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C–H Activation of π -Arene Ruthenium Complexes

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ABSTRACT: We present a C–H activation protocol for aromatic compounds that overcomes the current limitations of the need for directing group or covalently-bound activating groups, by exploiting the increase in C–H acidity of aromatic compounds when π -coordinated to a Ru(II) centre. The increased acidity facilitates catalytic concerted metalation-deprotonation and subsequent arylation reactions. We present the development and optimization of the C–H activation protocol and show the applicability of the reaction to a range of aromatic substrates, including the simplest of substrates (benzene). Furthermore, we demonstrate the recyclability of the activating Ru(II) fragment, using photolysis and give a mechanistic study, which provides strong evidence that this reaction occurs via a silver-mediated C–H bond activation. This is the first time Ru complexes have been shown to allow C–H activation of arenes by a π -coordination mechanism.

INTRODUCTION

C–H activation is a major current theme in synthetic chemistry, as it has the potential to simplify chemical transformations in an atom efficient manner.^{1–5} Applications of this versatile synthetic strategy range from pharmaceutical^{6–8} and agrochemical^{9,10} to bulk commodity chemical^{11,12} and materials syntheses^{13,14}. Activation protocols for sp, sp² and sp³ carbon centres have all been reported in the literature,¹⁵ but in each case privileged substrates are required to facilitate activation. The majority of C(sp²)–H activation reactions require substrates that fall in to one of three classes: (1) arenes incorporating a directing group (DG) that coordinates a transition metal catalyst; (2) electron rich arenes and (3) electron deficient arenes (Scheme 1). The directing group strategy requires arenes that incorporate a coordinating moiety, often amido or pyridyl that positions a metal catalyst close to a C–H bond and activation occurs via a cyclometalated intermediate. C–H activation is typically *ortho* to the DG,^{16–18} although *meta*^{19–21} and *para*²² C–H activation have also been achieved. Many precious (Pd,^{23,24} Ir,^{25,26} Rh^{27,28}) and non-precious metal (Mn,^{29,30} Fe,³¹ Co,³² Cu³³) catalyzed reactions have been reported that rely upon this directing group strategy. Heteroaromatics, with electron-rich π systems, such as furans, thiophenes and azoles, can all undergo Pd-catalysed C–H activation.³⁴ Directing groups are not required in these systems as the intrinsic electronic properties of the heteraromatics control regioselectivity. Electron-deficient arenes can undergo C–H activation, but typically require two electron-withdrawing groups (EWGs) *ortho* to the C–H bond of interest.³⁵ An important example in this class of reaction is the C–H activation of pentafluorobenzene,³⁶ reported by Fagnou, via a concerted metalation-deprotonation (CMD) mechanism.

(i) directing groups

(ii) electron-rich aromatics

(iii) electron-deficient aromatics

Scheme 1. Strategies towards C–H activation (DG = directing group, EWG = electron-withdrawing group)

Each of these three strategies for C–H activation requires either arenes with covalently bound substituents or heteroaromatics. As a result, substrate scope is limited and additional synthetic steps are required to incorporate the required substituents. This is a major drawback to the applicability of the current state-of-the-art C–H activations. Hence, new reaction pathways are required to overcome these limitations.

Metal complexes can activate aromatics through π -complexation,^{37–45} which typically leads to an increase in arene electrophilicity, as well as an increase in acidity of arene C–H bonds.⁴⁴ Larrosa has exploited the latter property to develop a C–H activation protocol that involves Pd-catalysed coupling between a $[(\eta^6\text{-arene})\text{Cr}(\text{CO})_3]$ complex and aryl iodides (Scheme 2i).⁴⁶ Subsequent oxidative cleavage of the Cr–arene bond with MnO_2 leads to formation of a selection of biaryls. Recently, we reported a catalytic $\text{S}_{\text{N}}\text{Ar}$ reaction of unactivated aryl halides,⁴⁷ which exploits the increase in electrophilicity of η^6 -bound arenes. This reaction

proceeds via a transient $[(\eta^6\text{-arene})\text{RuCp}]^+$ intermediate (Scheme 2ii), requires 10 mol% of the Ru catalyst and gives yields up to 90%.

