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Iridium-Catalyzed Carbon−Carbon σ-Bond Hydrogenation with Water: Rate Enhancement with Iridium Hydride

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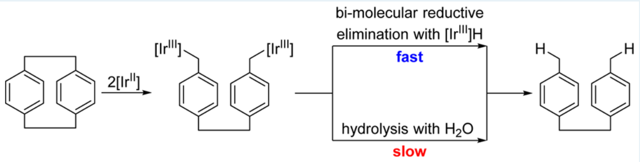
Supporting Information

ABSTRACT: Iridium porphyrins were found to be good catalysts for the carbon−carbon σ-bond hydrogenation of [2.2]paracyclophane using water in neutral conditions. Mechanistic investigations reveal the promoting effects of iridium porphyrin hydride, Ir^{III}(ttp)H, for efficient hydrogenation in the catalysis. The bimolecular reductive elimination from Ir^{III}(ttp)H and carbon−carbon bond activation intermediates speeds up the hydrogenation process.

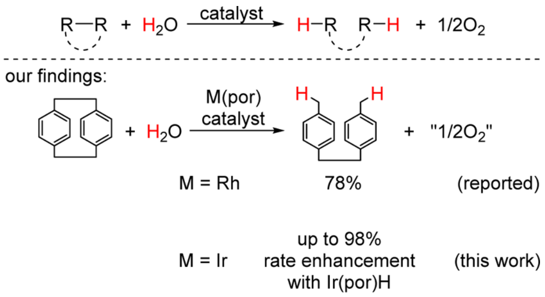


KEYWORDS: *C−C bond hydrogenation, water, iridium porphyrins, iridium hydride, bimolecular reductive elimination*

Catalytic aliphatic carbon−carbon σ-bond cleavage with transition-metal complexes in homogeneous solution is challenging due to the sterically hindered C−C bond by the surrounding C−H bonds.[1] Chelation assistance is a common strategy employed in homogeneous catalytic carbon−carbon bond activation (CCA).[2] Strain-relief is another method to achieve ring expansion,[3a] arylation,[3b] and polymerization,[3c] accompanied by a CCA process. However, these examples involve functionalized organic substrates. In contrast, examples of CCA in unfunctionalized hydrocarbon substrates are limited.[4]

Our group has reported the stoichiometric aliphatic CCA of nitrile (C(α)-C(β)) and TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) (C(Me)-C(ring)) with Rh^{II}(tmp) (tmp = tetramesitylporphyrinato dianion).[5a,b] The carbon−carbon bond of *c*-octane can be cleaved via a Rh^{II}(ttp)-catalyzed 1,2-addition of Rh^{III}(ttp)H (ttp = tetratolylporphyrinato dianion).[5c] Recently, we have developed the catalytic carbon−carbon σ-bond hydrogenation of [2.2]paracyclophane (PCP) using water as the convenient hydrogen source in neutral conditions (Scheme 1).[5d] Kinetic studies reveal a bimetalloradical CCA of PCP with Rh^{II}(tmp) in the stoichiometric reaction. We envisioned that this CCA process would be more favorable by replacing the rhodium porphyrin complexes with iridium congeners, taking the advantage of forming the stronger Ir−C bond (62 kcal/mol) than the Rh−C bond (56.9 kcal/mol) in the CCA step.[6] However, the chemistry of iridium(II) porphyrins is little explored, with the spin density equilibrating with porphyrin π radical in sterically bulky monomeric iridium(II) porphyrins, reducing its metalloradical character.[7]

Scheme 1. Catalytic Carbon−Carbon σ-Bond Hydrogenation using H_2O



There are only a few reports on stoichiometric bond activation with iridium(II) porphyrins, which are limited to H−H, C−H and aryl C-X (X = Cl, Br and I) bonds.[8] Stoichiometric C(CO)-C(α) bond activation of ketones by proposed Ir^{III}(ttp)OH intermediate has been documented.[9] Here, we report an iridium porphyrin catalyzed carbon−carbon σ-bond hydrogenation of PCP using water in neutral conditions with nearly quantitative yields and faster rate than the reported rhodium system. Furthermore, Ir^{III}(ttp)H plays an important promoting role in the catalysis. Mechanistic studies reveal the Ir^{III}(ttp)H undergoes rapid bimolecular reductive elimination with the CCA product Ir^{III}(ttp)R to give the hydrogenation product in accounting the faster hydrogenation.

