Electrophilic Rh^I catalysts for arene H/D exchange in acidic media: evidence for an electrophilic aromatic substitution mechanism

This paper is dedicated to Professor Georgiy B. Shul'pin whose research has profoundly impacted the field of C–H activation and functionalization.

Michael S. Webster-Gardiner,[a] Paige E. Piszel,[a] Ross Fu,[b] Bradley A. McKeown,[a] Robert J. Nielsen,[b] William A. Goddard III,*[b] and T Brent Gunnoe*[a]

[a] Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, USA

[b] Materials and Process Simulation Center, Department of Chemistry, California Institute of Technology, Pasadena, California 91125, USA

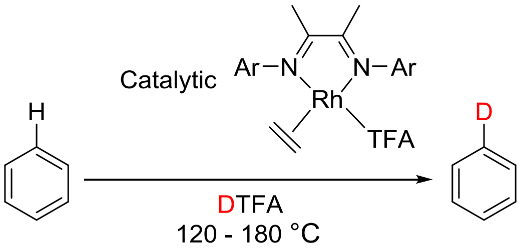
*Corresponding Author
E-mail address: tbg7h@virginia.edu
E-mail address: wag@wag.caltech.edu

Abstract

A series of new rhodium (I) complexes supported by bidentate nitrogen-donor ligands with varying electronic and steric properties were synthesized *in situ* and evaluated for catalytic arene C−H/D activation. In trifluoroacetic acid (HTFA), these complexes are proposed to mediate H/D exchange of arene C−H/D bonds by an electrophilic aromatic substitution mechanism that involves Rh-mediated activation of HTFA (or DTFA). DFT calculations support the proposed pathway for the H/D exchange reactions.

Keywords Rhodium, C–H Activation, Arene, Acid, Electrophilic

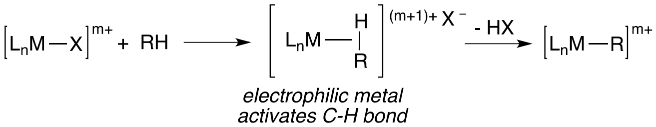
TOC Graphic



1. Introduction

Efficient and selective functionalization of hydrocarbon C−H bonds has been an area of intense study [1-14], but many examples of transition metal mediated C−H bond functionalization rely on directing groups to promote selectivity and activity [15-18]. Thus, developing catalysts that functionalize unactivated hydrocarbons (e.g., arenes and alkanes) remains challenging [2, 19-23]. The discovery by Shilov and coworkers that simple Pt^{II} salts can activate C–H bonds resulted in the demonstration that electrophilic metals are viable catalysts for alkane and arene C–H functionalization [4, 24-26]. The primary drawback of the initial Shilov process for alkane functionalization was the use of Pt^{IV} as a stoichiometric oxidant.

Studies of Shilov type catalysts have proposed that the rate limiting step is C−H activation through an electrophilic substitution mechanism (Scheme 1) [8, 14]. Since the discovery that electrophilic Pt^{II} can catalytically functionalize hydrocarbons, new catalysts based on electrophilic Hg^{II}[27], Pt^{II}[28], Pd^{II} [29, 30], $Au^{I}/^{III}$[31] and I_2[32] have been reported. Importantly, over oxidation can be avoided by protecting the functionalized hydrocarbyl with electron-withdrawing groups. For example, in one variant a Pt catalyst is used to functionalize methane in oleum to produce methylbisulfate, which is protected against further oxidation by the electron-withdrawing bisulfate group through an increase in the activation barrier toward electrophilic C–H activation for CH_3OSO_3H [28, 33]). These catalysts appear to only operate efficiently in concentrated and oxidizing super acids, such as oleum, which makes product separation and solvent recycling difficult[34]. In addition, these electrophilic catalysts are readily poisoned by water (or other Lewis bases) and can suffer from product inhibition [33]. More recently, main group elements and transition metal complexes have been shown to activate and functionalize hydrocarbons in less acidic, trifluoroacetic acid [35-41].

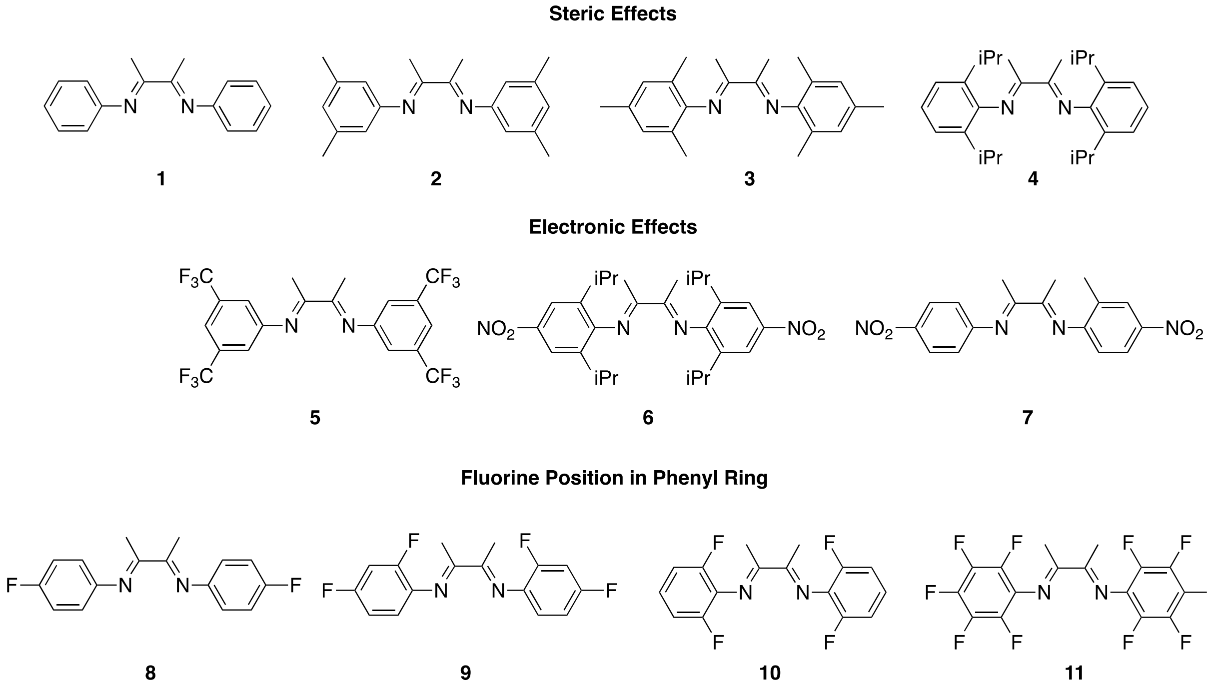


Scheme 1. Activation of C–H bonds by electrophilic substitution.

