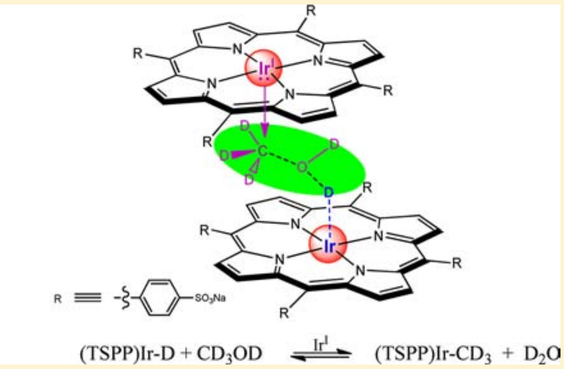
Inorganic Chemistry
Article
pubs.acs.org/IC

# Iridium Porphyrins in $CD_3OD$: Reduction of Ir(III), $CD_3$−OD Bond Cleavage, Ir−D Acid Dissociation and Alkene Reactions

Salome Bhagan, Gregory H. Imler, and Bradford B. Wayland*

Temple University, Department of Chemistry, 130 Beury Hall, 1901 North 13th Street, Philadelphia, Pennsylvania 19122, United States

Ⓢ *Supporting Information*



**ABSTRACT:** Methanol solutions of iridium(III) tetra(*p*-sulfonatophenyl)porphyrin $[(TSPP)Ir^{III}]$ form an equilibrium distribution of methanol and methoxide complexes $([(TSPP)Ir^{III}(CD_3OD)_{(2-n)}(OCD_3)_n]^{(3+n)-})$. Reaction of $[(TSPP)Ir^{III}$ with dihydrogen $(D_2)$ in methanol produces an iridium hydride $[(TSPP)Ir^{III}{-}D(CD_3OD)]^{4-}$ in equilibrium with an iridium(I) complex $([(TSPP)Ir^{I}(CD_3OD)]^{5-})$. The acid dissociation constant of the iridium hydride (Ir−D) in methanol at 298 K is $3.5 \times 10^{-12}$. The iridium(I) complex $([(TSPP)Ir^{I}(CD_3OD)]^{5-})$ catalyzes reaction of $[(TSPP)Ir^{III}{-}D(CD_3OD)]^{4-}$ with $CD_3$−OD to produce an iridium methyl complex $[(TSPP)Ir^{III}{-}CD_3(CD_3OD)]^{4-}$ and $D_2O$. Reactions of the iridium hydride with ethene and propene produce iridium alkyl complexes, but the Ir−D complex fails to give observable addition with acetaldehyde and carbon monoxide in methanol. Reaction of the iridium hydride with propene forms both the isopropyl and propyl complexes with free energy changes ($\Delta G°$ 298 K) of −1.3 and −0.4 kcal $mol^{-1}$ respectively. Equilibrium thermodynamics and reactivity studies are used in discussing relative Ir−D, Ir−$OCD_3$ and Ir−$CD_2$- bond energetics in methanol.

## ■ INTRODUCTION

Application of water and methanol as both solvent media and reactants is an important direction for organometallic catalysis research.[1−27] Current interest in group nine metalloporphyrin reactivity and catalysis studies in this area has been focused on the behavior of complexes with sulfonated porphyrin ligands in water[5,6,8,18−23,28] and methanol.[16,28] Water and methanol are high dielectric constant liquids[29,30] that have both hydrogen bonding and donor capability, which results in many analogous features. Methanol is distinguished by having both hydroxylic and hydrocarbon components which result in the unusual property of miscibility in both water and organic hydrocarbon solvents.

Rhodium porphyrins have a more highly developed reaction chemistry in diverse media[16,18−23,31−60] compared to iridium porphyrins.[18,61−74] This Article reports on reactivity and thermodynamic studies for methanol solutions of tetra(*p*-sulfonatophenyl)porphyrin iridium(III) methanol and methoxide complexes $([(TSPP)Ir^{III}(CD_3OD)_{2-n}(OCD_3)_n]^{(3+n)-})$. The Ir(III) complex reacts with $H_2(D_2)$ to form an iridium hydride complex $([(TSPP)Ir^{III}{-}D(CD_3OD)]^{4-})$ that has an Ir−D acid dissociation constant of $3.5 \times 10^{-12}$ in methanol. The Ir−D complex reacts with $CD_3OD$ in basic methanol by a net $CD_3$−OD bond cleavage to form an iridium methyl complex $([(TSPP)Ir^{III}{-}CD_3(CD_3OD)]^{4-})$ and $D_2O$. Alkenes react with $[(TSPP)Ir^{III}{-}D(CD_3OD)]^{4-}$ to form iridium alkyl complexes, but CO reacts to form only a carbon monoxide adduct$[(TSPP)Ir{-}D(CO)]^{4-}$ without observation of an iridium formyl species (Ir−CHO). Results from equilibrium thermodynamic and reactivity studies are used in discussing relative Ir−D, Ir−$OCD_3$ and Ir−$CD_2$- bond energetics in methanol.

## ■ RESULTS AND DISCUSSION

**Methanol and Methoxide Complexes of $(TSPP)Ir^{III}$ in $CD_3OD$.** Dissolution of iridium(III) tetra(*p*-sulfonatophenyl)porphyrin $(Na_3[(TSPP)Ir^{III}(CD_3OD)_2]\cdot 18CD_3OD)$ in $CD_3OD$ results in a pH dependent equilibrium distribution of a bis-methanol complex $[(TSPP)Ir(CD_3OD)_2]^{3-}$ (**1**) with mono- and bis-methoxide complexes $[(TSPP)Ir(OCH_3)(CD_3OD)]^{4-}$ (**2**) and $[(TSPP)Ir(OCD_3)_2]^{5-}$ (**3**) (eqs 1 and 2) (Figure 1). The axially coordinated methanol and methoxide ligands for **1**, **2** and **3** in methanol rapidly exchange protons with the bulk methanol (298 K) (Figure 1), which results in a single mole fraction averaged pyrrole $^1H$ NMR resonance for **1**, **2** and **3** (Figures 2 and 3).

$$[(TSPP)Ir(CD_3OD)_2]^{3-} \rightleftharpoons [(TSPP)Ir(OCD_3)(CD_3OD)]^{4-} + D^+ \qquad (1)$$