Initially, we explored the catalytic efficiency with a series of iridium(III) porphyrin alkyl precatalysts, Ir^{III}(ttp)R (R = Me, Bn and ^{i}Pr) under the previously reported conditions (Table 1, eq 1).[5d] To our delight, the iridium-catalyzed protocol yielded over 90% of the carbon−carbon bond hydrogenation product **1** (Table 1, eq 1, entries 3−5), with improved yield than the rhodium-catalyzed protocol (Table 1, eq 1, entries 1 and 2).[10] Deuterium labeling experiment using D_2O yielded **1**-*d* with 34% terminal benzylic deuterium contents with respect to the

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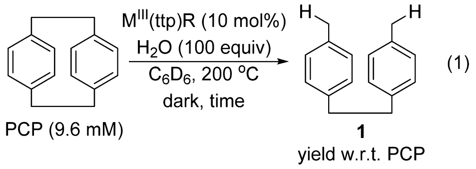
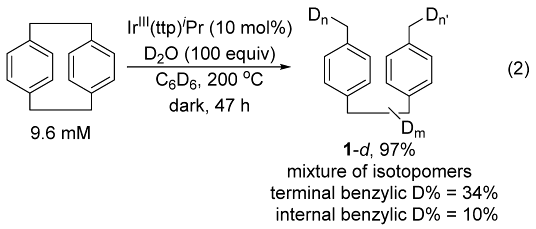
Table 1. Catalytic Carbon−Carbon σ-Bond Hydrogenation of PCP using Water

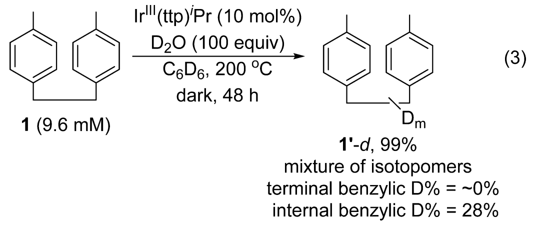


entry	M	R	time/h	yield of **1** (%)
1[a]	Rh	Me	54	78
2	Rh	^{i}Pr	50	68
3	Ir	Me	53	94
4	Ir	Bn	48	95
5	Ir	^{i}Pr	41	98
6[b]	Ir	^{i}Pr	55	97
7	Ir	H	35	96

[a] Ref 5d. [b] No H_2O added, except solvent residual H_2O (~3 equiv).

six terminal benzylic positions, in accordance to monodeuteration at both ends (eq 2).[11] A control experiment showed that **1** was inactive toward H/D exchange at the terminal benzylic positions (eq 3). This strongly supports that H_2O is the hydrogenating agent. Furthermore, dehydrogenation product of **1**, 4,4′-dimethylstilbene, was not observed. This accounts for the improved yields of **1** in the iridium-catalyzed protocol.[12] The much less internal benzylic H/D exchange further accounts for the slow rate of **1** in benzylic C−H activation which can lead to 4,4′-dimethylstilbene via β-H elimination. Indeed, the K_2CO_3-promoted benzylic C−H activation of toluene required higher temperature (200 °C vs 120 °C) and K_2CO_3 loading (20 equiv vs 10 equiv) for iridium than rhodium porphyrins, suggesting a less reactive nature of iridium porphyrins toward C−H activation.





The reactivity of the iridium(III) porphyrin alkyl precatalysts followed the order: $Ir^{III}(ttp)^iPr > Ir^{III}(ttp)Bn > Ir^{III}(ttp)Me$. When $Ir^{III}(ttp)Me$ was replaced with $Ir^{III}(ttp)^iPr$, the reaction time was reduced from 53 to 41 h (Table 1, eq 1, entries 3 and 5). The similar catalytic activity of $Rh^{III}(ttp)Me$ and $Rh^{III}(ttp)^iPr$ suggests the high reactivity of $Ir^{III}(ttp)^iPr$ is unique (Table 1, eq 1, entries 1 and 2). Interestingly, the catalytic hydrogenation also proceeded smoothly at very low water content, yielding 97% of **1** in 55 h, without significant lengthening of the reaction time (Table 1, eq 1, entry 6). At first we reasoned that the in situ generation of $Ir^{II}(ttp)$ for CCA from the precatalyst is important. Indeed, $Ir^{III}(ttp)H$ precatalyst, a facile precursor of $Ir^{II}(ttp)$ via dehydrogenation, catalyzed the hydrogenation of PCP to **1** in the shortest time of 35 h (Table 1, eq 1, entry 7). $Ir^{III}(ttp)H$ likely undergoes thermal dehydrogenative dimerization to give $Ir^{II}_2(ttp)_2$, which is in equilibrium with $Ir^{II}(ttp)$.[8c]

