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Acid-Induced Degradation and Ancillary Ligand Replacement of Biscyclometalated Iridium(III) Complexes

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Three biscyclometalated iridium(III) complexes with three different ancillary ligands have been investigated with respect to the final products of acid-induced transformation in coordinating or non-coordinating solvents. All of these complexes, represented as $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ and $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$, are susceptible to acid attack, followed by the departure of the ancillary ligand, $L_{O\wedge O}$ or $L_{N\wedge O}$. Depending on the coordinating ability of the solvent molecule and whether or not a coordinating anion exists, the final product will be either a solvento complex or a dichloro-bridged iridium(III) dimer. Although coexistence of the solvento complex and dichloro-bridged iridium(III) dimer was observed under certain conditions, the conversion of the solvento complex into the dichloro-bridged iridium(III) dimer has been proven.

Introduction

Owing to their high quantum efficiencies and excellent color-tuning capabilities through ligand structure control, cyclometalated iridium(III) complexes have been extensively studied in fundamental research[1] and are used as excellent phosphorescent emitters in organic light-emitting diodes (OLEDs).[2] In terms of the ligand combination mode, there are two types of these iridium(III) complexes, namely, homoleptic triscyclometalated and heteroleptic biscyclometalated complexes with an ancillary ligand, that is, $[Ir(L_{C\wedge N})_2L']$. The ancillary ligand (L′) is usually bidentate $L_{O\wedge O}$ (β-diketones, such as acetylacetone (acac)),[3] bidentate $L_{N\wedge O}$ (such as picolinic acid (pic),[4] quinoline-2-carboxylic acid (qui),[5] and others[6]). Bidentate $L_{O\wedge O}$ and $L_{N\wedge O}$ chelates are among the most frequently used ancillary ligands for the development of OLED phosphorescent emitters. With the successful industrialization of OLED technology, materials research has partially shifted to stability issues because they are associated with fabrication processes and long-term performance of the device.

For triscyclometalated iridium(III) complexes, certain stability issues have been reported and are mostly related to isomerization.[7] Isomerization during the sublimation process was also found in at least one heteroleptic biscyclometalated complex, $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$,[8] and the presence of isomers is detrimental to the performance of the device.[9] The utilization of solution processes in fabricating large-area OLED devices imposes new requirements on the materials with respect to their solution stability, rather than high-temperature stability. Recently, Baranoff et al. reported acid-induced degradation of $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ and two $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ complexes, in which $L_{C\wedge N}$ is 2-phenylpyridine and 2-(2,4-difluorophenyl)pyridine, $L_{N\wedge O}$ is picolinate, and $L_{O\wedge O}$ is deprotonated acac in the non-coordinating solvent chloroform.[10] At almost the same time, our group independently reported findings based on replacing acid-induced acac with the coordinating solvent acetonitrile.[11] Baranoff et al. observed the formation of dichloro-bridged iridium(III) complexes, $[\{Ir(L_{C\wedge N})_2(\mu\text{-}Cl)\}_2]$, from the degradation of $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ and $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$, in the presence of chloride from chloroform. We elucidated how $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ underwent a transformation leading to the formation of solvento complexes, $[Ir(L_{C\wedge N})_2(NCCH_3)_2]^+$, in acetonitrile. Although the products were differently derived in Baranoff's and our experiments, we consider that these findings from both groups are intrinsically correlated.

Although these studies addressed a fundamentally acid-induced chemical issue from different angles and are doubtlessly conclusive, three questions remain. First, could the ancillary ligand $L_{N\wedge O}$ in $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ be replaced with acetonitrile under acidic conditions? Second, could the dichloro-bridged compound $[\{Ir(L_{C\wedge N})_2(\mu\text{-}Cl)\}_2]$ be formed in coordinating acetonitrile in the presence of chloride? Whereas there is only one common $L_{O\wedge O}$ ligand, namely, deprotonated acac, there are at least two frequently used $L_{N\wedge O}$ ligands, that is, $L_{N\wedge O}$-pic and $L_{N\wedge O}$-qui. The third question that arises is what about $L_{N\wedge O}$-qui in these situations? To complement these studies and to allow general conclusions to be drawn, we continued stability research in a coordinating solvent, CH_3CN, in the presence of

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Table 1. A summary of studies on the stability of $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ and $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ in acidified solvents.[a]

