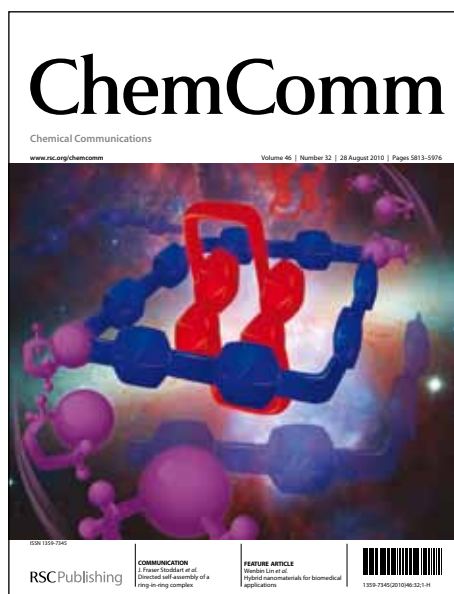


ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: P. J. Bonitatibus Jr, M. P. Rainka, A. J. Peters, D. L. Simone and M. D. Doherty, *Chem. Commun.*, 2013, DOI: 10.1039/C3CC46051G.



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard [Terms & Conditions](#) and the [ethical guidelines](#) that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

Highly selective electrocatalytic dehydrogenation at low applied potential catalyzed by an Ir organometallic complex

Peter J. Bonitatibus, Jr.,* Matthew P. Rainka, Andrea J. Peters, Davide L. Simone, and Mark D. Doherty

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

A homogeneous organometallic Ir complex was shown to catalyze the electro-oxidation of 4-methoxybenzyl alcohol to *p*-anisaldehyde at a very low applied potential with remarkably high selectivity and Faradaic efficiency. In the chemical catalysis, when stoichiometric oxidant and anionic base were used to separately accept electrons and protons, aldehyde selectivity was in agreement with electrolysis results.

Selective partial oxidation of alcohols by electrochemical means is important in the context of synthetic chemistry and direct alcohol fuel cell (DAFC) research. Examples of partial oxidation and dehydrogenation processes that take place in DAFCs have received attention in recent literature because this type of fuel cell generates electrical energy with zero CO₂ emissions.^{1,2} We are focused on the development of metal complexes to serve as molecular electro-oxidation catalysts in such systems. More specifically, engineering metal complex electrocatalysts for the energy generation (dehydrogenation) step in regenerative direct fuel cells.³

Kariya originally reported a regenerative (or rechargeable) direct fuel cell and investigated 2-propanol/acetone as a model rechargeable fuel system.² Electro-oxidation (dehydrogenation) of 2-propanol at a Pt anode generated electrical energy together with acetone, and electro-reduction (hydrogenation) of acetone back to 2-propanol was proposed as the charging cycle in this model system. Advancement of the technology requires development of efficient electrocatalysts that can perform partial electro-oxidation of fuel (dehydrogenation) and the reverse reaction of electro-reduction (hydrogenation) for charging.

Metal complex electrocatalysts are emerging as interesting anode materials in the development of molecular catalysis-based fuel cells.⁴ Recent examples include immobilized Rh complexes; such as Rh porphyrin, that convert glucose to gluconate in a glucose/O₂ fuel cell,⁵ and organorhodium catalysts, used to oxidize ethanol to acetate in organometallic fuel cells (OMFCs).⁶ Advantages of developing molecular electrocatalysts include the ability to energetically and/or structurally tune the active site *via* modification of the ligand framework, the potential to fundamentally investigate a reaction mechanism, and more efficient usage of precious noble metals.

Outlined in this context, we have pursued strategies to identify metal complex electro-oxidation catalysts that dehydrogenate alcohols to aldehydes (or ketones) with high product selectivity at

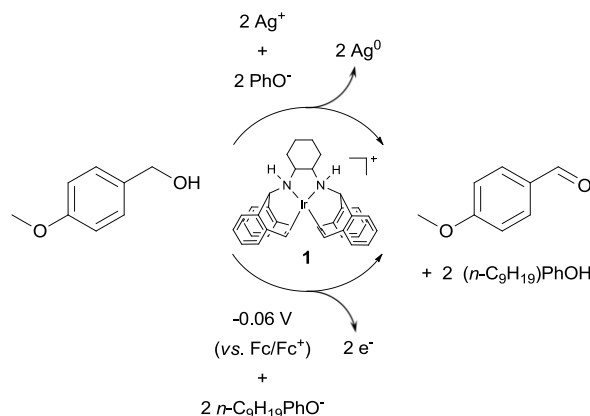
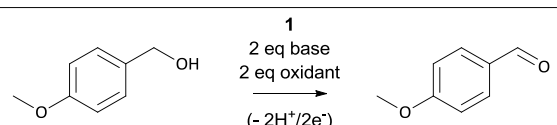


