Investigation of Cyclam Based Re-Complexes as Potential Electrocatalysts for the CO₂ Reduction Reaction

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Dedicated to Professor Dr. Peter Klüfers on the Occasion of his 70th Birthday

Among the various homogenous electrocatalysts, especially $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ and $[\text{Ni}(\text{cyclam})]^{2+}$ were shown to be highly efficient for the selective conversion of CO_2 to CO at moderate potentials. However, a purposeful combination of a Re^{I} tricarbonyl unit with a cyclam ligand hitherto received no

Introduction

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The earths major greenhouse gas, CO₂, contributes massively to the current global warming with a global radiative forcing of at least 2.076 Wm^{-2} , which accounts to 66% of the total anthropogenic radiative forcing.^[1–5] Since the ever-increasing global warming triggers an unstoppable climate change, which in turn affects the environment and its ecological systems adversely, a decrease of further CO₂ emissions and a reversal of the unnaturally high concentrations of CO₂ already accumulated in the atmosphere is of crucial importance.^[1,5-7] While the avoidance of CO₂ emissions can be achieved by increasing the efficiency of existing energy conversion processes based on fossil fuels and by establishing sustainable energy resources, the reduction of the existing high CO₂ concentrations in the atmosphere can be achieved through carbon capture and utilization (CCU), which deals with the chemical conversion and utilization of CO₂.^[1,6,8,9] Since the activation and conversion of CO2 into energy-rich products is associated with high energy

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attention. Herein, we report on a series of cyclam based Re complexes comprising the original $\{N_4\}$ as well as heteroatomaltered ligand frameworks, describe their synthesis, reveal their coordination behavior and furthermore investigate their performance towards the electrochemical CO₂ reduction.

demands, suitable strategies are required to achieve a selective and low-energy conversion.^[1,2,10,11]

Among the variety of CO₂ reduction approaches, electrocatalysis was suggested to be the most promising and sustainable, as it can be run directly with renewable power.^[2,12–14] However, finding suitable electrocatalysts that operate at low overpotentials and with a high selectivity for the CO₂ reduction is challenging.^[15–17] Although heterogeneous electrocatalysts are preferred for industrial applications due to their easy handling, high robustness and low price, homogeneous electrocatalysts are the key towards understanding and identification of essential features for an efficient electrocatalytic CO₂ reduction reaction (CO₂RR).^[14,18,19] The enormous bandwidth of homogeneous CO₂RR electrocatalysts can be divided into noble metal and non-noble metal containing catalysts.

One of the most prominent noble metal containing electrocatalyst is Re(bpy)(CO)₃Cl (1, bpy = 2,2'-bipyridine), that was first described by *Lehn et al.* in 1984 (Scheme 1).^[20] At a moderate potential of -1.25 V vs. NHE in DMF/water (9:1) in the presence of a glassy carbon working electrode, complex 1 catalyzes the selective reduction of CO₂ to CO with a Faraday Efficiency (FE) of up to 98%.^[20,21] The catalytically active species was identified as [Re(bpy)(CO)₃]⁻, which is generated by two successive electron uptakes, with the initial being located at the bpy ligand, leaving a vacant coordination site at the Re⁰ center upon loss of the chloride ligand.^[22-24] During catalysis, CO₂ is initially activated and bound to the vacant site of the rhenium center as η^1 -CO₂H. A subsequent electron and proton uptake,



Scheme 1. Schematic overview of complexes $Re(bpy)(CO)_3Cl 1$, [Ni $\{N_4\}^{2+} 2$ and $[Re(tacn)(CO)_3]^+ 3$.

accompanied by water release, generates the intermediary tetracarbonyl Re¹ complex [Re(bpy)(CO)₄]⁰. In a last step, CO is released after additional electron uptake and the catalytically active species is recovered.^[23,24]

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In order to further understand the electrocatalytic CO₂RR performance of complex **1** a broad variety of modulations of the bpy ligand and furthermore substitutions of bpy for comparable ligand platforms (e.g. pyNHC, pypz, pyiz) were investigated.^[23-37] Among the large number of modified rhenium complexes and within the most studied class, the 4,4'-substituted bpy rhenium complexes, the 'Bu-derivative Re-(bpy-^tBu)(CO)₃Cl (bpy-^tBu=4,4'-di-tert-butyl-2,2'-bipyridine) is particularly noteworthy.

