N-Heterocyclic Carbenes

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Anion-Exchange-Triggered 1,3-Shift of an NH Proton to Iridium in Protic N-Heterocyclic Carbenes: Hydrogen-Bonding and Ion-Pairing Effects**

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The chemistry of N-heterocyclic carbenes (NHCs) has become one of the most active and exciting topics in synthesis and catalysis.[1] NHCs bearing N-alkyl or -aryl wingtips are predominant, and there are only limited, although increasing, literature reports on NHC systems with hydrogen wingtips ligated on transition metals such as iridium,[2] rhodium,[3] osmium,[4] ruthenium,[4a–c,5] rhenium,[6] manganese,[7] chromium,[8] and platinum (Figure 1).[9] In general, these NH-protic NHC complexes can be synthesized by 1) protonation of 2- or 4-pyridyl or 2-imidazolyl complexes;[6,10] 2) cleavage of N–C[2c,5a] or N–Si[9] bonds within NHC units; 3) intramolecular attack of a ligated isonitrile by a pendent NH_2 or OH group generated in situ;[5c,8] and 4) metal-mediated tautomerization of N-heterocycles, a process involving C–H activation.[2–4,5a,b,11] Among these methods, metal-mediated tautomerization is most intriguing in that N-heterocycle to NHC tautomerization is important not only in biological process[12] but also in C–C bond formation, where rhodium[3] and ruthenium[5b] protic NHC complexes are established as active catalysts.

However, almost all the literature reports in this area are limited to the synthetic aspects, reactivity, catalytic applications of such complexes, and the energetics of N-bound and C-bound tautomers.[13] Mechanistic studies on this tautomerization process are rare and only two reports are known.[3a,4e] Furthermore, few experimental studies have been carried out on the the most important N–H bond-formation step that generates NHCs (or the microscopic-reverse process). Bergman, Ellman, and co-workers reported the first studies on the tautomerization of 3-methyl-3,4-dihydroquinazoline via a rhodium(III) hydride intermediate, which, on the basis of theoretical studies, undergoes β-hydride insertion to give the NHC product.[3a] We feel that controllable interconversions between the protic NHC and the metal hydride precursor can greatly alter the electronic effect of metal center, an important feature in catalysis and molecular recognition. Thus it is highly desirable that the thermodynamics between protic NHC complexes and the metal hydride precursors can be readily tuned. We now report the synthesis of a series of rare 18-electron iridium(I) protic NHC complexes, which upon anion exchange can undergo 1,3-shift of the NH proton to iridium to give iridium(III) hydrides. Significantly, the thermodynamics of this process can be readily tuned by the counteranion, the solvent, and the phosphine coligand.

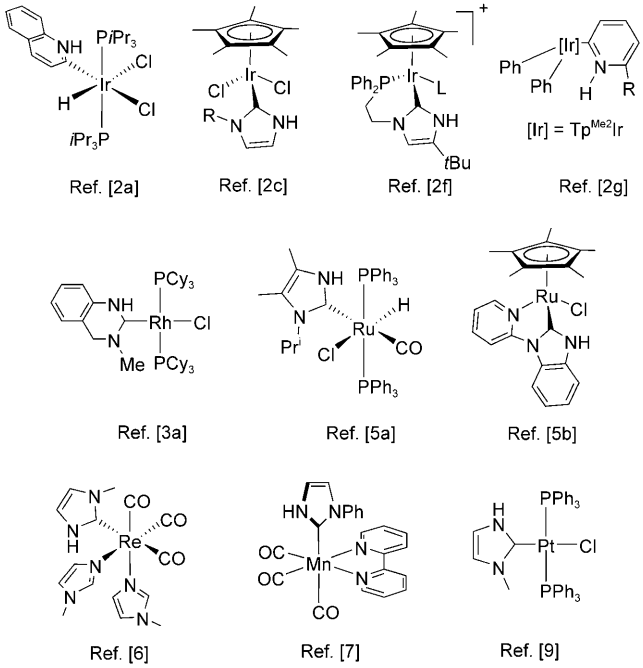

Figure 1. Examples of protic NHC complexes. Tp^{Me2} = tris(dimethylpyrazolyl)borate.