Fig. 1 Schematic representation of the separation of electrons and protons in the chemical and electrochemical dehydrogenation of 4-methoxybenzyl alcohol to *p*-anisaldehyde catalyzed by $[\text{Ir}(\text{trop}_2\text{DACH})]^+$, **1**.

low applied potential.⁷ While a few examples of such electrocatalysts have been reported (i.e. Ru-polypyridyl complexes),⁸ either product selectivity was not observed⁹ or the yield was extremely low.¹⁰ To our knowledge, only one report at a comparatively high applied potential,¹¹ matched selectivity and approached current efficiency and yield (of benzaldehyde) we now report (*vide infra*).

Ir-catalyzed oxidation reactions in organic synthesis have been studied extensively and those involving alcohols were recently reviewed.¹² Grützmacher has developed a highly efficient oxidation reaction of primary alcohols to aldehydes using an Ir-diamino-diolefin complex, $[\text{Ir}(\text{trop}_2\text{DACH})][\text{OTf}]$ ($\text{trop}_2\text{DACH} = N,N'$ -bis(5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-1,2-diaminocyclohexane), **1** (Fig. 1), in combination with a strong base (KO^tBu) and the oxidant 1,4-benzoquinone (BQ).¹³ Oxidation of benzylic and allylic alcohols proceeded at room temperature with 0.01 mol% catalyst and it was reported that both a catalytic amount of KO^tBu and stoichiometric BQ (used to accept both electrons and protons) were required.¹⁴ Given the catalytic efficiency observed in this system, we pursued conditions to replace BQ with an electrode and develop **1** as an electro-oxidation (electrodehydrogenation) catalyst.

Initially, we studied **1** by *chemical* dehydrogenation catalysis to identify conditions (i.e. combinations of chemical oxidants and anionic bases) that work to separate electron and proton transfer events in the catalytic dehydrogenation of 4-methoxybenzyl

Table 1 Chemical conditions for the catalytic dehydrogenation of 4-methoxybenzyl alcohol.^a


| entry | mol% of 1 | oxidant | base | time (hrs) | %yield |
|-------|------------------|---------------------|--|------------|--------|
| 1 | 0.03 | AgOTf | PhONa | 2 | 94 |
| 2 | 0.03 | AgOTf | <i>n</i> -C ₉ H ₁₉ PhONa | 2 | 99 |
| 3 | 0.03 | Ag ⁺ | TMHD ⁻ | 1 | 76 |
| 4 | 0.30 | air | PhONa | 24 | 53 |
| 5 | 0.03 | [Fc]PF ₆ | PhONa | 4 | 70 |

^aConditions: 1.5 mmol alcohol, 3 mmol oxidant and base, room temp in *o*-DCB, total reaction volume approx. 5 mL. HPLC yields determined against *o*-terphenyl spiked standard. ¹H NMR yields were complimentary based on the ratio of methoxy groups (3.91 and 3.84 ppm) or aromatic aldehyde (7.87 ppm) to alcohol (4.67 ppm). TMHD⁻ = tetramethylheptanedionate. Fc⁺ = ferrocenium.