**Received:** January 30, 2013
**Published:** March 29, 2013

dx.doi.org/10.1021/ic400240b | *Inorg. Chem.* 2013, 52, 4611−4617

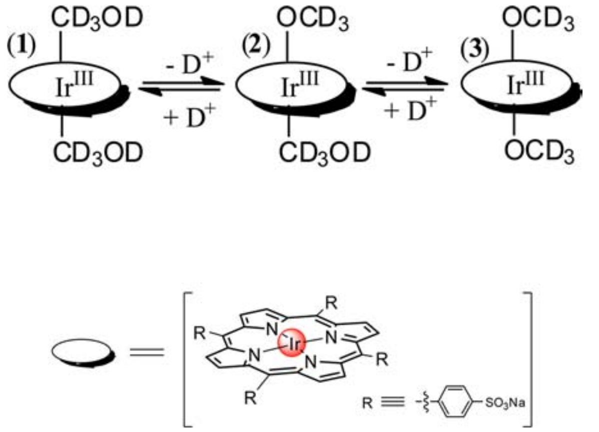


**Figure 1.** Methanol and methoxide complexes of (TSPP)$Ir^{III}$ in methanol.

$$[(TSPP)Ir(CD_3OD)]^{4-} \rightleftharpoons [(TSPP)Ir(OCD_3)_2]^{5-} + D^+ \tag{2}$$

The $^1H$ NMR of the bis-methanol complex **1** and bis-methoxide complex **3** can be directly obtained at limiting high and low hydrogen ion concentrations respectively. The mole fraction averaged pyrrole $^1H$ NMR resonances for equilibrium distributions of **1**, **2** and **3** as a function of $[D^+]$ were used in determining the acid dissociation constants for coordinated methanol by nonlinear least-squares curve fitting to the expression

$$\begin{aligned}\delta_{2,3,4(\mathrm{obs})}(\mathrm{pyr}) = {} & (K_1K_2\delta_3(\mathrm{pyr}) + K_1[D^+]\delta_2(\mathrm{pyr}) \\ & + [D^+]^2\delta_1(\mathrm{pyr})) \\ & /(K_1K_2 + K_1[D^+] + [D^+]^2)\end{aligned}$$

giving $K_1(298K) = 2.3 \times 10^{-8}$, $K_2(298K) = 2.1 \times 10^{-11}$ and $\delta_2(\mathrm{pyr}) = 8.61$ ppm; **1** $[(TSPP)Ir^{III}(CD_3OD)_2]^{3-}$ is $\delta_1(\mathrm{pyr}) = 8.76$ ppm, and **3** $[(TSPP)Ir^{III}(OCD_3)_2]^{5-}$ is $\delta_3(\mathrm{pyr}) = 8.43$ ppm (Figure 3). The coordinated methanol acid dissociation constants for $[(TSPP)Ir(CD_3OD)_2]^{3-}$ at 298 K ($K_1 = 2.3 \times 10^{-8}$, $K_2 = 2.1 \times 10^{-11}$) in methanol (Table 1) are similar to the values for the coordinated water acid dissociation constants in $D_2O$ at 298 K for $[(TSPP)Ir(D_2O)_2]^{3-}$ ($K_1(D_2O) = 4.8 \times 10^{-8}$, $K_2(D_2O) = 2.6 \times 10^{-11}$).[8]

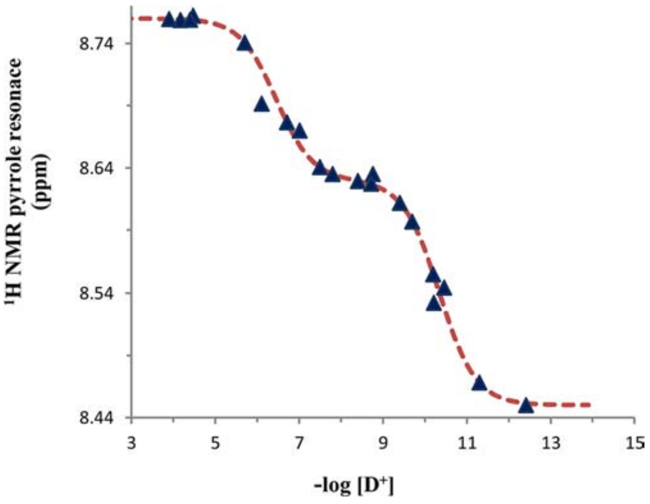


**Figure 3.** Observed limiting fast proton exchange mole fraction averaged pyrrole $^1H$ NMR shifts for (TSPP)$Ir^{III}$ complexes **1**, **2** and **3** in $CD_3OD$ as a function of pD. Triangular points are experimentally observed pyrrole shift values in methanol, and the line is calculated for $K_1(298K) = 2.3 \times 10^{-8}$ and $K_2(298K) = 2.1 \times 10^{-11}$.

**Reaction of Hydrogen ($H_2/D_2$) with [(TSPP)-$Ir^{III}(CD_3OD)_2]^{3-}$ in $CD_3OD$.** Methanol solutions of $[(TSPP)Ir^{III}(CD_3OD)_2]^{3-}$ at pD lower than 10 react with hydrogen ($P(H_2/D_2) \sim 0.4$–$0.9$ atm) in $CD_3OD$ to form a hydride (deuteride) complex $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ (**4**) (eq 3, Figure 4). Acidic solutions of the iridium hydride complex $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ in a mixture of $CH_3OH/CD_3OD$

