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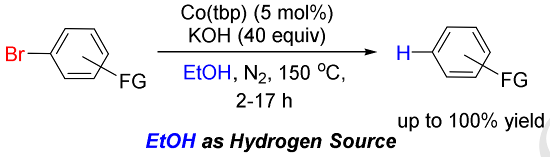
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China



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ABSTRACT

Hydrodebromination of aryl bromides catalyzed by electron rich and sterically unhindered cobalt 5,10,15,20-tetrabutylporphyrin was achieved at mild conditions in good yields employing EtOH as the hydrogen source. The catalytic efficiency was enhanced compared with previously reported by cobalt tetra-aryl porphyrin catalysts. A revised mechanism of single electron transfer was proposed.

1. Introduction

The reduction of aryl halides to the corresponding hydrocarbon is an important task not only in organic synthetic transformations,[1] but also in the detoxification of environmentally hazardous organic halides.[2]

Transfer hydrogenation (TH)[3] for hydrodehalogenation has been widely investigated as it is safer and more convenient than hydrogenation with H_2 gas.[4] Reducing agents used in TH such as sodium hydride,[5] borohydride,[6] silanes[1,7] and tin hydrides[1,8] are widely used but quite expensive and sometimes not environmentally friendly. Transfer hydrogenation with ^{i}PrOH is very common,[9] but the use of EtOH as hydrogen source is scarce.[10] Use of ethanol in TH represents an attractive alternative given its abundance, sustainability and low toxicity. However, the difficulties associated with EtOH are: the larger α-C-H bond dissociation energy of ethanol;[11] the poisonous dehydrogenation product acetaldehyde to many transition metal catalysts.[12]

Our group has reported the Co(ttp) (ttp = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion) catalyzed hydrodebromination of aryl bromides in hydrogen donor solvents of both ^{i}PrOH and THF.[13] The reaction mechanism operates through a halogen atom abstraction of an aryl bromide with Co(II) porphyrin to give an aryl radical and Co(III) bromide,[13,14] subsequent hydrogen atom abstraction of the aryl radical from solvent yields the arenes. We envisioned that a more electron rich porphyrin ligand would facilitate the key oxidative addition of Co^{II}(por),[15] thus possibly enhancing the hydrodebromination rate. We also discovered that the more attractive hydrogen donor ethanol can be used. Here we report the electron rich Co^{II}(tbp) (tbp = 5,10,15,20-tetrabutylporphyrinato dianion) catalyzed hydrodebromination of aryl halides employing EtOH as the hydrogen source with high efficiency. An updated reaction mechanism of single electron transfer was proposed.

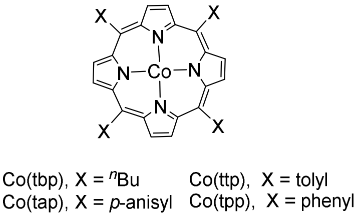

Fig. 1. Structure Illustration of Co(por) Catalysts

2. Reaction Conditions Optimization

Based on our reported work (eq. 1),[13] the catalytic hydrodebromination of 4-bromoanisole (**1a**) with more electron rich Co^{II}(tbp) in ^{i}PrOH solvent was examined. To our delight, the catalytic transformation proceeded smoothly with 100% yield at a lower temperature of 150 °C in a shorter time of 3 h (eq. 2). With this initial success in hand, the reaction conditions (porphyrin ligand, solvent, catalyst loading, temperature, KOH loading and reaction atmosphere) were further optimized.

The catalytic efficiency of various Co porphyrin ligand was then investigated. With the most electron rich and least sterically

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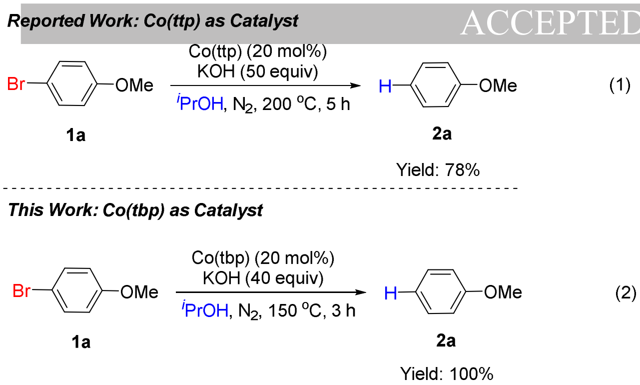
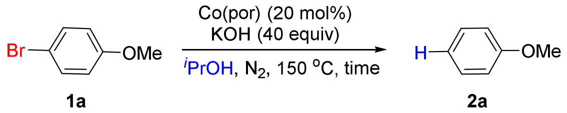
∗ Corresponding author. Tel.: +852 39436376; fax: +852 26035057; e-mail: ksc@cuhk.edu.hk (K.S.Chan)



hindered Co^{II}(tbp), the hydrodebromination process was complete in 3 h at 150 ^{o}C (Table 1, entry 1). While for Co^{II}(tap) and Co^{II}(ttp), the catalytic reactions were not complete after 6 h to give 82% and 17% yields of **2a**, respectively (Table 1, entries 2 and 3). Thus, Co^{II}(tbp) was chosen as the optimal catalyst for further investigation.

Table 1 Porphyrin Ligand Effect[a]

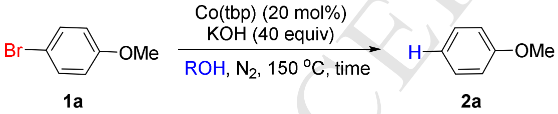


Entry	por	time	**2a** yield[b]%	**1a** recovery[b]%	(**1a**+**2a**) yield[b]%
1	tbp	3 h	100	0	100
2	tap	6 h	82	20	102
3	ttp	6 h	17	80	97

[a] Co(por) (0.014 mmol) with 4-bromoanisole (0.072 mmol) in 1.0 mL ^{i}PrOH; [b] GC-MS yield.

With the more reactive Co^{II}(tbp) catalyst, we examined the less reactive hydrogen donating solvent of EtOH and MeOH. The reaction in EtOH was similar with that in ^{i}PrOH and required 6 h to give 100% yield of **2a** (Table 2, entries 2 and 3). However, the reaction in MeOH required 3 d to reach 69% yield of **2a** with 5% of **1a** recovered (Table 2, entry 1). The stronger α-C-H bond[11] (96 kcal/mol) of MeOH and poor solubility of catalyst in MeOH account for the slower reaction. Therefore, the cheaper EtOH was chosen for further investigation.[11,12]

Table 2 Solvent Effect[a]

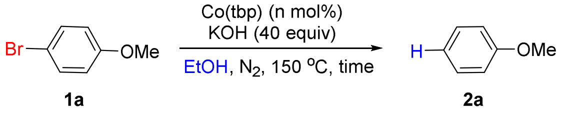


Entry	ROH	time	**2a** yield[b]%	**1a** recovery[b]%	(**1a**+**2a**) yield[b]%
1	MeOH	72 h	69	5	74
2	EtOH	6 h	100	0	100
3	^{i}PrOH	3 h	100	0	100

[a] Co(tbp) (0.014 mmol) with 4-bromoanisole (0.072 mmol) in 1.0 mL alcohol; [b] GC-MS yield.

