JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Highly Selective Hydrogenation of Aromatic Ketones and Phenols Enabled by Cyclic (Amino)(alkyl)carbene Rhodium Complexes

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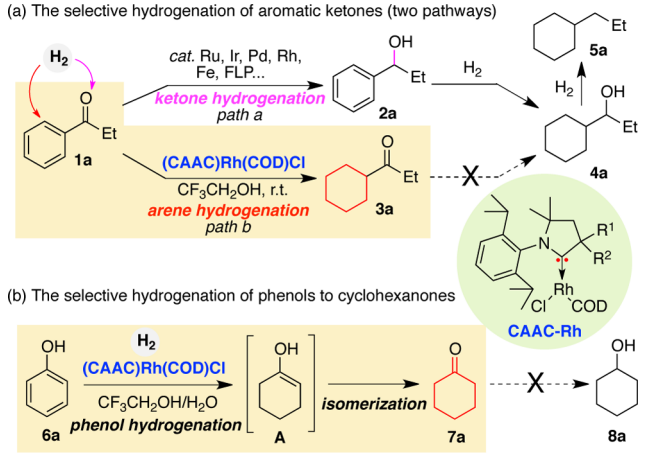
Supporting Information

ABSTRACT: Air-stable Rh complexes ligated by strongly σ-donating cyclic (amino)(alkyl)carbenes (CAACs) show unique catalytic activity for the selective hydrogenation of aromatic ketones and phenols by reducing the aryl groups. The use of CAAC ligands is essential for achieving high selectivity and conversion. This method is characterized by its good compatibility with unsaturated ketones, esters, carboxylic acids, amides, and amino acids and is scalable without detriment to its efficiency.

Selective hydrogenation is one of the most powerful and useful reactions because of its synthetic significance in the creation of pharmaceuticals, materials, and fundamental feedstock chemicals.[1,2] Despite considerable achievements, chemoselectivity has long been a prominent obstacle when several unsaturated scaffolds are present in the same substrates.[3] Compared with polar carbonyls, the aromatic hydrocarbons are difficult substrates for hydrogenation, probably because of the stability caused by aromaticity.[4,5] As a result, the hydrogenation of aromatic ketones often leads to aryl-containing alcohol products via a preferential carbonyl reduction (Scheme 1a, path a).[6] In contrast, switching the selectivity to realize arene hydrogenation while retaining an easily reducible carbonyl is more challenging and has not been achieved with structurally well-defined homogeneous catalysts to date (Scheme 1a, path b).[7] Another key problem is inhibiting the reduction of the resulting ketones to alcohols or dehydroxylated products (e.g., **4a** and **5a**). Especially for naturally abundant phenols, efficient strategies for reducing them to cyclohexanones by avoiding a carbonyl reduction are rare (Scheme 1b).[8,9] From both sustainable and synthetic points of view, developing a general protocol to address these selectivity challenges would help advance clean chemical syntheses.

Scheme 1. Selective Hydrogenation of Aromatic Ketones and Phenols



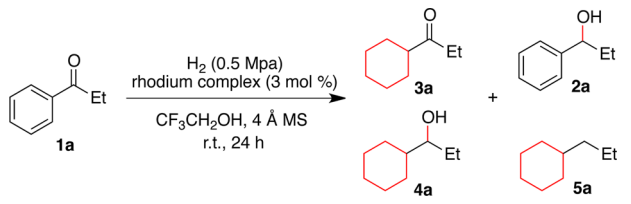
Recently, there has been significant progress in the rational design of effective organometallic catalysts using σ-donating *N*-heterocyclic carbenes (NHCs),[10,11] and a number of elegant examples of NHC ligand-promoted hydrogenation have been reported by Glorius,[12] Stephan,[13] Crabtree,[14] and others.[15] Differing from classic NHCs, cyclic (amino)(alkyl)carbenes (CAACs) show an enhanced nucleophilicity because of a σ-donating alkyl substituent, which was discovered by Bertrand and has received increasing interest recently.[16,17] However, the ligand effect of CAACs in organometallic catalysis has rarely been studied.[18] Herein we report the first CAAC ligand-enabled, highly selective hydrogenation of aromatic ketones and phenols with rhodium (Scheme 1). This method retains a synthetically valuable carbonyl group in the products, thus offering a straightforward and clean route to cyclohexyl-containing ketones and cyclohexanones, which are fundamental feedstock materials and widely used as key precursors to industrially important molecules such as caprolactam and adipic acid.[19]

