



Communication

Synthesis of a Half-Sandwich Hydroxidoiridium(III) Complex Bearing a Nonprotic *N*-Sulfonyldiamine Ligand and Its Transformations Triggered by the Brønsted Basicity

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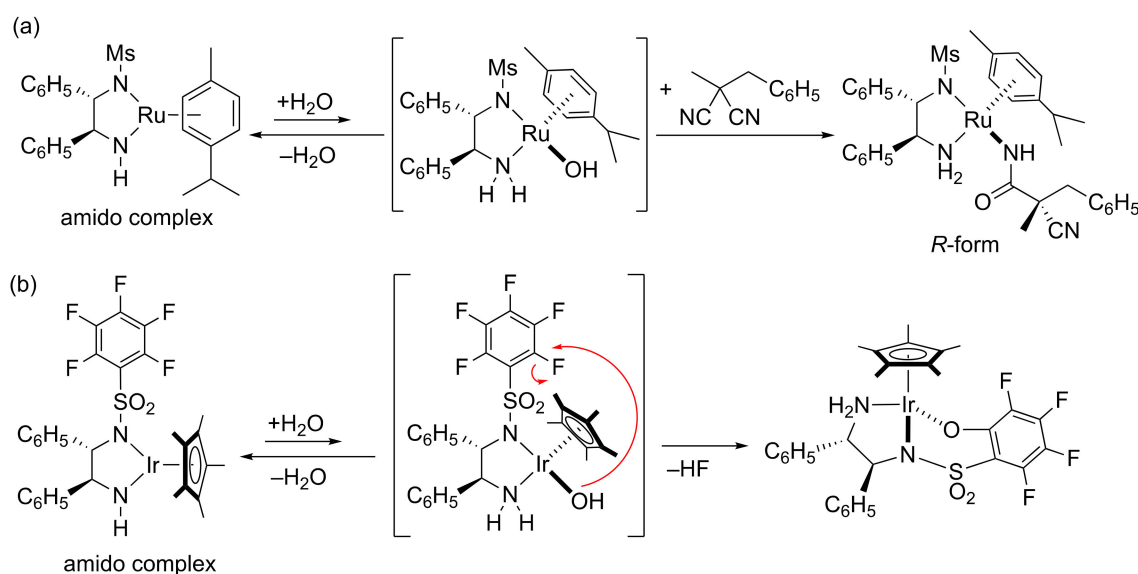
Abstract: Synthesis and reactivities of a new mononuclear hydroxidoiridium(III) complex with a pentamethylcyclopentadienyl (Cp*) ligand are reported. The hydroxido ligand was introduced into an iridium complex with a nonprotic amine chelate derived from *N*-mesyl-*N',N'*-dimethylethylenediamine by substitution of the chloride ligand using KOH. The resulting hydroxidoiridium complex was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The hydroxido complex was able to deprotonate benzamide and acetonitrile, and showed an ability to accept a hydride from 2-propanol to generate the corresponding hydrido complex quantitatively. In the reaction with mandelonitrile, a cyanide anion was transferred to the iridium center in preference to the hydride transfer. The cyanidoiridium complex was also identified in the reaction with acetone cyanohydrin, and could serve as catalyst species in the transfer hydrocyanation of benzaldehyde.

Keywords: iridium; hydroxido complex; deprotonation; hydride transfer; cyanido complex; transfer hydrocyanation; amidato complex; cyanomethyl complex

1. Introduction

Transition metal hydroxide complexes have received considerable attention as activators for small molecules and key intermediates in various catalytic transformations [1–3]. Despite the unmatched combination of hydroxide with a hard-base character and soft late transition metals, the utility of hydroxido complexes have been shown by careful synthetic approaches such as oxidative addition of water [4,5]. During the course of our studies on bifunctional catalysis based on the interconversion of amido/amine ligands [6], the O–H bond of water proved to be cleaved heterolytically by chiral amido–Ru complexes to generate amine-hydroxido complexes, and the process can contribute to the hydration of dinitriles in an enantioselective manner (Scheme 1a) [7]. Separately, we also reported the C–F bond breaking through nucleophilic aromatic substitution with a coordinated OH group generated from water and bifunctional amido–Ru and –Ir complexes (Scheme 1b) [8]. In these systems, the hydroxido complexes could not be isolated, possibly because the basicity of the hydroxido ligand promoted the reverse deprotonation of the protic amine ligands to give the parent amido complexes. We conceived that structural change of the amido/amine moiety with a nonprotic amine ligand would allow to stabilize the hydroxido complexes. Under the inspiration of achievements of Cp*Ir systems [9–13], we disclose herein, the synthesis and characterization of a new mononuclear hydroxidoiridium(III) complex having *N*-sulfonyldiamine without the NH moiety. As part from its reactivities toward

