

Electrocatalytic Dihydrogen Production with a Robust Mesoionic Pyridylcarbene Cobalt Catalyst

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Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday

Abstract: A Co^{III} complex with a mesoionic pyridylcarbene ligand is presented. This complex is an efficient electrocatalyst for H₂ production at very low overpotential and high turnovers when using a (glassy carbon) GC electrode. The corresponding triazole complexes display no catalytic activity whatsoever under identical conditions. The remarkable robustness of the Co–C(carbene) bond towards acids is likely responsible for the high efficiency of this catalyst. The present results thus open new avenues for carbene-based ligands for generating functional models for hydrogenases.

Dihydrogen is a promising fuel for the future and electrocatalysis is a key enabling technology for its use.^[1] The design of synthetic electrocatalysts for efficient proton reduction has been a goal for several decades. Ligand systems based on phosphines, porphyrins, and pyridines have been used in combination with first-row transition metals, which are arguably the most attractive candidates for generating the aforementioned catalyst.^[2] In current research in homogeneous catalysis, phosphine-based ligands are probably rivalled only by their N-heterocyclic carbene (NHC) counterparts.^[3] Thus, despite the presence of certain efficient phosphine-based electrocatalysts for dihydrogen production, it is surprising that almost no examples for such catalysts exist with NHC ligands. A possible reason for this is the intuitive assumption of the labile nature of metal–NHC bonds towards acids.

An emerging class of NHC ligands are mesoionic carbene (MIC) ligands of the form 1,2,3-triazol-5-ylidene (Figure 1).^[4] The modular synthesis of these ligands through the so-called click-reaction^[5a,b] have made them extremely popular in organometallic chemistry,^[5c] with homogeneous catalysis being a leading field of current research.^[6] Most examples of metal complexes reported with MIC ligands have been with the second- and third-row transition metals, with the only exceptions, to the best of our knowledge, being isolated

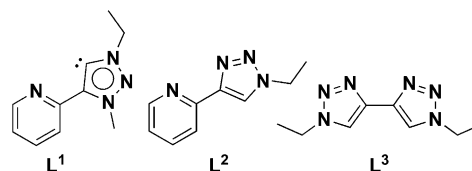


Figure 1. Ligands used in the present work.

examples of Fe, Ni, and Cu complexes.^[7] In the following, we present the Co complexes [Cp*CoL^{1–3}Cl](PF₆) (**1–3**, Cp* = 1,2,3,4,5-Pentamethylcyclopentadienyl) with click-synthesized triazoles or MIC ligands. We then show the capacity of the Co–MIC complex to act as an efficient electrocatalyst for dihydrogen production.

Complex **1** was synthesized by mixing the corresponding triazolium salt (HL¹)BF₄^[6f,n] in dry acetonitrile with basic silver(I) oxide and potassium chloride, and stirring the solution under exclusion of light. After 2 days, the chloro-bridged dimeric metal precursor [Cp*CoCl₂]₂ was added and the reaction was further stirred for 2 days under exclusion of light. The precipitate was filtered off and salt metathesis with potassium hexafluorophosphate from an acetone solution of the crude product afforded the pure complex **1** as a purple solid. For the preparation of **2** and **3**, the corresponding ligands **L**² and **L**³ were mixed with the same metal precursor [Cp*CoCl₂]₂ and potassium hexafluorophosphate in methanol and stirred for 2 h in air. After removal of the solvent, the residue was purified by filtration of a dichloromethane solution of the crude product over celite. Layering of this solution with hexane yielded **2** and **3** as purple solids. All the complexes were characterized by using ¹H and ¹³C NMR spectroscopy and mass spectrometry.

