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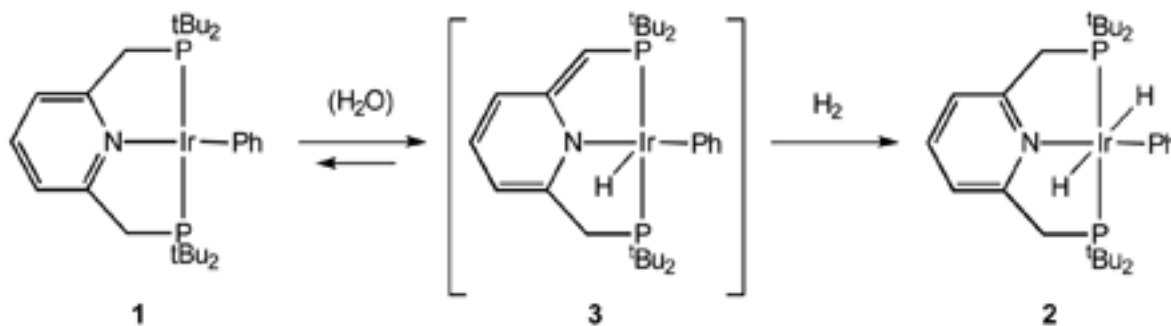
## Proton-catalyzed Hydrogenation of a $d^8$ Ir(I) Complex Yields a *trans* Ir(III) Dihydride

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Square planar  $d^8$  iridium(I) complexes, including the iconic Vaska's complex, (*trans*-IrCl(CO)[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>),<sup>1</sup> have been used to explore a wide range of oxidative addition reactions of  $d^8$  transition metal complexes. These studies established mechanisms ranging from concerted cleavage of nonpolar substrates, stepwise addition of polar substrates, and radical chain reactions of certain RX substrates.<sup>2</sup> In light of the importance of transition metal hydride complexes in numerous catalytic transformations, including olefin hydrogenation<sup>3</sup> and hydroformylation,<sup>4</sup> the concerted addition of dihydrogen to Ir(I) centers has received particular scrutiny.<sup>5</sup> Oxidative addition of dihydrogen to afford a kinetically preferred *cis*-dihydride complex is the prevailing pathway. Factors shown to influence the kinetics and thermodynamics of H<sub>2</sub> addition include the mode of substrate approach, metal basicity, and the steric and electronic nature of the ancillary ligands. In cases where the *trans*-dihydride isomer is observed, prior formation of a *cis*-dihydride intermediate is typically invoked.<sup>6</sup>

Milstein has recently reported that hydrogenation of Ir(I) phenyl complex **1** yields the *trans* dihydride complex **2** as the kinetic and thermodynamic product.<sup>7</sup> The mechanism proposed involved intermediacy of the dearomatized complex **3** formed by water-assisted proton transfer, followed by  $\alpha^2$ -binding of H<sub>2</sub> *cis* to the phenyl group and transfer of hydrogen from  $\alpha^2$ -H<sub>2</sub> to the methine carbon of the bridge. DFT calculations and deuterium labeling results supported this proposal.<sup>8</sup>



