Journal of Organometallic Chemistry 791 (2015) 82–89

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Aryl carbon–chlorine (Ar–Cl) and aryl carbon–fluorine (Ar–F) bond cleavages by rhodium porphyrins

Ying Ying Qian, Man Ho Lee, Wu Yang, Kin Shing Chan*

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

ARTICLE INFO

Article history:
Received 7 February 2015
Received in revised form
6 May 2015
Accepted 23 May 2015
Available online 27 May 2015

Keywords:
Rhodium porphyrin
Carbon–chlorine bond activation
Carbon–fluorine bond activation

ABSTRACT

Aryl carbon–chlorine (Ar–Cl) bond cleavage has been achieved with rhodium(III) tetrakis-4-tolylporphyrin chloride (Rh(ttp)Cl) to give Rh(ttp)Ar. For 4-chlorofluorobenzene, the aryl carbon–fluorine (Ar–F) bond cleavage competes with the Ar–Cl bond cleavage. Mechanistic investigations show that the Ar–Cl bond cleavage goes through metalloradical *ipso*-substitution mechanism, while the Ar–F bond cleavage goes through nucleophilic aromatic substitution. The selectivity of the Ar–F or Ar–Cl bond cleavage can be controlled by tuning the temperature and substrate concentration.

1. Introduction

Ar-X bond cleavage is important in organic synthesis, especially for aryl–aryl bond formation [1]. Since aryl chlorides are more readily available and less expensive starting materials than aryl bromides and iodides, the investigation of aryl–chlorine bond (Ar–Cl) is important [2]. Moreover, chlorinated dioxins and polychlorinated biphenyls are toxic chemical waste [3]. The hydrodechlorination is thus important in waste treatment. The mechanism of enzymatic dehalogenation of ArX is of very recent interest [4].

There are three kinds of mechanism reported for the Ar–Cl bond cleavage. First is the oxidative addition mechanism. Oxidative addition mechanism usually happens with electron rich d^8 and d^{10} metal complexes [5]. For example, Rh^{I}(PNP) (PNP = bis(2-(diisopropylphosphino)-4-methylphenyl)-amino), reacts with ArCl to give the Ar–Cl bond oxidative addition product [5a]. The Ar–Cl bond can also be cleaved through oxidative addition to the Pd center of $Pd^0(P^tBu_3)_2$ at 80 °C [5e]. Secondly, the Ar–Cl bond can be cleaved through chlorine atom abstraction. The chlorine atom of ArCl is abstracted by $LCo^0(N_2)$ (L = 2,6-bis[2,6-dimethylphenyliminoethyl] pyridine), which is generated from $LCo^{I}CH_2SiMe_3$ and H_2, to give LCoCl and Ar radical. The Ar radical further reacts with another $LCo^0(N_2)$ to give LCoAr and N_2 [6]. Thirdly, the Ar–Cl bond can also be cleaved by metalloradical *ipso*-substitution addition-elimination mechanism. Ir^{II}(ttp) (ttp = tetrakis-4-tolylporphyrinato dianion) radical, which is generated from reduction of Ir(ttp) (CO)Cl by KOH, cleaves the Ar–Cl bond to give Ir^{III}(ttp)Ar [7].

Due to the high bond dissociation energy of Ar–Cl bond (95 kcal/mol for Ph-Cl), Ar–H bond cleavage may compete with the Ar–Cl bond cleavage (112 kcal/mol for Ph-H) [8]. For example, when the Ir^{I}(PNP) complex, which is generated from Ir(PNP)H_2 and norbornene, reacts with ArCl to first give the kinetic Ar–H bond oxidative addition product and then converts to the thermodynamic Ar–Cl bond oxidative addition product [9]. Moreover, the reaction between $[Cp^*_2Zr^{IV}CH_3]^+$ and chlorobenzene gives *ortho*-C-H bond activation first, by the coordination effect of ortho-chlorine to Zr. Then, the Ar–Cl bond is cleaved by β-Cl elimination [10].

Our group has reported the selective Ar–Cl bond cleavage by iridium porphyrin. A metalloradical *ipso*-substitution addition-elimination mechanism has been proposed for the Ar–Cl bond cleavage process (Scheme 1) [7]. With the selective Ar–Cl bond cleavage by iridium porphyrin, we thus have extended our studies to rhodium porphyrin.

2. Results and discussion

2.1. Conditions optimization of Ar–Cl bond cleavage

Based on the optimal conditions in the reported Ar–I and Ar–Br bond cleavage with Rh(ttp)Cl [11], 10 equivalents of KOH and 10 equivalents of ArCl in benzene at 120 °C were applied for investigation of the Ar–Cl bond cleavage with Rh(ttp)Cl (Table 1, entry 1).

* Corresponding author.
E-mail address: ksc@cuhk.edu.hk (K.S. Chan).

http://dx.doi.org/10.1016/j.jorganchem.2015.05.039
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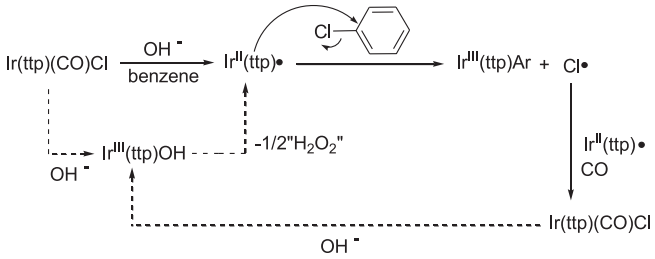


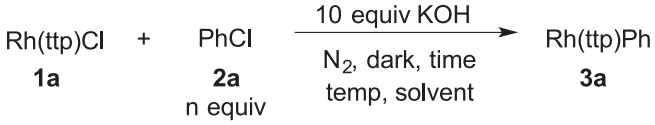
Scheme 1. Proposed mechanism for Ar–Cl bond cleavage with Ir(ttp) (CO)Cl.

