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Ligand-enabled and magnesium-activated hydrogenation with earth-abundant cobalt catalysts†

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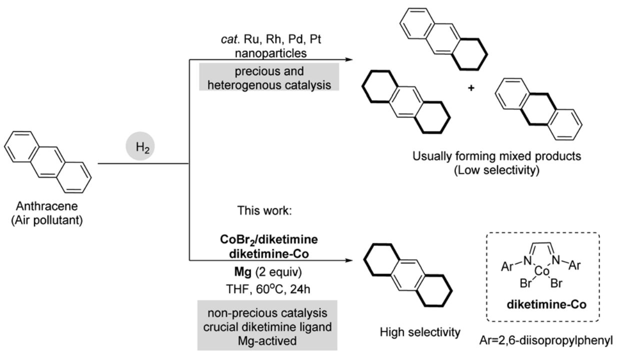
Replacing expensive noble metals like Pt, Pd, Ir, Ru, and Rh with inexpensive earth-abundant metals like cobalt (Co) is attracting wider research interest in catalysis. Cobalt catalysts are now undergoing a renaissance in hydrogenation reactions. Herein, we describe a hydrogenation method for polycyclic aromatic hydrocarbons (PAHs) and olefins with a magnesium-activated earth-abundant Co catalyst. When diketimine was used as a ligand, simple and inexpensive metal salts of $CoBr_2$ in combination with magnesium showed high catalytic activity in the site-selective hydrogenation of challenging PAHs under mild conditions. Co-catalyzed hydrogenation enabled the reduction of two side aromatics of PAHs. A wide range of PAHs can be hydrogenated in a site-selective manner, which provides a cost-effective, clean, and selective strategy to prepare partially reduced polycyclic hydrocarbon motifs that are otherwise difficult to prepare by common methods. The use of well-defined diketimine–ligated Co complexes as precatalysts for selective hydrogenation of PAHs and olefins is also demonstrated.

Earth-abundant metal-catalyzed hydrogenation provides a cost-effective and atom-economic strategy for sustainable chemical synthesis; thus, it has attracted considerable interest among the synthetic community.[1–4] Several inexpensive first-row transition metals such as iron,[5] nickel,[6] cobalt,[7] and manganese[8] have been shown to have appealing catalytic activities in the hydrogenation of olefins, ketones, imines, and even amides and esters.[9] In contrast, polycyclic aromatic hydrocarbons (PAHs) have rarely been hydrogenated by earth-abundant metal catalysts, probably due to their stability caused by aromaticity.[10] Catalytic hydrogenation of PAHs has been dominated by precious metals such as ruthenium, rhodium, palladium, and platinum *via* heterogeneous catalysis (Scheme 1).[11] Potassium bis(anthracene)cobaltate has been reported by Jacobi von Wangelin *et al.*[7a] for the hydrogenation reactions of unsaturated molecules (alkenes, arenes, carbonyl compounds). In addition, they have also reported the synthesis of potassium bis(η^4-anthracene) metalates of Fe and Co for catalytic hydrogenation of alkenes, ketones and imines at ambient H_2 pressure and temperatures.[7i]

Site selectivity in PAH hydrogenation has long been an important issue. Mixed products are usually formed upon hydrogenation of aromatic scaffolds at different sites, with limited PAH scope.[12] The use of earth-abundant metals for catalytic hydrogenation of PAHs with site-selective and cost-effective method would be of greater value for partially hydrogenated feedstock chemicals synthesis.

In nonprecious-metal-promoted catalysis, an activation strategy involving the reduction of simple, low-cost and commercially available metal salts for *in situ* formation of active metal catalysts has been established. It offer the advantages of easy handling and potential applications in large-scale



Scheme 1 Transition-metal-catalyzed hydrogenation of PAH (anthracene).