To ensure that the arene hydrogenation occurs preferentially over that of ketones, a suitable catalyst that allows interaction with the aryl group via a π-coordination is required. We postulated that electron-rich CAAC ligands, with their strong σ-electron donation to the metal center, might enhance the interaction of the metal with the aryl by the back-donation of electron density from the filled *d* orbitals of the metal into the unoccupied π^*_{aryl} antibonding orbital.[12b] This may favor the arene hydrogenation with H_2. Meanwhile, the electron-rich metal may be expected to show rather low oxophilicity.[20] Compared with other transition metals, rhodium shows high reactivity toward arene hydrogenation.[1] At the outset, the impact of Rh complexes on the selective hydrogenation of propiophenone was evaluated (Table 1). In the presence of Wilkinson's catalyst, a trace amount of the aryl-reduced product **3a** was detected by GC-MS analysis (entry 2). Similar results

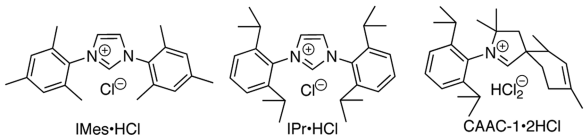
Received: June 6, 2015
Published: July 14, 2015

DOI: 10.1021/jacs.5b05868
J. Am. Chem. Soc. 2015, 137, 9250−9253

Table 1. Influence of Rhodium Complexes on the Aryl-Selective Hydrogenation of Propiophenone[a,b]



Entry	Rhodium complex	Yield (3a)	Yield (2a)	Yield (4a)	Yield (5a)
1	none	nd[c]	nd[c]	nd[c]	nd[c]
2	$Rh(PPh_3)_3Cl$	<1%	nd[c]	nd[c]	nd[c]
3[d]	$[Rh(cp^*)Cl_2]_2$	<5%	nd[c]	nd[c]	nd[c]
4	$RhCl_3•H_2O$	<5%	nd[c]	11%	nd[c]
5[d]	$[Rh(COD)Cl]_2$	29%	10%	25%	10%
6[e]	$[Rh(COD)Cl]_2$/ IMes•HCl /NaO^{t}Bu	9%	21%	10%	12%
7[e]	$[Rh(COD)Cl]_2$/ IPr•HCl /NaO^{t}Bu	12%	<1%	<5%	11%
8[e]	$[Rh(COD)Cl]_2$/ CAAC-1•2HCl /LDA	80%	nd[c]	<5%	<1%
9	(CAAC-1)Rh(COD)Cl	98% (94%)[f]	nd[c]	<1%	<1%
10	(CAAC-2)Rh(COD)Cl	96%	nd[c]	<1%	<1%

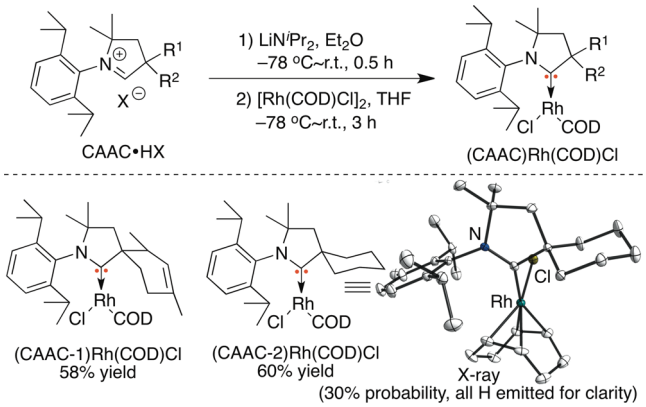


[a]Conditions: **1a** (0.1 mmol), Rh complex (0.003 mmol), 4 Å MS (50 mg), CF_3CH_2OH (2.0 mL), and H_2 (0.5 MPa) at room temperature for 24 h. [b]Yields were determined by ^1H NMR analysis. [c]Not detected. [d]$[Rh(cp^*)Cl_2]_2$ or $[Rh(COD)Cl]_2$ (0.0015 mmol) was used. [e]$[Rh(COD)Cl]_2$ (0.0015 mmol), iminium salt (0.004 mmol), and NaO^{t}Bu or LDA (0.004 or 0.008 mmol) in hexane or THF (2.0 mL) were stirred at 70 °C for 12 h. After the solvent was removed, the mixture was used directly. [f]Isolated yield on 0.5 mmol scale.

were obtained using $[Rh(cp^*)Cl_2]_2$ and $RhCl_3·H_2O$ (entries 3 and 4). A complex of $[Rh(COD)Cl]_2$ improves the reaction to give **3a** in 29% yield, but with various byproducts of **2a**, **4a**, and **5a** (entry 5).