However, no Ar–Cl bond cleavage product Rh(ttp)Ph was obtained after 6 h. Then, THF and PhCN were used as the solvent. No Rh(ttp)Ph was obtained neither (Table 1, entries 2 and 3). Since changing the solvent was not effective to achieve the Ar–Cl bond cleavage, the substrate concentration was increased. When 200 equivalents of PhCl was used at 150 °C, 31% yield of Rh(ttp)Ph was obtained (Table 1, entry 5). When the equivalent of PhCl was increased to 780, which is in solvent-free conditions, 62% yield of Rh(ttp)Ph was isolated (Table 1, entry 6). In order to further increase the product yield, the temperature effect was investigated. At 120 °C, only 30% yield of Rh(ttp)Ph was obtained after 3 days (Table 1, entry 7). When the reaction temperature was raised to 200 °C, although the reaction rate is faster, the yield of Rh(ttp)Ph was still 61% (Table 1, entry 8). Therefore, the better functional group compatible of 150 °C was used for further investigations.

2.2. Substrate scope of Ar–Cl bond cleavage

Various ArCl reacted with Rh(ttp)Cl to give the corresponding Ar–Cl bond cleavage products (Table 2). Electron rich 4-chloro-*tert*-butylbenzene (**2d**), electron deficient 1,4-dichlorobenzene (**2e**), 4-chlorobenzotrifluoride (**2g**) and 4-chloronitrobenzene (**2h**) reacted smoothly with Rh(ttp)Cl to give moderate to high yields of Ar–Cl bond cleavage products (Table 2, entries 4, 5, 7 and 8). However, substrates with reactive C–H and C–O bonds, such as 4-chloroanisole (**2b**) and 4-chlorotoluene (**2c**), reacted with Rh(ttp)Cl to give both the C–H or C–O bond cleavage products besides the Ar–Cl bond cleavage products (Table 2, entries 2 and 3) [12]. For 4-chlorofluorobenzene (**2f**), a higher temperature 200 °C was employed since the Ar–F bond cleavage competed dominantly with the Ar–Cl bond cleavage at 150 °C, which will be discussed in the following section. At 150 °C, still 6% yield of the Ar–F bond cleavage product **3e** was obtained (Table 2, entry 6).

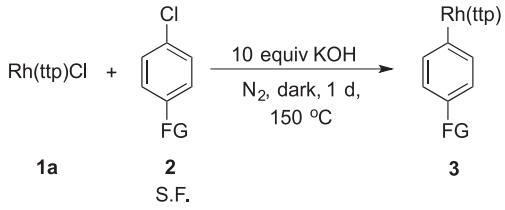
Table 1
Conditions Optimization of Ar–Cl Bond Cleavage with Rh(ttp)Cl.



Entry	Solvent	n	Temp/°C	Time	Rh(ttp)Ph yield/%
1	benzene	10	120	6 h	/
2	THF	10	120	3 h	/
3	PhCN	10	120	3 d	/
4	benzene	10	150	4 h	/
5	benzene	200	150	3 h	31
6	S.F.[a]	780	150	4 h	62
7	S.F.[a]	780	120	3 d	30
8	S.F.[a]	780	200	2 h	61

[a] S.F. = solvent-free.

Table 2
Substrate Scopes of Ar–Cl bond cleavage with Rh(ttp)Cl.

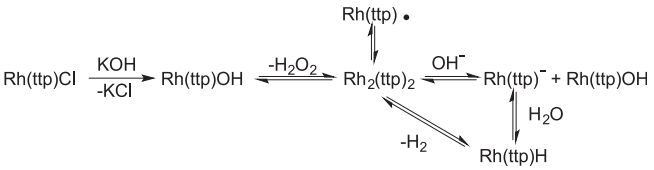


Entry	FG	Temp/°C	CCIA/%
1	H (**2a**)	150	**3a** (62)
2[a]	OMe (**2b**)	150	**3b** (7)
3[b]	Me (**2c**)	150	**3c** (29)
4	^{t}Bu (**2d**)	150	**3d** (85)
5	Cl (**2e**)	150	**3e** (47)
6[c]	F (**2f**)	200	**3f** (63)
7	CF_3 (**2g**)	150	**3g** (74)
8	NO_2 (**2h**)	150	**3h** (71)

[a] Rh(ttp)Me (**4**) was isolated in 43% yield and Rh(ttp)CH_2O(4-chlorophenyl) (**5**) was isolated in 41% yield.
[b] Rh(ttp) (4-chlorobenzyl) (**6**) was isolated in 11% yield.
[c] Rh(ttp) (4-chlorophenyl) (**3e**) was isolated in 6% yield.

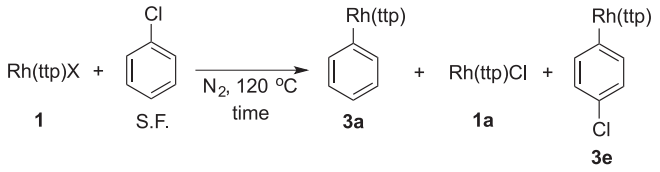
2.3. Mechanistic investigation for Ar–Cl bond cleavage

In order to gain further mechanistic understandings of the Ar–Cl bond cleavage, mechanistic investigations were carried out. It has been reported that Rh(ttp)OH, synthesized by ligand substitution with KOH, exists in equilibria with $Rh_2(ttp)_2$, Rh(ttp)H and $Rh(ttp)^-$ (Scheme 2) [13]. Since the thermal reductive elimination of Rh(ttp)OH to $Rh_2(ttp)_2$ is very rapid at 120 °C within 1 h [13a], $Rh_2(ttp)_2$, Rh(ttp)H and $Rh(ttp)^-$ are sufficiently long lived to be viable intermediates. Table 3 lists the results of these complexes with chlorobenzene. Among the three rhodium complexes, $Rh_2(ttp)_2$, which in thermo equilibrium with Rh(ttp) monomer [14], reacted the fastest with highest total yield (Table 3). Reactions of chlorobenzene with Rh(ttp)H and $Rh(ttp)^-K^+$ also occurred, however, with much longer reaction times. These two complexes thus play minor importance. Therefore, $Rh_2(ttp)_2$, or more accurately Rh(ttp) monomer, is the most likely intermediate for Ar–Cl bond cleavage, likely by a metalloradical substitution as we have previously established for related iridium (II) porphyrin activation of Ar-X bonds [7,11]. Two further detailed Ar-X bond cleavage processes of the metalloradical Ar–Cl bond cleavage still exist. One is the halogen atom transfer mechanism, and the other is the metalloradical *ipso*-substitution mechanism (Scheme 3). For the halogen atom transfer mechanism, the aryl radical is generated through cleavage of the strong Ar–Cl bond (Scheme 3, step i). The aryl radical can either react with Rh(ttp) radical to give Rh(ttp)Ar or with chlorobenzene to give biaryl through radical substitution reaction (Scheme 3, step ii). For the metalloradical *ipso*-substitution mechanism, cleavage of the relative weaker carbon–carbon π bond in benzene and subsequent formation of cyclohexadienyl radical intermediate [15], chlorine radical is then generated (Scheme 3,



Scheme 2. Equilibria between rhodium porphyrin intermediates under basic conditions.

