Dalton Transactions

PAPER

Cite this: *Dalton Trans.*, 2014, **43**, 7771

Received 16th January 2014,

Accepted 3rd March 2014

DOI: 10.1039/c4dt00155a

www.rsc.org/dalton

Base-promoted aryl-bromine bond cleavage with cobalt(II) porphyrins *via* a halogen atom transfer mechanism[†]

Chun Ran Liu, Ying Ying Qian and Kin Shing Chan*

Aryl-bromine bonds are successfully cleaved by cobalt(II) porphyrins in basic media to give Co(por)Ar (por = porphyrin) in good yields. Mechanistic studies suggested that the aryl-bromine bond is cleaved through a halogen atom transfer mechanism, which is different from the aryl-halogen bond cleavage mechanism with other group 9 metalloporphyrins.

1. Introduction

Aryl halides are commonly employed starting materials in transition metal-catalyzed cross-coupling reactions for the construction of carbon-carbon bonds.1 Aryl halides are used in Suzuki,² Stille,³ Negishi,⁴ Kumada,⁵ and Hiyama⁶ cross-coupling reactions to couple with aryl boronic acids, aryl tin complexes, aryl zinc complexes, aryl magnesium halides and aryl silanes to give biaryls. In these reactions, expensive palladium catalysts are usually employed. Recently, first row transition metals have been used as catalysts for cross-coupling reactions as they are cheaper and less toxic. For example, Fe,⁷ Ni,⁸ Cu,⁹ and Co¹⁰ have been used as catalysts for cross-coupling reactions. Detailed understanding of the aryl-halogen bond cleavage by first row transition metals are lacking. At the same time, first row transition metal-alkyl/aryl intermediates are difficult to isolate due to the weak metal-carbon bond.¹¹ This leads to the difficulty in conducting mechanistic studies.

Since the Ar–X bond cleavage has been reported to be the rate determining step in cross-coupling reaction, it is important to gain further understanding of the Ar–X bond cleavage by transition metals, especially first row transition metals.^{12,13} There are mainly four types of mechanisms for the cleavage of an aryl halogen bond (Ar–X): (1) oxidative addition, (2) nucleophilic aromatic substitution, (3) radical *ipso*-substitution, and (4) halogen atom transfer (Scheme 1).

Oxidative addition is the most reported mechanism for an aryl halogen bond (Ar-X) cleavage with a transition metal



Scheme 1 Four types of aryl halogen bond cleavage by transition metal complexes.

complex. Oxidative addition usually takes place with electronrich, low-valent middle-group transition metal complexes. For example, oxidative addition of PhX (X = I, Br, Cl) to the palladium(0) complex with the bidentate phosphine ligand (PP) gives the palladium(π) phenyl halo complex (PP)Pd(Ph) X.¹⁴ 2-Tolyl-bromobenzene has been reported to react with the nickel diaminocarbene complex (Ni⁰(timy)₂) through oxidative addition to form Ni^{II}(timy)(*o*-toyl)Br in 71% yield.¹⁵

Nucleophilic aromatic substitution usually occurs between an electron rich, low valent transition metal complex and an electron-deficient aryl halide. $[Cp*Rh^{I}(PMe_3)H]^-$, which is generated from the deprotonation of $Cp*Rh^{III}(PMe_3)H_2$ by pyridine, undergoes nucleophilic aromatic substitution with Ar^F-F to give $Cp*Rh^{III}(PMe_3)(Ar^F)H$ and pyridinium fluoride.¹⁶

A radical *ipso*-substitution mechanism for Ar–X bond cleavage with transition metals was first reported by the Chan group.¹⁷ Both iridium and rhodium porphyrin complexes cleave the Ar–X bond (X = I, Br) to give $Ir^{III}(ttp)Ar$ (ttp = 5,10,15,20-tetratolylporphyrin) and Rh^{III}(ttp)Ar in good to high yields. Under basic conditions, $Ir^{III}(ttp)(CO)CI$ and Rh^{III}(ttp)CI

View Article Online

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China. E-mail: ksc@cuhk.edu.hk; Fax: (+852) 3943-5057; Tel: (+852) 2609-6376

[†]Electronic supplementary information (ESI) available: Table, figure, and CIF file giving crystallographic data for Co(ttp)(4-methoxyphenyl) and ¹H and ¹³C NMR spectra. CCDC: 981392. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00155a

undergo ligand substitution with hydroxide ions to give $Ir^{III}(ttp)OH$ and $Rh^{III}(ttp)OH$, which then form $Ir_2{}^{II}(ttp)_2$ and $Rh_2{}^{II}(ttp)_2$, respectively, through reductive dimerization.¹⁸ $Ir^{II}(ttp)$ and $Rh^{II}(ttp)$, which exist in equilibria with the metalmetal bonded dimers, attack the *ipso*-carbon of ArX to give the $M^{III}(por)$ -cyclohexadienyl (M = Ir, Rh) radical intermediate. The radical intermediates then eliminate a halogen atom to give $Ir^{III}(ttp)Ar$ and $Rh^{III}(ttp)Ar$.

Halogen atom transfer commonly occurs between ArX (X = I, Br, Cl) and metalloradicals. $LCo^{0}(N_{2})$, generated from $LCo^{I}CH_{2}SiMe_{3}$ (L = 2,6-bis[2,6-dimethylphenyliminoethyl]-pydidine) and H₂, undergoes binuclear oxidative addition with ArCl to yield $LCo^{I}Ar$ and $LCo^{I}Cl$ through the halogen atom transfer mechanism.¹⁹ $[Co^{II}(CN)_{5}]^{3-}$ has also been proposed to abstract an iodine atom from the fairly reactive 2-iodopyridine to give $[ICo^{II}(CN)_{5}]^{3-}$.²⁰ Another $[Co^{II}(CN)_{5}]^{3-}$ then combines with the released pyridyl radical to generate [2-pyridyl- $Co^{III}(CN)_{5}]^{3-}$.

The Chan group has reported that iridium and rhodium porphyrins react with ArX (X = I, Br, Cl) to give iridium and rhodium porphyrin aryls, respectively, through a radical *ipso*-substitution mechanism.¹⁷ However, the halogen atom transfer mechanism has been reported for most examples of the Ar–X bond cleavage by cobalt complexes.^{19,20} The effects of metal in the Ar–X bond cleavage are thus interesting and intriguing, and we therefore examined the reaction scope as well as the mechanistic features.

