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Synthesis, Structure, and Reversible Deprotonation of a Half-sandwich Iridium Complex Bearing a Chelating Oxime Ligand

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A reaction of [{Cp*IrCl(μ-Cl)}$_2$] (Cp* = η^5-$C_5(CH_3)_5$) with 1-(pyridin-2-yl)ethanone oxime (PyNOH) afforded the cationic oxime complex [Cp*IrCl(PyNOH)]Cl (**3**) with an acidic OH group at the β-position to the metal center. Complex **3** underwent reversible deprotonation to give the corresponding oximato complex [Cp*IrCl-(PyNO)] (**4**), while treatment of **3** with silver triflate in acetonitrile led to the formation of the dicationic complex [Cp*Ir(PyNOH)-(CH_3CN)][OTf]$_2$ (**5**, OTf = OSO_2CF_3). The detailed structures of **3**–**5** have been determined by X-ray crystallography.

We have recently revealed that late-metal complexes ligated by N-heterocycles with an acidic β-NH group exhibit intriguing metal–ligand cooperating catalysis.[1] For example, the protic N-heterocyclic carbene complex **1** catalyzes dehydrative condensation of allyl alcohol and an imidazole,[2] whereas the pyrazole complex **2** serves as a precatalyst for cyclization of aminoalkenes (Chart 1).[3] The high catalytic performance of these complexes may be explained by the hydrogen bonding and reversible deprotonation of the β-NH group, which are coupled with events on the metal. We thus envisioned that chelating pyridyl oxime complexes such as **3** would become an additional class of the metal–ligand bifunctional catalysts, since they have a different type of protic functionality at the β-position to the metal.

Chelating oxime complexes have long been attracting much attention as bioinorganic model compounds and molecule-based magnetic materials.[4] In contrast, organometallic oxime complexes other than organocobaloximes[5] are rather scarce.[6–10] The catalytic application of these complexes has also rarely been explored, and the role of the β-OH group therein remains to be clarified.[7] We report here the synthesis, structures, and reactivities of the novel organometallic iridium oxime complex **3**, highlighting the proton and hydrogen-bond donating ability of the ligand as observed in the bifunctional catalysts **1** and **2**.

Treatment of [{Cp*IrCl(μ-Cl)}$_2$] with 1-(pyridin-2-yl)ethanone oxime (PyNOH)[11] afforded the organoiridium oxime complex **3** in 86% yield (eq 1).[12] The X-ray analysis[13] clearly revealed the three-legged piano-stool structure of **3** with a chelating oxime ligand as shown in Figure 1 and Table 1. The oxime hydrogen has been found in the difference Fourier map, although the ^{1}H NMR spectrum of **3** exhibits no signal ascribed to the OH proton even at −80 °C. The short H(1)···Cl(2) and O(1)···Cl(2) distances (1.97 and 2.871(3) Å) indicate the presence of the hydrogen bond between the coordinated oxime hydrogen atom and the outersphere chloride anion.

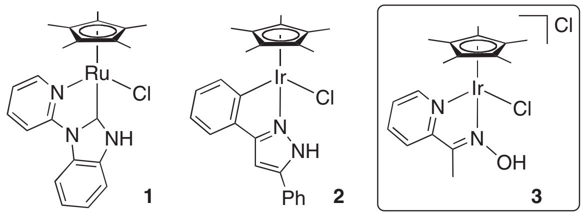


Chart 1.

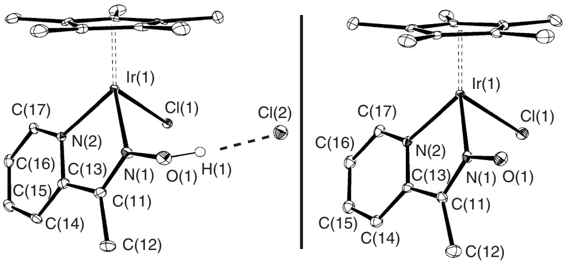
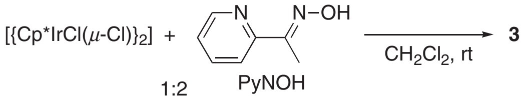


Figure 1. Crystal structures of **3** (left) and **4** (right). Hydrogen atoms except for the oxime hydrogen in **3** are omitted for clarity.

Table 1. Selected interatomic distances (Å) and angles (°) in **3**–**5**

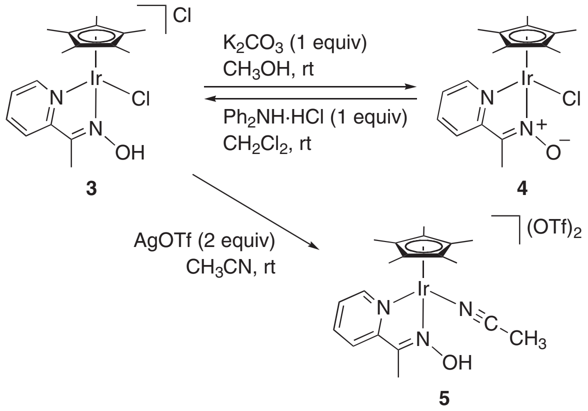
	3	**4**	**5**
Ir(1)–X[a]	2.3933(11)	2.3987(11)	2.046(3)
Ir(1)–N(1)	2.067(4)	2.070(3)	2.082(3)
Ir(1)–N(2)	2.083(3)	2.080(3)	2.089(4)
N(1)–O(1)	1.383(5)	1.291(5)	1.372(5)
N(1)–C(11)	1.292(6)	1.319(5)	1.291(7)
C(11)–C(12)	1.493(7)	1.503(6)	1.484(6)
C(11)–C(13)	1.461(7)	1.434(6)	1.476(6)
N(2)–C(13)	1.371(6)	1.362(6)	1.364(5)
O(1)–H(1)	0.93		0.74(10)
X[b]···H(1)	1.97		2.00(9)
Ir(1)–N(1)–O(1)	124.1(2)	121.3(2)	123.7(3)
Ir(1)–N(1)–C(11)	120.2(3)	117.3(3)	120.5(3)
O(1)–N(1)–C(11)	115.6(4)	121.2(3)	115.6(3)