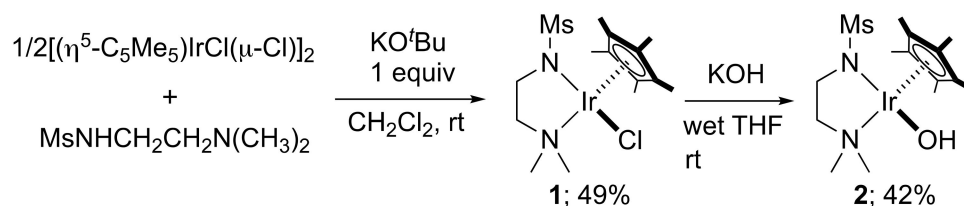
Brønsted acids, we also deal with the cyanide transfer from cyanohydrins in relation to the hydrogen transfer from secondary alcohols.



Scheme 1. Transformations via hydroxido complexes generated from amido–Ru (a) and –Ir (b) complexes in the presence of H₂O.

2. Results and Discussion

According to the established synthesis of 1,2-diphenylethylenediamine (DPEN)-derived complexes [14], coordination of *N*-mesyl-*N,N'*-dimethylethylenediamine (MsNHCH₂CH₂N(CH₃)₂) with [Cp*IrCl₂]₂ (diamine:Ir = 1:1) was performed in CH₂Cl₂ under basic conditions at room temperature. To avoid coordination of amine base competitively with the tertiary amine chelate, KO^tBu was better suited for the base additive. After recrystallization, the expected chlorido complex (**1**) was obtained as orange crystals in 49% yield (Scheme 2). The product was fully characterized by ¹H and ¹³C{¹H} NMR spectra, elemental analysis, and X-ray crystallography (see the Supplementary Materials and Figure 1 (left)). A set of nonequivalent dimethylamino signals at around 3.0 ppm in the ¹H NMR spectrum indicates the chelating structure of the amine ligand.



Scheme 2. Synthesis of hydroxidoiridium **2** derived from MsNHCH₂CH₂NMe₂.

When ligand substitution was performed by treatment of **1** with KOH pellets in tetrahydrofuran (THF) containing water with a *v/v* ratio of 1500/1, the desired hydroxido-amine complex (**2**) was formed and successfully isolated in 42% yield after recrystallization from THF. The ¹H NMR spectrum in CD₂Cl₂ at –70 °C displayed the hydroxido resonance at –0.79 ppm as a broad signal, which disappeared with increasing the temperature. Two separate aminomethyl signals observed at 2.83 and 2.88 ppm were also broadened and coalesced at room temperature. These results are indicative of facile dissociation of the tertiary amine and/or hydroxido ligands, allowing for dynamic behavior. A single-crystal X-ray diffraction analysis revealed that the structure of **2** resembles that of a monomeric

three-legged piano-stool shape of **1**, as shown in Figure 1. Although the OH hydrogen was located from the Fourier difference map, no significant hydrogen bonding interactions were observed.

