N-Heterocyclic Ligands

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Monodentate, N-Heterocyclic Carbene-Type Coordination of 2,2′-Bipyridine and 1,10-Phenanthroline to Iridium**

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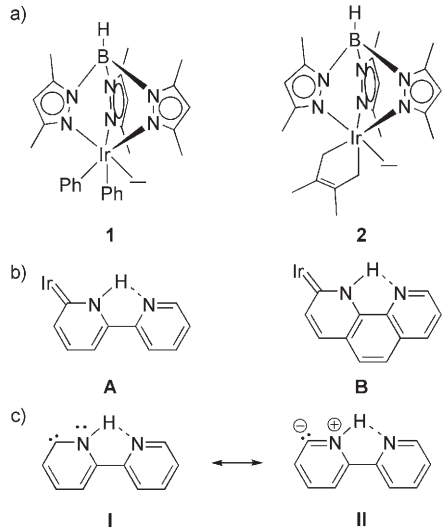
Aromatic nitrogen-containing heterocycles such as 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and related molecules are widely employed as ligands in coordination and organometallic chemistry,[1,2] especially in homogeneous catalysis.[3] Their interesting redox and photoredox chemistry means that they play a leading role in studies of electron and energy transfer.[4] Moreover, they are commonly utilized as building blocks in supramolecular chemistry.[5] The excellent donor properties of these ligands, which are usually viewed as α-diimines,[1b] stem from their sp^2-hybridized N atoms and result almost invariably in *N*,*N*′-chelating structures. Monodentate N-coordination has been proposed in several instances,[6] but has been authenticated by X-ray crystallography in only a few cases.[7]

Recent work has shown that some pyridines and related N-heterocycles can undergo metal-induced rearrangements to form N-heterocyclic carbenes (NHCs).[8–12] In our studies based on iridium,[11] tautomerization of the pyridines involves C–H bond activation chemistry with participation of an Ir–C σ bond of the precursor.[11b] Since the N adduct of 2-substituted pyridines becomes thermodynamically unfavorable with respect to the NHC complex isomer due to F-strain,[11a] we envisaged that bpy and phen could experience related rearrangements. In an attempt to prove this hypothesis, while at the same time establishing the generality of the tautomerization of six-membered N-heterocycles, we have investigated the reactions of bpy and phen with the readily accessible iridium fragments **1** and **2** (Scheme 1a) and have



Scheme 1. a) Iridium fragments **1** and **2**. b) Monodentate NHC coordination of bpy (**A**) and phen (**B**). c) Hydrogen-bonded C6 carbene (**I**) and ylidic (**II**) resonance structures for bpy.

demonstrated a new binding mode of these pervasive ligands as monodentate, N-heterocyclic carbenes (structures **A** and **B**, Scheme 1b). A further motivation for our work was provided by increasing interest in the photochemical properties of Ir^{III}–bpy and –phen complexes[13] and by the controversy that has long surrounded one of the $[Ir(bpy)_3]^{3+}$ cations[14,15] (sometimes referred to as Watt's complex[14a]), which has two *N*,*N*′-bpy and a third *N*,*C*-bpy ligand that chelates through the N atom of one ring and the C3 atom of the other in a manner "reminiscent of orthometalated complexes". As discussed later, the findings described herein suggest a renewed consideration of this system.

Previous work from our laboratory has shown that the compound $[Tp^{Me_2}Ir(C_6H_5)_2(N_2)]$ (**1**-N_2)[16a] reacts with 2-substituted pyridines to afford the corresponding NHC complexes.[11a] Heating a benzene solution of **1** in the presence of 1.2 equivalents of bpy yields the carbene complex **3** in high spectroscopic yields (>90% by ^{1}H NMR; Scheme 2). Complex **3** is isolated as an orange crystalline solid from its Et_2O