To further verify the reactivity trend of $Ir^{III}(ttp)R$ precatalysts (R = Me, Bn and ^{i}Pr), we examined the hydrolysis of $Ir^{III}(ttp)R$ individually at 200 °C and observed that their hydrolysis rates followed the order: $Ir^{III}(ttp)^iPr \approx Ir^{III}(ttp)Bn \gg Ir^{III}(ttp)Me$ (Table 2, eq 4). This trend roughly agrees with those observed in Table 1 (entries 3−5).

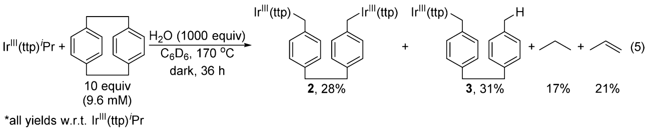
Table 2. Hydrolysis of $Ir^{III}(ttp)R$

$$\underset{0.96\ \text{mM}}{Ir^{III}(ttp)R} + \underset{1000\ \text{equiv}}{H_2O} \xrightarrow[-1/2O_2]{C_6D_6,\ 200\ ^\circ C,\ \text{dark, time}} Ir^{III}(ttp)H + R\text{-}H \quad (4)$$

entry	R	time/h	yield w.r.t. $Ir^{III}(ttp)R$ (%)	
			$Ir^{III}(ttp)H$	R−H
1[a]	Me	75	8	not observed[b]
2	Bn	43	56	72
3	^{i}Pr	44	76	26[c]

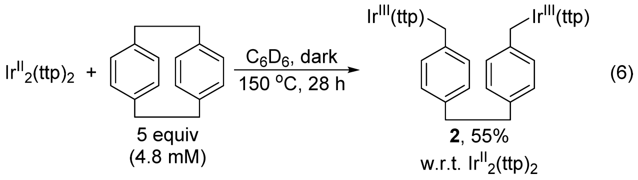
[a] 81% $Ir^{III}(ttp)Me$ recovery. [b] The $[CH_4]$ in C_6D_6 may be too low to be observed. [c] 68% propene was formed.

To gain understanding why $Ir^{III}(ttp)^iPr$ is the most active $Ir^{III}(ttp)R$ precatalyst, we monitored the initial stage of the catalysis at 170 °C by ^1H NMR spectroscopy (eq 5 and Table S1, eq S6, Figure S1). After 3 h, 15% of $Ir^{III}(ttp)^iPr$ was consumed to produce 10% of CCA product di-Ir **2**. $Ir^{III}(ttp)^iPr$ reacted via β-H elimination to give propene in 6% yield. However, $Ir^{III}(ttp)H$ was not observed and probably further reacted rapidly. Further heating to 6 h produced both CCA products di-Ir **2** and mono-Ir **3** in 16% and 8% yields, respectively. Hydrolysis of $Ir^{III}(ttp)^iPr$ was now observed to yield 5% of propane and $Ir^{III}(ttp)OH$, which was reduced quickly to give $Ir^{II}_2(ttp)_2$.[8d,13] $Ir^{II}_2(ttp)_2$ underwent rapid CCA with PCP and was not observed. After 36 h, $Ir^{III}(ttp)^iPr$ was completely consumed to yield 28% of **2**, 31% of **3**, 17% of propane and 21% of propene (eq 5). No benzylic C−H activation of PCP was observed to form any Ir^{III}(ttp)-(cyclophanyl) intermediates.[14] Hence, both $Ir^{II}_2(ttp)_2$ and $Ir^{III}(ttp)H$ were possible intermediates for the CCA of PCP. Their stoichiometric reactions with PCP were then examined independently.