Single crystals were obtained for all three complexes through the diffusion of *n*-hexane into a concentrated dichloromethane solution of the corresponding complex. All of the complexes display the three-legged piano-stool-type geometry (Figure 2) expected for half-sandwich complexes of this type: the Cp* binds in a *h*⁵ fashion and one chloride ligand is also coordinated to the metal center. The coordinating atoms from the chelating ligands are the carbene carbon C1 and the pyridyl nitrogen N4 in the case of **1**, the triazole nitrogen N1 and pyridyl nitrogen N4 in the case of **2**, and the triazole nitrogens N1 and N2 in the case of **3**. While the triazole rings in complexes **2** and **3** display bond localization, the triazolylidene ring of **1** shows a more delocalized electron density.^[4d]

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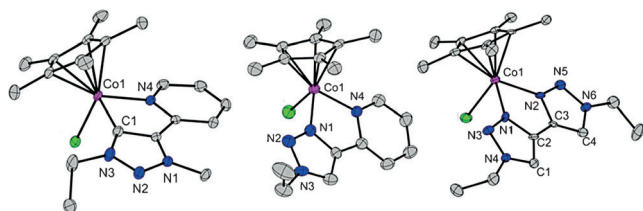


Figure 2. ORTEP plots of **1**, **2**, and **3** with ellipsoids shown at 50% probability. Hydrogen atoms and counteranions are omitted for clarity.

^1H NMR spectra of all three complexes were recorded in deuterated acetonitrile. Two signals are observed at $\delta = 8.52$ and 8.22 ppm in the ^1H NMR spectra of **2** and **3**, respectively. These signals can be assigned to the characteristic 5-*H* triazole proton. The absence of such a signal in the spectrum of **1** confirms the formation of a carbene complex. Interestingly, the methylene group of the ethyl residue of **1** and **3** shows a diastereotopic coupling pattern, while in the spectrum of **2**, a normal quartet was observed.

Cyclic voltammograms of **1**, **2**, and **3** were recorded in acetonitrile. All three complexes display two reduction processes (Figure S10 in the Supporting Information). The first reduction waves for **1** and **2** indicate the likely operation of an electron-transfer/chemical reaction (EC) mechanism, that is, the reduction of the complex (E) is accompanied by the dissociation of a chloride ligand (C). Similar behavior has been reported for the analogous Co–bipyridine complex.^[8] For all three complexes, the first reduction takes place almost at the same potential of -1.1 V vs. Fc/Fc^+ (unless otherwise noted, all potentials are referenced against the Fc/Fc^+ redox couple). The second reduction shifts from -1.38 V (**2**) to -1.59 V (**1**) to -1.84 V (**3**). The order of the second reduction potential roughly fits with the π -accepting capacity of the chelating ligands. These results likely point to the first reduction being Co-centered and the ligand playing a more active role in the second reduction step. The latter points to an electron density distribution between the metal center and the pyridylcarbene ligand, a phenomenon that has sometimes been referred to as ligand non-innocence.^[6a]

1, **2**, and **3** were investigated with respect to their activity for electrocatalytic H_2 production. Cyclic voltammograms in the presence of acetic acid ($\text{p}K_{\text{a}}^{\text{MeCN}} = 23.51$)^[9] in acetonitrile were recorded. A usual three-electrode set-up using a glassy carbon working electrode was employed. For **2**, almost no increase in current was observed on the addition of acid. The increase in current that was observed for **3** can be attributed to direct reduction of protons on the surface of the glassy carbon electrode owing to the high redox potential of **3** (Figure S20). For **1**, a new S-shaped reduction curve appeared at a potential slightly lower than the second reduction couple (Figure 3). The catalytic wave corresponds to dihydrogen evolution, as confirmed by mass spectrometry. Ongoing monitoring of the head space of the cell by MS during chronoamperometry experiments showed H_2 evolution at an applied potential of -1.54 V (Figures S21, S22). The dihydrogen evolution increased linearly with time and, as expected for an electrocatalytic process, it increased with increasing catalyst concentration. Importantly, the same chronoamper-

