CHAPTER 8. Synthesis of *N*-Heterocyclic Carbene-Containing Metal Complexes from 2-(Pentafluorophenyl) Imidazolidines*

8.1 ABSTRACT

N-heterocyclic carbene(NHC)-containing metal complexes are prepared through a simple, base-free method involving the decomposition of 2-(pentafluorophenyl)imidazolidines under mild thermolytic conditions. Ruthenium, iridium and rhodium complexes containing NHC ligands with different electronic and steric parameters are reported.

8.2 INTRODUCTION

N-heterocyclic carbene(NHC)-derived complexes have been used as powerful catalysts for effecting many transformations.[1-7] Despite their popularity, few methods are reported for their preparation. Current methods include the deprotonation[8-10] or oxidative addition of imidazolium salts,[11, 12] thermolysis of 2-(trichloromethyl)imidazolidine complexes,[13] oxidative addition of 2-chloro-imidazolium salts,[14] transmetallation of silver-NHC complexes[15] and sodium reduction of imidazolidin-2-thiones.[16] Recently, Crabtree and co-workers reported that *N*,*N*'-dialkylimidazolium-2-carboxylates can serve as precursors for the preparation of NHC-containing metal complexes with the release of CO_2.[17] Many of these methods utilize imidazolium salt precursors, which are insoluble in many media

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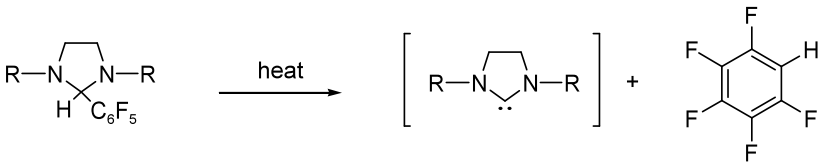
* *This work was done in collaboration with Dr. Tobias Ritter in the laboratory of Prof. Robert H. Grubbs and is adapted from:* Angela P. Blum, Tobias Ritter, Robert H. Grubbs, Synthesis of *N*-heterocyclic carbene-containing metal complexes from 2-(pentafluorophenyl)imidazolidines. *Organometallics* **2007**, 26, (8), 2122-24.

and difficult to further functionalize. "Protected" NHC adducts like 2-(alkoxy)imidazolidines, 2-(trichloromethyl)imidazolidines,[13] 2-(triethylborane) imidazolidines,[18] and 2-(dimethylamino)imidazolidines[19] are used to prepare NHC-containing complexes and offer the advantage that they can be chemically manipulated.[20] However, the base that is often required to synthesize these adducts limits the scope of complexes that can be prepared.

Waymouth, Hedrick and co-workers recently reported the base-free synthesis of a new set of air-stable NHC adducts that uses a pentafluorophenyl substituent as a protecting group. These adducts are formed by the condensation of diamines and pentafluorobenzaldehyde and were shown to decompose with mild heat to the corresponding carbenes (**equation 1**).[21] The only by-product of the reaction is pentafluorobenzene (b.p. 85^{o} C). Pentafluorophenyl adducts have been employed on three instances in the literature to prepare NHC-containing transition-metal complexes. Waymouth and Hedrick synthesized an NHC complex from allylpalladium chloride[21] and Bedford *et al*. reported phosphite-based palladacycle NHC compounds[22] as well as an iron-NHC complex that was formed *in situ*.[23] These reports illustrate the potential of utilizing pentafluorophenyl adducts for synthesizing metal-NHC complexes, and it was our goal to further explore the scope of compounds that can be prepared from these adducts. Here, we report the preparation of Ru-, Rh- and Ir-NHC complexes by the thermolysis of functionalized 2-(pentafluorophenyl)imidazolidines.



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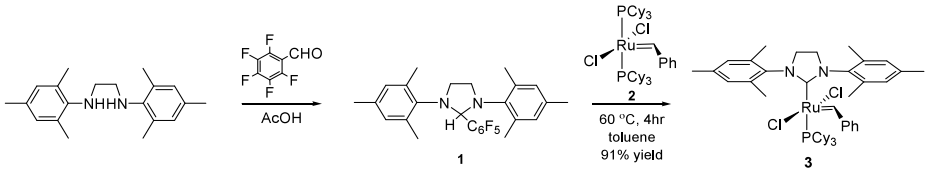
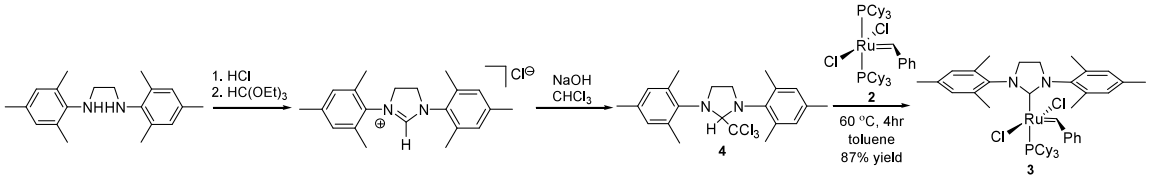
8.3 RESULTS

A direct comparison between the strategies involving the thermolysis of 1,3-bis(2,4,6-trimethylphenyl)-2-(pentafluorophenyl)imidazolidine **1** and 1,3-bis(2,4,6-trimethylphenyl)-2-(trichloromethyl)imidazolidine **4** in the synthesis of a common olefin metathesis catalyst **3** is shown in **Schemes 8.1** and **8.2**. Both methods afford **3** in comparable yield. The pentafluorophenyl adduct route offers several advantages in that it requires no base and fewer synthetic steps. In addition, **1** is stable at room temperature for greater than nine months while **4** shows signs of decomposition after a few weeks under the same conditions.

