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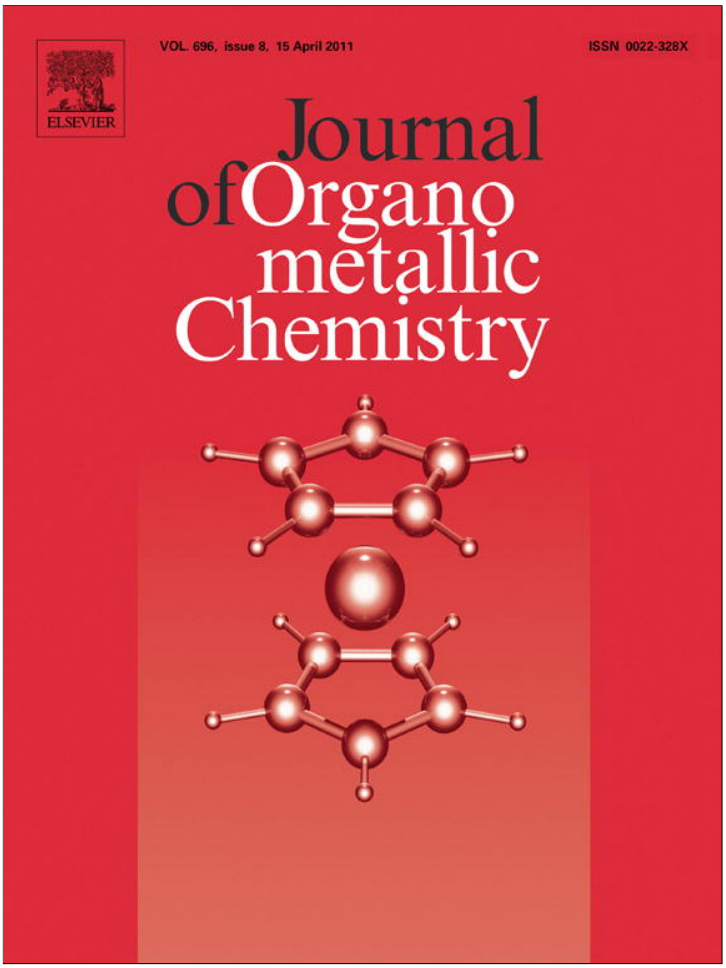

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Theoretical studies of iridium-mediated tautomerization of substituted pyridines

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ABSTRACT

Room temperature reaction of $[Ir(COD)_2]BF_4$ (COD = 1,5-cyclooctadiene) and amide-tethered or simple 2,3′-bipyridyls gave iridium(I) complexes bearing chelating protic pyridylidenes. This protic pyridylidene tautomer is stabilized by both chelation effect and by hydrogen bonding. The mechanistic details of this tautomerization of *N*-heterocycles to *N*-heterocyclic carbenes (NHCs) were investigated using the density functional theory (DFT). DFT studies suggested that cyclometalation of 2,3′-bipyridyls took place to give an iridium(III) hydride, which subsequently undergoes formal 1,3-hydrogen shift from the iridium to the pyridyl nitrogen atom. Two possible mechanisms of this formal 1,3-hydrogen shift process have been examined: the β-insertion of the hydride into an olefin followed by proton abstraction and the water-assisted proton transfer via a cyclic transition state. The latter mechanism is strongly favored in the presence of a catalytic amount of water, and this mechanism is applicable to the tautomerization of both amide-tethered and amide-free 2,3′-bipyridyls.

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1. Introduction

There has been increasing interest in using strongly donating ligands to stabilize transition metals in organometallic chemistry and in catalysis [1–3], owing to their strong donor capacity to stabilize metals and their labilizing effects to facilitate the rate-limiting steps. Carbenes are representative of such ligands [4–8] and have shown advantageous activity in reactions such as palladium-catalyzed C–C coupling [9,10] and ruthenium-catalyzed olefin metathesis reactions [11,12]. Syntheses of carbene complexes have been widely reported and extensively reviewed [13–18]. However, it is desirable to develop general synthetic methods for the preparation of NHC complexes by employing common, simple organic precursors that preclude pre-functionalization of heterocycles. This can be achieved by taking advantage of the interactions between metals and organic molecules. Indeed metal-mediated tautomerization of alkynes [19,20], vinyl ethers [21], aldehydes [22], and heterocycles such as pyridines has been recently reported [23,24], and it represents a simple route to access cyclic and acyclic carbenes (Chart 1). These tautomerization reactions are known to be mediated by various transition metals, and the metal–carbene interactions can strongly stabilize the otherwise unfavorable carbene tautomers.

