Angewandte Chemie International Edition

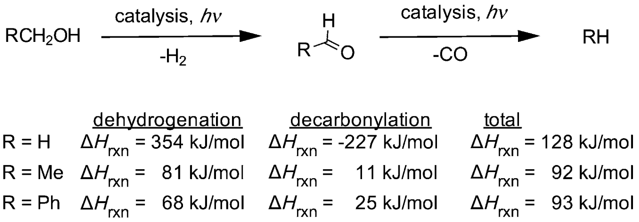
DOI: 10.1002/anie.201203556

**Photocatalysis**

# Acceptorless Photocatalytic Dehydrogenation for Alcohol Decarbonylation and Imine Synthesis**

*Hung-An Ho, Kuntal Manna, and Aaron D. Sadow**

Selective conversions of biorenewable materials for chemical feedstock and energy applications require chemical control of oxygen- and nitrogen-containing functional groups. Reductive catalytic transformations for their removal, such as hydrodeoxygenation and hydrodenitrogenation, generally require a terminal stoichiometric reductant such as hydrogen.[1] Alternative catalytic reactions which affect defunctionalization could be important components of biomass utilization strategies, particularly if these can be accomplished with hydrogen and carbon efficiency.[2] Herein we show that photocatalytic deoxygenation can be accomplished through a tandem dehydrogenation/decarbonylation process without sacrificial reagents (Scheme 1).



***Scheme 1.*** A dehydrogenation and decarbonylation sequence for the deoxygenation of primary alcohols.

Furthermore, the overall conversions in Scheme 1 show increased enthalpy content of the products versus reactants ($\Delta H_{rxn} > O$) and the production of $H_2$ and CO (syn-gas) as by-products.[3] A related photocatalytic amine dehydrogenation provides imines.

Although acceptorless alcohol dehydrogenations and aldehyde decarbonylations have been described,[4–6] catalytic alcohol decarbonylation typically requires a CO trap. Additionally, these two steps are rarely coupled in catalytic processes because dehydrogenation catalysts are often inhibited by the carbon monoxide product of decarbonylation. Pioneering studies showed that rhodium(I) phosphine complexes catalyze conversions of ethanol into CO/$CO_2$, $H_2$, and $CH_4$ under basic conditions at 150 °C.[7] Increased CO yield and greater rates are achieved by irradiation.[7] Likewise, alcohol decarbonylation generates CO for Pauson–Khand reactions catalyzed by [{(dppp)RhCl(CO)}$_2$] (dppp = bis(diphenylphosphino)propane).[8]

We envisioned photolysis as a method for catalyst reactivation through CO dissociation. Based on the above reports, several rhodium(I) compounds were screened as photocatalysts with cyclohexanemethanol (Cy$CH_2OH$) as a test substrate (Table 1). However, these rhodium(I) compounds are not effective under UV light at room temperature in neutral solutions (Table 1, entries 1–5). We then tested compounds known for C–H bond activation under photochemical conditions. [Cp*M(CO)$_2$] and [Tp*M(CO)$_2$] (Cp* = $\eta^5$-$C_5Me_5$, M = metal, Tp* = tris(3,5-dimethylpyrazolyl)borate) react with C–H bonds under mild irradiation.[9] These compounds were chosen because related systems mediate stoichiometric decarbonylations. For example, [Cp*(PMe$_3$)IrCl$_2$] reacts with primary alcohols at 135 °C to afford [Cp*(PMe$_3$)IrR(CO)]Cl (R = Me, Et, Ph),[10] while photolysis of [Tp*Rh(1,3-$C_8H_{12}$)] in methanol gives [Tp*Rh(H)$_2$CO], $H_2$, and 1,3-$C_8H_{12}$.[11] Also, a few iridium pincer compounds react with alcohols to give decarbonylation products.[12]