Scheme 8.1. Preparation of **3** from the thermolysis of 1,3-bis(2,4,6-trimethylphenyl)-2-(pentafluorophenyl)imidazolidine **1.**



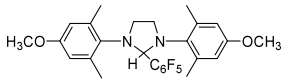
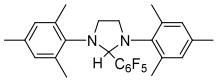
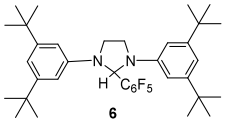
Scheme 8.2. Preparation of **3** from the thermolysis of 1,3-bis(2,4,6-trimethylphenyl)-2-(trichloromethyl)imidazolidine **4.**



The progress of the thermolysis of pentafluorophenyl adducts can be readily followed by ^{19}F NMR by monitoring the appearance of pentafluorobenzene. This fact enabled us to observe that the electron-rich adduct 1,3-bis(4-methoxy-2,6-dimethyl)-2-(pentafluorophenyl)imidazolidine (**5**) decomposes to pentafluorobenzene and the *N*-heterocyclic carbene at a faster rate (>95% conversion in 2 hours at 60 °C) than 1,3-

bis(2,4,6-trimethylphenyl)-2-(pentafluorophenyl)imidazolidine (**1**) (>95% conversion in 4 hours at 60 °C) as shown in **Table 8.1**. In addition, adducts lacking steric bulk in the *ortho* position of their phenyl rings do not form the carbene as readily. For example, the thermolysis of 1,3-bis[3,5-di(*tert*-butyl)phenyl)]-2-(pentafluorophenyl)imidazolidine (**6**), an adduct with steric bulk only in the *meta* position of its phenyl groups, required 14 days and 107 °C to reach >95% conversion to pentafluorobenzene while all adducts with substituents (methyl or isopropyl groups) in the *ortho* position, required less heat (60 °C) and shorter reaction times (four or five hours for the adducts containing methyl or isopropyl groups, respectively) to reach the same conversion.

Table 8.1. Comparison of the pyrolysis of 2-(pentafluorophenyl)imidazolidines to >95% in benzene or toluene.

Adduct	Time (h)	Temp (°C)
 **5**	2	60
 **1**	4	60
	5	60
 **6**	336	107

A study of the thermolysis of **1** at 45 °C in varying solvents (**eq 1**, R = Mes) showed a dramatic range of rates of conversion to pentafluorobenzene as determined by percent conversions after one hour quantified by ^{19}F NMR spectroscopy (**Table 8.2**). More polar solvents like acetone and acetonitrile were shown to yield higher conversions than less polar solvents like benzene. Although studies with acetone and acetonitrile

showed faster conversions to pentafluorobenzene, the apparent instability of some of the metal precursors prevented the preparation of NHC-containing organometallic complexes in these solvents. Studies in tetrahydrofuran and methylene chloride were also challenging because most of the reactions we attempted, which primarily involved ruthenium alkylidene species, required temperatures that exceeded the boiling points of these solvents. Despite prolonged reaction times, we found toluene to give the highest yields in our applications.

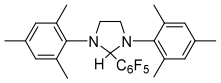
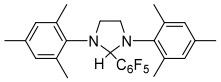
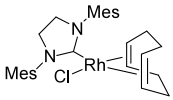
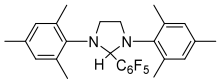
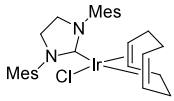
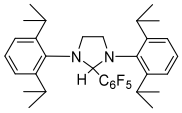
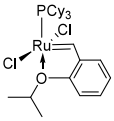
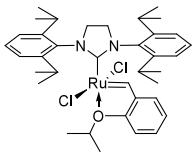
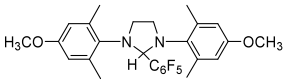
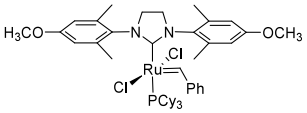
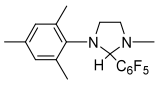
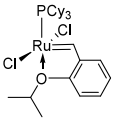
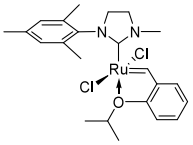
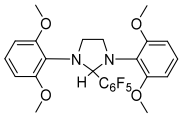
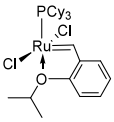
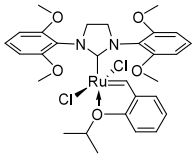
Table 8.2. Comparison of percent conversion to pentafluorobenzene in different solvents in the thermolysis of **1** after one hour at 45 °C.

solvent	%convn
C_6D_6	8
toluene-d_8	8
THF-d_8	29
CD_2Cl_2	32
acetone-d_6	90
CD_3CN	>95

Ruthenium, rhodium and iridium-NHC complexes were easily prepared from pentafluorophenyl adducts in generally high yield under mild thermolytic conditions as shown in **Table 8.3**. We investigated substrates with different electronic and steric properties, further illustrating the effectiveness of this strategy. The preparation of a complex containing an unsymmetrically-substituted NHC ligand (1-mesityl-3-methyl-imidazol-1-ylidene) is also reported (entry 6). The synthesis of the product of entry 7 presented a particular challenge. Other methods that were attempted to prepare the complex were unsuccessful due to the apparent instability of the product. The synthesis of this complex, although in low yield, highlights the utility of this method. It is likely that the *ortho* methoxy groups of this adduct do not present the steric environment needed to convert to pentafluorobenzene and the carbene at lower temperatures. Indeed, a lack

of hindered rotation around the C-$C_{aryl(C6F5)}$ bond is evident by the presence of only two resonances in the ^{19}F NMR spectrum of this adduct in contrast to the five resonances seen for **1**.

Table 8.3. *N*-heterocyclic carbene complexes prepared from 2-(pentafluorophenyl)imidazolidines.