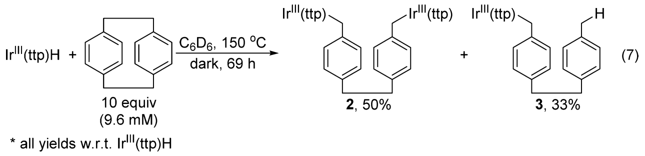
*all yields w.r.t. $Ir^{III}(ttp)^iPr$

At 150 °C, $Ir^{II}_2(ttp)_2$ was completely reacted with PCP to give 55% yield of **2** in 28 h (eq 6 and Table S3, eq S8). This

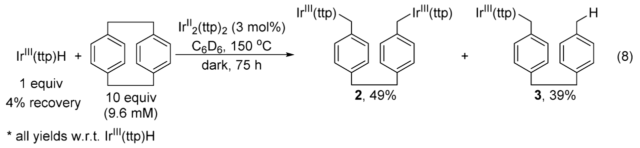


suggests a CCA process with Ir^{II}(ttp) metalloradical, formed from the thermal dissociation of the weak $(ttp)Ir^{II}-Ir^{II}(ttp)$ bond (~20 kcal/mol).[15] The moderate reaction yield was likely attributed to the decomposition of $Ir^{II}_2(ttp)_2$ via reaction with solvent residual water, which will be discussed in detail (eq 10).

Unexpectedly, Ir^{III}(ttp)H reacted with PCP at 150 °C in 35 h to give mono-Ir **3** as the major CCA product in 21% yield, and di-Ir **2** as the minor CCA product in 12% yield, with 37% recovery yield of Ir^{III}(ttp)H (eq 7 and Table S4, eq S9, Figure S2). Interestingly, **2** became the major product upon further heating to 69 h, yielding 50% of **2** and 33% of **3** as the minor product, with complete consumption of Ir^{III}(ttp)H (eq 7). The formation of **2** can be well accounted by the in situ formation of Ir^{II}(ttp) from Ir^{III}(ttp)H for the CCA of PCP. However, the preferential formation of **3** at the initial stage of reaction was unexpected. Owing to the slow hydrolysis of Ir^{III}(ttp)Bn at 200 °C (Table 2, eq 4, entry 2), which served as a simplified structural model of **2**, the hydrolysis of **2** to **3** by the solvent residual water present at 150 °C was not compatible with the fast formation of **3**. We suspect that the excess Ir^{III}(ttp)H present is promoting other reaction channels to form **3** in a much faster manner. Based on the precedented reactivity of Rh^{II}(por) and Rh^{III}(por)H (por = porphyrin ligand), the following two channels were proposed: (1) Ir^{II}(ttp)-catalyzed 1,2-addition of Ir^{III}(ttp)H across the benzylic C−C bond of PCP to form **3**;[5c] or (2) bimolecular reductive elimination from Ir^{III}(ttp)H and **2** to give **3** and $Ir^{II}_2(ttp)_2$.[16a] These two possibilities were then investigated.



Ir^{III}(ttp)H with 3 mol% of $Ir^{II}_2(ttp)_2$ reacted with PCP at 150 °C in C_6D_6 to yield 49% of **2** and 39% of **3** in 75 h (eq 8). No rate enhancement was observed for the formation of **3**. (Table S5, eq S10, Figure S3). Therefore, the Ir^{II}(ttp)-catalyzed 1,2-addition of Ir^{III}(ttp)H pathway does not operate.[17]