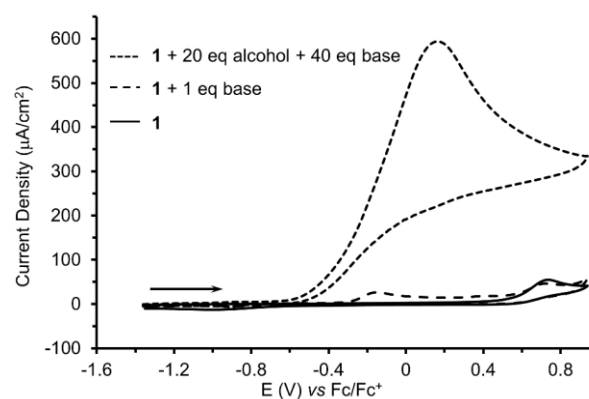


Fig. 2 CV scans at 50 mV s⁻¹ in *o*-DCB with 0.08 M TBAPF₆ of **1** (solid), **1** with 1 eq of sodium 4-nonylphenolate (heavily dashed), and **1** in the presence of 20 eq of 4-methoxybenzyl alcohol and 40 eq of sodium 4-nonylphenolate (lightly dashed). A linear increase in current for the peak at -0.15 V was observed with successively increased concentrations of alcohol and base, as well as a shift of the peak potential to 0.14 V.†

alcohol (Fig. 1). Since BQ supported coupled electron-proton transfer in the original system, we viewed successful decoupling of electron and proton transfer events as a fundamental first step toward BQ replacement and electrocatalysis. Leveraging these results with identification of a suitable base, we transitioned **1** to an *electrochemical* setting by replacement of the chemical oxidant with an electrode in the presence of a weak anionic base.

The oxidation of 4-methoxybenzyl alcohol to *p*-anisaldehyde was carried out using **1** as catalyst with 2 eq of oxidant and base relative to alcohol at room temperature in *o*-dichlorobenzene (*o*-DCB) under N₂ (Table 1). Reactions were monitored by ¹H NMR spectroscopy with yields determined using HPLC against *o*-terphenyl as a standard. We observed a 94% yield of *p*-anisaldehyde after 2 hrs when the reaction was carried out using 0.03 mol% **1** with 2 eq of AgOTf and sodium phenolate, whereas the same reaction with [Fc]PF₆ gave only 70% yield after 4 hrs (entries 1 and 5). Grützmacher reported a yield comparable to our result (entry 1) after 16 hrs in chlorobenzene using 0.01 mol% **1**, 0.03 mol% KO^tBu, and 1.3 eq BQ relative to alcohol.¹⁴ Catalytic dehydrogenations listed in Table 1 did not require initiation by strong base (KO^tBu) as in the original system that used BQ.

Silver tetramethylheptanedionate, [Ag(TMHD)], was found to be an interesting oxidant/base combination in that the TMHD⁻ ligand, which exhibits a structural type distinct from phenolate, served as an effective base (entry 3). It is worth noting O₂ can also serve as an oxidant in the catalytic oxidation of 4-methoxybenzyl alcohol to *p*-anisaldehyde when the vial was left open in the air with 0.3 mol% **1** (entry 4), even though literature suggests Ir-catalyzed oxidation of primary alcohols with molecular oxygen is rare.¹⁵ The most significant finding in Table 1, concerning adaptation of chemical conditions for electrolysis, was identification of sodium 4-nonylphenolate as a base because it allowed for quantitative yield of aldehyde (in combination with AgOTf) and had increased solubility in *o*-DCB over sodium phenolate (entry 2). In addition, we found sodium 4-nonylphenolate was not electrochemically active (i.e. was not oxidized in the presence of **1**) considering the high Faradaic efficiency observed in catalytic electro-dehydrogenation at the anode (*vide infra*).†

Electrochemical characterization of **1** in the absence and presence of sodium 4-nonylphenolate and 4-methoxybenzyl alcohol was performed using cyclic voltammetry (CV) (Fig. 2). The CV of a 1 mM solution of **1** in *o*-DCB with 0.08 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte showed an irreversible oxidation peak at 0.74 V (vs. Fc/Fc⁺). Addition of 1 eq of sodium 4-nonylphenolate to the solution of **1** resulted in the appearance of irreversible oxidation peaks at -0.15 V and 0.35 V, as well as a decrease in current for the peak at 0.74 V. Voltammograms of increased detail may be found in ESI. We attribute the peak at -0.15 V to oxidation of the neutral (mono-deprotonated) Ir-amido-amine complex [Ir(trop₂DACH-1H)], **2**. This is supported by ¹H NMR spectroscopy, in which a solution of **1** in THF-d₈ was treated with excess sodium phenolate, and clean conversion to complex **2** was observed.† Mono-deprotonation of **1** is consistent with pK_a values reported for **1** (pK_a¹ 10.5, pK_a² 19.6)¹³ and phenol (pK_a 16.5).¹⁶