Next, the effect of electron-donating NHC ligands on the selective hydrogenation was explored. Unfortunately, the rhodium complex prepared *in situ* by treating $[Rh(COD)Cl]_2$ with IMes·HCl or IPr·HCl results in low conversions (entries 6 and 7). In sharp contrast, a more nucleophilic CAAC bearing a 2,4-dimethylcyclohexenyl substituent adjacent to the carbene center dramatically improves the conversion, giving the desired product **3a** in 80% yield with high selectivity (entry 8). To identify the coordination mode of Rh with the CAAC ligand before catalysis, the CAAC-Rh complexes were prepared by a two-step operation (Scheme 2). Note that the complexes are air-stable and could be isolated by column chromatography. The ^{13}C NMR spectra show a greater downfield shift of the resonance for the carbene carbons (274.7 and 272.9 ppm) than that of classic NHCs (≈ 190 ppm).[21] The structure of the (CAAC-2)Rh(COD)Cl complex was fully characterized by single-crystal X-ray diffraction, evidencing a slightly shortened

Scheme 2. Synthesis of CAAC-Rh Complexes



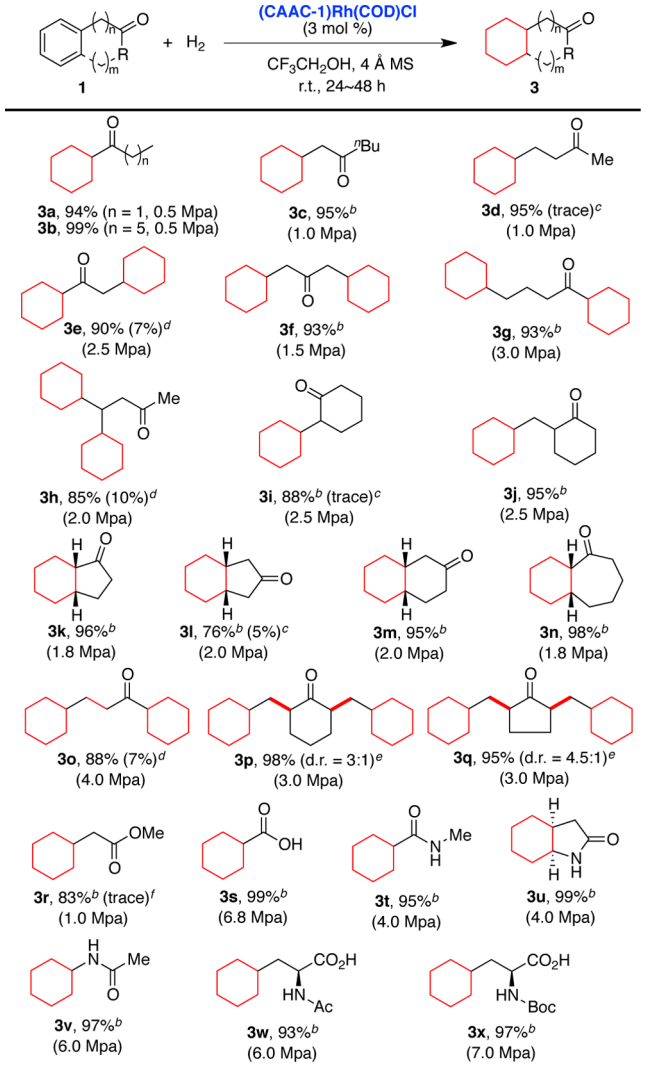
$Rh–C_{carbene}$ bond (2.0128(16) Å).[22] We were pleased to find that these structurally well-defined complexes show high catalytic activity for aryl-selective hydrogenation, leading to **3a** in excellent yield and selectivity (entries 9 and 10).[23,24]

