LETTER

Redox-active cyclopentadienyl Ni complexes with quinoid N-heterocyclic carbene ligands for the electrocatalytic hydrogen release from chemical fuels†

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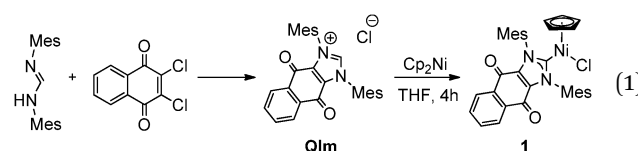
We now report the electrocatalytic dehydrogenation of tetra-hydroquinaldine by an electron-rich CpNi N-heterocyclic carbene (NHC) with quinoid ligand motifs and explore the effects of quinone additives on CpNi compounds without quinoid NHC ligands. Our CpNi(NHC) catalyst exhibits dehydrogenative electro-catalytic activity and demonstrates that a molecular catalyst precursor can be viable in the electrode-driven (H$^+$ + e$^-$) release step of "virtual hydrogen storage".

With the rising economic and environmental costs of natural gas and oil, much effort has been devoted to developing hydrogen fuel storage as an alternative, low-CO$_2$ fuel source. However, storage and transportation methods of free H$_2$ face many practical problems such as diffusion through metals and high flammability.[1] Easily storable liquid hydrogen carriers that can release H$_2$ equivalents as protons and electrons, therefore offer an attractive solution. The fuel can be thought of as "virtual hydrogen storage"[1] material that can be recycled by reversible electrohydrogenation–dehydrogenation.[2] The current infrastructure developed for the handling of liquid petroleum products may also be amenable to this technology.[2,3]

Only one electrode-driven electrochemical process of desaturation has been reported with a molecular catalyst precursor to date.[4] Even non-electrochemical hydrogenation–dehydrogenation catalytic systems for heterocycles are rare and require costly late transition metals like ruthenium[5] or iridium.[6] Research efforts have thus been focused on synthesizing catalysts with abundant first-row transition metals. In order to impart multi-electron reactivity to such base metal compounds, normally only

capable of 1e$^-$ chemical steps, incorporation of redox-active ligands has been proposed.[7]

Quinones have been of interest in electrochemical dehydrogenation chemistry as they readily accept (H$^+$ + e$^-$) equivalents and can be regenerated at an electrode.[4] They are also effective terminal H$_2$ acceptors for Pd catalyzed dehydrogenation reactions.[8,9] We have previously shown that high potential quinones such as 2,3-dichloro-5,6-dicyanoquinone (DDQ) are electrocatalysts for desaturation of C–N bonds, although having a limited substrate scope.[4] We believed that tethering quinones as (H$^+$ + e$^-$) acceptor motifs to electron-rich catalyst frameworks might impart reactivity towards dehydrogenation chemistry (Fig. 1).

The known reaction of nickelocene with azolium salts has been previously used as a versatile synthetic methodology leading to electron-rich CpNi(NHC) compounds.[10–13] Bielawski and coworkers[14] have previously reported the synthesis of
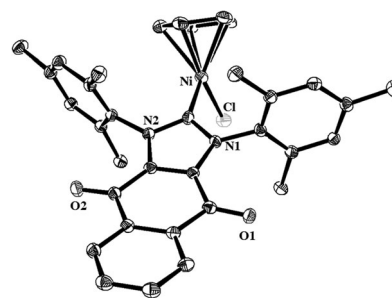
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† Electronic supplementary information (ESI) available: Additional CVs, controls, experimental details and X-ray information. CCDC 915452. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj00276d

Fig. 1 ORTEP representation of the X-ray structure of compound **1** (40% probability ellipsoids). H atoms were omitted for clarity.

quinone-annulated NHCs and the corresponding Rh and Ag complexes. We have now synthesized the quinone NHC compound **1** by the direct reaction of nickelocene with the imidazolium-annulated quinoid salt (**QIm** in eqn (1)). The new compound **1** was also successfully crystallized by slow evaporation from dichloromethane and the X-ray structure determined (see Section S2 (ESI†) for more details). The crystal structure shows very similar characteristics when compared to related CpNi NHC compounds[13] with similar "piano-stool" geometry. The diene distortion (the presence of two equally shortened non-adjacent C–C bonds) was also observed in the structure of compound **1**.

The cyclic voltammogram of **1** reveals two quasi-reversible oxidations the first of which at 0.78 V *vs.* NHE, we tentatively assign to a metal-centered oxidation (Fig. 2). The second signal at 1.35 V *vs.* NHE may be oxidation of Cl^-, although a definite assignment requires further investigation. A quasi-reversible quinone-centered reduction response is observed at -0.31 V *vs.* NHE, followed by another reduction at -1.1 V *vs.* NHE (Fig. 2) which we believe is associated with the metal center.