Although operating at a ~0.1 V higher overpotential, Re-(bpy- ¹Bu)(CO)₃Cl reveals a ten times higher catalytic activity compared to complex 1.^[23,25] Likewise, a series of rhenium tricarbonyl complexes containing aniline-substituted bpy derivatives with the amine function at *ortho-*, *meta-* and *para*position was investigated. While the *meta-*version reveals the best activity within the series with a more than three times higher turnover frequency (TOF) compared to complex 1, the *para-* version shows an inhibition, likely due to coordination of the aniline-amine function to the reduced rhenium center.^[31]

Among the non-noble metal containing electrocatalysts, $[Ni(cyclam)]^{2+}$ (2, $cyclam = \{N_4\} = 1,4,8,11$ -tetraazacyclotetra-decane) is one of the most efficient systems with a high FE of 96% and a reaction rate of 32 h⁻¹ for the selective reduction of CO₂ to CO at a potential of -1.05 V vs. NHE at pH 4.1 in water on a mercury working electrode (Scheme 1).^[38-42]

Along this line, we recently investigated the effects regarding electrocatalytic CO₂RR upon heteroatom replacement and geometric changes caused by the cyclam ligand.^[43,44] Although N/S replacement in case of $[Ni\{N_2S_2\}]^{2+}$ ($\{N_2S_2\}=1,8$ -dithia-4,12-diaazacyclotetradecane) resulted in a 0.2 V decreased overpotential for the electrocatalytic CO₂ reduction, the CO₂RR selectivity was severely mindered.^[43] Similar results were obtained for the Ni-isocyclam derivative (isocyclam = $\{i-N_4\}$ = 1,4,7,11-tetraazacyclotetradecane), $[Ni\{i-SN_3\}]^{2+}$ ($\{i-SN_3\}$ = 1-thia-4,8,12-triazacyclotetradecane).^[44]

We herein set out to combine both mentioned approaches and investigated rhenium complexes bearing macrocyclic cyclam and isocyclam based ligands for the CO_2RR . Notably, besides the synthesis and characterization of $[Re(tacn)(CO)_3]^+$ (**3**, tacn = 1,4,7-triaazacyclo-nonane) and its N/S or N/O heteroatom replaced derivatives, there are no studies on rhenium tricarbonyl complexes comprising azamacrocyclic ligands (Scheme 1).^[45–47] We thus herein present the synthesis and characterization of a novel series of cyclam based rhenium tricarbonyl complexes and their electrochemical properties.

Results and Discussion

Complex Syntheses and Characterization

While the $\{N_4\}$ ligand can be purchased, the cyclam based ligand $\{N_2S_3\}$ as well as the isocyclam based ligands $\{i-SN_3\}$, $\{i-$ ON₃} and {*i*-N₄} itself were synthesized according to literatureknown procedures.^[44,48] For the synthesis of the corresponding rhenium complexes, the macrocyclic ligands $\{N_{4}\}, \{N_{2}S_{2}\}, \{i-N_{4}\}, \{i-N_{4}\}$ {*i*-SN₃} and {*i*-ON₃} were reacted with equimolar amounts of Re(CO)₅Br in acetone under reflux conditions. After purification via recrystallization, the desired rhenium complexes $Re\{N_{4}\}$ (= $[\text{Re}(\kappa^{3}-N,N,N-\{N_{4}\}(\text{CO})_{3}]\text{Br},$ 87%), $Re\{N_2S_2\}$ $(=[Re(\kappa^3-S,S,N \{N_2S_2\}(CO)_3]Br$, 90%), **Re** $\{i-N_4\}$ (= [Re($\kappa^3-N_1,N_1,N_1-\{i-N_4\}(CO)_3]Br$, 74%), **Re**{*i*-SN₃} (= [Re(κ^3 -S,N,N-{*i*-SN₃}(CO)₃]Br, 92%) and **Re**{*i*-**ON**₃} (=[Re(κ^3 -N,N,N-{*i*-ON}_3)(CO)₃]Br, 98%) were obtained as colorless solids in good yields (Scheme 2). The successful complexation and furthermore the exact composition of the rhenium complexes was supported by electrospray-ionization mass spectrometry (ESI-MS), revealing characteristic peaks at m/ $z = 470.9 \ (\text{Re}\{N_4\}), \ 504.8 \ (\text{Re}\{N_2S_2\}), \ 470.9 \ (\text{Re}\{i-N_4\}), \ 487.9 \ (\text{Re$ SN₃) and 471.9 (Re{i-ON₃}) for the corresponding [Re(L)(CO)₃]⁺ fragments. Since the observed complex ions do not contain a bromine, it can be concluded that the rhenium complexes are cationic and bromide acts as non-coordinating counter ion.