With the optimal solvent and catalyst in hand, the loading of catalyst was also examined. Without any catalyst added, only 8% yield of the target product **2a** was formed with 80% yield of **1a** recovered after heating for 24 h, thus supporting the catalytic role of Co^{II}(tbp). In the presence of 5 mol% of Co^{II}(tbp) catalyst, the reaction proceeded smoothly and finished in 8 h with complete conversion (Table 3, entry 3). When the loading of catalyst was reduced to 2.5 mol%, the reaction rate decreased a lot and required 24 h to give 94% yield of **2a** with 5% of recovered **1a** (Table 3, entry 2). Increasing catalyst loading to 10 or 20 % enhanced the reaction rate slightly and required 6 h to finish the reaction (Table 3, entries 4 and 5). Thus, a 5 mol% of catalyst was chosen as the optimal catalyst loading.

Table 3 Catalyst Loading Effect[a]

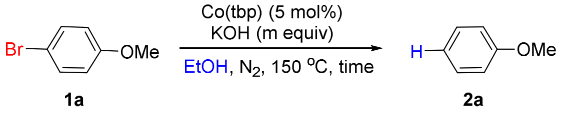


Entry	n	time	**2a** yield[b]%	**1a** recovery[b]%	(**1a**+**2a**) yield[b]%
1	0	24 h	8	80	88
2	2.5	24 h	94	5	99
3	5	8 h	100	0	100
4	10	6 h	98	0	98
5	20	6 h	100	0	100

[a] Co(tbp) (0.014 mmol) with 4-bromoanisole (0.072 mmol) in 1.0 mL EtOH; [b] GC-MS yield.

The loading of KOH was also examined. Without any base added, the starting material **1a** was recovered quantitatively after heating for 24 h (Table 4, entry 1). Increasing KOH loading to 20 equiv resulted in incomplete reaction after 24 h with 68% of **2a** and 30% of **1a** recovered (Table 4, entry 2). The reaction with 30 equiv of KOH required 16 h to give 98% yield (Table 4, entry 3). 40 equiv of KOH was essential to ensure fast hydrodebromination in 8 h (Table 4, entry 4). Reaction with 50 equiv of KOH still required 6 h to complete and the reaction rate was not improved dramatically (Table 4, entry 5). Thus, 40 equiv was found to be the optimal loading of KOH.

Table 4 KOH Loading Effect[a]

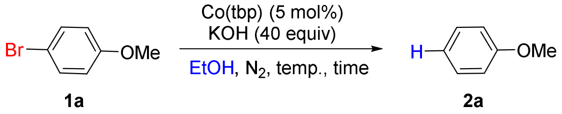


Entry	m	time	**2a** yield[b]%	**1a** recovery[b]%	(**1a**+**2a**) yield[b]%
1	0	24 h	0	100	100
2	20	24 h	68	30	98
3	30	16 h	98	0	98
4	40	8 h	100	0	100
5	50	6 h	96	0	96

[a] Co(tbp) (0.014 mmol) with 4-bromoanisole (0.072 mmol) in 1.0 mL EtOH; [b] GC-MS yield.

The reaction was carried out at a lower temperature of 120 ^{o}C and afforded 21% of **2a** together with 65% of recovered **1a** after 25 h (Table 5, entry 1). Therefore, 150 ^{o}C was chosen as the optimal reaction temperature.

Table 5 Temperature Effect[a]

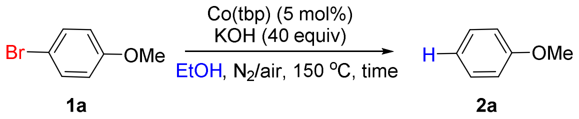


Entry	Temp. (˚C)	time	**2a** yield[b]%	**1a** recovery[b]%	(**1a**+**2a**) yield[b]%
1	120	25 h	21	65	86
2	150	8 h	100	0	100

[a] Co(tbp) (0.014 mmol) with 4-bromoanisole (0.072 mmol) in 1.0 mL EtOH; [b] GC-MS yield.

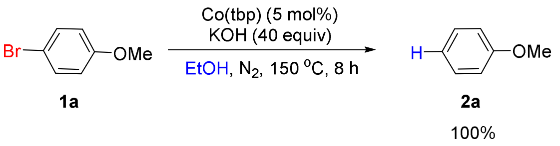
The hydrodebromination reaction was compatible with an air atmosphere to give similar yield in slightly longer time of 10 h (Table 6, entry 1). The optimal reaction conditions were shown below with 5 mol% of Co(tbp) catalyst and 40 equiv of KOH in EtOH solvent at 150 °C under N_2 (eq. 3).

Table 6 Atmosphere Effect[a]



Entry	N_2/air	time	**2a** yield[b]%	**1a** recovery[b]%	(**1a**+**2a**) yield[b]%
1	air	10 h	96	1	97
2	N_2	8 h	100	0	100

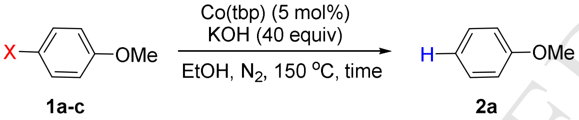
[a] Co(tbp) (0.014 mmol) with 4-bromoanisole (0.072 mmol) in 1.0 mL EtOH; [b] GC-MS yield.



(3)

The relative reactivities of Ar-X (X = Cl, Br, I) towards hydrodebromination were investigated in the optimized reaction conditions using *para* halogen atom substituted anisoles (**1a** to **1c**). Rates increased in the order Cl < Br < I (Table 7, entries 1 to 3). 4-Iodoanisole (**1c**) showed the highest reactivity and completed in 2 h with 92% yield (Table 7, entry 3). 4-Chloroanisole (**1b**) was inert towards hydrodechlorination with only 5% yield of **2a** formed and 80% of **1b** recovered after 24 h.