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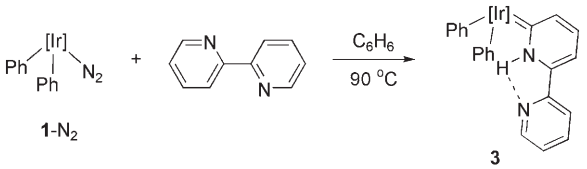
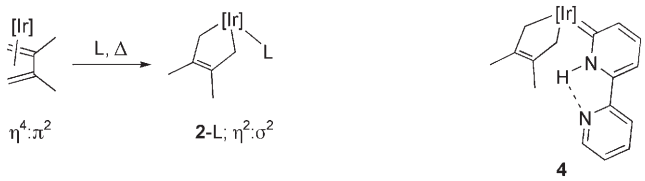


Scheme 2. Synthesis of the NHC compound **3**. In this and other schemes [Ir] is $Tp^{Me_2}Ir$ (Tp^{Me_2}: hydrotris(3,5-dimethylpyrazolyl)borate.



Scheme 3. Generation of species **2**-L and representation of the NHC complex **4**.

solution following column chromatography (silica gel) of the crude reaction product.

The IR spectrum of compound **3** shows a broad band centered at $\tilde{\nu} = 3265\ cm^{-1}$ due to the ν(N–H) stretching absorption, while a deshielded resonance at $\delta = 14.60$ ppm can be observed in the ^1H NMR spectrum for this functionality. A comparison with data for related compounds[11] suggests the existence of an intramolecular hydrogen bond between the NH unit of the coordinated ring and the N atom of the other ring (see below). The Ir-bound carbene carbon atom resonates at $\delta = 180.2$ ppm in the $^{13}C\{^1H\}$ NMR spectrum.

The analogous reaction of fragment **2** (Scheme 1a) was carried out to confirm the generality of this bpy tautomerization. It has been demonstrated previously that the Ir^I complex $[Tp^{Me_2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)]$ and analogous η^4-diene species react with Lewis bases[16b] to form Ir^{III} compounds in which the original $\eta^4{:}\pi^2$-diene becomes an $\eta^2{:}\sigma^2$-diyl ligand (**2**-L; Scheme 3). Accordingly, complex **4** forms as the major reaction product when benzene solutions of the above complex are heated with bpy (2 equiv; 90 °C, 20 h). ^1H NMR monitoring of this reaction reveals a spectroscopic yield higher than 80%. The spectroscopic data for **4** (see the Supporting Information) are similar to those of **3**, thereby indicating the monodentate NHC coordination of bpy. The NH resonance at $\delta = 12.60$ ppm in the ^1H NMR spectrum and the deshielded signal at $\delta = 185.5$ ppm in the $^{13}C\{^1H\}$ NMR spectrum due to the Ir-bound carbon atom of the bpy ring are particularly useful in this regard.

X-ray structure analyses of **3** and **4** (Figure 1) demonstrate the stabilization of the carbene tautomer of bpy (structures **I** and **II**, Scheme 1c) over classical N-coordination. The Ir–carbene bonds in these two molecules are similar in length (1.974(4) Å in **3** and 1.944(3) Å in **4**) and are significantly shorter than those of the two σ Ir–C bonds to phenyl (av. 2.06 Å in **3**) or CH_2 units (av. 2.07 Å in **4**). The two pyridyl rings are nearly coplanar in the solid state (dihedral angles of about 5–6°), thus confirming the existence of an N–H···N hydrogen bond. The N8···H7N distances of around 2.2(3) and 2.3(4) Å are shorter than the sum of the van der Waals radii of

