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Improved synthesis of *N*-heterocyclic olefins and evaluation of their donor strengths

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ABSTRACT

An improved synthesis of *N*-heterocyclic olefins (NHOs) containing terminal CH_2 donor groups was developed. A preliminary investigation of the bonding mode and donor strengths of various structurally distinct NHOs was conducted by analysis of the IR and NMR spectra of their corresponding rhodium carbonyl complexes NHO·RhCl(CO)$_2$, along with examination of pertinent metrical parameters via X-ray crystallography and Density Functional Theory (DFT) computations.

1. Introduction

N-Heterocyclic olefins (NHOs) represent a relatively new and emerging carbon-based ligand class with donor characteristics that complement those found within their well-known *N*-heterocyclic carbene (NHC) counterparts. *N*-Heterocyclic olefins were first reported by Kuhn and coworkers in the early 1990s [1], and the initially reported NHOs, such as $ImMe_4CH_2$ ($[(MeCNMe)_2C{=}CH_2]$), were shown to be sufficiently nucleophilic to coordinate as neutral two-electron donors to both main group and transition metal-based species (e.g., BH_3, $W(CO)_5$, RhCl(COD) [1]). From these initial studies it is expected that NHOs will exhibit similar coordination behavior as the widely explored phosphines and carbenes. However, NHOs are anticipated to be softer donors when compared to NHCs as they possess highly polarized exocyclic C=C double bonds which place considerable electron density of high p-orbital character at the terminal/ligating carbon atoms (Scheme 1) [1,2]; as a result, NHOs might show affinity for low oxidation state Ni(0) and Pd(0) sites present during many catalytic processes. These characteristics, along with a high inherent degree of structural tunability (attainable by either ring or methylene carbon substitution), could be utilized to advance both main group element and transition metal-based catalysis [3].

The exploration of *N*-heterocyclic olefins as Lewis bases in our group began in 2011 with the synthesis of $IPrCH_2$ adducts of the low oxidation state dihydrides, GeH_2 and SnH_2 ($IPrCH_2 = [(HCNDipp)_2C{=}CH_2]$; Dipp = 2,6-^{i}Pr$_2C_6H_3$) [2a]. Notably, widely utilized phosphine donors failed to yield stable EH_2 complexes (E = Ge and Sn), thus illustrating a case where NHOs were superior ligands to common benchmark donors. Accordingly, our group [4] and others [5] have been actively preparing NHO complexes of electron deficient main group species, while the sequestration of CO_2 [6] and the *N*-heterocyclic olefin-instigated polymerization of polar methacrylate-based monomers has been reported by the Lu group [7].

In this article, we report a new efficient method to prepare sterically encumbered NHOs and outline preliminary coordination chemistry to form rhodium carbonyl complexes. The latter species were examined by spectroscopic, crystallographic and computational methods in order to ascertain the donating ability of *N*-heterocyclic olefins in relation to the known carbene ligand, IPr (IPr = $(HCNDipp)_2C$:).

2. Discussion and results

2.1. Improved synthesis of N-heterocyclic olefins

There are currently three known methods in the literature to prepare the most thoroughly studied NHO, $IPrCH_2$ (IPr = $[(HCNDipp)_2C{:}]$, Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$; **1**) [1,2a,5a]. Each of these strategies, although successful, has its own considerable drawbacks. The first procedure listed in Scheme 2 (procedure A) was initially used by our own laboratory to prepare $IPrCH_2$ (**1**) [2a]. This one-pot method involves mixing two equivalents of IPr with methyliodide in toluene to install a terminal methylene group, $=CH_2$, at the carbenic carbon. In this process, one