(i) C-H activation of $(\eta^6\text{-arene})\text{-Cr}$ complex

(ii) $S_N\text{Ar}$ via transient $(\eta^6\text{-arene})\text{-Ru}$ complex

(iii) This work

Scheme 2. Arene activation through π -coordination.

We hypothesize that π -coordination of arenes to a $\text{Ru}^{\text{II}}\text{Cp}$ fragment will allow C–H activation of the bound arene through a CMD mechanism, due to the increase in acidity of the C–H bond. Supported by our catalytic $S_N\text{Ar}$, we suggest an analogous C–H activation reaction catalytic in Ru is feasible, via transient formation of the activated $(\eta^6\text{-arene})\text{-Ru}$ complex. Herein, we report the successful development of C–H activation of $[(\eta^6\text{-arene})\text{RuCp}]^+$ complexes, proceeding via a concerted metalation-deprotonation mechanism (Scheme 2iii). We show the application of this reaction to aryl fluorides and unactivated arenes, benzene and *p*-cymene. Furthermore, we demonstrate the potential to recover the activating $\text{Ru}^{\text{II}}\text{Cp}$ fragment via photolysis, which represents a key step towards the development of Ru-catalysed C–H activation of unfunctionalized substrates, via an arene exchange mechanism. This is the first time Ru complexes have been used to achieve C–H activation of arenes by this π -coordination strategy.

RESULTS AND DISCUSSION

Initially, we sought to investigate the C–H activation of *ortho*-fluorotoluene bound to a $[\text{CpRu}]^+$ fragment. Reaction of $[\text{CpRu}(\text{NCMe})_3]\text{PF}_6$ and *ortho*-fluorotoluene in 1,2-dichloroethane afforded $[\text{CpRu}(\eta^6\text{-}(o\text{-MeC}_6\text{H}_5\text{F}))\text{PF}_6$ (**1a**) in 88% yield. This complex was fully characterized by multinuclear NMR, mass spectrometry and C,H,N elemental analysis.

Reaction Optimization

Predicting a C–H activation mechanism involving concerted metalation-deprotonation, our initial catalytic reaction conditions emulated those of previous work, using catalytic $\text{Pd}(\text{PPh}_3)_4$ along with stoichiometric Ag(I) salt, carboxylic acid and base (Table 1, Entry 1).⁴⁶ Upon observing no reaction, we reasoned that solvent effects were likely to play an important role in stabilizing key transition states of the C–H activation. While several solvents also returned no product, reaction in 1,2-dichloroethane gave the desired product, albeit in low yield (Table 1, entry 3). The coupled product **1b** was easily identified by characteristic changes in the ^1H - and ^{19}F -NMR spectra, along with further confirmation by high resolution mass spectrometry. By increasing the reaction temperature to 120 °C, product conversion increased to 38% (Table 1, entry 5). A screen of potential bases (see Supp. Info. For full details) identified 2,2,6,6-tetramethylpiperidine (TMP) as the most effective, giving a conversion of 44% (Table 1, entry 9). The role of the TMP is likely the deprotonation of the carboxylic acid precursor.

Table 1 C-H activation reaction between complex **1a** and 4-iodoanisole under a variety of conditions (see Supp. Info. for full experimental detail). Conversions to **1b** were determined by ^1H - and ^{19}F -NMR against an internal standard. (Cp = cyclopentadienyl, 1-AdCO₂H = 1-adamantanecarboxylic acid, 1,2-DCE = 1,2-dichloroethane, DMF = *N,N*-dimethylformamide, TMP = 2,2,6,6-tetramethylpiperidine, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, NMI = *N*-methylimidazole).