Extension of the general strategy for Shilov type hydrocarbon functionalization would benefit from catalysts that are less susceptible to inhibition by Lewis bases, which could allow chemistry in non-super acidic media. Developing reactivity with earlier transition metals (i.e., earlier than the Ni, Pd and Pt triad) could provide more tolerance of Lewis basic groups, but major challenges include avoiding oxidation of the metal to higher valent states that are incapable of C–H activation and developing complexes that possess electrophilic hydrocarbyl ligands (after C–H activation) [42-53]. Recently, a number of catalysts based on Ir and Rh have been shown to be active for benzene C−H activation [50-61]. Rhodium complexes are particularly attractive due to the possibility of C−H activation by Rh^{I} [62] or Rh^{III} [55]. Further, oxidation of the rhodium center can be achieved with air recyclable Cu(II) salts, which provides a strategy for indirect use of dioxygen or air as the terminal oxidant [60, 63].

A common method for generating an active electrophilic metal center is to generate a coordinatively unsaturated complex through halide abstraction from the metal with a silver salt of the form AgX (X = triflate, acetate, tetrafluoroborate, etc.). The recent report that Lewis acids can facilitate H/D exchange between arenes and acidic media complicates analysis of transition metal-mediated C–H activation [64]. Thus, we sought a method to generate active catalysts *in situ* without the use of an additive Lewis acid, such as AgX.

Recently, two Rh^{I} complexes bearing neutral bidentate nitrogen donors were shown to be catalysts for the rapid H/D exchange between benzene and trifluoroacetic acid [62]. The most active catalyst for aromatic H/D exchange, (FlDAB)Rh(COE)(TFA) (FlDAB = *N*,*N'*-bis-(pentafluorophenyl)- 2,3-dimethyl-1,4-diaza-1,3-butadiene, COE = cyclooctene, TFA = trifluoroacetate) possesses easily modulated aryl groups and therefore was chosen for a study of the impact of substituent variation on catalytic benzene H/D exchange reactions. This report focuses on understanding the impact of the diimine ligand on catalytic H/D exchange activity of arenes in DTFA (Scheme 2). By varying the electronic character of the ligand, the influence of electron donating versus withdrawing is studied. Further, the impact of sterics on catalysis is reported. These catalysts were then explored for C−H functionalization of benzene in acidic and neutral media.



Scheme 2. Diimine proligands designed to vary the electron donor ability and steric profile of Rh^I catalysts (iPr = isopropyl).

2. Experimental

2.1 Materials and instruments

Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer ($O_2 < 15$ ppm for all reactions). Tetrahydrofuran, toluene, and *n*–pentane were dried by distillation from sodium. Benzene was purified by passage through a column of activated alumina. Hexamethylbenzene was used as received. C_6D_6 and toluene-d_8 were stored under a N_2 atmosphere over 4Å molecular sieves. Trifluoroacetic-d_1 acid was used as received. Nitrogen (99.99%) was purchased from GTS Welco and used as purchased. GC/MS analysis was performed using a Shimadzu GCMS–QP2010 Plus system with a 30 mm × 025 mm RTx-Qbond column with 8 µm thickness using electron impact ionization. All other reagents were used as purchased from commercial sources.

2.2 Ligand and complex synthesis

2.2.1 Ligand synthesis

Most of the diimine ligands (diazbutadienes, or DABs) were synthesized following a modified literature procedure [65]: To a round-bottomed flask, 2.1 equivalents of the aniline, 1 equivalent of 2,3-butanedione, 0.1 equivalents of *p*-toluenesulfonic acid, and 4 equivalents of trimethylorthoformate were combined in 10 mL of anhydrous methanol under air. The reaction mixture was stirred for 8 hours accompanied by the precipitation of a yellow solid. The solid was collected by filtration, washed with 5 mL of cold methanol, and dried under vacuum. The identity of the DABs was confirmed by comparison to reported NMR data for 3,5-diMeDAB = *N*,*N'*-bis-(3,5-dimethylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene)[66], 2,6-dippDAB = *N*,*N'*-bis-(2,6-diisopropylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) [67], 2,6-diClDAB = *N*,*N'*-bis-(2,6-dichlorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) [68], 3,5-diCF$_3$DAB = *N*,*N'*-bis-(3,5di(trifluoromethyl)phenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) [69], 2,6-diFlDAB = *N*,*N'*-bis-(2,6-difluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene)[70] (2,4-diFlDAB = *N*,*N'*-bis-(2,4-difluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene), (4-FlDAB = *N*,*N'*-bis-(4-fluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene)[71], (FlDAB = *N*,*N'*-bis-(pentafluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) [65]. The ligands (2,6-dip-4-nitroDAB = *N*,*N'*-bis-(2,6-diisopropyl,4-nitrophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) and (4-nitroDAB = *N*,*N'*-bis-(4-nitrophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) were prepared according to literature procedures [72], 4-nitroDAB was confirmed to reported NMR data [73].

2.2.2 Procedure for synthesis of in situ generated diimine rhodium complexes

Under nitrogen, the diimine ligand (2 equiv, 414.5 μmol) in THF (10 ml) was added to a stirring solution of $[Rh(\mu\text{-TFA})(\eta^2\text{-}C_2H_4)_2]_2$ (1 equiv, 207 μmol) in THF (15 mL). The solution immediately became deep purple to black. After 1 hour the solvent was removed *in vacuo*, and the resulting solid was washed with *n*-pentane (20 mL) and then dried under vacuum to yield the corresponding *in situ* rhodium catalyst.