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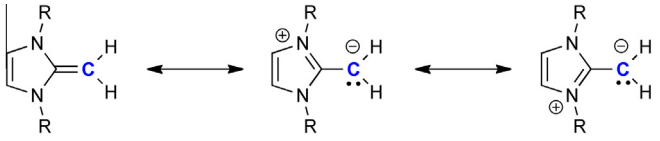
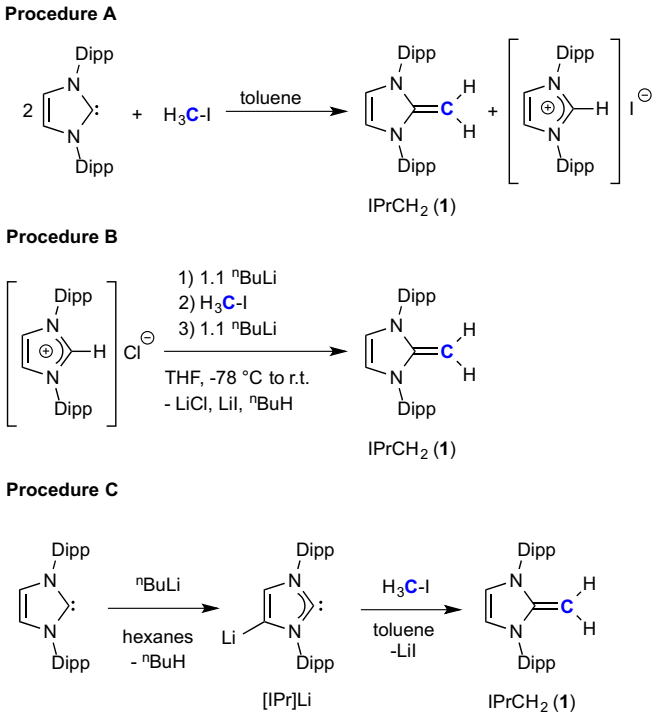


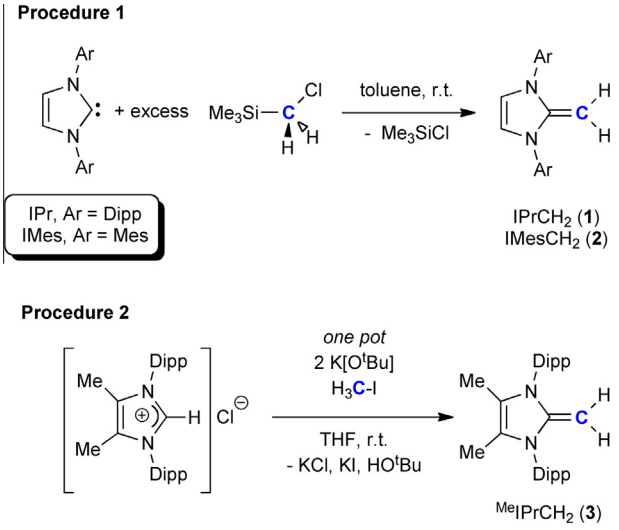
Scheme 1. Canonical forms for a generic NHO (R = aryl or alkyl groups).

equivalent of IPr reacts with MeI to yield the imidazolium salt [IPrCH$_3$]I *in situ*, which is then deprotonated by an additional equivalent of IPr to yield IPrCH$_2$ (**1**) in up to a 90% yield [2a]. However the final product contains variable amounts of residual IPr, which is difficult to separate from **1**. An alternative method to synthesize **1** was reported [1,3], which in our hands, leads to less IPr contamination in the final NHO product (Scheme 2; procedure B). In the first step, the strong Brønsted base, ^{n}BuLi, is used to deprotonate [IPrH]Cl to yield free IPr in solution, which is then alkylated by MeI to form [IPrMe]I; in the final step, more ^{n}BuLi is added to effect another deprotonation event leading to the formation of IPrCH$_2$ (**1**) [3]. Despite the larger number of steps associated with procedure B, each transformation can be sequentially carried out in a single reaction flask. However, this route yields [Li(THF)$_x$]I as a by-product, which has appreciable solubility in organic solvents (even in hexanes), rendering its separation from IPrCH$_2$ (**1**) difficult, resulting in low overall yields of pure **1**. Additionally, Robinson and coworkers reported a protocol (Scheme 2, procedure C) that involves backbone deprotonation of IPr using ^{n}BuLi in hexanes [5a]. The intermediately formed Li-salt, [IPr]Li, can be methylated with MeI in toluene leading to the generation of IPrCH$_2$ via proton-transfer. This method gives pure IPrCH$_2$ (**1**) on a small scale, however, on a large scale product separation from LiI can still be problematic.