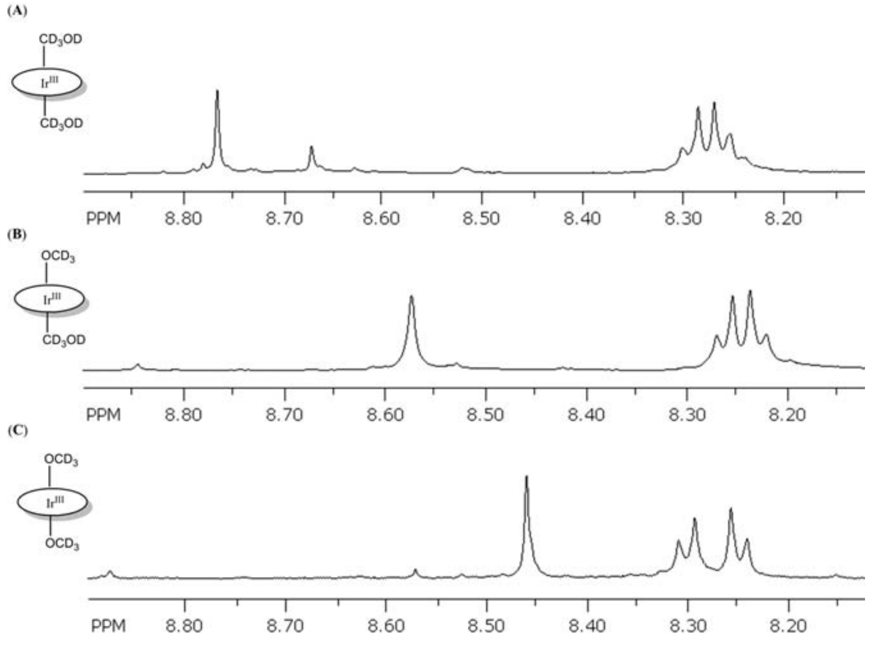


**Figure 2.** Mole fraction averaged $^1H$ HMR (500 MHz) porphyrin pyrrole singlet and phenyl AB pattern for complexes **1**, **2** and **3** in $CD_3OD$ ($T$ = 298 K): (A) pD = 4.0, (B) pD = 8.5 and (C) pD = 11.5.

**Table 1. Equilibrium Thermodynamic Values for $[(\mathrm{TSPP})\mathrm{Ir}]$ Reactions in Methanol ($T$ = 298 K)[a]**

| (TSPP)Ir reactions | $K$ | $\Delta G°$ |
|---|---|---|
| $[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{CD_3OD})_2]^{3-} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OCD_3})(\mathrm{CD_3OD})]^{4-} + \mathrm{D^+}$ | $2.3 \times 10^{-8}$ | +10.4 |
| $[(\mathrm{TSPP})\mathrm{Ir^{III}}((\mathrm{OCD_3})(\mathrm{CD_3OD})]^{4-} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir^{III}}((\mathrm{OCD_3})_2]^{5-} + \mathrm{D^+}$ | $2.1 \times 10^{-11}$ | +14.6 |
| $[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{CD_3OD})_2]^{3-} + \mathrm{D_2} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} + \mathrm{D^+} + \mathrm{CD_3OD}$ | 4.5 | −0.8 |
| $[(\mathrm{TSPP})\mathrm{Ir}(\mathrm{OCD_3})(\mathrm{CD_3OD})]^{4-} + \mathrm{D_2} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} + \mathrm{CD_3OD}$ | $1.9 \times 10^{8}$ | −11.2 |
| $[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir^{I}}(\mathrm{CD_3OD})]^{5-} + \mathrm{D^+}$ | $3.5 \times 10^{-12}$ | +15.6 |
| $[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} + \mathrm{C_2H_4} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir{-}CH_2CH_2D}(\mathrm{CD_3OD})]^{4-}$ | 63 | −2.5 |
| $[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} + \mathrm{C_3H_6} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir{-}CH(CH_2D)CH_3}(\mathrm{CD_3OD})]^{4-}$ | 9.2 | −1.3 |
| $[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} + \mathrm{C_3H_6} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir{-}CH_2CHDCH_3}(\mathrm{CD_3OD})]^{4-}$ | 2.0 | −0.4 |

[a] $\mathrm{CD_3OD} \rightleftharpoons \mathrm{D^+} + \mathrm{OCD_3^-}$; $K = 2.0 \times 10^{-17}$; $\Delta G^0 = 22.8$ kcal mol$^{-1}$.

were used to observe the high field iridium hydride resonance at −59.1 ppm.

$$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{CD_3OD})_2]^{3-} + \mathrm{D_2} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} + \mathrm{CD_3OD} + \mathrm{D^+} \qquad (3)$$

Reaction 3 was permitted to equilibrate for a period of two weeks at 298 K before determination of the equilibrium constant by integration of the $^1$H NMR for **2** and **4** and measurement of the solution pH ($K_3$(298K) = 4.5(0.5); $\Delta G°_3$ = −0.8(0.1) kcal mol$^{-1}$) (Table 1). The equilibrium constant for the reaction of dihydrogen with $[(\mathrm{TSPP})\mathrm{Ir}(\mathrm{OCD_3})(\mathrm{CD_3OD})]^{4-}$ (**2**) (eq 4) is too large for direct evaluation by $^1$H NMR, but the free energy change for reaction 4 can be derived from the measured $\Delta G°$ values for reactions 1 and 3 (Scheme 1, $\Delta G_4° = \Delta G_3° - \Delta G_1°$; $\Delta G_4°$(298K) = −11.2 kcal mol$^{-1}$).

$$[(\mathrm{TSPP})\mathrm{Ir}(\mathrm{OCD_3})(\mathrm{CD_3OD})]^{4-} + \mathrm{D_2} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} + \mathrm{CD_3OD} \qquad (4)$$

**Acid Dissociation Constant of $[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-}$ in Methanol.** The iridium hydride complex $[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-}$ (**4**) in methanol occurs in a $^1$H NMR observable equilibrium with the iridium(I) derivative $[(\mathrm{TSPP})\mathrm{Ir^{I}}(\mathrm{CD_3OD})]^{5-}$ (**5**) (eq 5) in the pD range of 10.5−11.5. Proton exchange between **4** and **5** at 298 K in methanol solution is sufficiently slow to permit observation of separate although slightly broadened porphyrin pyrrole hydrogen resonances for **4** and **5**.

$$[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-} \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir^{I}}(\mathrm{CD_3OD})]^{5-} + \mathrm{D^+} \qquad (5)$$

Evaluation of the $^1$H NMR integrated intensities for the pyrrole hydrogens of **4** and **5** along with the deuterium ion concentration were used in determining the acid dissociation constant for the deuteride complex ($[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-}$) in methanol ($K_5$(298K) = 3.5(0.2) × $10^{-12}$; $\Delta G°$(298K) = 15.6(0.1) kcal mol$^{-1}$) (Table 1). The acid dissociation constant for **4** in methanol ($K_5$(298K) = 3.5 × $10^{-12}$) is slightly larger than the value for $[(\mathrm{TMPS})\mathrm{Ir{-}D}(\mathrm{D_2O})]^{8-}$ in water ($K$(298K) = 1.8 × $10^{-12}$)[72] and much smaller than the acid dissociation constants for an analogous rhodium complex $[(\mathrm{TSPP})\mathrm{Rh{-}D}(\mathrm{CD_3OD})]^{4-}$ in methanol ($K$(298K) = 1.1 × $10^{-9}$; $\Delta G°$(298K) = 12.2 kcal mol$^{-1}$)[7] and $[(\mathrm{TSPP})\mathrm{Rh{-}D}(\mathrm{D_2O})]^{4-}$ in water ($K$(298K) = 8.0 × $10^{-8}$ ; $\Delta G°$(298K) = 9.7 kcal mol$^{-1}$) (Figure 5).[22]