Table 3
Possible intermediate for Ar–Cl bond cleavage.



Entry	Rh(ttp)X	Time	Yield **3a**/%	Yield **1a**/%	Yield **3e**/%	Total yield/%
1	$Rh_2(ttp)_2$ **1b**	1 h	22	7	10	39
2	Rh(ttp)H **1c**	1 d	8	/	/	8
3	$Rh(ttp)^-K^+$ **1d**	1 d	30	/	/	30

step iii). The chlorine radical can either react with Rh(ttp) radical to give Rh(ttp)Cl or with chlorobenzene to give 1,4-dichlorobenzene [15]. Rh(ttp) radical can further react with 1,4-dichlorobenzene, which is more reactive than chlorobenzene towards radical substitution with iridium(II) porphyrin [15], to give Rh(ttp) (4-chlorophenyl) (Scheme 3, step iv; Table 3, entry 1). Since Rh(ttp) (4-chlorophenyl) was obtained from the reaction between $Rh_2(ttp)_2$ and chlorobenzene, and no biaryl was observed by GC–MS analysis, the metalloradical *ipso*-substitution mechanism rather than the chlorine atom transfer process operates.

2.4. Competitive Ar–F and Ar–Cl bond cleavage

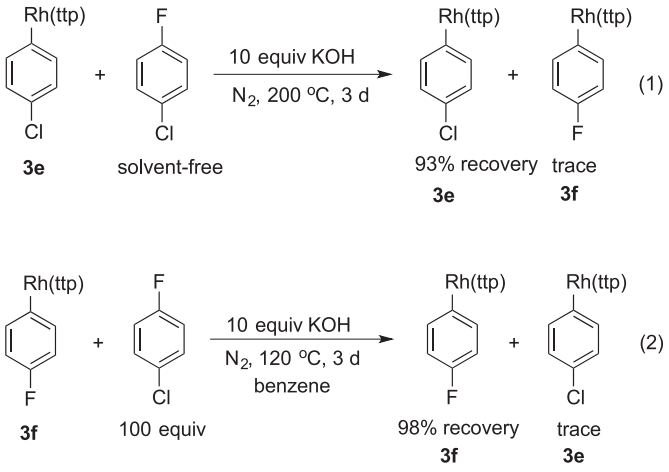
Interestingly, during the substrate investigation of the Ar–Cl bond cleavage, it was found that the much stronger Ar–F bond (~125 kcal/mol) [8] cleavage can compete with the Ar–Cl bond (~95 kcal/mol) [8] cleavage (Table 2, entry 6 and footnote c). We therefore optimized the conditions to achieve selective Ar–F bond cleavage. Initially, Rh(ttp)Cl reacted with 4-chlorofluorobenzene under solvent-free conditions at 200 °C to give the Ar–Cl bond cleavage product (**3f**) as the major product with 6% of the Ar–F bond cleavage product (**3e**) (Table 4, entry 1). When the reaction temperature was lowered to 150 °C, the Ar–F bond cleavage product Rh(ttp) (4-chlorophenyl) (**3e**) formed exclusively (Table 4, entry 2). A lower reaction temperature at 120 °C gave the Ar–F bond cleavage product **3e** in 92% yield almost exclusively (Table 4, entry 3). Moreover, 100 equivalents of 4-chlorofluorobenzene was enough for the selective Ar–F bond cleavage reaction (Table 4, entry 4). However, in the polar solvent, THF, unknown complexes together with only small amount Ar–F and Ar–Cl bond cleavage products were obtained (Table 4, entry 5). Therefore, selective Ar–F bond cleavage can be achieved at 120 °C with 10 equivalents of KOH and 100 equivalents of 4-chlorofluorobenzene in benzene solvent.

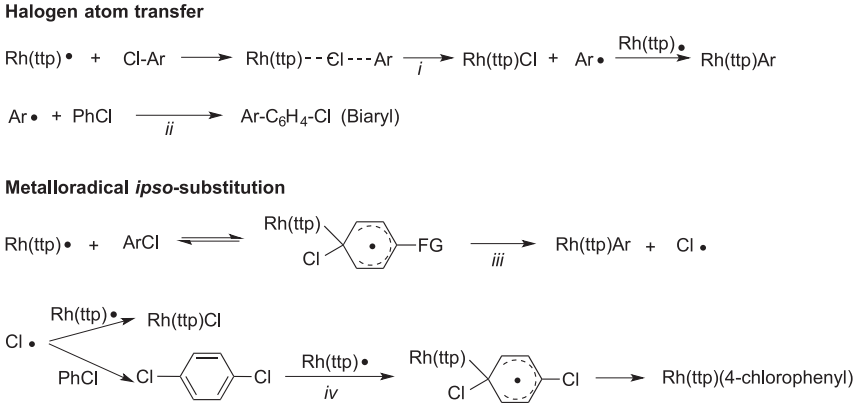
To ensure the product ratios are kinetic, the stability of the rhodium porphyrin aryls was examined. Rh(ttp) (4-chlorophenyl) (**3e**) and Rh(ttp) (4-fluorophenyl) (**3f**) were then reacted with 4-chlorofluorobenzene under the reaction conditions (eqs (1) and (2)). After 3 days, almost all the rhodium porphyrin aryls were recovered. Thus, the product ratios obtained were kinetic ratios.