Generation of the 2-pyridylidene from pyridine was first proposed in the gas-phase in mass spectrometry [23], and theoretical studies have shown that 2-pyridylidene lies 45–50 kcal mol^{-1} higher than pyridine in energy [24]. Experimentally documented metal-mediated tautomerization of pyridines haven't been reported until recently [25]. Poveda, Carmona et al and Esteruelas et al independently reported the synthesis of metal complexes of carbene tautomers of pyridines (Ir) [26–28], bipyridyls (Ir) [29], and other six-membered heterocycles (Os, Ru) [30–32]. In line with the rarity of complexes of protic pyridylidenes, examples of the carbene tautomers of imidazoles are also limited (Fig. 1) [33–35]. This tautomerization process is important not only in biological processes [36]but also in useful catalytic C–C coupling reactions, where the Rh and Ru protic NHC complexes are authenticated as active catalysts [32,33,37]. Interconversions between protic NHC complexes and N-bound complexes or the metal heteroaryl hydride complexes should greatly modify the electronic effects of the metal center, leading to desirable features in catalysis and in molecular recognition. Thus it is highly important to gain mechanistic insights into the mechanisms, particularly the N–H formation step.

Mechanistic studies on this tautomerization process, however, are rare [32,38,39]. Bergman, Ellman, and coworkers reported the first studies on the tautomerization of 3-methyl-3,4-dihydroquinazoline, and a rhodium(III) hydride intermediate was established as an intermediate, which, on the basis of theoretical studies, undergoes β–hydride insertion into the proximal

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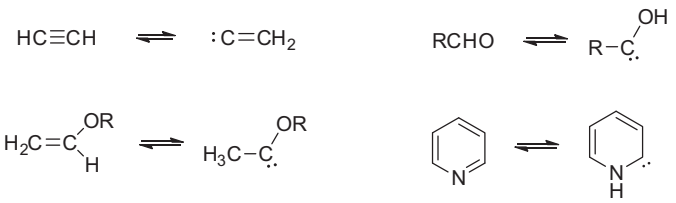
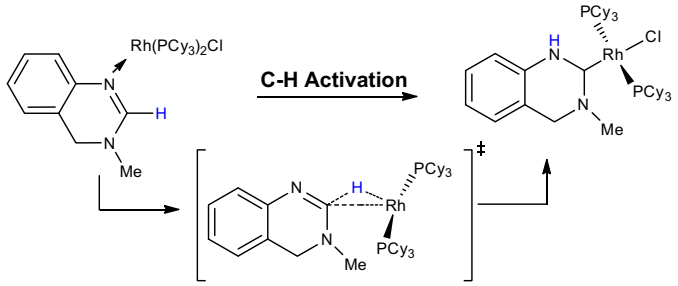


Chart 1. The carbene tautomer of alkyne, vinyl ether, aldehyde, and pyridine.



Scheme 1. Mechanism of carbene formation via C–H activation.

heteroaryl group to give the NHC product (Scheme 1) [32]. We recently reported the microscopic reverse process, and 1,3-shift of the NH proton to the iridium(I) center was observed upon anion exchange, leading to iridium(III) hydrides (Scheme 2) [39]. The sharp contrast of the kinetics of this proton shift process measured at different water concentrations in CD_2Cl_2 (20 ppm versus 0.14 M of water), together with DFT studies, all point to a water-assisted 1,3-proton shift mechanism via a six-member transition state. It should be noted that even 20 ppm of water in "anhydrous" CD_2Cl_2 would assist this process. We now focus on a deeper mechanistic understanding of our recently published work on protic NHCs by examining several 2,3′-bipyridyls and related systems using the density functional theory (DFT) [39,40]. Water-assisted proton transfer mechanism is consistently followed.

2. Experimental section

2.1. Computational methods

All the calculations were performed using the density functional theory (DFT) imbedded in the *Gaussian03* program package [41]. The DFT utilizes the Lee–Yang–Parr correlation (B3LYP) [42–44], which has been extensively proved to be a reliable method in handling transition metal complexes [45–48]. Geometries for all the species were fully optimized without any symmetry constraint. The LanL2DZ pseudo-potential basis set [49] was employed for the Ir atom, and the basis set for the other elements is the standard 6-31G(d, p). Each optimized structure was confirmed by the frequency analysis at the same level to be the real minimum without any imaginary vibration frequency. All transition states were ascertained by vibrational analysis with only one imaginary frequency mode. In all cases the vibrational mode with the imaginary frequency is verified to connect a specific pair of stationary points (reactants, products, or minima associated to intermediate species) by performing the necessary intrinsic reaction coordinate (IRC) calculations.