2. Results and discussion

2.1 Optimization of reaction conditions

Initially, $Co^{II}(ttp)$ did not react with PhBr in benzene at 150 °C for 2 days with 92% yield of $Co^{II}(ttp)$ recovered (Table 1, entry 1). Based on our previous success of base-promoted Ar–X cleavage reaction, when KOH was added, $Co^{II}(ttp)$ reacted with

Table 1	Base-promoted Ar–Br bond cleavage with Co ^{II}	ttp)
Table T	base-promoted Ar-br bond cleavage with Co	(up)

Co ^l 1	^I (ttp) + 1 I a	PhBr ⁻ 00 equiv 2a	n equiv m equiv ^t N ₂ , dark, te benze	KOH BuOH mp, time ene	Co(ttp)Ph 3a
Entry	n (KOH)	m (^t BuC	DH) Temp/	°C Time/h	Yield 3a/%
1	_	_	150	48	0
2	10	_	150	48	73
3	10	30	150	6	77
4	20	30	150	8	75
5	50	30	150	18	69
6	10	10	150	10	73
7^a	10	10	150	96	5
8	10	50	150	3	79
9	10	100	150	1.5	67
10	10	50	120	48	73
11	10	50	200	1.5	67

^a The reaction was carried out in THF solvent.

 Table 2
 Porphyrin electronic effects on the Ar-Br bond cleavage with Co^{II}(por)

Co ^{ll} (por) + 1	PhBr 100 equiv 2a	10 equiv KOH 50 equiv ^t BuOH N ₂ , dark, 150 °C, time benzene	Co(por)Ph 3
Entry	por	Time/h	Yield 3/%
1 2 3	tap (1b) ttp (1a) tpp (1c)	1.5 3 2	69 (3b) 79 (3a) 55 (3c)
4	$t_{4-Cl}pp(\mathbf{1d})$) 5	73 (3d)

tpp = 5,10,15,20-tetraphenyl
porphyrin; t_4-Clpp = 5,10,15,20-tetra-(p-chlorophenyl)porphyrin.

PhBr to give 73% yield of Co^{III}(ttp)Ph (Table 1, entry 2). ^tBuOH was then added to increase the solubility of KOH in benzene so as to increase the reaction rate. When 30 equivalents of ^tBuOH were added, the reaction time was significantly shortened to 6 h with similar yield of Co^{III}(ttp)Ph obtained (Table 1, entries 2 and 3). Higher base loading slowed down the reaction significantly (Table 1, entries 3-5). Optimization on increasing ^tBuOH loading to 50 equivalents reduced the reaction times from 10 h to 3 h (Table 1, entries 3, 6 and 8). Further increasing to 100 equivalents of ^tBuOH reduced the reaction time to 1.5 h, however, the yield of Co^{III}(ttp)Ph decreased from 79% to 67% (Table 2, entries 8 and 9). The temperature effect was then examined. At 120 °C, the reaction was very slow and required two days to complete (Table 1, entry 10). At 200 °C, although the reaction only required 1.5 h, the yield of Co^{III}(ttp)Ph was lower (Table 1, entry 11). Reaction in THF resulted in only 5% yield of Co(ttp)Ph after 4 days, which indicates that THF may coordinate to Co^{II}(ttp) and block the vacant sites (Table 1, entry 7). Therefore, 10 equivalents of KOH and 50 equivalents of ^tBuOH were used for the Ar-Br bond cleavage with Co^{II}(ttp) at 150 °C in benzene for further studies.

Various cobalt(π) porphyrin complexes were then used to study the electronic effects of porphyrin ligand on the Ar–Br bond cleavage reactions. Cobalt(π) porphyrins with both the electron rich and electron deficient substituents cleaved the Ar–Br bond successfully (Table 2). Although the more electron rich Co^{II}(tap) (tap = 5,10,15,20-tetra-4-anisylporphyrin) gave the fastest reaction rate, Co^{II}(ttp) gave the highest product yield (Table 2, entries 1 and 2). Therefore, Co^{II}(ttp) was used for further studies.

2.2 Substrate scopes

ArBr bearing both electron donating and withdrawing functional groups reacted with $\text{Co}^{\text{II}}(\text{ttp})$ smoothly to give moderate to good yields of $\text{Co}^{\text{III}}(\text{ttp})$ Ar within 1 day (Table 3). Functional groups such as NO₂ and C(O)Me were compatible under the reaction conditions (Table 3, entries 7 and 8).

These base-promoted Ar–Br cleavage reactions of ArBr with Co^{II}(por) provide a more convenient method for the synthesis

Table 3 Substrate scopes for the Ar–Br bond cleavage with Co^{II}(ttp)

Co ^{ll} (ttp)	+ Br	10 equiv KOH <u>50 equiv ¹BuOH</u> N ₂ , dark, 150 °C, time benzene	III(ttp)———————————————————————————————————
	100 equiv	201120110	
1a	2		3
Entry	FG	Time/h	Yield 3/%
1	OMe (2e)	7	75 (3e)
2	Me (2f)	2.5	89 (3f)
3	t Bu (2g)	24	72 (3g)
4	H (2a)	3	79 (3a)
5	Cl (2h)	2.5	61 (3h)
6	F (2i)	3	74 (3i)
7	$NO_2(2j)$	18	79 (3j)
8	C(O)Me (21	k) 3	57 (3k)



Fig. 1 ORTEP presentation of Co(ttp)(4-methoxyphenyl) (**3e**) (30% probability displacement ellipsoids). Hydrogen atoms are omitted for clarity.

of cobalt porphyrin aryls with reasonable rates and yields without using aryllithiums or Grignard reagents in their reactions with cobalt porphyrin halides.²¹

2.3 X-ray crystallographic details

The structure of $\text{Co}^{\text{III}}(\text{ttp})(4$ -methoxyphenyl) (**3e**) was shown in Fig. 1.‡ This complex crystallized in the monoclinic space group $P2_1/c$. It is a five coordinated cobalt complex in a square-pyramidal geometry with the cobalt-carbon bond length of 1.903 Å.

2.4 Mechanistic studies

The Ar–Br bond cleavage by $Co^{II}(por)$ may occur through one of the four possible mechanisms mentioned in Scheme 1. For the oxidative addition mechanism, the Ar–Br bond is oxidatively added to the cobalt(II) center and gives an aryl- $Co^{IV}(por)$ – Br intermediate (Scheme 2, pathway I). This intermediate is highly unstable since the *syn*-addition of two bulky substituI. Oxidaitve Addition



II. Nucleophilic Aromatic Substitution

- - - -

Scheme 2 Possible mechanisms for aryl-bromine bond cleavage by Coll(por).

ents to Co^{II}(por) is very sterically hindered due to the planar porphyrin ligand. Moreover, the cobalt(IV) oxidation state is very uncommon and generated as transients in chemical and electrochemical redox processes.²² Therefore, the oxidative addition mechanism is unlikely since it involves the generation of unstable cobalt(IV) porphyrin intermediates.

