

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

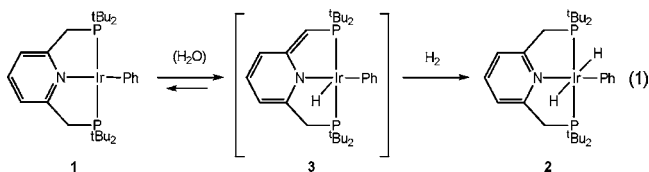
Michael Findlater, Wesley H. Bernskoetter, and Maurice Brookhart*

Department of Chemistry, The University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27599-3290

Received January 14, 2010; E-mail: brookhart@email.unc.edu

Square-planar d^8 iridium(I) complexes, including the iconic Vaska's complex, *trans*-IrCl(CO)[P(C₆H₅)₃]₂,¹ have been used to explore a wide range of oxidative addition reactions of d^8 transition-metal complexes. These studies have established a range of mechanisms, including concerted cleavage of nonpolar substrates, stepwise addition of polar substrates, and radical chain reactions of certain RX substrates.² In light of the importance of transition-metal hydride complexes in numerous catalytic transformations, including olefin hydrogenation³ and hydroformylation,⁴ the concerted addition of dihydrogen to Ir(I) centers has received particular scrutiny.⁵ Oxidative addition of dihydrogen to afford the kinetically preferred *cis*-dihydride complex is the prevailing pathway. Factors shown to influence the kinetics and thermodynamics of H₂ 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.⁶

Milstein has recently reported that hydrogenation of the Ir(I) phenyl complex **1** yields the *trans*-dihydride complex **2** as the kinetic and thermodynamic product (eq 1).⁷

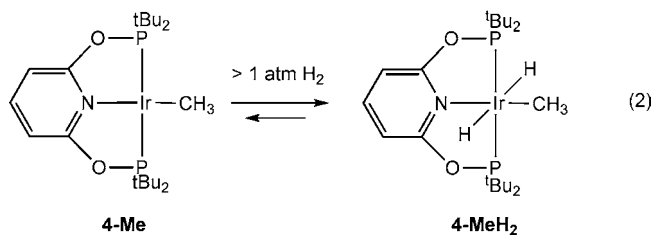


The proposed mechanism involves intermediacy of the dearomatized complex **3**, formed by water-assisted proton transfer, followed by η^2 -binding of H₂ cis to the phenyl group and transfer of hydrogen from η^2 -H₂ to the methine carbon of the bridge. Density functional theory calculations and deuterium-labeling results supported this proposal.⁸

We report here the hydrogenation of a related Ir(I) methyl complex, which yields a *trans*-dihydride species through a quite different mechanism involving proton-catalyzed H₂ cleavage, a pathway that circumvents the intermediacy of the *cis*-dihydride isomer.

We recently described the synthesis of the Ir(I) methyl complex (PONOP)Ir(CH₃) (**4-Me**), supported by the neutral pincer ligand 2,6-bis(di-*tert*-butylphosphinito)pyridine (PONOP), and its protonation with a noncoordinating acid to yield the remarkably stable five-coordinate, 16-electron complex (PONOP)Ir(H)(Me)⁺ (**4-MeH⁺**).⁹ This complex was found to equilibrate rapidly with an unobserved Ir(I) σ -methane complex, (PONOP)Ir(CH₄)⁺, prior to methane loss. To investigate the stability of the related Ir(III) methyl dihydride complex, a frozen benzene-*d*₆ solution of **4-Me** was treated with 1 atm dihydrogen at -196 °C. Warming the solution to ambient temperature and shaking overnight afforded com-

plete conversion to the unexpected *trans*-dihydride complex (PONOP)Ir(CH₃)H₂ (**4-MeH₂**) (eq 2):¹⁰



The ³¹P{¹H} NMR spectrum of **4-MeH₂** displays a singlet at 182.6 ppm that is shifted marginally upfield relative to that for **4-Me**. The corresponding ¹H NMR spectrum exhibits a 2H triplet of quartets at -9.06 ppm (²J_{P-H} = 17 Hz, ³J_{H-H} = 2.4 Hz) corresponding to the Ir-H fragments and a 3H triplet of triplets at 1.05 ppm (³J_{P-H} = 5 Hz, ³J_{H-H} = 2.8 Hz) assigned to the Ir-CH₃ moiety.¹⁰

Evacuation of the dihydrogen atmosphere from **4-MeH₂** resulted in reversion to **4-Me** over ~ 1 day at 23 °C under a static vacuum. **4-MeH₂** is stable under dihydrogen in benzene solution at 23 °C but eliminates CH₄ at temperatures above 60 °C. Monitoring of the concentrations of H₂ and both iridium methyl species by NMR spectroscopy in samples containing less than 1 atm dihydrogen afforded a K_{eq} of 748(34) M⁻¹ (23 °C) for the hydrogenation of **4-Me**.¹⁰

