Oxidative Addition of Water to Ir(I) Complexes Bearing a Pincer-Type Silyl Ligand

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ABSTRACT: Reaction of water with in situ generated $[(PSiP-R)Ir^I]$ $(PSiP-R = [\{2-(R_2P)C_6H_4\}_2MeSi]^-$; R = cyclohexyl, tBu or iPr) from $[(PSiP-R)Ir(H)_4]$ and *tert*-butylethylene (tbe) showed high ligand dependency. Oxidative addition of water cleanly proceeded in the reaction of $[(PSiP-tBu)Ir^I]$ in THF at room temperature to selectively afford a 16-electron hydrido−hydroxo complex $[(PSiP-^tBu)Ir(H)(OH)]$ almost quantitatively. In contrast, the reaction of cyclohexyl and iPr derivatives was unselective and formed various products containing Ir−H bonds. In the case of iPr-derivative, a small amount of 18-electron hydrido−hydroxo aqua complex $[(PSiP-iPr)Ir(H)(OH)(H_2O)]$ was isolated and structurally characterized by X-ray crystallography.
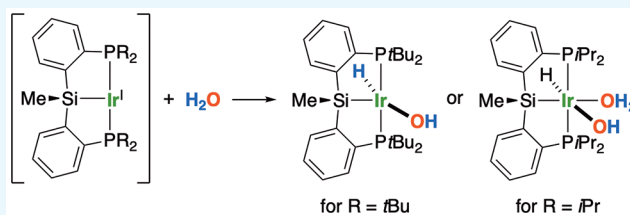
1. INTRODUCTION

Water is an abundant, ubiquitous, cheap, and ecologically benign substrate that acts as a source of oxy-functionalities for organic transformation. Transition-metal complexes act as catalysts for the transformation of water in organic synthesis, such as hydration of alkenes,[1] alkynes,[2] and nitriles,[3] C−H oxidation of organic compounds,[4] and Wacker−Tsuji reaction.[5] Artificial water splitting into H_2 and O_2 is a big challenge for the transition to renewal energy and transition-metal catalysis plays an important role.[6] The water gas shift reaction is also an important reaction catalyzed by transition metals.[7] Oxidative addition of water O−H bond to transition-metal complexes forming hydrido−hydroxo metal species would be involved as a crucial elemental step in the catalytic transformation of water in some of these reactions.[8] Clear examples of such species by the oxidative addition of water are rather limited and known for late transition metals.[9]

Silyl ligands have strong electron-donating and trans-labilizing properties and would bring unique reactivities to the transition-metal complexes. Recently, tridentate pincer-type[10] or tetradentate tripodal-type[11] ancillary silyl ligands have attracted considerable interest. Among these ligands, we had interest in a pincer-type silyl bis(phosphine) ligand $[\{2-(R_2P)C_6H_4\}_2MeSi]^-$ (PSiP-R, R = tBu, iPr, Cy).[12,13] Ir complexes bearing this silyl ligand undergo facile oxidative addition of aromatic sp² C−H bonds[13,14] and ammonia N−H bond.[15] Herein, we report a ligand-substituent-dependent selectivity of the oxidative addition reaction of water O−H bond to *in situ* generated $[(PSiP-R)Ir^I]$, giving a five-coordinate hydrido−hydroxo complex, $[(PSiP-tBu)Ir(H)(OH)]$, or a six-coordinate aqua hydrido−hydroxo complex $[(PSiP-iPr)Ir(H)(OH)(H_2O)]$.

2. RESULTS AND DISCUSSION

We initially examined the reaction of water with cyclohexyl (Cy)-substituted Ir complex **1a** (Figure 1). The reaction using
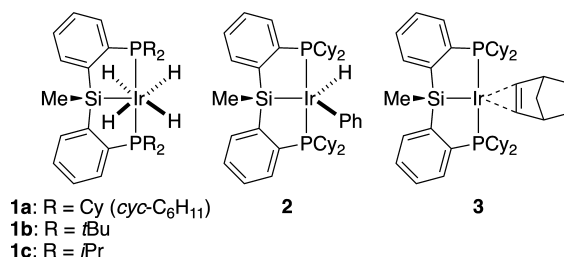

Figure 1. Structures of Ir complexes.