Entry	Adduct	Metal Precursor	Product	Time (hr)	Temp °C	% yield
1		**2**	**3**	4	60	91
2		$[Rh(cod)Cl]_2$		2	70	90
3		$[Ir(cod)Cl]_2$		2	70	89
4				5	60	80
5		**2**		4	60	75
6				5	60	65
7				5	100	25

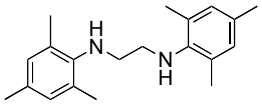
8.4 DISCUSSION

A strategy for preparing NHC-containing organometallic complexes from the thermolysis of 2-(pentafluorophenyl)imidazolidines was presented. It should be noted that this

method is not meant to replace traditional strategies for preparing metal complexes containing NHC ligands. Instead it is meant to be viewed as a simple, base-free alternative that may offer access to more complicated metal-NHC complexes by eliminating possible side reactions. The reaction scope was shown to include ligands with different electronic and steric properties. This method requires no base and fewer synthetic steps than many strategies currently in use, making possible the preparation of complexes with functionality that may be incompatible with other methods.

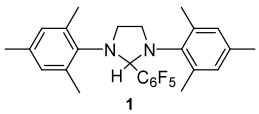
8.5 EXPERIMENTAL SECTION

All reactions involving metal complexes were conducted under nitrogen or argon atmospheres using standard glove box or standard Schlenk techniques. Solvents were purified by passage through alumina.[24] Resonances for NMR spectra are reported relative to Me_4Si (δ 0.0) for ^{1}H and ^{13}C and H_3PO_4 (δ 0.0) for ^{31}P. Spectra are reported as follows: chemical shift (δ ppm), integration, multiplicity and coupling constant (Hz). (2,6-dimethoxyphenyl)imidazoline, catalyst **2** and $RuCl_2(PCy_3)$(=CH-o-*i*Pr-Ph) were provided by Materia, Inc. 1,3-dimesitylimidazoline,[25] *N*-2-(mesitylimino)ethylidene-2,4,6-trimethylbenzenamine,[25] 1,3-bis(2,6-diisopropyl)2-pentafluorophenyl) imidazolidine,[23] and 2,4,6-trimethyl-N-(2-methylamino)ethyl)benzenamine[26] were prepared as described in the literature. All other reagents were purchased from Aldrich and used without prior purification. Crystallography data for S2 is available in Supplemental Material of Blum *et al*.[27]



S1

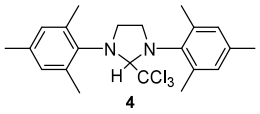
Synthesis of *N*-(2-(mesitylamino)ethyl)-2,4,6-trimethylbenzenamine (S1). A 250 mL round-bottom flask equipped with a stir bar was charged with *N*-2-(mesitylimino)ethylidene)-2,4,6-trimethylbenzenamine (2.0 g; 6.8 mmol) and sodium borohydride (1.1 g; 28 mmol), which were dissolved in 25 mL of THF at 0 °C. Concentrated HCl (1.1 mL) was added dropwise over a 30 minute period, and the solution became grey in color with the evolution of gas. The reaction stirred for an additional 20 minutes, and then 70 mL of 3 N HCl was added. The solution was allowed to warm to room temperature and was stirred for one hour. The reaction mixture was filtered through a glass frit, and the white precipitate was washed with H_2O (2 × 25 mL) and rinsed with 40 mL of a 5% acetone:hexanes mixture. The organics were extracted with CH_2Cl_2 (3 × 30 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to afford a white solid. Yield: 20%. ^{1}H NMR spectra match the data reported in the literature.[25]



1

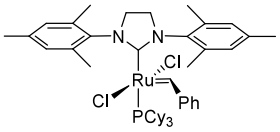
Synthesis of 1,3-dimesityl-2-(pentafluorophenyl)imidazoline (1). In a 10 mL flask equipped with a stir bar, **S1** (380 mg; 1.28 mmol) was dissolved in 0.7 mL of AcOH. Pentafluorobenzaldehyde (426 mg; 2.18 mmol) was then added and the reaction stirred overnight. The yellow precipitate was placed in a glass frit and washed with cold methanol to afford a white powder. Yield: 90%. ^{1}H and ^{19}F NMR spectra match the data

reported in the literature.[21] High-resolution MS analysis (FAB+) m/z: calcd 473.2016 [M+H], found 473.2007 [M+H].



4

Synthesis of 1,3-dimesityl-2-(trichloromethyl)imidazolidine (4). A 10 mL round-bottom flask equipped with a stir bar was charged with sodium hydroxide (232 mg; 5.80 mmol). To this was added 1.45 mL of chloroform. The solution stirred for two minutes and then 1,3-dimesitylimidazoline (101 mg; 0.294 mmol) was added. The solution stirred for two hours and was poured into 30 mL of ice water. The organics were extracted with CH_2Cl_2 (2 × 20 mL), rinsed with brine, dried over $MgSO_4$(s) and concentrated under vacuum to afford a white solid. The solid was dissolved in toluene and filtered through a small silica plug with (1:20 EtOAc:hexanes) to afford a white solid. Yield: 69%. ^{1}H and ^{31}P NMR spectra match the data reported in the literature.[25]

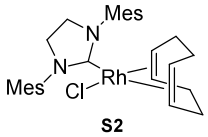


3

Synthesis of $(H_2IMes)(PCy_3)(Cl)_2Ru=CHPh$ (3) from 1. In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with **1** (100 mg; 0.211 mmol) and **2** (116 mg; 0.141 mmol). To this was added 4.2 mL of toluene. The vial was capped and removed from the glove box. It was then placed into an oil bath at 60 °C and stirred for four hours. The reaction mixture was purified by flash column chromatography on TSI Scientific silica gel (8% ether:pentane) to afford a reddish-brown solid. Yield: 91%. ^{1}H

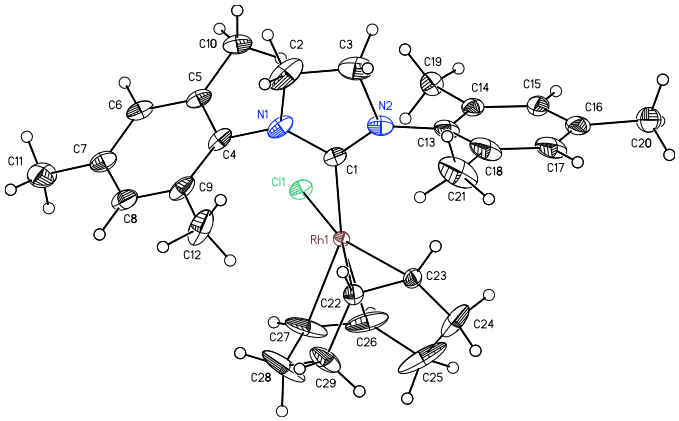
and ^{31}P NMR spectra match the data reported in the literature.[13] High-resolution MS analysis (FAB+) m/z: calcd 848.3306, found 848.3322.