Single-point calculations on the optimized geometry were subsequently performed with the larger basis set, LanL2DZ on Ir and the 6-311 + G(d, p) basis set on all other atoms. Zero-point vibrational corrections and thermal corrections to the Gibbs free energy were determined from the harmonic vibrational frequencies. To take the solvent effect into account, singlet-point solvent calculations were performed at the optimized gas-phase geometries using the CPCM [50,51] solvation method with dielectric constant (ϵ) of dichloromethane being 8.93. The UAHF (united atom Hartree-Fock) radii were used for all the atoms. All energies in this paper are given as relative solution-phase free energies ΔG in dichloromethane for the reference state of 1 mol L^{-1}, 298 K. The free energy was calculated by following a method that was previously reported. [52].

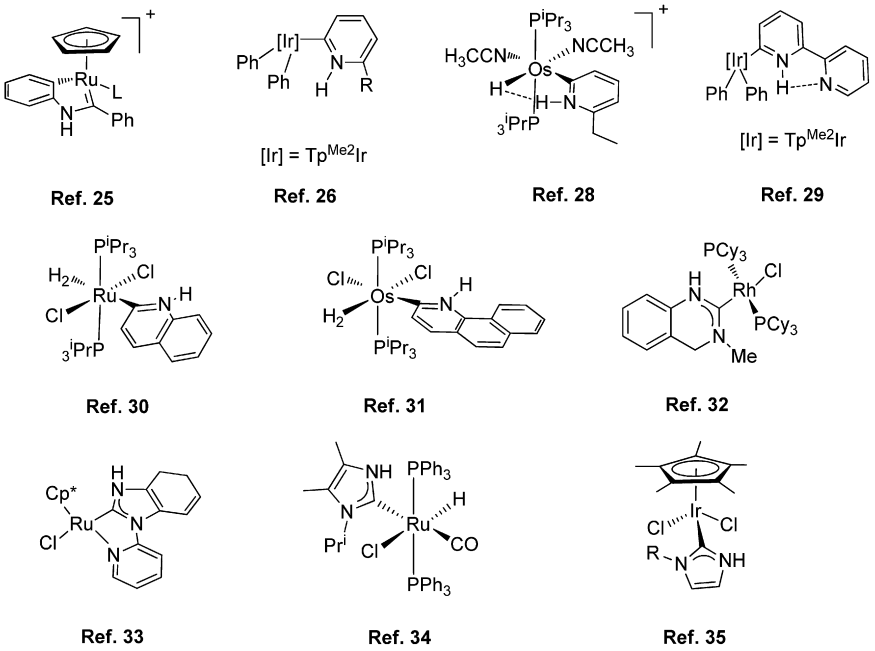


Fig. 1. Examples of protic NHC complexes. Tp^{Me2} = tris (dimethylpyrazolyl) borate.

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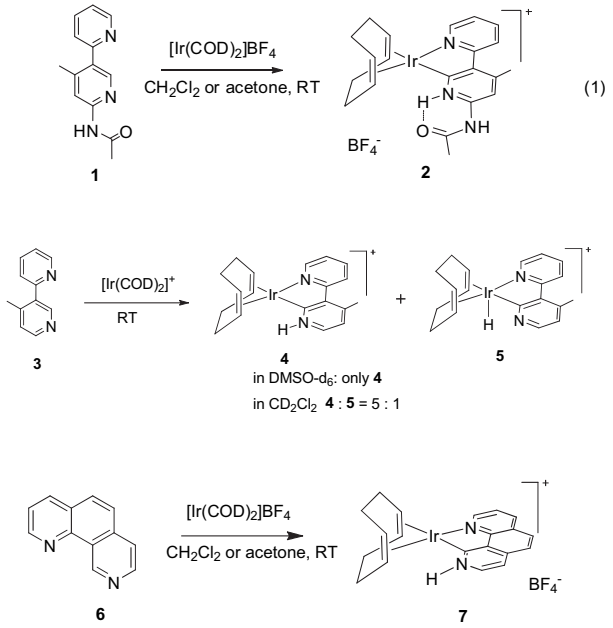