2.3. General Procedure for benzene H/D exchange

Stainless steel reactors were used for all H/D exchange reactions. Prior to use, the interior of the reactor and stir bars were treated with 35% hydrogen peroxide, washed with acetone and dried at 180 °C. A stock solution of catalyst was made by placing 0.02 mmol of the Rh complex into a glass vial and dissolving in 6.2 mL (80.4 mmol) of trifluoroacetic acid-d_1. C_6H_6 (360 μL, 4 mmol) was then added to the stock solution. Then, 1 mL of the stock solution was added to each pressure reactor, which was sealed under N_2, pressurized with 800 psi N_2, and placed in a heating block set to 120 °C, 150 °C or 180 °C. At the end of the reaction, the pressure reactor was allowed to cool to room temperature, slowly vented, and opened. An aliquot (1 μL) of the reaction mixture was placed into a vial that contained 1 mL of acetone. This vial was then analyzed by GC-MS. The extent of H/D exchange was analyzed by deconvolution of the GC-MS spectrum using an excel sheet developed by Periana, Goddard and coworkers [74].

2.4 General Procedure for toluene H/D exchange

To a glass vial, a stock solution was made by dissolving 12 μmol of Rh catalyst in 7.8 mL of trifluoroacetic acid and 240 μL of toluene-d_8. Then, 0.8 mL of stock solution was placed into a J-young NMR tube. The J-Young NMR tube was then placed in an oil bath at 120 °C, 150 °C or 180 °C. After 15 minutes, the J-Young NMR tube was removed from the high temperature oil bath, allowed to cool to room temperature, and a capillary tube filled with DMSO-d_6 was added. Then the reaction mixture was analyzed by ^{1}H NMR spectroscopy.

2.5 General Procedure for aliphatic H/D exchange

Stainless steel reactors were used for H/D exchange reactions. All pressure reactors and stir bars were treated with 35% hydrogen peroxide, washed with acetone and dried at 180 °C before use. For liquid aliphatics (cyclohexane) the same procedure described for benzene (see above) was used. For methane, the following procedure was followed: A stock solution was made by placing 0.02 mmol of Rh catalyst into a glass vial and dissolved into 6.2 mL (80.4 mmol) of trifluoroacetic acid-d_1. Then, 1 mL of the stock solution was added to each reactor, which was sealed under N_2, pressurized with 100 psi of methane, and placed in a heating block set to 120 °C, 150 °C or 180 °C. At the end of the reaction, the reactor was allowed to cool to room temperature. Then, 2 uL of reactor headspace was analyzed by GC-MS. Extent of H/D exchange was analyzed by deconvolution of the GC-MS spectrum using an excel sheet developed by Periana, Goddard and coworkers [74] .

2.6 General Procedure for arene functionalization in trifluoroacetic acid

A solution was made by placing 0.02 mmol of Rh catalyst into a glass pressure tube and dissolved in 6.125 mL (80 mmol) of trifluoroacetic acid. Benzene (90 μL, 1 mmol) and hexamethylbenzene (65mg, 0.4 mmol) was added to the solution. Then, 2 mmol of oxidant was added to the glass pressure tube. The pressure tube was sealed and then heated at 150 °C or 180 °C. At the end of the reaction, the reactor was allowed to cool to room temperature. An aliquot (1 μL) of the reaction mixture was placed into a vial with 1 mL of acetone. The solution was analyzed by GC-MS.

2.7 General Procedure for arene functionalization in non-acidic media

A solution was made by placing 0.02 mmol of Rh catalyst and hexamethylbenzene (65mg, 0.4 mmol) into a glass pressure tube and dissolved into 6.5 mL (80 mmol) of benzene. Then, 2 mmol of oxidant was added to the glass pressure tube. The pressure tube was sealed and then heated at 150 °C or 180 °C. At the end of the reaction, the reactor was allowed to cool to room temperature. An aliquot (1 μL) of the reaction mixture was placed into a vial with 1 mL acetone. The solution was then analyzed by GC-MS.

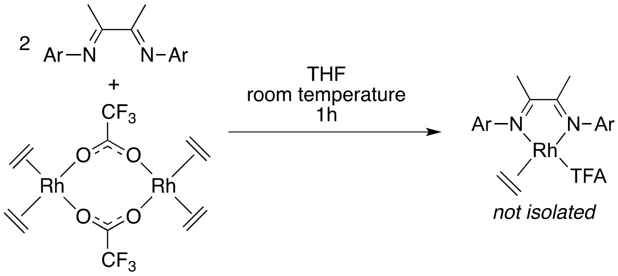
2.8 Calculations for mechanistic investigation

DFT calculations were performed using the M06 functional [75, 76] and the triple-zeta basis set 6-311G**++ [77, 78] for all atoms except for rhodium. For rhodium, the triple-zeta basis set and pseudopotential LACV3P**++ [79] was used. Further details may be found in the supporting information.

3. Results and discussion

3.1 Synthesis of (DAB)Rh(TFA)(η^2-C_2H_4) complexes

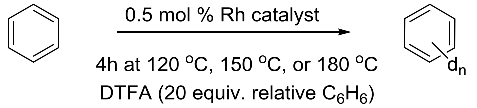
Diimine proligands were coordinated to Rh by reaction of $[Rh(\mu\text{-TFA})(\eta^2\text{-}C_2H_4)_2]_2$ with the diimine in THF (Scheme 3). To a yellow-brown stirring solution of $[Rh(\mu\text{-TFA})(\eta^2\text{-}C_2H_4)_2]_2$ in THF, the appropriate diimine ligand was added. Almost instantaneously, the solutions turn deep purple/black. The Rh complexes are not isolated, but rather were used after *in situ* generation.



Scheme 3. General *in situ* synthesis of rhodium catalyst precursors from diimines and $[Rh(\mu\text{-}TFA)(\eta^2\text{-}C_2H_4)_2]_2$.