Synthesis of $(H_2IMes)(PCy_3)(Cl)_2Ru=CHPh$ (3) from 4. By using the procedure described to prepare **3** from **1**, the reaction of **4** (77 mg; 0.18 mmol) and **2** (100 mg; 0.12 mmol) in 3.6 mL of toluene yielded **3** as a reddish-brown solid. Yield: 87%. ^{1}H and ^{31}P NMR spectra match the data reported in the literature.[13] High-resolution MS analysis (FAB+) m/z: calcd 848.3306, found 848.3315.



S2

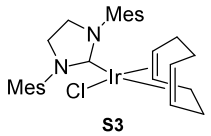
Synthesis of Chloro(h^4-1,5-cyclooctadiene)(1,3-dimesitylimidazole-2-ylidene) rhodium(I) (S2). In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with $[Rh(cod)Cl]_2$ (25 mg; 0.050 mmol) and **1** (0.048 mg; 0.10 mmol). To this was added 2.0 mL of toluene. The vial was capped and removed from the glove box. It was then placed into an oil bath at 70 °C and stirred for two hours.



S2

The reaction mixture was purified by flash column chromatography on silica gel (50% ether:hexanes) to afford a yellow crystalline solid. Yield: 90%. ^{1}H NMR and ^{13}C NMR data ($CDCl_3$) are reported for **S2** in the literature,[28] however, in our hands we found different data. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.98 (4H, d, J = 14.9 Hz, *m*-H), 4.45

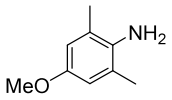
(2H, s, cod_{vinyl}), 3.84 (4H, m, J = 6.6, 2.0 Hz, NCH_2CH_2N), 3.35 (2H, s, cod_{vinyl}), 2.58 (6H, s, *p*-CH_3), 2.31 (12H, d, J = 7.15 Hz, *o*-CH_3), 1.75 (4H, m, J = 5.5 Hz, cod_{alkyl}), 1.49 (4H, m, J = 4.1 Hz, cod_{alkyl}). ^{13}C NMR (75MHz, $CDCl_3$, 298 K) δ 212.39 (d, J = 48.7 Hz, *C*–Rh), 137.9 (*p*-Ph), 136.0 (*o*-Ph), 134.9 (*m*-Ph), 129.7 (NCH_2CH_2N), 128.1 (NCH_2CH_2N), 96.9 (cod), 67.3 (cod), 51.1 (cod), 32.4 (cod), 27.9 (cod), 20.8 (cod), 19.7 (*o*-CH_3), 18.1 (*p*-CH_3). High-resolution MS analysis (FAB+) m/z: calcd 552.1778, found 552.1762. X-ray crystal structure confirms connectivity.[27]



S3

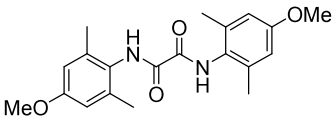
Synthesis of Chloro(h^4-1,5-cyclooctadiene)(1,3-dimesitylimidazole-2-ylidene) iridium(I) (S3). By using the procedure described to prepare (**S2**), the reaction of $[Ir(cod)Cl]_2$ (71 mg; 0.15 mmol) and **1** (50 mg; 0.74 mmol) in 3.0 mL of toluene yielded the product as an orange solid. The resulting reaction mixture was purified by flash column chromatography on silica gel (30% ether:hexanes) to afford an orange crystalline solid. Yield: 89%. ^{1}H NMR and ^{13}C NMR data ($CDCl_3$) are reported for **S3** in the literature,[28] however, in our hands we found different data. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.94 (4H, d, J = 10.7 Hz, *m*-H), 4.07 (2H, m, cod_{vinyl}), 3.88 (4H, s, NCH_2CH_2N), 3.06 (2H, m, cod_{vinyl}), 2.53 (6H, s, *p*-CH_3), 2.31 (12H, d, J = 9.07 Hz, *o*-CH_3), 1.62 (4H, m, cod_{alkyl}), 1.26 (4H, m, cod_{alkyl}). ^{13}C NMR (75MHz, $CDCl_3$, 298 K) δ 207.4 (*C*–Ir), 138.1 (*p*-Ph), 136.4 (*o*-Ph), 135.5 (*m*-Ph), 130.0 (NCH_2CH_2N), 128.6 (NCH_2CH_2N), 83.9 (cod), 51.9 (cod), 51.7 (cod), 33.6 (cod), 28.9 (cod), 21.3 (cod), 20.1

(*o*-CH_3), 18.7 (*p*-CH_3). High-resolution MS analysis (FAB+) m/z: calcd 642.2352 ($[M]^+$), found 642.2347 ($[M]^+$).



S4

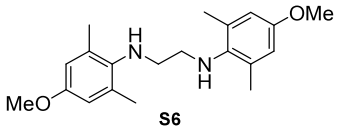
Synthesis of 4-methoxy-2,6-dimethylaniline (S4). A dry, two-neck 100 mL round-bottom flask equipped with a stir bar was charged with 4-amino-3,5-dimethylphenol (2.02 g; 14.8 mmol) and iodomethane (2.21 g; 15.6 mmol) under Ar(g). DMF (44 mL) was added and the reaction stirred at room temperature under Ar(g) for ten minutes to afford a dark solution. Potassium tertbutoxide (2.50 g; 22.3 mmol) was added, and the solution became tan and eventually dark green in color. The reaction stirred for a total of 16 hours and was then suspended in CH_2Cl_2. The organics were washed with 1 N KOH (3 × 50 mL) and brine, dried over $MgSO_4$(s) and concentrated under vacuum to yield a yellow solid. The crude product (with excess DMF) was used in the next reaction without characterization.