For the nucleophilic substitution mechanism, the disproportionation of $\text{Co}^{\text{II}}(\text{por})$ to form $\text{Co}^{\text{III}}(\text{por})\text{OH}$ and $\text{Co}^{\text{I}}(\text{por})^{-}$ can occur under basic conditions (Scheme 2, pathway II).²³ However, $\text{Co}^{\text{I}}(\text{por})^{-}$ (p K_{a} of Co(por)H is 10.5 in aqueous methanol), being a salt, is a poor nucleophile and is poorly soluble in benzene.²⁴ Therefore, it does not likely attack the Ar–Br bond.

The electron transfer mechanism is possible from energetic considerations but inconsistent with reactivity patterns. First, electron transfer from $\text{Co}^{\text{II}}(\text{ttp})$ to PhBr to give $\text{Co}^{\text{I}}(\text{ttp})^-$ and PhBr radical anions is uphill by about 1 V,²⁵ in line with the reaction rate at 150 °C. However, both more electron rich and poor FG–C₆H₄–Br (FG = OMe (2e), NO₂ (2j)) react slower than PhBr. The rate determining electron transfer is inconsistent with the substituent electronic effect.²⁶ Second, in polar solvent THF, which facilitates electron transfer, resulted in low yield of Co(ttp)Ar (Table 1, entry 7). Therefore, the electron transfer mechanism is unlikely.

Scheme 3 shows two possible mechanisms for the Ar-Br cleavage with Co^{II}(por). When a radical *ipso*-substitution operates (Scheme 3, pathway IV), Co^{II}(por) first attacks the *ipso*carbon of ArBr to generate Co^{III}(por)-cyclohexadienyl radical intermediate. Then a bromine atom is eliminated to generate Co^{III}(por)Ar. The bromine atom can either combine with another Co^{II}(por) to give Co^{III}(por)Br or attack benzene to give PhBr, which can further react with Co^{II}(por) to give Co^{III}(por)-Ph. Alternately, when the halogen atom transfer operates (Scheme 3, pathway V), Co^{II}(por) abstracts the bromine atom from ArBr to generate Co^{III}(por)Br and an aryl radical. The aryl radical can either combine with another Co^{II}(por) to give Co^{III}(por)Ar (Scheme 3, pathway (i)), or add to benzene solvent to give biaryl (Scheme 3, pathway (ii)). Co^{III}(por)Br further undergoes ligand substitution with KOH to produce Co^{III}(por)-OH (Scheme 3, pathway (iii)), which undergoes reductive elimination to give back Co^{II}(por) and H₂O₂.¹⁸

In order to differentiate pathway IV from pathway V, the substituent electronic effect by the Hammett study is an effective strategy as we have successfully applied in the studies with iridium and rhodium porphyrin chemistry.¹⁷ However,

[‡]Single crystal of Co(ttp)(4-methoxyphenyl) (**3e**) was recrystallised from dichloromethane and methanol. CCDC: 981392.



Scheme 3 Possible radical ipso-substitution and halogen atom transfer mechanism for Ar–Br bond cleavage of ArBr with Co^{ll}(por).

Co(ttp)Ar was not stable under the reaction conditions and exchange of Co(ttp)Ar also occurred (eqn (1) and (2)). Therefore, the Hammett study is not informative in mechanistic studies.



To figure out the reaction mechanism, the organic co-products were thus analyzed. In the reaction of $\text{Co}^{\text{II}}(\text{ttp})$ with 4-bromoanisole, apart from 73% yield of $\text{Co}^{\text{III}}(\text{ttp})$ (4-methoxyphenyl), 54% yield of anisole was detected by GC-MS analysis and 187% yield of 4-methoxylbiphenyl was isolated, which we have been previously reported as a product in the Co(por)catalyzed biaryl synthesis from Ar–Br in benzene (eqn (3)).¹³ Neither bromobenzene nor biphenyl was observed by GC-MS or ¹H NMR analysis. These observations are consistent with the halogen atom transfer mechanism.



However, an aryl radical can also form from the homolysis of $\text{Co}^{\text{III}}(\text{por})\text{Ar}$ if the *ipso*-substitution mechanism occurs. Thus, the control experiment was carried out to see if anisole and 4-methoxylbiphenyl formed from Co(ttp)(4-methoxy) phenyl). The results showed that only 50% of anisole was obtained without any 4-methoxylbiphenyl (eqn (4)). This confirmed that the 4-methoxylbiphenyl is formed from the aryl radical generated from halogen atom transfer. Anisole was probably formed from the hydrolysis of $\text{Co}^{\text{III}}(\text{ttp})(4\text{-methoxyphenyl})$ with ^{*t*}BuOH or residual water in KOH (Scheme 3, pathway iv).²⁷



 $4\text{Co}^{II}(\text{ttp}) + 4\text{ArBr} + 4\text{KOH} \longrightarrow 4\text{Co}^{III}(\text{ttp})\text{Ar} + 4\text{KBr} + 2\text{H}_2\text{O} + \text{O}_2$





From the above findings, the halogen atom transfer mechanism was concluded to be the most probable reaction mechanism (Scheme 4). First, $\text{Co}^{II}(\text{por})$ abstracts the bromine atom from ArBr through halogen atom transfer to give an aryl radical and $\text{Co}^{III}(\text{por})\text{Br}$ (Scheme 4, pathway 1). The aryl radical then combines with another $\text{Co}^{II}(\text{por})$ to form $\text{Co}^{III}(\text{por})\text{Ar}$ (Scheme 4, pathway 2). $\text{Co}^{III}(\text{por})\text{Br}$ undergoes ligand substitution with KOH to give $\text{Co}^{III}(\text{por})\text{OH}$, which undergoes reductive elimination to generate $\text{Co}^{II}(\text{por})$ and H_2O_2 (Scheme 4, pathways 3 and 4).¹⁸ H_2O_2 quickly decomposes to water and oxygen under basic conditions (Scheme 4, pathway 5).²⁸

2.5 Comparison of Ar-X bond cleavage mechanism

It is interesting to find that the mechanism for Ar–Br cleavage by cobalt porphyrins goes through a halogen atom transfer mechanism while that of iridium and rhodium porphyrins operate by the *ipso*-substitution mechanism. For a radical *ipso*substitution mechanism, the cyclohexadienyl radical forms first (Scheme 5, pathway A). For rhodium and iridium porphyrins, the Rh–C and Ir–C bonds are stronger than that of Co–C bond.^{11,29} When the weaker π bond of an aryl halide is broken and forms the M–C (M = Co, Rh, Ir) bond, the rhodium and



iridium intermediates are much more stabilized than the cobalt one.³⁰ On the other hand, in the halogen atom transfer mechanism, the partial formation of a Co–Br bond and partial breaking of an Ar–Br bond in the transition state can decrease the activation barrier of the Ar–Br bond cleavage by cobalt porphyrins (Scheme 5, pathway B). Thus, the strength of M–C bond plays an important role in controlling the Ar–Br bond cleavage mechanism.