3.2 *Catalytic Benzene H/D Exchange*

In 1958 H/D exchange of arenes with trifluoroacetic acid-d_1 was shown to occur, albeit quite slowly (especially at lower temperatures) [80]. Therefore, for all reactions reported herein, we determined the extent of uncatalyzed H/D exchange between the substrates and trifluoroacetic acid-d_1. The background H/D exchange reaction increased with temperature and was determined to be the equivalent of 7(1), 15(4), and 96(9) turnovers (TO) (relative to standard amount of Rh catalyst, see below) at 120 °C, 150 °C and 180 °C, respectively (numbers in parenthesis are standard deviations from multiple experiments). These TO were subtracted from the results for catalytic H/D exchange using the various Rh catalysts. Our standard screening conditions incorporated 0.5 mol % (relative to benzene) of Rh catalyst with 20 equivalents of trifluoroacetic acid-d_1 relative to benzene for 4 hours (eq 1).



(1)

Figure 1 shows the results of the catalytic H/D exchange between benzene and trifluoroacetic acid-d_1. The effect of temperature was studied for all catalysts. The optimal temperature for catalysts **1**, **5**, and **7-11** is 150 °C. Complexes **2-4** and **6** showed minimal catalytic activity at all temperatures studied. Catalysts **1, 5**, and **7-11** are all active at 120 °C; however, only complexes **5**, **7**, **9** and **11** show activity at 180 °C. The inactivity of complexes **1**, **8,** and **10** at 180 °C is likely due to catalyst decomposition. In general, more electron-withdrawing ligands appear to enhance catalysis. Catalyst **11** shows the highest TO at 150 °C with 140(14) TO after 4 hours, which corresponds to an apparent turnover frequency (TOF, calculated by TO/time) of 9.7(9) x 10^{-3} s^{-1} (Table 1). Relative to the catalyst with a phenyl substituent (complex **1**), which gives 25(7) TO after 4 hours (TOF ~ 1.7(5) x 10^{-3} s^{-1}), the apparent activity of **5** is approximately 5.5 times greater. The complexes **8-10** all show TO after 4 hours between catalyst precursors **1** and **11**. This is expected due to the increased number of electron withdrawing fluorine substituents on the aryl ring relative to **1** but decreased relative to **11**. Comparison of data using complexes **8-10** reveals that the position of fluorine substituents on the phenyl rings makes little difference to catalytic activity. Comparison of data using catalytic precursors **2** and **5** highlights the impact of electron-withdrawing groups. Complex **2** possesses electron-donating methyl groups in the 3 and 5 positions on the phenyl ring whereas **5** has trifluoromethyl groups in the 3 and 5 positions on the ring. No TO above background reactivity is observed using **2**; however, complex **5** is an active precatalyst with 55(2) TO which corresponds to an apparent TOF of 3.8(1) x 10^{-3} s^{-1} at 150 °C. Furthermore, installing electron-withdrawing nitro groups in the para position of the the DAB phenyl results in the second most active catalyst of the series, as catalyst as **7** gives 82(2) TO (apparent TOF of 5.7(1) x 10^{-3} s^{-1}).

We propose three possible rationalizations for increased efficacy for benzene/trifluoroacetic acid-d_1 H/D exchange using Rh complexes with electron-withdrawing substituents on the DAB ligand: 1) The C–H activation occurs at the Rh^{I} oxidation state, and less donating ligands stabilize Rh^{I} in the presence of oxidizing trifluoroacetic acid whereas more donating ligands result in oxidation to Rh^{III}; 2) the C–H activation occurs by an electrophilic substitution process (regardless of the exact mechanism, which could be "classic" electrophilic substitution, see Scheme 1, or concerted-metalation deprotonation) [81] and is enhanced by less electron-rich Rh catalysts; 3) the C–H "activation" occurs by an electrophilic aromatic substitution pathway, as we have previously demonstrated for other metals in acidic media [64], and more electrophilic Rh complexes enhance reactivity. We have no evidence that the DAB-Rh^{I} complexes are oxidized in the presence of trifluoroacetic acid. For example, no color changes are observed as would be expected for oxidation from Rh^{I} to Rh^{III}. As discussed below, the results of H/D exchange with toluene is most consistent with the electrophilic aromatic substitution pathway.

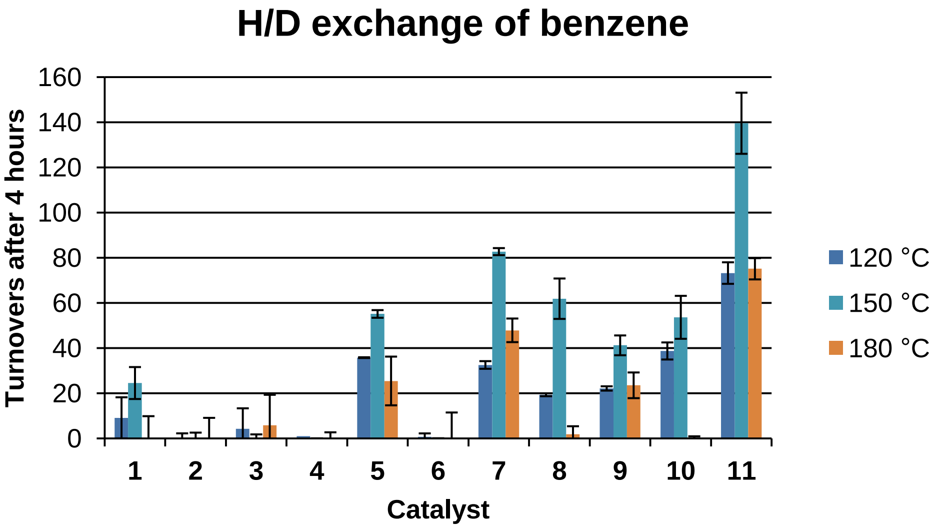


Fig. 1. Results from Rh catalyzed H/D exchange between benzene and trifluoroacetic acid-d_1 using complexes 1-11 (see Scheme 2). Conditions: 0.5 mol % Rh relative to benzene, 20 equivalents of trifluoroacetic acid-d_1 relative to benzene for 4 hours at 120 °C, 150 °C or 180 °C.