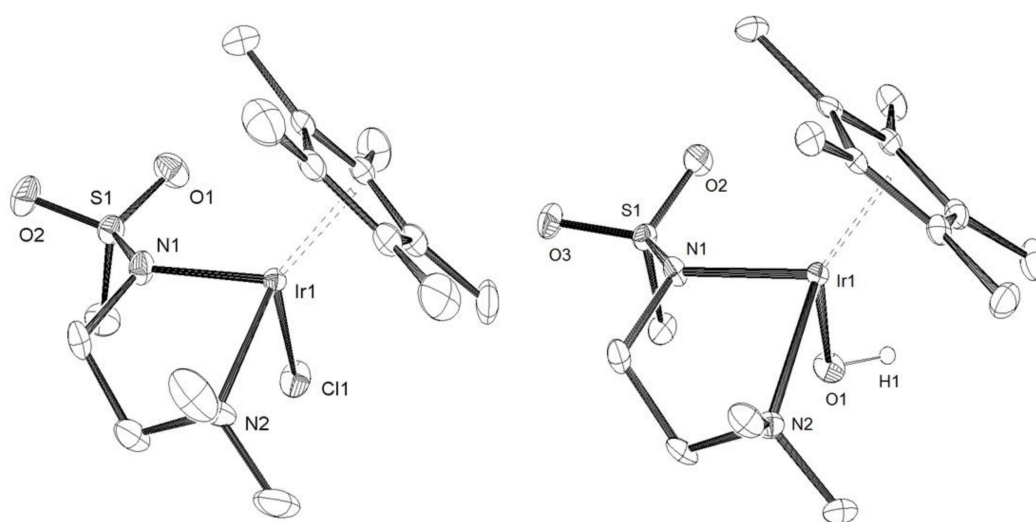
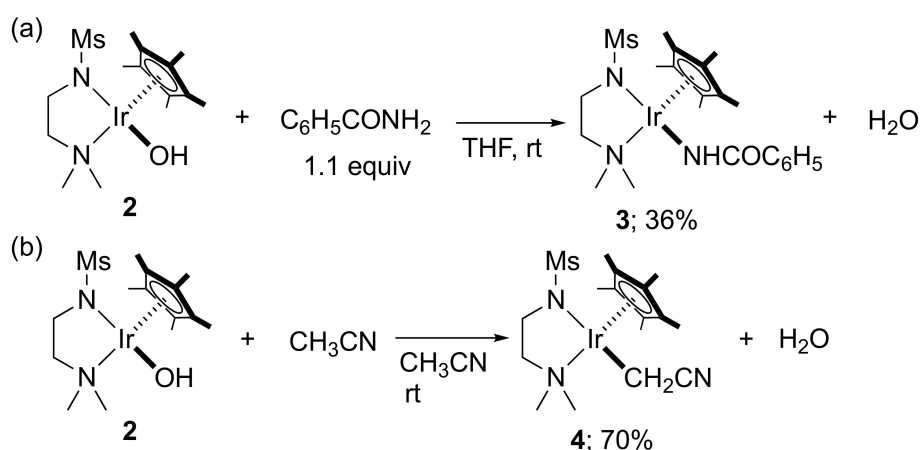


Figure 1. ORTEP drawings of **1** (left) and **2** (right). Hydrogen atoms other than the OH ligand in **2** are omitted for clarity, and the ellipsoids represent 30% probability.

The isolated mononuclear complex **2** can deprotonate benzamide to form the corresponding benzamidato (**3**) complex at room temperature (Scheme 3a). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra and elemental analysis agree with the substitution. The $\kappa^1(N)$ -benzamidato coordination making a reasonable hydrogen bond to the sulfonyl oxygen in **3** was verified by X-ray diffraction analysis, as shown in Figure 2 (left). Moreover, the hydroxido complex proved to have sufficient basicity to abstract a proton from acetonitrile ($\text{p}K_a$ in DMSO = 31.3) [15]. When an acetonitrile solution (4.0×10^{-2} M) of **2** was stirred at room temperature for 3.5 h, a cyanomethyl complex (**4**) was isolated in 70% yield (Scheme 3b) [16]. The ^1H NMR spectrum in CD_2Cl_2 displayed a characteristic AB pattern for the diastereotopic CH_2 protons of the cyanomethyl ligand at 2.14 ppm. The presence of the cyanomethyl moiety was confirmed by $^{13}\text{C}\{^1\text{H}\}$ NMR signals observed at -18.8 and 129.7 ppm and a CN stretching band at 2187 cm^{-1} in the IR spectrum.



Scheme 3. Deprotonation of benzamide (a) and acetonitrile (b) with **2**.