3. Results and discussions

We have recently reported our preliminary results on Ir(I)-induced tautomerization of a pyridine moiety to a carbene in 2,3-bipyridyls under mild conditions (Eq (1)) [40]. Further studies indicated that, in contrast to the clean formation of 2 from 1, reaction of the simple 4-methyl-3-(2-pyridyl)pyridine (3) under the same conditions leads to a mixture of a protic NHC complex and a hydride species in 5:1 ratio in CD2Cl2 (Eq (2)). This indicates that the amide group plays a key role as a hydrogen bonding acceptor to enhance the selectivity of tautomerization (complex 4) over C–H oxidative addition (complex 5). The selectivity of this reaction is strongly dependent on the solvent. Thus when the reaction of 3 and $[Ir(COD)2]^{+}$ was carried out in DMSO-d6 at room temperature, only the carbene product was observed (Eq (2)). Similarly, the reaction of 1,9-phenanthroline (6) and [Ir(COD)2]BF4 (acetone or dichloromethane, room temperature) gave carbene complex 7 in 95% yield.

3.1. Geometries of the NHC product and the starting agostic complex

We use N-(5-(pyridin-2-yl)pyridin-2-yl)acetamide (**8**) as a model reactant that gives complex **9** upon tautomerization (Eq (4)), and the experimental data have been previously reported [40]. The optimized structural data of complex **9** (Fig. 2) were found to closely match those of the directly analogous methyl derivative (**2**), and in almost all cases, the calculated bonds are within 0.05 Å longer than the corresponding experimental ones, and this overestimation is typical for the B3LYP functional. Therefore these consistent data support the general reliability of our method and the proper selection of the basis sets.

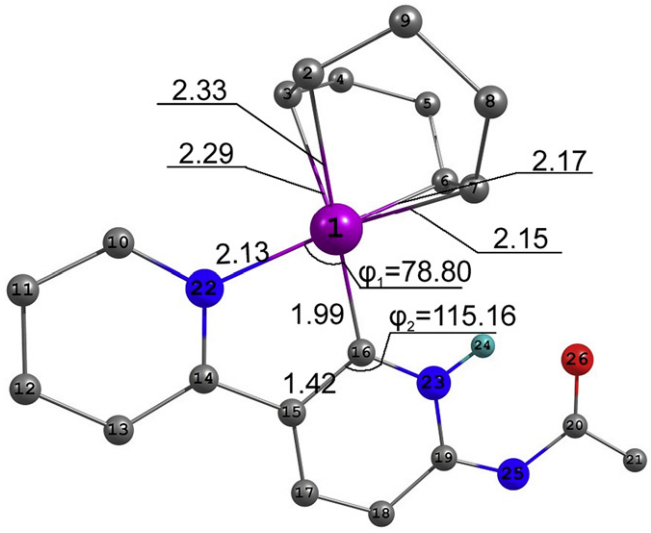
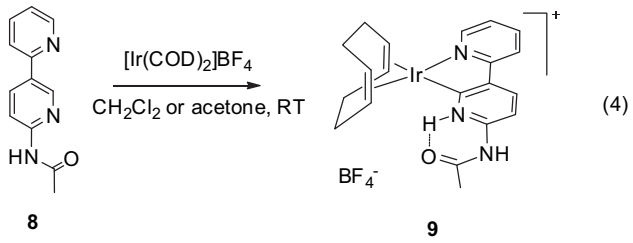
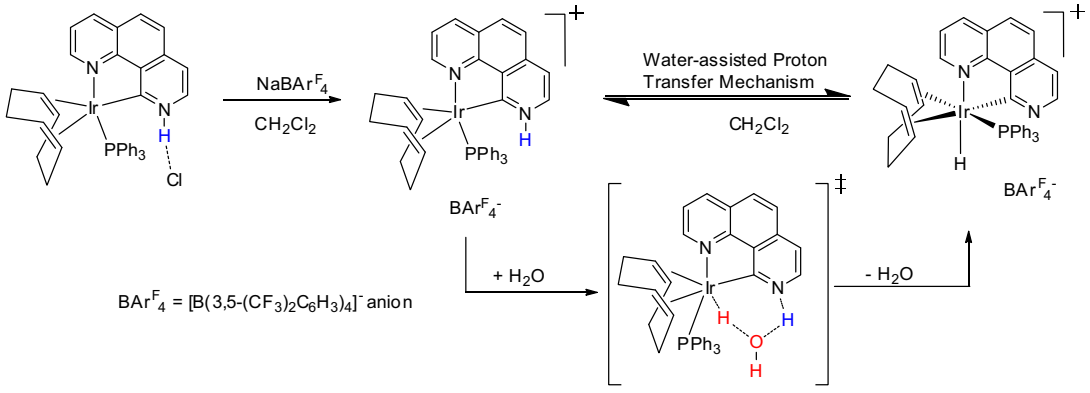


Fig. 2. Selected calculated geometric data (lengths in angstroms and angles in degrees) of **9**.