***Table 1:*** Catalysts investigated for photocatalytic decarbonylation of cyclohexanemethanol (Cy$CH_2OH$).[a]

| Entry | Catalyst | *t* [h] | Yield [%][b] |
|---|---|---|---|
| 1 | [{RhCl($C_8H_{12}$)}$_2$] | 24 | 0 |
| 2 | [{RhCl($C_8H_{14}$)$_2$}$_2$] | 24 | 0 |
| 3 | [{RhCl(CO)$_2$}$_2$] | 24 | 0 |
| 4 | [{RhCl(CO)$_2$}$_2$] + dppm | 24 | 0 |
| 5 | [{RhCl(CO)$_2$}$_2$] + dppp | 72 | 1.6 |
| 6 | [Cp*Ir(CO)$_2$] | 24 | 0 |
| 7 | [Cp*Rh(CO)$_2$] | 24 | 0 |
| 8 | [Tp*Rh(CO)$_2$] | 72 | 36 |
| 9 | [To$^M$Rh(CO)$_2$] (**1**)[c] | 24 | > 95 |
| 10 | [To$^P$Rh(CO)$_2$] (**2**) | 72 | 56 |
| 11 | [To$^M$Rh(H)$_2$CO] (**3**) | 72 | > 95 |
| 12 | [To$^M$Ir(CO)$_2$] (**4**) | 24 | 0 |

[a] Reaction conditions: Cy$CH_2OH$ (0.09 mmol), catalyst (0.009 mmol), benzene (0.7 mL), 450 W medium pressure Hg lamp. [b] Yield as determined by NMR spectroscopy using cyclooctane as an internal standard. [c] Similar yields are obtained in toluene, but only starting material is observed when the solvent is $CH_2Cl_2$, THF, or $CH_3CN$.

[Cp*M(CO)$_2$] (M = Rh, Ir) compounds do not give detectable conversion of Cy$CH_2OH$ upon irradiation. Interestingly, cyclohexane is observed upon photolysis of

---

[*] Dr. H.-A. Ho, K. Manna, Prof. A. D. Sadow
Department of Chemistry and US DOE Ames Laboratory
Iowa State University
1605 Gilman Hall, Ames IA 50011 (USA)
E-mail: sadow@iastate.edu

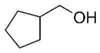
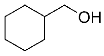
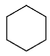
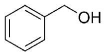
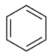
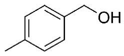
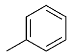
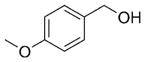
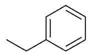
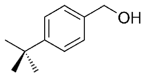
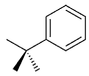
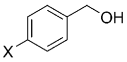
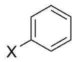
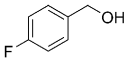
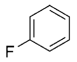
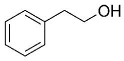
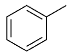
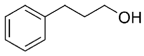
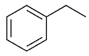
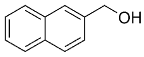
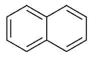
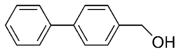
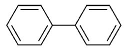
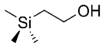
[**] This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through the Ames Laboratory (Contract No. DE-AC02-07CH11358). Aaron D. Sadow is an Alfred P. Sloan Fellow.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203556.

$CyCH_2OH$ in the presence of [Tp*Rh(CO)$_2$]. GC analysis confirmed that CO and $H_2$ are formed in the reaction. Furthermore, a compound prepared in our group, [To$^M$Rh(CO)$_2$] (To$^M$ = tris(4,4-dimethyl-2-oxazolinyl)phenylborate),[13] is an order of magnitude more effective than [Tp*Rh(CO)$_2$]. The related optically active [To$^P$Rh(CO)$_2$] (**2**; To$^P$ = tris(4*S*-isopropyl-2-oxazolinyl)phenylborate)[13] is less active. [To$^M$Rh(H)$_2$CO] (**3**) is approximately three times slower than **1**, and the iridium analogue **4** is not active.

