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# Secondary Coordination Sphere Interactions Facilitate the Insertion Step in an Iridium(III) $CO_2$ Reduction Catalyst

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S *Supporting Information*

**ABSTRACT:** There is considerable interest in both catalysts for $CO_2$ conversion and understanding how $CO_2$ reacts with transition metal complexes. Here we develop a simple model for predicting the thermodynamic favorability of $CO_2$ insertion into Ir(III) hydrides. In general this reaction is unfavorable; however, we demonstrate that with a hydrogen bond donor in the secondary coordination sphere it is possible to isolate a formate product from this reaction. Furthermore, our $CO_2$ inserted product is one of the most active water-soluble catalysts reported to date for $CO_2$ hydrogenation.

The decline in the world's petroleum reserves and concerns about the environmental consequences of fossil fuel use have led to a search for alternative carbon sources.[1] $CO_2$ is a particularly attractive feedstock owing to its high abundance, low cost and toxicity, and relative ease of transport.[2,3] However, the catalytic conversion of $CO_2$ is complicated by its high kinetic and thermodynamic stability. One promising approach has been the catalytic hydrogenation of $CO_2$ to formic acid, which is in wide use as a preservative and an insecticide and as an acid, a reductant, and a carbon source in synthetic chemistry.[4−6] Homogeneous Fe,[7] Ru,[4,8] Rh,[4,8] and Ir[9,10] catalysts have all been shown to be active for $CO_2$ hydrogenation. Nozaki and co-workers recently described a remarkable advance in catalyst activity, with turnover numbers up to $3.5 \times 10^6$ reported at 120 °C and 6.0 MPa (of a 1:1 mixture of $CO_2$ and $H_2$) (Figure 1).[11] The first step in the catalytic cycle was proposed to be the insertion of $CO_2$ into an Ir−H bond to generate an Ir formate, but no intermediates were isolated. Related computational work by Ahlquist suggests that the $CO_2$ insertion proceeds through an unusual outer sphere mechanism in which a nucleophilic hydride attacks $CO_2$.[12]

A goal of our laboratory is to understand how $CO_2$ inserts into M−R $\sigma$-bonds, and we have previously explored $CO_2$ insertion into a variety of four-coordinate Ni and Pd hydride, methyl, and allyl complexes.[13−16] In this work we have built a simple model for determining the thermodynamic favorability of $CO_2$ insertion into six-coordinate Ir hydrides and show that it is unfavorable in most cases.

Several difficult reactions have recently been facilitated through the use of noncovalent interactions between a substrate and the secondary coordination sphere of a transition metal complex.[17] For example, DuBois has used a pendant amine to assist in the reduction of $H^+$ to hydrogen,[18] Bercaw and Labinger have used a pendant borane to facilitate hydride transfer and C−C bond forming reactions,[19] and Borovik and co-workers have used H-bonds to assist in dioxygen activation.[20] Here, by incorporating an H-bond donor in the secondary coordination sphere, we experimentally demonstrate the first example of $CO_2$ insertion into an Ir−H bond and show computationally that the H-bond donor lowers the kinetic barrier for the reaction. Furthermore we show that this $CO_2$ inserted product is an *air stable* highly active *water-soluble* catalyst for the hydrogenation of $CO_2$.