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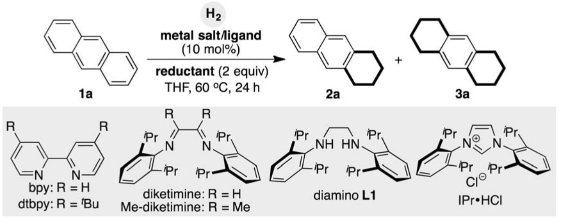
manufacturing, with minimal associated hazards in the purification of metal catalysts.[13,14]

We hypothesized whether it will be possible to use earth-abundant metal salts as precatalysts to replace expensive metal catalysts, using an *in situ* activation strategy for achieving the hydrogenation of PAHs with controllable selectivity. Hydrogenation using robust Fe, Co, and Mn catalysts has been reported. However, the hydrogenation of PAHs using these inexpensive metal catalysts has been rather limited.[15,16] Zeng's group has developed low-valent cobalt *in situ* using methylmagnesium bromide as a reducing agent for the hydrogenation of fused PAHs to give two terminal aromatic carbocycles.[17]

Herein, we report a ligand-enabled and magnesium-activated hydrogenation of PAHs and olefins with in-expensive metal Co catalysis. Site selectivity in the hydrogenation of PAHs can be controlled by these two different, earth-abundant metal catalysts. A combination of $CoBr_2$ and diketimine or a diketimine–ligated Co complex with magnesium as a reductant showed good catalytic activity in the selective hydrogenation of two side aromatics of PAHs (Scheme 1). Preactivation with Mg was performed by placing Mg turnings and $CoBr_2$ in Schlenk tube and heating under vacuum for 5–8 minutes using a heat gun.

In our efforts to form low-oxidation-state active Co species *in situ*, we commenced our studies by selecting metallic magnesium as reductant, to test its reactivity in the hydrogenation of anthracene (Table 1).[18] Initially, we selected $CoCl_2$ salt as the catalyst and examined it under various reaction conditions. In the absence of external ligands, the low-cost $CoCl_2$ salt with magnesium as reductant was unable to promote the hydrogenation (entry 1). Screening of ligands showed that 2,2′-bipyridine was inefficient in the hydrogenation (entry 2). Interestingly, Co-catalyzed hydrogenation occurred when using dtbpy as ligand; a product with one reduced aromatic side arm was formed (entry 3), only a trace amount of the two-side-aromatic-reduced product **3a** was detected. We recognized that the ligand could play an important role in promoting hydrogenation with Co. Other ligands such as IPr, dppp, Xantphos, and diamino L1 were inefficient in the promotion of the Co-catalyzed hydrogenation (entries 4–7). *N*-2,6-Diisopropylphenyl-bearing diketimine greatly enhanced the catalytic activity of Co to afford **3a** in 59% yield (entry 8). However, with 2,3-dimethyl-substituted diketimine, a trace amount of product **3a** was detected (entry 9). Encouraged by the results, we chose different cobalt salts as catalysts. When using $Co(acac)_2$ salt, no hydrogenation took place (entry 10). To our delight, the salt of $CoBr_2$ exhibited high reactivity; it resulted in catalytic hydrogenation of two side aromatics of anthracene in the formation of product **3a** (entry 11). Manganese and zinc could not serve as efficient reductants in Co catalysis (entry 12).

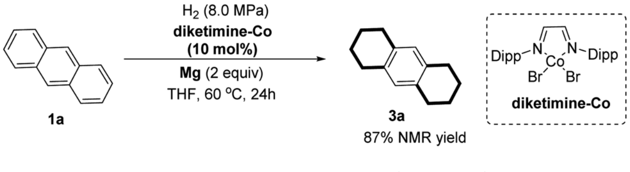
Table 1 Studying the effect of metal salts, ligands and reductants on selective hydrogenation of anthracene^a



Entry	Metal salt	Ligand	Reductant	[2a %]	[3a %]
1	$CoCl_2$	None	Mg	nd^b	nd^b
2	$CoCl_2$	Bpy	Mg	nd^b	nd^b
3	$CoCl_2$	Dtbpy	Mg	38	Trace
4	$CoCl_2$	IPr·HCl	Mg	nd^b	nd^b
5	$CoCl_2$	Dppp	Mg	nd^b	nd^b
6	$CoCl_2$	Xantphos	Mg	nd^b	nd^b
7	$CoCl_2$	Diamino L1	Mg	nd^b	nd^b
8	$CoCl_2$	Diketimine	Mg	26	59
9	$CoCl_2$	Me-diketimine	Mg	37	Trace
10	$Co(acac)_2$	Diketimine	Mg	nd^b	nd^b
11	$CoBr_2$	Diketimine	Mg	nd^b	90 [84]^c
12	$CoBr_2$	Diketimine	Mn or Zn	nd^b	nd^b
13	$CoBr_2$	No	Mg	nd^b	nd^b
14	$CoBr_2$	Diketimine	No	nd^b	nd^b
15	$CoBr_2$	Diketimine	CH_3Li	nd^b	nd^b
16	$CoBr_2$	Diketimine	NaO^{t}Bu	nd^b	nd^b
17	$CoBr_2$	Diketimine	$NaHBEt_3$	nd^b	nd^b
18	$CoBr_2$	Diketimine	NaO^{t}Bu/HBPin	nd^b	nd^b
19^d	$CoBr_2$	Diketimine	NaO^{t}Bu/HBPin	nd^b	nd^b