Since the cleavage of the CH bond adjacent to the N atom in **8** is a key step in this overall tautomerization process, we started our model studies by constructing the precursor to the C–H activation product. This reactant is a four-coordinate Ir(I) agostic complex, and the coordination geometry around the Ir atom can be described as a distorted square plane (**RC**, Figs. 3 and 4.). In this complex, the iridium has weak interactions with both the C and the H atoms



Scheme 2. Reversible 1,3-H shift between Ir(I) protic NHCs and the cationic Ir(III) hydride aryl complexes.

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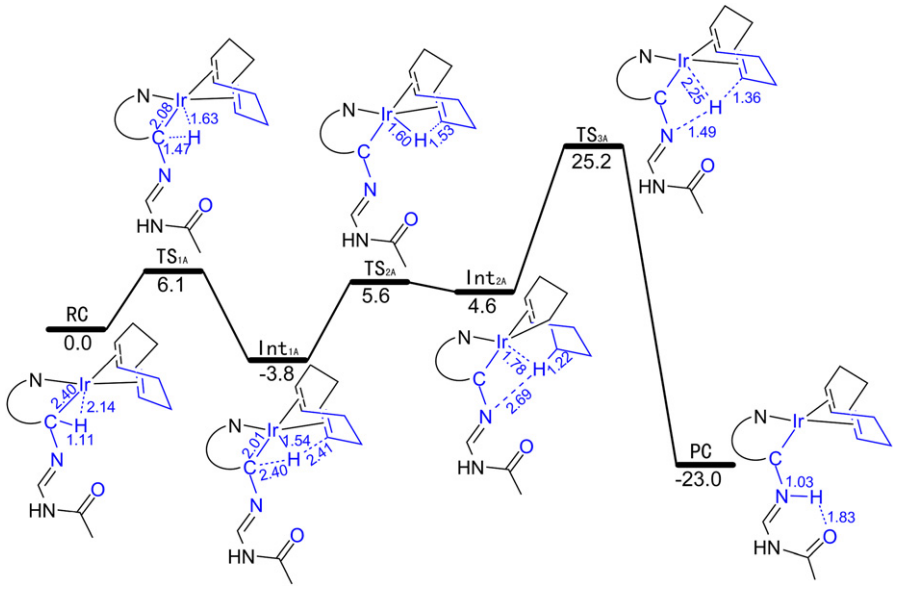

Fig. 3. Free energy profile for the β-hydrogen insertion mechanism. All the free energies are in kcal mol^{-1} relative to the reactant and all bond lengths are in Å. See Figure S1 for the full structure of the N–C chelating ligand.

(Ir–C = 2.40 Å and Ir–H = 2.14 Å), and accordingly the C–H bond is slightly elongated (C–H = 1.11 Å). These data are typical for agostic interactions between iridium and a C(sp^2)–H bond [53–56].

3.2. Possible reaction mechanisms

3.2.1. The β-hydrogen insertion mechanism

3.2.1.1. C–H oxidative addition. Agostic complex (RC) undergoes cyclometalation to give an iridium(III) hydride complex (Int_{1A}, Fig. 3 and Figure S1.). A transition state (TS_{1A}) has been located with a low barrier ($\Delta G^{\neq}$ = 6.1 kcal mol^{-1}) on the potential energy surface for this elementary process. This low barrier is consistent with the facile kinetics in the cyclometalation of related heterocycles [57–59]. In TS_{1A} the C–H distance is considerably elongated (1.47 Å), and both the Ir–C (2.08 Å) and the Ir–H (1.63 Å) distances are shortened. The Ir–C distance is close to the typical value for Ir–C_{aryl} bonds in the ground state (1.99 Å in **2**), suggesting a late transition state. The oxidative addition product (Int_{1A}) is a five-coordinate iridium(III) hydride complex in which the hydride occupies the apical position, and the resulting Ir–C (2.01 Å) and Ir–H (1.54 Å) bonds are within the normal range. This oxidative addition process is slightly thermodynamically favorable (−3.8 kcal mol^{-1}). We reason that this five-coordinate Ir(III) hydride complex is likely an intermediate in the real reaction system since it is less likely for the poorly coordinating CH_2Cl_2 or BF_4^- anion to occupy the vacant coordination site trans to the hydride, a high trans effect ligand.

