 (2015) 14–19. doi:10.1016/j.cattod.2014.06.023.
[9] S. Manzini, C.A.U. Blanco, S.P. Nolan, Ruthenium Phenylindenyl Complex as an Efficient Transfer Hydrogenation Catalyst, Adv. Synth. Catal. 354 (2012) 3036–3044. doi:10.1002/adsc.201200411.
[10] E. Putignano, G. Bossi, P. Rigo, W. Baratta, MCl_2(ampy)(dppf) (M = Ru, Os): Multitasking Catalysts for Carbonyl Compound/Alcohol Interconversion Reactions, Organometallics 31 (2012) 1133–1142. doi:10.1021/om201189r.
[11] S. Baldino, S. Facchetti, A. Zanotti-Gerosa, H.G. Nedden, W. Baratta, Transfer Hydrogenation and Hydrogenation of Commercial-Grade Aldehydes to Primary Alcohols Catalyzed by 2-(Aminomethyl)pyridine and Pincer Benzo[h]quinoline Ruthenium Complexes, ChemCatChem. 8 (2016) 2279–2288. doi:10.1002/cctc.201600420.
[12] S.S. Bhosale, K.S. Singh, Ruthenium(II)-Catalyzed Transfer Hydrogenation of Aromatic and Heteroaromatic Aldehydes in Air, Synth. Commun. 45 (2015) 1411–1420. doi:10.1080/00397911.2015.1022793.
[13] C. Sui-Seng, F. Freutel, A.J. Lough, R.H. Morris, Highly Efficient Catalyst Systems Using Iron Complexes with a Tetradentate PNNP Ligand for the Asymmetric Hydrogenation of Polar Bonds, Angew. Chem. Int. Ed. 47 (2008) 940–943. doi:10.1002/anie.200705115.
[14] G. Zhang, S.K. Hanson, Cobalt-catalyzed transfer hydrogenation of CO and CN bonds, Chem. Commun. 49 (2013) 10151–10153. doi:10.1039/C3CC45900D.
[15] A. Azua, J.A. Mata, E. Peris, F. Lamaty, J. Martinez, E. Colacino, Alternative Energy Input for Transfer Hydrogenation using Iridium NHC Based Catalysts in Glycerol as Hydrogen Donor and Solvent, Organometallics 31 (2012) 3911–3919. doi:10.1021/om300109e.
[16] R. Maity, S. Hohloch, C.-Y. Su, M. van der Meer, B. Sarkar, Cyclometalated Mono- and Dinuclear Ir ^{III} Complexes with “Click”-Derived Triazoles and Mesoionic Carbenes, Chem. - Eur. J. 20 (2014) 9952–9961. doi:10.1002/chem.201402838.
[17] D. Talwar, N.P. Salguero, C.M. Robertson, J. Xiao, Primary Amines by Transfer Hydrogenative Reductive Amination of Ketones by Using Cyclometalated Ir ^{III} Catalysts, Chem. - Eur. J. 20 (2014) 245–252. doi:10.1002/chem.201303541.
[18] D. Talwar, X. Wu, O. Saidi, N.P. Salguero, J. Xiao, Versatile Iridicycle Catalysts for Highly Efficient and Chemoselective Transfer Hydrogenation of Carbonyl Compounds in Water, Chem. - Eur. J. 20 (2014) 12835–12842. doi:10.1002/chem.201403701.
[19] Q. Lei, Y. Wei, D. Talwar, C. Wang, D. Xue, J. Xiao, Fast Reductive Amination by Transfer Hydrogenation “on Water,” Chem. - Eur. J. 19 (2013) 4021–4029. doi:10.1002/chem.201204194.
[20] C. Wang, A. Pettman, J. Basca, J. Xiao, A Versatile Catalyst for Reductive Amination by Transfer Hydrogenation, Angew. Chem. Int. Ed. 49 (2010) 7548–7552. doi:10.1002/anie.201002944.
[21] Y. Wei, D. Xue, Q. Lei, C. Wang, J. Xiao, Cyclometalated iridium complexes for transfer hydrogenation of carbonyl groups in water, Green Chem. 15 (2013) 629–634. doi:10.1039/C2GC36619C.
[22] J.R. Miecznikowski, R.H. Crabtree, Hydrogen Transfer Reduction of Aldehydes with Alkali-Metal Carbonates and Iridium NHC Complexes, Organometallics 23 (2004) 629–631. doi:10.1021/om034393x.