[a] Conditions: **1a** (0.2 mmol), metal salt (0.02 mmol), ligand (0.02 mmol), reductant (0.4 mmol), H_2 (8 MPa), THF (2 mL), 60 °C, 48 h. ^1H NMR yields using 1,3,5-trimethoxybenzene as internal standard. [b] Not detected. [c] Isolated yield. dppp = 1,3-bis(diphenylphosphino)propane. Xantphos = 4,5-bis(diphenyl phosphino)-9,9-dimethylxanthene. [d] Without H_2.

Once we had the optimal hydrogenation conditions with $CoBr_2$ and diketimine ligand in hand, we were curious as to whether well-defined diketimine–ligated Co complexes could serve as precatalysts to promote the hydrogenation of PAH. According to known procedures,[19] we prepared the diketimine–ligated Co complexes and tested their reactivities in the hydrogenation of anthracene. Briefly, diketimine–ligated Co complexes were prepared by mixing equimolar anhydrous $CoBr_2$ and diketimine in THF and stirred for 24 h at room temperature, filtered, washed with hexane, and dried in vacuum. The diketimine–Co complex afforded the product **3a** in almost equal conversion to that using $CoBr_2$/diketimine (Scheme 2). Catalytic hydrogenation of PAHs was carried out by heating Mg turnings (10 mg, 0.4 mmol) and $CoBr_2$ (5 mg, 0.02 mmol) in a Schlenk tube using a heat gun at around 300 °C under vacuum for 5 min. The mixture was cooled to room temperature in nitrogen atmosphere, PAH (0.2 mmol), diketimine (8 mg, 0.02 mmol) and THF (2.0 mL) were added. The

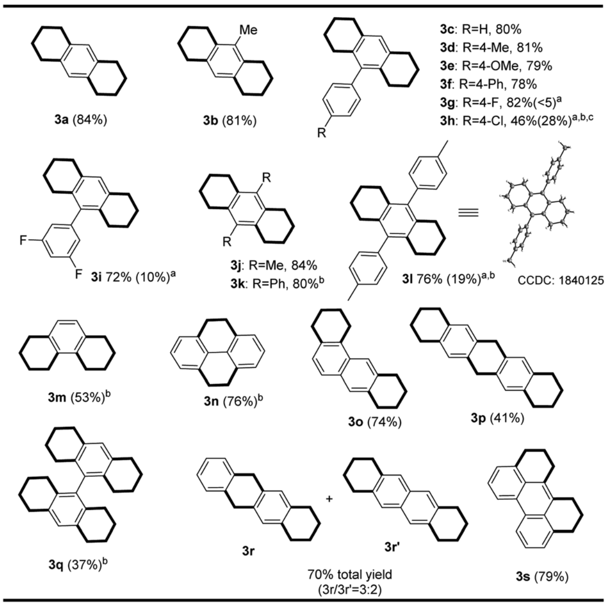


Scheme 2 Testing the catalytic activities of well-defined diketimine–Co complexes in hydrogenation of anthracene.

resulting mixture was heated at 80 °C for 2 hours. Then the resulting mixture was quickly moved to a high-pressure autoclave. The reaction mixture was stirred under an atmosphere of H_2 (8 Mpa) at 60 °C for 50 h and then quenched with saturated NH_4Cl/H_2O (4 mL). The crude product was extracted with EtOAc (3 × 4 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. After removal of the volatiles under vacuum, the crude products were purified by column chromatography to afford the desired hydrogenation compounds.

With optimal reaction conditions in hand, $CoBr_2$/diketimine was further used as a precatalyst to explore the scope of Co-catalyzed hydrogenation for the synthesis of two-side-aromatic-reduced motifs (Scheme 3).