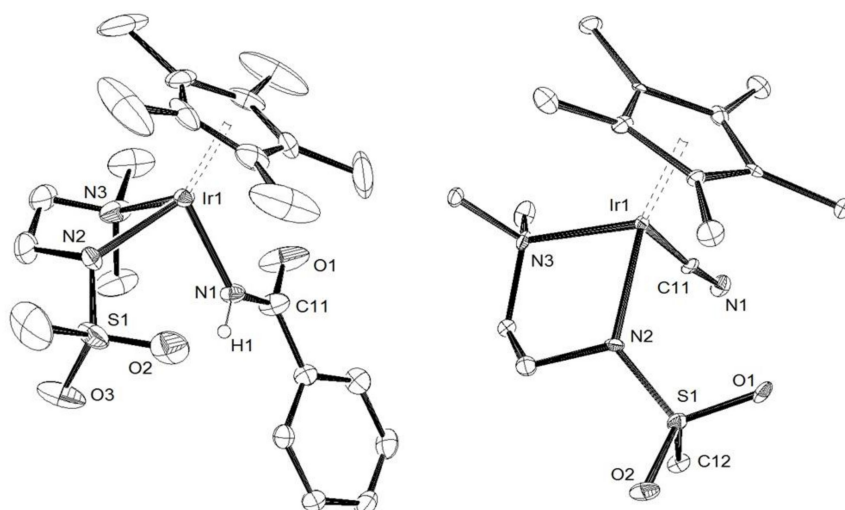
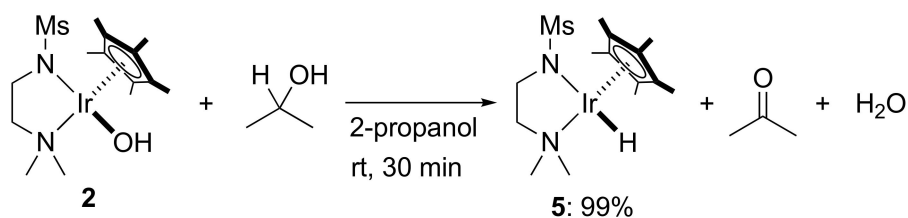
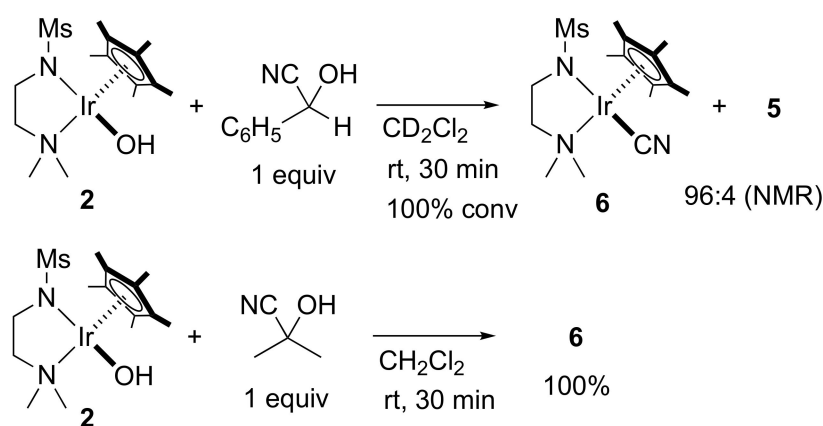


Figure 2. ORTEP drawings of **3** (left) and **6** (right). Hydrogen atoms are omitted for clarity, and the ellipsoids represent 30% probability.

Treatment of **2** in 2-propanol at ambient temperature resulted in the smooth formation of a hydrido complex (**5**) in an almost quantitative yield (Scheme 4). The ^1H NMR spectrum in CD_2Cl_2 displayed a hydrido resonance at -11.6 ppm. Presumably, **2** deprotonated the alcohol group to generate a coordinatively saturated alkoxido complex and hemilabile nature of the tertiary amine ligand allowed spontaneous β -hydrogen elimination to afford **5**. The β -H elimination of alkoxidoiridium species generated from a hydroxido ligand was discussed with relevant to hydrogen evolution from aliphatic alcohols catalyzed by cyclometalated iridium complexes [17]. Notably, the isolable hydroxido complex **2** was found to undergo cyanide transfer from cyanohydrins in an analogous fashion to the hydride transfer (Scheme 5). Monitoring the reaction of **2** with 1 equivalent of mandelonitrile in CD_2Cl_2 at room temperature by ^1H NMR revealed that the hydroxido moiety was fully consumed within 30 min and a new cyanidoiridium complex **6** was formed in preference to the hydride transfer product **5** with the ratio of 96:4. The same complex **6** could be synthesized quantitatively by treatment of **2** with an equimolar amount of acetone cyanohydrin in CH_2Cl_2 for 30 min at room temperature. The product was unambiguously characterized by spectroscopic methods and elemental analysis. The cyanido ligand was identified by a ^{13}C NMR signal at 121.3 ppm and a CN stretching absorption at 2103 cm^{-1} in the IR spectrum. Single crystal X-ray analysis also confirmed a typical half-sandwich structure of **6** as shown in Figure 2 (right). The Ir–C and C–N distances of 2.005(10) and 1.171(14) Å were nearly identical to those of 1.990(8) and 1.146(9) Å in a related cyanidoiridium complex having a TsDPEN ligand [18].

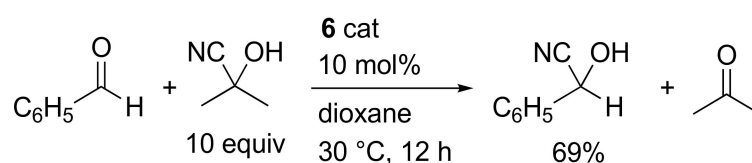


Scheme 4. Hydrogen transfer reaction of **2** in 2-propanol.



