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Base-Controlled Directed Synthesis of Metal−Methyleneimidazoline (MIz) and Metal−Mesoionic Carbene (MIC) Compounds

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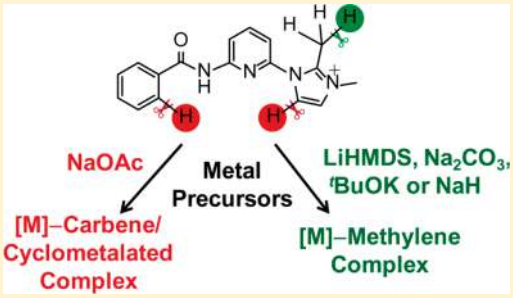
Supporting Information

ABSTRACT: Reactions of a host of metal precursors with pyridyl-(benzamide)-functionalized C^2-methyl-protected imidazolium salts $[L^1H_2]I$ and $[L^2H]I$ afforded the metal−methyleneimidazoline (MIz) compounds $[Ru(L^1\text{-}\kappa C^1)(p\text{-cymene})]I$ (**1**), $[Mn(L^1\text{-}\kappa C^1)(CO)_3]$ (**2**), $[Ru(L^2\text{-}\kappa C^1)(p\text{-cymene})Cl]PF_6$ (**3**), and $[Ir(L^2\text{-}\kappa C^1)(Cp^*)Cl]PF_6$ (**4**) in the presence of different external bases, such as LiHMDS, Na_2CO_3, ^{t}BuOK, and NaH. However, the use of NaOAc led to the selective formation of the metal−mesoionic carbene (MIC) compounds $[Ru(L^2\text{-}\kappa C^5)(p\text{-cymene})Cl]PF_6$ (**5**), $[Ir(L^2\text{-}\kappa C^5)(Cp^*)Cl]PF_6$ (**6**), $[Ir_2(L^1\text{-}\kappa C^5)(Cp^*)_2I]PF_6$ (**8**), and the ortho-metalated compound $[Ir(L^1)(Cp^*)I]$ (**7**). All compounds have been characterized by spectroscopic techniques and X-ray crystallography. Being more acidic, the C^2-methyl is readily deprotonated by the external base to give the metal−MIz products. A metal-bound acetate, in contrast, interacts selectively with the imidazolium C^5−H and drives the reaction toward the metal−MIC formation. DFT calculations support a concerted metalation−deprotonation pathway for selective C−H activation and metalation.

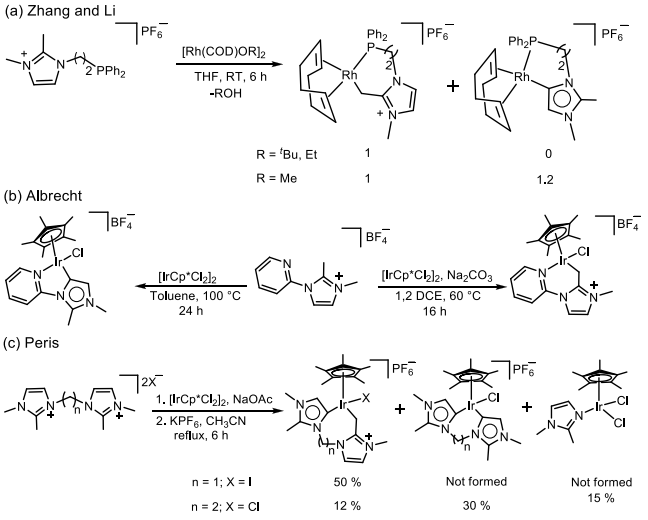


INTRODUCTION

N-heterocyclic carbenes (NHCs) have found widespread use in organometallic chemistry and catalysis, primarily due to their relatively easy synthetic accessibility, broad structural and stereoelectronic diversity, and their ability to form stable compounds with different metal ions.[1] Mesoionic carbenes (MICs) are a subclass of NHCs featuring reduced heteroatom stabilization of the carbenic carbon and hence stronger σ donation for metal coordination.[2] The remarkable properties and reactivities of metal−MIC complexes have led to numerous exciting applications,[3] particularly in catalysis.[4] In contrast to the classical metal−NHC complexes, the synthesis of metal−MIC compounds is a challenging task, as the targeted C^4/C^5−H of the imidazolium precursor is weakly acidic and therefore less vulnerable for metalation than the C^2−H bond.[5] The various methods used to synthesize metal−MIC compounds include the use of bulky wingtip groups,[6] substitution of the C^2−H with nitrogen, i.e. the employment of the triazolium salts,[7] and oxidative addition of C^4/C^5−X (X = halides, H) to low-valent metals.[8] Apart from these, the most commonly employed strategy involves blocking of the C^2 position with an alkyl/aryl group.[9,10] Installing a methyl group at the C^2 position has not been particularly successful because of its high acidity,[11] which has largely afforded the metal−methyleneimidazoline compounds, henceforth referred to as metal−MIz, and metal−MIC compounds as well. The product identity depends on the structure of the imidazolium salts, the nature of the base, and the reaction conditions.

Zhang and Li utilized a phosphine-tethered 2-methylimidazolium salt to selectively access the metal−MIz complex either by direct reaction with $[Rh(COD)(OR)]_2$ (R = ^{t}Bu, Et) (Scheme 1a) or via reaction of $[Rh(COD)Cl]_2$ with the proligand in the presence of ^{t}BuOK. The use of the relatively less bulky methoxide (R = Me) afforded a mixture of Rh−MIz and Rh−MIC complexes in 1:1.2 ratio.[12] The Albrecht group achieved the selective synthesis of both Ir−MIC and Ir−MIz

Scheme 1. Metalation of C^2-Methyl-Protected Imidazolium Salts



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