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)IrI] (PSiP-R = [(2-(R2P)C6H4)2MeSi]−; R = cyclohexyl, tBu or iPr) from [(PSiP-R)Ir(H)4] and tert-butyldimethylethylene (tbe) showed high ligand dependency. Oxidative addition of water cleanly proceeded in the reaction of [(PSiP-tBu)IrI] 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)(H2O)] 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 H2 and O2 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-type10 or tetradentate tripodal-type11 ancillary silyl ligands have attracted considerable interest. Among these ligands, we had interest in a pincer-type silyl bis(phosphine) ligand [(2-(R2P)C6H4)2MeSi]− (PSiP-R, R = tBu, iPr, Cy).12,13 Ir complexes bearing this silyl ligand have attracted considerable interest. Among these complexes, we had interest in a pincer-type silyl bis(phosphine) ligand [(2-(R2P)C6H4)2MeSi]− (PSiP-R, R = tBu, iPr, Cy).12,13 Ir complexes bearing this silyl ligand undergo facile oxidative addition of aromatic sp2 C−H bonds14,15 and ammonia N−H bond.16 Herein, we report a ligand-substituent-dependent selectivity of the oxidative addition reaction of water O−H bond to in situ generated [(PSiP-R)IrH], 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)(H2O)]−.

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.](https://www.ACSomega.org/journal/acsodf/2022/7/20237-20240/01.png)

1a was done under strictly N2-free conditions because it easily forms a stable unreactive dinitrogen complex (PSiP-Cy)IrH2(N2) even with a trace amount of N2.16 The reaction of Ir(I) species, in situ generated from tetrahydride complex 1a and tert-butyldimethylethylene (tbe), with H2O 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 bonds. After heating the mixture at 65 °C for 2 h, 31P NMR showed that the conversion increased by

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more than 50% with many new signals, suggesting that the reaction was unselective. We tried the reactions of 1a with H$_2$O under various conditions, including those in benzene where complex 2 was initially formed, 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 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$_4$ 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$_2$O liberated from 1b.

The $^{31}$P($^1$H) NMR spectrum of the benzene-$d_4$ solution of 4 showed one sharp singlet signal at 76.5 ppm, suggesting that the two phosphorus atoms are in equal environment. The $^1$H NMR spectrum showed a triplet signal at $-23.78$ ppm ($J_{P-H}$ = 14 Hz) for the hydride ligand of 4; the multiplicity of the signal also suggests the presence of two equivalent phosphorus nuclei. The $^1$H 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$_5$NF$_4$)(H)(OH)(P(P$_3$)$_2$)$_2$] at 3.59 ppm$^{9m}$ and [(2,6-($t$Bu$_2$PCH$_2$)$_2$C$_6$H$_3$)$_2$Ir-$\mu$-OH] at 5.6 ppm.$^{9n}$ The presence of the hydroxy 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$_5$-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), Ir1–P2: 2.3208(9), and Ir1–Si1: 2.2532(12).

In an effort to obtain an analogous isopropyl derivative, excess of the was added to a cyclohexane solution of (PSiP-$\mu$-Pr)$_2$IrH, and also the reaction with water smoothly proceeded at room temperature. $^1$H 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$_2$O 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$_2$O 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-$i$Pr)$_2$Ir] with water. The reaction of $t$Bu derivative, [(PSiP-$t$Bu)$_2$Ir], with water smoothly proceeded at room temperature to selectively afford a 16-electron five-coordinate hydrido–hydroxo complex, [(PSiP-$t$Bu)$_2$Ir(H)(OH)], quantitatively. On the other hand, the reaction of Cy and $i$Pr derivatives with water was unselective and formation of various Ir–H species was observed. In the reaction of [(PSiP-$i$Pr)$_2$Ir], a small amount of 18-electron six-coordinate hydrido–hydroxo aqua complex, [(PSiP-$i$Pr)$_2$Ir(H)(OH)(H$_2$O)], was isolated and its structure was characterized by X-ray diffraction analysis.
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