

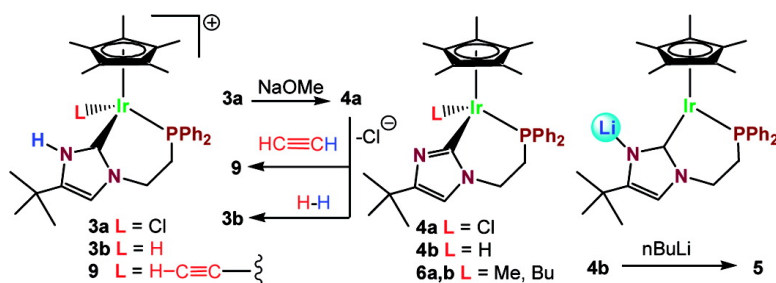
Communication

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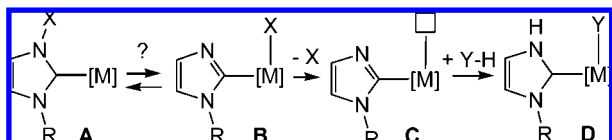
Imidazol-2-yl Complexes of Cp*Ir as Bifunctional Ambident Reactants

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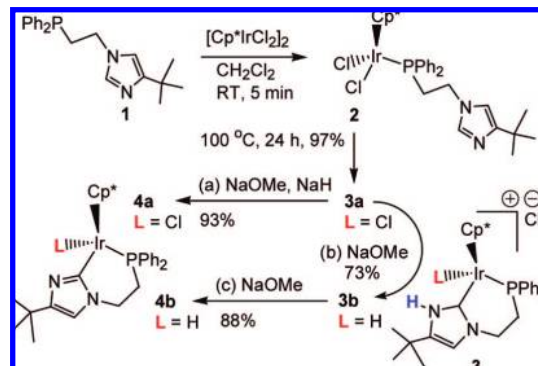
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Exploring the chemistry and uses of N-heterocyclic carbenes (NHCs) has become one of the most active and exciting areas of organometallic chemistry, because of the useful reactivity which NHC ligands impart on catalysts.¹ The vast majority of reported NHC ligands are substituted at nitrogen(s) by alkyl, aryl, or other groups (e.g., structure A with X = R = alkyl or aryl). There are a few but growing number of imidazole-derived NHC complexes bearing an NH-wingtip (A, X = H),² and a few cases of related NH-bearing carbenes derived from pyridines.³



Scheme 1. Synthesis of Imidazol-2-ylidene and Imidazol-2-yl Complexes^a



^a Conditions: (a) CD₂Cl₂, 70 °C, 1 h; (b) EtOH, room temp, 1 d; (c) THF, 70 °C, 1 d.

However, relatively little is known about the reactivity of NHC complexes containing an unusual free NH. Our interest in bifunctional catalysis involving proton transfer or hydrogen bonding⁴ led us to consider not only structure A (X = H), but its tautomer B with higher formal oxidation state at the metal,⁵ and C, with a vacant coordination site at the metal and a basic nitrogen⁶ in close proximity, which could facilitate breaking a bond, forming D. Here we report the synthesis of a new series of imidazol-2-yl complexes of Cp*Ir and their bifunctional behavior as ambident reactants consistent with A–D.

Reaction of **1**⁷ (Scheme 1) with [Cp*IrCl₂]₂ rapidly afforded **2** at room temperature; heating led to complete tautomerization of the imidazole^{2a,f,g} and yellow carbene complex **3a**. The presence of a low field ¹H NMR signal (δ 10.13, NH), together with the appearance of a doublet in the ¹³C {¹H} NMR spectrum (δ 140.3, ²J_{CP} = 21.3 Hz, C-2) are consistent with structure **3a**. The NH group could be deprotonated to give **4a**. X-ray structures of **3a** (Figure 1) and **4a** (Figure S1)⁷ confirm the presence of an N–H group in the acid **3a** and its absence in conjugate base **4a**. Interestingly, **3a** crystallizes with two H₂O molecules, where one oxygen accepts a hydrogen bond from the N–H of the carbene [H₂O ⋯H = 1.949(12) Å].^{7,8} The structure of **4a** showed a C_{imidazolyl}–Ir distance of 2.059(3) Å, whereas the C_{carbene}–Ir distance in **3a** is shorter [2.026(2) Å], likely a reflection of the single Ir–C bond in **4a** and the stronger Ir–carbene bond in **3a**.