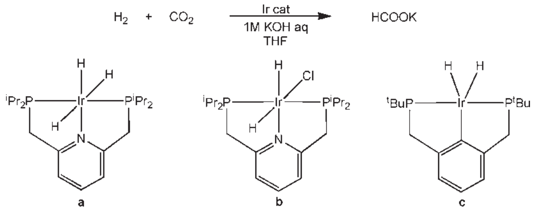

**Figure 1.** Ir catalysts utilized by Nozaki for homogeneous $CO_2$ hydrogenation.[10]

Our initial computational studies focused on the proposed first step in the Nozaki system which involves $CO_2$ insertion into one of the *trans* hydrides of complex **a** (Figure 1).[11] We chose a model Ir trihydride complex $(PN^{Py}P)IrH_3$ ($PN^{Py}P$ = 2,6-$C_6H_3$-$(CH_2PMe_2)_2$) with methyl substitutions in place of the bulky $^i$Pr groups of **a**. We find computationally that insertion of $CO_2$ into one of the *trans* hydrides is thermodynamically unfavorable by 3.1 kJ $mol^{-1}$ (Gibbs free energy, 298.15 K, 1 atm, with solvent corrections for THF; Table 1).[21] This is consistent with Nozaki's experimental data, which showed that, in THF, $CO_2$ insertion did not proceed to completion but gave a mixture of starting materials and a proposed Ir formate product at rt.[11] Insertion into the hydride coplanar with the pincer ligand (*trans* to the N) is significantly more unfavorable (65.5 kJ $mol^{-1}$), presumably because the Ir−H bond which needs to be broken is stronger. Nozaki also demonstrated that the Ir chloride complex **b** is an active catalyst for $CO_2$ hydrogenation. Our calculations indicate that $CO_2$ insertion into $(PN^{Py}P)IrH_2Cl$ is significantly more thermodynamically unfavorable than for $(PN^{Py}P)IrH_3$, which may explain the slower rates observed in catalysis using the chloride complex (Table 1). Insertion into the hydride *trans* to the Cl is uphill by 82.4 kJ $mol^{-1}$, whereas insertion into the hydride coplanar with the $PN^{Py}P$ ligand is uphill by only 67.7 kJ $mol^{-1}$. This suggests that, for $(PN^{Py}P)IrH_2Cl$, $CO_2$ insertion occurs with the opposite selectivity than in the case of $(PN^{Py}P)IrH_3$.[22]

Our results for $CO_2$ insertion into **a** and **b** suggest that a major factor in determining the thermodynamic favorability for $CO_2$

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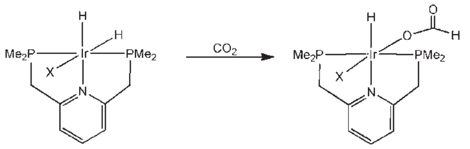
Table 1. Comparative Computational Energetics for $CO_2$ Insertion into a Series of Ir−H Complexes Supported by $PN^{Py}P$ Ligands with Variation of the Ligand *trans* to the Hydride



| *Trans*-substituent (X) | $\Delta G°$ (kJ $mol^{-1}$)$^a$ | Ir−H Bond Length (Å) | NBO Charge on H ($e^-$) |
|---|---|---|---|
| H | 3.1 (65.5) | 1.680 (1.589) | −0.012 (0.129) |
| Ph | 4.7 (59.5) | 1.666 (1.586) | −0.009 (0.126) |
| Me | 6.0 (62.2) | 1.665 (1.589) | −0.012 (0.127) |
| OH | 46.3 (48.8) | 1.607 (1.591) | 0.050 (0.090) |
| Cl | 82.4 (67.7) | 1.586 (1.585) | 0.104 (0.113) |
| I | 87.4 (71.4) | 1.588 (1.584) | 0.113 (0.127) |

[a] $\Delta G°$ is Gibbs free energy, 298.15 K, 1 atm, with solvent corrections for THF. Numbers in parentheses refer to values for the hydride coplanar with the pincer ligand.