Complex	Non-coordinating solvent ($CHCl_3$)		Coordinating solvent (CH_3CN)	
	Acid with coordinating anion (HCl)	Non-coordinating acid (TFA) and coordinating anion (Cl^-)	Acid with coordinating anion (HCl)	Acid with non-coordinating anion (TFA)
$[Ir(L_{C\wedge N})_2L_{O\wedge O}]$	○[b]	○[b]	×	○[c]
$[Ir(L_{C\wedge N})_2L_{N\wedge O}$-pic]	○[b]	○[b,d]	×	×
$[Ir(L_{C\wedge N})_2L_{N\wedge O}$-qui]	×	×	×	×

[a] × = no conclusive remarks; ○ = conclusions drawn. TFA = trifluoroacetic acid. [b] Ref. [10]. [c] Ref. [11]. [d] No experiment was carried, but a conclusion was drawn in Ref. [10].

a coordinating anion (chloride), and furthermore, examined an additional iridium(III) complex with qui as an ancillary ligand. In Table 1, we summarize previous work reported in the literature, from which conclusive remarks have been made (marked with "○"), and the studies reported herein (marked with "×"). The compounds used herein, either as reactants or as reference compounds, are shown in Scheme 1. We hope that this work, in combination with previously reported findings, will provide insight not only for understanding deterioration in the device performance, but also to guide the preparation of the solvent systems (potentially with residual acid) for solution-processed light-emitting devices.

Results and Discussion

$[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ in coordinating CH_3CN with a non-coordinating acid (TFA)

The acid-induced replacement of $L_{O\wedge O}$ in $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ by the solvent molecule has been thoroughly investigated in our previous work. Herein, we report the same acid-induced ligand replacement in two $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$: compounds **1** and **2**.

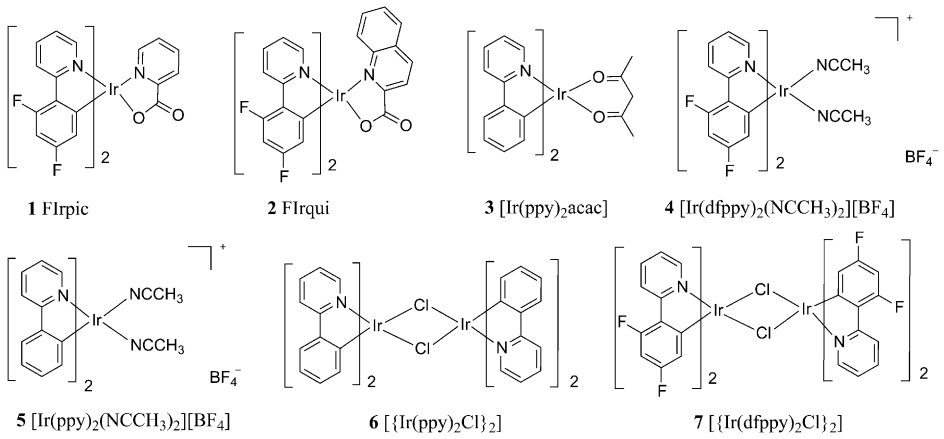
Following the protocol for spectroscopic monitoring,[11] we first observed the decrease and eventually disappearance of the photoluminescence of **1** in acetonitrile upon the addition of TFA (Figure 1 A). To elucidate the chemical nature of the spectral changes, we employed the same methodology described in our previous work[11] and that by Baranoff et al.,[10] to monitor compound **1** by ^1H NMR spectroscopy in progressively acidified solutions in acetonitrile (Figure 2). We found that [D]TFA caused the changes of the ^1H NMR spectra. The spectra in Figure 2 B and C have features of the mixing of $[Ir(L_{C\wedge N})_2(NCCH_3)_2]^+$ and the ancillary ligand, that is, **4** and pic. The ^1H NMR spectroscopy and ESI-MS data (see Figure S1 in the Supporting Information) confirmed the anticipated ligand replacement of $L_{N\wedge O}$ in $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ with the coordinating solvent molecule CD_3CN.

For compound **2**, with its emission at $\lambda = 565$ nm diminishing, a new emission at around $\lambda = 450$ nm emerged upon the addition of TFA (Figure 1 B). Nevertheless, monitoring by ^1H NMR spectroscopy (Figure S2) unambiguously confirmed that **2** was converted into **4** in the same way as the conversion of **1** in acidified acetonitrile.