Turning toward reactivity studies relevant to B, C, and D, **4a** dehydrogenates primary and secondary alcohols giving aldehydes and ketones, respectively. In particular, the stoichiometric reaction of **4a** with ethanol in CD₂Cl₂ gives acetaldehyde and **3b**, possibly through C and D (Y = OEt), followed by β-hydride elimination. The colorless carbene hydride **3b** could be better obtained in a one-pot synthesis from **3a** using NaOMe in ethanol. The ¹H NMR

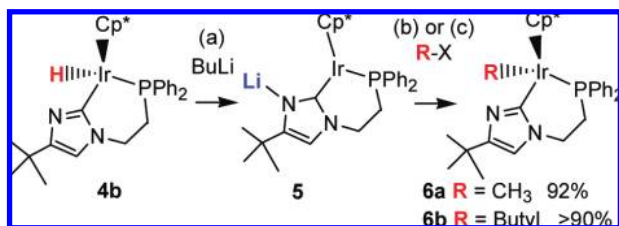
Figure 1. Molecular structure of N-heterocyclic carbene complex **3a**. Of the two water molecules, only the one involved in hydrogen bonding is shown.

spectrum of **3b** showed the presence of an N–H (δ 10.53, br) and a hydride (−16.0 ppm, d, ²J_{HP} = 28.4 Hz); the ¹³C spectrum showed a doublet for the carbene carbon (139.2 ppm, ²J_{CP} = 14.6 Hz). Deprotonation of **3b** using NaOMe gave **4b**, with a hydride resonance at −17.01 ppm (d, ²J_{HP} = 32.4 Hz) and absence of a downfield NH signal. Solutions of **4b** in CDCl₃ or CD₂Cl₂ at room temperature led to **4a** and CDHCl₂ or CD₂HCl.

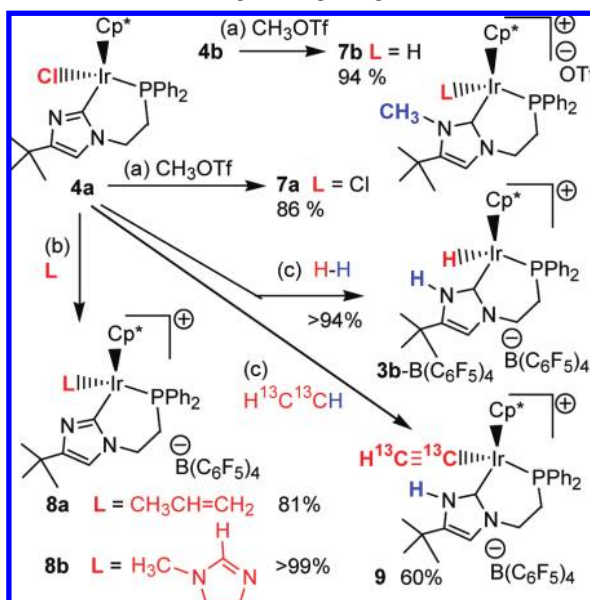
Treatment of a pale yellow solution of **4b** (Scheme 2) with 1 equiv of BuLi at room temperature gives a deep red solution. The single organometallic product is formulated as Ir(I) species **5** with a plane of symmetry because its ¹H and ¹³C NMR spectra showed resonances for equivalent phenyl rings as well as only two signals for the (CH₂)₂ protons, even at −10 °C,⁹ whereas pseudotetrahedral complexes **3** and **4** showed more complex spectra. In comparison with **3a,b**, the carbene resonance is shifted to lower field [sl br s at δ 149.2 (C₆D₆), a sharp doublet δ 150.0, ²J_{CP} = 16.6 Hz (THF-d₈)]. Complex **5** is highly moisture sensitive, reforming **4b** on

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Scheme 2. Interconversions of Ir(III) and Ir(I) Species^a

^a Conditions: (a) C₆D₆, toluene-*d*₈, or THF-*d*₈, room temp, <10 min; (b) CH₃OTf, C₆D₆, -40 °C to room temp; (c) CH₃CH₂CH₂CH₂-I, THF-*d*₈, -78 °C to room temp.

