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Oxidative Addition of Water to Novel Ir(I) Complexes Stabilized by Dimethyl Sulfoxide Ligands

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Oxidative addition of water to transition-metal complexes has received much attention in recent years by virtue of its relevance to a number of catalytic processes and its potential importance in the design of new catalysis based on water. The isolation of hydrido hydroxo complexes as primary products from such a reaction is uncommon,[1] and the crystal structures of only a few complexes of this type have been reported.[1d,g,i−k,2] In all of these cases, this reactivity is achieved by using late transition-metal complexes bearing phosphine ligands.

Ir(III) DMSO complexes containing no other dative ligands have been used as catalysts for various transformations,[3] although their synthesis and characterization is not straightforward and has been the subject of some debate.[4] Only one such complex has been characterized by X-ray crystallography.[5] To the best of our knowledge, Ir(I) DMSO complexes bearing no other dative ligands are unknown.[6]

We report here the synthesis and characterization of the first Ir(I) DMSO complexes (which contain no other ligands except chloride) including the X-ray crystal structure of one of them. Remarkably, these complexes can easily activate water at ambient temperature, leading to hydrido hydroxo addition products which have been characterized by X-ray diffraction.

The complex IrCl(DM*S*O)$_3$ (**1**) is prepared in high yield by treating a toluene slurry of [Ir$_2$Cl$_2$(COE)$_4$] (COE = cyclooctene) with excess DMSO. The resulting lemon-yellow complex **1** loses 1 equiv of DMSO in a CH$_2$Cl$_2$ solution, and addition of diethyl ether leads to the isolation of [Ir$_2$Cl$_2$(DM*S*O)$_4$] (**2**) as an orange microcrystalline solid. An X-ray diffraction study of **1** (Figure 1) shows the expected square-planar geometry around the metal with Ir−S bond distances of 2.1957(9) Å (DMSO trans to Cl) and 2.2643(10) Å (DMSO cis to Cl).[7] Addition of water to a yellow acetone slurry of **1** leads to the formation of pale yellow crystals of **3** within 2 h. Starting with **2**, the formation of **3** is much slower and requires 2 days for completion (Scheme 1).

This striking difference in reactivity of **1** and **2** toward oxidative addition of H$_2$O seems to indicate that the active species for the oxidative addition is the 14-electron species [IrCl(DMSO)$_2$], which is expected to be much more easily generated from **1** than from **2**. Another indication for a reaction pathway involving such an intermediate stems from the fact that excess DMSO retards the water addition to **1**, which does not take place in a neat DMSO solution at room temperature. In both cases, analytically pure crystals of **3** are obtained in high yield. The ^{1}H NMR spectrum of **3** shows the expected hydride peak at −20.19 ppm and three singlets between 3.39 and 3.56 ppm for the coordinated DMSO. An additional broad resonance at 5.27 ppm might be attributed to the bridging hydroxo ligand. The formulation of **3** is also supported by IR and elemental analysis. Surprisingly, dissolving **3** in pyridine-d_5 yields a solution whose ^{1}H NMR spectrum shows two sharp peaks at 3.61 and 3.70 ppm for the DMSO ligands, a singlet at 4.94 ppm attributable to free H$_2$O and no hydride. Thus, reductive elimination takes place readily in this solvent. Indeed, the same complex can be synthesized directly by dissolving **1** or **2** in pyridine-d_5. NMR data and elemental analysis of the nondeuterated complex are in agreement with the formulation of IrCl(py)(DM*S*O)$_2$ (**4**).

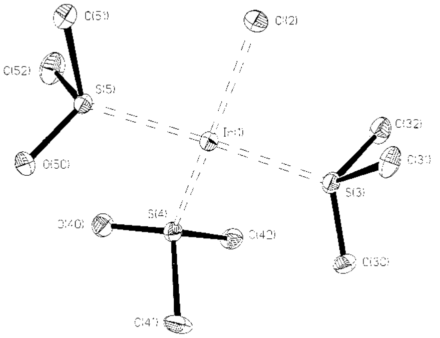
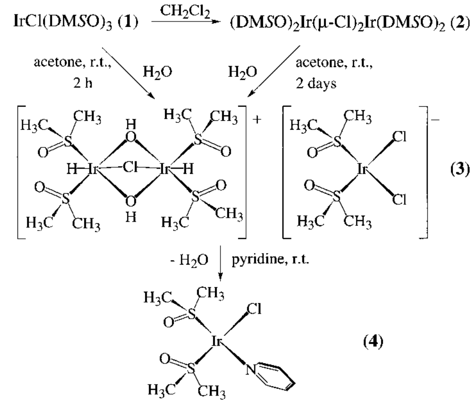


Figure 1. ORTEP drawing of complex **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms omitted for clarity.

Scheme 1



An X-ray crystal structural study (Figure 2) shows that the cationic part of **3** has a dinuclear structure with each iridium atom being located in a highly distorted octahedral environment.[7] Each iridium atom is bound to two DMSO molecules via the sulfur atom and to bridging chloro- and two hydroxo ligands. The terminal hydride ligands were not located, but their position is inferred to be trans to the μ-chloro ligand and cis to the hydroxy bridges. Closely related derivatives of such a triply bridged dinuclear structure are the methoxy-bridged [(BINAP)HIr(μ-OMe)$_2$(μ-Cl)-IrH(BINAP)]Cl and the mixed species [(Et$_3$P)$_2$HIr(μ-OH)(μ-Cl)-