S5

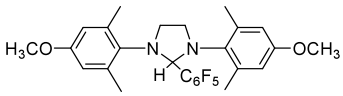
Synthesis of N^1,N^2-bis(4-methoxy-2,6-dimethylphenyl)oxalamide (S5). In a 250 mL Erlenmeyer flask, sodium hydroxide (1.8 g, 45 mmol) was dissolved in 75 mL of H_2O. The solution was placed into an ice bath and **S4** (2.24 g; 14.8 mmol) was added. Oxalyl chloride (1.05 mL; 12.0 mmol) was then added slowly by syringe. Gas evolved and a

light brown precipitate formed instantaneously. The crude product was used in the next reaction without characterization. Yield: 19% over two steps.



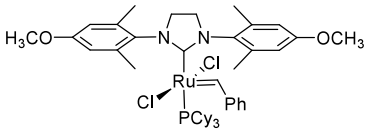
S6

Synthesis of *N*-(2-(4-methoxy-2,6-dimethylphenylamino)ethyl)-4-methoxy-2,6-dimethylbenzenamine(S6). A 100 mL pressure tube equipped with a stir bar was charged with **S5** (0.50 g; 1.4 mmol) under Ar(g). To this was added 12 mL of BH_3-THF (1.0 M in THF). The reaction vessel was capped and placed into an oil bath at 75 ºC behind a safety shield. The solution was stirred for 16 hours at this temperature. The reaction was allowed to cool to room temperature and poured into 20 mL of MeOH in a 100 mL round-bottom flask. Then, 0.50 mL of HCl was added. A precipitate formed and the solution was concentrated under vacuum to reveal a white solid. The solid was redissolved in methanol and concentrated to dryness two more times. The white solid was suspended in CH_2Cl_2 and 2 N KOH. The organics were extracted with CH_2Cl_2 (3 × 25 mL), washed with brine, dried over $MgSO_4$(s) and concentrated under vacuum to afford an off-white powder. Yield: 63%. ^{1}H NMR (300MHz, C_6D_6, 298 K) δ 6.79 (4H, s, *m*-H), 3.54 (6H, s, OCH_3), 3.02 (4H, s, NCH_2CH_2N), 2.32 (12H, s, *o*-CH_3). ^{13}C NMR (75MHz, C_6D_6, 298 K) δ 155.8 (*p*-C), 139.8 (*C*(Ar)–N), 132.3 (*o*-C), 114.5 (*m*-C), 55.0 (O*C*H$_3$), 49.9 (N*C*H$_2$*C*H$_2$N), 18.7 (*o*-*C*H$_3$). High-resolution MS analysis (FAB+) m/z: calcd 328.2151 ([M]$^+$), found 328.2150 ([M]$^+$).



S7

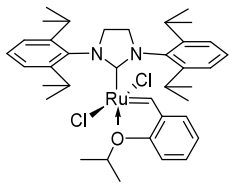
Synthesis of 1,3-Bis(4-methoxy-2,6-dimethylphenyl)-2-(pentafluorophenyl) imidzolidine (S7). In a 10 mL round-bottom flask equipped with a stir bar, **S6** (68 mg; 0.18 mmol) was suspended/dissolved in 0.7 mL of secBuOH. Pentafluorobenzaldehyde (61 mg; 0.31 mmol) was then added and the reaction stirred for two hours at room temperature. The reaction mixture was suspended in hexanes and 2 N KOH. The organics were extracted with hexanes (3 × 30 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to afford a yellow oil. The oil was purified by flash column chromatography on Brockmann IV alumina. Yield: 87%. ^{1}H NMR (crude) (300MHz, C_6D_6, 298 K) δ 6.54 (4H, b, *m*-H), 3.68 (2H, m, NCH_2CH_2N), 3.25 (8H, m, NCH_2CH_2N and OCH_3), 2.21 (12H, b, *o*-CH_3). ^{19}F NMR (282MHz, C_6D_6, 298 K) δ −137.3 (1F, J = 14.48, 8.28 Hz), −150.3 (1F, J = 16.55, 6.21 Hz), −155.5 (1F, J = 22.8, 20.7 Hz), −162.7 (1F, J = 14.48, 8.28 Hz), −164.5 (1F, J = 14.48, 8.28 Hz). High-resolution MS analysis (FAB+) m/z: calcd 506.1993, found 506.2002.



S8

Synthesis of $RuCl_2$(1,3-Bis(4-methoxy-2,6-dimethylphenyl)-2-ylidene)(PCy_3) (=CHPh) (S8). In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with **S7** (35 mg; 0.068 mmol) and **2** (28 mg; 0.034 mmol). To this was added 1.4 mL of toluene. The purple solution was then transferred into a screw-top NMR tube,

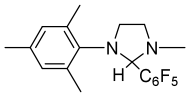
removed from the glove box and then placed into an oil bath at 60 ºC for 4 hours. The reaction mixture was purified by flash column chromatography on TSI Scientific silica gel (20% ether:pentane) to afford a reddish-brown solid. Yield: 75%. ^{1}H NMR (300MHz, CD_2Cl_2, 298 K) δ 19.1 (1H, s), 6.8-5.4 (9H, m), 3.9-3.4 (10H, m), 1.6-1.0 (45H, m). ^{31}P NMR (121MHz, CD_2Cl_2, 298 K) δ 29.8. High-resolution MS analysis (FAB+) m/z: calcd 880.3205, found 880.3208.