Table 7 Relative Reactivity of Ar-X[a]

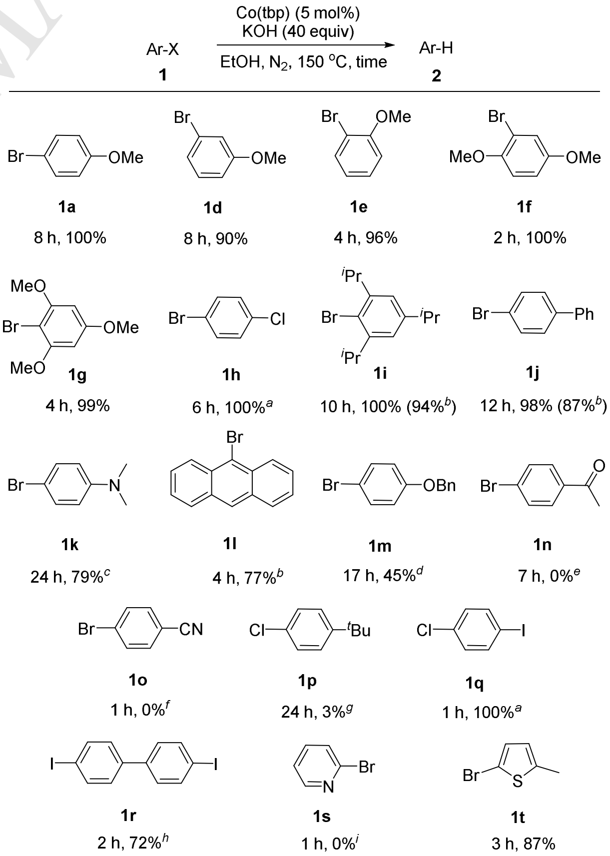


Entry	X	time	**2a** yield[b]%	**1** recovery[b]%	(**1**+**2a**) yield[b]%
1	Cl (**1b**)	24 h	5	80	85
2	Br (**1a**)	8 h	100	0	100
3	I (**1c**)	2 h	92	0	92

[a] Co(tbp) (0.014 mmol) with 4-haloanisole (0.072 mmol) in 1.0 mL EtOH; [b] GC-MS yield.

Substituted aryl bromides and aryl iodides were tolerated and reacted smoothly. (Scheme 1). Dehalogenation of *para* and *meta* bromoanisole (**1a** and **1d**) were completed in 8 h to give anisole in 100% and 90% yield, respectively. The *ortho* bromoanisole (**1e**) was more reactive and gave clean conversion in 4 h with 96% yield of **2a**. When the phenyl ring was substituted with more methoxy groups, the reaction times were shortened to 2 h for **1f** and 4 h for **1g**. Hydrodehalogenation of 1-bromo-4-chlorobenzene (**1h**) and 1-chloro-4-iodobenzene (**1q**) afforded chlorobenzene quantitatively without further reduction to benzene. Sterically hindered 2,4,6-triisopropylbromobenzene (**1i**) was hydrogenated smoothly within 10 h with quantitative conversion. Hydrodebromination of 1-bromo-4-(dimethylamino) benzene (**1k**) was slow and generated 79% of *N*, *N*-dimethylbenzenamine after 24 h with 20% of **1k** recovered. 1-Bromo-4-phenylbenzene (**1j**) was hydrogenated completely in 12 h. Hydrodebromination of 9-bromoanthracene (**1l**) was accomplished in 4 h with slightly low yield of 77%. When 1-bromo-4-(benzyloxy)benzene (**1m**) was treated with the optimal reaction conditions, 45% yield of benzyl phenyl ether was achieved as the hydrodebromination product together with 60% yield of toluene and 60% yield of 4-bromophenol as the C-O bond hydrogenation product after heating for 17 h. For 4-bromoacetophenone (**1n**), the reduction of carbonyl group to hydroxy group occurred fast to afford 4-bromo-*α*-methylbenzyl alcohol within 1 h, followed by further hydrodebromination to generate *α*-methylbenzyl alcohol in 32% yield with 4-bromo-*α*-methylbenzyl alcohol in 12% yield after 7 h. 4-Bromobenzonitrile (**1o**) was consumed completely after heating for 1 h without any formation of benzonitrile. After neutralization of the reaction mixture with HCl, 86% of 4-bromocarboxylic acid and 12% of benzoic acid were achieved. Alkaline hydrolysis of nitrile occurred rapidly to generate the corresponding carboxylate. Only 3% of hydrodechlorination product of **1p** was achieved with 95% of **1p** recovered. The poor reactivity of C–Cl bond in **1b**, **1p** and **1q** suggests that aryl chlorides are inert towards hydrodechlorination in the optimized reaction conditions. **1r** was reduced to biphenyl with 72% of isolated yield. The efficient C–I bond reduction in **1c**, **1q** and **1r** support the high reactivity of aryl iodides in the cobalt porphyrin catalyzed hydrodehalogenation reactions. The hydrodebromination of heteroaromatic bromides were also examined. 2-Bromopyridine (**1s**) was consumed completely within 1 h with the formation of complex mixture. The hydrodebromination of **1t** went on smoothly to afford 2-methylthiophene in 87% yield.

Scheme 1 Substrate Scope of Co(tbp) Catalyzed Hydrodehalogenation.



[a] chlorobenzene as sole product; [b] isolated yield; [c] 20% of **1k** recovered; [d] 50% of toluene and 50% of 4-bromophenol were achieved; [e] *α*-methylbenzyl alcohol in 32% yield and 4-bromo-*α*-methylbenzyl alcohol in 12% yield were achieved; [f] 86% of 4-bromobenzoic acid and 12% of benzoic acid were achieved after neutralization with HCl. [g] 95% of **1p** recovered after reaction; [h] isolated yield, biphenyl as sole product; [i] complex mixture.

3. Mechanistic Investigation

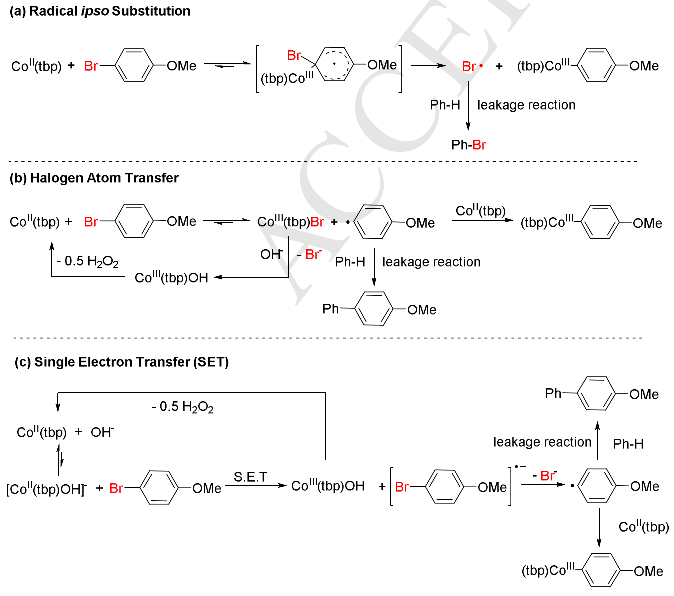
Based on the established mechanism for Ar-X bond activation with group 9 metalloporphyrins and cobalt porphyrin catalyzed hydrodebromination of aryl bromides,[13-17] 3 plausible mechanistic pathways were proposed for the C-Br bond activation step: (a) radical *ipso* substitution mechanism, (b) halogen atom transfer mechanism, (c) single electron transfer mechanism (Scheme 2).