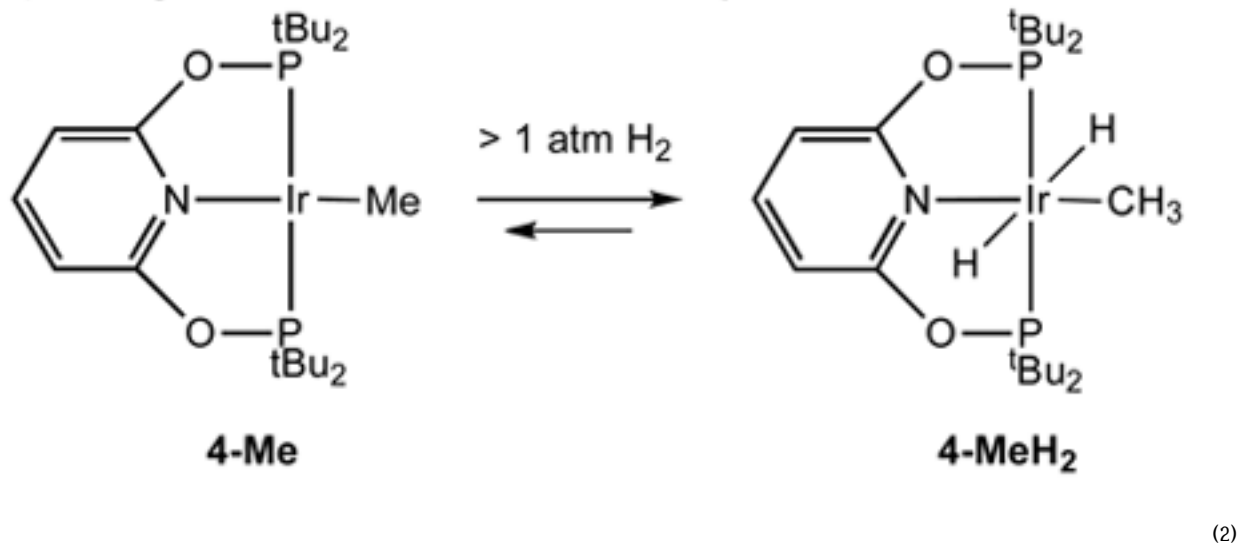
(1)

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 Supporting Information Available: Experimental details and pertinent NMR spectra. This material is available free of charge at <http://pubs.acs.org>.

We report here the hydrogenation of a related Ir(I) methyl complex which yields a *trans*-dihydride species but via a quite different mechanism involving proton-catalyzed H<sub>2</sub> cleavage, a pathway which circumvents the intermediacy of the *cis*-dihydride isomer.

We recently described the synthesis of an Ir(I) methyl complex supported by the neutral pincer ligand 2,6-bis(di-*tert*-butylphosphinito)pyridine, (PONOP)Ir(CH<sub>3</sub>) (**4-Me**), and its protonation with a non-coordinating acid to yield a remarkably stable five-coordinate, sixteen-electron complex, (PONOP)Ir(H)(Me)<sup>+</sup> (**4-MeH**<sup>+</sup>).<sup>9</sup> This complex was found to equilibrate rapidly with an unobserved Ir(I) *s*-methane complex, (PONOP)Ir(CH<sub>4</sub>)<sup>+</sup>, prior to methane loss. To investigate the stability of the related Ir(III) methyl dihydride complex, a frozen benzene-*d*<sub>6</sub> solution of **4-Me** was treated with 1 atm of dihydrogen at -196°C. Warming the solution to ambient temperature and shaking overnight afforded complete conversion to the unexpected *trans*-dihydride complex (PONOP)Ir(CH<sub>3</sub>)H<sub>2</sub> (**4-MeH**<sub>2</sub>).<sup>10</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **4-MeH**<sub>2</sub> displays a singlet at 182.6 ppm, shifted marginally upfield relative to that for **4-Me**. The corresponding <sup>1</sup>H NMR spectrum exhibits a 2H triplet of quartets at -9.06 ppm (<sup>2</sup>J<sub>P-H</sub> = 17 Hz, <sup>3</sup>J<sub>H-H</sub> = 2.4 Hz) corresponding to the Ir-H fragments and a 3H triplet of triplets at 1.05 ppm (<sup>3</sup>J<sub>P-H</sub> = 5 Hz, <sup>3</sup>J<sub>H-H</sub> = 2.8 Hz) assigned to the Ir-CH<sub>3</sub> moiety.<sup>10</sup>



Evacuation of the dihydrogen atmosphere from **4-MeH**<sub>2</sub> resulted in reversion to **4-Me** over ca. 1 day at 23°C under a static vacuum. **4-MeH**<sub>2</sub> is stable under dihydrogen in benzene solution at 23°C, but eliminates CH<sub>4</sub> at temperatures above 60°C. Monitoring of the concentrations of [H<sub>2</sub>] and both iridium methyl species by NMR spectroscopy in samples containing less than 1 atm of dihydrogen afforded a K<sub>eq</sub> of 748(34) M<sup>-1</sup> (23 °C) for the hydrogenation of **4-Me**.<sup>10</sup>