S9

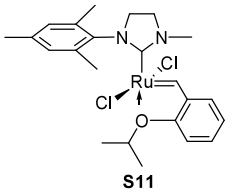
Synthesis of $RuCl_2$(1,3-Bis(2,6diisopropylphenyl)-2-ylidene)(=CH-o-iPr-Ph) (S9). In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with 1,3-bis(2,6-diisopropyl)-2-(pentafluorophenyl)imidazolidine (82 mg; 0.15 mmol) and $RuCl_2(PCy_3)$(=CH-o-iPr-Ph) (0.59 mg; 0.097 mmol). To this was added 3.0 mL of toluene. The vial was capped and removed from the glove box. It was then placed into an oil bath at 60 °C and stirred for five hours. The reaction mixture was purified by flash column chromatography on TSI Scientific silica gel (5% ether:hexanes) to afford a green solid. Yield: 80%. ^{1}H NMR and ^{13}C NMR data (C_6D_6) are reported for **S9** in the literature,[29] however, in our hands we found different data. ^{1}H NMR (300MHz, C_6D_6, 298 K) δ 16.5 (1H, s, Ru=C*H*Ph), 7.35 (2H, *J* = 6.58 Hz), 7.24 (4H, m, *J* = 7.02 Hz), 6.58 (2H, m, *J* = 7.45 Hz), 6.57 (1H, t, *J* = 7.45 Hz), 6.26 (1H, d, *J* = 8.78 Hz) 4.38 (1H, sept, OC*H*$(CH_3)_2$), 3.80 (8H, m, NCH_2CH_2N and ArC*H*$(CH_3)_2$), 1.15 (6H, d, *J* = 7.02 Hz), 0.89 (24H, d, *J* = 6.14 Hz) ^{13}C NMR (75MHz, C_6D_6, 298 K) δ 287.0 (*C*–Ru), 215.5,

153.0, 149.6, 144.8,137.5, 130.0, 129.1, 124.7, 122.4, 122,2, 113.2, 71.1, 54.9, 30.2, 29.2, 26.7, 23.9, 21.8. High-resolution MS analysis (FAB+) m/z: calcd 710.2344 ($[M]^+$), found 710.2371 ($[M]^+$).



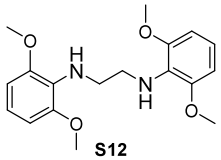
S10

Synthesis of 1-Mesityl-3-methyl-2-(pentafluorophenyl)imidzolidine (S10). In a 10 mL flask equipped with a stir bar, 2,4,6-trimethyl-*N*-(2-(methylamino)ethyl)benzenamine (207 mg; 1.08 mmol) was dissolved in 0.9 mL of AcOH. Pentafluorobenzaldehyde (359 mg; 1.82 mmol) was then added and the reaction mixture stirred for 1 hr at room temperature. The yellow solution was suspended in 50 mL of 2 N KOH and 50 mL of hexanes. The organics were extracted with hexanes (3 × 25 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to yield a yellow oil. The yellow oil was purified by flash column chromatography (5% EtOAc:hexanes) on Brockmann IV alumina and concentrated under vaccum to afford a light yellow oil. Yield: 85%. ^{1}H NMR (300MHz, C_6D_6, 298 K) δ 6.7 (2H, s, *m*-H), 5.4 (1H, s, NC*H*(C_6F_5)N), 3.5 (2H, m, *J* = 6.4 Hz, NCH_2CH_2N), 3.0 (3H, m, NCH_3), 2.7 (2H, m, NCH_2CH_2N), 2.18 (3H, s, *p*-CH_3), 2.02 (6H, d, 15.0 Hz, *o*-CH_3). ^{19}F NMR (282MHz, C_6D_6, 298 K) δ −143.0 (2F, b), −155.8 (1F, t, *J* = 20.7 Hz), −163.3 (2F, dd, *J* = 14.5, 8.3 Hz). High-resolution MS analysis (FAB+) m/z: calcd 369.1390 ($[M]^+$), found 369.1393 ($[M]^+$).



S11

Synthesis of $RuCl_2$(1-mesityl-3-methyl-2-ylidene)(=CH-o-iPr-Ph) (S11). Compound **S10** (113 mg; 0.304 mmol) was added to a 10 mL round-bottom flask and dissolved in degassed toluene (6 mL). Ar(g) was then bubbled through the solution via syringe for 20 minutes. A separate 50 mL round-bottom Schlenk flask containing $RuCl_2(PCy_3)$(=CH-o-*i*Pr-Ph) (122 mg; 0.203 mmol) was equipped with a stir bar and removed from the glove box. It was then placed under Ar(g) (via pump/backfill × 3). To this second flask was added the solution containing 2,4,6-trimethyl-*N*-(2-(methylamino)ethyl)benzenamine via syringe. The flask was sealed and placed in an oil bath at 60 °C for 5 hours with stirring. The flask was cooled to room temperature and then placed under Ar(g) (pump/backfill × 3). Copper(I) chloride (20.0 mg; 0.203 mmol) was then added and the resulting solution was allowed to stir for 1 hr at room temperature. The reaction mixture was purified by flash column chromatography (3% MeOH:CH_2Cl_2) on TSI Scientific silica gel and concentrated under vacuum to afford a green solid. Yield: 65%. ^1H and ^{13}C NMR spectra match the data reported in the literature.[26] High-resolution MS analysis (FAB+) m/z: calcd 522.0779, found 522.0759.