Redox-active **1** has now been shown to act as an operationally homogeneous dehydrogenation catalyst for the dehydrogenation of the saturated *N*-heterocyclic substrate: 1,2,3,4-tetrahydroquinaldine to give the corresponding arene. Cyclic voltammograms of compound **1** in the presence of incremental additions of this substrate show a sharp increase in current response, characteristic of a catalytic process (Fig. 3). As derivatives of anilines often show polyaniline-forming side-reactions,[15] the current responses had to be correlated with isolated yields of the desired fully desaturated product (eqn (2)) to show efficient and selective charge consumption (details in the ESI†). The reaction was shown to occur in 70–90% faradaic and chemical yield (Table 1) at a Pt surface, with the largest chemical yield of 78% obtained with **1**. We also investigated the role of a free quinone additive on an otherwise electrocatalytically unreactive non-quinoid CpNi NHC derived from
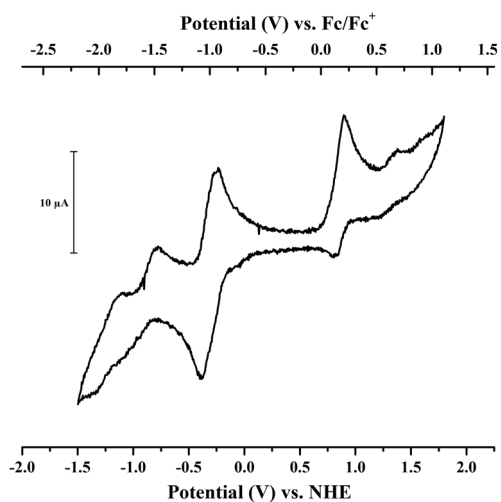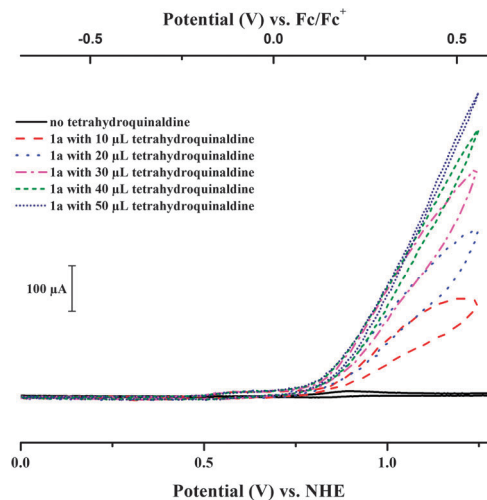

Fig. 3 Cyclic voltammetry of **1**-catalytic run: 2 mM **1** in a 2 mL solution of 0.1 M NBu_4BF_4 in acetonitrile at a Pt electrode with increments of added tetrahydroquinaldine.
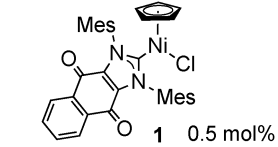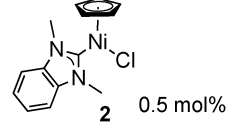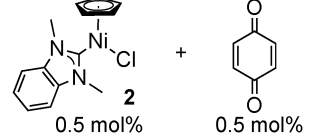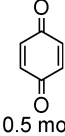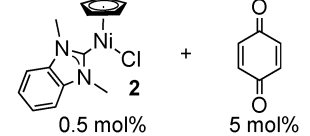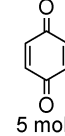
N,N-dimethylbenzimidazolium chloride (**2**, Fig. S3-2 (ESI†) for CVs). Compound **2** was prepared as previously reported *via* the method depicted in eqn (1).[13] The results of our electrocatalytic studies with **2** are summarized in Table 1, entries b–d.

The utility of quinones as ligand components in metal catalysts has been limited by difficulty of synthesis.[16] Moreover, recent studies have explored the nature of metal–quinone interactions in catalytic processes.[17] We therefore looked at the possibility of adding a free quinone to a CpNiNHC catalyst that lacked a tethered quinone ligand. The results shown in entries c and d of Table 1 indicate that the free quinone is indeed capable of activating the catalysts for the desaturation process without needing to be incorporated in the ligand. The result with **2** and no added quinone (entry b) suggests the quinone is necessary for the dehydrogenation process to occur in quantifiable yields, but it does not necessarily have to be attached to the metal catalyst. Moreover, the addition of 10 equivalents of benzoquinone (related to the 0.5 mol% catalyst loading) raises the product yield by 19% from the catalytic run with only one equivalent (Table 1, entry c) of benzoquinone (Table 1, entry d).

Electrode materials other than Pt also proved suitable under the conditions, albeit with lower yields: Reticulated Vitreous Carbon (RVC)—55% and Stainless Steel 60 (SS60)—30%. Plots of charge *vs.* time after 4 h of electrolysis at 1 V *vs.* NHE with the three electrode materials are shown in Fig. 4. and the product yields in Table 2.

Ni/Pt has previously been shown to be a viable catalyst option for a fuel cell operating with an organic fuel.[18] In our own work, controls with suspended NiO and metallic Ni powders suspended in solution have shown significant current consumption; however modest product (40 and 30% respectively) and faradaic yields (53 and 34% respectively) were observed (Table S2, ESI†). This is indicative of parasitic non-productive processes occurring under these conditions, likely associated with substrate side-reactivity due to polyaniline formation, as has been previously observed.[15]

Fig. 2 Cyclic voltammetry of **1**: 2 mM **1** in a 0.1 M NBu_4BF_4 solution at a Pt working electrode at 100 mV s^{-1}.