Compound **1** is a photocatalyst for the conversion of a range of primary alcohols into hydrocarbons in good overall yield (Table 2). The catalyst tolerates silyl, ether, phenyl, and fluorophenyl groups under these reaction conditions. Benzylic alcohol moieties, central components of lignin,[14] are readily decarbonylated, and the aromatic groups and ether linkages are tolerated. Notably, aliphatic alcohols are readily decarbonylated, thus indicating that β-hydrogen elimination of the presumed alkylrhodium intermediate is slower than reductive dealkylation. Simple alcohols, such as methanol and ethanol are also readily decarbonylated with **1** as the photocatalyst. The nitro- and chloroarene groups, as well as esters, were not tolerated (Table 2, entries 7 and 8).

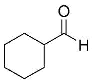
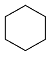
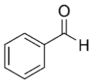
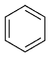
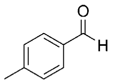
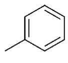
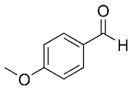
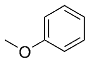
***Table 2:*** [To$^M$Rh(CO)$_2$]-catalyzed alcohol conversion into RH, $H_2$, and CO.[a]

| Entry | Alcohol | RH | *t* [h] | Yield [%][b,c] |
|---|---|---|---|---|
| 1 |  |  | 24 | 93 |
| 2[c] |  |  | 24 | 94 |
| 3[d] |  |  | 24 | 92 |
| 4 |  |  | 24 | 92 |
| 5 |  |  | 24 | 88[e] |
| 6 |  |  | 24 | 90 (85) |
| 7[f] |  |  | 24 | 0 |
| 8 |  |  | 36 | 95 |
| 9 |  |  | 24 | 99 |
| 10 |  |  | 24 | 94 |
| 11 |  |  | 72 | 84 (81) |
| 12 |  |  | 72 | 81 |
| 13 |  |  | 36 | 90 (87) |

[a] Reaction conditions: alcohol (0.09 mmol), **1** (0.009 mmol), benzene (0.7 mL), RT, 450 W medium pressure Hg lamp. [b] Yield as determined by GC using cyclooctane as an internal standard. [c] Yield of isolated product. [d] Used toluene as the solvent. [e] 5 mol% **1** gives 95% yield after 41 h. [f] X = $CO_2Me$, $NO_2$, or Cl.

In these catalytic reactions, the sequence depicted in Scheme 1 is supported by the detection of a small quantity of cyclohexanecarbaldehyde (CyCHO) by $^1$H NMR spectroscopy and GC/MS. Additionally, aldehydes are decarbonylated under the photocatalytic reaction conditions with precatalysts **1** or **3** (Table 3). In the absence of light, there is no conversion of either the aldehyde or alcohol.

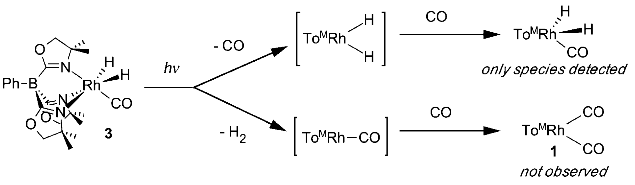
***Table 3:*** Photocatalytic decarbonylation of aldehydes.[a]

| Entry | Aldehyde | RH | *t* [h] | Yield [%][b] |
|---|---|---|---|---|
| 1 |  |  | 6 | 89 |
| 2 |  |  | 6 | 87 |
| 3 |  |  | 6 | 92 |
| 4 |  |  | 6 | 89 |

[a] Reaction conditions: aldehyde(0.09 mmol), **1** or **3** (0.0023 mmol), benzene (0.7 mL), RT, 450 W medium pressure Hg lamp. [b] Yield as determined by GC using cyclooctane as an internal standard.