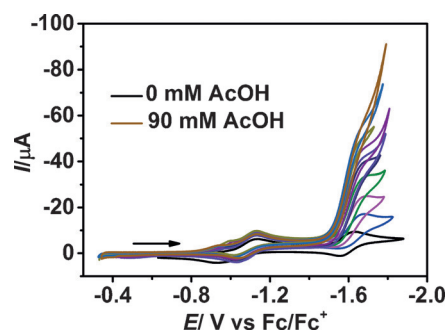


Figure 3. Cyclic voltammogram of a solution of **1** and acetic acid. Conditions: glassy carbon working electrode, 71 mm^2 , CH_3CN , $0.77 \times 10^{-3} \text{ M}$ **1**, $0.77 \times 10^{-3} \text{ M}$ to $92.4 \times 10^{-3} \text{ M}$ acetic acid, 0.1 M Bu_4NPF_6 , and a scan rate of 25 mV s^{-1} .

ometry experiment in the absence of the catalyst did not lead to any hydrogen production. This proves that the dihydrogen is evolved electrocatalytically. An average Faraday efficiency of 80% ($\pm 20\%$) was determined from the two bulk electrolysis experiments (Figure S22).^[10]

The onset of the catalytic wave occurs at a potential of -1.48 V and the half wave potential is reached at -1.56 V. In order to evaluate our catalyst, the turn over frequency (TOF) and the overpotential (η) of the reaction were determined. η can be calculated from the electrode potential and the apparent standard potential of proton reduction under the reaction conditions (see the Supporting Information for the derivation).^[11] The TOF and overpotential were determined by the recently reported foot-of-the-wave analysis (FOWA).^[12,2q] A maximum TOF of $4 \times 10^2 \text{ s}^{-1}$ was calculated and the Tafel plot revealed that the maximum TOF was already reached at a very low overpotential of 0.13 V (Figure 4). Bulk electrolysis confirmed H_2 evolution at an overpotential of $\eta = 0.08$ V at the remarkably low catalyst concentration of 0.42 mM . The Tafel plot for **1** and various well-known electrocatalysts (see Figure 4, for example, $\text{Co}(\text{dmgH})_2\text{py}$ ($\text{dmgH} = \text{dimethylglyoxime}$) reported by Artero et al.^[2c] or $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}})_2](\text{BF}_4)_2$ ($\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}} = 1,3,6\text{-triphenyl-1-aza-3,6-diphosphacycloheptane}$) reported by DuBois and Bullock^[2s,12]) shows that our system is very potent because it provides a satisfactory TOF at low overpotentials.^[12]

Complex **1** was tested for its stability towards acids to establish its integrity under catalytic conditions. 50 equivalents acetic acid were added and ^1H NMR spectra were recorded after 1, 4 and 24 h. Despite the potentially labile Co–C bond, no decomposition of the complex was observed under the conditions of the catalysis (Figure S7), thus establishing the robustness of such Co–carbene bonds towards acids. Further, a solution of **1** and acetic acid was electrolyzed and a cyclic voltammogram was measured every 1.5 h. It could be seen that the catalyst is stable under these conditions for at least 3 h. The kinetics of the dihydrogen evolution electrocatalyzed by **1** was then further investigated. To a solution with a constant concentration of **1**, several equivalents of acetic acid were added portionwise. By plotting i_c/i_p against the square root of the acid concentration,

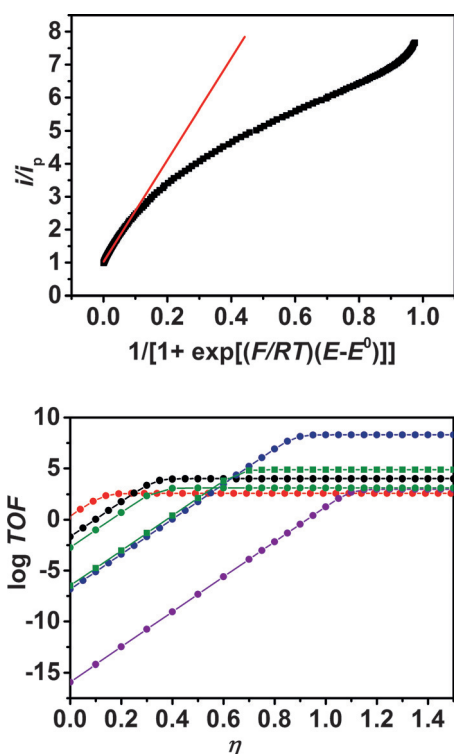
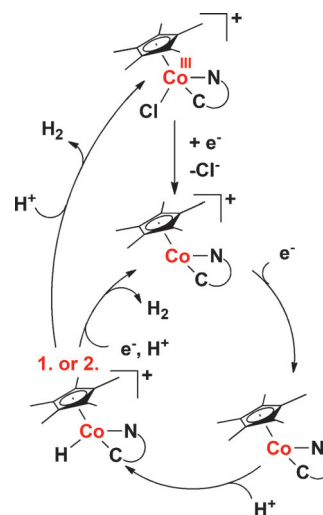