Increased steric bulk around the rhodium metal inhibits the catalytic H/D exchange. At all temperatures studied, complexes **2** and **4** show minimal to no activity above the background reactions.

There is a possibility that the alkyl groups are too electron-donating resulting in a rhodium center that is not sufficiently electrophilic. Installing a nitro group should mitigate the electron-donating effects of the alkyl groups. However, even installing a nitro group on the ligand, as in the comparison of **4** and **6**, does not result in catalytic H/D exchange. This observation provides support that alkyl groups on the aryl 2,6-positions sterically hinder access to the rhodium center, which likely inhibits coordination of benzene or trifluoroacetic acid.

Table 1. Rhodium catalyst precursors and apparent TOFs (s^{-1}) after 4 hours at 120 °C, 150 °C and 180 °C for H/D exchange between benzene (C_6H_6) and trifluoroacetic acid-d_1.[a]

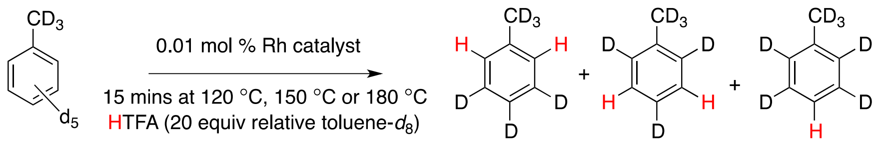
Catalyst Precursor	**TOF (s^{-1})** **120 °C**	**150 °C**	**180 °C**
1	$6(3) \times 10^{-4}$	$1.7(9) \times 10^{-3}$	0
2	0	0	0
3	0	0	0
4	0	0	0
5	$2.5(2) \times 10^{-3}$	$3.8(2) \times 10^{-3}$	$1.8(8) \times 10^{-3}$
6	0	0	0
7	$2.3(1) \times 10^{-3}$	$5.7(2) \times 10^{-3}$	$3.3(7) \times 10^{-3}$
8	$1.3(5) \times 10^{-3}$	$4(1) \times 10^{-3}$	0
9	$1.5(7) \times 10^{-3}$	$2.9(6) \times 10^{-3}$	$1.6(8) \times 10^{-3}$
10	$2(1) \times 10^{-3}$	$3(1) \times 10^{-3}$	0
11	$5(2) \times 10^{-3}$	$9(2) \times 10^{-3}$	$5.2(7) \times 10^{-3}$

[a] Reactions performed using 1 mL of a solution containing 80.4 mmol (6.2 mL) of trifluoroacetic acid with 4 mmol (360 μL) of benzene with the Rh catalyst (0.5 mol % relative to benzene).

3.3 *Attempted H/D exchange with toluene, cyclohexane and methane*

The Rh catalyzed H/D exchange between toluene-d_8 and trifluoroacetic acid was studied. The regioselectivity of the reactions was determined using ^{1}H NMR spectroscopy (eq 2). For reactions with toluene, electrophilic aromatic protonation mechanisms favor the *ortho* and *para* positions whereas organometallic complexes often favor activation of the *meta* and *para* positions [64, 82]. The Rh complexes (0.5 mol % relative to toluene-d_8) were heated (120 °C, 150 °C, or 180 °C) in trifluoroacetic acid with toluene-d_8. After 15 minutes, the solutions were analyzed by ^{1}H NMR spectroscopy to determine *o*:*m*:*p* ratio for proton exchange (Table 2). All of the Rh catalysts exhibited selectivity for H/D exchange at the *ortho* and *para* positions with (*ortho* + *para*) to *meta* ratios > 6:1, which is very similar to the ratio for trifluoroacetic acid electrophilic aromatic substitution (Table 2, Entry 1). None of the Rh catalysts activate the methyl group of toluene. These results point to a likely reaction pathway that involves protic electrophilic aromatic substitution rather than Rh mediated C–H activation. In this proposed reaction pathway, the Rh catalyst activates HTFA to liberate H^+ (from HTFA) or D^+ (from

DTFA), which then adds to the arene to form a Wheland type arenium intermediate. We have previously proposed a similar reaction pathway for Lewis acid mediated H/D exchange between arenes and acidic media [64].



(2)

Table 2. Evaluation of Rh catalyst precursors **1-11** for the H/D exchange of toluene-d_8 with trifluoroacetic acid and *ortho*:*meta*:*para* selectivity.[a]

Entry	Catalyst Precursor	Ratio of *o:m:p*		
		120 °C	**150 °C**	**180 °C**
1	HTFA	8(2) :1 : 7(2)	12(1) : 1 : 11(1)	9(0.2) : 1 : 7(0.4)
2	$[Rh(\mu\text{-}TFA)(\eta^2\text{-}C_2H_4)_2]_2$	8(0.3) : 1 : 7(0.3)	14(0.7) : 1 : 13(0.5)	12(1) : 1 : 9(1)
3	**1**	12(3) : 1 : 16(3)	5(1) : 1 : 6.4(1)	8(2) : 1 : 8(2)
4	**2**	5.8(1) : 1 : 7(2)	9(2) : 1 : 9(2)	12(4) : 1 : 10(3)
5	**3**	4(2) : 1 : 3(2)	9.1(1) : 1 : 9(1)	11(1) : 1 : 10(1)
6	**4**	5(2) : 1 : 6(2)	8(2) : 1 : 8(1)	7(1) : 1 : 6(1)
7	**5**	9(0.2) : 1 : 8(0.2)	16(2) : 1 : 14(2)	14(2) : 1 : 10(1)
8	**6**	9(0.1) : 1 : 9(1)	10(0.4) :1 : 10(0.3)	10(1) : 1 : 10(0.3)
9	**7**	7(2) : 1 : 8(0.3)	7(0.03) : 1 : 7(0.2)	14(2) : 1 : 15(2)
10	**8**	6(1) : 1 : 7(0.01)	8(0.3) : 1 : 8(0.3)	9(0.2) : 1 : 10(1)
11	**9**	9(0.04) : 1 : 9(0.1)	8(1) : 1 : 7(1)	9(1) : 1 : 7(1)
12	**10**	4(2) : 1 : 3(1)	9(0.7) : 1 : 9(1)	11(1) : 1 : 10(1)
13	**11**	9(2) : 1 : 8(2)	10(0.3) : 1 : 9(0.3)	12(2) : 1 : 10(1)

[a] Reactions performed using 0.8 mL of a solution containing 101 mmol (7.8 mL) of trifluoroacetic acid with 2.26 mmol (240 μL) of toluene with the Rh catalyst (0.5 mol % relative to toluene).