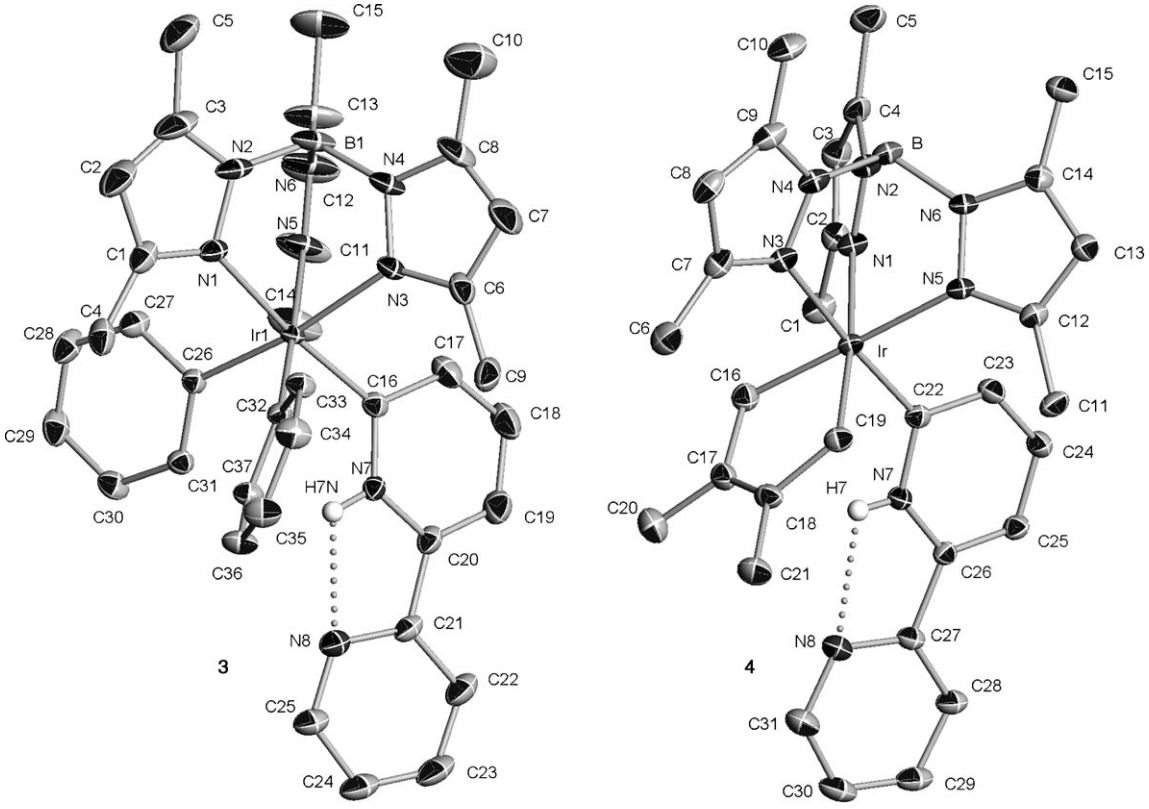


Figure 1. ORTEP drawings (50% probability ellipsoids) of complexes **3** and **4**. The hydrogen bonds are represented by dotted lines.

H (1.2 Å) and N (1.5 Å).[17] A comparison of the bond lengths for free bpy and bpy bonded through C6 to iridium in **3** and **4** (Figure 2) nicely illustrates the distortion of the pyridyl ring bonded to iridium. Thus, whereas the C–C bond lengths in

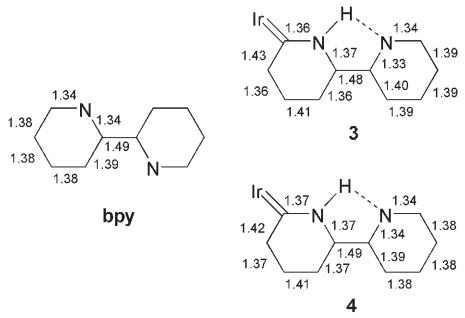
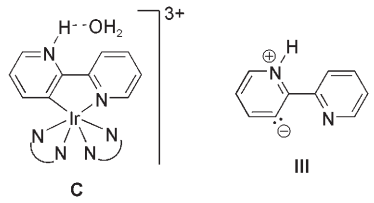


Figure 2. Bond lengths in free bpy[18a] and as an NHC ligand in **3** and **4**.

free bpy are identical (1.38 Å)[18a] and in the uncoordinated ring of **3** and **4** they cluster in the narrow range 1.38–1.40 Å, the coordinated rings of the two complexes exhibit two C–C bonds with lengths of around 1.36 Å, which are distinctly shorter than the other two (around 1.42 Å). The coordinated rings therefore exhibit some diene character.