Initial kinetic experiments revealed the rates of hydrogenation were non-uniform. These observations led to speculation that trace amounts of water played a role in the reaction. Indeed, parallel NMR tube experiments in which samples of **4-Me** were spiked with >10 equiv. of water or methanol (added via syringe) revealed complete hydrogenation to **4-MeH**<sub>2</sub> in a matter of minutes for the methanol or water treated samples compared to hours for the control hydrogenation reaction. Two possible mechanisms for the methanol- or water-assisted cleavage of dihydrogen to produce the *trans*-dihydride, **4-MeH**<sub>2</sub>, are shown in Figure 1.<sup>11</sup> An alternative mechanism in which  $\alpha$ -elimination from **4-Me** forms a

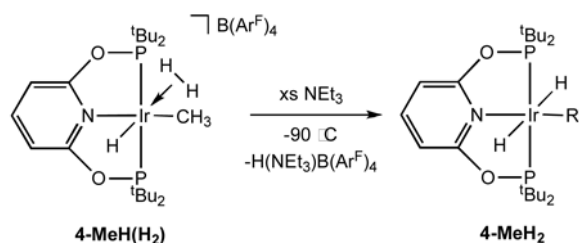
transient carbene intermediate, followed by 1,2-addition of H<sub>2</sub>, was ruled out on the basis of kinetic isotope effect experiments.<sup>10</sup>

The first mechanism (Figure 1a) proceeds by the classic *cis*-addition of H<sub>2</sub> to the metal center followed by base-assisted isomerization of the unobserved *cis*-dihydride complex to the *trans*-dihydride species. Water (or alcohol) acts as the base, permitting transient formation of an iridium(I) methyl hydride anion, which could isomerize to reestablish the methyl group *trans* to the pyridyl nitrogen, followed by protonation with the conjugate acid to afford **4-MeH<sub>2</sub>**. To assay the ability of base to catalyze the formation of **4-MeH<sub>2</sub>**, parallel hydrogenation reactions with **4-Me** were conducted. One sample of the hydrogenation mixture was treated with approximately 5 equiv of triethylamine at -196 °C prior to the warming of benzene-*d*<sub>6</sub> solutions. Monitoring by NMR spectroscopy revealed no detectable rate enhancement for conversion of **4-Me** to **4-MeH<sub>2</sub>** for the amine-containing sample. Since no rate enhancement was observed in the presence of a superior base, it is unlikely that water/alcohol is acting as a base to accelerate the formation of the *trans*-dihydride species.

The second mechanism (Figure 1b), utilizes water/alcohol as a weak acid to protonate **4-Me**, generating small quantities of the iridium(III) methyl hydride cation, **4-MeH<sup>+</sup>**. Subsequent coordination of dihydrogen *trans* to the iridium-hydride ligand and deprotonation by the conjugate base would yield the observed *trans*-dihydride complex. Previous isolation of **4-MeH<sup>+</sup>** (*vide supra*), offers strong evidence for the viability of this species as an intermediate and permits direct investigation of the subsequent reactions along the proposed hydrogenation pathway.

A frozen solution of **4-MeH<sup>+</sup>** in methylene chloride-*d*<sub>2</sub> was treated with 1 atm of dihydrogen at -196 °C and the tube transferred to a pre-cooled (-100 °C) NMR probe. Upon thawing, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy indicated near complete conversion (>90%) to the dihydrogen-hydride species, **4-MeH(H<sub>2</sub>)<sup>+</sup>**. The presence of the hydride was confirmed by a 1H triplet at -13.37 ppm (<sup>2</sup>J<sub>P-H</sub> = 17 Hz) and the coordinated dihydrogen was observed as a 2H broad singlet at -1.98 ppm (*J*<sub>HD</sub> = 34 Hz in the α<sup>2</sup>-HD complex). Additionally the Ir-CH<sub>3</sub> resonance appears at 0.39 ppm and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibits a singlet at 174.1 ppm.