We then examined whether Ir^{III}(ttp)H promoted the bimolecular reductive elimination using Ir^{III}(ttp)Bn as the model to give toluene as an alternative hydrogenation pathway. Wayland has reported the bimolecular reductive elimination of *n*-propylbenzene from Rh^{III}(oep)H and $Rh^{III}(oep)(CH(Ph)CH_2CH_3)$ (oep = octaethylporphyrinato dianion).[16a] Elimination of MeOH from Rh^{III}(oep)H and $Rh^{III}(oep)CH_2OH$ has also been observed.[16b] In the reversible C−H bond activation of alkanes and toluene (R-H) with rhodium(II) porphyrin complexes Rh^{II}(por) to give Rh^{III}(por)R and Rh^{III}(por)H, the bimolecular reductive elimination of R-H from Rh^{III}(por)H and Rh^{III}(por)R is more favorable at elevated temperature.[16c,d] We propose that Ir^{III}(ttp)H can react similarly with **2** and **3** to afford **1** as the final product in the catalytic system to speed up the hydrogenation process. To our delight, Ir^{III}(ttp)H reacted with Ir^{III}(ttp)Bn at 200 °C to give 78% yield of toluene in 43 h (eq 9). The initial rates of Ir^{III}(ttp)Bn consumption and toluene formation were 3 times faster than that of Ir^{III}(ttp)Bn hydrolysis, estimated from the initial 3 h of the two reaction profiles (Table S6, eq S11, Figures S4, S5 and S6), supporting the promoting effect of Ir^{III}(ttp)H on faster hydrogenation. Hence, higher water loading for the hydrolysis of **2** and **3** is not a must, which agrees with the results depicted in Table 1, eq 1, entry 6.

$$\underset{\substack{\text{1 equiv}\\ \text{(0.96 mM)}}}{Ir^{III}(ttp)Bn} + \underset{\text{1 equiv}}{Ir^{III}(ttp)H} \xrightarrow[\text{200 °C, 43 h}]{C_6D_6} \underset{\text{78\% w.r.t. }Ir^{III}(ttp)Bn}{BnH} \qquad (9)$$

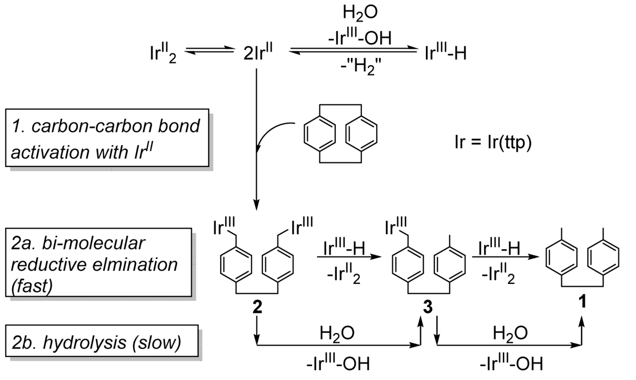
The proposed bimolecular reductive elimination with Ir^{III}(ttp)H is consistent with the catalytic hydrogenation of PCP because Ir^{III}(ttp)H can be generated continuously in the catalysis. $Ir^{III}(ttp)^iPr$ undergoes *β*-H elimination to give Ir^{III}(ttp)H. Alternatively, $Ir^{II}_2(ttp)_2$ reacts with H_2O to give Ir^{III}(ttp)H and Ir^{III}(ttp)OH. Independent study showed that $Ir^{II}_2(ttp)_2$ reacted readily with excess H_2O in C_6D_6 at mild temperatures of 27 to 50 °C to give 55% yield of Ir^{III}(ttp)H (eq 10 and Table S7, eq S12, Figure S7).[18] The yield was only moderate as we observed gradual formation of deep brown precipitates in the sealed NMR tube, presumably due to the oxidative decomposition of the iridium porphyrin species.

$$\underset{\substack{\text{0.3 mM}\\ \text{8\% recovery}}}{Ir^{II}_2(ttp)_2} + \underset{\text{3200 equiv}}{H_2O} \xrightarrow[\text{27-50 °C, 110 h}]{C_6D_6\text{, dark}} \underset{\text{55\%}}{Ir^{III}(ttp)H} \qquad (10)$$

* all yields w.r.t. $Ir^{II}_2(ttp)_2$

On the basis of the previous understandings of rhodium porphyrin catalyzed hydrogenation of PCP using H_2O and current findings, a catalytic cycle with three key steps is proposed in Scheme 2 using Ir^{III}(ttp)H precatalyst as example: (1) C−C bond activation and (2) hydrogenation.