2.5. Mechanistic investigation of Ar–F bond cleavage

In order to find out the origin of the selectivity, mechanistic investigations of Ar–F bond cleavage were carried out. The Ar–F bond cleavage of fluorobenzene in benzene with KOH was achieved with 77% yield of Rh(ttp)Ph (eq (3)). To rule out the possibility of direct C–H activation of benzene, fluorobenzene was reacted with Rh(ttp)Cl in benzene-d_6 with 10 equivalents of KOH. Only Rh(ttp)Ph in 50% yield was obtained without any Rh(ttp)Ph-d_5 (eq (4)). Moreover, $Rh(ttp)C_6H_5$ in C_6D_6 with KOH (10 equiv) at 120 °C in 1 day did not exchange to give any $Rh(ttp)C_6D_5$, so Rh(ttp)Ph is not formed from the Ar–H bond cleavage of benzene.

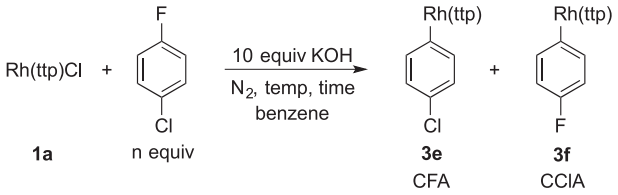
Then, Rh(ttp)H, $Rh_2(ttp)_2$ and $Rh(ttp)^-$ were tested with 1,4-difluorobenzene or fluorobenzene. Neither Rh(ttp)H nor $Rh_2(ttp)_2$ gave any Ar–F bond cleavage product (Table 5, entries 1 and 2). $Rh(ttp)^-$ however, reacted with fluorobenzene to give 40% yield of Rh(ttp)Ph (**3a**) (Table 5, entry 3). Therefore, $Rh(ttp)^-$ is the most reasonable intermediate for Ar–F bond cleavage through nucleophilic aromatic substitution mechanism as we have identified in the iridium analogues in the Ar–F bond cleavage [16].





Scheme 3. Possible mechanisms for Ar–Cl bond cleavage.

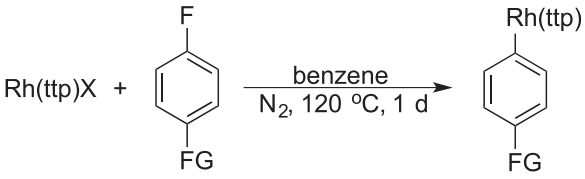
Table 4
Conditions optimization for the competitive Ar–F and Ar–Cl bond cleavage with rhodium porphyrin complexes.



Entry	n	Temp/°C	Time	Yield **3e** (CFA)/%	Yield **3f** (CClA)/%	Total yield/%
1	S.F.	200	1.5 h	6	63	69
2	S.F.	150	2 h	82	trace	82
3	S.F.	120	10 h	92	/	92
4	100	120	1 d	91	trace	91
5[a]	100	120	1 d	10	6	16

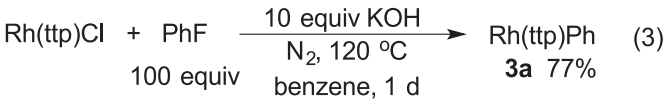
[a] THF was used as solvent.

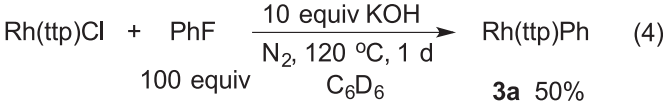
Table 5
Possible intermediate for Ar–F bond cleavage.



Entry	Rh(ttp)X	FG	Yield CFA/%
1	$Rh_2(ttp)_2$ **1b**	F	/
2	Rh(ttp)H **1c**	F	/
3[a]	$Rh(ttp)^-K^+$ **1d**	H	40

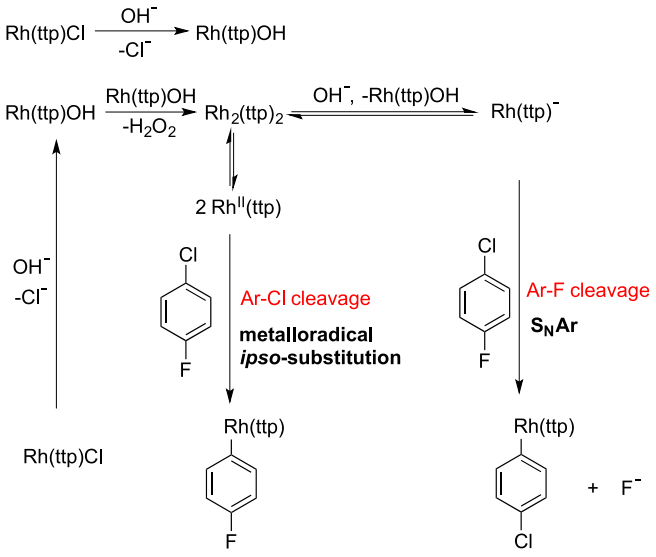
[a] 18% Rh(ttp) (2-fluorophenyl) was obtained.





2.6. Proposed mechanism for competitive Ar–F and Ar–Cl bond cleavage

From the above mechanistic investigations, we suggest that the Ar–Cl bond is cleaved by $Rh^{II}(ttp)$ radical through metalloradical *ipso*-substitution, while the Ar–F bond is cleaved by $Rh(ttp)^-$ through nucleophilic aromatic substitution (Scheme 4). From the competitive Ar–F and Ar–Cl bond cleavage reactions by Rh(ttp)Cl, the Ar–F bond cleavage was selective at lower temperature (120 °C) and the Ar–Cl bond cleavage was selective at higher temperature (200 °C). We reason the results as follows. First, the dissociation of $Rh_2(ttp)_2$ to $Rh^{II}(ttp)$ monomer requires high temperature. Moreover, at 120 °C, $Rh_2(ttp)_2$ does not cleave the Ar–Cl bond due to the strong Ar–Cl bond strength (95 kcal/mol) [8]. Thus, the $Rh(ttp)^-$ can be generated under basic conditions and cleave the Ar–F bond at lower temperature through nucleophilic substitution, which is a heterolytic cleavage. At 200 °C, in solvent-free conditions, the homolytic cleavage of Ar–Cl bond by Rh(ttp) radical operates. Likely the homolysis of $Rh_2(ttp)_2$ into $Rh^{II}(ttp)$ radical is much faster than the reaction with KOH to give $Rh(ttp)^-K^+$, the Ar–Cl bond cleavage then becomes dominant. Therefore, the selectivity of Ar–Cl or Ar–F bond cleavage can be controlled by reaction temperature and substrate concentration.



