Cycloaddition Reactions

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Metallacyclic Pyridylidene Structures from Reactions of Terminal Pyridylidenes with Alkenes and Acetylene**

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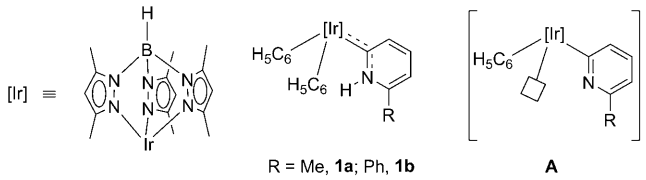
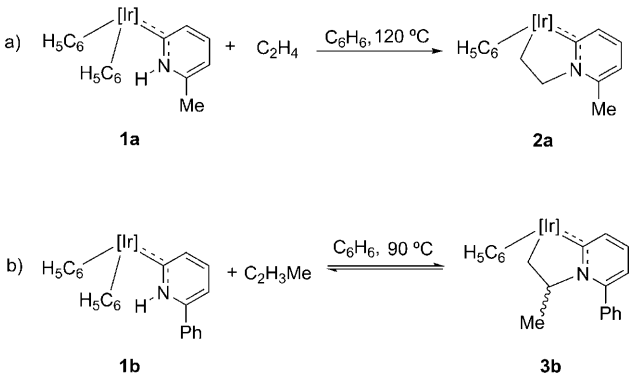
In recent years, N-heterocyclic carbenes (NHCs) have emerged as an important family of catalytically useful ligands[1,2] whose relevance is considered comparable to that of the cyclopentadienyl and phosphine ligands.[1] Pyridylidenes are an interesting subclass of NHCs capable of forming normal, abnormal, and remote carbenes.[2,3] They may be obtained from pyridinium salt precursors,[4] although various alternative procedures are available, including functionalization of metallated pyridyl ligands,[5] or C–H bond activation of N-heterocycles.[4c,d,5,6] Recently, pyridines and related N-heterocycles have been shown to experience metal-induced rearrangements that lead to N-heterocyclic carbenes.[7–9]

In work based on the use of [Tp′Ir(R)(R′)] fragments (Tp′ = hydrotris(pyrazolyl)borate groups; R,R′ = alkyl or aryl groups), we observed isomerization of pyridine, 2-substituted pyridines, and polypyridines to NHCs.[10] As a continuation of this work, we have studied the reactivity of pyridylidene complexes **1** toward ethene, propene, and acetylene to yield novel iridacyclic pyridylidene structures that stem from C–N bond formation. As discussed below, with the exception of C_2H_4 reactions, the C–N couplings are reversible and entail the participation of phenyl pyridyl intermediates of type **A**.



When complex **1a** (R = Me)[10a] is heated in benzene under 2 bar of C_2H_4 (120 °C, 12 h, Scheme 1 a), clean conversion to **2a** is observed in quantitative yields (by ^{1}H NMR spectroscopy). Compound **1b** (R = Ph) reacts similarly,



Scheme 1. a) Synthesis of iridacyclic pyridylidene **2a**. b) Reversible formation of the metallacyclic pyridylidene **3b**. In this and other schemes, [Ir] is iridium{hydrotris(3,5-dimethylpyrazolyl)borate}.

although faster (C_6H_6, 90 °C, 12 h), to give the related compound **2b**. The metallacyclic structure proposed for compounds **2** is supported by elemental analysis and spectroscopic data (see the Supporting Information) and by X-ray studies performed with **2b** (see below).

Compounds **1** react also with propene, as illustrated in Scheme 1 b for pyridylidene complex **1b**, derived from 2-phenyl pyridine. C–N bond formation is regioselective and occurs at the substituted olefin carbon atom. Two diastereomers form in an approximate 5:1 ratio, of which the major presents diagnostic ^{1}H NMR signals at $\delta = 3.04$ and 2.75 ppm (both multiplets, Ir–CH_2) and ^{13}C{^{1}H} resonances at $\delta = 2.7$ (Ir–CH_2) and 194.2 ppm (Ir=C). As expected, **1a** furnished the related complex **3a** in a somewhat slower reaction as a 1:3 diastereomer mixture. By contrast with the C_2H_4 case, propene incorporation is reversible; heating solutions of **3** in C_6H_6, under an atmosphere of dinitrogen, eliminates propene and regenerates cleanly pyridylidene complexes **1**. This contrasting behavior is probably a reflection of the weaker N–C(Me)H bond of **3**, relative to the N–CH_2 bond in **2**.[11]