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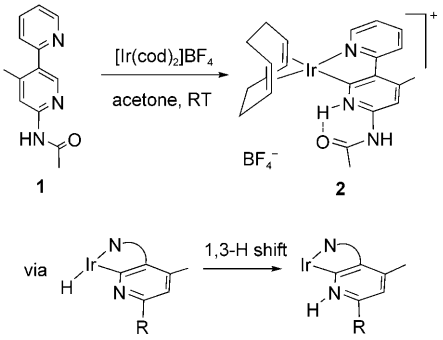
We have recently reported the tautomerization of amide-functionalized 2,3-bipyridyl (**1**)[2d] to give protic NHC complex **2** (Scheme 1), during which process a hydride species ($\delta(^1H) = -14.9$ ppm) has been detected by ^1H NMR spectros-



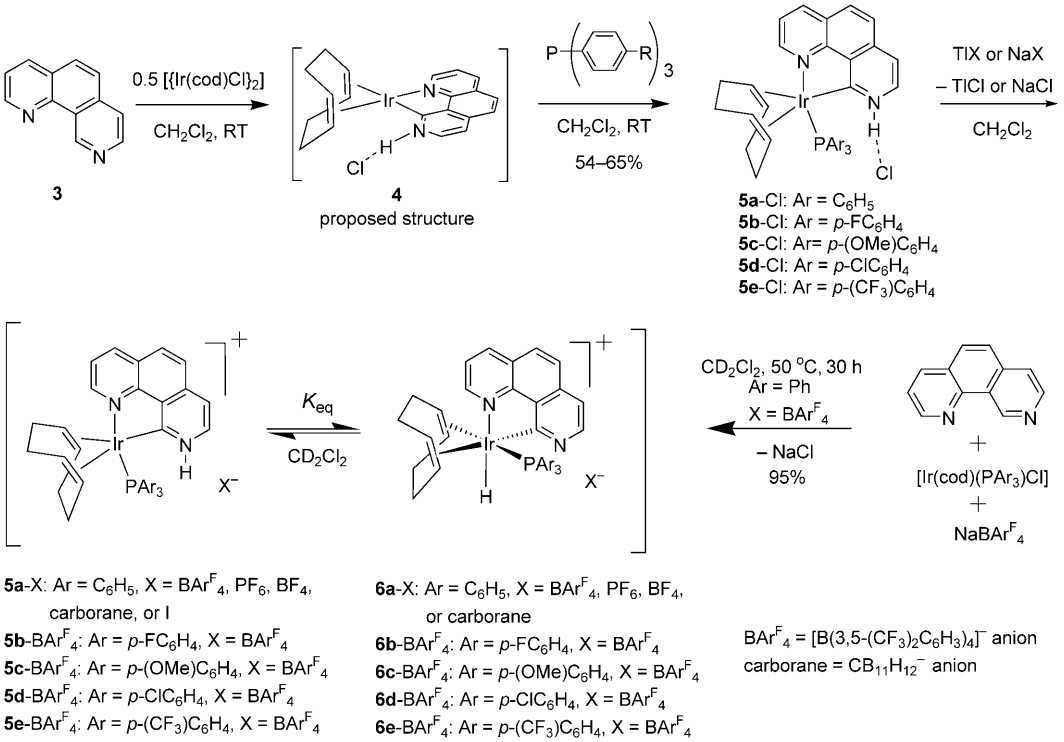
Scheme 1. Hydrogen-bonding-assisted tautomerization of 2,3-bipyridyls. cod = cycloocta-1,5-diene.

copy.[2d] In contrast, switching **1** to its amide-free analogue leads to a mixture of a protic NHC complex and a hydride species (5:1 ratio) under the same conditions. It is likely that the amide group in **1** facilitates the 1,3-migration of the hydride to the pyridyl nitrogen, resulting in an enhanced selectivity of the Ir^I carbene over the Ir^{III} hydride. In this work we focus on the microscopic-reverse 1,3-hydrogen-shift process.