Pathway (a) (Scheme 2) involves a radical *ipso* substitution by Co^{II}(tbp) based on the known mechanism of aryl carbon halogen bond activation with rhodium and iridium porphyrin complexes.[16,17] Co^{II}(tbp) attacks the *ipso*-carbon of Ar-Br to give the Co^{III}(tbp)-cyclohexadienyl radical intermediate. The radical intermediate then eliminates a bromine atom to generate Co(tbp)aryl. In benzene solvent, the bromine atom generated can be trapped by benzene to afford bromobenzene through a leakage reaction.

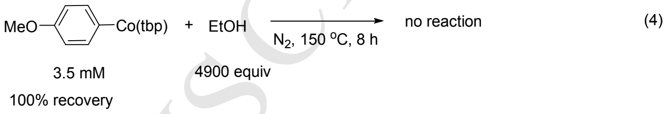
Pathway (b) (Scheme 2) starts from a bromine atom abstraction of aryl bromide by Co^{II}(tbp) to give an aryl radical and Co^{III}(tbp)Br, analogous to the well-known halogen atom transfer process between $Co^{II}(CN)_5^{3-}$ and an alkyl halide.[15(a)] The aryl radical formed can combine with Co^{II}(tbp) to generate Co(tbp)aryl. When benzene solvent is employed, the aryl radical intermediate can be trapped by benzene to afford 4-methoxy biphenyl as a coupling product. In the presence of KOH, Co^{III}(tbp)Br can be converted to Co(tbp)OH through ligand substitution, which regenerates Co^{II}(tbp) and H_2O_2 through reductive elimination.[14,16]

Pathway (c) (Scheme 2) goes through a single electron transfer mechanism.[16] In strongly basic media, $[Co^{II}(tbp)OH]^-$ complexes were formed from the coordination between OH^- and Co^{II}(tbp), which subsequently reduce aryl bromides through single electron transfer to afford the corresponding radical anion.[19] The radical anion undergoes fast C-Br bond cleavage to afford an aryl radical and bromide anion.[19(b)] The aryl radical can combine with Co^{II}(tbp) to afford Co(tbp)aryl. Since Co^{II}(tbp) is electron rich[20] (Oxidation potential for Ni analouges: 0.6 eV for tbp and 1.04 eV for tpp) with small steric hindrance, the single electron transfer process is likely favored and faster than other Co porphyrin complexes.

Scheme 2. Possible Mechanisms for Aryl C-Br Bond Activation with Co^{II}(tbp).



Co(tbp)aryl are important intermediates generated in the bond activation process. To gain further mechanistic support and understanding of the catalysis, the reaction (eq. 3) was closely monitored by thin layer chromatography. The formation of Co(tbp)Ph(*p*-OMe) in the reaction process was observed and further confirmed by both TLC and HRMS through comparing with an authentic sample.[14] The conversion of Co(tbp)Ph(*p*-OMe) to anisole in the optimized reaction conditions was also investigated. In the absence of base, Co(tbp)Ph(*p*-OMe) was stable and did not react with ethanol to generate any anisole after heating for 8 h at 150 °C (eq. 4). When KOH was added, Co(tbp)Ph(*p*-OMe) was hydrolyzed smoothly to give anisole and Co^{II}(tbp) quantitatively in 1.5 h at 150 °C (eq. 5). KOH is therefore needed in the hydrolysis of Co(tbp)aryl. The experimental results strongly support the intermediacy of Co(tbp)aryl in the formation of hydrodebromination product under basic conditions and all 3 possible mechanisms are reasonable.



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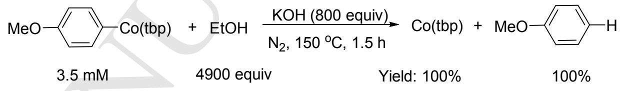
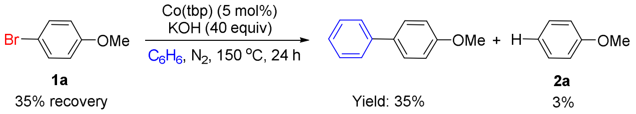


(5)

To determine whether any aryl radical intermediate exists in the reaction process, benzene solvent was employed instead of EtOH as a radical trapping reagent.[14,16] 35% of 1-phenyl-4-methoxybenzene was formed after 24 h as the biaryl coupling product between benzene and 4-methoxyphenyl radical together with 3% of anisole as the hydrodebromination product (eq. 6). Therefore, the existence of an aryl radical in the reaction process is supported. Halogen atom abstraction and single electron transfer mechanisms are more reasonable (Scheme 2, pathways b and c). Furthermore, no bromobenzene product was detected from the leakage reaction between bromine atom and benzene solvent, which rules out the presence of bromine atom intermediate. The radical *ipso* substitution mechanism (Scheme 2, pathway a) is thus disfavored.[14,16] The catalysis is promoted by electron withdrawing *para*-substituent (**1h**) and suppressed by electron donating *para*-substituent (**1k**), which is not consistent with a Co(tbp)-cyclohexadienyl radical intermediate stabilized by both electron-rich and -poor *para*-substituents via resonance interaction.[17] Therefore, pathway (a) is ruled out.



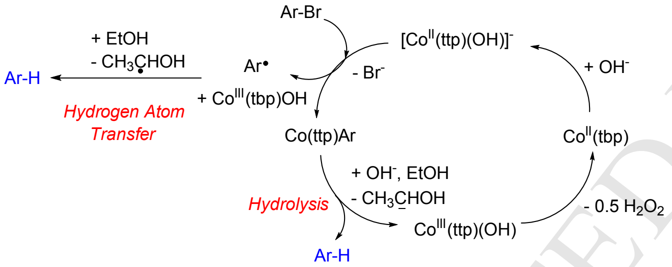
(6)

Pathway (b) (Scheme 2) includes a C(aryl)-Br bond activation through direct bromine atom abstraction by Co^{II}(tbp). However, the absence of any stoichiometric product between Co^{II}(tbp) and 4-bromoanisole (**1a**) without base (Table 4, entry 1) highly disfavors this mechanism.