This discovery led us to probe the scope of the aryl-selective hydrogenation using active (CAAC)Rh(COD)Cl complexes (Scheme 3). The phenyl group could be introduced at the *α*- or *β*-position of the ketone with no effect on its hydrogenation and retains the carbonyl intact (**3c** and **3d**). The bisphenyl fragments could be reduced simultaneously, allowing the rapid buildup of complex biscyclohexyl structural motifs (**3e**–**3h**). As expected, fused biscyclic ketones **3k**–**3n** are easily accessible from readily available benzocyclic precursors. Interestingly, the reactions with conjugated chalcones result in a synchronous hydrogenation of the unsaturated phenyl and alkenyl (**3o**–**3q**). It is particularly noteworthy that the approach uniformly retains the C═O moiety and generally achieves high conversion (76–99%). For instance, the aromatic rings on the ester and carboxylic acid can be reduced effectively, while keeping reactive alkoxycarbonyl and carboxyl intact (**3r** and **3s**). Strikingly, the hydrogenation tolerates the synthetically valuable amidyl group, forming substituted amides such as cyclohexanecarboxamide, hexahydro-1*H*-indol-2(3*H*)-one, and *N*-cyclohexylacetamide in 95–99% yields (**3t**–**3v**). In addition, the motifs of *N*-protected amino acids are also perfectly retained, offering a new avenue to functionalize phenyl-substituted amino acids (**3w** and **3x**).

Inspired by these results, we examined the efficiency of this CAAC-Rh catalyst system in the selective hydrogenation of phenols to cyclohexanones. Gratifyingly, the (CAAC-1)Rh(COD)Cl complex shows high reactivity in phenol hydrogenation in a mixed solvent of trifluoroethanol and water (ratio of 19:1), exclusively producing the product **7a** in almost quantitative yield (Scheme 4).[25] Common substituents such as methyl, isopropyl, *tert*-butyl, and methoxy on the phenols did not significantly interfere with the performance of the complexes (**7b**–**7i**). Importantly, the reaction with sterically hindered di- and trisubstituted phenols proceeded smoothly (**7j**–**7m**). Interestingly, unsaturated phenol and phenyl are hydrogenated together in the reaction (**7n**). Furthermore, polycyclic and heterocyclic substrates, such as naphthols, 2-hydroxypyridine, and 2-hydroxyquinoline, are amenable to the transformation, giving the related ketones and lactams in good to excellent yields (**7o**–**7r**). Notably, the protocol can be successfully applied to the selective reduction of bioactive estrone, allowing access to functionalized bisketone **7s**.

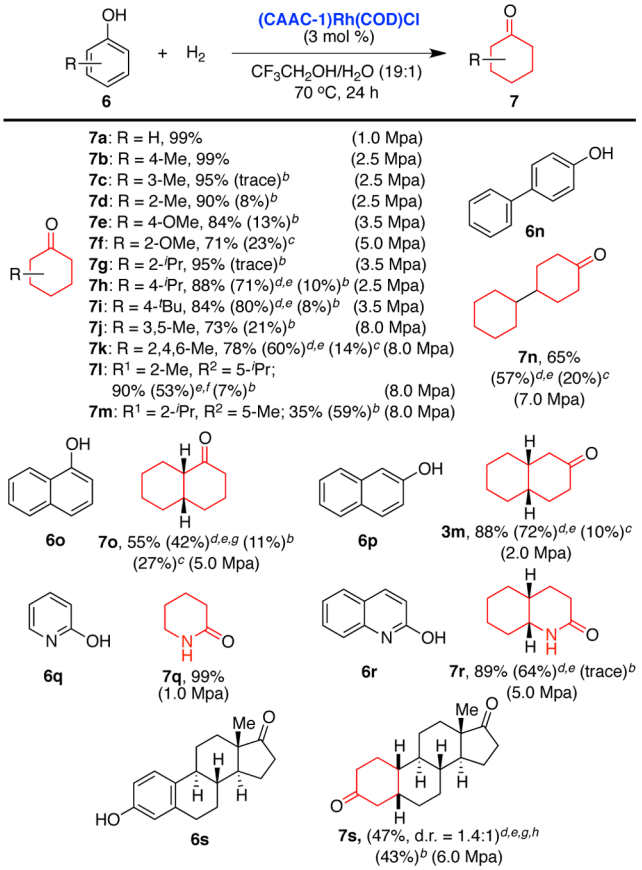
DOI: 10.1021/jacs.5b05868
J. Am. Chem. Soc. 2015, 137, 9250–9253