We reason that 1,9-phenanthroline (**3**) is a more reactive cyclometalating reagent owing to its structural rigidity. Indeed, it reacted with the less reactive $[\{Ir(cod)Cl\}_2]$ in CH_2Cl_2 to give a yellow precipitate (Scheme 2). Unfortunately, this product is essentially insoluble in any common organic solvent and defies NMR analysis. In the IR spectrum, no Ir–H stretching band was evident. Instead, a broad NH (3480 cm^{-1}) resonance peak was observed. Thus we tentatively assign this compound to complex **4**. Addition of triarylphosphines to a suspension of **4** (CH_2Cl_2) gave red solutions, from which analytically pure 18-electron iridium(I) NHC phosphine complexes **5a**-Cl–**5e**-Cl could be isolated (54–65%) and spectroscopically characterized. In particular, in the ^{13}C NMR spectra (CD_2Cl_2) the $Ir{-}C_{carbene}$ of **5a**-Cl–**5e**-Cl resonates characteristically as a doublet signal within a narrow range of $\delta(^{13}C) = 193.5$–196 ($^2J_{PC} = 8.4$–8.8 Hz), in line with typical values reported for pyridylidene complexes.[2d,4a,14] The small $^2J_{PC(carbene)}$ coupling constant suggests the *cis* relationship between the phosphine and the NHC. In the ^1H NMR spectra of **5a**-Cl–**5e**-Cl, a characteristic broad low-field signal ($\delta(^1H) = 14.74$ to 15.63) was observed for the NH proton.

X-ray crystallographic analysis of **5b**-Cl unambiguously confirmed its 18-electron, distorted trigonal-bipyramidal structure (Figure 2).[15] The Ir–C9 distance (2.0052(19) Å) is within the normal range expected for pyridylidene complexes.[1f,2d,14] Consistent with previous observations,[2d,4a,14] the C–C bond lengths in the pyridylidene ring show large variations, with the C10–C11 bond (1.333(3) Å) being significantly short. The H···Cl distance (2.267 Å) is smaller than the sum of the van der Waals radii, suggestive of hydrogen bonding.[4a,13]

In general, 18-electron, five-coordinate Ir^I complexes are less common,[16] and we reason that the NH hydrogen in **5a**-



Scheme 2. Synthesis and subsequent conversion of Ir^I complexes having with protic NHC ligands.

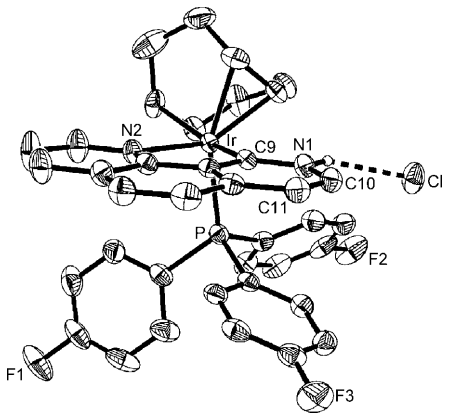


Figure 2. X-ray crystal structure of **5b**-Cl shown with 50% thermal ellipsoids.