Entry	Solvent	Temp. (°C)	Base	Conversion (%)
1	Toluene	60	K ₂ CO ₃	0
2	DMF	60	K ₂ CO ₃	0
3	1,2-DCE	60	K ₂ CO ₃	10
4	1,2-DCE	100	K ₂ CO ₃	28
5	1,2-DCE	120	K ₂ CO ₃	38
6	1,2-DCE	120	Pyridine	7
7	1,2-DCE	120	DBU	0
8	1,2-DCE	120	NMI	0
9	1,2-DCE	120	TMP	44

Throughout our initial investigations, in all reactions that had undergone C–H activation, we observed 5–30% conversion to a reaction side-product, which we identified as complex **1c**, in which a phenyl group replaces the anisyl group in the reaction product (Scheme 3). We supposed that this species may have formed by a demethoxylation process, in which the aryl ether bond is broken.⁴⁸ To test this hypothesis, we subjected **2a** to the reaction conditions in Table 1, entry 9 and found only formation of the expected C–H activation product **2b** and the phenyl-containing side-product **1c**, but, importantly, no formation of **2c**, a potential product of breaking the aryl ether bond. This result led us to reason that the source of the phenyl coupled product must be the

PPh_3 ligand of the Pd catalyst. Such scrambling of the aryl groups has previously been observed.^{49,50} To avoid formation of this side-product, we explored the use of alternative Pd catalysts, along with a selection of phosphine ligands. We also chose to investigate the effect of the carboxylic acid and silver salt upon the reaction (Table 2).

Scheme 3 Formation of phenylated by-product **1c**. *a* reaction conditions shown in Table 1, Entry 9.

The C–H activation reaction proceeded in the absence of ligand using PdCl_2 , $\text{Pd}_2(\text{dba})_3$ and $\text{Pd}(\text{OAc})_2$ (Table 2, entries 1, 3 and 6). However, addition of phosphine ligands increased conversion significantly. Phosphine ligands containing no phenyl groups (Table 2, entries 5, 7 and 8) circumvented the formation of phenylated product **1c** and generally gave the highest conversions. The combination of $\text{Pd}(\text{OAc})_2$ and DavePhos gave 69% conversion to the desired product. An exploration into the effect of the carboxylic acid revealed that the absence of acid severely hindered the reaction (Table 2, entry 9) and that 1-adamantanecarboxylic acid (1-AdCO₂H) was the optimum choice of acid. The conjugate base of the carboxylic acid is involved in a key transition state of the CMD reaction (*vide infra*). Removing silver from the reaction mixture completely turned off product formation (Table 2, entry 11). Alternative silver salts to

Ag₂CO₃ gave no improvement in reaction conversion, but increasing the quantity of Ag₂CO₃ to 2 equivalents showed a further increase in reaction conversion. Overall optimized reaction conditions gave 83% conversion (Table 2, entry 16).

Table 2 C-H activation reaction between complex **1a** (1 equivalent) and 4-iodoanisole (1.5 equivalents) under a variety of conditions (see Supp. Info. for full experimental detail). Conversions to **1b** were determined by ¹H- and ¹⁹F-NMR against an internal standard. (Cp = cyclopentadienyl, 1-AdCO₂H = 1-adamantanecarboxylic acid, 1,2-DCE = 1,2-dichloroethane, TMP = 2,2,6,6-tetramethylpiperidine, dppe = 1,2-bis(diphenylphosphino)ethane, dba = dibenzylideneacetone, DavePhos = 2-dicyclohexylphosphino-2'-(*N,N*-dimethylamino)biphenyl); SPhos = 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl).