Scheme 4. Proposed mechanism for competitive Ar–Cl and Ar–F Bond cleavage with Rh(ttp)Cl.

3. Conclusions

In summary, the Ar–Cl bond of aryl chlorides can be cleaved successfully by Rh(ttp)Cl/KOH through metalloradical *ipso*-substitution mechanism to give a variety of Rh(ttp)Ar. For 4-chlorofluorobenzene, selective Ar–F bond cleavage was achieved. Ar–F bond cleavage by $Rh(ttp)^-$ through nucleophilic aromatic substitution is identified. Selective Ar–F bond cleavage is achieved at lower temperature and selective Ar–Cl bond cleavage is achieved at higher temperature.

4. Experimental section

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used without further purification.

Hexane for chromatography was distilled from anhydrous calcium chloride. Benzene and THF used as solvent were distilled from sodium. Thin-layer chromatography was performed on precoated silica gel 60 F254 plates for thin-layer analyses for the reaction mixture. All preparation reactions were carried out in a teflon screw-head stoppered pressure tube in N_2 heated in drilled holes in an aluminum block. All reactions were carried out without light irradiation by wrapping with aluminum foil. Silica gel (Merck, 70-230 and 230–400 mesh) was used for column chromatography for rhodium porphyrin aryls in air. Rh(ttp)Cl [17] $Rh_2(ttp)_2$ [18] Rh(ttp)H [18] and Rh(ttp)$^-Na^+$ [19] were prepared according to the literature procedures.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 at 300 MHz or Bruker AV400 spectrometer at 400 MHz and Bruker DPX-300 at 75 MHz or Bruker AV400 at 100 MHz respectively. Chemical shifts were reported with reference to the residual solvent protons in C_6D_6 (δ 7.15 ppm) or in $CDCl_3$ (δ 7.26 ppm) as the internal standard. ^{19}F NMR spectra were recorded on a Varian XL-400 spectrometer at 376 MHz. Chemical shifts were referenced with the external standard fluorine in $C_6H_5CF_3$ using a sealed melting point tube and put into the NMR tube (d = 0.00 ppm). Chemical shifts (d) were reported as part per million (ppm) in (d) scale downfield from $C_7H_5F_3$.Coupling constants (J) are reported in hertz (Hz) [20]. Chemical shifts (δ) were reported as part per million (ppm). Coupling constants (J) were reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were performed on a ThermoFinnigan MAT 95 XL mass spectrometer in fast atom bombardment (FAB) mode using 3-nitrobenzyl alcohol (NBA) matrix and CH_2Cl_2 as the solvent or in electrospray ionization (ESI) mode using MeOH/CH_2Cl_2 (1/1) as the solvent.

4.1. Experimental procedure

4.1.1. Reaction of Rh(ttp)Cl with PhCl, and KOH in benzene

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (7.0 mg, 0.125 mmol) and PhCl (**2a**) (0.013 mL, 0.124 mmol) were added in benzene (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C under N_2 for 6 h. Excess benzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). No product was isolated.

4.1.2. Reaction of Rh(ttp)Cl with PhCl, and KOH in THF

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (7.0 mg, 0.125 mmol) and PhCl (**2a**) (0.013 mL, 0.124 mmol) were added in THF (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C under N_2 for 3 h. Excess THF was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). No product was isolated.

4.1.3. Reaction of Rh(ttp)Cl with PhCl, and KOH in PhCN

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (7.0 mg, 0.125 mmol) and PhCl (**2a**) (0.013 mL, 0.124 mmol) were added in PhCN (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C under N_2 for 3 days. Excess PhCN was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). No product was isolated.

4.1.4. Reaction of Rh(ttp)Cl with PhCl, and KOH in benzene at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (7.0 mg, 0.125 mmol) and PhCl (**2a**) (0.013 mL, 0.124 mmol) were added in benzene (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 4 h. Excess benzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). No product was isolated.

4.1.5. Reaction of Rh(ttp)Cl with PhCl, and KOH in benzene at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (7.0 mg, 0.125 mmol) and PhCl (**2a**) (0.26 mL, 2.48 mmol) were added in benzene (0.8 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 3 h. Excess benzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp)Ph (**3a**) [11] (3.2 mg, 0.004 mmol, 31%) was collected. Rh(ttp)Ph (**3a**) ^1H NMR ($CDCl_3$, 400 MHz) δ 0.26 (d, 2H, J = 8.0 Hz), 2.69 (s, 12H), 4.75 (t, 2H, J = 7.6 Hz), 5.22 (t, 1H, J = 7.1 Hz), 7.52 (t, 8H, J = 7.8 Hz), 8.00 (d, 4H, J = 7.7 Hz), 8.06 (d, 4H, J = 7.6 Hz), 8.75 (s, 8H).

4.1.6. Reaction of Rh(ttp)Cl with PhCl, and KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in PhCl (**2a**) (1.0 mL, 9.53 mmol). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 4 h. Excess chlorobenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp)Ph (**3a**) [11] (6.3 mg, 0.007 mmol, 62%) was collected.

4.1.7. Reaction of Rh(ttp)Cl with PhCl, and KOH at 120 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in PhCl (**2a**) (1.0 mL, 9.53 mmol). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C under N_2 for 3 days. Excess chlorobenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp)Ph (**3a**) [11] (3.1 mg, 0.004 mmol, 30%) was collected.

4.1.8. Reaction of Rh(ttp)Cl with PhCl, and KOH at 200 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in PhCl (**2a**) (1.0 mL, 9.53 mmol). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 200 °C under N_2 for 2 h. Excess chlorobenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp)Ph (**3a**) [11] (6.2 mg, 0.007 mmol, 61%) was collected.