Initial kinetic experiments revealed that the rates of hydrogenation were nonuniform. 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-MeH₂** in a matter of minutes for the methanol- or water-treated samples, compared with hours for the control hydrogenation reaction. Two possible mechanisms for the methanol- or water-assisted cleavage of dihydrogen to produce the *trans*-dihydride, **4-MeH₂**, are shown in Figure 1.¹¹ An alternative mechanism, in which α -elimination from **4-Me** to form a transient carbene intermediate is followed by 1,2-addition of H₂, was ruled out on the basis of kinetic isotope effect experiments.¹⁰

The first mechanism (Figure 1a) proceeds by the classic *cis* addition of H₂ 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-MeH₂**. To assay the ability of base to catalyze the formation of **4-MeH₂**, parallel hydrogenation reactions with **4-Me** were conducted. One sample of the hydrogenation mixture was treated with

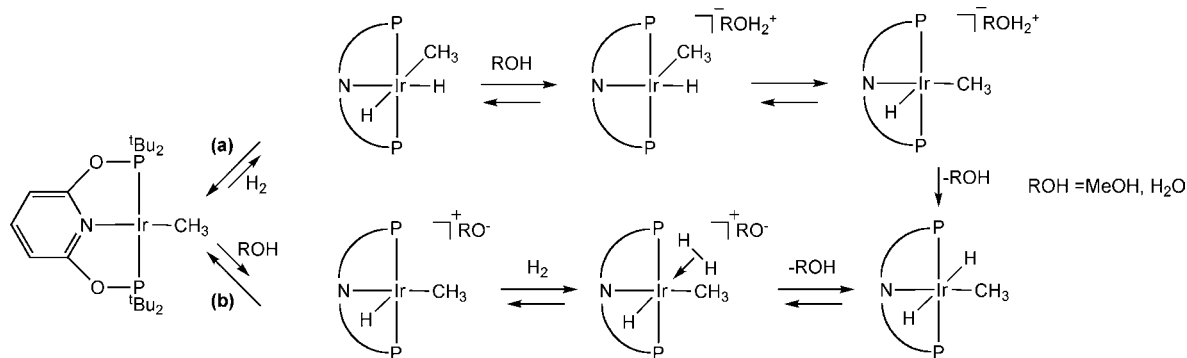


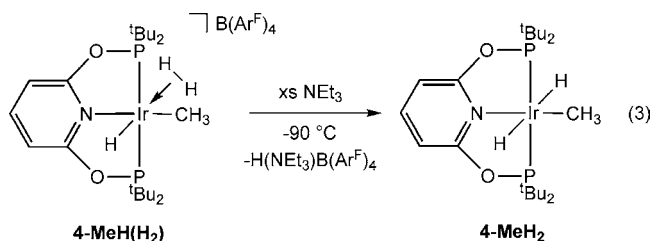
Figure 1. Proposed mechanisms for water-catalyzed dihydrogen cleavage: (a) water as a base; (b) water as an acid.

~5 equiv of triethylamine at $-196\text{ }^{\circ}\text{C}$ prior to warming of the benzene- d_6 solutions. Monitoring by NMR spectroscopy revealed no detectable rate enhancement for conversion of **4-Me** to **4-MeH₂** for the amine-containing sample. Since no rate enhancement was observed in the presence of a superior base, it is unlikely that water/alcohol acts 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⁺**. 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⁺** (see above) 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⁺** in methylene chloride- d_2 was treated with 1 atm dihydrogen at $-196\text{ }^{\circ}\text{C}$, and the tube was transferred to a precooled ($-100\text{ }^{\circ}\text{C}$) NMR probe. After the solution was thawed, ^1H and ^{31}P NMR spectroscopy indicated near complete conversion (>90%) to the dihydrogen-hydride species, **4-MeH(H₂)⁺**. The presence of the hydride was confirmed by a 1H triplet at -13.37 ppm ($^2J_{\text{P-H}} = 17\text{ Hz}$), and the coordinated dihydrogen was observed as a broad 2H singlet at -1.98 ppm ($J_{\text{HD}} = 34\text{ Hz}$ in the η^2 -HD complex). Additionally the Ir-CH₃ resonance appeared at 0.39 ppm , and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibited 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(H₂)⁺**. 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_2 solution of **4-MeH(H₂)⁺** at $-90\text{ }^{\circ}\text{C}$ resulted in complete conversion to **4-MeH₂** with concomitant formation of the (H)NEt₃B(Ar^F)₄ salt [Ar^F = 3,5-(CF₃)₂C₆H₃] (eq 3):



Experiments employing either D₂O or CH₃OD revealed rapid incorporation of deuterium into the methyl group of **4-Me**. This

exchange clearly occurs via deuteration at iridium to give **4-MeD⁺** followed by reversible reductive coupling to yield **4-(CH₃D)⁺**. This observation is consistent with the equilibrium indicated in the proposed mechanism (Figure 1b).⁹

In summary, we have reported 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.¹¹ Since the bridge atoms are oxygen, the “Milstein mechanism” cannot apply here.^{7,8} 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 that are sufficiently basic to be protonated by weak acids such as water.

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

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

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