1a was done under strictly N_2-free conditions because it easily forms a stable unreactive dinitrogen complex (PSiP-Cy)Ir-$(H)_2(N_2)$ even with a trace amount of N_2.[13] The reaction of Ir(I) species, *in situ* generated from tetrahydride complex **1a** and *tert*-butylethylene (tbe), with H_2O in cyclohexane under Ar slowly proceeded at room temperature; monitoring the reaction by ¹H NMR spectroscopy showed the formation of 2,2-dimethylbutane from tbe and appearance of five new signals between −15 and −30 ppm after 4 days, suggesting the formation of new Ir−H species. After heating the mixture at 65 °C for 2 h, ³¹P NMR showed that the conversion increased by
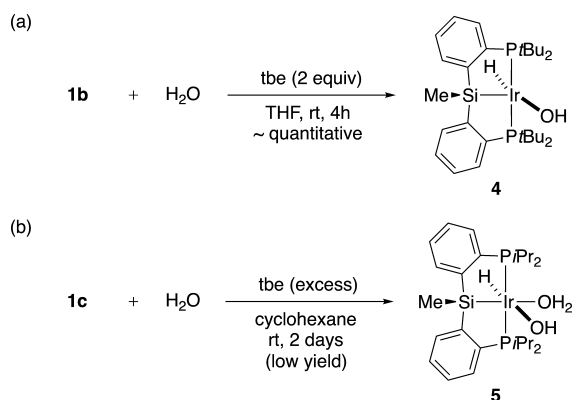
more than 50% with many new signals, suggesting that the reaction was unselective. We tried the reactions of **1a** with H_2O under various conditions, including those in benzene where complex **2** was initially formed,[13] and also the reaction using Ir(I) norbornene complex **3**. However, no selective reaction was observed and we could not obtain any clear evidence for the formation of Ir(H)(OH) species.

On the other hand, the reaction of the *tBu*-substituted Ir complex with water proceeded very selectively. In the presence of an excess amount of water (ca. 20 equiv), Ir complex **1b** was treated with tbe in THF at room temperature. After 4 h, the Ir complex was converted to complex **4** as a single isomer nearly quantitatively (Scheme 1a). Removal of volatiles afforded **4** as

Scheme 1. Reactions of (a) Complex 1b with Water and (b) Complex 1c with Water

(a)

1b + H_2O $\xrightarrow[\sim \text{quantitative}]{\text{tbe (2 equiv)} \atop \text{THF, rt, 4h}}$ **4**

(b)

1c + H_2O $\xrightarrow[\substack{\text{cyclohexane} \\ \text{rt, 2 days} \\ \text{(low yield)}}]{\text{tbe (excess)}}$ **5**

analytically pure, yellow crystals. Alternatively, this reaction can be performed in cyclohexane, although the formation of **4** required longer reaction time (2 days) and heating (50 °C). The reaction of **1b** with water also proceeded without the addition of tbe; THF-d_8 solution of **1b** in the presence of excess water in a closed NMR tube was monitored by NMR spectroscopy. The reaction cleanly proceeded to selectively form **4** at room temperature, though the conversion stopped at ca. 50% in the presence of H_2 liberated from **1b**.

The $^{31}P\{^1H\}$ NMR spectrum of the benzene-d_6 solution of **4** showed one sharp singlet signal at 76.5 ppm, suggesting that the two phosphorus atoms are in equal environment. The ^1H NMR spectrum showed a triplet signal at −23.78 ppm ($^2J_{P-H}$ = 14 Hz) for the hydride ligand of **4**; the multiplicity of the signal also suggests the presence of two equivalent phosphorus nuclei. The ^1H NMR signal for the hydroxy hydrogen was observed at 3.88 ppm as a broad singlet. A similar broad resonance was observed for the hydroxy hydrogen of the related 16-electron iridium complexes *trans*-[Ir(4-C_5NF_4)(H)-(OH)(P*i*Pr$_3$)$_2$] at 3.59ppm[9i] and [{2,6-(tBu_2PCH$_2$)$_2$C$_6$H$_3$}Ir-(H)(OH)] at 5.6 ppm.[9f] The presence of the hydrido ligand in **4** was also supported by the absorption at 2183 cm^{-1} in the infrared spectrum.

Light yellow crystals of **4** suitable for X-ray diffraction were directly obtained from the reaction mixture. The molecular structure of complex **4** determined by single crystal X-ray diffraction analysis is shown in Figure 2. The X-ray crystal structure of **4** confirms the formation of a C_s-symmetric five-coordinated complex in which the pincer phosphine donors are trans-oriented. The geometry at the metal center can be described as a distorted square-based pyramidal, with Si occupying the apical coordination site. Ir1−P1: 2.3219(10),
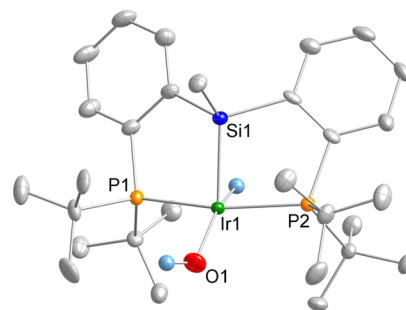

Figure 2. Molecular structure of complex **4**. Hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1−P1: 2.3219(10), Ir1−P2: 2.3208(9), Ir1−Si1: 2.2532(12), Ir1−O1: 2.053(3); P1−Ir1−P2: 163.49(4), P1−Ir1−Si1: 85.71(4), P1−Ir1−O1: 99.25(11), P2−Ir1−Si1: 85.64(4), P2−Ir1−O1: 97.11(11), Si1−Ir1−O1: 129.23(11).