In terms of the change in emission, these two compounds seemed to behave differently, that is, whereas compound **1** experienced a progressive reduction and eventually became nonemissive, the addition of TFA to the solution of compound **2** generated a new emission wave. At first glance, one may not be surprised because the two types of behavior were previously observed and clarified.[11] For $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$, after undergoing acid-induced ligand replacement, the resulting product, $[Ir(L_{C\wedge N})_2(NCCH_3)_2]^+$, may be emissive or nonemissive, depending on $L_{C\wedge N}$. However, unlike the situation in which various $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ share a common ancillary ligand (acac), here we have the same $L_{C\wedge N}$ ligand, but different $L_{N\wedge O}$ ancillary ligands. After acid-induced replacement of the ancillary ligand, the same solvento product, **4**, formed.

It is known that some $[Ir(L_{C\wedge N})_2(NCCH_3)_2]^+$ complexes, such as $[Ir(MeCN)_2(thq)_2]$ (thq = 2-(thiophen-2-yl)quinoline)[12] and $[Ir(ppy)_2(NCCH_3)_2]$[13] (**5**) in Scheme 1, are nonemissive in solution at room temperature. The examination of the compound **4** proved its nonemissive nature at room temperature; this is consistent with the results given in Figure 1 A.

Given the NMR spectroscopy data in Figure S2, we suggested that the luminescence peak at $\lambda = 450$ nm (Figure 1 B) was



Scheme 1. The chemical structures of the iridium(III) complexes used in this work. FIrpic = bis[2-(4,6-difluorophenyl)pyridinato-C2,*N*](picolinato)iridium(III), FIrqui = bis[2-(4,6-difluorophenyl)pyridinato-C2,*N*](quinolinato)iridium(III), ppy = 2-phenylpyridinato, dfppy = (4,6-difluorophenyl)pyridinato.

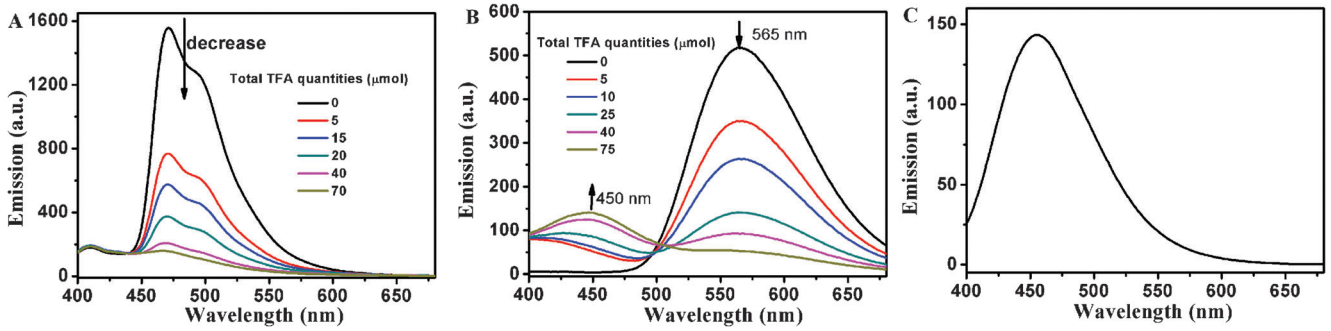


Figure 1. Changes in the emission of $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ (20 μM in CH_3CN) upon the addition of TFA. A) complex **1**, exciting light $\lambda_{ex}=365$ nm; B) complex **2**, $\lambda_{ex}=345$ nm; C) emission of a solution of qui in acetonitrile acidified with TFA, $\lambda_{ex}=345$ nm.