4.1.9. Reaction of Rh(ttp)Cl with 4-chloroanisole, and KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in 4-chloroanisole (**2b**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 1 day. Excess 4-chloroanisole was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp)(4-methoxyphenyl) (**3b**) [11] (4.0 mg, 0.001 mmol, 7%), Rh(ttp)Me (**4**) [12b] (0.7 mg, 0.005 mmol, 43%) and Rh(ttp)CH_2O(4-chlorophenyl) (**5**) (4.0 mg, 0.005 mmol, 41%) were collected. Rh(ttp)(4-methoxyphenyl) (**3b**) ^1H NMR ($CDCl_3$, 400 MHz) δ 0.15 (d, 2H, J = 7.9 Hz), 2.69 (s, 12H), 2.77 (s, 3H), 4.44 (d, 2H, J = 9.1 Hz), 7.53 (t, 8H, J = 6.6 Hz), 8.01 (d, 4H, J = 7.4 Hz), 8.06 (d, 4H, J = 7.4 Hz), 8.76 (s, 8H). Rh(ttp)Me (**4**) ^1H NMR ($CDCl_3$, 400 MHz) δ −5.82 (d, 3H,

$J = 3.0$ Hz), 2.96 (s, 12H), 7.53 (d, 8H, $J = 7.5$ Hz), 8.01 (dd, 4H, $J = 2.4$, 8.4 Hz), 8.07 (dd, 4H, $J = 2.4$, 8.4 Hz), 8.73 (s, 8H). Rh(ttp)CH_2O(4-chlorophenyl) (**5**), R_f = 0.72 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.83 (d, 2H, $J = 3.2$ Hz), 2.71 (s, 12H), 3.56 (d, 2H, $J = 8.8$ Hz), 6.33 (d, 2H, $J = 8.8$ Hz), 7.54 (m, 8H), 8.00 (m, 8H), 8.71 (s, 8H). Calcd. For $(C_{55}H_{42}ClN_4ORh)^+$: *m/z* 912.2097 Found: *m/z* 912.2094.

4.1.10. Reaction of Rh(ttp)Cl with 4-chlorotoluene, and KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in 4-chlorotoluene (**2c**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 1 day. Excess 4-chlorotoluene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp) (4-toly) (**3c**) [11] (3.0 mg, 0.003 mmol, 29%), Rh(ttp) (4-Cl)Bn (**9**) [12a] (1.2 mg, 0.001 mmol, 11%) were collected. Rh(ttp) (4-toly) (**3c**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.17 (d, 2H, $J = 6.9$ Hz), 1.08 (s, 3H), 2.69 (s, 12H), 4.61 (d, 2H, $J = 8.4$ Hz), 7.52 (t, 8H, $J = 6.0$ Hz), 8.01 (d, 4H, $J = 8.7$ Hz), 8.05 (d, 4H, $J = 8.6$ Hz), 8.75 (s, 8H). Rh(ttp) (4-Cl)Bn (**9**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ −3.83 (d, 2H, $J = 3.9$ Hz), 2.71 (s, 12H), 2.84 (d, 2H, $J = 8.4$ Hz), 5.80 (d, 2H, $J = 8.4$ Hz), 7.55 (t, 8H, $J = 7.2$ Hz), 7.96 (d, 4H, $J = 8.0$ Hz), 8.06 (d, 4H, $J = 7.8$ Hz), 8.69 (s, 8H).

4.1.11. Reaction of Rh(ttp)Cl with 4-chloro-tert-butylbenzene, and KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in 4-chloro-*tert*-butylbenzene (**2d**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 1 day. Excess 4-chloro-*tert*-butylbenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp) (4-*tert*-butylphenyl) (**3d**) [11] (9.2 mg, 0.010 mmol, 85%) was collected. Rh(ttp) (4-*tert*-butylphenyl) (**3d**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.23 (d, 2H, $J = 8.5$ Hz), 0.35 (s, 9H), 2.70 (s, 12H), 4.80 (d, 2H, $J = 8.8$ Hz), 7.53 (t, 8H, $J = 6.4$ Hz), 8.03 (d, 4H, $J = 7.2$ Hz), 8.08 (d, 4H, $J = 7.5$ Hz), 8.78 (s, 8H).

4.1.12. Reaction of Rh(ttp)Cl with 1,4-dichlorobenzene, and KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in 1,4-dichlorobenzene (**2e**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 1 day. Excess 1,4-dichlorobenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp) (4-chlorophenyl) (**3e**) [11] (5.0 mg, 0.006 mmol, 47%) was collected. Rh(ttp) (4-chlorophenyl) (**3e**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.16 (d, 2H, $J = 8.8$ Hz), 2.70 (s, 12H), 4.78 (d, 2H, $J = 8.8$ Hz), 7.54 (t, 8H, $J = 6.0$ Hz), 8.00 (d, 4H, $J = 4.5$ Hz), 8.07 (d, 4H, $J = 4.6$ Hz), 8.79 (s, 8H).

4.1.13. Reaction of Rh(ttp)Cl with 4-chlorofluorobenzene, and KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in 4-chlorofluorobenzene (**2f**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 200 °C under N_2 for 1 day. Excess 4-chlorofluorobenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp) (4-fluorophenyl) (**3f**) [11] (6.5 mg, 0.008 mmol, 63%) was collected. Rh(ttp) (4-fluorophenyl) (**3f**) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.16 (dd, 2H, $^4J_{H\text{-}F} = 1.8$, $J = 8.9$ Hz), 2.69 (s, 12H), 4.55 (dd, 2H, $^3J_{H\text{-}F} = 8.6$, $J = 8.9$ Hz), 7.54 (d, 8H, $J = 6.3$ Hz), 7.99 (dd, 4H, $J = 2.2$, 8.5 Hz), 8.02 (dd, 4H, $J = 2.2$, 8.7 Hz), 8.74 (s, 8H).

4.1.14. Reaction of Rh(ttp)Cl with 4-chlorobenzotrifluoride, and KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in 4-chlorobenzotrifluoride (**2g**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 1 day. Excess 4-chlorobenzotrifluoride was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp) (4-trifluoromethylphenyl) (**3g**) (8.1 mg, 0.008 mmol, 74%) was collected. Rh(ttp) (4-trifluoromethylphenyl) (**3g**), R_f = 0.58 (hexane/CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.34 (d, 2H, $J = 8.3$ Hz), 2.69 (s, 12H), 5.01 (d, 2H, $J = 8.7$ Hz), 7.54 (t, 8H, $J = 6.5$ Hz), 8.00 (d, 4H, $J = 7.6$ Hz), 8.06 (d, 4H, $J = 7.6$ Hz), 8.80 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.69, 30.00, 120.09, 123.10, 127.62, 128.88, 131.62, 131.93, 133.88, 134.26, 137.59, 138.98, 143.10. Calcd. for $(C_{55}H_{40}F_3N_4Rh)^+$: *m/z* 916.2255 Found: *m/z* 916.2258.