Entry	[Pd]	Ligand	Acid	Ag salt (equiv.)	Conversion (%)
1	PdCl ₂	—	1-AdCO ₂ H	Ag ₂ CO ₃ (0.75)	30
2	PdCl ₂	dppe	1-AdCO ₂ H	Ag ₂ CO ₃ (0.75)	51
3	Pd ₂ (dba) ₃	—	1-AdCO ₂ H	Ag ₂ CO ₃ (0.75)	10
4	Pd ₂ (dba) ₃	dppe	1-AdCO ₂ H	Ag ₂ CO ₃ (0.75)	34
5	Pd ₂ (dba) ₃	DavePhos	1-AdCO ₂ H	Ag ₂ CO ₃ (0.75)	28
6	Pd(OAc) ₂	—	1-AdCO ₂ H	Ag ₂ CO ₃ (0.75)	16
7	Pd(OAc) ₂	SPhos	1-AdCO ₂ H	Ag ₂ CO ₃ (0.75)	49
8	Pd(OAc) ₂	DavePhos	1-AdCO ₂ H	Ag ₂ CO ₃ (0.75)	69
9	Pd(OAc) ₂	DavePhos	—	Ag ₂ CO ₃ (0.75)	8
10	Pd(OAc) ₂	DavePhos	PivCO ₂ H	Ag ₂ CO ₃ (0.75)	17
11	Pd(OAc) ₂	DavePhos	1-AdCO ₂ H	—	0
12	Pd(OAc) ₂	DavePhos	1-AdCO ₂ H	AgOTf (1.50)	2
13	Pd(OAc) ₂	DavePhos	1-AdCO ₂ H	Ag ₂ O (0.75)	22
14	Pd(OAc) ₂	DavePhos	1-AdCO ₂ H	Ag ₂ CO ₃ (0.50)	29
15	Pd(OAc) ₂	DavePhos	1-AdCO ₂ H	Ag ₂ CO ₃ (1.00)	74
16	Pd(OAc)₂	DavePhos	1-AdCO₂H	Ag₂CO₃ (2.00)	83

In a final investigation we varied the solvent choice under optimized conditions. The reaction proceeded in dioxane (46%) and CHCl_3 (23%), but 1,2-dichloroethane remained the best reaction solvent. Varying the quantity of carboxylic acid showed no improvement in reaction conversion, whilst increasing the amount of Pd, led to the formation of di-substituted product, with 20 mol% $\text{Pd}(\text{OAc})_2$ giving 75% mono-substituted- and 5% di-substituted product (see Supp. Info. for full details).

Reaction Scope

With optimized conditions in hand, we set out to explore the scope of the C-H activation reaction (Table 3). We found that aryl iodides outperformed aryl bromides (Table 3, entry 2) and aryl chlorides were inactive under the reaction conditions, consistent with a mechanism that proceeds via oxidative addition. A selection of aryl iodides underwent reaction in varying yields, with electron-rich aryl iodides (Table 3, entries 1, 5 and 8) giving higher conversions than electron-deficient substrates (Table 3, entry 6). This is more likely due to the less efficient transmetalation of the subsequent Pd-Ar species, as opposed to slower oxidative addition, which is generally successful for electron-deficient arenes. Hindered aryl iodides also showed a reduction in reaction conversion (Table 3, entry 7) and iodobutane and vinyl iodide gave no coupled product under the reaction conditions.

With iodoanisole as a coupling partner, we also explored the C-H activation of a range of η^6 -coordinated arenes. The fluorobenzene complex proceeded to give 60% mono-substituted product and approximately 5% di-substitution, resulting from C-H activation at each *ortho* position (Table 3, Entry 9). η^6 -Bound nitrobenzene and chlorotoluene showed no C-H activation, returning only starting material, while trifluorotoluene gave a small amount of conversion.

Pleasingly, under the optimized reaction conditions, η^6 -bound benzene and *p*-cymene gave coupled products, albeit in moderate yields (16% and 20%, respectively, Table 3, entries 13 and 14), demonstrating the potential for C–H activation of non-fluorinated arenes. The ability to activate unfunctionalized arenes via this reaction mechanism is extremely exciting, as the vast majority of C–H activation mechanisms require the presence of directing or activating groups. η^6 -Bound electron-rich arene were not tested, as it is unlikely they will undergo concerted metalation-deprotonation. Isolated yields are generally low, due to the small scale of reaction (15 mg starting complex).

Table 3 C-H Activation reaction between various Ru(II) complexes (1 equivalent) and aryl halides (1.5 equivalents) under the optimized reaction conditions (see Supporting Information for full list of conditions). Conversions were determined by ^1H - and ^{19}F -NMR against an internal standard. Isolated yields in parentheses. Reactions with conversions less than 20% were not isolated. ^aReaction of the fluorobenzene complex led to 5% formation of di-substituted product.