Single crystals of complexes $Re\{N_4\}$, $Re\{i-N_4\}$, $Re\{i-SN_3\}$ and $Re\{i-ON_3\}$ were obtained either from acetone or methanol solutions and provided further information about the coordination environment of the rhenium centers and binding modes of the corresponding macrocycles.

All rhenium centers are coordinated octahedrally as *fac*isomers by three carbonyl ligands and additional three donor atoms of the macrocycles in a κ^3 -manner, leaving one donor atom of the macrocycles uncoordinated (Figure 1). Due to the symmetry of ligand {**N**₄} there is only one κ^3 -isomer possible in the case of complex **Re**{**N**₄}. The averaged Re–N distance of **Re** {**N**₄} is 2.235 Å and the averaged Re–C and C–O bond lengths are 1.913 Å and 1.153 Å, respectively. Analysis of the bond angles furthermore reveals that the octahedral coordination sphere of complex **Re**{**N**₄} is highly distorted with the L–Re–L binding angles ranging from 102.9° to 77.8° (Table S1).



Scheme 2. Syntheses of the rhenium complexes $Re\{N_4\}$, $Re\{N_2S_2\}$, $Re\{i-N_4\}$, $Re\{i-SN_3\}$ and $Re\{i-ON_3\}$.



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Figure 1. Molecular structures of the complexes $Re\{N_{4}\}$ (A), $Re\{i-N_{4}\}$ (B), Re{i-SN₃} (C) and Re{i-ON₃} (D) shown with thermal ellipsoid drawn at the 50% probability level. Hydrogen atoms and bromide counterions are omitted for clarity. Gray: carbon, blue: nitrogen, yellow: sulfur, red: oxygen and dark blue: rhenium.

In contrast to {N₄}, three κ^3 -isomers are possible for the simplest structurally related ligand {i-N₄}. However, only one isomer is obtained in case of $Re{i-N_4}$ with the nitrogen atom between the propyl units uncoordinated. With an averaged Re–N distance of 2.214 Å the nitrogen atoms in $Re{i-N_4}$ are slightly stronger bonded to the rhenium center compared to Re $\{N_{4}\}$. However, the averaged Re–C and C–O bond lengths of Re {*i*-N₄} remain comparatively equal with 1.912 Å and 1.150 Å.

Furthermore, bond angle analysis shows that the octahedron of Re{i-N₄} is overall less distorted compared to Re{N₄} (Table S1).

Similar to ligand $\{i-N_4\}$, three κ^3 -isomers for the corresponding $[\text{Re}(\kappa^3-\{L\})(\text{CO})_3]^+$ complexes are possible for the ligands {*i*-SN₃} and {*i*-ON₃}. While the formation of the κ^3 -isomer of Re{*i*- N_{4} seems to be exclusively dependent on geometrical factors, the κ^3 -isomer choices of **Re**{*i*-SN₃} and **Re**{*i*-ON₃} are additionally dependent on the nature of the donor atoms due to the mixed donor sets provided.

In case of Re{i-SN₃} the sulfur donor atom of the macrocycle binds to the rhenium center and similar to Re{i-N₄} the nitrogen atom between the propyl units remains uncoordinated. The formation of this specific κ^3 -isomer is favored by two factors. On the one hand the complex occupies a preferred thermodynamic geometry and on the other hand sulfur is coordinated as preferred donor atom according to the HSAB concept. Complex Re{i-SN₃} has a Re–S distance of 2.456 Å and an averaged Re–N bond length of 2.237 Å. Moreover, due to the influence of the sulfur donor atom the Re-C bond lengths is altered significantly compared to Re{i-N₄}. While the averaged C–O distance of Re{i-SN₃} is maintained with 1.150 Å, the averaged Re–C bond length is comparatively elongated with 1.928 Å, indicating a weaker π -backbonding in case of **Re**{*i*-**SN**₃}. Moreover, the octahedral geometry in Re{i-SN₃} is less distorted compared to **Re**{*i*-**N**₄} with L–Re–L binding angles ranging from 98.6° to 78.7° (Table S1).