Pathway (c) (Scheme 2) is the most reasonable mechanism based on the following experimental results. The increasing reactivities of **1k**, **1a** and **1h** towards hydrodebromination match well with the decreased LUMO energy of each molecule (-0.09 eV for **1k**. -0.35 eV for **1a** and -0.76 eV for **1h**),[21] consistent with the increasing ease of an aryl bromide towards single electron reduction.[22] 9-Bromoanthracene (**1l**) showed fast reduction rate of 4 h due to the reduced LUMO energy (-1.93 eV for **1m**)[21] through extended conjugation. Rate enhancement by *ortho* methoxy group substituent was achieved from **1a**, **1e**, **1f** and **1g**, which can be explained by the stabilization of the corresponding σ radical anion[23] through inductive effect. Little steric effect was observed in the reduction of hindered substrates **1g**, **1i** and **1l** taking 4, 10 and 4 h to complete, respectively. Thus, an outer sphere electron transfer mechanism is likely to operate from [Co^{II}(tbp)(OH)]$^-$ complexes to an aryl bromide. The inner sphere reduction process of halogen atom transfer (Pathway b, Scheme 2) is less likely to operate as the sterically hindered aryl bromides (**1g**, **1i** and **1l**) still yield high product yields.[24]

Scheme 3 depicts a general catalytic cycle for the hydrodebromination process. Co^{II}(tbp) coordinates with OH$^-$ in strongly basic conditions to afford [Co^{II}(tbp)(OH)]$^-$ complexes, which subsequently transfer one electron to an aryl bromide to generate an aryl bromide radical anion. The radical anion undergoes fast carbon bromide bond cleavage to generate an aryl radical and a bromide anion. In ethanol solvent, the aryl radical formed can directly abstract a hydrogen atom from EtOH to afford the corresponding arene as the hydrogenation product. On the other hand, Co(tbp)aryl intermediate can further be hydrolyzed to generate the corresponding arene and Co^{III}(tbp)OH in basic conditions as reported in our previous work.[14] Co^{III}(tbp)OH then undergoes reductive dimerization to regenerate Co^{II}(tbp) and H_2O_2, thus completing the catalytic cycle.

Scheme 3 Catalytic Cycle for Co^{II}(tbp) Catalyzed Hydrodebromination



4. Conclusion

In conclusion, the Co^{II}(tbp) catalyzed hydrodebromination of aryl bromides using EtOH as the hydrogen source was achieved with high yields. Mechanistic investigation shows the single electron transfer is the most plausible pathway for aryl carbon bromine bond cleavage.

5. Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane was distilled from anhydrous calcium chloride. Benzene was distilled over sodium under nitrogen. All reactions were protected from light by wrapping with alumina foils. The reaction in Teflon screw capped pressure tubes were heated in heat blocks on heaters, monitored by TLC and GC-MS. Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates. H_2(tbp)[25] and Co(tbp)[26] have been characterized and were prepared according to the literature process. Silica gel (Merck, 70-230 and 230-400 mesh) was used in column chromatography to isolate. Neutral alumina (Merck, 90 active neutral, 70-230 mesh)/H_2O (~10:1 v/v) was used in column chromatography to isolate.

^{1}H NMR spectra was recorded on a Bruker AV-400 instrument at 400 MHz. Chemical shifts were referenced with the residual solvent protons in $CDCl_3$ (δ 7.26 ppm), C_6D_6 (δ 7.15 ppm). Chemical shifts (δ) are reported as parts per million (ppm) in δ scale downfield from TMS. Coupling constants (J) are reported in Hertz (Hz). High-resolution mass spectrometry (HRMS) was performed on a Bruker SolariX 9.4 Tesla FTICR MS instrument in electrospray ionization (ESI) mode using MeOH/CH_2Cl_2 (1/1) as the solvent. GC-MS analyses were conducted on a GCMS-QP2010 Plus system using an Rtx-5MS column (30 m × 0.25 mm). Details of the GC program are as follows. The column oven temperature and injection temperature were 100 and 250 °C. Helium was used as the carrier gas. The flow control mode was chosen as linear velocity (36.3 cm s^{-1}) with a pressure of 68.8 kPa. The total flow, column flow, and purge flow were 13.5, 0.95, and 3.0 mL min^{-1}, respectively. Split mode injection with a split ratio of 10.0 was applied. After injection, the column oven temperature was kept at 100 °C for 2 min and was then elevated at a rate of 30 °C min^{-1} for 5 min until 250 °C. The temperature of 250 °C was kept for 4 min. The retention time and mass spectrum of organic products obtained were identical with those of commercially available authentic samples.

5.1. Preparation of H_2(tbp).

H_2(tbp) was prepared according to literature method.[25] Pyrrole (4.2 mL, 0.061 mol) and pentanal (3.5 mL, 0.033 mol) were added to 300 mL of propionic acid containing 12 mL of H_2O and 1 mL of pyridine at 100-105 °C and reflux for 30 min. Another 1.8 mL of pentanal (0.017 mol) was added and refluxed for another 2 h. Chloroform (300 mL) was added to the cooled reaction mixture, and the reaction mixture was washed with water (300 mL × 3), 50 mM NaOH (300 mL × 3) and water (300 mL × 3) to remove propionic acid. The chloroform solution was evaporated to dryness. The dark residue was recrystallized from DCM and MeOH and washed with MeOH repeatedly to give fine purple crystal as H_2(tbp) (291 mg, 0.545 mmol) in 4% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ -2.63 (s, 2 H), 1.14 (t, ^2J = 5.9 Hz, 12 H), 1.83 (m, 8 H), 2.51 (m, 8 H), 4.95 (t, ^2J = 6.5 Hz, 8 H), 9.47 (s, 8 H).

5.2. Preparation of Co(tbp).

Co(tbp) was prepared according to literature method.[26] H_2(tbp) (150 mg, 0.28 mmol), Co(OAc)$_2$·4H_2O (300.1 mg, 1.2 mmol) was added to 20 mL DMF and heated to reflux for 3 h. 60 mL water was added to the cooled reaction mixture and filtrated to get the brown solid as product. The product was further recrystallized from MeOH and DCM to get Co(tbp) (140 mg, 0.24 mmol) in 84% yield as purple solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.93 (brs, 12 H), 3.47 (brs, 8 H), 6.69 (brs, 8 H), 12.65 (brs, 8 H), 15.93 (brs, 8 H).

5.3. Catalytic Hydrodebromination of Aryl Bromides at Various Reaction Conditions

5.3.1. Porphyrin Ligand Effect

With Co(tbp). 4-Bromoanisole (**1a**) (9 µL, 0.072 mmol), Co(tbp) (8.3 mg, 0.014 mmol) and KOH (155.1 mg, 2.8 mmol) were added in ^{i}PrOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 °C for 3 h. 100% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

With Co(tap). 4-Bromoanisole (**1a**) (9 µL, 0.072 mmol), Co(tap) (11.3 mg, 0.014 mmol) and KOH (154.5 mg, 0.11 moL) were added in ^{i}PrOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 °C for 6 h. 80% yield of anisole (**2a**) and 20% of recovered 4-bromoanisole (**1a**) were detected by GC-MS analysis using decalin as internal standard.