Scheme 3. Substrate Scope for CAAC-Rh-Catalyzed Aryl-Selective Hydrogenation[a]



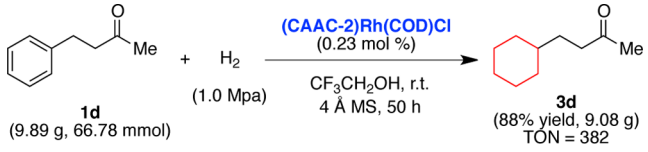
[a]Conditions: **1** (0.5 mmol), (CAAC-1)Rh(COD)Cl (0.015 mmol), 4 Å MS (250 mg), CF_3CH_2OH (10 mL); reaction was conducted under the conditions listed in each case at room temperature for 24−48 h. Isolated yields. [b](CAAC-2)Rh(COD)Cl was used. [c]GC yields of the compounds that were formed by the hydrogenation of the aromatic ring and carbonyl synchronously. [d]GC yields of the products that were formed by the reduction of one benzene ring. [e]The diastereomeric ratio was determined by HPLC analysis. [f]Trace amount of the starting materials was detected.

Scheme 4. CAAC-Rh-Catalyzed Selective Hydrogenation of Phenols[a]



[a]Conditions: **6** (0.1 mmol), (CAAC-1)Rh(COD)Cl (0.003 mmol), CF_3CH_2OH/H_2O (2.0 mL), and hydrogenation was conducted under the conditions listed in each case at 70 °C for 24 h. The yield was determined by GC analysis. [b]The recovery of the starting materials. [c]GC yields of the related cyclohexanol compounds. [d]**6** (0.5 mmol), (CAAC-2)Rh(COD)Cl (0.015 mmol), and CF_3CH_2OH/H_2O (10 mL) were used. [e]Isolated yields are given in parentheses. [f]**6l** (0.5 mmol). [g]48 h. [h](CAAC-1)Rh(COD)Cl (0.025 mmol) was employed, and the diastereomeric ratio was determined by HPLC analysis.

Scheme 5. Gram-Scale Hydrogenation of 1d



Finally, the selective hydrogenation is scalable and can be conducted on the 10-g scale with a 0.23 mol % loading of CAAC-Rh complex, forming **3d** in 88% yield with a turnover number (TON) of 382 (Scheme 5).

In summary, we have developed an efficient CAAC-Rh catalyst system for the hydrogenation of aromatic ketones and phenols to cyclohexyl-containing ketones and cyclohexanones, through the selective reduction of the aryl scaffolds while retaining functional carbonyl groups. The unique electronic structural properties of CAAC ligands open up a new opportunity for significantly improving selectivity and conversion by ligating to rhodium, achieving high compatibility with a variety of C═O-containing structural motifs, such as ketones, esters, carboxylic acids, amides, and amino acids. Further studies on the mechanistic understanding of the role of CAAC ligands and exploring chiral catalyst systems are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed optimization data; experimental procedures; characterization data of all new compounds; ORTEP drawing of (CAAC-2)Rh(COD)Cl and crystallographic data (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05868.

DOI: 10.1021/jacs.5b05868
J. Am. Chem. Soc. 2015, 137, 9250−9253

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support was provided by NSFC [No. 21202128 (X.Z.)] and XJTU. We thank Prof. Guy Bertrand (UCSD) for the donation of parts of iminium salts and Prof. Yan-Zhen Zheng (XJTU) for X-ray crystallographic analysis. We also thank Prof. Frank Glorius (WWU) and Prof. Laurean Ilies (UT) for valuable suggestions.

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(22) CCDC 1058808 [(CAAC-2)Rh(COD)Cl] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallo graphic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(23) Hg(0) poisoning experiments support the homogeneous nature of this CAAC-Rh catalyst system. See Supporting Information.

(24) The hydrogenation of propylbenzene also occurs smoothly to give propylcyclohexane (78% yield) under standard conditions, excluding chelation assistance of the carbonyl in the selective catalysis.

(25) Please see Supporting Information for details on the optimizing reaction parameters for the selective hydrogenation of phenols.

DOI: 10.1021/jacs.5b05868
J. Am. Chem. Soc. 2015, 137, 9250−9253