Apparent turnover rates for **1**- and **3**-photocatalyzed RCHO decarbonylations are much greater than the $RCH_2OH$ conversions. Thus, even though light is required for catalysis, catalytic turnover frequencies also depend on the interaction of the substrate and photoactivated catalyst. Relatively small amounts of CO (ca. 1 atm) do not appear to inhibit the catalysis, although conversion is slower at higher CO pressures (5 atm).

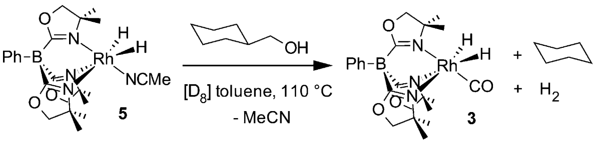
For catalyst **1**, photolytic CO dissociation gives [To$^M$Rh(CO)], and this is the necessary first step for both alcohol and aldehyde activation processes (see below). Photolysis of the catalyst **3** could give either [To$^M$Rh(CO)] or [To$^M$RhH$_2$] as intermediates. Because **3** is less efficient than **1** for alcohol conversion, the reactive intermediate obtained from **3** is likely not the same as the one from **1**. That photolysis of **1** and **3** give non-equivalent intermediates is also suggested by the results of thermal experiments (see below). Additionally, photolysis of **3** in the presence of CO affords only **3**, and dicarbonyl **1** could not be detected (Scheme 2). Thus, [To$^M$RhH$_2$], rather than [To$^M$Rh(CO)], is implicated as the



***Scheme 2.*** Photochemical reductive elimination of $H_2$ from [To$^M$Rh(H)$_2$CO] (**3**) is disfavored versus CO dissociation.

intermediate from catalyst **3** in the dehydrogenation and decarbonylation.

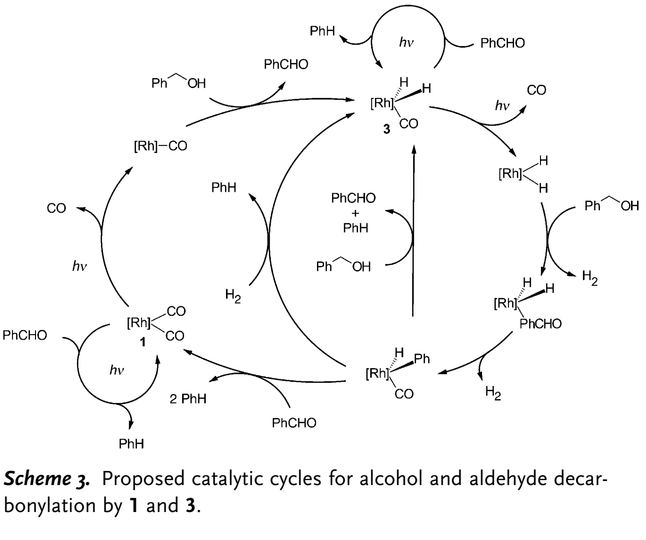
The dehydrogenation/decarbonylation sequence could require either one or two photons. The proposed intermediate, [To$^M$RhH$_2$], was sought to address this question. [To$^M$RhH$_2$(NCMe)] (**5**) was reacted with CyCH$_2$OH [Eq. (1)] under thermal conditions with the expectation that acetonitrile dissociation would give [To$^M$RhH$_2$]. The overall reaction gives cyclohexane and **3** as the products of stoichiometric dehydrogenation and decarbonylation. Once **3** is formed, no further conversion of CyCH$_2$OH occurs. Additionally, CyCHO is not detected in the reaction mixture, thus providing additional evidence for rate-limiting dehydrogenation with subsequent decarbonylation.