1,2,3,4,5,6,7,8-Octahydroanthracene derivatives bearing methyl and substituted phenyl substituents at the C9/C10 positions were prepared by selectively reducing two side carbocycles (**3b–3l**). As expected, the hydrogenation of phenanthrene readily took place with Co catalysis (**3m**). When using pyrene, we found that internal carbocycles were reduced to afford 4,5,9,10-tetrahydropyrene (**3n**). This protocol was extended to the preparation of partially reduced compounds of 1,2,3,4,8,9,10,11-octahydrotetraphene and 1,2,3,10,11,12-hexahydroperylene, by the reduction of related PAH precursors (**3o** and **3s**). It was interesting to note that the hydrogenation of pentacene unexpectedly afforded 1,2,3,4,6,8,9,10,11,13-decahydropentacene **3p** by selective reduction of three carbocycles. A further interesting observation was that four side carbocycles in bianthracene were hydrogenated to form hexadecahydro-9,9′-bianthracene (**3q**). This differs from what was observed in the Cr catalysis protocol; the formation of a mixed regioisomer (**3r** and **3r′**) was found in the hydrogenation of tetracene by Co catalysis. This reaction was not tolerable for substrates bearing reducible groups such as Br, COOR, COOH, CHO, CN and NO_2.

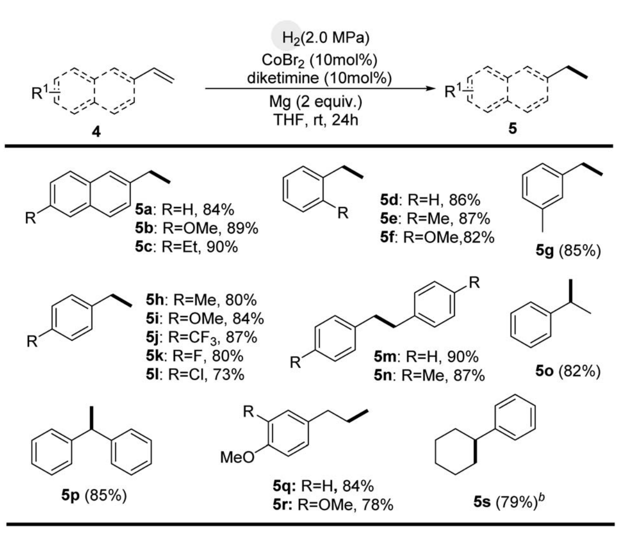


Scheme 3 Co-catalyzed selective hydrogenation of PAHs. PAH (0.2 mmol), $CoBr_2$ (0.02 mmol), diketimine (0.02 mmol), Mg (0.4 mmol), H_2 (8 MPa), THF (2 mL), 60 °C, 48 h. Isolated yields. [a]Yields of compounds that were formed by reducing one side arenes of PHAs. [b]60 h. [c]Mg (3.5 equiv.) was used.

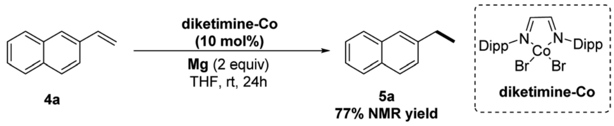
The diketimine–Co-catalyzed hydrogenation protocols can be utilized to reduce substituted olefins (Scheme 4).[5c,5d,7a,7b] The double bonds were reduced, with retention of the phenyl and naphthyl groups, affording linear or branched alkylarene motifs in good yields. Moreover, olefin hydrogenation using diketimine–ligated Co complexes took place smoothly (Scheme 5).

To examine whether a low-oxidation-state Co species is formed by the reduction of a $CoBr_2$ salt with magnesium, we performed X-ray photoelectron spectroscopy (XPS) analysis of the oxidation states of Co in the stoichiometric reactions of $CoBr_2$ with diketimine in the absence or presence of magnesium. Downshift signals with a shift distance of 0.89 eV for the Co 2p components in the related spectra were observed when conducting the reaction with magnesium in THF (Fig. 1). This shows that low-oxidation-state Co species are formed *in situ* by the reduction of $CoBr_2$ with magnesium, which then serve as active species to initiate the hydrogenation. The π-acceptors (arenes, olefins *etc.*) are able to stabilize low oxidation state reactive metal spices. Previously, it has been reported that Co catalyzed reaction were initiated by the substitution of the labile arenes molecules by π-acceptor substrates.[7i] Jacobi von Wangelin *et al.* have reported arene–Co and arene–Fe catalysts for hydrogenations of olefins, alkenes, *etc.* and found that slow hydrogenation of anthracene occurred when there was no suitable π-acceptor.[7i] We also performed controlled experiments of the low-cost $CoBr_2$ salt with magnesium in the absence of diketimine ligand (Table 1, entry 13), but were failed to get hydrogenated anthracene. Additionally, we also checked the Jacobi von Wagelin's arene–M(0) complexes,[7i] using anthracene instead of diketimine as ligand for the catalytic hydrogenation of olifens but were unable to get hydrogenated products.