3.2.1.2. 1,3-Shift of the hydride to the N. Bergman, Ellman and coworkers reported on the basis of DFT studies the mechanism of

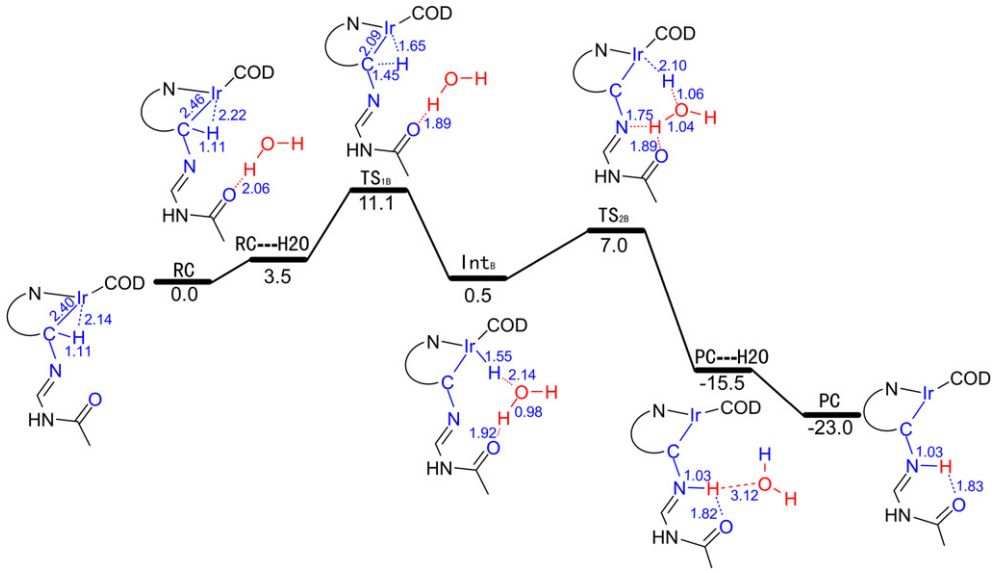

Fig. 4. Free energy profile for water-assisted proton relay mechanism. All the free energies are in kcal mol^{-1} relative to the reactant and all bond lengths are in Å. See Figure S2 for the full structure of the N–C chelating ligand.

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the conversion of a Rh(III) pyridyl hydride complex to the Rh(I) protic NHC product, and the formal 1,3-shift of the hydride proceeds via the β-insertion mechanism [32]. In our system, however, this mechanism is unlikely in that the H–Ir–C–N fragment cannot adopt the required syn coplanar conformation. Furthermore, the tethering effect of the pyridine ring renders the pyridyl N difficult to approach the hydride.

Instead, DFT studies reveal that Int_{1A} undergoes β-insertion of the hydride to the olefin moiety in the COD ligand that is trans to the N atom via the TS_{2A}. This step carriers a barrier of $\Delta G^{\neq} = 9.4$ kcal mol^{-1} to give an alkyl intermediate Int_{2A}, and it is thermodynamically unfavorable ($\Delta G = 8.4$ kcal mol^{-1}). The length of the resultant Ir–C_{alkyl} bond is 2.31 Å (see Figure S1), and Int_{2A} is best described as an agostic complex with characteristic lengths for the incipient Ir–H (1.78 Å), C–H (1.22 Å) and Ir–C (2.31 Å) bonds. We also noted that the hydride in TS_{2A} is closer to the carbon atom of COD (H–$C_{(COD)}$ = 1.53 Å, H–Ir = 1.60 Å), so TS_{2A} is a late transition state and is only 1.0 kcal mol^{-1} higher than Int_{2A} in energy.

In the last step, Int_{2A} undergoes proton abstraction by the pyridyl N atom. This is a process analogous to the classical β-elimination in organic chemistry, with the metal fragment being the leaving group. Significant structural reorganization is experienced via transition state TS_{3A} with a high barrier (20.6 kcal mol^{-1}). In this transition state, the distances of Ir–H, N–H and $C_{(COD)}$–H are 2.25 Å, 1.49 Å and 1.36 Å, respectively (Fig. 3). The final NHC complex is 23.0 kcal mol^{-1} more stable than the reactant and is stabilized by the chelation effect and by intramolecular hydrogen bonding (NH–O = 1.83 Å). The high overall energy barrier of this pathway (29.0 kcal mol^{-1}) indicates that it is not likely to occur at ambient temperature.