Cl–**5e**-Cl might migrate to the iridium to yield rather common 18-electron iridium(III) hydride aryl complexes if the H···Cl hydrogen bond is properly disrupted. Indeed, a hydride species was observed by ^{1}H NMR spectroscopy when $NaBAr^F_4$ (equimolar) was added to a CD_2Cl_2 solution of **5a**-Cl, to give an equilibrium system between **5a**-BAr^F_4 and **6a**-BAr^F_4 (Scheme 2). The same equilibrium mixture can be alternatively synthesized from the reaction of [Ir(cod)-(PPh_3)Cl], 1,9-phenanthroline, and $NaBAr^F_4$ (equimolar) in CD_2Cl_2 by a C–H activation approach (Scheme 2). The equilibrium constant K_{eq} was determined to be 1.17 ($\Delta G_{298} = -0.09$ kcal mol^{-1}) for the conversion of **5a**-BAr^F_4 to **6a**-BAr^F_4 (CD_2Cl_2), and the ΔH was estimated to be -1.3 kcal mol^{-1} based on a van't Hoff plot (-10 to 37 °C). The hydride of **6a**-BAr^F_4 resonates characteristically at $\delta(^1H) = -13.58$ ppm (d, $^2J_{HP} = 10.8$ Hz, -50 °C) in CD_2Cl_2. In addition, the Ir–C_{aryl} carbon resonates as a doublet ($\delta(^{13}C) = 161.6$ ppm, $^2J_{PC} = 10.2$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum. These small coupling constants suggest that both the hydride and the C_{aryl} are *cis* to the phosphine ligand. Although the structure of **6a**-BAr^F_4 could not be elucidated unambiguously, DFT was employed to further support this proposed structure. The calculated ΔG_{298} value of -0.8 kcal mol^{-1} (CH_2Cl_2) between **5a**$^+$ and **6a**$^+$ agrees well with the experimental value (-0.09 kcal mol^{-1}), while the calculated free energy (298 K, CH_2Cl_2) of other possible cationic *cis* hydride phosphine complexes is at least 6.8 kcal mol^{-1} higher than that of **5a**$^+$ (see the Supporting Information). The essentially non-coordinating nature of $BAr^F_4{}^-$ should provide the best scenario for DFT modeling where the anion is ignored.

Pronounced counteranion effects (Table 1) have been observed for the equilibra between PPh_3 complexes **5a**-X and **6a**-X (X$^-$ = $BAr^F_4{}^-$, $PF_6{}^-$, $BF_4{}^-$, I$^-$, carborane$^-$, and Cl$^-$) in CD_2Cl_2. The K_{eq} can be tuned to range from < 0.02 (lowest limit of NMR detection) to 1.17, as a result of the hydrogen-bonding and/or ion-pairing effects. The largest K_{eq} was observed for the least coordinating $BAr^F_4{}^-$, while for halide counteranions only the iridium(I) NHC complexes were observed in the ^{1}H NMR spectra. More coordinating or interfering anions help to stabilize the carbene complexes likely through NH···X interactions.[17] DFT studies further revealed that the conversion of **5a**-Cl to the hypothetical **6a**-Cl is endergonic by 8.3 kcal mol^{-1}, consistent with the unidirectional formation of complex **5a**-Cl in experiments. Counteranion effects have been reported in catalysts; switching counteranions can change the catalytic activity or lead to different selectivity as in [Au(PR_3)X]-catalyzed (X = OTf or OTs) cyclization reactions.[18] However, well-characterized counteranion effects in carbene complexes are rare.[17,19]

Table 1: Effects of the counteranion on the equilibrium [**5a-X** ⇄ **6a-X**].

	BAr^F_4	Carborane ($CB_{11}H_{12}$)	PF_6	BF_4	Cl or I
K_{eq}	1.17	0.82	0.30	0.15	< 0.02

Solvents are also shown to strongly influence the equilibrium between **5a**-BAr^F_4 and **6a**-BAr^F_4. In solvents that are potentially hydrogen-bonding acceptors such as CD_3CN, [D_6]acetone, [D_8]THF, and [D_4]MeOH, only **5a**-BAr^F_4 was observed in the ^{1}H NMR spectra, and these solvents serve to "lock" the NH species by means of hydrogen bonding. Changing the solvent from CD_2Cl_2 to $CDCl_3$ resulted in an increase of the K_{eq} from 1.17 to 2.80. This is probably because of the enhanced acidity of $CDCl_3$ such that it acts as a weak proton donor[20] and can stabilize the pyridyl N atom in **6a**-BAr^F_4. However, the difference in solvent polarity might be also responsible. We also noted that addition of D_2O or CD_3OD to an equilibrium mixture of **5a**-BAr^F_4 and **6a**-BAr^F_4 in CD_2Cl_2 caused the disappearance of both the NH and the IrH signals in the ^{1}H NMR spectrum, indicative of the exchange between labile NH, OD, and IrH protons/deuteriums.