(1)

These results indicate that a) CO dissociation in **1** and **3** is required for alcohol dehydrogenation, b) aldehydes are more reactive than alcohols toward [To$^M$Rh(CO)] and [To$^M$RhH$_2$], and thus c) catalytic turnover is limited by a competition between CO re-coordination and substrate activation. The catalytic decarbonylation of primary alcohols by **3** requires only one photon. In contrast, dehydrogenation of alcohol with [To$^M$RhCO] forms [To$^M$RhH$_2$(CO)], and therefore a second photon is required for **1**-catalyzed decarbonylation. These conclusions can be summarized to include several concurrent catalytic cycles (Scheme 3).

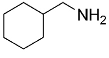
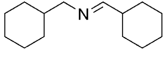
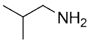
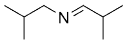
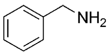
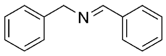
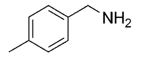
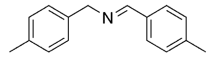
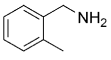
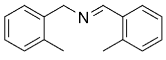
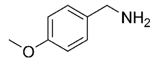
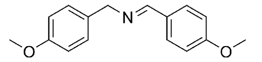
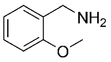
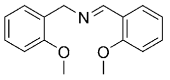
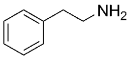
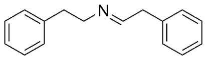
Dehydrogenation of primary amines would generate aldimine products.[15] Following the reductive amination sequence, these aldimines would react with a second equivalent of a primary amine and, upon reduction, give the alkylated products.[16] However, [To$^M$Rh$^I$] compounds are not effective for imine hydrogenation, and the final products might be imines and H$_2$. The photocatalytic dehydrogenation of amines to imines, under oxidative conditions, has recently attracted significant attention.[17] Therefore, we investigated oxidant-free conversions of primary amines with our photocatalyst.



**Scheme 3.** Proposed catalytic cycles for alcohol and aldehyde decarbonylation by **1** and **3**.

Indeed, [To$^M$Rh(CO)$_2$] is a photocatalyst for the dehydrogenation of primary amines to imines (Table 4). Linear and cyclic/branched aliphatic amines provide the corresponding imines with good yield. Benzylamine and substituted derivatives also afford the coupled imine products in high yields (Table 4).

**Table 4:** Oxidant-free imine synthesis from various primary amines.[a]

| Entry | Amine | Imine | Yield [%][b,c] |
|---|---|---|---|
| 1 | $n$-$C_6H_{13}NH_2$ | $n$-$C_6H_{13}N{=}CH(nC_5H_{11})$ | 79 |
| 2 | $n$-$C_7H_{15}NH_2$ | $n$-$C_7H_{15}N{=}CH(nC_6H_{13})$ | 77 |
| 3 |  |  | 85 (78) |
| 4 |  |  | 86 |
| 5 |  |  | 92 (83) |
| 6 |  |  | 90 |
| 7 |  |  | 85 |
| 8 |  |  | 88 |
| 9 |  |  | 86 |
| 10 |  |  | 79 |

[a] Reaction conditions: amines (0.09 mmol), **1** (0.009 mmol), benzene (0.7 mL), RT, 450 W medium pressure Hg lamp. [b] Yield as determined by GC using cyclooctane as an internal standard. [c] Yield of isolated product.

Thus, **1** is a photocatalyst for the conversion of both primary alcohols and primary amines. In fact, we are not aware of previous reports of oxidant-free photocatalytic amine coupling. Additionally, these catalysts are effective for decarbonylations of aliphatic aldehydes which are difficult under thermal catalysis because of β-hydrogen elimination.[4]