With Co(ttp). 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(ttp) (10.3 mg, 0.014 mmol) and KOH (157.5 mg, 0.11 moL) were added in ^{i}PrOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 6 h. 17% yield of anisole (**2a**) and 80% of recovered 4-bromoanisole (**1a**) were detected by GC-MS analysis using decalin as internal standard.

5.3.2. Solvent Effect

With MeOH. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (8.4 mg, 0.014 mmol) and KOH (153.7 mg, 2.7 mmol) were added in MeOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 72 h. 69% yield of anisole (**2a**) and 5% of recovered 4-bromoanisole (**1a**) were detected by GC-MS analysis using decalin as internal standard.

With EtOH. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (8.3 mg, 0.014 mmol) and KOH (156 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 6 h. 100% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

5.3.3. Catalyst Loading Effect

With 0 mol%. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol) and KOH (154 mg, 2.7 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 24 h. 8% yield of anisole (**2a**) and 80% of recovered 4-bromoanisole (**1a**) were detected by GC-MS analysis using decalin as internal standard.

With 2.5 mol%. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (1.1 mg, 0.0018 mmol) and KOH (160 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 24 h. 94% yield of anisole (**2a**) and 5% of recovered 4-bromoanisole (**1a**) were detected by GC-MS analysis using decalin as internal standard.

With 5 mol%. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (156.7mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 8 h. 100% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

With 10 mol%. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (4.2 mg, 0.007 mmol) and KOH (157.9mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 6 h. 98% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

5.3.4. KOH Loading Effect

Without base. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol) and Co(tbp) (2.1 mg, 0.0035 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 24 h. 0% yield of anisole (**2a**) and 100% of recovered 4-bromoanisole (**1a**) were detected by GC-MS analysis using decalin as internal standard.

With 20 equiv of base. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (80.9 mg, 1.4 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 24 h. 68% yield of anisole (**2a**) and 30% of recovered 4-bromoanisole (**1a**) were detected by GC-MS analysis using decalin as internal standard.

With 30 equiv of base. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (120.1 mg, 2.1 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 16 h. 98% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

With 50 equiv of base. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (199.8 mg, 3.6 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 6 h. 96% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

5.3.5. Temperature Effect

At 120 ˚C. 4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (160 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 120 °C for 25 h. 21% yield of anisole (**2a**) and 65% of recovered 4-bromoanisole (**1a**) were detected by GC-MS analysis using decalin as internal standard.

5.3.6. Atmosphere Effect

4-Bromoanisole (**1a**) (9 μL, 0.072 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (159.4 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was heated to 150 °C for 10 h. 96% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

5.4. Substrate Scope

4-Chloroanisole. 4-Chloroanisole (**1b**) (9 μL, 0.073 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (160 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 24 h. 5% yield of anisole (**2a**) and 80% of recovered 4-chloroanisole (**1b**) were detected by GC-MS analysis using decalin as internal standard.

4-Iodoanisole. 4-Iodoanisole (**1c**) (16.7 mg, 0.071 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (158.7 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 2 h. 92% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

2-Bromoanisole. 2-Bromoanisole (**1e**) (9 μL, 0.072 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (160.0 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 4 h. 96% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

3-Bromoanisole. 3-Bromoanisole (**1d**) (9 μL, 0.071 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (157.2 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 8 h. 90% yield of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard.

1-Bromo-2,5-dimethoxybenzene. 1-Bromo-2,5-dimethoxybenzene (**1f**) (11 μL, 0.073 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (161.8 mg, 2.9 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 2 h. 100% yield of 1,4-dimethoxybenzene was detected by GC-MS analysis using decalin as internal standard.

Bromo-2,4,6-trimethoxybenzene. 1-Bromo-2,4,6-trimethoxybenzene (**1g**) (17.6 mg, 0.071 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (157.5 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N$_2$, and heated to 150 °C for 4 h.

99% yield of 1,3,5-trimethoxybenzene was detected by GC-MS analysis using decalin as internal standard.

1-Bromo-4-chlorobenzene. 1-Bromo-4-chlorobenzene (**1h**) (13.7 mg, 0.071 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (156.2 mg, 2.78 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 6 h. 100% yield of chlorobenzene was detected by GC-MS analysis using decalin as internal standard.

1-Bromo-2,4,6-triisopropylbenzene. 1-Bromo-2,4,6-triisopropylbenzene (**1i**) (36 μL, 0.142 mmol), Co(tbp) (4.2 mg, 0.007 mmol) and KOH (319.5 mg, 5.7 mmol) were added in EtOH (2.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 10 h. 100% yield of 1,3,5-triisopropylbenzene was detected by GC-MS analysis using decalin as internal standard. The reaction mixture was purified with silica gel column chromatography using hexane as eluent to get the first fast moving fraction as 1,3,5-triisopropylbenzene (27.4 mg, 0.13 mmol) in 94% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (d, 18H, ^{2}J = 6.9 Hz), 2.85-2.95 (m, 3 H), 6.94 (s, 3 H).

9-Bromoanthracene. 9-Bromoanthracene (**1l**) (35.4 mg, 0.14 mmol), Co(tbp) (4.1 mg, 0.007 mmol) and KOH (316.3 mg, 5.6 mmol) were added in EtOH (2.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 4 h. The reaction mixture was purified with silica gel column chromatography using hexane as eluent to get the first fast moving fraction as product of anthracene (18.8 mg, 0.11 mmol) in 77% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.49 (m, 4 H), 8.00-8.03 (m, 4 H), 8.44 (s, 2 H).

4-Bromobiphenyl. 4-Bromobiphenyl (**1j**) (32.7 mg, 0.14 mmol), Co(tbp) (4.1 mg, 0.007 mmol) and KOH (318.5 mg, 5.7 mmol) were added in EtOH (2.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 12 h. 98% yield of biphenyl was detected by GC-MS analysis using decalin as internal standard. The reaction mixture was purified with silica gel column chromatography using hexane as eluent to get the first fast moving fraction as biphenyl (18.7 mg, 0.12 mmol) in 87% yield.

4-Bromo-(N, N-dimethyl)aminoanisole. 4-Bromo-(*N*, *N*-dimethyl)aminoanisole (**1k**) (14.3 mg, 0.072 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (156.8 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 24 h. 79% yield of (*N*, *N*-dimethyl)aminoanisole and 20% of recovered 4-Bromo-(*N*, *N*-dimethyl)aminoanisole (**1k**) were detected by GC-MS analysis using decalin as internal standard.