Scheme 2. Proposed Catalytic Cycle



(1). Precatalyst activation. Ir^{III}(ttp)H and $Ir^{II}_2(ttp)_2$ can be interconverted via dehydrogenation[8c] or oxidative addition with H_2O,[18] respectively. $Ir^{II}_2(ttp)_2$ equilibrates with Ir^{II}(ttp) metalloradical upon the thermolysis of (ttp)Ir−Ir(ttp) bond.[15] In a productive process, Ir^{II}(ttp) cleaves the benzylic C−C bond of PCP to give di-Ir **2**.

(2). Hydrogenation. With continuous generation of Ir^{III}(ttp)H in the catalysis, the CCA products **2** and **3** undergo faster bimolecular reductive elimination with Ir^{III}(ttp)H to yield **1** as the final hydrogenation product (step 2a). The slow hydrolysis of **2** and **3** acts as a minor hydrogenation process (step 2b).

In summary, we have discovered a fast and high yielding iridium porphyrin catalyzed hydrogenation of PCP using H_2O in neutral conditions. Despite the partial metalloradical character of iridium(II) porphyrins, this report shows its promising potential on C−C bond activation. In addition, Ir^{III}(ttp)H, continuously derived from $Ir^{II}_2(ttp)_2$ and H_2O, promoted the bimolecular reductive elimination with the CCA intermediates to achieve faster hydrogenation. This provides new insight on more efficient hydrogenation by speeding up the in situ formation of Ir^{III}(ttp)H.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, ^1H, $^{13}C\{^1H\}$ NMR and HRMS spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01005.

(PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(10) The saturated $[H_2O]$ in C_6H_6 at 200 °C has been reported to be ∼2 M. We assume H_2O/C_6D_6 system would behave similarly. Therefore, H_2O was completely dissolved to give $[H_2O]$ in C_6D_6 = 0.96 M in the catalysis conditions. For the solubility of H_2O in C_6H_6 from 0 to 250 °C, see: Góral, M.; Wiśniewska-Goclowska, B.; Mączyński, A. *J. Phys. Chem. Ref. Data* **2004**, *33*, 1159−1188.

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(12) In the rhodium-catalyzed protocol, ∼10% of 4,4′-dimethylstilbene was formed, likely from the dehydrogenation of **1**.

(13) (a) The OH^- axial ligand can act as one electron reducing agent, see: Sawyer, D. T.; Roberts, J. L., Jr. *Acc. Chem. Res.* **1988**, *21*, 469−476. (b) For Rh^{III}(ttp)OH example, see: Choi, K. S.; Lai, T. H.; Lee, S. Y.; Chan, K. S. *Organometallics* **2011**, *30*, 2633−2635.

(14) In a separate deuterium labelling experiment with gradual temperature increase from 60 to 130 °C, benzylic H/D exchange of PCP was not observed before the CCA (Table S2 and eq S7).

(15) There are no reports on the Ir-Ir BDE in $Ir^{II}_2(ttp)_2$. Hence, estimation from sterically similar $Ir^{II}_2(txp)_2$ is adopted, reference 6a. The equilibrium constants at 150 and 200 °C were estimated to be 3.1×10^{-4} and 3.8×10^{-3}, respectively.

(16) For rhodium porphyrin examples, see: (a) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* **1985**, *107*, 7941−7944. (b) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887−1888. (c) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305−5311. (d) Cui, W.; Wayland, B. B. *J. Am. Chem. Soc.* **2004**, *126*, 8266−8274.

(17) The Ir^{II}(ttp)-catalyzed 1,2-addition pathway is estimated to be 2.5 kcal/mol less favorable than the bimetalloradical CCA with Ir^{II}(ttp). See p S24 in SI.

(18) The oxidative addition of iridium(II) porphyrin complexes with H_2O has been suggested to be thermodynamically more favorable than the rhodium(II) analogues. (a) Bhagan, S.; Wayland, B. B. *Inorg. Chem.* **2011**, *50*, 11011−11020. For rhodium(II) porphyrin examples, see: (b) Fu, X.; Li, S.; Wayland, B. B. *Inorg. Chem.* **2006**, *45*, 9884−9889. (c) Sarkar, S.; Li, S.; Wayland, B. B. *J. Am. Chem. Soc.* **2010**, *132*, 13569−13571. For a cobalt(II) complex example, see: (d) Sokol, C. S.; Brubaker, C. H., Jr. *J. Inorg. Nucl. Chem.* **1968**, *30*, 3267−3271.