3.2.2. Water-assisted proton transfer mechanism

We feel that the mechanism of the metal-free NH–NH tautomerization of simple organic heterocycles may provide useful insights. Recent DFT work by Kim and coworkers has shown that the tautomerization of adenine is assisted by a catalytic amount of water, and the transfer of the NH proton to the adjacent N atom is assisted by a water molecule via a six-membered ring transition state [60]. Likewise, Milstein recently reported on the basis of theoretical studies that water considerably lowers the barrier of oxidative proton transfer from a benzylic methylene group to the metal in a pyridine based PNP iridium complex [61], which are recent examples among solvent-assisted proton transfer processes [39,52,62–65]. In this system, a water molecule can be incorporated via hydrogen bonding and can participate in proton transfer through a cyclic transition state, particularly if the hydride is acidic enough. We thus examined this alternative mechanism.

In this mechanism, water is incorporated into the reaction system and acts as a catalyst, as shown in Fig. 4 and Figure S2. Hydrogen bonding between water and the amide functionality (HOH–O=C = 2.06 Å) gives an intermediate (RC–H_2O) with a slightly unfavorable thermodynamics ($\Delta G_{298} = 3.5$ kcal mol^{-1}), and this endergonicity is likely caused by entropic effect. The hydrate intermediate undergoes cyclometalation to give a hydride intermediate Int_B. This analogous CH activation process is thermodynamically favorable by 3.0 kcal mol^{-1}, and the activation barrier is slightly higher than that of the water-free analogue in Fig. 3. Subsequently, formation of the N–H bond was achieved from Int_B through further proton transfer via TS_{2B} with a barrier of only 6.5 kcal mol^{-1} to give PC–H_2O. The geometric data of TS_{2B} indicate that the water hydrogen is accessible to the pyridyl nitrogen (N–H = 1.75 Å), and there is only slight structural reorganization from Int_B to TS_{2B}. In PC–H_2O, The NH proton is hydrogen-bonded to the amide group, and the water molecule is essentially separated from the rest of the metal complex. Complete dissociation of water from the system affords the final product and finishes this catalytic cycle. The overall kinetic barrier for this water-assisted pathway is only 11.1 kcal mol^{-1}. The significant drop of the barrier is in part accountable by the facile proton transfer processes, which is even more prominent in the metal-free NH–NH tautomerization of organic heterocycles [60]. These theoretical results suggest that the water-assisted proton transfer mechanism is more likely.

3.3. Reaction mechanisms of amide-free analogues

Amide-free 2-(pyridin-3-yl)pyridine (**3**) and 1,9-phenanthroline (**6**) were further studied for comparison purposes (See the Supporting Information for the data of **3**). Figs. 5 and 6 give the comparisons of the two mechanisms for ligand **6**. In the β-hydrogen insertion mechanism (Fig. 5), the free energy barrier of the rate-determining proton abstraction by the pyridyl N atom is calculated to be 25.0 kcal mol^{-1} for **6** (Fig. 5), and this is slightly higher than that for ligand **8** (20.6 kcal mol^{-1}, Fig. 3). Since only the pyridyl N atom and water can participate in hydrogen bonding in the water-assisted proton transfer mechanism (Fig. 6), the hydrated hydride compounds (Int_B) undergo direct proton transfer via a cyclic transition state (TS_{2B}). The free energy cost for this step is calculated to be 7.6 kcal mol^{-1} for ligand **6**, (Fig. 6). Similarly, this