insertion into the Ir−H bond is the *trans*-influence of the ligand opposite the hydride. We propose that ligands which exert a strong *trans*-influence weaken the Ir−H bond, increase the nucleophilicity of the hydride, and make $CO_2$ insertion more favorable. Moreover, we propose that the cleavage of the Ir−H bond is the dominant factor in predicting the thermodynamics of $CO_2$ insertion, so that the energy differences associated with the strength of the new Ir−O bond can essentially be ignored. Computationally, the nucleophilicity of the hydride can be estimated by calculating the NBO charge on the hydride (a related method has been used previously);[23] the more negative the charge, the greater the nucleophilicity. To test our hypothesis that more nucleophilic hydrides make $CO_2$ insertion more favorable, we varied the ligand *trans* to the hydride in the $PN^{Py}P$ framework and calculated the energies for $CO_2$ insertion (Table 1). Our results show that a strongly donating *trans* ligand makes $CO_2$ insertion more thermodynamically favorable. There is a strong correlation between the NBO charge on the hydride and the thermodynamics of $CO_2$ insertion, suggesting that this provides a simple model for predicting the favorability of insertion (Figure 2).

Hydrides are one of the strongest *trans* influence ligands.[24] We were interested in synthesizing an Ir−H complex that could perform a thermodynamically favorable $CO_2$ insertion in order to design better catalysts for $CO_2$ hydrogenation. To direct our synthetic studies we performed additional calculations on the energetics of $CO_2$ insertion into a number of different Ir−H complexes with *trans* hydrides (Table 2). These species included *trans*-$(PMe_3)_3IrH_3$, *trans*-$(NHC)_3IrH_3$ (NHC = 1,3-dimethyl-4,5-dihydro-2*H*-imidazol-2-ylidene), *trans*-$(PMe_3)_2(NHC)IrH_3$, and $(PNP)IrH_3$ (**1**) (PNP = $HN(^iPr_2PC_2H_4)_2$), which features an H-bond donor in the secondary coordination sphere. All of these systems except for the tris NHC complex are related to experimentally observed complexes.[25−27] In general $CO_2$ insertion is disfavored; the exceptions are insertion into one of the *trans*-hydrides of $(NHC)_3IrH_3$ and **1**. Furthermore, the phosphine and NHC supported complexes displayed a similar trend between the NBO charge on the hydride and the thermodynamics of $CO_2$ insertion, consistent with our results on the $PN^{Py}P$ system (vide supra), indicating that our model also applies to monodentate ligand sets (Figure 2). However, Figure 2 clearly shows that $CO_2$ insertion into **1** is significantly more favorable than our model would predict. Examination of the optimized structure of the $CO_2$ inserted product **2** showed the expected hydrogen bond between the N−H moiety of the ligand and the noncoordinated oxygen atom of the formate ligand. Our simple model based on the NBO charge of the hydride in the starting material is unable to account for this interaction in the secondary coordination sphere of the product.

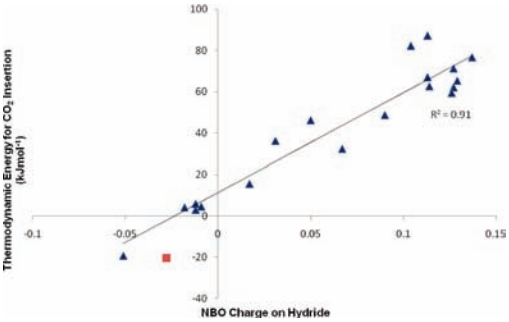


**Figure 2.** Graph of NBO charge on hydride against the thermodynamic favorability of $CO_2$ insertion into the Ir−H bond. Square point is compound **1** (which was not used for calculating the $R^2$ value).

Table 2. Comparative Computational Energetics for $CO_2$ Insertion into a Series of Ir−H Complexes with Variation of the L Type Ligands

| Compound | $\Delta G°$ (kJ $mol^{-1}$)$^a$ | Ir−H Bond Length (Å) | NBO Charge on H ($e^-$) |
|---|---|---|---|
| *trans*-$(PMe_3)_3IrH_3$ | 15.7 (62.8) | 1.681 (1.613) | 0.017 (0.114) |
| *trans*-$(NHC)_3IrH_3$ | −19.2 (36.3) | 1.662 (1.640) | −0.051 (0.031) |
| *trans*-$(PMe_3)_2(NHC)IrH_3$ | 4.23 (32.4) | 1.673 (1.640) | −0.018 (0.067) |
| $(PNP)IrH_3$ (**1**) | −20.4 (76.8) | 1.678 (1.584) | −0.028 (0.137) |

[a] $\Delta G°$ is Gibbs free energy, 298.15 K, 1 atm, with solvent corrections for THF. Numbers in parentheses refer to values for the hydride *trans* to the L type ligand.