[23] X. Wu, J. Liu, X. Li, A. Zanotti-Gerosa, F. Hancock, D. Vinci, J. Ruan, J. Xiao, On Water and in Air: Fast and Highly Chemoselective Transfer Hydrogenation of Aldehydes with Iridium Catalysts, Angew. Chem. Int. Ed. 45 (2006) 6718–6722. doi:10.1002/anie.200602122.
[24] G.W. Huber, S. Iborra, A. Corma, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering, Chem. Rev. 106 (2006) 4044–4098. doi:10.1021/cr068360d.
[25] Y. Jiang, A.J.J. Woortman, G.O.R. Alberda van Ekenstein, D.M. Petrović, K. Loos, Enzymatic Synthesis of Biobased Polyesters Using 2,5-Bis(hydroxymethyl)furan as the Building Block, Biomacromolecules. 15 (2014) 2482–2493. doi:10.1021/bm500340w.
[26] P.D. Bloom, P. Venkitasubramanian, P. US 20090018300, A1, January 15, 2009.
[27] Y. Nakagawa, M. Tamura, K. Tomishige, Catalytic Reduction of Biomass-Derived Furanic Compounds with Hydrogen, ACS Catal. 3 (2013) 2655–2668. doi:10.1021/cs400616p.
[28] Y. Zu, P. Yang, J. Wang, X. Liu, J. Ren, G. Lu, Y. Wang, Efficient production of the liquid fuel 2,5-dimethylfuran from 5-hydroxymethylfurfural over Ru/Co_3O_4 catalyst, Appl. Catal. B Environ. 146 (2014) 244–248. doi:10.1016/j.apcatb.2013.04.026.
[29] J. Jae, W. Zheng, A.M. Karim, W. Guo, R.F. Lobo, D.G. Vlachos, The Role of Ru and RuO_2 in the Catalytic Transfer Hydrogenation of 5-Hydroxymethylfurfural for the Production of 2,5-Dimethylfuran, ChemCatChem. 6 (2014) 848–856. doi:10.1002/cctc.201300945.
[30] W. Hao, W. Li, X. Tang, X. Zeng, Y. Sun, S. Liu, L. Lin, Catalytic transfer hydrogenation of biomass-derived 5-hydroxymethyl furfural to the building block 2,5-bishydroxymethyl furan, Green Chem. (2015). doi:10.1039/C5GC01221J.
[31] A. Ruff, C. Kirby, B.C. Chan, A.R. O'Connor, Base-Free Transfer Hydrogenation of Ketones Using Cp*Ir(pyridinesulfonamide)Cl Precatalysts, Organometallics 35 (2016) 327–335. doi:10.1021/acs.organomet.5b00864.
[32] P.J. Alaimo, B.A. Arndtsen, R.G. Bergman, Alkylation of Iridium via Tandem Carbon−Hydrogen Bond Activation/Decarbonylation of Aldehydes. Access to Complexes with Tertiary and Highly Hindered Metal−Carbon Bonds, Organometallics 19 (2000) 2130–2143. doi:10.1021/om9910064.
[33] C.M. Beck, S.E. Rathmill, Y.J. Park, J. Chen, R.H. Crabtree, L.M. Liable-Sands, A.L. Rheingold, Aldehyde Decarbonylation Catalysis under Mild Conditions, Organometallics 18 (1999) 5311–5317. doi:10.1021/om9905106.
[34] C. White, A. Yates, P.M. Maitlis, D.M. Heinekey, (η^5-Pentamethylcyclopentadienyl) Rhodium and -Iridium Compounds, in: R.N. Grimes (Ed.), Inorg. Synth., John Wiley & Sons, Inc., 1992: pp. 228–234. http://onlinelibrary.wiley.com/doi/10.1002/9780470132609.ch53/summary
[35] M.H. Klingele, B. Moubaraki, K.S. Murray, S. Brooker, Synthesis and Some First-Row Transition-Metal Complexes of the 1,2,4-Triazole-Based Bis(terdentate) Ligands TsPMAT and PMAT, Chem. – Eur. J. 11 (2005) 6962–6973. doi:10.1002/chem.200500387.
[36] J.K. Harrington, R.D. Trepka, N-(2-benzimidazolyl)fluoroalkanesulfonamides, US 3897449 A, July 29, 1975.

Highlights

- Selective transfer hydrogenation of aldehydes under base-free conditions in air
- Electron-poor aryl aldehydes are reduced faster than electron-rich substrates
-Iridium precatalysts bearing electron-donating substituents on the sulfonamide moiety of the ligand leads to more product in less time
-Competition experiments show selective reduction of aldehydes in the presence of ketones
-Mercury poisoning experiments support a homogeneous species as the active catalyst