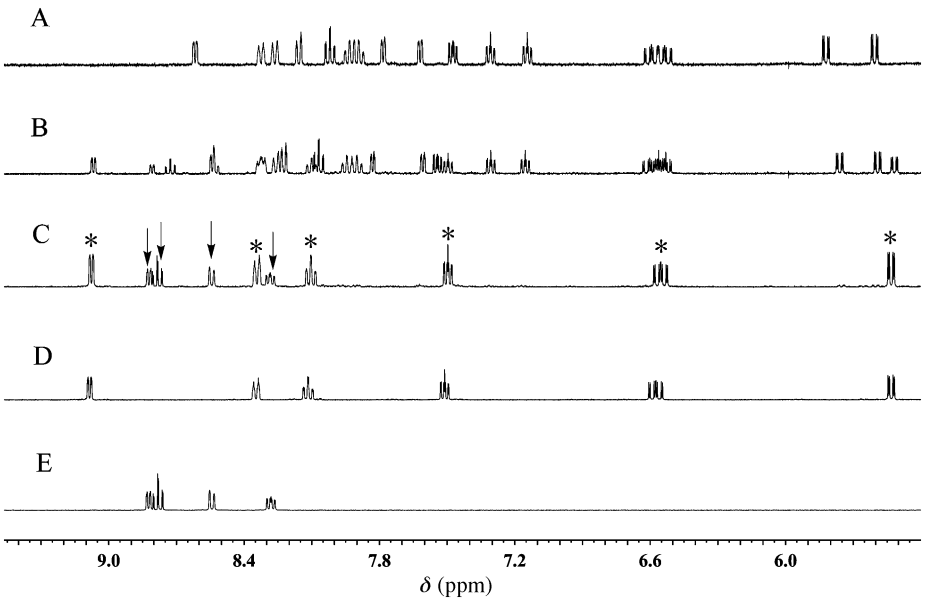


Figure 2. ^1H NMR spectroscopy monitoring of **1** in CD_3CN upon the addition of [D]TFA. A) 4 mM of **1** without [D]TFA; B) 10 min after the addition of [D]TFA (20 μL); C) 10 min after the addition of an extra 40 μL of [D]TFA; D) 4 mM of **4** in CD_3CN; E) mixture of pic and [D]TFA in CD_3CN. ^1H NMR signals marked with * are from **4** and ↓ are from pic.

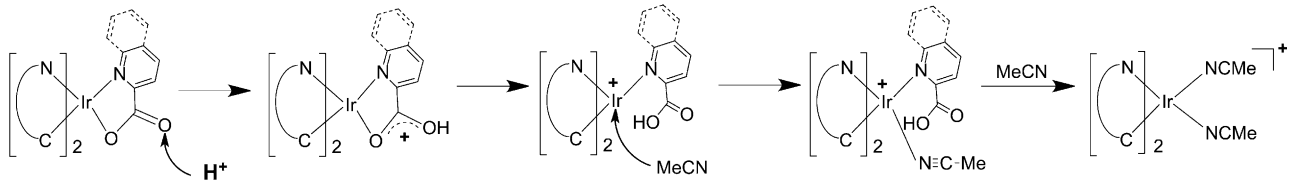
from free qui, which formed after $L_{N\wedge O}$-qui was replaced with CH_3CN. To prove this hypothesis, we investigated the photoluminescence of the ancillary ligand qui in acetonitrile containing TFA (Figure 1C). The solution of qui emitted at $\lambda=456$ nm under the same excitation wavelength ($\lambda=345$ nm). Thus, we can safely conclude that the observed emission at $\lambda=450$ nm was from liberated qui. Combining this observation with those reported previously,[11] the emission spectra of $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ and $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ may change in different ways (shifting or diminishing) for the same reason, or may change in apparently similar ways (diminishing) for different reasons, depending on the properties of the solvento complexes $[Ir(L_{C\wedge N})_2(NCCH_3)_2]^+$ and the liberated ancillary ligands.

Based on the acid-induced ligand replacement mechanism previously proposed for biscyclometalated iridium(III) acetylacetonato complexes, $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$, we suggest a similar mechanism for $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ (Scheme 2), in which $L_{N\wedge O}$ can be either pic or qui. These studies and the proposed acid-induced mechanism answer the first question raised in the Introduction.

Notably, although **1** and **2** both underwent the ligand replacement in TFA-acidified acetonitrile following the mechanism shown in Scheme 2, they may have different reaction kinetics at different steps. Compared with **1**, it took much longer for **2** to complete ligand replacement and eventually become **4**. The detailed kinetic study is, however, beyond the scope of this work.

$[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ and $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ in coordinating CH_3CN with a coordinating acid (HCl)

In this section, we address the second question raised in the Introduction, that is, could dichloro-bridged compound [{Ir-



Scheme 2. Acid-induced transformation of $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ in acetonitrile with a non-coordinating acid (TFA).