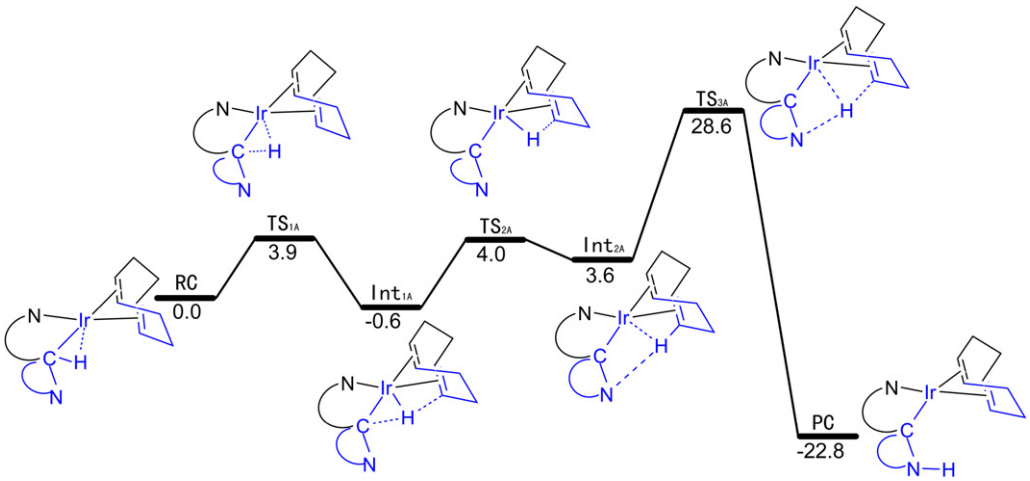

Fig. 5. Free energy profile for the β-hydrogen insertion mechanism. All the free energies are in kcal mol^{-1} relative to the reactant and all bond lengths are in Å. The N–C chelating ligand is 1,9-phenanthroline.

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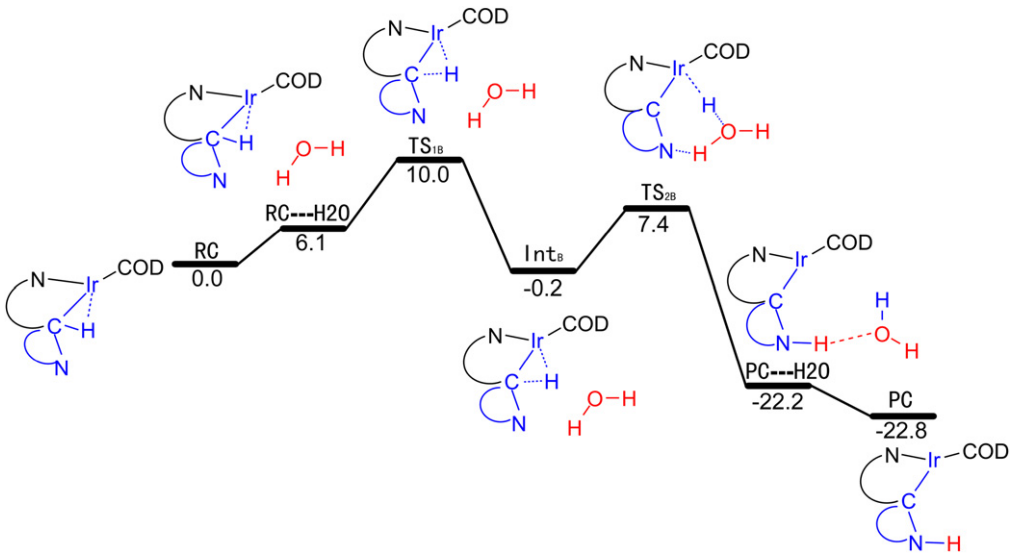

Fig. 6. Free energy profile for water-assisted proton relay mechanism. All the free energies are in kcal mol^{-1} relative to the reactant and all bond lengths are in Å. The N–C chelating ligand is 1,9-phenanthroline.

barrier is also slightly higher than that for ligand **8**. Comparisons of the calculated data for the tautomerization of ligands **8** (Fig. 4) and **6** (Fig. 6) point to the prediction that the tautomerization of these ligands should proceed at rates of the same order of magnitude under the same concentration of water. Indeed, the reaction time necessary for the synthesis of complex **7** (3 h) is similar to that for complex **2** (0.5 h).

4. Conclusions

In summary, the reactions of $[Ir(COD)_2]BF_4$ and 2,3′-bipyridyls or 1,9-phenanthroline lead to the tautomerization of the pyridine moiety with the assistance of the pre-coordination of the nitrogen atom. The NH species could be stabilized by hydrogen bonding with adjacent amide functionality. DFT studies indicate that C–H oxidative addition proceeds first to give a five-coordinate iridium(III) hydride intermediate. Subsequent 1,3-shift of the Ir*H* to the pyridyl nitrogen might follow two possible pathways: the β-insertion pathway and the water-assisted proton transfer pathways. On the basis of DFT studies, water-assisted proton relay mechanism is most likely for the tautomerization of 2,3′-bypyridyls with or without any adjacent amide group.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.01.029.

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