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The metallacyclic linkage of complexes **2** and **3** was characterized by X-ray crystallography of compound **2b** as a representative example. The five-membered metallacyclic ring (Figure 1, left) exhibits an Ir–C carbene bond of

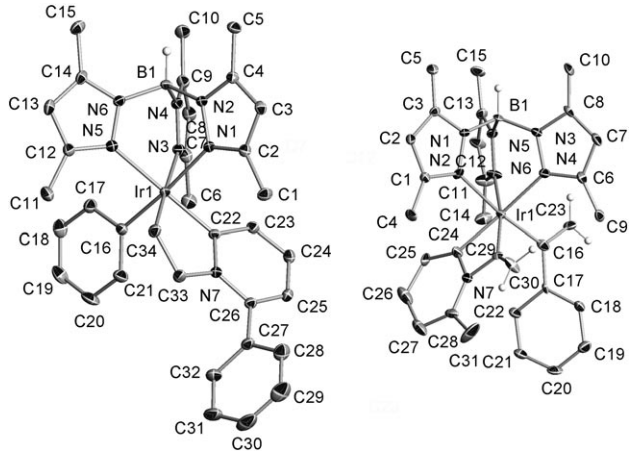
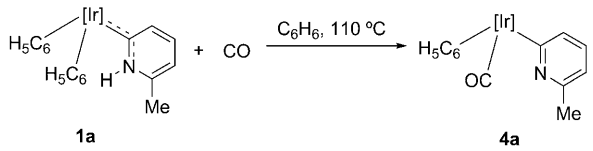


Figure 1. ORTEP representations (30% probability) for complexes **2b** (left) and **6a** (right).

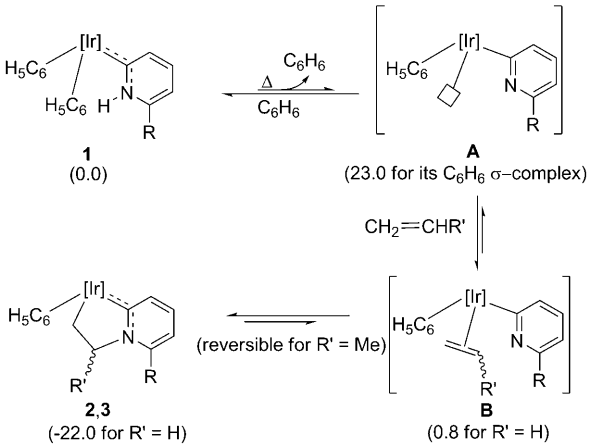
1.949(3) Å, which is very similar to that found in related monodentate pyridylidenes.[10] The pyridinium N7–C33 bond has a normal[12] length of 1.500(4) Å, whereas the two originally olefinic carbon atoms C33 and C34 form in **2b** a single C–C bond of regular length (1.534(4) Å).

The constitution of compounds **2** and **3** hints that they originate from a common intermediate **A**, generated from precursors **1** by reversible elimination of a molecule of C_6H_6. Underpinning this hypothesis is the fact that both complexes **1** undergo deuterium incorporation at their phenyl and N–H groups in C_6D_6 (90 °C, $t_{1/2} \approx 0.5$ h for **1b** and 8 h for **1a**). Additionally, carbonyl adduct **4a** forms upon treatment of **1a** with carbon monoxide (Scheme 2). Notice that the carbonyl



Scheme 2. Reaction of complex **1a** with carbon monoxide.

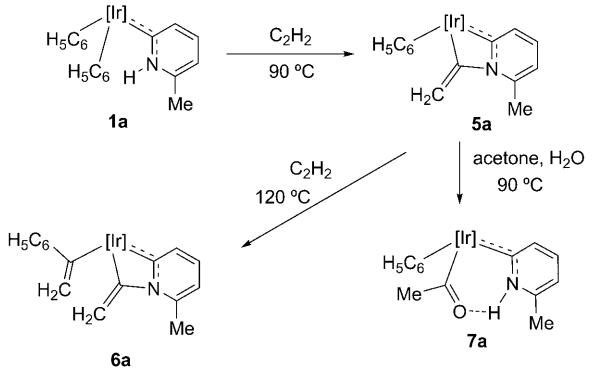
carbon atom is not sufficiently electrophilic to form a lactam ring. Accordingly, complexes **2** and **3** may form as represented in Scheme 3, which is in full agreement with the energy profile shown in Figure S1 (see the Supporting Information). Initial hydrogen migration from the N–H group to one of the Ir–C_6H_5 bonds results eventually in the generation of a σ-benzene complex.[13] Interestingly, N coordination in intermediate **A** seems to be hindered by F-strain,[14] the purported κ^2-pyridyl having higher energy (ca. 12 kcal mol^{-1}) than the σ-benzene complex, whereas the related C_2H_4 adduct **B** (R′ = H) has stability comparable to that of **1a** (approximately



Scheme 3. Proposed mechanism for the formation of pyridylidenes **2** and **3**. Calculated energies (kcal mol^{-1}) for the species involved when R = Me are indicated in parenthesis.