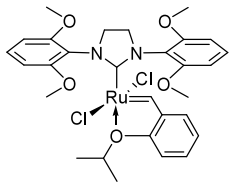
S12

Synthesis of *N*-(2-(2,6-dimethoxyphenylamino)ethyl)-2,6-dimethoxybenzenamine (S12). A two-neck 100 mL round-bottom flask equipped with a stir bar and condenser was charged with 1,3-(2,6-dimethoxyphenyl)imidazoline (172 mg; 0.452 mmol). To this was added 30 mL of 3 N HCl. The mixture was placed in an oil bath at 80 °C and stirred for 12 hours. The solution was then cooled to room temperature and suspended in CH_2Cl_2 and 2 N KOH. The organics were extracted with CH_2Cl_2 (3 × 25 mL), washed with brine, dried over $MgSO_4$(s) and concentrated under vacuum. The resulting yellow oil was then purified by flash column chromatography on Brockmann IV alumina (0.5% EtOAc: hexanes) Yield: 41%. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.82 (2H, t, J = 7.98 Hz, *p*-H), 6.54 (4H, d, J = 8.25 Hz, *m*-H), 4.24 (2H, s, N*H*), 3.82 (12H, s, OCH_3), 3.28 (4H, NCH_2CH_2N). ^{13}C NMR (75MHz, $CDCl_3$, 298 K) δ 151.6 (*o*-C), 126.7 (*p*-C), 120.2 (*C*(Ar)–N), 104.6 (*m*-C), 55.9 (O*C*H$_3$), 47.0 (N*C*H$_2$*C*H$_2$N). High-resolution MS analysis (FAB+) m/z: calcd 333.1814 ([M+H]), found 333.1806 ([M+H]).

S13

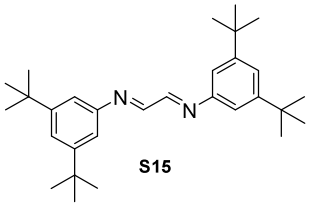
Synthesis of 1,3-Bis(2,6-dimethoxyphenyl)-2-(pentafluorophenyl)imidzolidine (S13). In a 10 mL round-bottom flask equpped with a stir bar, **S12** (60.8 mg; 0.183 mmol) was suspended/dissolved in 0.7 mL of secBuOH. Pentafluorobenzaldehyde (61.0 mg; 0.311 mmol) was then added and the reaction stirred for 12 hours at room temperature. The

reaction mixture was suspended in hexanes and 2 N KOH. The organics were extracted with hexanes (3 × 30 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to afford a yellow oil. The oil was purified by flash column chromatography on Brockmann IV alumina (1% methanol:CH_2Cl_2) to afford a yellow solid. Yield: 70%. ^{1}H NMR (300MHz, C_6D_6, 298 K) δ 6.83 (2H, t, *J* = 10.1 Hz, *p*-H), 6.25 (4H, d, *J* = 8.25, *m*-H), 4.11 (2H, m, NC*H*$_2$C*H*$_2$N), 3.64 (2H, m, NC*H*$_2$C*H*$_2$N), 3.34 (12H, s, OC*H*$_3$). ^{19}F NMR (282 MHz, C_6D_6, 298 K) δ −158.8 (2F, m, *J* = 20.69 Hz), −166.6 (3F, m, *J*= 14.48, 6.21 Hz). High-resolution MS analysis (FAB+) m/z: calcd 511.1656 ([M+H]), found 511.1649 ([M+H]).



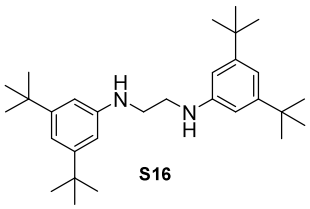
S14

Synthesis of $RuCl_2$[1,3-Bis(2,6-dimethoxyphenyl)-2-ylidene](=CH-o-iPr-Ph) (S14). In the glove box, a 20 mL scintillation vial equipped with a stir bar was charged with **S13** (10 mg; 0.020 mmol) and $RuCl_2(PCy_3)$(=CH-o-*i*Pr-Ph) (7.8 mg; 0.013 mmol). To this was added 0.5 mL of toluene. The brown solution was then transferred into a screw-top NMR tube, removed from the glove box and then placed into an oil bath at 60 °C for 4 hours. The reaction mixture was purified by flash column chromatography on TSI Scientific silica gel (20% ether:pentane) to yield an olive-green solid. Yield: 25%. ^{1}H NMR (300MHz, CD_2Cl_2, 298 K) δ 18.4 (1H, s), 7.9-6.3 (10H), 5.0 (1H, sept, *J* = 6.4, 3.84 Hz), 4.2-3.6 (16H), 1.5 (6H). High-resolution MS analysis (FAB+) m/z: calcd 662.0889, found 662.0872.



S15

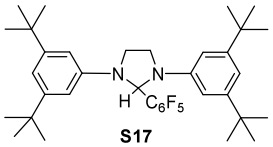
Synthesis of *N*-2-(3,5-di-*tert*-butylphenylimino)ethylidene)-3,5-di-*tert*-butyl-benzenamine (S15). 3,5-di-*tert*-butylaniline (2.50g; 12.2 mmol) was added to a 100 mL round-bottom flask equipped with a stir bar and dissolved in a 1:1 mixiture of isopropanol:water at 0 °C. Glyoxal (40% in H_2O) (0.7 mL; 6.1 mmol) was added. The solution was stirred vigorously for 2.5 hours and allowed to warm to room temperature. The yellow precipitate was dissolved in CH_2Cl_2 and passed through a glass frit. The yellow solution contained in the receiving flask was concentrated under vacuum to afford a yellow solid that was used in the next reaction without characterization.



S16

Synthesis of *N*-(2-(3,5-di-*tert*-butylphenylamino)ethyl)-3,5-di-*tert*-butylbenzenamine (S16). A 10 mL round-bottom flask equipped with a stir bar was charged with **S15** (2.86 g; 6.62 mmol) and sodium borohydride (1.02 g; 27.0 mmol), which were dissolved in 24 mL of THF at 0 °C. Concentrated HCl (1.09 mL) was added dropwise over a 30 minute period, and the solution became grey in color with gas evolution. The solution stirred for an additional 20 minutes and 67 mL of 3 N HCl was added. The solution was allowed to warm to room temperature and stirred for one hour. The reaction mixture was filtered through a glass frit and the white precipitate was washed with H_2O (2 × 25 mL) and

rinsed with 40 mL of a 5% acetone:hexanes mixture. The percipitate was suspended in CH_2Cl_2 and 2 N KOH. The organics were extracted with CH_2Cl_2 (3 × 30 mL), washed with brine, dried over Na_2SO_4(s) and concentrated under vacuum to afford a white solid. Yield: 10%. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.60 (2H, s, *p*-H), 6.39 (4H, s, *o*-H), 5.42 (2H, s, N*H*), 3.21 (4H, s, NCH_2CH_2N), 1.21 (36H, s, CH_3).