The iridium(I) complex ($[(\mathrm{TSPP})\mathrm{Ir^{I}}(\mathrm{CD_3OD})]^{5-}$ (**5**)) reacts as a nucleophile with methyl iodide ($\mathrm{CH_3I}$) in methanol to form the methyl complex ($[(\mathrm{TSPP})\mathrm{Ir{-}CH_3}(\mathrm{CD_3OD})]^{4-}$ (**6**)), which is readily identified in solution by the characteristic high field methyl $^1$H NMR resonance ($\delta$ = −7.15 ppm) (Supporting Information). Addition of triphenyl phosphite to the methanol solution of the methyl complex (**6**) produces the phosphite complex, which is readily detected in methanol solution by $^{31}\mathrm{P{-}C}H_3$ coupling ($\delta$ = −7.37 ppm, 15 Hz) between the trans phosphite and methyl groups in $[(\mathrm{TSPP})\mathrm{Ir{-}CH_3}(\mathrm{P(OC_6H_5)_3})]^{4-}$ (Supporting Information).

**Reduction of Ir(III) to Ir(I) by Methanol.** Methanol solutions of $[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OCD_3})_2]^{5-}$ (**3**) (pD > 11) are kinetically stable for days at 298 K, but upon warming to 343 K the $(\mathrm{TSPP})\mathrm{Ir^{III}}$ is quickly reduced to $[(\mathrm{TSPP})\mathrm{Ir^{I}}(\mathrm{CD_3OD})]^{5-}$ (**5**) and methanol is oxidized to formaldehyde (Scheme 2).

Iridium(III) porphyrins are thus only metastable reagents for substrate reactions in strongly basic methanol. Oxidation of methanol becomes catalytic through quantitative dioxygen oxidation of $(\mathrm{TSPP})\mathrm{Ir^{I}}$ to $(\mathrm{TSPP})\mathrm{Ir^{III}}$ (Scheme 2), and formaldehyde oxidizes further under these conditions to formate. The methanol oxidation to formaldehyde is currently viewed as occurring by an intermolecular $\beta$ C−H deprotonation of methoxide coordinated to Ir(III) in the basic high

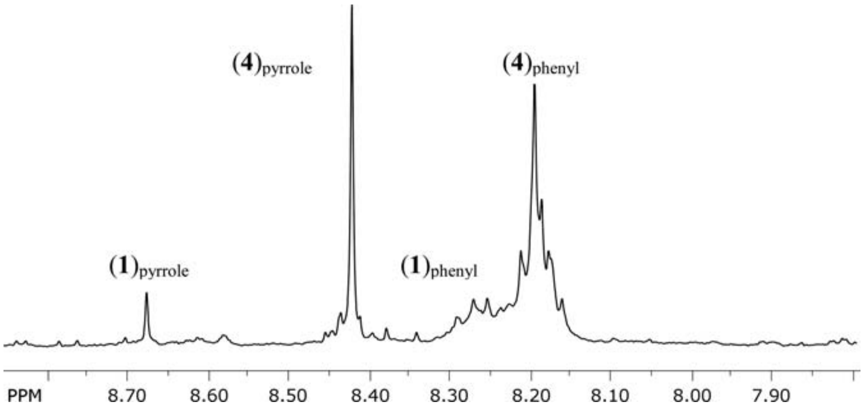


**Figure 4.** $^1$H NMR (500 MHz, $\mathrm{CD_3OD}$,pD = 4.8). Equilibrium among $[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{CD_3OD})_2]^{3-}$, $\mathrm{H_2}$ and $[(\mathrm{TSPP})\mathrm{Ir{-}D}(\mathrm{CD_3OD})]^{4-}$.

**Scheme 1. Thermodynamic Cycle for $D_2$ Reaction with $[(TSPP)Ir(OCD_3)(CD_3OD)]^{4-}$**

$$[(Ir^{III}(CD_3OD)_2]^{3-} + D_2 \rightleftharpoons [Ir\text{-}D(CD_3OD)]^{4-} + D^+ + CD_3OD \qquad (3)$$

$$[Ir(OCD_3)(CD_3OD)]^{4-} + D^+ \rightleftharpoons [Ir^{III}(CD_3OD)_2]^{3-} \qquad (\text{-}1)$$

$$[(TSPP)Ir(OCD_3)(CD_3OD)]^{4-} + D_2 \rightleftharpoons [(TSPP)Ir\text{-}D(CD_3OD)]^{4-} + CD_3OD \qquad (4)$$

$$\Delta G_4{}^\circ = \Delta G_3{}^\circ - \Delta G_1{}^\circ = -11.2\ \text{kcal mol}^{-1}$$

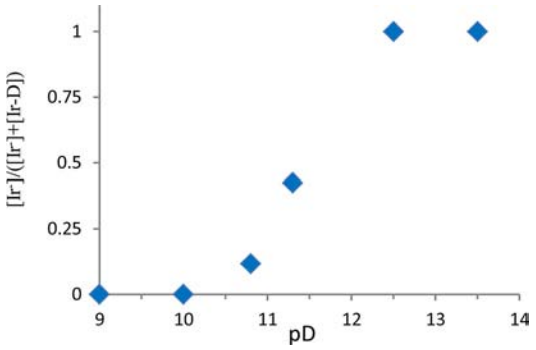


**Figure 5.** Acid dissociation constant for $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ in $CD_3OD$ from $[(TSPP)Ir^I(CD_3OD)]^{5-}$ in equilibrium with the $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ as a function of pD from $^1H$ NMR. Nonlinear least-squares fit gives $K_5(298K) = 3.5 \times 10^{-12}$.

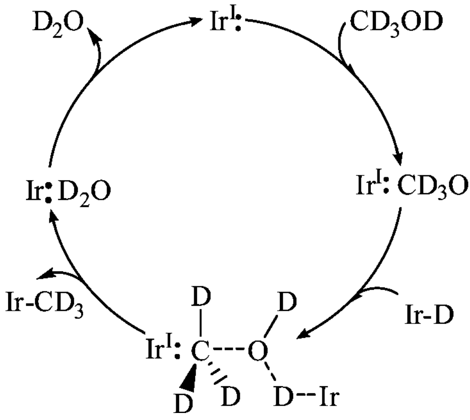
dielectric medium. Fast quantitative air oxidation of iridium(I) to iridium(III) is an important feature of the iridium porphyrin system that permits iridium(III) porphyrins to function as oxidation catalysts by directly using $O_2$ without the need for a cocatalyst.