Unlike Re{i-SN₃}, where the non-nitrogen donor atom of the macrocycle binds to the rhenium center, in Re{i-ON₃} the oxygen atom of the $\{i-ON_3\}$ macrocycle remains uncoordinated. The formation of this specific κ^3 -isomer of Re{*i*-ON₃} can be justified by the HSAB concept. Since Re¹ is a soft transition metal, the coordination of the comparatively softer nitrogen donor atoms is favored over the relatively hard oxygen donor atom. Although the κ^3 -N coordination mode herein is geometrically unfavored, Re{i-ON₃} is adopting this binding mode to avoid the coordination of oxygen. With an averaged distance of 2.253 Å the Re-N bond length in Re{i-ON₃} is significantly longer compared to Re{i-N₄} and slightly longer compared to **Re**{ N_4 }. The averaged Re–C and C–O bond lengths of **Re**{*i*-ON₃} are with 1.917 Å and 1.154 Å in a similar range as those of Re{i-N₄} and Re{N₄}. However, complex Re{i-ON₃} is compared to Re $\{i-N_{A}\}$ overall less distorted with L-Re-L binding angles ranging from 97.6° to 79.4° (Table S1).

Especially for carbonyl complexes, IR spectroscopy is a valuable tool in order to gain information about the geometry and symmetry of the complexes and to determine the effects of the remaining ligands on the electronic properties of the metal center. The IR spectra of complexes Re{N₄}, Re{N₂S₂}, Re{i-N₄}, Re{i-SN₃} and Re{i-ON₃} reveal a similar band structure in the carbonyl region, with a sharp band over 2000 cm⁻¹ and a broad band around 1900 cm⁻¹, which is characteristic for [Re(L)(CO)₃]⁺ fac-isomers (Figure 2).^[46] However, within the different rhenium complexes there are small alterations in the general band structure, that can be explained by the different donor atom sets and the differently distorted octahedron geometries. While for all κ^3 -N complexes Re{N₄}, Re{i-N₄} and Re{i-ON₃} the sharp



Figure 2. Solid ATR-IR spectra of the rhenium complexes Re{N₄} (red), Re{N₂S₂} (blue), Re{i-N₄} (yellow), Re{i-SN₃} (green) and Re{i- ON_3 (violet). For comparison, the band positions of $Re\{N_4\}$ are shown as grey dotted lines.

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Although no molecular structure of complex Re{N₂S₂} was obtained, we can now predict the κ^3 -binding mode of the $\{N_2S_2\}$ ligand based on the IR data of complexes $Re\{N_2S_2\}$ and $Re{i-SN_3}$ and the molecular structure of $Re{i-SN_3}$. Since the CO bands of $Re\{N_2S_2\}$ are observed at significantly higher wavenumbers compared to the bands of complex Re{i-SN₃}, where one sulfur atom is coordinated to the rhenium center, and the coordination of sulfur atoms is known to result in a weaker π backbonding, complex **Re**{N₂S₂} is most likely the κ^3 -S,S,N isomer.

While the thermodynamically preferred coordination modes of the rhenium complexes Re{N₄}, Re{i-N₄}, Re{i-SN₃} and Re{i-ON₃} in the solid state were revealed by crystal structure analyses, no information is provided about the structures in solution. In order to shed light on the structures of the rhenium complexes in solution ¹³C{¹H} NMR spectroscopic experiments in deuterated methanol were carried out. Since for the C1 symmetric complex **Re**{N₄} only one κ^3 -isomer is thinkable, ten different signals for the macrocyclic ligand are expected and found in the corresponding ${}^{13}C{}^{1}H$ NMR spectrum (Figure S1). Contrary to complex $Re\{N_4\}$, in case of the C₁ symmetric

Table 1. Chelectrochen	naracteristic nical data of !{i-ON ₃}.	IR and UV spe complexes R	ectroscopic fea e{N ₄ }, Re{N ₂ S ₂ }	tures and , Re{i-N₄}, Re{i-
complex	IR solid \tilde{v} (cm ⁻¹)	UV MeCN λ (nm)	E _{pc} ^[a] MeCN (V)	$E_{pc}^{[a]}$ MeCN/ H ₂ O (V)
Re{N ₄ }	2014 1898 1880	317 322 (sh)	-2.68	-2.55
$Re{N_2S_2}$	2027 1906	318 324	-2.31	-2.23
Re{ <i>i</i> -N ₄ }	2014 1873	318 323 (sh)	-2.57	-2.47
Re{ <i>i</i> -SN₃}	2019 1886	318 324	-2.56	-2.31
Re{ <i>i</i> -ON₃}	2015 1894 1875 1853	318 323 (sh)	-2.69	-2.48
[a] Cathodio	c peak pote	ntial vs. Fc/Fc	t ⁺ at 100 mVs ⁻	-1