Entry			Conversion (%)	Entry			Conversion (%)
1			83 (33)	8			54 (5)
2			52 (29)	9			60 ^a (10)
3			0	10			0
4			68 (15)	11			10
5			61 (8)	12			0
6			6	13			16

Photolysis

One advantage to using the $[\text{CpRu}^{\text{II}}]$ fragment as a method to activate η^6 -bound arenes is the ease with which the bound arene can be liberated upon completion of the reaction, with regeneration of $[\text{CpRu}(\text{NCMe})_3]^+$.⁵¹ To investigate the potential of metal complex recovery, we carried out a reaction between η^6 -bound *o*-fluorotoluene and iodoanisole under the optimized reaction conditions. Following purification by column chromatography, a solution of the η^6 -bound product in d_3 -MeCN was exposed to UV light (365 nm, 9 W). Photolysis was monitored by ^1H -NMR (Figure 1). After 2 h irradiation 85% photolysis had occurred, leading to the unbound arene product and $[\text{CpRu}(\text{d}_3\text{-NCMe})_3]^+$. After 6 h, the photolysis had proceeded to 99% completion. The liberated Ru complex, $[\text{CpRu}(\text{NCMe})_3]^+$ is the same complex used to generate the initial η^6 -bound *o*-fluorotoluene that underwent C–H activation. This demonstrates the potential for a C–H activation protocol that is overall catalytic in Ru. In our previous work, we have shown reactions of arenes that are catalysed by transient formation of η^6 -arene–Ru complexes and our future work will focus on producing a one-pot C–H activation, catalytic in Ru.

Figure 1. Photolysis (365 nm, 9 W, d₃-MeCN, 298 K) over 6 h showing full conversion to the free arene **1d** and [CpRu(d-NCMe)₃]⁺.

Mechanistic Study

Two mechanisms have been proposed in the literature by which electron-deficient arenes may undergo concerted metalation-deprotonation C–H activation. Early reports suggested a Pd-mediated CMD process, with Ag(I) salts used as scavengers for liberated halides (see Supp. Info. Scheme S2).³⁶ However, more recently, it has been demonstrated that Ag(I) may in fact be involved in the key CMD reaction step, followed by transmetalation of the activated [Ag]–arene to Pd.^{52–54}

Scheme 4 Ag-catalyzed H/D exchange experiment.

In an attempt to better understand the reaction mechanism by which our protocol is proceeding, we subjected complex **1a** to the optimized reactions conditions in the absence of $\text{Pd}(\text{OAc})_2$, but with addition of 10 equivalents of D_2O (Scheme 4). Under these conditions around 50% H/D exchange took place at the hydrogen in the *ortho* position to fluorine (see Supp. Info. Schemes S2 and S3). This provides strong evidence for a Ag-mediated C–H activation, consistent with the mechanism shown in Scheme 5. In additional control experiments, we omitted systematically each component of the reaction mixture. We found that absence of Pd or absence of Ag gives no reaction product or intermediates, with complete retention of starting material. Reactions will proceed slowly in the absence of 1-AdCO₂H, likely due to the presence of alternative sources of carboxylate (AcO^- , Ag_2CO_3). Overall, we reason that C–H activation occurs through a CMD mechanism and that Ag is indeed responsible for the initial C–H activation step.

Scheme 5 Proposed mechanism via concerted metalation-deprotonation (CMD) C–H activation.

CONCLUSION

Catalytic C–H activation leads to more efficiency and atom economical syntheses. The vast majority of reactions rely upon privileged substrates, incorporating activating groups. We report an exciting new C–H activation protocol, which overcomes these limitations, allowing formation of biaryls. Activation of the C–H bond is achieved through η^6 -coordination of arenes to [CpRu^{II}]. This is the first time that Ru complexes have been used to allow C–H activation by this mechanism. The Ru complex used to synthesise the η^6 -arene substrates can be recovered at the end of the reaction through photolysis in MeCN, thus highlighting the potential for a reaction overall catalytic in Ru, via an arene exchange mechanism. Furthermore, the simplest of arenes (benzene) will undergo C–H activation under the optimized reaction conditions.

CONFLICTS OF INTEREST

The authors declare no conflicts of interest or competing financial interests.

ASSOCIATED CONTENT

Supporting Information is available and contains: experimental detail, full optimization data, mechanistic evaluation and photolysis experiments.

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