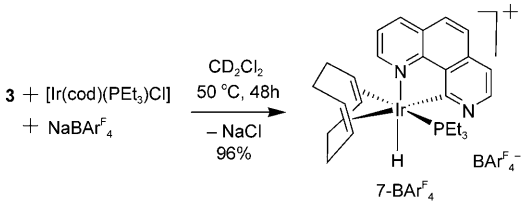
The electronic effects of isosteric phosphines can further tune this equilibrium (CD_2Cl_2), where a more donating phosphine ligand leads to a larger K_{eq} (Table 2). This trend is expected for this formal Ir^I to Ir^{III} oxidation process, and a metal in a higher oxidation state is stabilized by an electron-rich phosphine. Quantitative analyses indicate that the ln K_{eq} correlates well ($R^2 = 0.999$) with the pK_a[21] of the phosphine and with the σ_p value of the *para* substituent in substituted triphenylphosphines (see Table 2 and the Supporting Information). Thus the basicity of the phosphine affects the ΔG of this equilibrium by imparting its electron density directly to the metal. To obtain the unidirectional formation of the iridium(III) hydride product, a more electron-rich phosphine is necessary. Thus hydride complex **7**-BAr^F_4 was obtained as the only isomer in CD_2Cl_2 from equimolar 1,9-phenanthroline, [Ir(cod)(PEt_3)Cl], and $NaBAr^F_4$ [Eq. (1)]. Here the

Table 2: The electronic effects of isosteric phosphine ligands on the equilibrium between BAr^F_4 complexes in Scheme 2.

	6a$^+$/**5a**$^+$	**6c**$^+$/**5c**$^+$	**6d**$^+$/**5d**$^+$	**6e**$^+$/**5e**$^+$
K_{eq}	1.17	5.61	0.37	0.074
pK_a of $HPAr_3{}^+$	2.73	4.57	1.03	−1.2

unidirectionality might originate from a combination of electronic (pK_a of $HPEt_3^+ = 8.69$) and steric effects of PEt_3.

We further explored the electronic effects of the chelating ligand on this equilibrium. Analogous to the synthesis of **7**-BAr^F_4, 2,3′-bipyridine was allowed to react with [Ir(cod)-(PPh_3)Cl] and $NaBAr^F_4$ (equimolar) in CD_2Cl_2. Interestingly, when the reaction was conducted under relatively mild conditions (46 °C, 30 h), essentially only the hydride complex **8**-BAr^F_4 was observed by NMR spectroscopy (Scheme 3). Prolonged heating (52 °C, 60 h) of the reaction mixture or a solution of isolated **8**-BAr^F_4 produced an equilibrium mixture of hydrides **8**-BAr^F_4 and **9**-BAr^F_4 in 3.9:1 ratio at 298 K. In all cases, no isomeric protic NHC complexes were observed. Thus the migration of the hydride to the nitrogen is probably thermodynamically unfavorable as a result of the electronic effects of this chelating ligand.



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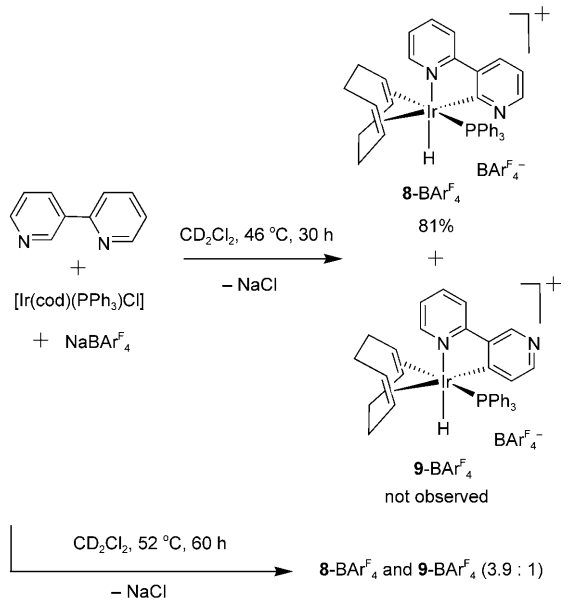

Scheme 3. Cyclometalation of 2,3′-bipyridine.