Complex **1** was prepared via a literature protocol[27] and tested for $CO_2$ insertion reactivity. Gratifyingly, **1** inserted $CO_2$ in less than 5 min at rt to form air and moisture stable **2**, which was fully characterized (eq 1). In the $^1H$ NMR spectrum, compound **2** features a characteristic resonance for the formate proton at $\delta$ 8.98 ppm along with two hydride signals at $\delta$ −19.01 and −28.48 ppm. The IR spectrum displays two inequivalent $CO_2$ stretches at 1600 and 1335 $cm^{-1}$, which shift to 1560 and 1315 $cm^{-1}$ when the complex was prepared from $^{13}C$-labeled $CO_2$ (calcd: 1564 and 1305 $cm^{-1}$).[21] The difference between the two $CO_2$ stretches is greater than 200 $cm^{-1}$, characteristic of a monodentate carboxylate ligand.[28] The N−H stretch at 3182 $cm^{-1}$ suggests that the N−H group is involved in a H-bond, as demonstrated by computation. Further evidence for a H-bond was obtained from the X-ray structure of **2** (Figure 3). Although the H-atom of the N−H moiety could not be located, the formate group is oriented appropriately to form a N−H···O hydrogen bond.[27] The O−H bond distances for the two independent molecules in the unit cell are 1.95 and 1.93 Å. Other bond angles and distances are consistent with those previously observed in $(PNP)IrH_2Cl$.[27] The insertion of $CO_2$ is reversible, as exposure of **2** to 1 atm of

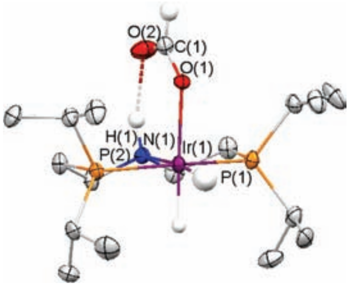


**Figure 3.** X-ray structure of **2** (selected hydrogen atoms omitted for clarity; only one of two independent molecules shown). Selected bond lengths (Å) and angles (deg): Ir(1)−P(1) 2.222(2), Ir(1)−P(2) 2.239(2), Ir(1)−N(1) 2.149(6), Ir(1)−O(1) 2.155(5), O(1)−C(1) 1.247(11), O(2)−C(1) 1.196(12), P(1)−Ir(1)−P(2) 166.85(8), P(1)−Ir(1)−N(1) 83.82(18), P(2)−Ir(1)−N(1) 83.32(18), P(1)−Ir(1)−O(1) 92.04(16), P(2)−Ir(1)−O(1) 92.20(15), N(1)−Ir(1)−O(1) 96.7(2), Ir(1)−O(1)−C(1) 125.2(5), O(1)−C(1)−O(2) 127.2(9).

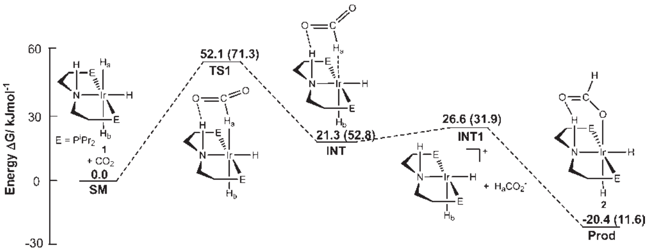
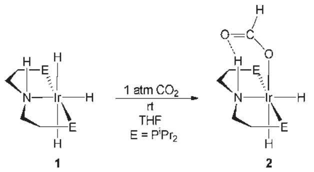


**Figure 4.** Reaction pathway for insertion of $CO_2$ into **1**. All energies are solvent corrected (THF) Gibbs free energies. Numbers in parentheses are for insertion into $H_b$.