Further evidence in support of the proposed mechanism of hydrogenation (Figure 1b) was garnered via *in situ* deprotonation of **4-MeH(H<sub>2</sub>)<sup>+</sup>**. Deprotonation of the bound dihydrogen molecule by a conjugate base is a key step in the proposed mechanism for formation of the *trans*-dihydride species without the intermediacy of the *cis*-dihydride isomer. Significantly, addition of 10 equiv. of triethylamine to a methylene chloride-*d*<sub>2</sub> solution of **4-MeH(H<sub>2</sub>)<sup>+</sup>** at -90 °C (eq 2) resulted in complete conversion to **4-MeH<sub>2</sub>** with concomitant formation of the (H)NEt<sub>3</sub>B(Ar<sup>F</sup>)<sub>4</sub> salt (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>).



(3)

Experiments employing either D<sub>2</sub>O or CH<sub>3</sub>OD revealed rapid incorporation of deuterium into the methyl group of **4-Me**. This exchange clearly occurs via deuteration at iridium to give **4-MeD**<sup>+</sup> followed by reversible reductive coupling to yield **4-(CH<sub>3</sub>D)**<sup>+</sup>. This observation is consistent with the equilibrium indicated in the proposed mechanism (Figure 1b).<sup>9</sup>

In summary, we report that proton-catalyzed hydrogenation of an Ir(I) complex yields a *trans*-dihydride iridium(III) complex without the intermediacy of the *cis*-dihydride isomer. The proposed mechanism, shown in Figure 1b, is supported by independent verification of the elementary reaction steps along the proposed pathway.<sup>11</sup> Since the bridge atoms are oxygen, the “Milstein mechanism” cannot apply here.<sup>7,8</sup> It is remarkable that two quite different mechanisms, both water-mediated, can apply to very similar systems. The unusual proton-catalyzed net oxidative addition of dihydrogen seen here serves as an alternative pathway for dihydrogen cleavage by metal complexes sufficiently basic to be protonated by weak acids such as water.

## Supplementary Material

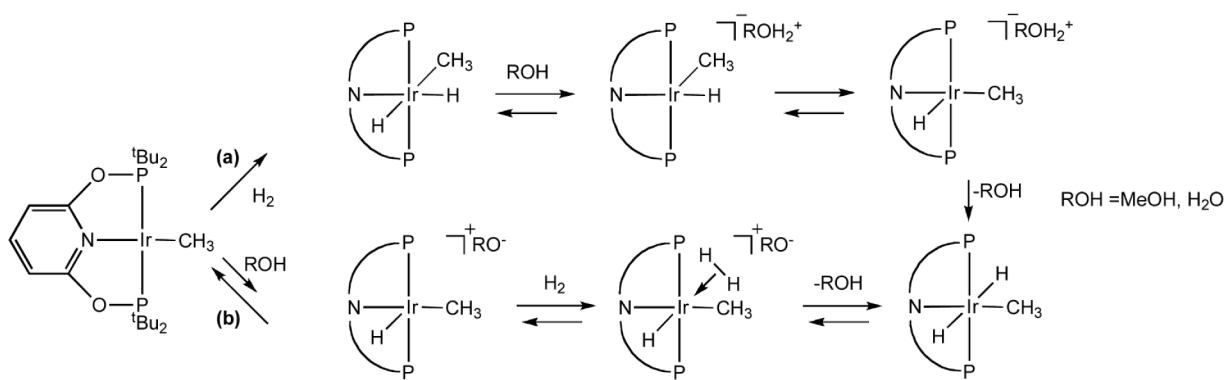
Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

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- See Supporting Information for these details and an alternative mechanism suggested by a reviewer.
- A reviewer notes that the counteranions differ for the water and methanol catalysed reactions ( $\text{OH}^-$  or  $\text{OCH}_3^-$ ) versus the low temperature protonation studies ( $\text{B}(\text{Ar}^{\text{F}})_4^-$ ), thus the latter species should be viewed as model compounds.



**Figure 1.** Proposed mechanisms for water-catalyzed dihydrogen cleavage: (a) water as base, and (b) water as acid