**Reaction of $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ with $CD_3OD$ To Form $[(TSPP)Ir{-}CH_3(CD_3OD)]^{4-}$ and Water Catalyzed by $[(TSPP)Ir^I(CD_3OD)]^{5-}$ in Methanol.** Methanol solutions that contain only the hydride ($[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ (**4**)) (pD < 10.5) or the iridium(I) complex ($[(TSPP)Ir^I(CD_3OD)]^{5-}$ (**5**)) (pD > 12.0) are kinetically stable over periods of months. When the pD is in the range of 10.8−11.8 the iridium hydride complex ($[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ (**4**)) is observed to react with methanol to form the methyl complex $[(TSPP)Ir{-}CD_3(CD_3OD)]^{5-}$ (**6**) and water (eq 6). Formation of an iridium−methyl complex from reaction with methanol was first reported by Chan.[18] Reaction 6 in $CH_3{-}OH$ results in formation of $[(TSPP)Ir{-}CH_3(CH_3OH)]^{4-}$, which is easily observed in solution by the characteristic high field methyl resonance in the $^1H$ NMR spectrum ($\delta Ir{-}CH_3 = -7.15$).

$$[(TSPP)Ir{-}D(CD_3OD)]^{4-} + CD_3OD \rightleftharpoons [(TSPP)Ir{-}CD_3(CD_3OD)]^{4-} + D_2O \qquad (6)$$

Formation of the $[(TSPP)Ir{-}CD_3(CD_3OD)]^{4-}$ complex only occurs at a finite rate in the pD range (10.8−11.8) where both $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ (**4**) and $[(TSPP)Ir^I(CD_3OD)]^{5-}$ (**5**) occur at $^1H$ NMR observable concentrations. The net process corresponds to reaction of the hydride (**4**) with $CD_3OD$ to form the methyl complex (**6**) and $D_2O$ (eq 6) where $[(TSPP)Ir^I(CD_3OD)]^{5-}$ (**5**) functions as a catalyst. The proposed reaction pathway is illustrated in Scheme 3 . This process is an unusual example of $CD_3{-}OD$ bond cleavage which is driven thermodynamically by formation of water.

**Scheme 3. Reaction of $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ and $CD_3OD$ To Form $[(TSPP)Ir{-}CD_3(CD_3OD)]^{4-}$ and Water Catalyzed by $[(TSPP)Ir^I(CD_3OD)]^{5-}$ in Methanol**



**Reaction of $[(TSPP)Ir{-}D\ (CD_3OD)]^{4-}$ with Alkenes in $CD_3OD$.** Methanol ($CD_3OD$) solutions of the iridium hydride complex **4** ($[(TSPP)Ir{-}D(CD_3OD)]^{4-}$) ($1 \times 10^{-3}$ M) in vacuum adapted NMR tubes were pressurized with ethene, propene, 1-pentene and 1-hexene gases each at 100 Torr pressure, and changes in the $^1H$ NMR spectra were followed over a period of days. The $^1H$ NMR spectra for $CD_3OD$ solutions of **4** with ethene and propene showed the appearance of the characteristic high field porphyrin ring current shifted resonances for metalloporphyrin alkyl complexes ((por)M−R), but the longer chain alkenes did not produce $^1H$ NMR observable concentrations of organoiridium porphyrin species.

Reaction of $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ with ethene produces the iridium ethyl complex $[(TSPP)Ir{-}CH_2CH_2D(CD_3OD)]^{4-}$ (**7**), which is identified in methanol solution by the high field region of the $^1H$ NMR (−1.85 (br, 2H, $-CH_2$) and −5.68 (br, 2H, $-CH_2D$) (eq 7). Equilibrium concen-

**Scheme 2. Proposed Pathway for Methanol Reduction of Iridium(III) Porphyrins at High pD**

$$[(TSPP)Ir^{III}(OCD_3)_2]^{5-} \rightleftharpoons [(TSPP)Ir^I(OCD_3)(OCD_2)]^{6-} + D^+$$

$$[(TSPP)Ir^I(OCD_3)(OCD_2)]^{6-} + D^+ \rightleftharpoons [(TSPP)Ir^I(CD_3OD)]^{5-} + CD_2O$$

$$[(TSPP)Ir^I(CD_3OD)]^{5-} + O_2 + CD_3OD \rightleftharpoons [(TSPP)Ir^{III}(OCD_3)_2]^{5-} + D_2O_2$$

$$D_2O_2 \rightleftharpoons \tfrac{1}{2}\, O_2 + D_2O$$

$$CD_3OD + \tfrac{1}{2}\, O_2 \rightleftharpoons CD_2O + D_2O$$

trations of the iridium ethyl complex $[(TSPP)Ir{-}CH_2CH_2D(CD_3OD)]^{4-}$, $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ and ethene determined by integration of the $^1H$ NMR were used in evaluating the equilibrium constant for reaction 7 at 298 K ($K_7 = 63$ and $\Delta G_7° = -2.5$ kcal mol$^{-1}$) (Table 1). Addition of the (TSPP)Ir−D to ethene in methanol ($\Delta G_7° = -2.5$ kcalmol$^{-1}$) is similar to that for the reaction of ethene with (TMPS)Ir−D in water($\Delta G° = -3.7$ kcal mol$^{-1}$).[72]

$$[(TSPP)Ir{-}D(CD_3OD)]^{4-} + C_2H_4 \rightleftharpoons [(TSPP)Ir{-}CH_2CH_2D(CD_3OD)]^{4-} \tag{7}$$