3. Conclusions

In conclusion, the base-promoted Ar–Br bond cleavage with Co^{II}(por) has been achieved in basic media to give Co^{III}(por)Ar in moderate to high yields. Mechanistic studies showed that the Ar–Br bond cleavage step follows a halogen atom transfer mechanism.

4. Experimental section

4.1 General procedure

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Benzene and benzene- d_6 were distilled from sodium and were stored in a Teflon-capped tube under nitrogen gas prior to use. Thin layer chromatography was performed on aluminum oxide 150 F254 neutral. All reactions carried out in a Teflon screw capped tube under N2 with the mixture degassed for three freeze-thaw-pump cycles were wrapped with aluminum foil to prevent undesired photochemical reactions. The reaction mixtures in Teflon-screwcapped tubes were heated in heat blocks on heaters. The reactions in sealed NMR tubes were heated in GC-ovens. The crude mixture was dried under high vacuum. The products were further purified by aluminum oxide (Merck, 70-230 mesh, neutral, pre-treated with 10 wt% of water) column chromatography eluting with a solvent mixture of hexane-CH₂Cl₂. Single crystal of 3e for X-ray crystallography was grown from CH₂Cl₂-MeOH via slow evaporation. Unless otherwise specified, the residual benzene proton signal of benzene- d_6 solvent was used as an internal standard to estimate the vield of cobalt porphyrin species by ¹H NMR spectroscopy. Co^{II}(ttp) (1a), $Co^{II}(tap)$ (1b), $Co^{II}(tpp)$ (1c), and $Co^{II}(t_{4-Cl}pp)$ (1d) were prepared according to literature procedures.31

4.2. Experimental instrumentation

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 at 400 MHz). Chemical shifts were referenced with the residual solvent protons in chloroform-*d* (δ = 7.26 ppm) or tetramethylsilane (δ = 0.00 ppm) and benzene-*d*₆ (δ = 7.15 ppm) in ¹H NMR spectra, CDCl₃ (δ = 77.16 ppm) in ¹³C NMR spectra as the internal standards. Chemical shifts (δ) were reported as part per million (ppm) in (δ) scale downfield from TMS. Coupling constants (*J*) were reported in hertz (Hz).

High resolution mass spectra (HRMS) were recorded on a ThermoFinnigan MAT 95 XL mass spectrometer. Fast atom bombardment spectra were recorded with 3-nitrobenzyl alcohol (NBA) as the matrix.

GC/MS analysis conducted on a Shimadzu was GCMS-OP2010 Plus system using an Rtx-5MS column (30 m × 0.25 mm). The details of the GC program are as follows. The column oven temperature and injection temperature are 50.0 °C and 270.0 °C, respectively. Split injection mode was applied. The carrier gas used was helium with primary pressure of 500-900 kPa. Linear velocity was chosen as the flow control mode. The pressure, total flow, column flow, linear velocity, purge flow and split ratio were 53.5 kPa, 24.0 mL min⁻¹, 1.00 mL min⁻¹, 36.3 cm s⁻¹, 3.0 mL min⁻¹ and 20.0, respectively. The column oven temperature was kept at 50 °C for 5 minutes and then elevated at a rate of 20 °C min⁻¹ until 270 °C and the temperature was kept for 4 minutes. The ion source temperature and interface temperature were 230 °C and 270 °C, respectively.

4.3. Optimization of base-promoted Ph–Br bond cleavage by $Co^{II}(por)$

(a) Reaction between $Co^{II}(ttp)$ and PhBr without a base. Co^{II}(ttp) (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 µL, 1.400 mmol) were added to benzene (1.0 mL) and the mixture was degassed for three freeze-pump-thaw cycles in a Teflon screw capped tube and filled with N₂. The reaction was then heated at 150 °C for 2 days. The solvent was then removed under vacuum and the crude product was purified by column chromatography over alumina eluted with CH₂Cl₂-hexane (1:2). No product was obtained.

(b) Reaction between Co^{II}(ttp) and PhBr with KOH. Co^{II}(ttp) (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 µL, 1.400 mmol) and KOH (7.8 mg, 0.140 mmol) were added to benzene (1.0 mL) and the mixture was degassed for three freeze-pump-thaw cycles in a Teflon screw capped tube and filled with N₂. The reaction was then heated at 150 °C for 2 days. The solvent was then removed under vacuum and the crude product was purified by column chromatography over alumina eluted with CH₂Cl₂-hexane (1:2) to give Co^{III}(ttp)Ph (3a, 8.2 mg, 0.010 mmol, 73%). $R_{\rm f} = 0.84$ (CH₂Cl₂-hexane = 1:2). ¹H NMR (400 MHz, CDCl₃): δ 0.27(d, 2H, *o*-Ph), 2.66 (s, 12H, methyl-H), 4.67 (t, 2H, *m*-Ph), 5.26 (t, 1H, *p*-Ph), 7.49 (d, 8H, tolyl-H), 7.93 (s, 8H, tolyl-H), 8.83 (s, 8H, pyrrole-H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 121.4, 122.0, 123.0, 127.7, 132.6, 133.0, 133.7, 137.5, 138.8, 145.5; HRMS (FABMS): calcd for $[C_{54}H_{41}CoN_4]^+([M]^+)$: m/z 804.2658. Found: m/z. 804.2682.

(c) Reaction between $Co^{II}(ttp)$ and PhBr with KOH and 10 equiv. ^tBuOH. $Co^{II}(ttp)$ (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 µL, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (13.0 µL, 0.140 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 10 hours to give $Co^{III}(ttp)Ph$ (3a, 8.2 mg, 0.010 mmol, 73%).

(d) Reaction between $Co^{II}(ttp)$ and PhBr with 10 equiv. KOH and 30 equiv. ^tBuOH. $Co^{II}(ttp)$ (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 µL, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (40.0 µL, 0.421 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 6 hours to give $Co^{III}(ttp)$ Ph (3a, 8.7 mg, 0.011 mmol, 77%).

(e) Reaction between $Co^{II}(ttp)$ and PhBr with 10 equiv. KOH and 50 equiv. ^tBuOH. $Co^{II}(ttp)$ (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 µL, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (65.0 µL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 3 hours to give $Co^{III}(ttp)$ Ph (3a, 8.9 mg, 0.011 mmol, 79%).

(f) Reaction between Co^{II}(ttp) and PhBr with 10 equiv. KOH and 100 equiv. ^tBuOH. Co^{II}(ttp) (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 μ L, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (133.0 μ L, 1.400 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 6 hours to give Co^{III}(ttp)Ph (3a, 7.5 mg, 0.011 mmol, 67%).

(g) Reaction between Co^{II}(ttp) and PhBr with 20 equiv. KOH and 30 equiv. ^tBuOH. Co^{II}(ttp) (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 μ L, 1.400 mmol), KOH (15.6 mg, 0.280 mmol) and ^tBuOH (40.0 μ L, 0.421 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 8 hours to give Co^{III}(ttp)Ph (3a, 8.4 mg, 0.010 mmol, 75%).