$^{13}$C-labeled $CO_2$ at rt resulted in rapid incorporation of $^{13}$C into the formate ligand of **2**.



(1)

DFT calculations were performed to probe the pathway for $CO_2$ insertion into **2**. The effect of the H-bond donor can be established by comparing $CO_2$ insertion into the hydrides syn and anti to the N−H bond and thus into $H_a$ or $H_b$, respectively (Figure 4). $CO_2$ insertion into $H_b$ is thermodynamically uphill by 11.6 kJ mol$^{-1}$ without H-bond assistance but favorable by −20.4 kJ mol for $H_a$ with H-bonding. This suggests that the H-bond provides ~30 kJ mol$^{-1}$ of stabilization, although it should be noted that a six-membered ring incorporating the H-bond is formed in **2**.

The pathway for $CO_2$ insertion into both $H_a$ and $H_b$ is the same and involves nucleophilic attack on $CO_2$, leading to a H-bound formate intermediate, followed by dissociation of the formate and recoordination as an O-bound species. This is summarized in Figure 4. The rate-limiting step is nucleophilic attack on $CO_2$ by the hydride, and there is no precoordination of $CO_2$ to Ir. This pathway is similar to that proposed by Ahlquist for Nozaki's complex **a**.[12]

Our calculations show that, in addition to making $CO_2$ insertion more thermodynamically favorable, the H-bond donor also lowers the activation energy by 19.2 kJ mol$^{-1}$, from 71.3 to 52.1 kJ mol$^{-1}$. The effect of the H-bond donor on the transition state geometry (Figure 5) can be seen by comparing the Ir−$H_a$−C bond angle for $CO_2$ insertion into $H_a$ (152.2°) with the corresponding bond angle Ir−$H_b$−C for $CO_2$ insertion into $H_b$ (172.4°). This reduction in bond angle allows for a stabilizing H-bonding interaction between O(2) and H(1). A similar effect causes stabilization of the first intermediate in which the formate is bound through the H-atom to the Ir.[21]

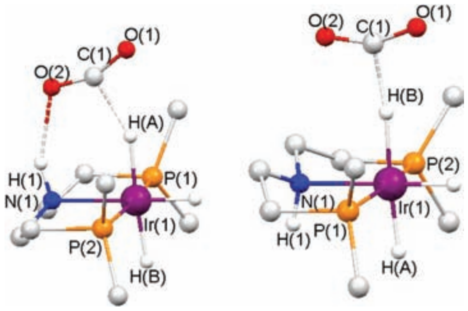


**Figure 5.** (a) Calculated transition state for $CO_2$ insertion into $H_a$ of **1**. Selected hydrogen atoms and isopropyl groups have been removed for clarity. Selected bond lengths and angles (Å or deg): Ir(1)−H(A) 1.72, C(1)−H(1) 1.80, C(1)−O(1) 1.18, C(1)−O(2) 1.20, O(2)−H(1) 2.08, Ir(1)−H(B) 1.64, Ir(1)−H(A)−C(1) 152.2. (b) Calculated transition state for $CO_2$ insertion into $H_b$ of **1**. Selected hydrogen atoms and isopropyl groups have been removed for clarity. Selected bond lengths and angles (Å or deg): Ir(1)−H(B) 1.73, C(1)−H(1) 1.69, C(1)−O(1) 1.19, C(1)−O(2) 1.20, Ir(1)−H(A) 1.64, Ir(1)−H(B)−C(1) 172.4.