Ir1−P2: 2.3208(9), and Ir1−Si1: 2.2532(12) bond lengths show no significant deviation from those determined for **1b**. The 16-electron configuration of **4** is unusual because common iridium(III) hydrido−hydroxo complexes generally show an 18-electron configuration with very few exceptions, such as [Ir(PCP)(H)(OH)] (PCP = 2,6-(CH$_2$PtBu$_2$)$_2$C$_6$H$_3$)[9f] and *trans*-[Ir(4-C_5NF_4)(H)(OH)(P*i*Pr$_3$)$_2$].[9i]

In an effort to obtain an analogous isopropyl derivative, excess of tbe was added to a cyclohexane solution of (PSiP-*i*Pr)Ir(H)$_4$ (**1c**) in the presence of excess water at room temperature. ^1H NMR analysis of the resulting intractable reaction mixture confirmed the formation of multiple Ir−H species. In the ^{31}P NMR spectrum, many new signals were observed. Fortunately, a small amount of orange crystals were formed in the reaction mixture after standing for several days at room temperature. X-ray structure analysis confirmed that the crystal is a water oxidative addition product **5** (Scheme 1b and Figure 3). However, it is not a five-coordinate complex similar to **4** but a six-coordinate complex with a H_2O ligand in addition to the hydrido and hydroxo ligands. The Ir atom of complex **5** has a distorted octahedral geometry. It is noteworthy to mention that the Ir−O bond distances *trans* to the silicon atom, 2.281(3)/2.312(3) Å, are at the longest end among the aqua−iridium complexes found in CSD (150 complexes, Ir−OH$_2$ distances range 2.03−2.34 Å), which results from the strong trans-influence of the silyl ligand and would suggest that the H_2O ligand is readily dissociable. In fact, complex **5** decomposes in solution at room temperature, leading to the formation of multiple unidentified products and thus preventing the identification of **5** by NMR spectroscopy. In the crystal, complex **5** forms a dimer through hydrogen bonding, as shown in Figure 3b.

3. CONCLUSIONS

High ligand dependency was disclosed in the reaction of [(PSiP-R)Ir^I] with water. The reaction of *tBu* derivative, [(PSiP-*tBu*)Ir^I], with water smoothly proceeded at room temperature to selectively afford a 16-electron five-coordinate hydrido−hydroxo complex, [(PSiP-*tBu*)Ir(H)(OH)], quantitatively. On the other hand, the reaction of Cy and *iPr* derivatives with water was unselective and formation of various Ir−H species was observed. In the reaction of [(PSiP-*iPr*)Ir^I], a small amount of 18-electron six-coordinate hydrido−hydroxo aqua complex, [(PSiP-*iPr*)Ir(H)(OH)(H$_2$O)], was isolated and its structure was characterized by X-ray diffraction analysis.
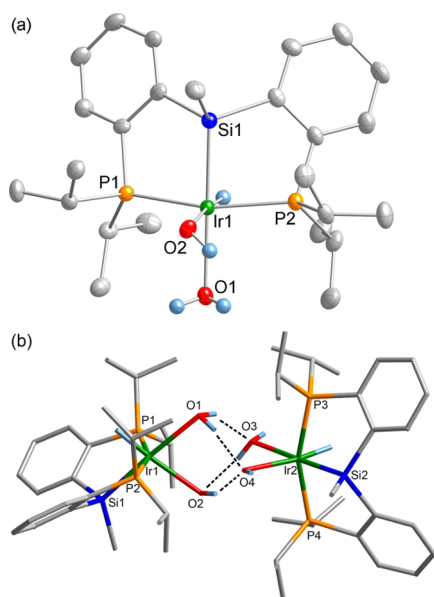
Figure 3. (a) Molecular structure of complex **5** (one of two crystallographically independent molecules is shown). Hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1−P1: 2.2906(9), Ir1−P2: 2.3005(9), Ir1−Si1: 2.2846(10), Ir1−O1: 2.281(3), Ir1−O2: 2.200(3); P1−Ir1−P2: 159.75(3), P1−Ir1−Si1: 84.77(3), P1−Ir1−O1: 93.88(7), P1−Ir1−O2: 99.27(7), P2−Ir1−Si1: 84.50(3), P2−Ir1−O1: 96.89(7), P2−Ir1−O2: 99.57(7), Si1−Ir1−O1: 178.61(8), Si1−Ir1−O2: 100.66(7), O1−Ir1−O2: 79.20(10). (b) Dimeric structure of complex **5** in the crystal through hydrogen bonding.

ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02168.

> Experimental details, NMR spectra, and details of X-ray crystallographic studies (PDF)
>
> Crystallographic data for the 16-electron hydrido−hydroxo complex **4** (CIF)
>
> Crystallographic data for the 18-electron hydrido−hydroxo aqua complex **5** (CIF)

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Notes

The authors declare no competing financial interest.

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