complex Re{N₂S₂} twenty signals are observed in the corresponding ¹³C¹H NMR spectrum, indicating either an equilibrium between the two possible κ^3 -isomers or the presence of two different conformational isomers in solution (Figure S2). In case of the, according to their crystal structures, C_{2v} symmetric isocyclam based complexes Re{i-N₄}, Re{i-SN₃} and Re{i-ON₃}, five different signals are expected in their ¹³C{¹H} NMR spectra for the corresponding macrocyclic ligand. However, all ¹³C NMR spectra of the complexes $Re{i-N_4}$, $Re{i-SN_3}$ and $Re{i-ON_3}$ reveal additional signals besides the expected dominant five signals, also indicating the presence of different κ^3 -or conformational isomers in solution (Figures S3–S5).

Further investigations of the rhenium complexes using UV/ vis/NIR spectroscopy show in all cases a similar double absorption band structure in the UV region around 320 nm, whereby the exact band positions of the rhenium complexes differ only by 1–2 nm (Table 1 and Figure S6). Furthermore, while in case of the κ^3 -N complexes Re{N₄}, Re{i-N₄} and Re{i-ON₃} the band at lower wavelengths can be seen as shoulder of the absorption at higher wavelengths, the same band is more pronounced in case of the κ^3 -S/N complexes Re{N₂S₂} and Re{*i*-SN₃} and can be seen as discrete band.

Electrochemical Characterization

All rhenium complexes Re{N₄}, Re{N₂S₂}, Re{i-N₄}, Re{i-SN₃} and Re{i-ON₃} were characterized by cyclic voltammetry (CV) in dry acetonitrile with 0.1 M ["Bu₄N]PF₆ as supporting electrolyte in an argon atmosphere at a scan rate of 100 mV s^{-1} (Figure 3).

Comparison of the CVs of the different complexes reveals that all rhenium complexes have the same shape and features in their voltammograms. At potentials more negative than -2.30 V vs. Fc/Fc⁺ they show an irreversible Re^{1/0} redox couple and at potentials more positive than 0.35 V vs. Fc/Fc^+ they show an irreversible Re^{II/I} redox couple. In all cases, the mentioned Re^{1/0} and Re^{11/1} couples stay fully irreversible, when altering the scan rate (Figures S7–S11).

Although the CVs of all rhenium complexes have the same shape, the individual complexes differ significantly in their cathodic peak potentials E_{pc} for the $Re^{1/0}$ couple (Table 1). Compared to $Re\{N_4\}$, which reveals an E_{pc} of -2.68 V vs. Fc/Fc⁺ for the $\text{Re}^{1/0}$ couple, the exchange of two nitrogen donor atoms against sulfur while maintaining the ligand geometry leads to an anodic shift of the E_{pc} by 0.37 V to -2.31 V vs. Fc/Fc⁺, as in the case of Re{N₂S₂}. Changing the geometry compared to Re $\{N_{4}\}$ while maintaining the donor atoms, as in the case of Re{*i*- N_4 , also results in an anodic but comparatively smaller shift of the E_{pc} by 0.1 V to -2.57 V vs. Fc/Fc⁺. When combining the effects of geometric change and donor atom exchange, which individually cause a shift of the E_{pc} to more anodic potentials, a more anodic E_{pc} would be expected in the case of Re{i-SN₃} compared to Re{i-N₄}. However, with -2.56 V vs. Fc/Fc⁺ the E_{pc} of Re{i-SN₃} remains unaltered compared to Re{i-N₄}. Furthermore, complex **Re**{*i*-**ON**₃}, with the actual unfavored κ^3 - N geometry shows an expected and compared to Re{i-N₄} more cathodic E_{pc} of -2.69 V vs. Fc/Fc⁺ for the Re^{1/0} redox couple.

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Figure 3. Cyclic voltammograms of 1 mM solutions of complexes $Re\{N_4\}$, $Re\{N_2S_2\}$, $Re\{i-N_4\}$, $Re\{i-SN_3\}$ and $Re\{i-ON_3\}$ in acetonitrile with 0.1 M ["Bu₄N]PF₆ at 100 mV s⁻¹.