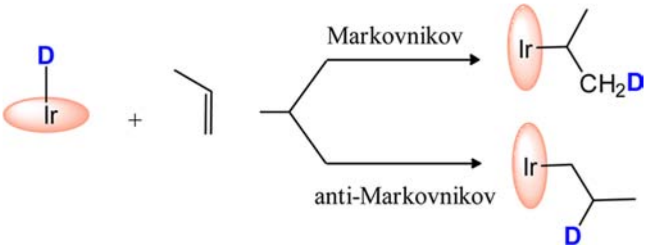
The reaction of $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ with propene results in observation of an equilibrium distribution of two isomers. The major isomer corresponds to the iridium isopropyl complex $[(TSPP)Ir{-}CH(CH_2D)CH_3(CD_3OD)]^{4-}$ (**8**) which is identified in solution by distinct doublets at −2.20 ppm ($-CH(CH_2D)CH_3$) and a broad peak at −6.33 ppm ($-CH(CH_2D)CH_3$)) (eq 8). The minor isomer is the iridium *n*-propyl derivative $[(TSPP)Ir{-}CH_2CHDCH_3(CD_3OD)]^{4-}$ (**9**), which is identified by the distinctive high field resonances for the iridium propyl complex at −1.70 ppm ($-CH_2CHDCH_3$), −3.01 ppm ($-CH_2CHDCH_3$) and −5.82 ppm ($-CH_2CHDCH_3$) (eq 9). Equilibrium constants and $\Delta G°$ values for reactions 8 and 9 were evaluated at 298 K by $^1H$ NMR ($K_8 = 9.2(0.2)$, $\Delta G_8° = -1.3$ kcal mol$^{-1}$; $K_9 = 2.0(0.5)$, $\Delta G_9° = -0.4$ kcal mol$^{-1}$) (Table 1).

$$[(TSPP)Ir{-}D(CD_3OD)]^{4-} + CH_2{=}CHCH_3 \rightleftharpoons [(TSPP)Ir{-}CH(CH_2D)CH_3(CD_3OD)]^{4-} \tag{8}$$

$$[(TSPP)Ir{-}D(CD_3OD)]^{4-} + CH_2{=}CHCH_3 \rightleftharpoons [(TSPP)Ir{-}CH_2CHDCH_3(CD_3OD)]^{4-} \tag{9}$$

Thermodynamic preference for the Ir−D addition with propene to give the Markovnikov regioisomer is opposite to that observed for propene reactions with (TMPS)Ir−D in water[72] and with (TSPP)Rh−D and (TMPS)Rh−D complexes in water and methanol (Scheme 4).[20,22] Repulsive steric interactions favor placing the metalloporphyrin on a primary carbon, but M−C covalent bonding is maximized by placing the metal center on a secondary carbon which better stabilizes the negative charge.[75] The increased importance of covalent bonding compared to rhodium and the smaller steric requirements of TSPP compared to TMPS may combine in the (TPPS)Ir−D system to alter the regioselective addition with propene. The small free energy change in the addition reaction of propene with **4** to produce $[(TSPP)Ir{-}CH_2CHDCH_3(CD_3OD)]^{4-}$ ($\Delta G_9° = -0.4$ kcal mol$^{-1}$)) compared to related Rh−D reaction in water (∼−5 kcal mol$^{-1}$) results in part from the previously recognized increase in the difference between the Ir−D and Ir−$CH_2$ BDFEs compared to the Rh−D and Rh−$CH_2$ BDFE values.

**Scheme 4. Addition Reactions of Propene with $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ in Methanol**



**Reaction of $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ with CO in $CD_3OD$ in Methanol.** The hydride complex $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ (**4**) does not react with CO ($P_{CO}$ = 700 Torr) in methanol to form an iridium formyl complex ($[(TSPP)Ir{-}CDO(CD_3OD)]^{4-}$), but simply produces a trans hydrido carbonyl adduct ($[(TSPP)Ir{-}D(CO)]^{4-}$ (**10**)) (eq 10). The inability to obtain observable quantities of an iridium formyl complex contrasts with rhodium porphyrin hydrides where reaction with CO ($P_{CO}$ < 1 atm) to produce metallo−formyl complexes is a prominent characteristic reaction in benzene,[36,76] water[27] and methanol.[17]

$$[(TSPP)Ir{-}D(CD_3OD)]^{4-} + CO \rightleftharpoons [(TSPP)Ir{-}D(CO)]^{4-} + CD_3OD \tag{10}$$

An increase in the Ir−H relative to the Ir−C is consistent with the inability of the iridium hydride complex (**4**) to produce observable quantities of the $\alpha$-hydroxyethyl complex ($[(TSPP)Ir{-}CH(OD)CH_3(CD_3OD)]^{4-}$), which is a thermodynamically favorable reaction of the corresponding rhodium porphyrin system.[42]

**Difference between the Bond Dissociation Free Energy of Ir−$OCD_3$ and Ir−D for $[(TSPP)Ir{-}X(CD_3OD)]^{4-}$ Complexes in $CD_3OD$.** The difference between the $[(TSPP)Ir{-}OCH_3]$ and $[(TSPP)Ir{-}D]$ units can be estimated as shown from analysis of the bonds breaking and forming as derived from eq 4 (Scheme 5).

The iridium hydride $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ (**4**) bond dissociation free energy (BDFE) is larger than the iridium methoxide BDFE for $[(TSPP)Ir(OCD_3)(CD_3OD)]^{4-}$ (**2**) in methanol by 13.3 kcal mol$^{-1}$ ([Ir−D] − [Ir−$OCH_3$] = 13.3 kcal mol$^{-1}$). The iridium hydroxide BDFE is 3.6 kcal mol$^{-1}$ larger than the iridium hydride BDFE ([Ir−OD] − [Ir−D] = 3.6 kcal mol$^{-1}$) for the similar (TMPS)Ir complexes in water,[72] which places the Ir−OH BDFE in water at ∼17 kcal mol$^{-1}$ larger than the Ir−$OCH_3$ BDFE in methanol. The difference of 14 kcal mol$^{-1}$ in H−$OCH_3$ and H−OH bond dissociation energies[77] is dominated by the difference in the radical stabilization energies of the methoxy and hydroxyl radicals,

**Scheme 5. BDFE of [(Ir−$OCD_3$)- (Ir−D)] Derived from the Reaction of $[Ir\text{-}OCD_3(CD_3OD)]^{4-}$ and $D_2$**

$$[Ir\text{-}OCD_3(CD_3OD)]^{4-} + [D\text{-}D] - [Ir\text{-}D(CD_3OD)]^{4-} - [CD_3O\text{-}D] = \Delta G_4°$$

$$\begin{aligned}[Ir\text{-}OCD_3(CD_3OD)]^{4-} - [Ir\text{-}D(CD_3OD)]^{4-} &= \Delta G_4° - [D\text{-}D] + [CD_3O\text{-}D]\\ &= ([-11.3] - [103.6] + [101.6])\ \text{kcal mol}^{-1}\\ &= -13.3\ \text{kcal mol}^{-1}\end{aligned}$$

and this term also dominates the difference in the Ir−$OCD_3$ and Ir−OD bond dissociation free energies.

