

## A Useful Method for Preparing Iridium Alkoxides and a Study of Their Catalytic Decomposition by Iridium Cations: A New Mode of $\beta$ -Hydride Elimination for Coordinatively Saturated Metal Alkoxides

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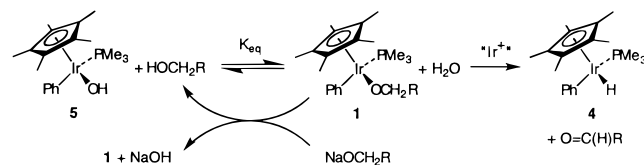
Compared with late transition metal alkyls, the corresponding metal alkoxides are difficult to prepare, especially if C–H bonds at the carbon connected to the oxygen atom are present.<sup>1b</sup> Attempts to obtain these compounds by the displacement of halides or other good leaving groups from transition metal centers with alkali metal alkoxides (in analogy to the general method used to prepare metal alkyls) often lead to the corresponding metal hydrides. In fact, this occurs so frequently that the treatment of metal halides with alcoholic base is a classical method for preparing hydrides.<sup>2</sup> It is normally assumed, and in some cases established,<sup>3–7</sup> that aldehydes are produced in these reactions. This provides evidence that metal alkoxides are intermediates, but undergo rapid  $\beta$ -H elimination (eq 1, X = halide, OTf).



As in the related  $\beta$ -H eliminations of metal alkyls, it is normally assumed that a site of coordinative unsaturation cis to the alkoxo ligand is required for this process to occur.<sup>3,5,8</sup> Kinetically inert late transition metal complexes with M–O bonds have been prepared which lack  $\alpha$ -oxy hydrogens, do not have an open coordination site, or have a sterically disfavored transition state for  $\beta$ -H elimination,<sup>9</sup> but for many systems, coordinatively saturated alkoxides are difficult to prepare or, once generated, are relatively unstable kinetically.<sup>1,10</sup>

In a recent study of apparent ethylene insertion into a metal–hydroxide bond, we proposed the binuclear complex ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(PMe<sub>3</sub>)(Ph)Ir-CH<sub>2</sub>CH<sub>2</sub>-O-Ir(Ph)(PMe<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) as a crucial intermediate, and obtained evidence that its decomposition occurred by  $\beta$ -H elimination catalyzed by a third cationic iridium center.<sup>11</sup> Because this intermediate has an Ir–O bond at a formally coordinatively saturated iridium center, we considered the possibility that simpler iridium alkoxides might decompose by analogous metal-catalyzed mechanisms. Testing this possibil-

Scheme 1



ity required the development of effective methods for the synthesis of such alkoxides, so that their decompositions could be studied directly. We now report the successful preparation of a series of coordinatively saturated iridium alkoxides and evidence that their decomposition to aldehydes and iridium hydrides is in fact catalyzed by a second iridium center.

In accord with the previous experience summarized above, our initial attempts to prepare alkoxides of the general formula ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(PMe<sub>3</sub>)Ir(Ph)(OCH<sub>2</sub>R) (1) (here abbreviated Ph[Ir]OCH<sub>2</sub>R) by metathesis of Ph[Ir]X (X = OTf (2), Cl (3)) with the corresponding sodium alkoxides in various solvents were unsuccessful. Instead, apparent  $\beta$ -H elimination products were observed. For example, addition of 1 equiv of NaOEt to a solution of 3 in EtOH led to quantitative formation of Ph[Ir]H (4) and acetaldehyde (90–95% by <sup>1</sup>H NMR).<sup>12</sup> Suspecting that traces of cationic iridium species present in solution were responsible for catalyzing the decomposition of Ph[Ir]OEt (1a) to hydride 4, we turned to a hydroxyl/alkoxyl exchange approach in which the concentration of Ph[Ir]<sup>+</sup> ions is deliberately kept as low as possible. Treating Ph[Ir]OH (5) with a primary alcohol in THF-d<sub>8</sub> results in an equilibrium mixture containing the starting materials, the alkoxide Ph[Ir]OCH<sub>2</sub>R (1), and H<sub>2</sub>O, with  $K_{eq} \approx 0.1$  (Scheme 1). The mixtures are stable for several days at room temperature, confirming that uncatalyzed  $\beta$ -H elimination is not a rapid process in this system. Upon addition of standard drying agents to remove the water<sup>13</sup> and drive the equilibrium toward alkoxide product, clean decomposition to Ph[Ir]H (4) and aldehyde is observed.<sup>14</sup>