The demonstration of this unprecedented coordination mode of bpy may mean that further studies on Watt's complex, for which structure **C** (Scheme 4) was ascertained



Scheme 4. Schematic representation of Watt's complex **C** and ylidic structure **III** for its *C,N*-coordinated ring.

after a long and often intense controversy, are warranted.[14] It seems plausible that this structure could be described as containing an ylidic bpy ligand **III** rather than being "reminiscent of orthometalated compounds".[14] Deshielded resonances in the ^{1}H (NH) and ^{13}C NMR spectra (ylidic carbon) should be sought to confirm or refute this suggestion.

Complex **2** reacts with phen under conditions identical to those needed to generate **4** to provide the NHC compound **5**, albeit with a lower spectroscopic yield and lower yield of isolated product (approx. 40% and 20%, respectively). The IR and NMR spectroscopic data for **5** are similar to those of **3** and **4**. Thus, a broad IR absorption at around $\tilde{\nu} = 3160\ cm^{-1}$ and a ^{1}H NMR resonance at $\delta = 13.20$ ppm are due to the NH unit, while the carbene (or ylidic) carbon atom resonates at $\delta = 189.7$ ppm in the ^{13}C NMR spectrum. A single-crystal X-ray study (Figure 3) proved the monodentate NHC coordination suggested by the spectroscopic data unequivocally: once again, the Ir–carbene bond is appreciably shorter than

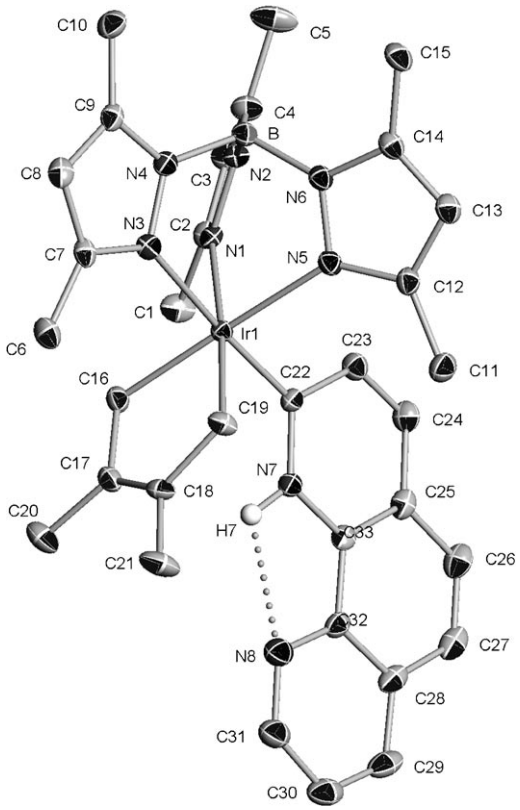


Figure 3. ORTEP drawing (50% probability ellipsoids) of complex **5**. The hydrogen bond is represented by a dotted line.

the Ir–CH_2 bonds to the η^2:σ^2 diyl linkage (1.931(3) Å vs. 2.088(4) Å), and the N8···H7N separation of 2.25 Å indicates an intramolecular hydrogen bond between the two nitrogen-containing rings of phen. The C–N and C–C bonds formed by the carbene carbon atom are clearly longer than the corresponding bonds in free phenanthroline (1.36 vs. 1.31 Å for C–N and 1.46 vs. 1.39 Å for C–C).[18b]

In conclusion, this work confirms that the tautomerization of 2-substituted pyridines by $Tp^{Me_2}Ir^{III}$ fragments[11] is a general reaction that is extendable to polypyridine ligands such as 2,2′-bipyridine and 1,10-phenanthroline. A new coordination mode of these important and ubiquitous ligands as monohapto N-heterocyclic carbenes (or alternatively as ylidic structures) has been discovered. Extension of this chemistry to different $Tp'Ir^{III}$ units and polypyridine ligands appears feasible and is currently being pursued in our laboratory.

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