4-Bromo-benzylphenyl ether. 4-Bromo-benzylphenyl ether (**1m**) (37.7 mg, 0.143 mmol), Co(tbp) (4.2 mg, 0.007 mmol) and KOH (312 mg, 5.56 mmol) were added in EtOH (2.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 17 h. The reaction mixture was neutralized with HCl (3 M) before GC-MS analysis. 45% yield of benzyl phenyl ether, 50% of toluene and 50% of 4-bromophenol were detected by GC-MS analysis using decalin as internal standard.

4-Bromobenzonitrile. 4-Bromobenzonitrile (**1o**) (12.6 mg, 0.07 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (161.6 mg, 2.9 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 1 h. The reaction mixture was diluted with water and extracted with dichloromethane for 3 times to get rid of Co(tbp). The water layer was acidified with HCl (3M) and extracted with Et_2O for 3 times. The organic layer was combined and dried with rotary evaporator. 86% 4-bromobenzoic acid and 12% of benzoic acid were detected by ^{1}H NMR using 10 μL $CHCl_2CHCl_2$ as internal standard.

4-Bromobenzaldehyde. 4-Bromobenzaldehyde (**1n**) (14.1 mg, 0.07 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (156.3 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 7 h. 32% of α-methylbenzyl alcohol and 12% of 4-bromo-α-methylbenzyl alcohol were detected by ^{1}H NMR using 10 μL $CHCl_2CHCl_2$ as internal standard.

1-tert-Butyl-4-chlorobenzene. 1-*tert*-Butyl-4-chlorobenzene (**1p**) (12 μL, 0.07 mmol), Co(tbp) (2.2 mg, 0.0037 mmol) and KOH (155.7 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 24 h. 3% of *tert*-butylbenzene and 95% of recovered 1-*tert*-Butyl-4-chlorobenzene were detected by GC-MS analysis using decalin as internal standard.

1-Chloro-4-iodobenzene. 1-Chloro-4-iodobenzene (**1q**) (16.9 mg, 0.07 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (153.3 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 1 h. 100% of chlorobenzene was detected by GC-MS analysis using decalin as internal standard.

4,4'-Diiodobiphenyl. 4,4'-Diiodobiphenyl (**1r**) (28.5 mg, 0.07 mmol), Co(tbp) (2.2 mg, 0.0037 mmol) and KOH (157.0 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 2 h. The reaction mixture was purified with silica gel column chromatography using hexane as eluent to get the first fast moving fraction as biphenyl (7.8 mg, 0.05 mmol) in 72% yield.

2-Bromopyridine. 2-Bromopyridine (**1s**) (7 μL, 0.073 mmol), Co(tbp) (2.1 mg, 0.0035 mmol) and KOH (150.3 mg, 2.7 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 1 h. Complex mixture was achieved after reaction with 2-bromopyridine consumed completely.

2-Bromo-5-methylpyridine. 2-Bromo-5-methylpyridine (**1t**) (8 μL, 0.07 mmol), Co(tbp) (2.2 mg, 0.0037 mmol) and KOH (154.7 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 1 h. 87% of 2-methylthiophene was detected by GC-MS analysis using decalin as internal standard.

5.5. Mechanistic Investigation

Independent Synthesis of Co(tbp)Ph(p-OMe). Co(tbp)Ph(*p*-OMe) was prepared according to literature method.[14] Co(tbp) (9.0 mg, 0.015 mmol), 4-bromoanisole (175 μL, 1.4 mmol), KOH (8.9 mg, 0.15 mmol) and ^{t}BuOH (65 μL, 0.70 mmol) were added in benzene (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^{o}C for 4 h. Benzene solvent was removed with evaporation. The residue was purified with column chromatography on silica gel and using hexane/DCM (v:v/3:1) as eluent to get the second red fraction as product of Co(tbp)Ph(*p*-OMe) (12.5 mg, 0.018 mmol) in 56% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.14 (d, ^{2}J = 8.9 Hz, 2 H), 0.86 (t, ^{2}J = 7.3Hz, 12 H), 1.24 (m, 8 H). 2.16-2.23 (m, 8 H), 2.74 (s, 3 H), 4.31 (d, ^{2}J = 8.9 Hz, 2 H), 4.58 (t, ^{2}J = 7.6Hz, 8 H), 9.37 (s, 8 H). ^{13}C NMR ($CDCl_3$, 176 MHz) δ 14.16, 23.01, 34.23, 38.90, 54.07, 108.65, 119.63, 130.35, 132.35, 143.91, 154.96. HRMS (ESI-MS): calcd for $C_{43}H_{51}CoN_4O$ $[M]^+$ m/z 698.3389; found m/z 698.3392.

Trap experiment. 4-Bromobenzene (**1a**) (9 μL, 0.072 mmol), Co(tbp) (2.1 mg, 0.035 mmol) and KOH (161 mg, 2.9 mmol) were added in benzene (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^oC for 24 h. 3% of anisole (**2a**) was detected by GC-MS analysis using decalin as internal standard. 35% of 4-methoxybiphenyl and 35% of recovered 4-bromoanisole (**1a**) were detected by ^1H NMR analysis using $CHCl_2CHCl_2$ as internal standard.

Reaction between Co(tbp)Ph(p-OMe) and EtOH in neutral conditions. Co(tbp)Ph(*p*-OMe) (2.5 mg, 0.0035 mmol) was added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^oC for 8 h. Both TLC and GC-MS analysis showed no reaction occurred.

Reaction between Co(tbp)Ph(p-OMe) and EtOH in basic conditions. Co(tbp)Ph(*p*-OMe) (2.5 mg, 0.0035 mmol), KOH (154.9 mg, 2.8 mmol) were added in EtOH (1.0 mL). The mixture was degassed for three freeze-pump-thaw cycles, purged with N_2, and heated to 150 ^oC for 1.5 h. 100% of anisole (**2a**) was detected by GC-MS analysis with quantitative formation of Co(tbp).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at