(h) Reaction between $Co^{II}(ttp)$ and PhBr with 50 equiv. KOH and 30 equiv. ^tBuOH. $Co^{II}(ttp)$ (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 µL, 1.400 mmol), KOH (39.0 mg, 0.700 mmol) and ^tBuOH (40.0 µL, 0.421 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 18 hours to give $Co^{III}(ttp)$ Ph (3a, 7.8 mg, 0.010 mmol, 69%).

(i) Reaction between $Co^{II}(ttp)$ and PhBr with 10 equiv. KOH and 50 equiv. ^tBuOH at 120 °C. $Co^{II}(ttp)$ (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 µL, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (65.0 µL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 120 °C for 2 days to give $Co^{III}(ttp)Ph$ (3a, 8.2 mg, 0.010 mmol, 73%).

(j) Reaction between Co^{II}(ttp) and PhBr with 10 equiv. KOH and 50 equiv. ^{*t*}BuOH at 200 °C. Co^{II}(ttp) (1a, 10.0 mg, 0.014 mmol), PhBr (2a, 145.0 μ L, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^{*t*}BuOH (65.0 μ L, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then (k) Reaction between $Co^{II}(ttp)$ and PhBr with 10 equiv. KOH and 10 equiv. ^tBuOH at 150 °C in THF. $Co^{II}(ttp)$ (10.0 mg, 0.014 mmol), PhBr (145.0 µL, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (65.0 µL, 0.685 mmol) were added to THF (1.0 mL) and the mixture was degassed and then heated at 150 °C for 4 days to give $Co^{III}(ttp)$ Ph (0.6 mg, 0.001 mmol, 5%).

4.4. Porphyrin ligand electronic effect

(a) Reaction with Co^{II}(tap). Co^{II}(tap) (1b, 10.0 mg, 0.013 mmol), PhBr (2a, 133.0 µL, 1.263 mmol), KOH (7.1 mg, 0.126 mmol) and ^tBuOH (60.0 µL, 0.632 mmol) were added to benzene (1.0 mL) and the mixture was degassed for three freeze-pump-thaw cycles in a Teflon screw capped tube and filled with N₂. The reaction was then heated at 150 °C for 1.5 hours. The solvent was then removed under vacuum and the crude product was purified by column chromatography over alumina eluted with CH₂Cl₂-hexane (1:2) to give Co^{III}-(tap)Ph³² (3b, 7.6 mg, 0.009 mmol, 69%). ¹H NMR (CDCl₃, 400 MHz) δ 0.32 (d, 2 H, *o*-Ph), 4.04 (s, 12 H, methyl-H), 4.71 (m, 2 H, *m*-Ph), 5.28 (d, 1 H, *p*-Ph), 7.22 (d, 2 H, tolyl-H), 7.98 (s, 8 H, tolyl-H), 8.88 (s, 8 H, pyrrole-H).

(b) Reaction with Co^{II}(tpp). Co^{II}(tpp) (1c, 10.0 mg, 0.015 mmol), PhBr (2a, 157.0 μL, 1.491 mmol), KOH (8.3 mg, 0.148 mmol) and ^tBuOH (70.0 μL, 0.737 mmol) were added to benzene (1.0 mL) and the mixture was degassed then heated at 150 °C for 2 hours to give Co^{III}(tpp)Ph³³ (3c) (6.1 mg, 0.008 mmol, 55%). $R_{\rm f} = 0.68$ (CH₂Cl₂-hexane = 2 : 1) ¹H NMR (CDCl₃, 400 MHz) δ 0.28 (d, 2 H, *o*-Ph), 4.70 (t, 2 H, *m*-Ph), 5.28 (d, 1 H, *p*-Ph), 7.71 (m, 12 H, por-Ph), 8.03 (s, 8 H, por-Ph), 8.83 (s, 8 H, pyrrole-H).

(c) Reaction with Co^{II}(t_{4-Cl}pp). Co^{II}(t_{4-Cl}pp) (1d, 10.0 mg, 0.012 mmol), PhBr (2a, 130.0 µL, 1.234 mmol), KOH (7.0 mg, 0.125 mmol) and ^tBuOH (58.0 µL, 0.611 mmol) were added to benzene (1.0 mL) and the mixture was degassed for three freeze-pump-thaw cycles in a Teflon screw capped tube and filled with N2. The reaction was then heated at 150 °C for 5 hours. The solvent was then removed under vacuum and the crude product was purified by column chromatography over alumina eluted with CH_2Cl_2 -hexane (1:2) to give $Co^{III}(t_{4-Cl}pp)$ -Ph (**3d**) (7.8 mg, 0.009 mmol, 73%). ¹H NMR (CDCl₃, 400 MHz) δ 0.18 (d, 2 H, o-Ph), 4.68 (t, 2 H, m-Ph), 5.28 (t, 1 H, p-Ph), 7.68 (d, 8 H, por-Ph), 7.96 (s, 8 H, por-Ph), 8.82 (s, 8 H, pyrrole-H). ¹³C NMR (CDCl₃, 100 MHz) δ 120.8, 121.7, 123.3, 127.3, 132.4, 133.2, 134.5, 134.8, 139.8, 145.3; HRMS (FABMS): calcd for $[C_{50}H_{29}Cl_4CoN_4]^+([M]^+)$: m/z 884.0478. Found: m/z884.0480.

4.5. Scope of base-promoted Ar–Br cleavage with Co^{II}(ttp)

(a) Reaction with 4-bromoanisole. Co^{II} (ttp) (1a, 10.0 mg, 0.014 mmol), 4-bromoanisole (2e, 257.0 mg, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^{*t*}BuOH (65.0 µL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 7 hours to give Co^{III} (ttp) C_6H_4 -

(*p*-OMe) (**3e**, 8.6 mg, 0.010 mmol, 75%). $R_{\rm f} = 0.20$ (CH₂Cl₂-hexane = 1 : 2) ¹H NMR (CDCl₃, 400 MHz) δ 0.15 (d, 2 H, *o*-Ph), 2.65 (s, 12 H, methyl-H), 2.83 (s, 3 H, OMe-H), 4.43 (d, 2 H, *m*-Ph), 7.49 (d, 8 H, por-Ph), 7.93 (s, 8 H, por-Ph), 8.83 (s, 8 H, pyrrole-H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 54.3, 109.2, 122.0, 127.7, 131.8, 133.0, 133.7, 137.5, 138.8, 145.6, 155.3; HRMS (FABMS): calcd for [C₅₅H₄₃CoN₄O]⁺([M]⁺): *m/z* 834.2769. Found: *m/z*. 834.2780.