S17

Synthesis of 1,3-Bis(3,5-di-*tert*-butylphenyl)-2-(pentafluorophenyl)imidzolidine (S17). In a 10 mL flask equipped with a stir bar, **S16** (181 mg; 0.416 mmol) was dissolved in 0.7 mL of AcOH. Pentafluorobenzaldehyde (170 mg; 0.867 mmol) was then added and a yellow precipitate began to form instantaneously. The reaction mixture stirred for 90 minutes. The precipitate was placed in a glass frit and washed with cold methanol to afford a white powder. Yield: 52%. ^{1}H NMR (300MHz, $CDCl_3$, 298 K) δ 6.88 (2H, s, *p*-H), 6.52 (4H, s, *o*-H), 5.30 (1H, s, N*H*), 4.00 (2H, m, NCH_2CH_2N), 3.79 (2H, m, NCH_2CH_2N) 1.6-1.3 (36H, m, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$, 298 K) δ −142.0 (2F, b), −154.3 (1F, t, J = 21.4 Hz), −162.9 (2F, b).

Solvent dependence of the thermolysis of 1. To evaluate the dependence of the thermolysis of **1** on the solvent composition, six 5 mL scintillation vials were charged with 20 mg of **1**. A different solvent (benzene-d_6, toluene-d_8, CD_2Cl_2, THF-d_8, acetone-d_6 or acetonitrile-d_3) was added to each vial. The vials were shaken until all of **1** dissolved. The solutions were then transferred into six screw-cap NMR tubes, which

were immediately placed into an oil bath at 45 °C. After 1 hr, the NMR tubes were removed from the bath, cooled to −78 °C and ^{19}F NMR spectra were taken immediately.

^{19}F NMR data for **1**: (282 MHz, C_6D_6, 298 K) δ −137.6 (1F, m, J = 14.5, 8.3, 6.2 Hz), −150.4 (1F, m, J = 14.5, 8.3 Hz), −155.5 (1F, m, J = 22.8, 20.2 Hz), −162.7 (1F, m), −164.5 (1F, m, J = 14.5, 8.3, 6.2 Hz). ^{19}F NMR (282 MHz, THF-d_8, 298 K) δ −140.6 (1F, m, J = 12.4, 10.2, 8.3 Hz), −151.1 (1F, m, J = 14.5, 8.3 Hz), −158.1 (1F, m, J = 20.7 Hz), −165.4 (2F, m). ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) δ −136.9 (1F, m, J = 14.5, 8.3 Hz), −150.1 (1F, m, J = 14.5, 8.3 Hz), −157.3 (1F, m, J = 20.7 Hz), −164.4 (2F, m). ^{19}F NMR (282 MHz, CD_3CN, 298 K) δ −135.9 (1F, m, J = 10.3, 8.3 Hz), −151.9 (1F, m, J = 14.5, 8.3 Hz), −157.5 (1F, m, J = 20.7 Hz), −164.8 (1F, m), −165.8 (1F, m, J = 15.3, 6.1 Hz). ^{19}F NMR (282 MHz, acetone-d_6, 298 K) δ −137.4 (1F, m, J = 21.4, 9.1 Hz), −151.3 (1F, m, J = 15.3, 9.2 Hz), −157.9 (1F, m, J = 21.4, 18.3 Hz), −165.3 (1F, m, J = 21.4, 9.2 Hz), −165.7 (1F, m, J = 15.3, 6.1 Hz). ^{19}F NMR (282 MHz, toluene-d_8, 298 K) δ −137.4 (1F, m, J = 14.5, 7.3 Hz), −150.3 (1F, m, J = 14.5, 9.7 Hz), −155.9 (1F, m, J = 21.8 Hz), −163.2 (1F, m, J = 12.1, 9.7 Hz), −164.5 (1F, m, J = 20.7 Hz).

^{19}F NMR data for pentafluorobenzene: (282 MHz, C_6D_6, 298 K) δ −139.5 (2F, m, J = 10.3, 8.3 Hz), −154.4 (1F, t, J = 20.7 Hz), −162.7 (2F, m). ^{19}F NMR (282 MHz, THF-d_8, 298 K) δ −137.5 (2F, m, J = 14.5, 8.3 Hz), −156.7 (1F, t, J = 20.7, 18.6 Hz), −164.5 (1F, m, J = 8.3, 6.3 Hz). ^{19}F NMR (282 MHz, CD_2Cl_2, 298 K) δ −136.9 (1F, m, J = 14.5, 8.3 Hz), −150.1 (1F, m, J = 14.5, 8.3 Hz), −157.3 (1F, m, J = 20.7 Hz), −164.4 (1F, m). ^{19}F NMR (282 MHz, CD_3CN, 298 K) δ −141.1 (1F, m, J = 12.4, 10.3 Hz), −141.4 (1F, m, J = 12.4, 8.3 Hz), −156.7 (1F, m, J = 20.7, 18.6 Hz), −164.6 (2F, m). ^{19}F NMR (282 MHz,

acetone-d_6, 298 K) δ −140.9 (1F, m, J = 10.3, 8.3 Hz), −141.2 (1F, m, J = 12.4, 8.3 Hz), −156.8 (1F, m, J = 20.7, 18.6 Hz), −164.7 (2F, m).^{19}F NMR (282 MHz, toluene-d_8, 298 K) δ −139.6 (2F, m, J = 12.1, 9.7 Hz), −154.6 (1F, m, J = 21.8, 19.3 Hz), −162.8 (2F, m, J = 14.5, 7.3 Hz).

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