4.1.15. Reaction of Rh(ttp)Cl with 4-nitrochlorobenzene, and KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol) and KOH (7.0 mg, 0.125 mmol) were added in 4-nitrochlorobenzene (**2h**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C under N_2 for 1 day. Excess 4-nitrochlorobenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp) (4-nitrophenyl) (**3h**) [11] (7.6 mg, 0.008 mmol, 71%) was collected. Rh(ttp) (4-nitrophenyl) (**3h**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.37 (d, 2H, $J = 8.2$ Hz), 2.70 (s, 12H), 5.61 (d, 2H, $J = 9.1$ Hz), 7.55 (t, 8H, $J = 5.9$ Hz), 8.00 (d, 4H, $J = 7.2$ Hz), 8.06 (d, 4H, $J = 7.1$ Hz), 8.83 (s, 8H).

4.1.16. Reaction of $Rh_2(ttp)_2$ with PhCl

$Rh_2(ttp)_2$ (**1b**) (9.3 mg, 0.006 mmol) was added in PhCl (**2a**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C under N_2 for 1 h. Excess chlorobenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp)Cl (**1a**) (0.7 mg, 0.001 mmol, 7%), Rh(ttp) (4-chlorophenyl) (**3e**) [11] (1.0 mg, 0.001 mmol, 10%) and Rh(ttp)Ph (**3a**) [11] (2.2 mg, 0.003 mmol, 22%) were collected.

4.1.17. Reaction of Rh(ttp)H with PhCl

Rh(ttp)H (**1c**) (9.3 mg, 0.012 mmol) was added into PhCl (**2a**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C under N_2 for 1 day. Excess chlorobenzene was removed by vacuum distillation. The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp)Ph (**3a**) [11] (0.8 mg, 0.001 mmol, 8%) was collected.

4.1.18. Reaction of $Rh(ttp)^-K^+$ with PhCl

$Rh(ttp)^-K^+$ (**1d**) (9.3 mg, 0.012 mmol) was added into PhCl (**2a**) (1.0 mL). The red mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C under N_2 for 1 day. Excess chlorobenzene was removed by vacuum distillation.

The red residue was purified by column chromatography on silica gel eluting with a solvent mixture of hexane/CH_2Cl_2 (1:1). Red solid Rh(ttp)Ph (**3a**) [11] (3.0 mg, 0.004 mmol, 30%) was collected.

4.1.19. Reaction between Rh(ttp)Cl and 4-chlorofluorobenzene with 10 equiv KOH at 200 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (6.7 mg, 0.12 mmol, 10 equiv) were added to 4-chlorofluorobenzene (**2f**) (1.0 mL). The mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 200 °C for 1.5 h. Excess 4-chlorofluorobenzene was removed by vacuum distillation. The brown residue was purified by column chromatography on silica gel eluting with a mixture of hexane/CH_2Cl_2 (1:1). Purple solid of Rh(ttp) (4-chlorophenyl) (**3e**) [11] (0.7 mg, 0.001 mmol, 6%) and Rh(ttp) (4-fluorophenyl) (**3f**) [11] (7.2 mg, 0.008 mmol, 63%) were isolated.

4.1.20. Reaction between Rh(ttp)Cl and 4-chlorofluorobenzene with 10 equiv KOH at 150 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (6.7 mg, 0.12 mmol, 10 equiv) were added to 4-chlorofluorobenzene (**2f**) (1.0 mL). The mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 150 °C for 2 h. Excess 4-chlorofluorobenzene was removed by vacuum distillation. The brown residue was purified by column chromatography on silica gel eluting with a mixture of hexane/CH_2Cl_2 (1:1). Purple solid of Rh(ttp) (4-chlorophenyl) (**3e**) [11] (9.6 mg, 0.010 mmol, 82%) and Rh(ttp) (4-fluorophenyl) (**3f**) [11] (trace, < 5%) were isolated.

4.1.21. Reaction between Rh(ttp)Cl and 4-chlorofluorobenzene with 10 equiv KOH at 120 °C

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (6.7 mg, 0.12 mmol, 10 equiv) were added to 4-chlorofluorobenzene (**2f**) (1.0 mL). The mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C for 10 h. Excess 4-chlorofluorobenzene was removed by vacuum distillation. The brown residue was purified by column chromatography on silica gel eluting with a mixture of hexane/CH_2Cl_2 (1:1). Purple solid of Rh(ttp) (4-chlorophenyl) (**3e**) [11] (10.1 mg, 0.011 mmol, 92%) was isolated.

4.1.22. Reaction between Rh(ttp)Cl and 4-chlorofluorobenzene with 10 equiv KOH at 120 °C in benzene solvent

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (6.7 mg, 0.12 mmol, 10 equiv) and 4-chlorofluorobenzene (**2f**) (0.15 mL, 100 equiv) were added in benzene (1.0 mL). The mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C for 1 day. Excess benzene was removed by vacuum distillation. The brown residue was purified by column chromatography on silica gel eluting with a mixture of hexane/CH_2Cl_2 (1:1). Purple solid of Rh(ttp) (4-chlorophenyl) (**3e**) [11] (10.7 mg, 0.011 mmol, 91%) and Rh(ttp) (4-fluorophenyl) (**3f**) [11] (trace, < 5%) were isolated.

4.1.23. Reaction between Rh(ttp)Cl and 4-chlorofluorobenzene with 10 equiv KOH at 120 °C in THF

Rh(ttp)Cl (**1a**) (10.0 mg, 0.012 mmol), KOH (6.7 mg, 0.12 mmol, 10 equiv) and 4-chlorofluorobenzene (**2f**) (0.15 mL, 100 equiv) were added in THF (1.0 mL). The mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C for 1 day. Excess THF was removed by vacuum distillation. The brown residue was purified by column chromatography on silica gel eluting with a mixture of hexane/CH_2Cl_2 (1:1). Purple solid of Rh(ttp) (4-chlorophenyl) (**3e**) [11] (1.0 mg, 0.001 mmol, 10%) and Rh(ttp) (4-fluorophenyl) (**3f**) [11] (0.7 mg, 0.001 mmol, 6%) were isolated.