(b) Reaction with 4-bromotoluene. Co^{II}(ttp) (1a, 10.0 mg, 0.014 mmol), 4-bromotoluene (2f, 169.0 mg, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^{*t*}BuOH (65.0 μL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 2.5 hours to give Co^{III}(ttp)-C₆H₄(*p*-Me) (3f, 10.0 mg, 0.012 mmol, 89%). $R_{\rm f}$ = 0.52 (CH₂Cl₂-hexane = 1 : 2) ¹H NMR (CDCl₃, 400 MHz) δ 0.20 (d, 2 H, *o*-Ph), 1.21 (s, 3 H, tolyl-Me), 2.67 (s, 12 H, por-Me), 4.57 (d, 2 H, *m*-Ph), 7.50 (d, 8 H, por-Ph), 7.95 (s, 8 H, por-Ph), 8.85 (s, 8 H, pyrrole-H). ¹³C NMR (CDCl₃, 100 MHz) δ 19.0, 21.7, 122.0, 124.1, 127.7, 130.5, 131.9, 132.9, 133.7, 137.4, 138.9, 145.6; HRMS (FABMS): calcd for [C₅₅H₄₃CON₄]⁺([M]⁺): *m/z* 818.2820. Found: *m/z*. 818.2814.

(c) Reaction with 1-bromo-4-*tert*-butylbenzene. $Co^{II}(ttp)$ (1a, 10.0 mg, 0.014 mmol), 1-bromo-4-*tert*-butylbenzene (2g, 242.5 µL, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (65.0 µL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 1 day to give $Co^{III}(ttp)C_6H_4(p-tert$ -butyl) (3g, 8.7 mg, 0.010 mmol, 72%). $R_f = 0.53$ (CH₂Cl₂-hexane = 1:2). ¹H NMR (CDCl₃, 400 MHz) δ 0.21 (d, 2 H, *o*-Ph), 0.39 (s, 9 H, ^tBu), 2.66 (s, 12 H, por-Me), 4.71 (m, 2 H, *m*-Ph), 7.49 (d, 8 H, por-Ph), 7.93 (s, 8 H, por-Ph), 8.85 (s, 8 H, pyrrole-H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 30.8, 120.4, 121.9, 127.7, 131.7, 132.9, 133.7, 137.4, 138.9, 145.5; HRMS (FABMS): calcd for $[C_{58}H_{49}CON_4]^+([M]^+)$: *m/z* 860.3289. Found: *m/z* 860.3284.

(d) Reaction with 1-bromo-4-chlorobenzene. $Co^{II}(ttp)$ (1a, 10.0 mg, 0.014 mmol), 1-bromo-4-chlorobenzene (2h, 263.0 mg, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (65.0 µL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 2.5 hours to give $Co^{III}(ttp)C_6H_4(p-Cl)$ (3h, 7.0 mg, 0.008 mmol, 61%). $R_f = 0.45$ (CH₂Cl₂-hexane = 1 : 2). ¹H NMR (CDCl₃, 400 MHz) δ 0.22 (d, 2 H, *o*-Ph), 2.67 (s, 12 H, por-Me), 4.74 (d, 2 H, *m*-Ph), 7.50 (d, 8 H, por-Ph), 7.92 (s, 8 H, por-Ph), 8.86 (s, 8 H, pyrrole-H).¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 122.1, 122.5, 127.7, 133.1, 133.6, 137.6, 138.6, 145.5; HRMS (FABMS): calcd for $[C_{54}H_{40}ClCoN_4]^+([M]^+): m/z$ 838.2274. Found: m/z. 838.2258.

(e) Reaction with 1-bromo-4-fluorobenzene. $\text{Co}^{II}(\text{ttp})$ (1a, 10.0 mg, 0.014 mmol), 1-bromo-4-fluorobenzene (2i, 150.0 µL, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^{*t*}BuOH (65.0 µL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 3 hours to give $\text{Co}^{III}(\text{ttp})\text{C}_6\text{H}_4(p\text{-F})$ (3i, 8.4 mg, 0.010 mmol, 74%). $R_f = 0.42$ (CH₂Cl₂-hexane = 1:2). ¹H NMR (CDCl₃, 400 MHz) δ 0.19 (t, 2 H, *o*-Ph), 2.66 (s, 12 H, por-Me), 4.57 (t, 2 H, *m*-Ph), 7.50 (d, 8 H, por-Ph), 7.92 (s, 8 H, por-Ph), 8.86 (s, 8 H, pyrrole-H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 109.4, 109.6, 122.0, 127.8,

132.1, 132.2, 133.1, 133.6, 137.6, 138.7, 145.5; HRMS (FABMS): calcd for $[C_{54}H_{40}CoFN_4]^+([M]^+)$: m/z 822.2569. Found: m/z. 838.2564.

(f) Reaction with 4-bromo-nitrobenzene. $\text{Co}^{II}(\text{ttp})$ (1a, 10.0 mg, 0.014 mmol), 4-bromo-nitrobenene (2j, 278.0 mg, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (65.0 µL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 18 hours to give $\text{Co}^{III}(\text{ttp})\text{C}_{6}\text{H}_{4}(p\text{-NO}_{2})$ (3j, 9.2 mg, 0.011 mmol, 79%). $R_{\rm f} = 0.19$ (CH₂Cl₂-hexane = 1 : 2). ¹H NMR (CDCl₃, 400 MHz) δ 0.53 (d, 2 H, o-Ph), 2.66 (s, 12 H, por-Me), 5.55 (d, 2 H, m-Ph), 7.51 (d, 8 H, por-Ph), 7.91 (s, 8 H, por-Ph), 8.88 (s, 8 H, pyrrole-H). ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 115.9, 122.3, 127.9, 132.7, 133.3, 133.6, 137.6, 138.3, 144.0, 145.4. HRMS (FABMS): calcd for $[\text{C}_{54}\text{H}_{40}\text{CoN}_5\text{O}_2]^{+}([\text{M}]^+)$: m/z 849.2514. Found: m/z 849.2503.

(g) Reaction with 4-bromoacetophenone. $\text{Co}^{\text{II}}(\text{ttp})$ (1a, 10.0 mg, 0.014 mmol), 4-bromoacetophenone (2k, 274.0 mg, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (65.0 µL, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed and then heated at 150 °C for 3 hours to give $\text{Co}^{\text{III}}(\text{ttp})\text{C}_{6}\text{H}_{4}(p\text{-C}(\text{O})\text{Me})$ (3k, 6.6 mg, 0.008 mmol, 57%). $R_{\rm f}$ = 0.10 (CH₂Cl₂-hexane = 1:2). ¹H NMR (CDCl₃, 400 MHz) δ 0.47 (d, 2 H, *o*-Ph), 1.66 (s, 3 H, C(O)Me-H), 2.66 (s, 12 H, por-Me), 5.26 (d, 2 H, *m*-Ph), 7.50 (d, 8 H, por-Ph), 7.94 (s, 8 H, por-Ph), 8.86 (s, 8 H, pyrrole-H). ¹³C NMR (CDCl₃, 100 Hz) δ 21.7, 25.6, 26.8, 121.7, 122.2, 127.4, 127.8, 128.4, 129.1, 132.7, 133.1, 133.6, 137.7, 138.6, 145.5; HRMS (FABMS): calcd for [C₅₆H₄₃CON₄O]⁺([M]⁺): *m*/z 846.2769. Found: *m*/z. 846.2763.