**Table 3. Hydrogenation of $CO_2$ Catalyzed by 2**

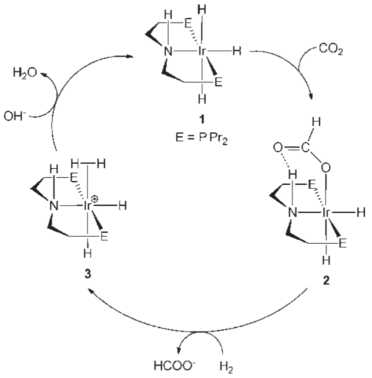
$$\underset{(1:1)}{H_2 + CO_2} \xrightarrow[\text{1 M KOH aq. (10 mL)}]{\substack{\textbf{2}\ \text{(20 nmol)} \\ 2\times10^{-4}\ \text{mol\% relative to KOH}}} \text{HCOOK}$$

| Entry | *T* (°C) | *P* (psi)$^a$ | Time (h) | Yield (%)$^b$ | TON$^c$ | TOF$^d$ |
|---|---|---|---|---|---|---|
| 1 | 125 | 800 | 24 | 1 | 3820 | 159 |
| 2 | 145 | 800 | 24 | 10 | 49400 | 2058 |
| 3 | 165 | 800 | 24 | 24 | 118000 | 4917 |
| 4 | 185 | 800 | 24 | 70 | 348000 | 14500 |
| 5 | 185 | 600 | 24 | 8 | 39000 | 1625 |
| 6 | 185 | 400 | 24 | 6 | 27828 | 1160 |
| 7 | 185 | 200 | 24 | 1 | 3932 | 164 |
| 8 | 185 | 800 | 1 | 4 | 18780 | 18780 |
| 9 | 185 | 800 | 2 | 7 | 37340 | 18670 |

$^a$ Total pressure at rt. $^b$ Yield based on $^1$H NMR analysis using sodium $d_4$-(trimethylsilyl)-1-propionate as an internal standard. The yield represents conversion of the added KOH (10 mmol). $^c$ TON = turnover number; number of moles of product formed per mole of catalyst. $^d$ TOF = turnover frequency; number of moles of product formed per mole of catalyst per hour.

With **2** in hand, we were interested in assessing its competence as a catalyst for $CO_2$ hydrogenation. The results in Table 3 show that **2** gives the highest turnover number (TON) ever reported for an air stable, water-soluble catalyst and is comparable with the best system described by Nozaki (albeit at slightly higher temperature and pressure).[11] The maximum TON is 348 000, and yields of up to 70% formate are produced.[29] The highest TOF of 18 780 is similar to the best systems reported.[6] Importantly the TOF does not decrease dramatically with time (entries 4, 8, and 9) suggesting that there is little catalyst

**Scheme 1**



decomposition. Unsurprisingly as the temperature and pressure were lowered, catalytic activity decreased.

We propose a simple mechanism for $CO_2$ hydrogenation involving displacement of coordinated formate by $H_2$ to generate the coordinated molecular hydrogen species **3**, deprotonation of **3** to form the trihydride **1**, and subsequent $CO_2$ insertion to produce **2** (Scheme 1). Compound **1** can also be used as a catalyst for $CO_2$ hydrogenation, although precautions need to be taken to ensure the solution is kept oxygen-free before pressurization.[21] Given that our stoichiometric studies indicate $CO_2$ insertion is facile, we believe that displacement of formate by $H_2$ is rate-determining. Nozaki has also previously speculated that this is the rate-limiting step for many $CO_2$ hydrogenation catalysts.[11] In our case the high pressure of $H_2$ and elevated temperatures are presumably required to promote ligand substitution.