$(L_{C\wedge N})_2(\mu\text{-Cl})\}_2]$ be formed in coordinating acetonitrile in the presence of chloride?

This is actually an issue of competitive coordination between CH_3CN and chloride to iridium(III). Díaz-Torres and Alvarez thoroughly compared the coordinating abilities of a number of solvents and anions by defining a coordinating ability index.[14] In their system, the index of chloride is 1.3, which is higher than that of CH_3CN (−0.2). Based on this comparison, we anticipated the formation of the dichloro-bridged compound $[\{Ir(L_{C\wedge N})_2(\mu\text{-Cl})\}_2]$ in the presence of chloride. We first performed emission measurements upon the addition of HCl to solutions of **1** and **2** in CH_3CN under similar conditions to those described in the previous section. We observed almost the same spectral changes (see Figure S3) as those seen in Figure 1. However, these spectral changes did not answer the question as to whether $[Ir(L_{C\wedge N})_2(NCCH_3)_2^+]$ or $[\{Ir(L_{C\wedge N})_2(\mu\text{-Cl})\}_2]$ formed as a product of acid-induced ligand replacement or degradation.

Although no more information could be obtained from the emission spectra (Figure S3), the ^{1}H NMR spectra recorded during the chemical change told a different story from the simple mechanism described in Scheme 2 and reported previously.[11] Figure S4 shows how the ^{1}H NMR spectrum of one of $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ complexes, that is, **3**, changed with the addition of HCl over time. After the addition of HCl, we found some new signals in the NMR spectra (Figure S4, marked with * and ↓), which were from the solvento complexes $[Ir(L_{C\wedge N})_2(NCCH_3)_2]^+$ (**5**) and $[\{Ir(L_{C\wedge N})_2(\mu\text{-Cl})\}_2]$ (**6**). Figure S4B demonstrates the coexistence of **3**, **5**, and a very small amount of **6**. With time, and the extra addition of HCl, the initial NMR signal of **3** disappeared completely (Figure S4C). We found that the overnight storage of the NMR tube at room temperature caused the formation of some yellow precipitate, which, after isolation and dissolution in $[D_6]$DMSO, proved to be dichloro-bridged compound **6** (see Figure S5 for its ^{1}H NMR in $[D_6]$DMSO). The observed NMR signal from **6** and its gradual precipitation in CD_3CN suggests that **6** has a certain solubility in CD_3CN.

For **1** and **2**, we performed the same monitoring experiments by ^{1}H NMR spectroscopy. The addition of HCl to a solution of **1** in CD_3CN led the solution becoming immediately cloudy. A light greenish yellow precipitate could be seen quickly. In the end, the initial (Figure S6A) and intermediate NMR signals (Figure S6B) disappeared. The only visible signals left in Figure S6C are those from the ligand pic. The ^{1}H NMR spectroscopic evolution (Figure S7 in the Supporting Information) of **2** followed the same model as that of **1**, while the greenish yellow precipitate gradually became clear. That is, after a certain transition period, the only visible signals were those from the liberated ligand qui. The precipitates from **1** and **2**, which were totally insoluble in CD_3CN, were soluble in $[D_6]$DMSO and proved to be dichloro-bridged compound **7** (see ^{1}H NMR spectra in Figure S8A and B and ESI-MS data in Figure S9).

Notably, under the experimental conditions, whereas **1** and **3** underwent fairly fast degradation to become dichloro-bridged compounds **7** and **6**, respectively, in 10–20 min, it took more than one day for **2** to degrade completely.

In the above-described experiments, compounds **1**, **2**, and **3** degraded to form the dichloro-bridged dimer and, in the meantime, to liberate the ancillary ligands. These results unambiguously answered the second question raised in the Introduction. In brief, even in the coordinating solvent CH_3CN, the coordinating chloride led to the formation of a dichloro-bridged dimer $[\{Ir(L_{C\wedge N})_2(\mu\text{-Cl})\}_2]$, although the competition of solvento complex **5** and dichloro-bridged complex **6** existed at the beginning of the reaction. These results are consistent with the higher coordinating ability index of chloride compared with that of CH_3CN.[14]

The above discussion is purely based on the coordinating abilities of chloride and CH_3CN. The experimental results were consistent with their relative coordinating abilities. Another favorable factor for the formation of dichloro-bridged dimers lies in the poor solubility of **6** and the insolubility of **7**. Precipitation drives the equilibrium towards the formation of dichloro-bridged dimers. In light of the large excess of CH_3CN, this factor could be equally important or more important than the relative coordinating abilities.