During our general explorations of the reactivity of **1** towards various electrophiles, we noticed that pure IPrCH$_2$ (**1**) could be prepared in a very efficient manner by combining IPr (*ca.* 0.5 g scale) with an excess of ClCH$_2$SiMe$_3$ (*ca.* 4 equiv.) in toluene at ambient temperature (Scheme 3, procedure 1). After the mixture is stirred for four days, a small amount of precipitate is formed that is easily separated by filtration, and removal of the volatiles from the filtrate yields **1** in good yield (*ca.* 70% yield) as a spectroscopically pure solid (determined by ^{1}H NMR spectroscopy). As shown in Scheme 3, this reaction produces ClSiMe$_3$ as a by-product and this transformation likely goes via the transient alkylsilyl imidazolium salt [IPr-CH$_2$-SiMe$_3$]Cl; it should also be mentioned that ClSiMe$_3$ does not react with IPr or IPrCH$_2$ at room temperature, thus simplifying the nature of the reaction profile in Scheme 3. This route allowed the preparation of large quantities of **1**: starting from 5.5 g of IPr and ca. 5 equiv. ClCH$_2$SiMe$_3$ in 150 mL toluene, complete conversion was achieved after stirring for 7 days and yielded after filtration 4.51 g of analytically pure **1** in a 79% yield (based on IPr). This new synthesis is a large improvement over the protocols used to date, and interestingly, the same route can be used to prepare the related *N*-heterocyclic olefin IMesCH$_2$ (IMes = [(HCNMes)$_2$C:] [7], Mes = 2,4,6-Me$_3$C$_6$H$_2$; **2**). In this case, full conversion of IMes into IMesCH$_2$ is achieved in 12 h with three equiv. of ClH$_2$CSiMe$_3$; the acceleration in reaction rate is likely due to the less hindered nature of the IMes nucleophile in relation to IPr. Unfortunately the backbone-methylated carbene ^{Me}IPr (^{Me}IPr = [(MeCNDipp)$_2$C:]), only reacts slowly with ClCH$_2$SiMe$_3$ at room temperature, and formation of high yields of ^{Me}IPrCH$_2$ (**3**) does not occur even after two weeks of stirring. A possible explanation for the sluggish reactivity between ^{Me}IPr and ClCH$_2$SiMe$_3$, is that the backbone positioned Me groups in ^{Me}IPr push the flanking Dipp groups forward, leading to greater steric crowding about the nucleophilic carbene donor center relative to in IPr [8]. As a result of these challenges, we decided to move to a procedure described earlier by von Wangelin et al. in which they combined [IPrH]Cl with two equivalents of K[O^{t}Bu] in THF at room temperature, and after 20 min added the respective alkyl halides to obtain a wide variety of 2-alkylidine imidazolines [9]. In order to prepare ^{Me}IPrCH$_2$ (**3**), MeI was added to a mixture of [^{Me}IPrH]Cl and two equiv. of K[O^{t}Bu] in THF at room temperature, and the mixture was stirred overnight (Scheme 3, procedure 2). This resulted in the isolation of the backbone-substituted NHO, ^{Me}IPrCH$_2$ (**3**), in a yield of 86% as an analytically pure crystalline solid (Fig. S2, see ESI). Thus we now have two effective routes to prepare a library of different NHOs, and in the next section of this paper we will compare the donating abilities of these NHOs with their *N*-heterocyclic carbene counterparts.



Scheme 2. Literature procedures for the preparation of IPrCH$_2$ (**1**) using an excess of IPr (procedure A), an exogenous base (procedure B) or via backbone-activated IPr (procedure C).



Scheme 3. Improved syntheses of NHOs using ClCH$_2$SiMe$_3$ (procedure 1) or K[O^{t}Bu] as external base in a one-pot reaction (procedure 2).