However, if the corresponding sodium salt of the alcohol is used as a drying agent the corresponding alkoxides can be isolated in 95–100% yields as yellow crystalline compounds (Scheme 1; R = CH<sub>3</sub>, 1a; R = CMe<sub>3</sub>, 1b; R = CH<sub>2</sub>CMe<sub>3</sub>, 1c). In this acid/conjugate base metathesis approach, hydroxide 5 is treated with 2 equiv of NaOCH<sub>2</sub>R and 0.2 equiv of RCH<sub>2</sub>OH in pentane.<sup>15</sup> Analytically pure material can be obtained by crystallization from toluene/pentane mixtures. All of the alkoxides are stable at room temperature as neat compounds and in solution. Their <sup>1</sup>H NMR spectra show a characteristic pattern for the diastereotopic  $\alpha$ -methylene protons (C<sub>6</sub>D<sub>6</sub>;  $\delta$  3.5–4.0 ppm) Single-crystal X-ray diffraction studies of ethoxide 1a and neopentoxide 1b confirm the covalent nature of their Ir–O bonds in the solid state. ORTEP diagrams of both compounds are shown in Figure 1 and details of the structure determinations are provided as Supporting Information.

To account for the clean formation of 1a–c during the acid/conjugate base metathesis, we assume that under these basic and

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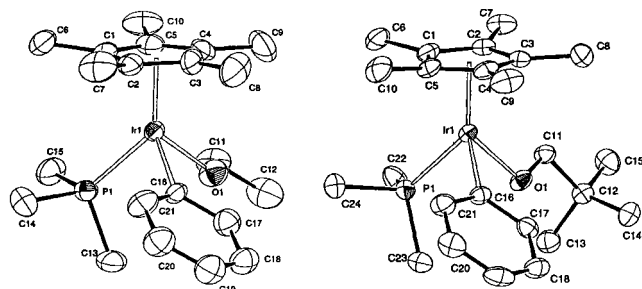
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(13) We employed 4 Å sieves, Al<sub>2</sub>O<sub>3</sub>, MgSO<sub>4</sub>, NaSO<sub>4</sub>, and azeotropic distillation.

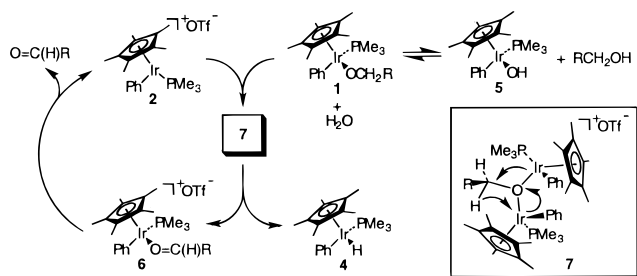
(14) In contrast Ph[Ir]OPh is formed quantitatively from a 1:1 mixture of 5 and PhOH when mixed in THF, indicating that electron-withdrawing substituents attached to the oxygen thermodynamically stabilize the M–OPh complex relative to the hydroxide: see ref 20.

(15) Minimal amounts of alcohol and the use of pentane as a solvent in which NaOCH<sub>2</sub>R and NaOH are insoluble are essential to avoid hydride formation (the iridium hydroxide and alkoxide are both soluble in the pentane/alcohol mixtures). This contrasts with the synthesis of some platinum alkoxides where an alcohol/benzene solution of the alkoxide was used for metathesis: see ref 5.



**Figure 1.** ORTEP diagrams of Ph[Ir]OEt (**1a**) (top) and Ph[Ir]OCH<sub>2</sub>CMe<sub>3</sub> (**1b**) (bottom).

### Scheme 2



relatively nonpolar conditions the formation of iridium cations is suppressed.<sup>16</sup> The unfavorable equilibrium is presumably driven by a surface reaction of NaOCH<sub>2</sub>R with the H<sub>2</sub>O formed to produce insoluble NaOH and the corresponding alcohol (Scheme 1). Since no overall consumption of alcohol takes place, only catalytic amounts of RCH<sub>2</sub>OH are necessary to achieve quantitative conversion. We believe that hydrogen bonding from the alcohol to the strongly basic oxygen in hydroxide **5** is important for the facilitation of the metathesis. In the absence of RCH<sub>2</sub>OH the above transformation is very slow or does not occur at all. Hydrogen bonding in late transition metal alkoxides has been found to be important for alkoxide exchange reactions.<sup>10,17,18</sup>

Treating a solution of Ph[Ir]OCH<sub>2</sub>R (**1**) with a catalytic amount of Ph[Ir]OTf (**2**)<sup>19</sup> known to be a source of the corresponding cation,<sup>20</sup> leads to quantitative formation of Ph[Ir]H (**4**) and aldehyde (Scheme 2). Dissolved in benzene or THF in the absence of **2**, the alkoxides require temperatures above 60 °C to undergo slow decomposition to a mixture of β-H elimination and other unidentified products. We believe that under conditions where ionization of Ph[Ir]X (X = OH, OTf, OR, Cl) occurs, catalytic hydride transfer from the alkoxide **1** to the cationic species **2** initiates the formal β-H elimination (Scheme 2). This catalytic cycle constitutes a rare example of bimetallic catalysis involving cooperative participation of two iridium centers.<sup>21</sup>

This novel hydride transfer reaction can be used to selectively oxidize primary alcohols in the presence of secondary alcohols.