$[Ir(L_{C\wedge N})_2L_{N\wedge O}$-qui] in acidified non-coordinating solvent ($CDCl_3$)

The third question raised in the Introduction is related to **2**, which was not studied previously by us and Baranoff et al. In the aforementioned experiments, the behavior of **2** in coordinating CD_3CN was investigated.

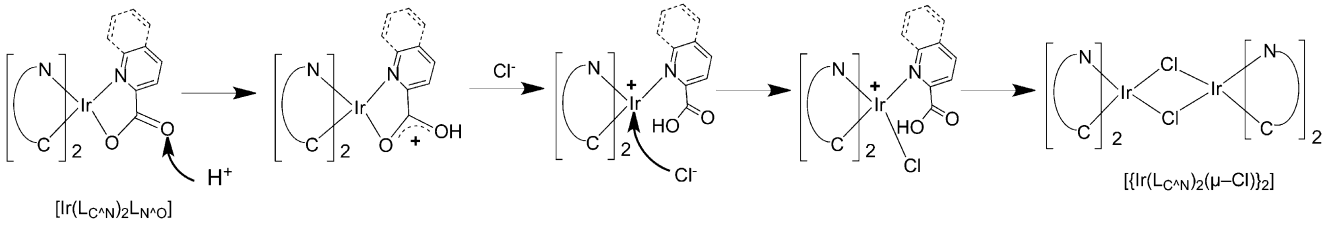
With respect to its behavior in acidified non-coordinating solvent, owing to the structural similarity between pic and qui and the above study on **2**, we can safely predict that $[Ir(L_{C\wedge N})_2L_{N\wedge O}$-qui] will degrade into a dichloro-bridged dimer and release the ligand qui. Our ^{1}H NMR spectroscopy (Figures S10 and S11) and ESI-MS (Figure S12) data for monitoring experiments performed in $CDCl_3$ with both HCl and [D]TFA confirmed our prediction.

Thus, we are able to expand the mechanism proposed by Baranoff et al.[10] for $[Ir(L_{C\wedge N})_2L_{N\wedge O}$-pic] and $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ to cover $[Ir(L_{C\wedge N})_2L_{N\wedge O}$-qui] (Scheme 3).

A summary of the studies on $[Ir(L_{C\wedge N})_2L_{O\wedge O}]$ and $[Ir(L_{C\wedge N})_2L_{N\wedge O}]$ in different acidified solvents is given in Table 2 with the identified solvento complexes (**4** and **5**) and degraded products (**6** and **7**).

Transformation from $[Ir(L_{C\wedge N})_2(NCCH_3)_2]^+$ to $[\{Ir(L_{C\wedge N})_2(\mu\text{-Cl})\}_2]$

Despite the fact that chloride has a stronger coordination ability, competitive coordination between CH_3CN and chloride to iridium(III) has been found in CH_3CN, leading to $[Ir(L_{C\wedge N})_2(NCCH_3)_2^+]$. We wish to stress that the (mono- or di-)solvento complexes could be intermediates (Figures S4B, S6B, and S7B and C) and the final products will be dichloro-bridged dimers. The transition from solvento complexes $[Ir(L_{C\wedge N})_2(NCCH_3)_2]^+$ into $[\{Ir(L_{C\wedge N})_2(\mu\text{-Cl})\}_2]$ was facile (Scheme 4). Figures S13 and S14 show the transition monitored by ^{1}H NMR spectroscopy. Owing to precipitation of dichloro-bridged dimer **7** and its insolubility in both $CDCl_3$ and CD_3CN, the signals measured by

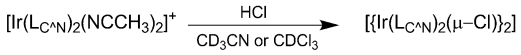


Scheme 3. Mechanism for the chemical transformation of $[Ir(L_{C^N})_2L_{N^O}]$ in $CDCl_3$ with coexisting protons and coordinating anions (Cl^-).

Table 2. A conclusive summary of the results from treating $[Ir(L_{C^N})_2L_{O^O}]$ and $[Ir(L_{C^N})_2L_{N^O}]$ with acid.