Scheme 5. Cyanide transfer from cyanohydrins using **2**.

Considering the homologous hydride and cyanide transfer processes from alcoholic compounds, we envisioned that the cyanidoiridium complex will be able to promote hydrocyanation of aldehydes. In the trial reaction of benzaldehyde (0.5 mmol) with 10 equiv of acetone cyanohydrin using 10 mol % of **6** in 1,4-dioxane at 30 °C, the expected product, mandelonitrile, was reasonably formed in 69% yield after 12 h (Scheme 6). Hydrocyanation using acetone cyanohydrin is an attractive transformation without using hazardous HCN and could be operated without special setups [19,20]. Aside from successful applications in which base and Lewis acid catalysts and biocatalysts have been utilized for transfer hydrocyanation from cyanohydrin to aldehydes [21–34], transition metal-based cyanido complexes can be regarded as potential catalyst candidates to advance the HCN-free process.



Scheme 6. Transfer hydrocyanation of benzaldehyde with acetone cyanohydrin catalyzed by **6**.

3. Materials and Methods

3.1. General Information

All manipulations of oxygen and moisture-sensitive materials were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and dried by refluxing over sodium benzophenone ketyl (THF, 1,4-dioxane, and diethyl ether), P₂O₅ (CH₃CN and CH₂Cl₂), or CaH₂ (2-propanol), and distilled under argon before use. Chloroform-*d*₁ was used as delivered. Other deuterated solvents were degassed by three freeze-pump-thaw cycles and purified by trap-to-trap distillation after being dried with CaH₂ (THF-*d*₈) or P₂O₅ (CD₂Cl₂). Benzaldehyde and acetone cyanohydrin were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), degassed, and stored under argon atmosphere. The other reagents were purchased from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA), Nacalai Tesque Inc. (Kyoto, Japan), and FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan), and used as delivered. ¹H and ¹³C{¹H} NMR spectra were recorded on a JEOL JNM-LA300 and JNM-ECX400 spectrometers (JEOL Ltd., Tokyo, Japan) at around 25 °C unless otherwise noted. The NMR chemical shifts were referenced to an external tetramethylsilane signal (0.0 ppm) by using the signals of residual proton impurities in the deuterated solvents for ¹H and ¹³C{¹H} NMR. IR spectra were recorded on a JASCO FT/IR-610 spectrometer (JASCO Corporation, Tokyo, Japan). Elemental analyses were carried out using a PE2400 Series II CHN analyser (PerkinElmer, Waltham, MA, USA).

3.2. X-Ray Crystal Structure Determination

All measurements were made on a Rigaku Saturn 70 (Rigaku Corporation, Tokyo, Japan) using graphite-monochromated Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$) under nitrogen stream at 193 or 93 K. Single crystals suitable for X-ray analyses were mounted on glass fibers. Intensity data were collected for Lorentz-polarization effects and for absorption. Details of crystal and data collection parameters for the complexes **1**, **2**, **3**, and **6** are summarized in Tables S1 and S2. Structure solution and refinements were performed with the CrystalStructure program package [35]. The heavy atom positions were determined by a direct program method (SIR92) [36], and the remaining non-hydrogen atoms were found by subsequent Fourier syntheses and refined by full-matrix least-squares techniques against F^2 using the SHELXL-2014/7 program [37]. The OH hydrogen atom in **2** was found in the difference Fourier map, while the rest hydrogen atoms were placed at calculated positions; these hydrogen atoms were included in the refinements with a riding model.

4. Conclusions

In summary, the hydroxido-ligated Cp*Ir complex was successfully synthesized by employment of the nonprotic *N*-sulfonyldiamine chelate. The isolated mononuclear complex reacted with a range of protic compounds. In a striking contrast with the hydride transfer from 2-propanol, the specific cyanide transfer from cyanohydrins was demonstrated. The resulting cyanidoiridium complex can serve as the catalyst, which can deliver HCN from cyanohydrin to benzaldehyde. Further studies aimed at improving the catalytic performance, as well as exploration of the chemical properties of the related hydroxido complexes are underway.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2304-6740/7/10/125/s1>. The CIFs and CheckCIFs; Experimental procedures and characterization of products; Tables of X-ray crystallographic data for **1**, **2**, **3**, and **6**, and NMR spectra.

Author Contributions: S.K. (Shoko Kamezaki) performed experiments and measurements. Y.K. designed the experiments, carried out the X-ray crystallography, and wrote the paper. S.K. (Shigeki Kuwata) supervised and reviewed the final manuscript. T.I. supervised the project.

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