Isoelectronic [Cp*M(CO)$_2$] and [Tp*Rh(CO)$_2$]are much less active than **1**. Because the compounds reported in the literature are well known for photochemical C–H bond oxidative addition reactions, and those reactions are proposed to involve electronically unsaturated [M]-CO intermediates, one might expect that [To$^M$Rh(CO)$_2$] would be very effective for photochemically activated alkane oxidative addition. Instead, C–H bond activation with **1** is less facile than in the [Cp*M] and [Tp*M] systems (e.g., we have not yet found evidence for aliphatic C–H bond oxidative addition with **1**). Thus, the highly reactive [M]-CO and [M](H)$_2$ intermediates exhibit a wide range of reactivity toward alcohol, aldehyde, and hydrocarbon substrates as the ancillaries are varied. These results emphasize the need for new catalysts, for conversion of oxygenates, which are distinct from catalysts for hydrocarbon conversions. While we are currently developing catalysts with improved photon and chemical efficiency, the present studies provide significant insight into the reaction scope and mechanism, and highlight strategies for future catalyst development for conversion of oxygenates.

Received: May 8, 2012

**Keywords:** alcohols · dehydrogenation · homogeneous catalysis · imines · photochemistry

---

[1] a) E. Furimsky, *Appl. Catal. A* **2000**, *199*, 147–190; b) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098.

[2] a) G. K. Cook, M. A. Andrews, *J. Am. Chem. Soc.* **1996**, *118*, 9448–9449; b) K. P. Gable, B. Ross, in *Feedstocks for the Future*, Eds.: J. J. Bozell, M. K. Patel, ACS, **2006**, 143–155; c) J. E. Ziegler, M. J. Zdilla, A. J. Evans, M. M. Abu-Omar, *Inorg. Chem.* **2009**, *48*, 9998–10000; d) M. Schlaf, P. Ghosh, P. J. Fagan, E. Hauptman, R. M. Bullock, *Adv. Synth. Catal.* **2009**, *351*, 789–800; e) S. Vkuturi, G. Chapman, I. Ahmad, K. M. Nicholas, *Inorg. Chem.* **2010**, *49*, 4744–4746; f) I. Ahmad, G. Chapman, K. M. Nicholas, *Organometallics* **2011**, *30*, 2810–2818; g) S. Stanowski, K. M. Nicholas, R. S. Srivastava, *Organometallics* **2012**, *31*, 515–518.

[3] a) J. D. Cox, G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, **1970**; b) J. H. S. Green, *Chem. Ind.* **1960**, 1215–1216; c) M. W. Chase, Jr., NIST-JANAF Thermochemical Tables, *4th ed.*, J. Phys. Chem. Ref. Data. Monograph 9, **1998**; d) M. V. Roux, M. Temprado, J. S. Chickos, Y. Nagano, *J. Phys. Chem. Ref. Data* **2008**, *37*, 1855–1996; e) D. Ambrose, J. E. Connett, J. H. S. Green, J. L. Hales, A. J. Head, J. F. Martin, *J. Chem. Thermodyn.* **1975**, *7*, 1143–1157; f) T. S. Papina, S. M. Pimenova, V. A. Luk'yanova, V. P. Kolesov, *Russ. J. Phys. Chem.* **1995**, *69*, 1951–1953.

[4] a) K. Ohno, J. Tsuji, *J. Am. Chem. Soc.* **1968**, *90*, 99–107; b) D. H. Doughty, L. H. Pignolet, *J. Am. Chem. Soc.* **1978**, *100*, 7083–7085; c) F. Abu-Hasanayn, M. E. Goldman, A. S. Goldman, *J. Am. Chem. Soc.* **1992**, *114*, 2520–2524; d) C. M. Beck, S. E. Rathmill, Y. J. Park, J. Chen, R. H. Crabtree, L. M. Liable-Sands, A. L. Rheingold, *Organometallics* **1999**, *18*, 5311–5317; e) M. Kreis, A. Palmelund, L. Bunch, R. Madsen, *Adv. Synth. Catal.* **2006**, *348*, 2148–2154; f) T. Iwai, T. Fujihara, Y. Tsuji, *Chem. Commun.* **2008**, 6215–6217; g) A. E. Roa, V. Salazar, J. López-Serrano, E. Oñate, M. Paneque, M. L. Poveda, *Organometallics* **2012**, *31*, 716–721.