Following the formation of complex **2**, aliquots of a mixture containing a 1:2 ratio of 4-methoxybenzyl alcohol:sodium 4-nonylphenolate in *o*-DCB/0.08M TBAPF₆ were successively added and the CV was recorded after each addition. A linear increase in current was observed at the catalyst wave with increasing concentrations of alcohol and base.† The CV after 20 eq of 4-methoxybenzyl alcohol and 40 eq of sodium 4-nonylphenolate were added is shown in Fig. 2. A large increase in current for the peak at -0.15 V was observed as well as a shift of the peak potential to 0.14 V. This behaviour is consistent with electrocatalysis¹⁷ and led us to study **1** in a constant potential electrolysis experiment with 4-methoxybenzyl alcohol and sodium 4-nonylphenolate.

Electrolysis experiments were performed in a cell with working and counter electrode compartments separated by a porous glass frit. A CV of an *o*-DCB/0.08M TBAPF₆ solution of **1** (0.67 mM), 4-methoxybenzyl alcohol (67 mM) and sodium 4-nonylphenolate (134 mM) was recorded in the electrolysis cell prior to performing the electrolysis. The onset oxidation of the mixture was observed to be shifted to slightly more positive potentials in this setup. Based on this data, a constant potential

electrolysis was conducted by applying a potential of -0.06 V (vs. Fc/Fc⁺) for 20 hrs using Pt gauze working and counter electrodes.

A total of 38 C of charge were passed and GC/GC-MS (with pentadecane as internal standard) analysis of the reaction mixture determined that *p*-anisaldehyde was produced with a 32% yield. This product yield corresponds to a Faradaic efficiency of >95% for the two electron oxidation process. A control experiment was run in parallel with the same solution mixture in the absence of an applied potential, and after stirring at room temperature under Ar (20 hrs) only a 4% yield of *p*-anisaldehyde was detected. An additional control experiment was performed in which the electrolysis conditions were the same as above, however **1** was excluded. In this electrolysis experiment, 20 C of charge were passed after applying a potential of -0.06 V for 20 hrs, and GC analysis again determined only a 4% yield of *p*-anisaldehyde. Charge passed in the latter electrolysis experiment resulted from oxidation of sodium 4-nonylphenolate (in the absence of **1**) based on its CV data.† At the potential applied in electrolysis experiments, both 4-methoxybenzyl alcohol and *p*-anisaldehyde showed negligible oxidation currents by CV (voltammograms may be found in ESI). Control experiments and data substantiated that **1** was involved in the electrochemical oxidation process and necessary for producing higher yields of selective aldehyde product.

When the electrolysis was repeated with **1**, but allowed to run for a total of 96 hrs, 78 C of charge passed resulting in a 64% yield of *p*-anisaldehyde corresponding to a Faradaic efficiency of 94%. Electrolysis with **1** at -0.06 V (vs. Fc/Fc⁺) is a comparatively low applied potential relative to the only reported example (to our knowledge) of an electrocatalytic system that similarly produced benzaldehyde selectively from benzyl alcohol with an 82% current efficiency (32% yield).¹¹ The electrocatalyst in that report, [Ru(bpea)(bpy)(H₂O)]²⁺, required a fairly high applied potential of 0.51 V (vs. Fc/Fc⁺) compared to -0.06 V (vs. Fc/Fc⁺) used for **1**.¹⁸

In this report, **1** was developed as an electro-oxidation catalyst and displayed high Faradaic efficiency and selectivity in the oxidation of 4-methoxybenzyl alcohol to *p*-anisaldehyde at low applied potential. The investigation of **1** in chemical catalysis experiments demonstrated separation of electron and proton transfer events in the dehydrogenation process, and enabled identification of an anionic base that was compatible for electrochemistry. Future studies will focus on establishing a mechanistic understanding of the electrocatalytic process outlined here, as well as the catalytic activity of **1** in the reverse electro-reduction of *p*-anisaldehyde.

This work was supported as part of the Center for Electrocatalysis, Transport Phenomena, and Materials (CETM) for Innovative Energy Storage, an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001055. PJB would like to devote his contribution to the loving memory of his father.