Scheme 3. Reactions Using Ionizing Reagents^a

^a Conditions: (a) C₆D₆, -40 °C to room temp, 1–2 h; (b) KB(C₆F₅)₄, THF-*d*₈, 70 °C, 16 h (9a), 21 h (9b); (c) KB(C₆F₅)₄, THF-*d*₈, room temp, 67 h (3b), 4 d (9).

contact with water. Conversion of **4b** to **5** would be an example of transforming **B** to **A**, perhaps driven by the highly electropositive nature of X = Li in the latter species.

Thus far, alkylation reactions of **5** have occurred at the metal (Scheme 2), giving **6a** or **6b**. In **6a**, the Ir-CH₃ unit showed ¹H and ¹³C NMR resonances at -0.03 ppm (d, ³J_{HP} = 5.2 Hz) and -21.1 (d, ²J_{CP} = 8.2 Hz), respectively.

Ionization of the chloride ligand in **4a** could allow formation of structure **C**, at least transiently. Adding CH₃OTf to **4a,b** gave carbenes **7a,b** (Scheme 3), rather than formation of either CH₄ or CH₃Cl. The N-CH₃ protons of **7a** and **7b** appeared as singlets near 4 ppm, whereas the hydride in **7b** was revealed by a doublet (-15.90, ²J_{HP} = 27.6 Hz). In contrast, chloride abstraction from **4a** by KB(C₆F₅)₄ was observed, though not until other reactants were added. Propene or 1-methylimidazole coordinated to the metal, giving **8a** or **8b**. In principle, two diastereomers of **8a** are possible, but the ratio must be >10:1 because only one major isomer could be seen in 81% yield, along with two minor species. In the case of acetylene, the heterocyclic nitrogen acts as a base, forming acetylide carbene complex **9**, an example of **B** → **C** → **D**. The use of H¹³C¹³CH allowed full identification of the structure shown, ¹J_{CC}

= 131.8 Hz. Similarly, ionization of **4a** in the presence of hydrogen led to heterolysis of the latter and formation of **3b-B(C₆F₅)₄**.

In summary, fundamental reactivity of NH-bearing NHC complex **3a**, its conjugate base **4a**, and related species provide evidence for structures **A–D**. Notably, the relationship of **B** and **A** with different formal oxidation states is highlighted in Scheme 2. Reactivity of **4a** perhaps via **C** with acetylene or hydrogen leads to **D** by bond activation prompted by the basic heterocyclic nitrogen. Taken together, these results highlight new transformations made possible in an NHC complex by the presence of an NH group, as well as reactivity of the conjugate base at the free heterocyclic nitrogen. Both types of secondary interaction are expected to expand the possibilities of NHC complexes in organometallic chemistry and catalysis.

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Supporting Information Available: Details of compound preparation and characterization, and CIF files for structures of **3a** and **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) See Supporting Information for full details.
- (8) See for example, ref 3d, with a hydrogen bond between an NHC NH and metal-bound OH ligand.
- (9) As a solution made in toluene-*d*₈ is cooled below -10 °C, decoalescence of the peaks for the CH₂CH₂PPh₂ unit begins, plausibly consistent with slowing of the flipping of the metallacycle ring in **5** or with slowing of interconversion of Ir(III) valence tautomer **6c** (R = Li) and its enantiomer. If indeed **6c** is the ground state structure, in order for the Li to move from one (hindered) face of the complex to the other, it would seem that **5** is a likely intermediate. For whatever site exchange process is occurring, VT NMR data show E_a = 11.8 kcal mol⁻¹. ⁷Li NMR chemical shift data were not diagnostic. Attempts to crystallize **5** for X-ray diffraction continue.

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