0.8 kcal mol^{-1}). Once this adduct is formed, nucleophilic attack of the pyridyl nitrogen atom onto the coordinated ethylene ligand still finds a high barrier ($\approx$23 kcal mol^{-1}), which is nevertheless smaller (by about 11 kcal mol^{-1}) than that corresponding to the N–H transfer step. The overall reaction is exothermic by approximately 22 kcal mol^{-1}. Notably, conversion of adducts **B** to products **2** or **3** reflects unusual chemoselectivity, as the expected hydrocarbon insertion into either the Ir–C_6H_5[15] or the Ir–pyridyl[16,17] bonds is not detected.

An ideal molecule for further scrutiny of the unusual reactivity of metal pyridylidenes with unsaturated hydrocarbons is acetylene.[18,19] When picoline-derived complex **1a** is allowed to react with C_2H_2 in C_6H_6 (2 bar, 90 °C, 16 h, Scheme 4) under strictly anaerobic and anhydrous conditions,



Scheme 4. Reaction manifold for **1a**, C_2H_2, and H_2O.

quantitative conversion (according to ^{1}H NMR spectroscopy) into the novel four-membered iridacycle **5a** is observed. Heating to 120 °C yields instead the related complex **6a**, whereas if water is not removed carefully from commercially obtained C_2H_2 or the reaction solvent, acetyl complex **7a** may become the main reaction product independently of temperature. Compounds **5a** and **6a** contain an unusual four member

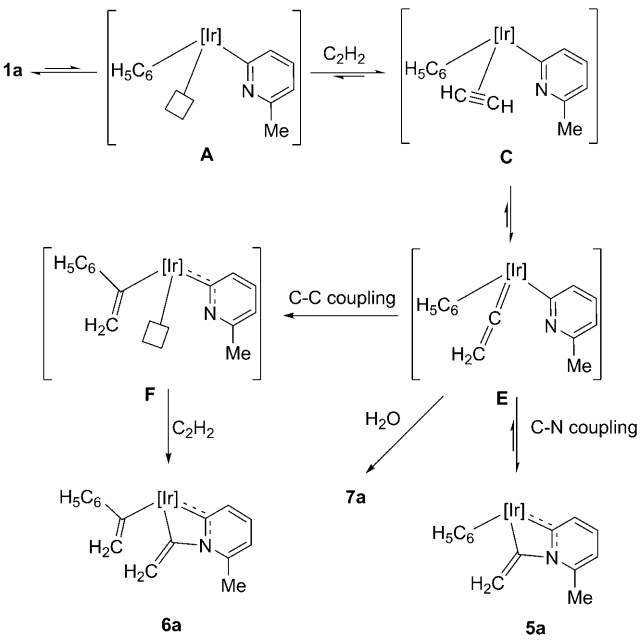
IrCNC ring. In the two compounds, the resonance of the carbene carbon atom is found around $\delta = 160$ ppm, that is, less deshielded that in the parent carbene **1a** ($\delta = 176.6$ ppm). Another molecule of C_2H_2 makes up the alkenyl terminus of **6a**, which can be obtained from **5a** and C_2H_2, whereas **7a** can be demonstrated to form directly from **5a** and water (Scheme 4).

The formulation of complex **7a** as an acetyl–pyridylidene, rather than as the hydroxycarbene–pyridyl tautomer,[20] is supported by X-ray studies to be reported elsewhere, as well as by solution NMR data. Specifically, the acetyl carbonyl resonance is recorded at $\delta = 240.2$ ppm and the carbene one at $\delta = 174.0$ ppm, the latter chemical shift being very close to the carbene resonance of the parent carbene **1a**. An IR absorption at around 1600 cm^{-1} can also be taken as diagnostic for the acetyl moiety of **7a**.