Complex	Non-coordinating solvent ($CHCl_3$)		Coordinating solvent (CH_3CN)	
	Acid with coordinating anion (HCl)	Non-coordinating acid (TFA) and coordinating anion (Cl^-)	Acid with coordinating anion (HCl)	Acid with non-coordinating anion (TFA)
$[Ir(L_{C^N})_2L_{O^O}]$	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$[a]	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$[a]	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$ and $[Ir(L_{C^N})_2(NCCH_3)_2]^+$[c]	$[Ir(L_{C^N})_2(NCCH_3)_2]^+$[b]
$[Ir(L_{C^N})_2L_{N^O}$-pic]	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$[a]	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$[a]	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$[c]	$[Ir(L_{C^N})_2(NCCH_3)_2]^+$[c]
$[Ir(L_{C^N})_2L_{N^O}$-qui]	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$[c]	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$[c]	$[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$[c]	$[Ir(L_{C^N})_2(NCCH_3)_2]^+$[c]

[a] Ref. [10]. [b] Ref. [11]. [c] This work.



Scheme 4. An acid with a coordinating anion (HCl) induced the transformation from $[Ir(L_{C^N})_2(NCCH_3)_2]^+$ into $[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$.

^{1}H NMR spectroscopy disappeared completely at the end of the transition. The identification of the precipitates was achieved by isolating them and characterizing them by ^{1}H NMR spectroscopy in $[D_6]$DMSO (see Figure S8C and S8D) and ESI-MS (see Figure S15).

Conclusion

Biscyclometalated iridium(III) complexes with an ancillary ligand chosen from acac and pic were unstable in acidified solutions. By including a new iridium(III) complex with quinoline-2-carboxylate as the ancillary ligand into the $[Ir(L_{C^N})_2L_{N^O}]$ family and varying the conditions (coordinating or non-coordinating solvents and anion), this work expands upon prior knowledge. Both $[Ir(L_{C^N})_2L_{N^O}]$ and $[Ir(L_{C^N})_2L_{O^O}]$ are susceptible to acid: In a coordinating solvent, proton attack causes the departure of the ancillary ligand and the coordination of solvent molecules to iridium(III). In non-coordinating solvents, or if a stronger coordinating anion exists in solution, the degradation of $[Ir(L_{C^N})_2L_{N^O}]$ and $[Ir(L_{C^N})_2L_{O^O}]$ leads to the formation of dichloro-bridged dimer $[\{Ir(L_{C^N})_2(\mu\text{-}Cl)\}_2]$, which may be slightly soluble or completely insoluble in different solvents. Depending on the coordinating ability of solvent molecules and anions, competitive coordination may take place, leading to the formation of both solvento complexes and dichloro-bridged dimers at certain stages of the acid-induced reactions. Finally, the solvento complexes were able to transform into dichloro-bridged dimers through the stronger coordinating ability of chloride and the insolubility of the product.

Experimental Section

Chemicals and measurements

Except **2**, which was synthesized previously,[5c] all other complexes (**1**, **3**, **4**, **5**, **6**, and **7**) were received from SunaTech Inc. Picolinic acid (pic; Alfa Aesar), quinoline-2-carboxylic acid (qui; Alfa Aesar), [D]TFA (Cambridge Isotope Laboratories, Inc.), tetrabutylammonium chloride (TBACl, Sinopharm Chemical Reagent Co., Ltd.), and concentrated hydrochloric acid (36–38%, Sinopharm Chemical Reagent Co., Ltd.) were used as received.

^{1}H NMR spectra were acquired on a VARIAN 400 MHz spectrometer. To monitor changes in ^{1}H NMR spectra of biscyclometalated iridium(III) complexes upon addition of acid ([D]TFA or concentrated HCl), 0.5 mL of CD_3CN or $CDCl_3$ was added to NMR tubes loaded with the iridium(III) complexes. After mixing and shaking with aliquots of acid, the tubes were placed in the NMR spectrometer for measurement. Photoluminescent spectra were obtained on a HITACHI F-4600 spectrophotometer equipped with a xenon lamp as the light source. Excitation and emission slits were set at $\lambda =$ 10 nm. ESI-MS analysis was performed on an Agilent TOF spectrometer.

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Keywords: coordination chemistry · iridium · ligand effects · N,O ligands

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