[a]X = Cl(1) (**3** and **4**), N(3) (**5**). [b]X = Cl(2) (**3**), O(2) (**5**).

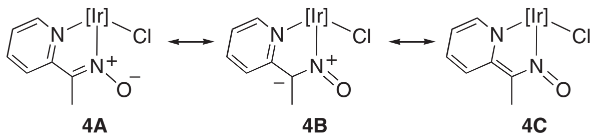


(1)

We next examined the Brønsted acidity of the β-OH group in **3**. When the cationic oxime complex **3** was treated with an equimolar amount of potassium carbonate, the oximato complex **4** was isolated as the deprotonation product in 54% yield (Scheme 1). In the ^{1}H NMR spectrum of **4**, the methyl signal of the oxime ligand (δ 2.11) appears upfield with respect to the oxime complex **3** (δ 2.81) in line with observations by Beck and co-workers.[8] The ^{13}C NMR signal for the azomethine carbon (δ 156.0 (**3**) vs. 146.9 (**4**)) is also shifted upfield upon deprotonation. The X-ray analysis of **4**, shown in Figure 1 and



Scheme 1.



Scheme 2.

Table 1, demonstrated the considerable structural difference in the chelating ligand between the protonated and deprotonated forms **3** and **4**,[14] in contrast to the related pyrazole–pyrazolato couples.[3] The N(1)–O(1) bond in **4** is shorter than that in **3** by 0.09 Å, whereas the N(1)–C(11) bond in **4** is slightly elongated. These metric parameters may suggest sizable contribution of the canonical structure **4B** in Scheme 2, which has been proposed for other oximato complexes;[8,9] however, the azomethine carbon atom in **4** is almost perfectly planar with the angle sum around the C(11) atom 359.9°. The nitrosoalkene structure **4C** without the pyridine aromaticity is much less plausible, because the C(11)–C(13) distance in **4** is almost the same as that in the protonated form **3** and there seems no bond alternation in the pyridine ring in **4**. As expected, protonation of the oximato **4** with an amine hydrochloride readily took place to regenerate the oxime complex **3** in 54% isolated yield.

In addition to the oxime hydrogen, the chlorido ligand in **3** proved to be removed smoothly. Thus, the reaction of **3** with two equivalents of silver triflate in acetonitrile led to the formation of the dicationic nitrile–oxime complex **5** in 82% yield (Scheme 1). In contrast to the chlorido complex **3**, the ^1H NMR spectrum of **5** diplays a low-field, sharp singlet assigned to the oxime proton at δ 12.21, which disappears upon treatment with D_2O. The presence and acidic nature of the oxime hydrogen were further supported by an X-ray diffraction study (Figure 2); the β-OH group forms a hydrogen bond with a triflate anion with the H(1)···O(2) and O(2)···Cl(2) distances of 2.00(9) and 2.675(5) Å.[15]

In summary, we have synthesized an interconvertible couple of chelating oxime and oximato complexes **3** and **4** with exactly the same auxiliary organometallic coligands. The X-ray analysis revealed that the hydrogen-bond-donating ability of the oxime complexes as well as detailed structural changes associated with reversible deprotonation of the β-OH group. The catalytic application of the oxime complexes with the metal/(β-OH) bifunctionality will be reported in due course.

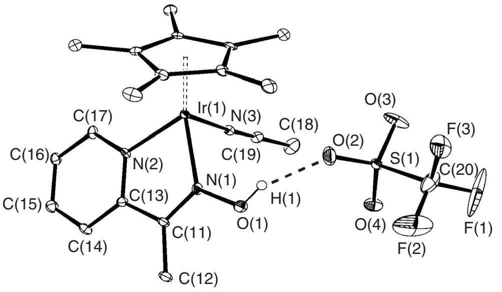


Figure 2. Crystal structure of **5**. One of the triflate anions, which does not form apparent hydrogen bonds with the cationic part, as well as hydrogen atoms except for the oxime hydrogen is omitted for clarity.

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13 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-777525 (**3**), 777526 (**4**), and 777527 (**5**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

14 Beck and co-workers have reported some half-sandwich type chelating oxime and oximato complexes.[8–10] However, comparison of the crystal structures between oxime and oximato complexes with the same ligand sets has not been achieved.

15 Preliminary experiments revealed that **5** also undergoes facile deprotonation with K_2CO_3 to give the corresponding monocationic oximato complex. Details will be reported elsewhere.