Table 1 Chemical and faradaic yields for tetrahydroquinaldine dehydrogenation experiments at a Pt electrode 0.5 mol% catalysts **1** and **2**

Entry	Catalyst	Chemical yield[a] (%)	Faradaic yield[b] (%)
a	**1** 0.5 mol%	78	80
b	**2** 0.5 mol%	N/A	N/A
c	**2** 0.5 mol% + 0.5 mol%	51	71
d	**2** 0.5 mol% + 5 mol%	68	90
e	None	0	0
f	5 mol% benzoquinone	0	0

[a] Isolated yields. [b] Determined from the ratio of current used for current used for efficient product formation vs. total passed current.

Table 2 Chemical and faradaic yields for tetrahydroquinaldine dehydrogenation at a Pt electrode (entry 1), SS60 (2) and RVC (3) by **1** (0.5%). Plots of current vs. time shown in Fig. 4

Entry	Electrode material	Chemical yield (%)	Faradaic efficiency (%)
1	Pt	78	80
2	SS60	30	86
3	RVC	55	95

Conclusions

Dehydrogenation of 1,2,3,4-tetrahydroquinaldine is not only possible with quinone catalyst **1**, but also with free quinone added to the non-quinoid catalyst **2** (entries c and d in Table 1) that in the absence of the quinone is inactive. Our CpNi(NHC) catalyst is one of the first examples of first-row transition metal complexes exhibiting dehydrogenative electrocatalytic activity at room temperature and shows that a molecular catalyst precursor can be viable in the electrode-driven H_2 release step of "virtual hydrogen storage".[1]

Experimental

Synthesis and characterization of compound 1

To a 20 mL solution of 1.1 equivalents of nickelocene (41 mg, 0.22 mmol) in anhydrous THF, the yellow quinone-annulated dimesitylimidazolium chloride **ImQ** (0.2 mmol) was added as a solid as shown in eqn (1). The resulting suspension was then refluxed for 4 hours. **1** was isolated as a red solid in 69% yield by column chromatography in 4:1 hexanes–ethylacetate as a brown-red solid. FT-ICR MS analysis was performed at the Yale Keck Proteomics facility on a 9.4 T Bruker Qe FT-ICR MS. Elemental Analysis was performed by Robertson Microlit.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.01 (s, 2H, Ar_{CH}), 7.74 (s, 2H, Ar_{CH}), 7.20 (s, 4H, Mes_{CH}), 4.58 (s, 5H, Cp_{CH}), 2.50 (s, 6H, Mes_{p-CH3}), 2.08 (s, 12H, $Mes_{o,o'-CH3}$). $^{13}C\{^1H\}$ (126 MHz, CD_2Cl_2) δ 141.19, 135.85, 135.35, 133.00, 130.66, 128.25, 94.34, 22.46, 19.66. FT ICR MS: [M-Cl] calculated 557.1734, found 557.1721. Elemental analysis. Expected: C: 68.77%, H: 5.26%, N: 4.72% Found: C: 68.59%, H: 5.23%; N: 4.44%.

Acknowledgements

Notes and references

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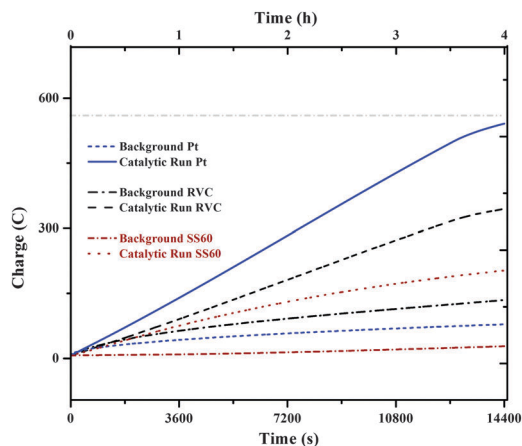2 R. Crabtree and O. Luca, WO Pat. 2,012,112,758, 2012.

Fig. 4 Plots of charge passed vs. time during 4 h of electrolysis at 1 V vs. NHE with the three different electrode materials. Background runs with just the model fuel (200 μL 1,2,3,4-tetrahydroquinaldine) in the absence of catalyst are shown in short dash-dot—SS60, dash-dot—RVC, dot-dot—Pt. Catalytic runs were performed at 0.5 mol% **1**. The top dashed gray line indicates the level of charge expected to pass for 100% efficient current conversion for the reaction depicted in eqn (2). Background current consumptions observed in the absence of catalyst **1** (at the bare electrode) in the presence of substrate does not correlate with formation of desired product and are depicted by dashed lines. Benzoquinone was unable to mediate the heterocycle desaturation in the absence of **2** at 5 mol% (entry f in Table 1).

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