Reference

1. (a) V.V. Grushin, H. Alper, Chem. Rev. 94 (1994) 1047; (b) A. Ramanathan, L.S. Jimenez, Synthesis 2010 (2010) 217.
2. F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 102 (2002) 4009.
3. D. Wang, D. Astruc, Chem. Rev. 115 (2015) 6621.
4. (a) C. Cheng, J. Sun, L. Xing, J. Xu, X. Wang, Y. Hu, J. Org. Chem. 74 (2009) 5671; (b) M.L. Buil, M.A. Esteruelas, S. Niembro, M. Oliván, L. Orzechowski, C. Pelayo, A. Vallribera, Organometallics 29 (2010) 4375; (c) B. Sahoo, A.-E. Surkus, M.-M. Pohl, J. Radnik, M. Schneider, S. Bachmann, M. Scalone, K. Junge, M. Beller, Angew. Chem. Int. Ed. 56 (2017) 11242.
5. (a) G. Chelucci, G.A. Pinna, G. Pinna, Eur. J. Org. Chem. 2014 (2014) 3802-3807; (b) D.Y. Ong, C. Tejo, K. Xu, H. Hirao, S. Chiba, Angew. Chem. Int. Ed. 56 (2017) 1.
6. (a) G. Chelucci, S. Baldino, A. Ruiu, J. Org. Chem. 77 (2012) 9921; (b) K. Inoue, A. Sawada, I. Shibata, A. Baba, J. Am. Chem. Soc. 124 (2002) 906.
7. (a) G.L. Larson, J.L. Fry, in: Org. React., John Wiley & Sons, Inc.: 2008; (b) A. Bhattacharjya, P. Klumphu, B.H. Lipshutz, Org. Lett. 17 (2015) 1122; (c) C. Chatgilialoglu, C. Ferreri, Y. Landais, V.I. Timokhin, Chem. Rev. 118 (2018) 6516.
8. M. Katsukiyo, I. Yoshifumi, N. Kyoko, F. Keigo, O. Koichiro, U. Kiitiro, Bull. Chem. Soc. Jpn. 62 (1989) 143.
9. (a) Y. Ukisu, T. Miyadera, J. Mol. Catal. A: Chem. 125 (1997) 135; (b) T. You, Z. Wang, J. Chen, Y. Xia, J. Org. Chem. 82 (2017) 1340; (c) V.H. Mai, G.I. Nikonov, ACS Catal. 6 (2016) 7956; (d) M.C. Haibach, B.M. Stoltz, R.H. Grubbs, Angew. Chem. Int. Ed. 56 (2017) 15123; (5) H. Sakamoto, J. Imai, Y. Shiraishi, S. Tanaka, S. Ichikawa, T. Hirai, ACS Catal. 7 (2017) 5194.
10. (a) T. Zweifel, J.-V. Naubron, T. Büttner, T. Ott, H. Grützmacher, Angew. Chem. Int. Ed. 47 (2008) 3245; (b) W.-P. Liu, M.-L. Yuan, X.-H. Yang, K. Li, J.-H. Xie, Q.-L. Zhou, Chem. Comm. 51 (2015) 6123; (c) Y. Wang, Z. Huang, X. Leng, H. Zhu, G. Liu, Z. Huang, J. Am. Chem. Soc. 140 (2018) 4417.
11. Y.R. Luo, in: Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Boca Raton, 2002.
12. (a) R.H. Crabtree, A.J. Pearman, J. Organomet. Chem. 157 (1978) 335; (b) S.R. Klei, J.T. Golden, T.D. Tilley, R.G. Bergman, J. Am. Chem. Soc. 124 (2002) 2092. (c) C.M. Yung, M.B. Skaddan, R.G. Bergman, J. Am. Chem. Soc. 126 (2004) 13033; (d) H. Maki, S. Yasutomo, Y. Makoto, N. Kyoko, Angew. Chem. Int. Ed. 51 (2012) 6956.
13. K.S. Chan, C.R. Liu, K.L.Wong, Tetrahedron Lett. 56 (2015) 2728.
14. C.R. Liu, Y.Y. Qian, K.S. Chan, Dalton Trans 43 (2014) 7771.
15. (a) J. Halpern, J.P. Maher, J. Am. Chem. Soc. 87 (1965) 5361; (b) D. Zhu, I. Korobkov, P.H.M. Budzelaar, Organometallics 31 (2012) 3958; (c) V. Lyaskovskyy, B. de Bruin, ACS Catal. 2 (2012) 270.
16. K.L. Wong, C. Chen, K.S. Chan, Organometallics 35 (2016) 1847.
17. (a) C.W. Cheung, K.S. Chan, Organometallics 30 (2011) 1768; (b) C.W. Cheung, K.S. Chan, Organometallics 30 (2011) 4269; (c) C.W. Cheung, K.S. Chan, Organometallics 30 (2011) 4999; (d) Y.Y. Qian, K.S. Chan, Organometallics 31 (2012) 5452; (e) B.Z. Li, Y.Y. Qian, J. Liu, K.S. Chan, Organometallics 33 (2014) 7059; (f) Y.Y. Qian, M.H. Lee, W. Yang, K.S. Chan, J. Organomet. Chem. 791 (2015) 82; (g) W. Yang, H.P. Zuo, W.Y. Lai, S.Y. Feng, Y.S. Pang, K.E. Hung, C.Y. Yu, Y.F. Lau, H.Y. Tsoi, K.S. Chan, Organometallics 34 (2015) 4051; (h) H. Zuo, Z. Liu, W. Yang, Z. Zhou, K.S. Chan, Dalton Trans. 44 (2015) 20618.
18. C.T. To, K.S. Choi, K.S. Chan, J. Am. Chem. Soc. 134 (2012) 11388.
19. (a) D.T. Sawyer, J.L. Roberts, Acc. Chem. Res. 21 (1988) 469; (b) C. Costentin, M. Robert, J.-M. Savéant, J. Am. Chem. Soc. 126 (2004) 16051; (c) P. K. S. Tsang, P. Cofre, D.T. Sawyer, Inorg. Chem. 26 (1987) 3604.
20. K.M. Kadish, K.M. Smith, R. Guilard, in: The Porphyrin Handbook: Database of Redox Potentials and Binding Constants. Vol. 9. Elsevier, 2000.
21. Calculated at B3LYP/6-311G* level with DFT on Spartan 16.
22. E. Cahard, F. Schoenebeck, J. Garnier, S.P.Y. Cutulic, S. Zhou, J.A. Murphy, Angew. Chem. Int. Ed. 51 (2012) 3673.
23. (a) R.A. Rossi, J. Chem. Educ. 59 (1982) 310; (b) N. Kimura, S. Takamuku, J. Am. Chem. Soc. 117 (1995) 8023; (c) J.-M. Savéant, in: *Adv. Phys. Org. Chem.* Academic Press, 1990.
24. (a) C.P. Andrieux, L. Gelis, J.M. Saveant, J. Am. Chem. Soc. 112 (1990) 786; (b) R.S. Miller, J.M. Sealy, M. Shabangi, M.L. Kuhlman, J.R. Fuchs, R.A. Flowers, J. Am. Chem. Soc. 122 (2000) 7718.
25. S. Neya, N. Funasaki, J. Heterocycl. Chem. 34 (1997) 689.
26. K. Maruyama, H. Tamiaki, J. Org. Chem. 51 (1986) 602.