Overall, our outer sphere based mechanism is similar to one we have recently proposed for the hydrogenation of quinolines by an Ir trihydride[26] and is consistent with that proposed by Alhquist for compound **a**.[12] However, at this stage we cannot rule out deprotonation of the amine linker to convert **2** into an amido species and subsequent release of formate.[27] The deprotonation of the ligand could also affect the $CO_2$ insertion step, and we will explore this possibility in future work. At this stage the possibility that **2** decomposes to $Ir^0$ under the reaction conditions is unlikely because control experiments indicate that Ir/C is not an active catalyst for $CO_2$ hydrogenation, but the formation of a heterogeneous system cannot be excluded.[21]

In conclusion we report that with a H-bond donor in the secondary coordination sphere we can isolate the product of $CO_2$ insertion into an Ir(III) hydride. In addition, our $CO_2$ inserted product is a highly active water-soluble catalyst for $CO_2$ hydrogenation. Further work will involve elucidating the full mechanism of $CO_2$ hydrogenation and investigating if the incorporation of a H-bond donor in the secondary coordination sphere can facilitate other reactions involving $CO_2$.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENT

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## ■ REFERENCES

(1) United States Department of Energy. Energy Information Administration, *International Energy Annual 2010*. July 2010; EIA-0484.
(2) Aresta, M.; Dibenedetto, A. *Catal. Today* **2004**, *98*, 455.
(3) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975.
(4) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259.
(5) Jessop, P. G.; Joo, F.; Tai, C.-C. *Coord. Chem. Rev.* **2004**, *248*, 2425.
(6) Federsel, C.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6254.
(7) Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 9777.
(8) Jessop, P. G.; Joo, F.; Tai, C.-C. *Coord. Chem. Rev.* **2004**, *248*, 2425.
(9) Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H.; Kasuga, K. *Organometallics* **2007**, *26*, 702.
(10) Ogo, S.; Kabe, R.; Hayashi, H.; Harada, R.; Fukuzumi, S. *Dalton Trans.* **2006**, 4657.
(11) Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14168.
(12) Ahlquist, M. S. G. *J. Mol. Catal. A: Chem.* **2010**, *324*, 3.
(13) Wu, J.; Green, J. C.; Hazari, N.; Hruszkewycz, D. P.; Incarvito, C. D.; Schmeier, T. J. *Organometallics* **2010**, *29*, 6369.
(14) Schmeier, T. J.; Hazari, N.; Incarvito, C. D.; Raskatov, J. R. *Chem. Commun.* **2011**, *47*, 1824.
(15) Hruszkewycz, D. P.; Wu, J.; Hazari, N.; Incarvito, C. D. *J. Am. Chem. Soc.* **2011**, *133*, 3280.
(16) Wu, J.; Hazari, N.; Incarvito, C. D. *Organometallics* **2011**DOI: 10.1021/om2002238.
(17) Crabtree, R. H. *New J. Chem.* **2011**, *35*, 18.
(18) DuBois, M. R.; DuBois, D. L. *Chem. Soc. Rev.* **2009**, *38*, 62.
(19) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 11874.
(20) Shook, R. L.; Borovik, A. S. *Inorg. Chem.* **2010**, *49*, 3646.
(21) See Supporting Information for more details.
(22) We assume that under the harsh reaction conditions, 200 °C, 6 MPa, some $CO_2$ insertion does occur, as **b** is an active catalyst for hydrogenation.[10] However, we cannot discount the possibility that in basic conditions ligand metathesis occurs and the chloride ligand is replaced by a hydroxide ligand. Insertion into the hydroxide supported complex is slighly more favorable than insertion into the chloride species; see Table 1.
(23) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485.
(24) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 5th ed.; Wiley: 2009.
(25) Hayter, R. G. *J. Am. Chem. Soc.* **1961**, *83*, 1259.
(26) Dobereiner, G. E.; Nova, A.; Schley, N. D.; Hazari, N.; Miller, S. J.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 7547.
(27) Clarke, Z. E.; Maragh, P. T.; Dasgupta, T. P.; Gusev, D. G.; Lough, A. J.; Abdur-Rashid, K. *Organometallics* **2006**, *25*, 4113.
(28) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.
(29) Using $^{13}C$ NMR spectroscopy bicarbonate is detected as a product along with formate, although only the yield of formate is reported. Presumably the bicarbonate is formed through the reaction of $CO_2$ with KOH.