Reaction profiles for the Co-catalyzed hydrogenation of anthracene were investigated. The formation of two-side-



Scheme 4 Diketimine–Co-catalyzed hydrogenation of olefins.



Scheme 5 Testing the catalytic activities of diketimine–Co complexes in hydrogenation of olefins.

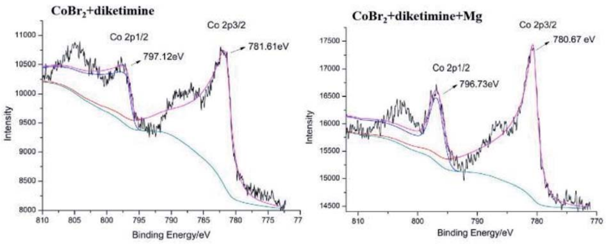


Fig. 1 XPS analysis of stoichiometric reaction mixtures of $CoBr_2$ with diketimine ligand in the absence or presence of metallic magnesium.

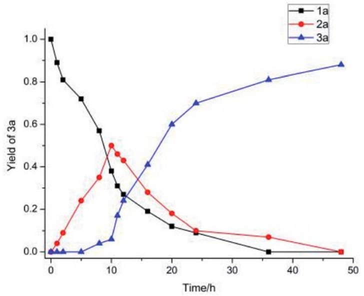
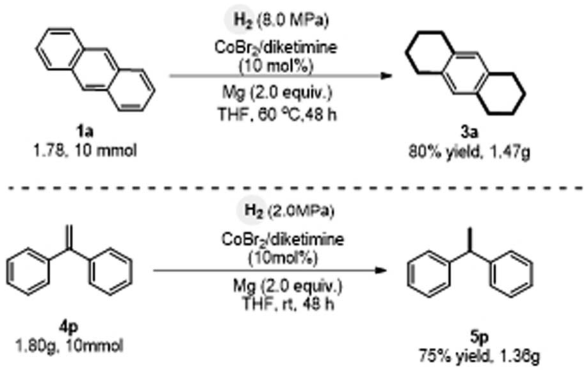


Fig. 2 Reaction profiles for Co-catalyzed hydrogenation of anthracene.

aromatic-reduced product **3a** was observed in Co catalysis within the first 10 hours (Fig. 2), and the hydrogenation rate for the conversion of **2a** to **3a** increased.

The scalability of the hydrogenation of anthracene was examined on gram scale. It was found that performing the Co-catalyzed reactions on the scale of 10 mmol did not affect the efficiency of site-selective hydrogenation, hence permitting the scalable preparation of **3a** and **5p** (Scheme 6).



Scheme 6 Gram-scale hydrogenation of **1a** and **4p**.

Conclusions

In summary, we have developed an economic and site-selective hydrogenation of challenging PAHs with earth-abundant Co catalysis.[20] arene–Co and arene–Fe catalysts for hydrogenations of olefins, alkenes, ketones, and imines have been previously reported by Jacobi von Wangelin *et al.*[7i] in this study, we used low-cost and commercially available $CoBr_2$ salts as precatalysts combined with diketimine ligand and air-stable magnesium as the reductant for site-selective hydrogenation of two side aromatic hydrocarbons of PAHs and olefins. A wide range of PAHs such as tetracene, tetraphene, perylene, pentacene, and bianthracene were amenable to the hydrogenation, providing a cost-effective and clean strategy for the synthesis of two-side-aromatic-reduced polycyclic hydrocarbon motifs in high site selectivity. The high reactivity of Co catalysis with diketimine ligand indicates that the methodology outlined herein will have potential applications in the hydrogenation of challenging substrates.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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