A recent report by Ison and coworkers disclosed that the mechanism for catalytic H/D exchange between arenes and acids using Cp*Ir(III) complexes varies as a function of acid identity [82]. The study showed that electrophilic aromatic protonation dominates in trifluoroacetic acid whereas an organometallic mechanism, where an Ir−Ph is formed and is subsequently protonated by the deuterated solvent, occurs in methanol and acetic acid. Under our standard conditions with rhodium complexes **7** and

11, no catalytic H/D exchange was observed between benzene and acetic acid, trifluoroethanol or methanol. These weaker acids (compared to trifluoroacetic acid) are most likely insufficiently acidic to promote the protic electrophilic aromatic substitution. These results suggest that Rh−Ph bonds are not likely formed under these conditions.

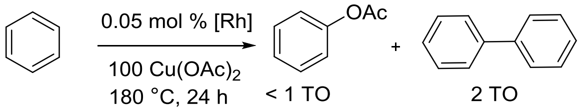
C−H activation reactivity with other hydrocarbon substrates was attempted with the most active Rh catalyst precursors. Solutions of 0.5 mol % of **7** or **11** in trifluoroacetic acid-d_1 were pressurized with 100 psi of CH_4 and heated to 120 °C, 150 °C or 180 °C. After 4 hours, the headspace of the reactors was analyzed by GC/MS. Analysis revealed no deuterium incorporation into methane beyond the natural isotope abundance. Under the same conditions C−H activation of cyclohexane was also examined, but again no deuterium incorporation was detected. This lack of reactivity is consistent with the proposed mechanism for arenes in trifluoroacetic acid which relies on the formation of an arenium ion.

3.4 Attempted benzene oxidation in trifluoroacetic acid

Rhodium complexes **7** and **11** were examined for benzene oxidation with a number of chemical oxidants. In previous work, we have shown (FlDAB)Rh(μ-TFA)(η^2-C_2H_4) catalyzes the oxidative hydrophenylation of ethylene (using Cu(II) salts as oxidant) to produce styrene [60]. Therefore attempts to generate other oxidation products from benzene were undertaken. A 0.5 mol % solution of **11** in trifluoroacetic acid with 50 equivalents of benzene and 100 equivalents of copper(II) acetate was heated to 150 °C for 4 hours. The reaction mixture was then analyzed by GC-MS. However, no evidence of benzene oxidation was obtained (i.e., no observation of PhOAc, PhTFA or biphenyl). Silver oxidants (AgTFA, Ag_2O) and hyper-valent iodine (III) compounds, such as (Ph)I(OAc)$_2$, were also used as potential oxidants, but the only functionalized arene products detected were from direct reaction with the oxidant alone.

3.5 Benzene oxidation in non-acidic media

The lack of benzene oxidation in HTFA (see above) could result from the failure of the Rh complexes to mediate benzene C–H activation in trifluoroacetic acid. We speculated that non-acidic solvents might allow arene functionalization chemistry (eq. 3). A 0.5 mol % solution of **7** or **11** in benzene with 100 equivalents of copper (II) acetate was heated to 150 °C and 180 °C for 4 hours. Analysis by GC/MS revealed no benzene functionalization at 150 °C. However, at 180 °C the production of biphenyl and a minor quantity of PhOAc was observed when using Cu(OAc)$_2$. Control experiments at 180 °C without rhodium catalyst produced the same quantity of phenyl acetate; however, no biphenyl was observed. The formation of PhOAc presumably is due to reaction with Cu(OAc)$_2$. This was confirmed by running a control reaction in toluene and producing significantly more benzylic acetate than tolylacetate (see Supporting Information, Scheme S1). The production of biphenyl was also observed with catalyst **4, 7**, **11** and [Rh(μ-TFA)(η^2-C_2H_4)$_2$]$_2$ in similar yields.



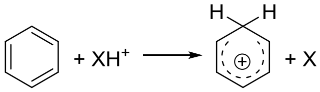
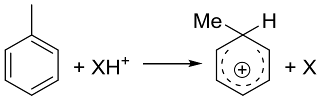
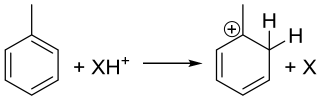
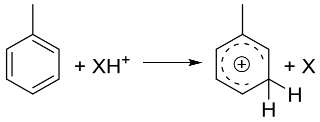
(3)

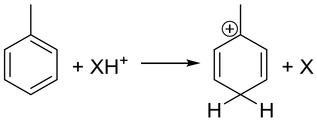
3.6 *Computational investigation of mechanism*

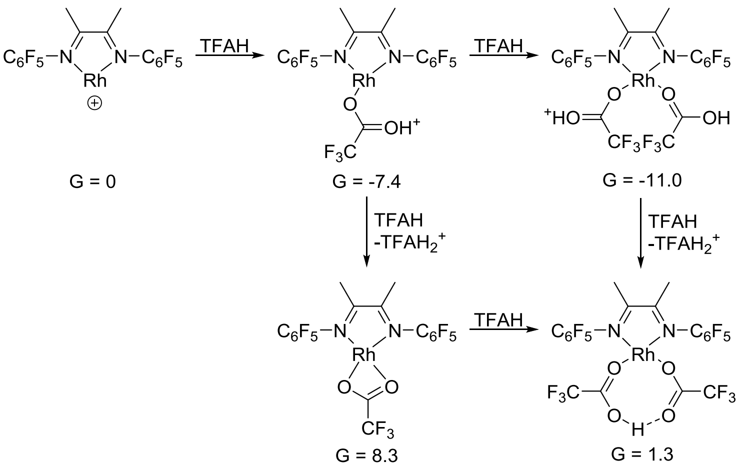
Our assertion that H/D exchange occurs by a Rh-mediated electrophilic aromatic substitution pathway is supported by DFT calculations. Table shows the calculated change in Gibbs free energy for protonation of arenes (benzene and toluene) by either HTFA or H_2TFA^+. H_2TFA^+ is formed upon Rh-mediated activation of HTFA: $[Rh]^{n+} + 2HTFA \rightarrow \{[Rh]\text{-}TFA\}^{(n-1)+} + H_2TFA^+$. In Table 3 column 3, we see that HTFA solvent can indeed support the formation of arenium cations, since they are less acidic than $TFAH_2^+$. Also, protonation of the meta position in toluene is comparable to that of benzene since there is no stabilization of resonance structures due to a tertiary carbocation. Protonation of the ortho or para positions is more favorable due to the resonance structure with a tertiary carbocation. However, due to the high self-ionization energy of HTFA, formation of the arenium cation in neutral HTFA solution is quite uphill (Table 3 column 4).