Mechanistic studies of the 1,3-H-shift process were conducted both experimentially and theoretically. As was proposed by Bergman, Ellman et al.,[3a] a β-hydrogen insertion mechanism is a possible pathway. However, the four-membered-ring transition state may be less accessible owing to the tethering effect of the pyridine ring. In addition to this pathway, we note that water as a catalyst can facilitate the classical metal-free NH to NH tautomerization of adenine,[22] where a cyclic transition state has been established. This mechanism is applicable if the Ir^I center acts as a reasonable proton acceptor. Thus these two pathways were analyzed by DFT methods (Figure 3). In the β-hydrogen insertion pathway a transition state ($\mathbf{TS_1}$) is located (d(Ir–H) = 1.82 Å and d(N–H) = 1.40 Å), and the large calculated $\Delta G^{\ddagger}_{298}$ (33.5 kcal mol^{-1} in CH_2Cl_2) for the forward reaction suggests that it is unlikely at room temperature. In the water-assisted 1,3-hydrogen-shift mechanism, water is bound to NH moiety to give an intermediate ($\mathbf{5a}^+\cdots H_2O$) with a calculated ΔG_{298} of 6.6 kcal mol^{-1} for hydration. Subsequently $\mathbf{5a}^+\cdots H_2O$ undergoes facile proton transfer via a six-membered metallacyclic transition state ($\mathbf{TS_2}$). This proton-transfer process has a low

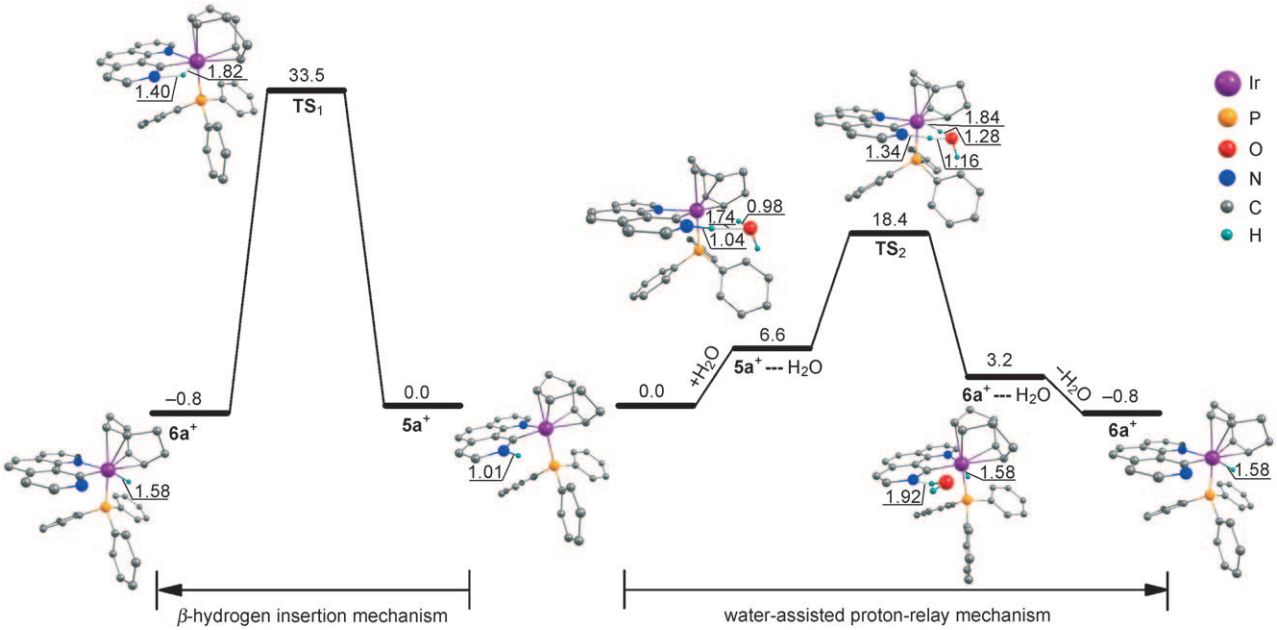

Figure 3. Free-energy diagram of two possible pathways for the conversion of $\mathbf{5a}^+$ to $\mathbf{6a}^+$. Important distances [Å] are given.

barrier ($\Delta G^{\ddagger}_{298} = 11.8$ kcal mol^{-1}), and an overall barrier of 18.4 kcal mol^{-1} is located for this pathway. Thus it can be predicted that the actual kinetics may depend on the concentration of water in CD_2Cl_2.