[5] a) H. B. Charman, *J. Chem. Soc. Phys. Org.* **1967**, 629–632; b) D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1988**, 1154–1156; c) J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg, D. Milstein, *Organometallics* **2004**, *23*, 4026–4033; d) K.-i. Fujita, N. Tanino, R. Yamaguchi, *Org. Lett.* **2007**, *9*, 109–111; e) R. Kawahara, K.-i. Fujita, R. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 3643–3646.

[6] a) Y. Blum, Y. Shvo, *J. Organomet. Chem.* **1985**, *282*, C7–C10; b) J. Zhao, J. F. Hartwig, *Organometallics* **2005**, *24*, 2441–2446.

[7] a) E. Delgado-Lieta, M. A. Luke, R. F. Jones, D. J. Cole-Hamilton, *Polyhedron* **1982**, *1*, 836–838; b) D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1987**, 248–249; c) D. Morton, D. J. Cole-Hamilton, I. D. Utuk, M. Paneque-Sosa, M. Lopez-Poveda, *J. Chem. Soc. Dalton Trans.* **1989**, 489–495.

[8] J. H. Park, Y. Cho, Y. K. Chung, *Angew. Chem.* **2010**, *122*, 5264–5267; *Angew. Chem. Int. Ed.* **2010**, *49*, 5138–5141.

[9] a) J. K. Hoyano, W. A. G. Graham, *J. Am. Chem. Soc.* **1982**, *104*, 3723–3725; b) A. J. Rest, I. Whitwell, W. A. G. Graham, J. K. Hoyano, A. D. McMaster, *J. Chem. Soc. Chem. Commun.* **1984**, 624–626; c) C. K. Ghosh, W. A. G. Graham, *J. Am. Chem. Soc.* **1987**, *109*, 4726–4727.

[10] S. R. Klei, J. T. Golden, T. D. Tilley, R. G. Bergman, *J. Am. Chem. Soc.* **2002**, *124*, 2092–2093.

[11] a) Y.-Z. Chen, W. C. Chan, C. P. Lau, H. S. Chu, H. L. Lee, G. Jia, *Organometallics* **1997**, *16*, 1241–1246; b) R. Boaretto, G. Paolucci, S. Sostero, O. Traverso, *J. Mol. Catal. A* **2003**, *204*, 253–258.

[12] a) D. Morales-Morales, R. Redón, Z. Wang, D. W. Lee, C. Yung, K. Magnuson, C. M. Jensen, *Can. J. Chem.* **2001**, *79*, 823–829; b) S. M. Kloek, D. M. Heinekey, K. I. Goldberg, *Organometallics* **2006**, *25*, 3007–3011; c) J. G. Melnick, A. T. Radosevich, D. Villagrán, D. G. Nocera, *Chem. Commun.* **2010**, *46*, 79–81.

[13] H.-A. Ho, J. F. Dunne, A. Ellern, A. D. Sadow, *Organometallics* **2010**, *29*, 4105–4114.

[14] J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* **2010**, *110*, 3552–3599.

[15] R. Yamaguchi, C. Ikeda, Y. Takahashi, K.-i. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 8410–8412.

[16] G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703.

[17] a) S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka, *ACS Catal.* **2011**, *1*, 1150–1153; b) F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang, S. Blechert, *Angew. Chem.* **2011**, *123*, 683–686; *Angew. Chem. Int. Ed.* **2011**, *50*, 657–660; c) X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao, *Angew. Chem.* **2011**, *123*, 4020–4023; *Angew. Chem. Int. Ed.* **2011**, *50*, 3934–3937; d) X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji, J. Zhao, *Chem. Eur. J.* **2012**, *18*, 2624–2631; e) H. Huang, J. Huang, Y.-M. Liu, H.-Y. He, Y. Cao, K.-N. Fan, *Green Chem.* **2012**, *14*, 930–934.