X-ray studies were performed to authenticate structurally the four-membered metallacycles **5a** and **6a**. Data for **5a** are of poor quality, in part because of the existence of a disordered solvent molecule of crystallization. X-ray data for **6a** are of better quality and allow description of its molecular structure, despite the fact that racemic twinning was detected and twin refinement had to be applied (see Figure 1 and the Supporting Information). Moreover, different crystals were investigated and they all present a high degree of mosaicity. The ring is puckered (dihedral angle between planes of 10.9°), and the Ir–$C_{carbene}$ bond length of 1.970(16) Å, Ir–$C_{alkenyl}$ bond length of 2.016(13) Å, and the C–N (1.424(18) Å) and $C_{alkenyl}$–N (1.430(18) Å) bond lengths are consistent with the proposed structure.

It should be mentioned at this stage that the reactivity pattern that leads to compound **5a**, although unprecedented, finds strong support in recent, prominent work from Grotjahn and co-workers on ruthenium complexes with imidazolyl- and pyridyl-substituted phosphine ligands.[20] Production of **5a** (and of **6a**) from **1a** and C_2H_2 may proceed as represented in Scheme 5. Acetylene coordination to intermediate **A** could generate **C** and its vinylidene tautomer **E**, the latter converting into metallacycle **5a** by nucleophilic attack of the pyridyl nitrogen atom onto the carbene carbon atom.

Theoretical calculations summarized in Figure 2 support this proposal, and moreover disclose an unprecedented, ligand-assisted intramolecular mechanism for the acetylene-to-vinylidene rearrangement.[20,21] This process starts with migration of a hydrogen atom from the bound acetylene to the pyridyl nitrogen atom to yield acetylide–pyridylidene species **D**[20f] in a facile rearrangement that needs to overcome an energy barrier of only 12.2 kcal mol^{-1}. A second prototropic redistribution would bring the N–H hydrogen atom of **D** back into the acetylide ligand preferentially on its β-carbon atom to afford vinylidene intermediate **E**, which is calculated to be around 9 kcal mol^{-1} more stable than its π-alkyne isomer **C**. Finally, almost barrierless C–N coupling furnishes metallacycle **5**. Alternative pathways for the acetylene-to-vinylidene transformation, such as oxidative addition of one of the acetylene C–H bonds, direct 1,2-H shift on η^2-coordinated acetylene, or 1,2-H shift via a σ-C–H acetylene complex, have also been explored. However, they require significantly higher energy intermediates and have been discarded. It is important to note that the computed acetylene-to-vinylidene rearrangement may be viewed as an intramolecular version of the protonation/deprotonation route reported by Puerta and co-workers for the isomerization of 1-alkynes on the $[(\eta^5\text{-}C_5Me_5)Ru(dippe)]^+$ fragment (dippe = 1,2-bis(diisopropylphosphino)ethane).[22]



Scheme 5. Proposed, simplified mechanism for the formation of the compounds **5a**–**6a**.

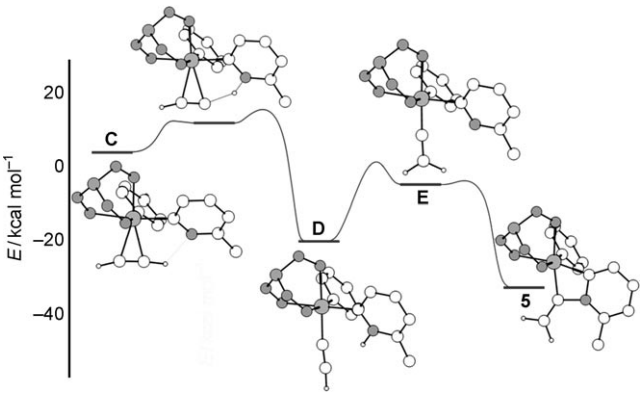


Figure 2. DFT-calculated potential-energy profile for the ligand-assisted intramolecular mechanism for acetylene-to-vinylidene rearrangement.

Under harsh conditions (120 °C), formation of **5a** can be reversed. Thus, treatment with C_2H_4 leads to **2a**, whereas reaction with C_2D_2 affords [D_4]-**6a** with fully deuterated methylene units. Since the calculated barrier for the reverse **5a**-to-**C** transformation of Scheme 5 is prohibitively high (ca. 49.3 kcal mol^{-1}; $\Delta G^{\ddagger}_{298.15} = 46.0$ kcal mol^{-1}), it is possible that reactions of **5a** with the above molecules may proceed by a mechanism that does not require formation of **C** from **5a** (Scheme 5).

In summary, terminal pyridylidenes resulting from tautomerization of 2-substituted pyridines react with C_2H_2, C_2H_4,

and C_2H_3Me to form metallacyclic pyridylidenes. The reactions occur through pyridyl intermediates with structure of type **A** that activate the hydrocarbon, or structures derived thereof, toward nucleophilic attack by the pyridyl nitrogen atom.

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