Our assertion is that our Rh complexes act as Lewis acids, coordinating to HTFA and enhancing its Brønsted acidity. We performed calculations for this process with **11** and our results are shown in Scheme 4. The calculations reveal that $(FlDAB)Rh^+$ is a very strong Lewis base and will coordinate two equivalents of TFAH in solution, forming $(FlDAB)Rh(TFAH)_2^+$ (top right). It is only 12.3 kcal/mol uphill to produce $TFAH_2^+$ from this species, much lower than the 45.8 kcal/mol required by HTFA self-ionization. These results are provide an explanation for the catalytic ability of **11** and related complexes to help arenes undergo H/D exchange.

Table 3. Calculated free energies of the formation of various arenium cations in uncatalyzed TFAH solution. In all cases, the temperature was set to 150°C. Note that the difference in ΔG's for the two rightmost columns is due to the self-ionization free energy of TFAH: 45.8 kcal/mol for $2\mathrm{TFAH} \longrightarrow \mathrm{TFAH}_2^+ + \mathrm{TFA}^-$ at 150 °C.

Entry	Reaction	**ΔG (kcal/mol)** **X = TFAH**	**ΔG (kcal/mol)** **X = TFA$^-$**
1		-9.7 kcal/mol	36.0 kcal/mol
2 (ipso)		-2.8 kcal/mol	43.0 kcal/mol
3 (ortho)		-12.1 kcal/mol	33.6 kcal/mol
4 (meta)		-8.1 kcal/mol	37.6 kcal/mol

5 (para)		-13.4 kcal/mol	32.4 kcal/mol



Scheme 4. Energetics of (**11**)Rh$^+$ complexing with TFAH. All free energies calculated at 150 °C and in kcal/mol. Note that the lowest energy species is (**11**)Rh(TFAH)$_2^+$ (top right) and that release of a proton from this species to form (**11**)Rh(TFAH)(TFA) (bottom right) is uphill by only 12.3 kcal/mol.

4. Conclusion

Eleven new Rh^I diimine complexes have been generated *in situ* and examined for catalytic H/D exchange between arenes and acidic media. The most active catalyst precursors possess electron-withdrawing substituents on the diimine ligands. The mechanism of the arene H/D exchange reactions most likely involves protic electrophilic aromatic substitution with Rh acting as a Lewis acid to activate DTFA and provide access to D_2TFA^+. This was shown by monitoring the selectivity for H/D exchange of toluene, which revealed selectivity for the *ortho* and *para* positions over the *meta* position. DFT calculations demonstrate the viability of our proposed mechanism of H/D exchange. Attempts to extend catalysis to other solvents and aliphatic hydrocarbons were unsuccessful, which is consistent with the proposed protic electrophilic aromatic substitution. Although, attempts to functionalize benzene in acidic media were unsuccessful with a range of chemical oxidants, catalysis in neat arene was successful, but with low turnover number of ~2.

Acknowledgements

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Supplementary Material

Electrophilic Rh^I catalysts for arene C−H activation: electrophilic aromatic substitution mechanism

Special issue dedicated to Professor Georgiy B. Shul'pin

Michael S. Webster-Gardiner,[a] Paige E. Piszel,[a] Ross Fu,[b] Bradley A. McKeown,[a] Robert J. Nielsen,[b] William A. Goddard III,*[b] and T Brent Gunnoe*[a]

[a] Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, USA

[b] Materials and Process Simulation Center, Department of Chemistry, California Institute of Technology, Pasadena, California 91125, USA

*Corresponding Author
E-mail address: tbg7h@virginia.edu
E-mail address: wag@wag.caltech.edu

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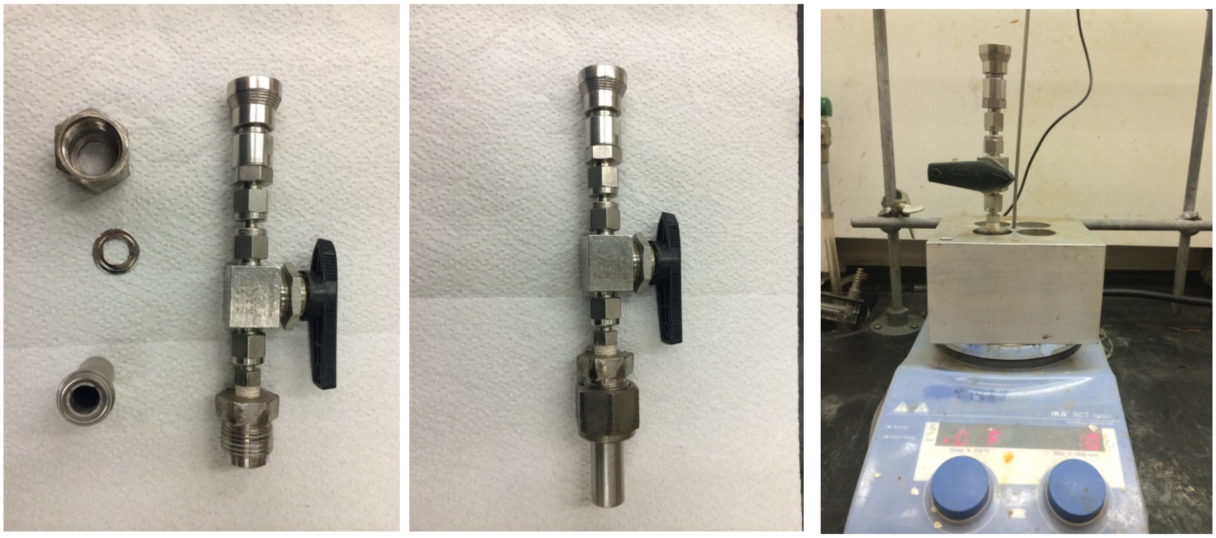

Figure S1. Pressure reactors used in H/D exchange. Left – Unassembled reactor parts. Middle - Assembled reactor. Right – Fully assembled reactor in aluminum heating block.