4.6. Stability of Co^{III}(ttp)C₆H₄(*p*-OMe) in benzene at 150 °C

Co^{III}(ttp)C₆H₄(*p*-OMe) (**3e**, 11.0 mg, 0.014 mmol), KOH (7.8 mg, 0.140 mmol) and ^{*t*}BuOH (65.0 μ L, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed for three freeze-pump-thaw cycles in a Teflon screw capped tube and filled with N₂. The reaction was then heated at 150 °C for 5 hours. The solvent was then removed under vacuum and the crude product was purified by column chromatography over alumina eluted with CH₂Cl₂-hexane (1 : 2) to give Co^{II}(ttp) (**1a**, 1.6 mg, 0.002 mmol, 16%) and Co^{III}(ttp)C₆H₄(*p*-OMe) (**3e**, 8.3 mg, 0.010 mmol, 71%).

4.7. Exchange reaction between $\mathrm{Co}^{\mathrm{II}}(\mathrm{ttp})\mathrm{Ph}$ and 4-methoxy-1-bromobenzene at 150 $^{\mathrm{o}}\mathrm{C}$

Co^{III}(ttp)Ph (**3a**, 11.0 mg, 0.014 mmol), 4-bromoanisole (**2e**, 257.0 mg, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^{*t*}BuOH (65.0 μ L, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed for three freeze–pump–thaw cycles in a Teflon screw capped tube and filled with N₂. The reaction was then heated at 150 °C for 6 hours. The solvent was then removed under vacuum and the crude product was purified by column chromatography over alumina eluted with CH₂Cl₂–hexane (1:2) to give Co^{III}(ttp)C₆H₄(*p*-OMe) (**3e**, 3.2 mg, 0.004 mmol, 27%), Co^{III}(ttp)Ph (**3a**, 6.9 mg, 0.009 mmol, 61%) and trace of Co^{II}(ttp) (**1a**).

4.8. Detection of anisole and 4-methoxybiphenyl from reaction between Co^{II}(ttp) and 4-methoxylbromobenzene in benzene

Co^{II}(ttp) (1a, 10.0 mg, 0.014 mmol), 4-bromoanisole (2e, 257.0 mg, 1.400 mmol), KOH (7.8 mg, 0.140 mmol) and ^{*t*}BuOH (65.0 μ L, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed for three freeze-pump-thaw cycles in a Teflon screw capped tube and filled with N₂. The reaction was then heated at 150 °C for 7 hours. The solvent was then collected in a liquid-N₂ cooled trap under vacuum and subjected to GC/MS analysis using Decalin as the internal standard. Anisole (54%) was detected. The crude product was purified by column chromatography over alumina eluted with CH₂Cl₂-hexane (1:2) to give Co^{III}(ttp)C₆H₄(*p*-OMe) (3e, 8.5 mg, 0.010 mmol, 73%) and 4-methoxylbiphenyl (4.8 mg, 0.026 mmol, 187%).

4.9. Detection of anisole and 4-methoxybiphenyl from the hydrolysis of $Co^{III}(ttp)C_6H_4(p$ -OMe) in benzene

Co^{III}(ttp)C₆H₄(*p*-OMe) (**3e**, 11.0 mg, 0.014 mmol), KOH (7.8 mg, 0.140 mmol) and ^tBuOH (65.0 μ L, 0.685 mmol) were added to benzene (1.0 mL) and the mixture was degassed for three freeze-pump-thaw cycles in a Teflon screw capped tube and filled with N₂. The reaction was then heated at 150 °C for 7 hours. The solvent was then collected in a liquid-N₂ cooled trap under vacuum and subjected to GC-MS analysis using Decalin as the internal standard. Anisole (50%) was detected. The crude product was purified by column chromatography over alumina eluted with CH₂Cl₂-hexane (1 : 2) to give Co^{II}(ttp) (**1a**, 3.3 mg, 0.004 mmol, 36%).

Acknowledgements

We thank the Research Grants Council (no. 400308) and a Special Equipment Grant (no. SEG/CUHK09) from the University Grants Committee of Hong Kong SAR, People's Republic of China, for financial support.

Notes and references

- (a) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, 2002, **102**, 1359; (b) J. P. Corbet and G. Mignani, *Chem. Rev.*, 2006, **106**, 2651.
- 2 (a) X. Cui, T. Qin, J.-R. Wang, L. Liu and Q.-X. Guo, Synthesis, 2007, 393; (b) S. Li, Y. Lin, J. Cao and S. Zhang, J. Org. Chem., 2007, 72, 4067.
- 3 (a) H. Huang, H. Jiang, K. Chen and H. Liu, J. Org. Chem., 2009, 74, 5599; (b) S. P. H. Mee, V. Lee and J. E. Baldwin, Angew. Chem., Int. Ed., 2004, 43, 1132.
- 4 (a) C. Han and S. L. Buchwald, J. Am. Chem. Soc., 2009, 131, 7532; (b) A. Krasovskiy, C. Duplais and B. H. Lipshutz, J. Am. Chem. Soc., 2009, 131, 15592.