Figure 4. FOWA for the CV of **1** and acetic acid measured with 0.77 mM [**1**] and 90 mM [AcOH] (top, see Figure S17 and the Supporting Information for details). Tafel plot for various electrocatalysts: Red: **1**, (MeCN, AcOH); black: $\text{Co}(\text{dgmH})_2\text{py}$, (DMF, Et_3NH^+);^[12c] blue: $\text{Fe}^{\text{II}}\text{TPP}$ (DMF, Et_3NH^+);^[12d] green: $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_5\text{H}_4\text{X}})_2]^{2+}$ (Dots: (X = $\text{CH}_2\text{P}(\text{O})(\text{OEt}_2)$, MeCN, HDMF^+), squares: (X = H, MeCN, HDMF^+));^[12c] purple: $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}})_2]^{2+}$ (MeCN, DMFH^+).^[20]

a reaction order of 2 with respect to the acid was determined (Figure S13). Furthermore, **1** was titrated to a solution of constant acid concentration. By plotting the catalytic current versus the concentration of **1**, it could be seen that the reaction order is 1 with respect to the catalyst (Figure S14).

On the basis of all of the electrochemical data for **1** in the absence and presence of acetic acid, a first, although still ambiguous, mechanism can be postulated (Scheme 1). A heterolytic pathway is likely the dominant pathway, because we utilized a reasonably strong acid, observed first-order kinetics with respect to **1** (Figure S13), and the plot of the half-wave potential $E^{1/2}$ against the square root of the acid concentration give a constant (Figure S24).^[12a] The latter two observations are diagnostic criteria for a heterolytic pathway, although at the current stage, we cannot rule out a homolytic pathway.^[12b] The first reduction of **1** is followed by decoordination of the chlorido ligand (see above). Subsequently, the second reduction occurs, which is followed by protonation of the doubly reduced species, most likely with the formation of a hydrido complex. After the above steps, two reaction pathways are likely: 1) The Co^{III} hydride is reduced to a Co^{II} hydride, which releases H_2 upon protonation (ECEC mechanism) or 2) the Co^{III} hydride is directly protonated again and H_2 is formed (EECC mechanism). Detailed mechanistic investigation will be part of a future project.



Scheme 1. Postulated mechanism of electrocatalytic proton reduction.

In conclusion, we have synthesized a new series of cobalt complexes with three different types of bidentate chelating ligands bearing a (bis)triazole (**3**), a pyridyl triazole (**2**), and a pyridyl MIC (**1**) moiety. We tested all three complexes for activity in electrocatalytic H_2 production by employing acetic acid as a very inexpensive proton source. Electrocatalytic experiments showed that **1** is an excellent catalyst, providing a maximum TOF of $4 \times 10^2 \text{ s}^{-1}$, which is achieved even at a very low overpotential of 0.13 V when using glassy carbon as electrode material. Turnover numbers (TONs) of about 650 000 were reached during 30 min of electrocatalysis in the reaction–diffusion layer.^[12a] To the best of our knowledge, **1** is not only the first reported mesoionic cobalt carbene complex but also a rare case in which a metal–carbene complex has been investigated as a catalyst in proton reduction. The present results thus provide a new class of robust molecules for generating functional models for hydrogenases. Future work will focus on optimizing the catalytic conditions as well as the catalyst, and on gaining detailed mechanistic insight into the working of this intriguing class of catalysts.

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