4.1.24. Reaction between Rh(ttp) (4-fluorophenyl) and 4-fluorochlorobenzene with 10 equiv KOH at 120 °C for 3 days in benzene solvent

Rh(ttp) (4-fluorophenyl) (**3f**) (10.0 mg, 0.010 mmol), KOH (6.2 mg, 0.11 mmol, 10 equiv) and 4-fluorochlorobenzene (2f) (0.24 ml, 200 equiv) were added in benzene (1.0 mL). The mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 120 °C for 3 day. Excess benzene was removed by vacuum distillation. The brown residue was purified by column chromatography on alumina eluting with a mixture of hexane/CH_2Cl_2 (2:1). Purple solid of Rh(ttp) (4-fluorophenyl) (3f) [11] (9.3 mg, 0.010 mmol, 93%) and Rh(ttp) (4-chlorophenyl) (3e) [11] (trace, < 5%) were isolated.

4.1.25. Reaction between Rh(ttp) (4-chlorophenyl) and 4-chlorofluorobenzene with 10 equiv KOH at 200 °C for 3 days

Rh(ttp) (4-chlorophenyl) (**3e**) (10.0 mg, 0.010 mmol), KOH (6.2 mg, 0.11 mmol, 10 equiv) were added into 4-fluorochlorobenzene (**2f**) (1.0 mL). The mixture was degassed for three freeze-thaw-pump cycles, purged with N_2 and heated at 200 °C for 3 days. Excess 4-chlorofluorobenzene was removed by vacuum distillation. The brown residue was purified by column chromatography on alumina eluting with a mixture of hexane/CH_2Cl_2 (2:1). Purple solid of Rh(ttp) (4-chlorophenyl) (**3e**) [11] (9.8 mg, 0.010 mmol, 98%) and Rh(ttp) (4-fluorophenyl) (**3f**) [11] (trace, < 5%) were isolated.

4.1.26. Reaction of fluorobenzene with Rh(ttp)Cl in benzene

A mixture of Rh(ttp)Cl (**1a**) (30.0 mg, 0.037 mmol), 10 equiv of KOH (20.8 mg, 0.37 mmol) and fluorobenzene (0.30 mL, 3.7 mmol) with benzene (1.50 mL, 18.5 mmol) were degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 1 d. The solvent was then removed in vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Ph (**3a**) [11] (23.1 mg, 0.028 mmol, 77%).

4.1.27. Reaction of fluorobenzene with Rh(ttp)Cl in C_6D_6

A mixture of Rh(ttp)Cl (**1a**) (30.0 mg, 0.037 mmol), 10 equiv of KOH (20.8 mg, 0.37 mmol) and fluorobenzene (0.30 mL, 3.7 mmol) with C_6D_6 (1.50 mL, 18.5 mmol) were degassed for three freeze-−thawpump cycles and heated at 120 °C under N_2 for 1 d. The solvent was then removed in vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Ph (**3a**) [11] (15.3 mg, 0.018 mmol, 50%).

4.1.28. Reaction of 1,4-difluorobenzene with $Rh_2(ttp)_2$

A solution of $Rh_2(ttp)_2$ (**1b**) (15.0 mg, 0.010 mmol), 1,4-difluorobenzene (0.19 mL, 1.9 mmol) in benzene (0.93 mL, 8.5 mmol) was degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 1 d. The solvent was then removed in vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a mixture of hexane: CH_2Cl_2 (1:1) to give an unidentified mixture of complexes.

4.1.29. Reaction of 1,4-difluorobenzene with Rh(ttp)H

A solution of Rh(ttp)H (**1c**) (15.0 mg, 0.019 mmol), 1,4-difluorobenzene (0.19 mL, 1.9 mmol) in benzene (0.93 mL, 8.5 mmol) was degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 1 d. The solvent was then removed in vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a mixture of hexane: CH_2Cl_2 (1:1) to give an unidentified mixture of complexes.

4.1.30. Reaction of fluorobenzene with Rh(ttp)$^-K^+$ precursor Rh(ttp)SiEt$_3$ with KOH

A mixture of Rh(ttp)SiEt$_3$ (15.0 mg, 0.017 mmol) and 10 equiv of KOH (9.6 mg, 0.17 mmol) and fluorobenzene (0.17 mL, 1.7 mmol) in benzene (1 mL) were degassed for three freeze-thaw-pump cycles and heated at 120 °C under N_2 for 4 d. The solvent was then removed by vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a mixture of hexane: CH_2Cl_2 (1:1) to give Rh(ttp)Ph (**3a**) (6.0 mg, 7 μmol, 40%) and Rh(ttp) (2-fluorophenyl) (2.7 mg, 3 μmol, 18%). Rh(ttp) (2-fluorophenyl) R_f = 0.58 (hexane: CH_2Cl_2 = 1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.01 (m, 1H), 2.69 (s, 12H), 4.48 (t, 1H, J = 7.3 Hz), 4.68 (dd, 1H, J = 7.3, $^1J_{H\text{-}F}$ = 8.3 Hz), 5.28 (dd, 1H, J = 7.3, 7.5 Hz) 7.53 (t, 8H, J = 7.3 Hz), 8.02 (dd, 4H, J = 2.2, 8.6 Hz), 8.07 (dd, 4H, J = 2.2, 8.6 Hz), 8.79 (s, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.76, 107.43 (d, $^1J_{C\text{-}F}$ = 25.2 Hz), 112.10, (d, $^1J_{C\text{-}Rh}$ = 27.8 Hz), 119.43, 122.09, 122.87, 127.52, 131.75, 132.30, 133.75, 134.25, 137.38, 139.18, 143.55. ^{19}F NMR ($CDCl_3$, 376 MHz) δ −45.15 (s, 1F, *o*-F). Calcd for $(C_{54}H_{40}N_4FRh)^+$: m/z 866.2238. Found: m/z 866.2287.

Acknowledgments

We thank the Research Grants Council (No 400212) of the HKSAR and a Special Equipment Grant (SEG/CUHK09) from University Grants Committee for financial support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.05.039.

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