- 5 (a) C. Wolf and H. Xu, J. Org. Chem., 2008, 73, 162;
 (b) S. Y. W. Lau, G. Hughes, P. D. O'Shea and I. W. Davies, Org. Lett., 2007, 9, 2239.
- 6 (a) B. Sreedhar, A. S. Kumar and D. Yada, Synlett, 2011, 1081; (b) E. Alacid and C. Nájera, J. Org. Chem., 2008, 73, 2315; (c) S. Shi and Y. Zhang, J. Org. Chem., 2007, 72, 5927.
- 7 (a) F. Vallée, J. J. Mousseau and A. B. Charette, J. Am. Chem. Soc., 2010, 132, 1514; (b) W. Liu, H. Cao and A. Lei, Angew. Chem., Int. Ed., 2010, 49, 2004.
- 8 (a) O. Kobayashi, D. Uraguchi and T. Yamakawa, Org. Lett., 2009, 11, 2679; (b) M. Tobisu, I. Hyodo and N. Chatani, J. Am. Chem. Soc., 2009, 131, 12070.
- 9 H.-Q. Do, R. M. K. Khan and O. Daugulis, J. Am. Chem. Soc., 2008, 130, 15185.
- 10 (a) T. Hatakeyama, S. Hashimoto, K. Ishizuka and M. Nakamura, J. Am. Chem. Soc., 2009, 131, 11949;
 (b) H. Ohmiya, H. Yorimitsu and K. Oshima, Chem. Lett., 2004, 33, 1240; (c) T. J. Korn and P. Knochel, Angew. Chem., Int. Ed., 2005, 44, 2947.
- 11 (a) A. Qiu and D. T. Sawyer, J. Porphyrins Phthalocyanines, 1997, 1, 125; (b) H. Dong, T. Hou, Y. Zhao, X. Fu and Y. Li, Comput. Theor. Chem., 2012, 1001, 51.
- 12 L. M. Alcazar-Roman and J. F. Hatwig, Organometallics, 2002, 21, 491.
- (a) C. T. To, T. L. Chan, B. Z. Li, Y. Y. Hui, T. Y. Kwok, S. Y. Lam and K. S. Chan, *Tetrahedron Lett.*, 2011, 52, 1023;
 (b) Y. Y. Qian, K. L. Wong, M. W. Zhang, T. Y. Kwok, C. T. To and K. S. Chan, *Tetrahedron Lett.*, 2012, 53, 1571.
- 14 H. M. Senn and T. Ziegler, Organometallics, 2004, 23, 2980.
- D. S. McGuinness and A. H. White, *Organometallics*, 1999, 18, 1596.
- 16 B. L. Edelbach and W. D. Jones, J. Am. Chem. Soc., 1997, 119, 7734.
- 17 (a) C. W. Cheung and K. S. Chan, Organometallics, 2011, 30, 1768; (b) C. W. Cheung and K. S. Chan, Organometallics, 2011, 30, 4269; (c) Y. Y. Qian and K. S. Chan, Organometallics, 2012, 31, 5452.
- 18 (a) K. S. Choi, T. H. Lai, S. Y. Lee and K. S. Chan, Organometallics, 2011, 30, 2633; (b) C. W. Cheung and K. S. Chan, Organometallics, 2011, 30, 4999; (c) D. T. Sawyer and J. L. Roberts Jr., Acc. Chem. Res., 1988, 21, 469.
- (a) D. Zhu, F. F. B. J. Janssen and P. H. M. Budzelaar, *Organometallics*, 2010, 29, 1897; (b) D. Zhu and P. H. M. Budzelaar, *Organometallics*, 2010, 29, 5759; (c) D. Zhu, I. Thapa, I. Korobkov, S. Gambarotta and P. H. M. Budzelaar, *Inorg. Chem.*, 2011, 50, 9879.
- 20 J. Halpern and J. P. Maher, J. Am. Chem. Soc., 1965, 87, 5361.
- 21 D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson and H. A. Pinnock, *J. Chem. Soc. C*, 1968, 881.
- 22 (a) J. Halpern, M. S. Chan, J. Hanson, T. S. Roche and J. A. Topich, *J. Am. Chem. Soc.*, 1975, 97, 1606;
 (b) D. Dolphin, D. J. Halko and E. Johnson, *Inorg. Chem.*, 1981, 20, 4348;
 (c) S. Fukuzumi, K. Miyanoto, T. O. Suenobu, E. V. Caemelbecke and K. M. Kadish, *J. Am. Chem. Soc.*, 1998, 120, 2880;
 (d) S. Fukuzumi, I. Nakanishi,

K. Tanaka, A. Tabard, R. Guilard, E. V. Caemelbecke and K. M. Kadish, *Inorg. Chem.*, 1999, **38**, 5000.

- 23 (a) P. B. Chock, R. B. K. Dewar, J. Haplern and L. Y. Wong, J. Am. Chem. Soc., 1969, 91, 82; (b) J. Halpern, Acc. Chem. Res., 1970, 3, 386; (c) D. Lexa, J. M. Saveant and J. Zickler, J. Am. Chem. Soc., 1980, 102, 2654; (d) B. B. Wayland, K. J. Balkus Jr. and M. D. Farnos, Organometallics, 1989, 8, 950; (e) V. Grass, D. Lexa, M. Momenteau and J. M. Saveant, J. Am. Chem. Soc., 1997, 119, 3536.
- 24 M. K. Richard and G. S. Thomos, Inorg. Chem., 1985, 24, 2373.
- 25 The energetics of the electron transfer reaction was calculated to be -0.97 V. (a) M. Tezuka, Y. Ohkatsu and T. Osa, Bull. Chem. Soc. Jpn., 1976, 49, 1435; (b) M. Louis, Electrochemical Data, Wiley, New York, 1974.
- 26 D. D. Davis and J. K. Kochi, J. Am. Chem. Soc., 1964, 86, 5264.
- 27 (a) K. Weissermel and H. Arpe, *Industrial Organic Chemistry*, Wiley-VCH, Weinheim, 4th edn, 2003; (b) H. S. Fung, B. Z. Li and K. S. Chan, *Organometallics*, 2012, 31, 570.
- 28 (a) J. L. Roberts Jr., H. Sugimoto, W. C. Barrette Jr. and
 D. T. Sawyer, J. Am. Chem. Soc., 1985, 107, 4556;

(b) H. S. Harned, J. Am. Chem. Soc., 1918, 40, 1461;
(c) A. Kumar and R. J. McCluskey, Ind. Eng. Chem. Res., 1987, 26, 1323.

- (a) Y. R. Luo, Comprehensive Handbook of Chemical Bond Energies, CRC Press, Boca Raton, FL, 2007; (b) G. Li and F. F. Zhang, Chem. Lett., 2001, 284; (c) B. B. Wayland, S. Ba and A. E. Sherry, J. Am. Chem. Soc., 1991, 113, 5305; (d) W. Cui and B. B. Wayland, J. Am. Chem. Soc., 2004, 126, 8266; (e) J. A. Martinho Simões and J. L. Beauchamp, Chem. Rev., 1990, 90, 629.
- 30 Estimated by subtraction C−C bond strength of pentane (87.3 kcal mol⁻¹) from C=C bond strength of (*E*)-1,3-pentadiene (117.2 kcal mol⁻¹).^{28a}.
- 31 (a) A. K. S. Tse, K. W. Mak and K. S. Chan, Organometallics, 1988, 17, 2651; (b) K. Maruyama and H. Tamiaki, J. Org. Chem., 1986, 51, 602.
- 32 T. V. Magdesieva, P. S. Ivanov, D. N. Kravchuk and K. P. Butin, *Mendeleev Commun.*, 2003, **13**, 56.
- 33 (a) H. J. Callot and F. Metz, J. Chem. Soc., Chem. Commun., 1982, 947; (b) H. J. Callot, F. Metz and R. Cromer, Nouv. J. Chem., 1984, 8, 759.