## SUMMARY AND CONCLUSIONS

Solutions of iridium(III) tetrakis(*p*-sulfonatophenyl)porphyrin $[(TSPP)Ir^{III}]$ in methanol form a hydrogen ion dependent equilibrium distribution between three species $[(TSPP)Ir(CD_3OD)_2]^{3-}$, $[(TSPP)Ir(OCD_3)(CD_3OD)]^{4-}$ and $[(TSPP)Ir(OCD_3)_2]^{5-}$. The coordinated $CD_3OD$ acid dissociation constants for $[(TSPP)Ir(CD_3OD)_2]^{3-}$ are $K_1 = 2.3 \times 10^{-8}$ and $K_2 = 2.1 \times 10^{-11}$, which are somewhat smaller than those of $[(TSPP)Ir(D_2O)_2]^{3-}$ in water ($K_1(H_2O) = 4.8 \times 10^{-8}$, $K_2(H_2O) = 2.6 \times 10^{-11}$). Reaction of $[(TSPP)Ir^{III}]$ species in $CD_3OD$ with dihydrogen ($H_2/D_2$) results in formation of an iridium hydride complex $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ with an equilibrium constant of $K_3 = 4.5$, $\Delta G°(298K) = -0.8$ kcal $mol^{-1}$, which is smaller than the corresponding reaction of $[(TSPP)Rh^{III}]$) in methanol ($K = 1.0 \times 10^3$, $\Delta G°(298K) = -4.1$ kcal $mol^{-1}$). The less favorable $\Delta G°$ for the $(TSPP)Ir^{III}$ compared to $(TSPP)Rh^{III}$ system results from larger Ir−methanol binding compared to Rh−methanol that more than compensates for the increase in metal hydride bond energy $(([Ir{-}(CD_3OD] - [Rh(CD_3OD]) > ([Ir{-}D] - [Rh{-}D]))$. The acid dissociation constant for $[(TSPP)Ir{-}D(CD_3OD)]^{4-}$ measured in methanol is $3.5 \times 10^{-12}$ ($\Delta G°(298K) = 15.6$ kcal $mol^{-1}$) and is comparable to that for $[(TMPS)Ir{-}D(D_2O)]^{8-}$ in water ($K = 1.8 \times 10^{-12}$, $\Delta G°(298K) = 16.0$ kcal $mol^{-1}$) and much smaller than that for $[(TSPP)Rh{-}D(CD_3OD)]^{8-}$ in methanol ($K = 1.1 \times 10^{-9}$) which primarily reflects the larger Ir−D bond energy. The Ir(I) complex $([(TSPP)Ir(I){-}(CD_3OD)]^{5-})$ in the pD range of 10.8 to 11.8 is observed to catalyze reaction of the iridium hydride $([(TSPP)Ir{-}D{-}(CD_3OD)]^{4-})$ with methanol to form an Ir−$CH_3$ complex $[(TSPP)Ir{-}CD_3(CD_3OD)]^{4-}$ and water. This thermodynamically favorable $CD_3$−OD bond cleavage occurs at a significant rate only in the pD range where both the Ir−D and Ir(I) have substantial equilibrium concentrations which maximize the opportunity for a concerted process.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

Materials and experimental procedures and $^1H$ NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: bwayland@temple.edu.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research was initiated with support from the Department of Energy, Division of Chemical Sciences and the Office of Science through Grant DE-FG02-09ER-16000.

## REFERENCES

(1) Crabtree, R. H. *Organometallics* **2011**, *30*, 17.
(2) Moreno, T.; Garcia-Serna, J.; Cocero, M. J. *Green Chem.* **2010**, *12*, 282.
(3) Capello, C.; Fischer, U.; Hungerbuehler, K. *Green Chem.* **2007**, *9*, 927.
(4) Labinger, J. A.; Bercaw, J. E. *Top. Organomet. Chem.* **2011**, *35*, 29.
(5) Zhang, J.; Li, S.; Fu, X.; Wayland, B. B. *Dalton Trans.* **2009**, 3661.
(6) Zhang, J.; Wayland, B. B.; Yun, L.; Li, S.; Fu, X. *Dalton Trans.* **2010**, *39*, 477.
(7) Li, S.; Sarkar, S.; Wayland, B. B. *Inorg. Chem.* **2009**, *48*, 8550.
(8) Bhagan, S.; Sarkar, S.; Wayland, B. B. *Inorg. Chem.* **2010**, *49*, 6734.
(9) Ozerov, O. V. *Chem. Soc. Rev.* **2009**, *38*, 83.
(10) Eisenberg, R. *Science* **2009**, *324*, 44.
(11) Dempsey, J. L.; Esswein, A. J.; Manke, D. R.; Rosenthal, J.; Soper, J. D.; Nocera, D. G. *Inorg. Chem.* **2005**, *44*, 6879.
(12) Hong, S. H.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 3508.
(13) Demirhan, F.; Çağatay, B.; Demir, D.; Baya, M.; Daran, J.-C.; Poli, R. *Eur. J. Inorg. Chem.* **2006**, *2006*, 757.
(14) Joó, F.; Kovács, J.; Bényei, A. C.; Kathó, Á. *Angew. Chem., Int. Ed.* **1998**, *37*, 969.
(15) Breno, K. L.; Ahmed, T. J.; Pluth, M. D.; Balzarek, C.; Tyler, D. R. *Coord. Chem. Rev.* **2006**, *250*, 1141.
(16) Sarkar, S.; Li, S.; Wayland, B. B. *J. Am. Chem. Soc.* **2010**, *132*, 13569.
(17) Sarkar, S.; Li, S.; Wayland, B. B. *Inorg. Chem.* **2011**, *50*, 3313.
(18) Cheung, C. W.; Fung, H. S.; Lee, S. Y.; Qian, Y. Y.; Chan, Y. W.; Chan, K. S. *Organometallics* **2010**, *29*, 1343.
(19) Fu, X.; Li, S.; Wayland, B. B. *J. Am. Chem. Soc.* **2006**, *128*, 8947.
(20) Fu, X.; Li, S.; Wayland, B. B. *Inorg. Chem.* **2006**, *45*, 9884.
(21) Fu, X.; Wayland, B. B. *J. Am. Chem. Soc.* **2004**, *126*, 2623.
(22) Fu, X.; Wayland, B. B. *J. Am. Chem. Soc.* **2005**, *127*, 16460.
(23) Fu, X.; Basickes, L.; Wayland, B. B. *Chem. Commun.* **2003**, 520.
(24) Helfer, D. S.; Phaho, D. S.; Atwood, J. D. *Organometallics* **2006**, *25*, 410.
(25) Pryadun, R.; Sukumaran, D.; Bogadi, R.; Atwood, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 12414.
(26) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181.
(27) Demirhan, F.; Taban, G.; Baya, M.; Dinoi, C.; Daran, J.-C.; Poli, R. *J. Organomet. Chem.* **2006**, *691*, 648.
(28) Li, S.; Sarkar, S.; Wayland, B. B. *Inorg. Chem.* **2009**, *48*, 8550.
(29) Jouyban, A.; Soltanpour, S. *J. Chem. Eng. Data* **2010**, *55*, 2951.
(30) Chmielewska, A.; Zurada, M.; Klimaszewski, K.; Bald, A. *J. Chem. Eng. Data* **2008**, *54*, 801.
(31) Biffinger, J. C.; Uppaluri, S.; Sun, H.; DiMagno, S. G. *ACS Catal.* **2011**, *1*, 764.
(32) Sun, H.; Xue, F.; Nelson Andrew, P.; Redepenning, J.; DiMagno Stephen, G. *Inorg. Chem.* **2003**, *42*, 4507.
(33) Bunn, A. G.; Wayland, B. B. *J. Am. Chem. Soc.* **1992**, *114*, 6917.
(34) Coffin, V. L.; Brennen, W.; Wayland, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 6063.
(35) Cui, W.; Wayland, B. B. *J. Am. Chem. Soc.* **2006**, *128*, 10350.
(36) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941.
(37) Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.
(38) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1989**, *111*, 5010.
(39) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 1259.
(40) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305.
(41) Wayland, B. B.; Newman, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 6472.
(42) Wayland, B. B.; Sherry, A. E.; Bunn, A. G. *J. Am. Chem. Soc.* **1993**, *115*, 7675.
(43) Wayland, B. B.; Sherry, A. E.; Poszmik, G.; Bunn, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 1673.
(44) Wayland, B. B.; Van Voorhees, S. L.; Del Rossi, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 6513.
(45) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302.
(46) Zhang, X.-X.; Parks, G. F.; Wayland, B. B. *J. Am. Chem. Soc.* **1997**, *119*, 7938.
(47) Zhang, X.-X.; Wayland, B. B. *J. Am. Chem. Soc.* **1994**, *116*, 7897.

