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Notes

Synthesis of N-Heterocylic Carbene-Containing Metal Complexes from 2-(Pentafluorophenyl)imidazolidines

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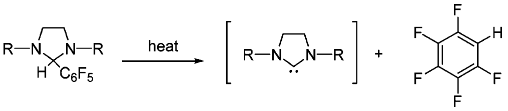
Summary: N-Heterocyclic carbene (NHC)-containing metal complexes are prepared through a simple, base-free method involving the decomposition of 2-(pentafluorophenyl)imidazolidines under mild thermolytic conditions. Ruthenium, iridium, and rhodium complexes containing NHC ligands with different electronic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

N-Heterocyclic carbene (NHC)-derived complexes have been used as powerful catalysts for effecting many transformations.[1] Despite their popularity, few methods are reported for their preparation. Current methods include the deprotonation[2a−c] or oxidative addition[2d,e] of imidazolium salts, thermolysis of 2-(trichloromethyl)imidazolidine complexes,[2f] oxidative addition of 2-chloroimidazolium salts,[2g] transmetalation of silver−NHC complexes,[2h] and sodium reduction of imidazolidin-2-thiones.[2i] 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.[3] Many of these methods utilize imidazolium salt precursors, which are insoluble in many media and difficult to further functionalize. "Protected" NHC adducts like 2-(alkoxy)imidazolidines, 2-(trichloromethyl)imidazolidines,[2f] 2-(triethylborane)imidazolidines[4] and 2-(dimethylamino)imidazolidines[5] are used to prepare NHC-containing complexes and offer the advantage that they can be chemically manipulated.[6] 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 (eq 1).[7]



(1)

The only byproduct of the reaction is pentafluorobenzene (bp 85 °C). Pentafluorophenyl adducts have been employed in three instances in the literature to prepare NHC-containing transition-metal complexes. Waymouth and Hedrick synthesized an NHC complex from allylpalladium chloride,[7] and Bedford et al. reported phosphite-based palladacycle NHC compounds[8a] as well as an iron−NHC complex that was formed in situ.[8b] 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.

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 1 and 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 9 months, while **4** shows signs of decomposition after a few weeks under the same conditions.

The progress of the thermolysis of pentafluorophenyl adducts can be readily followed by ^{19}F NMR by monitoring the

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Scheme 1. Preparation of 3 from the Thermolysis of 1,3-Bis(2,4,6-trimethylphenyl)-2-(pentafluorophenyl)imidazolidine, 1

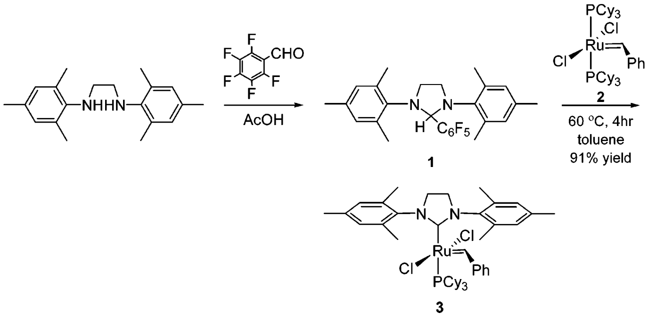
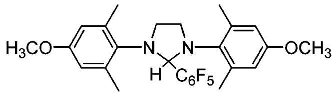
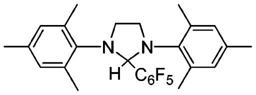
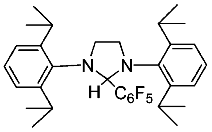
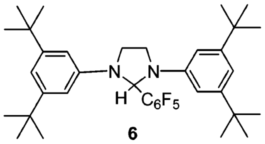


Table 1. Comparison of the Thermolysis of 2-(Pentafluorophenyl)imidazolidines to >95% in Benzene or Toluene

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

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 h at 60 °C) than 1,3-bis(2,4,6-trimethylphenyl)-2-(pentafluorophenyl)imidazolidine (**1**) (>95% conversion in 4 h at 60 °C), as shown in Table 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 (4 or 5 h for the adducts containing methyl or isopropyl groups, respectively) to reach the same conversion (Table 1).