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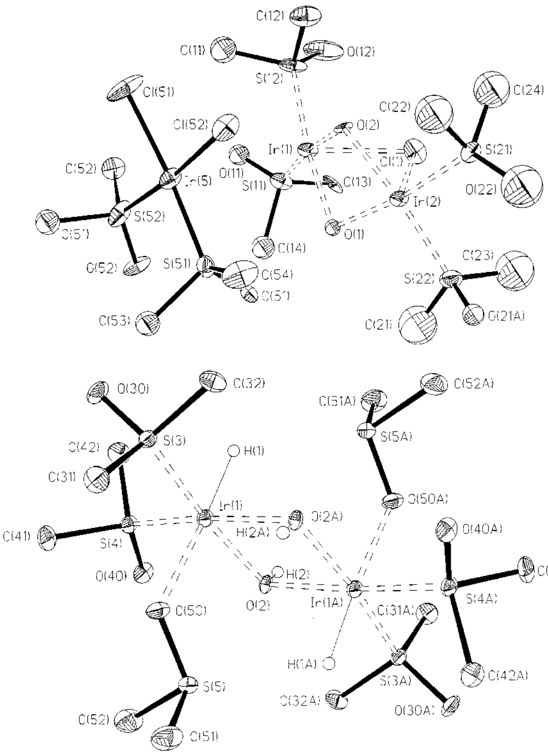
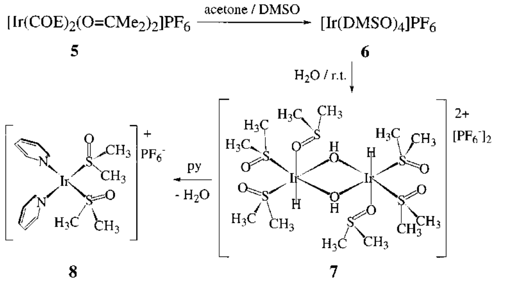


Figure 2. ORTEP views of complexes **3** (above) and **7** (below). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and PF_6^- (in **7**) omitted for clarity.

Scheme 2



(μ-NHPh)IrH(PEt_3)$_2$]Cl.[1i,8] The counteranion consists of a unique $[IrCl_2(DMSO)_2]^-$ fragment with distorted square planar configuration.

Treating the complex $[Ir(COE)_2(O{=}CMe_2)_2]PF_6$ (**5**) in an acetone solution with 10 equiv of DMSO leads most probably to the formation of $[Ir(DMSO)_4]PF_6$ (**6**).[9] Although unambiguous characterization of this complex was not possible, we base this formulation on the fact that rhodium complexes analogous to **1** and **6**, RhCl(DM*S*O)$_3$ and [Rh(DM*S*O)$_2$(DMS*O*)$_2$]PF_6, have both been characterized by X-ray crystallography by us.[10] Complex **6** readily activates water. Adding excess water to an acetone solution of **6** leads to the formation of **7** (Scheme 2). As in the case of **3**, characterization of **7** by NMR spectroscopy is hampered by its low solubility in common organic solvents. Its formulation is supported by IR and elemental analysis and is confirmed by an X-ray analysis.[7] Again, dissolving **7** in pyridine leads to ready reductive elimination of water, and the resulting complex has the formulation [Ir(py)$_2$(DM*S*O)$_2$]PF_6 (**8**). This complex is also obtained directly by treating **5** in an acetone solution with 10 equiv of DMSO and 5 equiv of pyridine.[11]

As shown in Figure 2, compound **7** displays a distorted octahedral geometry at the Ir(III) centers, with two bridging hydroxo ligands and terminal hydrido donors. Interestingly, the DMSO ligands exhibit two coordination modes in the same molecule. Each iridium atom is coordinated to two DMSO molecules through the sulfur atoms and to one DMSO molecule through the oxygen atom. It is noteworthy that the hydride is located trans to the latter.

In conclusion, we have reported the first Ir(I) DMSO complexes which contain no other dative ligands including an X-ray diffraction study of one of them (**1**). These complexes can be obtained quantitatively starting from Ir(I) olefin precursors. Surprisingly, these complexes can easily activate water at room temperature to give the isolated novel hydrido hydroxo complexes **3** and **7** in good yield. Both **3** and **7** have been characterized by X-ray crystallography showing dinuclear structures, and in complex **7** both *O*- and *S*-bonded DMSO ligands are present. Reductive elimination in pyridine leads to quantitative isolation of mixed Ir(I) DMSO−pyridine complexes **4** and **8** respectively. Studies are underway toward better understanding of the mechanism of these reactions, to extend the chemistry of these low-valent sulfoxide complexes and to explore the catalytic potential of such compounds.

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Supporting Information Available: Experimental procedures and characterization of complexes **1**−**8** and X-ray data for **1**, **3**, **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Selected bond distances [Å] for **1**: Ir1−S4 2.1957(9), Ir1−S3 2.2643(10), Ir1−S5 2.2763(10), Ir1−Cl2 2.3566(10). For **3:** Ir1−O1 2.054(17), Ir1−O2 2.100(17), Ir1−S11 2.197(8), Ir1−S12 2.211(7), Ir1−Cl1 2.661(8), Ir1···Ir2 3.0277(17), Ir2−O1 2.055(17), Ir2−O2 2.070(17), Ir2−S22 2.201(8), Ir2−S21 2.219(8), Ir2−Cl1 2.510(7); Ir5−S52 2.174(8), Ir5−S51 2.180(8), Ir5−Cl51 2.359(8), Ir5−Cl52 2.403(8). For **7**: Ir1−O2 2.074(3), Ir1−O1A 2.093(3), Ir1−S3 2.2077(13), Ir1−S4 2.2142(12), Ir1−O50 2.218(3), Ir1−H 1.66(9), Ir1···Ir1A 3.235. See Supporting Information for full details.

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