(48) Choi, K. S.; Lai, T. H.; Lee, S. Y.; Chan, K. S. *Organometallics* **2011**, *30*, 2633.
(49) Fung, H. S.; Li, B. Z.; Chan, K. S. *Organometallics* **2010**, *29*, 4421.
(50) Choi, K. S.; Chiu, P. F.; Chan, K. S. *Organometallics* **2010**, *29*, 624.
(51) Au, C. C.; Lai, T. H.; Chan, K. S. *J. Organomet. Chem.* **2010**, *695*, 1370.
(52) Lai, T. H.; Chan, K. S. *Organometallics* **2009**, *28*, 6845.
(53) Fung, H. S.; Chan, Y. W.; Cheung, C. W.; Choi, K. S.; Lee, S. Y.; Qian, Y. Y.; Chan, K. S. *Organometallics* **2009**, *28*, 3981.
(54) Chan, K. S.; Mak, K. W.; Tse, M. K.; Yeung, S. K.; Li, B. Z.; Chan, Y. W. *J. Organomet. Chem.* **2008**, *693*, 399.
(55) Zhang, L.; Chan, K. S. *Organometallics* **2007**, *26*, 679.
(56) Zhang, L.; Chan, K. S. *J. Organomet. Chem.* **2007**, *692*, 2021.
(57) Nelson, A. P.; DiMagno, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 8569.
(58) Wayland, B. B.; Ba, S.; Sherry, A. E. *Inorg. Chem.* **1992**, *31*, 148.
(59) Wayland, B. B.; Coffin, V. L.; Farnos, M. D. *Inorg. Chem.* **1988**, *27*, 2745.
(60) Chan, Y. W.; Chan, K. S. *Organometallics* **2008**, *27*, 4625.
(61) Del Rossi, K. J.; Zhang, X.-X.; Wayland, B. B. *J. Organomet. Chem.* **1995**, *504*, 47.
(62) Del Rossi, K. J.; Wayland, B. B. *Chem. Commun.* **1986**, 1653.
(63) Collman, J. P.; Kim, K. *J. Am. Chem. Soc.* **1986**, *108*, 7847.
(64) Collman, J. P.; Chng, L. L.; Tyvoll, D. A. *Inorg. Chem.* **1995**, *34*, 1311.
(65) Zhai, H.; Bunn, A.; Wayland, B. *Chem. Commun.* **2001**, 1294.
(66) Li, B. Z.; Fung, H. S.; Song, X.; Chan, K. S. *Organometallics* **2011**, *30*, 1984.
(67) Cheung, C. W.; Chan, K. S. *Organometallics* **2011**, *30*, 1768.
(68) Li, B. Z.; Song, X.; Fung, H. S.; Chan, K. S. *Organometallics* **2010**, *29*, 2001.
(69) Lee, S. Y.; Cheung, C. W.; Hsu, I. J.; Chan, K. S. *Inorg. Chem.* **2010**, *49*, 9636.
(70) Li, B.; Chan, K. S. *Organometallics* **2008**, *27*, 4034.
(71) Cheung, C. W.; Chan, K. S. *Organometallics* **2008**, *27*, 3043.
(72) Bhagan, S.; Wayland, B. B. *Inorg. Chem.* **2011**, *50*, 11011.
(73) Dong, S. S.; Nielsen, R. J.; Palmer, J. H.; Gray, H. B.; Gross, Z.; Dasgupta, S.; Goddard, W. A., III *Inorg. Chem.* **2011**, *50*, 764.
(74) Palmer, J. H.; Brock-Nannestad, T.; Mahammed, A.; Durrell, A. C.; VanderVelde, D.; Virgil, S.; Gross, Z.; Gray, H. B. *Angew. Chem., Int. Ed.* **2011**, *50*, 9433.
(75) Harvey, J. N. *Organometallics* **2001**, *20*, 4887.
(76) Wayland, B. B.; Coffin, V. L.; Sherry, A. E.; Brennen, W. R. *ACS Symp. Ser.* **1990**, *428*, 148.
(77) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.