The kinetics of the conversion of **5a**-BAr^F_4 to **6b**-BAr^F_4 has been experimentally evaluated at two different water concentrations. The observed rate k_{obs} was measured to be 3.0×10^{-4} s^{-1} at 298 K for the forward reaction (2.5×10^{-4} s^{-1} for the reverse reaction) in CaH_2-dried CD_2Cl_2, which typically contains 20 ppm water.[23] In contrast, the equilibrium was achieved within only seven minutes (time needed to acquire an NMR spectrum) when water-saturated CD_2Cl_2 was used ($[H_2O] = 0.14$ M), where the K_{eq} is slightly changed to 1.03. The strongly water-dependent kinetics suggest that the water-assisted 1,3-hydrogen-shift mechanism is more likely. In particular, the estimated experimental value of $\Delta G^{\ddagger}_{298}$ is 18.3 kcal mol^{-1} for the forward reaction using $k_{obs} = k[H_2O]$, where $[H_2O] = 1.5$ mM (20 ppm) (see the Supporting Information), which matches well with that calculated for the water-assisted mechanism (18.4 kcal mol^{-1}). Although the probability of having a water dimer is low at low concentrations of water, we further examined the mechanism of a water-dimer-assisted formal 1,3-proton shift; this is kinetically unlikely with a calculated $\Delta G^{\ddagger}_{298}$ of 29.8 kcal mol^{-1} (see the Supporting Information). We noted the report of water dependence in the synthesis of a related protic pyridylidene complex,[2g] but in this case no conclusion could be drawn on the intermediacy of metal hydride and on the role of water in metal–H bond cleavage or formation.

In summary, we have synthesized a series of 18-electron iridium(I) protic NHC complexes by the C–H activation of 1,9-phenanthroline. The protic NHC ligand is stabilized by NH···Cl hydrogen bonds, disruption of which by anion exchange leads to an equilibrium between iridium(I) protic NHC complexes and the corresponding cationic iridium(III) hydride aryl complexes, as a result of a reversible 1,3-hydrogen shift from the nitrogen to the iridium center. The effects of the solvent, counteranion, chelating ligand, and phosphine have been studied. A combination of DFT and experimental studies strongly supports a novel water-assisted proton-relay mechanism in this transformation. The tuning of the energies of protic NHC complexes and their hydride precursors by readily controllable parameters should make it possible for each species to perform its role to full capacity in catalytic systems. Further studies on the reactivity and catalytic properties of iridium protic NHC complexes are in progress.

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[15] Crystal data of **5b**-Cl were collected on a Bruker X8 Kappa CCD diffractometer at 173 K using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The APEX2 Software Suite (Bruker, 2005) was used for data acquisition, structure solution, and refinement. Absorption corrections were applied using SADABS. The structure was solved by direct methods and refined by full-matrix least squares method on F^2 using X-shell. Crystal data: $C_{38}H_{32}ClF_3IrN_2P$, red, 832.28 g mol^{-1}, $F(000) =$

1640, orthorhombic, space group $P2_12_12_1$, $a=11.7727(5)$, $b=15.5461(7)$, $c=17.4063(8)$ Å, $V=3185.7(2)$ Å^3, $Z=4$, $d=1.735\ g\,cm^{-3}$, $\mu=3.374\ mm^{-1}$, no. data collected = 158967, R(int) = 0.0375, goodness-of-fit on $F^2=1.050$, R(all data) = 0.0227, $R_w=0.0363$, largest peak and hole 0.590 and $-0.406\ e\,Å^{-3}$. CCDC 743784 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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