Notes and references

*GE Global Research, Chemistry & Chemical Engineering Global Technology Organization, Niskayuna, NY 12309 USA.
E-mail: bonitati@ge.com

† Electronic Supplementary Information (ESI) available: Experimental details for the deprotonation of **1** to form **2** with ¹H NMR spectra, plot of the linear increase in catalytic current, and other data.
See DOI: 10.1039/b000000x/

‡ An average of two runs determined *p*-anisaldehyde was produced with a 32% yield.

- S. P. Annen, V. Bambagioni, M. Bevilacqua, J. Filippi, A. Marchionni, W. Oberhauser, H. Schönberg, F. Vizza, C. Bianchini, and H. Grützmacher, *Angew. Chem. Int. Ed.*, **2010**, *49*, 7229.
- N. Kariya, A. Fukuoka, and M. Ichikawa, *Phys. Chem. Chem. Phys.*, **2006**, *8*, 1724.
- C. M. Araujo, D. L. Simone, S. J. Konezny, A. Shim, R. H. Crabtree, G. L. Soloveichik, and V. S. Batista, *Energy Environ. Sci.*, **2012**, *5*, 9534; P. F. Driscoll, E. Deunf, L. Rubin, O. Luca, R. H. Crabtree, C. Chidsey, J. Arnold, and J. B. Kerr, *ECS Trans.*, **2011**, *35*, 3.
- T. Matsumoto, K. Kim, and S. Ogo, *Angew. Chem. Int. Ed.*, **2011**, *50*, 11202; T. Matsumoto, K. Kim, H. Nakai, T. Hibino, and S. Ogo, *Chem. Cat. Chem.*, **2013**, *5*, 1368.
- K. Elouarzaki, A. Le Goff, M. Holzinger, J. Thery, and S. Cosnier, *J. Am. Chem. Soc.*, **2012**, *134*, 14078.
- M. Bevilacqua, C. Bianchini, A. Marchionni, J. Filippi, A. Lavacchi, H. Miller, W. Oberhauser, F. Vizza, G. Granozzi, L. Artiglia, S. P. Annen, F. Krumeich, and H. Grützmacher, *Energy Environ. Sci.*, **2012**, *5*, 8608.
- "Low" applied potential is defined by quantitative comparison of applied potentials between known catalysts. See ESI for a Table comparing catalytic systems for the electro-oxidation of benzyl alcohol.
- K.-C. Cheung, W.-L. Wong, D.-L. Ma, T.-S. Lai, and K.-Y. Wong, *Coord. Chem. Rev.*, **2007**, *251*, 2367.
- S. Yamazaki, M. Yao, N. Fujiwara, Z. Siroma, K. Yasuda, and T. Ioroi, *Chem. Commun.*, **2012**, *48*, 4353; T. Hino, T. Wada, T. Fujihara, and K. Tanaka, *Chem. Lett.*, **2004**, *33*, 1596; D. Serra, M. C. Correia, and L. McElwee-White, *Organometallics*, **2011**, *30*, 5568.
- Y. Miyazato, T. Wada, and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **2006**, *79*, 745; H. Ozawa, T. Hino, H. Ohtsu, T. Wada, and K. Tanaka, *Inorg. Chim. Acta*, **2011**, *366*, 298; A. K. Vannucci, J. F. Hull, Z. Chen, R. A. Binstead, J. J. Concepcion, and T. J. Meyer, *J. Am. Chem. Soc.*, **2012**, *134*, 3972.
- M. Rodríguez, I. Romero, A. Llobet, A. Deronzier, M. Biner, T. Parella, and H. Stoeckli-Evans, *Inorg. Chem.*, **2001**, *40*, 4150.
- T. Suzuki, *Chem. Rev.*, **2011**, *111*, 1825.
- N. Donati, M. Königsmann, D. Stein, L. Udino, and H. Grützmacher, *C. R. Chimie*, **2007**, *10*, 721.
- M. Königsmann, N. Donati, D. Stein, H. Schönberg, J. Harmer, A. Sreekanth, and H. Grützmacher, *Angew. Chem. Int. Ed.*, **2007**, *46*, 3567.
- A. Gabrielsson, P. van Leeuwen, and W. Kaim, *Chem. Commun.*, **2006**, 4926.
- K. Roy and P. L. A. Popelier, *J. Phys. Org. Chem.*, **2009**, *22*, 186.
- A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, 1980.
- V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, **2000**, *298*, 97 (Table 1 provided conversion constants to relate potentials measured versus different reference electrodes).