Table 2. Comparison of Percent Conversion to Pentafluorobenzene in Different Solvents in the Thermolysis of 1 after 1 h 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

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 1 h quantified by ^{19}F NMR spectroscopy (Table 2). More polar solvents such as acetone and acetonitrile were shown to yield higher conversions than less polar solvents such as 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.

Ruthenium−, rhodium−, and iridium−NHC complexes were easily prepared from pentafluorophenyl adducts in generally high yield under mild thermolytic conditions, as shown in Table 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-methylimidazol-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**.

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

Scheme 2. Preparation of 3 from the Thermolysis of 1,3-Bis(2,4,6-trimethylphenyl)-2-(trichloromethyl)imidazolidine, 4

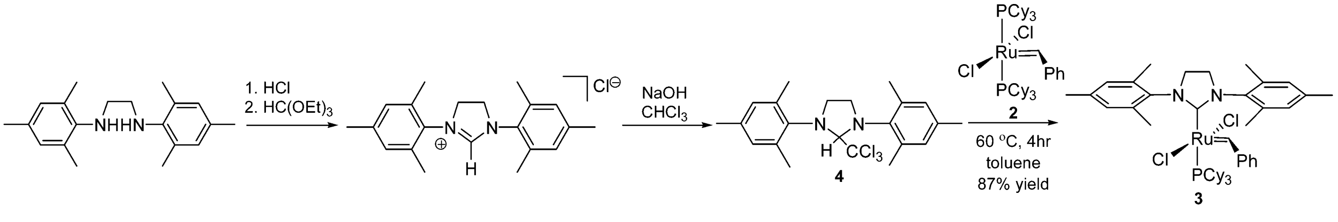
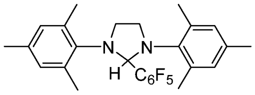
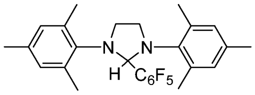
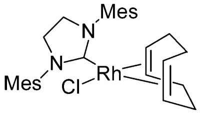
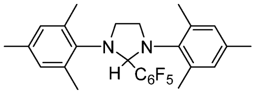
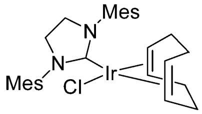
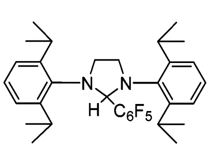
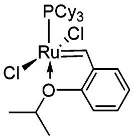
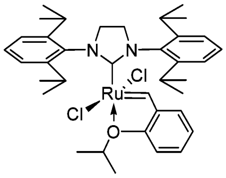
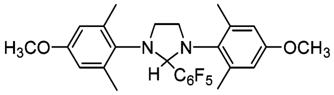
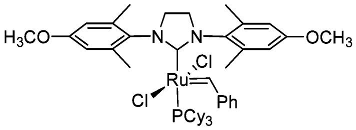
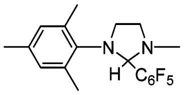
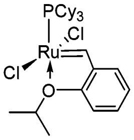
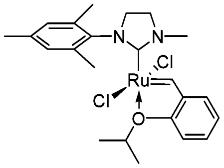
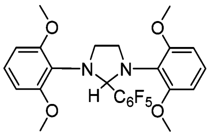
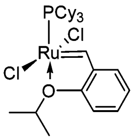
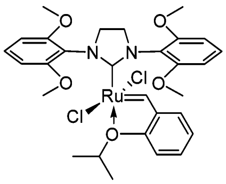


Table 3. N-Heterocyclic Carbene Complexes Prepared from 2-(Pentafluorophenyl)imidazolidines

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

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.

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Supporting Information Available: Crystallographic data for chloro(η^4-1,5-cyclooctadiene)(1,3-dimesitylimidazole-2-ylidene)-rhodium(I), experimental procedures, and NMR data for all new compounds are available free of charge via the Internet at http://pubs.acs.org.

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