(16) Alternatively, **1b** and **1c** can be isolated, only as oils (95% purity), from mixtures of Ph[Ir]OTf and the corresponding sodium alkoxides in THF/1-hexene 1:2 (the 1-hexene is added to keep the concentration of iridium cations as low as possible by complexing to the alkene) or by removing the solvent (THF/(Me<sub>3</sub>Si)<sub>2</sub>O) and water from mixtures of **5** and RCH<sub>2</sub>OH under vacuum. In the case of **1a**, however, the formation of 10–30% hydride **4** and acetaldehyde was still observed.

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For example, when a mixture of 1 equiv of EtOH, 1 equiv of *i*-PrOH, and 1 equiv of Ph[Ir]OH (**5**) in benzene or THF is treated with 0.05 equiv of iridium triflate **2** at room temperature, quantitative oxidation to acetaldehyde is observed by NMR within minutes, whereas the amount of *i*-PrOH is unchanged (in a separate experiment, no reaction was observed between Ph[Ir]OH and excess *i*-PrOH by NMR). During the reaction Ph[Ir]OEt (**1a**) is observed as an intermediate, with no evidence for the formation of either Ph[Ir]Oi-Pr or acetone. The catalyst can easily be deactivated by addition of PPh<sub>3</sub>.<sup>11</sup> The hydride transfer most likely proceeds via a hydride shift (Scheme 2) or by a SET mechanism.<sup>22</sup> In either case we expect that the C–H bond is broken as part of the rate determining transition state.

To gain additional information on the exchange processes occurring in solution during the hydride transfer reaction, we conducted double crossover experiments. Addition of 0.5–1 equiv of Ph(Ir)OTf (**2'**)<sup>20</sup> (Ir = (C<sub>5</sub>Me<sub>4</sub>Et)Ir(PMe<sub>3</sub>)) to a solution of Ph[Ir]OCH<sub>2</sub>CH<sub>2</sub>CMe<sub>3</sub> (**1c**) in C<sub>6</sub>D<sub>6</sub> results in equilibration to give substantial amounts of Ph[Ir]OTf (**2**) and Ph(Ir)OCH<sub>2</sub>CH<sub>2</sub>CMe<sub>3</sub> (**1c'**). The equilibrium was established immediately (*t* < 1 min, *K*<sub>eq</sub> ≈ 1) at room temperature (RT), prior to the appearance of any hydride products **4** and **4'**. Subsequent decomposition to Ph[Ir]H (**4**) and Ph(Ir)H (**4'**) was complete after 1 h. In addition, rapid scrambling was observed upon mixing a solution of **1c** with a solution of **1b'** under exclusion of air and moisture without further reaction at RT. Both experiments show that bond-breaking and -forming processes between the iridium center and the alkoxide oxygen are much faster than the H abstraction.<sup>18</sup>

Comparison of the relative kinetic stability of the alkoxides Ph[Ir]OCH<sub>2</sub>R (R = Me, *t*-Bu, neopentyl) in the presence of 0.1 equiv Ph[Ir]OTf (**2**) indicates that the barrier for hydrogen transfer to the iridium cation is affected mostly by steric factors. Whereas quantitative decomposition of **1a** (R = Me) occurs immediately at ambient temperatures, decomposition of **1c** (R = neopentyl) under the same conditions requires 4 h. The sterically hindered alkoxide **1b** (R = *t*-Bu) is stable at RT when treated with 0.1 equiv of **2** but decomposes over the course of 12 h when heated at 75 °C.

In summary, we have synthesized a series of primary iridium alkoxides by utilizing a novel acid/conjugate base metathesis approach and demonstrated that in the case of coordinatively saturated alkoxides R[Ir]OCH<sub>2</sub>R (**1**), decomposition to give the corresponding iridium hydrides and aldehydes is catalyzed by iridium cations. This report provides the first direct evidence that β-H elimination can involve the cooperative participation of two metal centers. It seems likely that other examples of apparent mononuclear β-elimination may also proceed by this more complicated binuclear mechanism. This novel catalytic process can be used to selectively oxidize primary alcohols to aldehydes in the presence of secondary alcohols. Further investigation of the reactivity of these alkoxides is under way.

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**Supporting Information Available:** Spectroscopic and analytic data for **1a–c** and X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional parameters, and intramolecular distances and angles) for **1a** and **1b** (24 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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