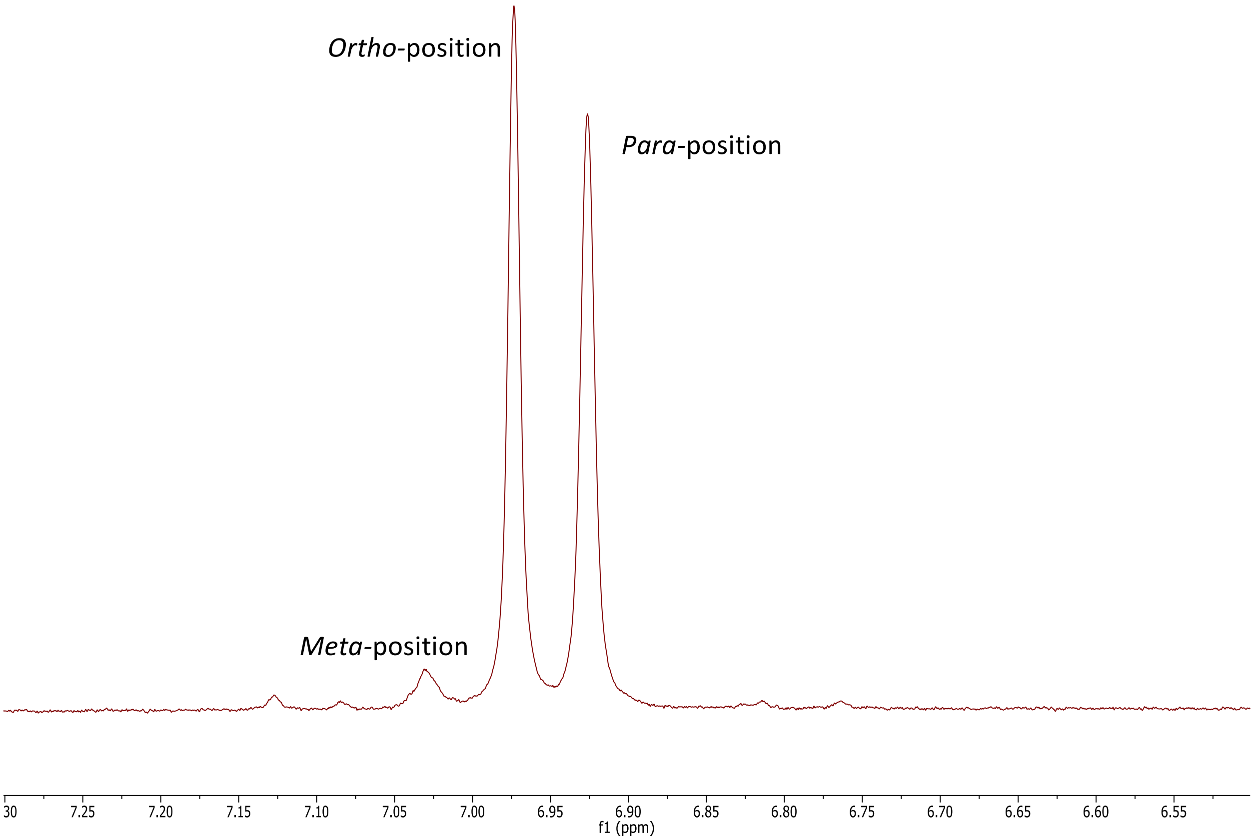

Figure S2. Representative ^{1}H NMR spectrum of H/D exchange of toluene-D_8 in HTFA.

Details on the DFT calculations

All DFT calculations were carried out using the Jaguar software version 8.4 developed by Schrödinger Inc. [1] Geometry optimizations were carried out on initial guess structures, and vibrational frequencies were calculated to confirm the optimized geometries as intermediates (no negative curvatures) and to calculate the zero-point energy, entropy, and temperature corrections to obtain the free energy profile. Solvation energies were calculated using the PBF Poisson-Boltzmann implicit continuum solvation model [2] in Jaguar, with a dielectric constant of 8.55 and a probe radius of 2.451 Å based on trifluoroacetic acid.

All geometry optimization and vibrational data were calculated using the double-ζ basis set 6-31G** [3] for all elements except Rh, and the double-ζ basis set and pseudopotential LACVP** for Rh [4]. The B3LYP density functional [5] was used for Rh species whereas M06 [6] was used for the organic molecules. In both cases, the Grimme post-SCF D3 correction for van der Waals interactions was added *a posteriori* [7]. After geometry optimization and vibrational calculations, single point gas-phase and solvated energies were calculated using M06-D3 with the triple-ζ Los Alamos basis set and pseudopotential (LACV3P**++) modified to include *f* functions and diffuse functions for rhodium [8], and the 6-311G**++ basis set [9] for the other atoms.

The enthalpy for each molecular species in solution was calculated using the formula $H = E_{\text{gas}} + \Delta E_{\text{solv}} + \text{ZPE} + H_{\text{tot}}$, whereas the free energy was calculated using the formula $G = H - TS_{\text{tot}} + RT\ln(34.7)$ where the last term represents the free energy change of compressing 1 mol of an ideal gas (volume 34.7 L at 150°C) to 1 L (for 1 M standard concentration). Note that all calculations were performed with T set to 423.15 K (150 °C).

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