The anodic peak potentials E_{pa} for the $Re^{1/1}$ couple also differ for the individual rhenium complexes. However, the difference between all complexes is much less pronounced and within a range of 80 mV. Moreover, the E_{pc} for the $Re^{1/0}$ couple is more relevant compared to the E_{pa} for the $Re^{11/1}$ couple, since the Re^{0} species is expected to be the potentially catalytic active species for the CO_2 reduction reaction.

Finally, the electrochemical properties of complexes $Re\{N_4\}$, $Re\{N_2S_2\}$, $Re\{i-N_4\}$, $Re\{i-SN_3\}$ and $Re\{i-ON_3\}$ were analyzed in an acetonitrile/water mixture (4:1), since water acts as proton source for the later examined electroreduction of CO_2 (Figure 4, dashed lines).

The CVs of the rhenium complexes in the presence of water reveal the same features as the measurements in pure acetonitrile. All complexes show a fully irreversible Re^{1/0} couple and a compared to the measurements in pure acetonitrile slightly more reversible Re^{11/1} couple. While the Re^{1/0} couples of all rhenium complexes and the Re^{11/1} couples of Re{N₂S₂}, Re{*i*-N₄} and Re{*i*-SN₃} stay irreversible when increasing the scan rate, the nature of the Re^{11/1} couples of Re{N₄} and Re{*i*-ON₃} can be identified as quasi-reversible based on the measurements with increased scan rates (Figures S12–S16).

Although in presence of water the cathodic peak potentials of the $\text{Re}^{1/0}$ couples are generally shifted to more anodic potentials compared to the measurements in acetonitrile, the individual shifts of the rhenium complexes are different (Table 1). While for complexes $\text{Re}\{N_4\}$, $\text{Re}\{N_2S_2\}$ and $\text{Re}\{i-N_4\}$ the potential shift is around 0.1 V, the shift for complexes $\text{Re}\{i-SN_3\}$ and $\text{Re}\{i-ON_3\}$ is with 0.2 V significantly higher.



Figure 4. Cyclic voltammograms of 1 mM solutions of complexes $Re\{N_4\}$, $Re\{N_2S_2\}$, $Re\{i-N_4\}$, $Re\{i-SN_3\}$ and $Re\{i-ON_3\}$ in acetonitrile/water (4:1) under argon (dashed lines) and saturated with CO₂ (solid lines) with 0.1 M ["Bu₄N]PF₆ at 100 mV s⁻¹.

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> After saturation of the acetonitrile/water (4:1) solutions of the rhenium complexes with CO₂, the shape of the CVs changed drastically in all cases compared to the measurements in an argon atmosphere (Figure 4, solid lines). In the presence of CO₂ a significant reductive current increase is observed for complexes Re{N₄}, Re{N₂S₂}, Re{*i*-N₄} and Re{*i*-ON₃} after generation of the Re⁰ species, indicating a potential interaction with CO₂. For complex Re{i-SN₃}, the same kind of current increase is observed, however, much less pronounced. Moreover, a much higher reductive current maximum i_{pc} around 100 μ A is observed for all κ^3 -N complexes Re{N₄}, Re{*i*-N₄} and Re{*i*-ON₃}, compared to the i_{pc} around 40 μ A observed for the κ^3 -S,N complexes Re{N₂S₂} and Re{*i*-SN₃}. Furthermore, in the presence of CO₂ all complexes reveal an additional oxidative signal prior the wave associated with the Re^{II/I} redox couple. This oxidation peak only appears when generating the Re⁰ species beforehand. If the CV scan is performed solely in oxidative direction, the wave is missing in all cases (Figure S17). This finding further suggests that the electrochemically generated Re⁰ species interact with CO₂ and potentially catalyze its reduction.

> Analysis of the i_{cat}/i_{pc} ratios of the complexes **Re{N₄**} (1.63), Re{N₂S₂} (1.45), Re{*i*-N₄} (1.66), Re{*i*-SN₃} (1.14) and Re{*i*-ON₃} (2.15) in acetonitrile/water (4:1) shows that the catalytic activities of the rhenium complexes studied here are significantly lower compared to the benchmark electrocatalysts Re(bpy)(CO)₃Cl (4.4 in anhydrous acetonitrile, 13.4 in acetonitrile +4% TFE) and $[Ni(cyclam)]^{2+}$ (~4 in acetonitrile/ water (4:1)).[31,49]

Electrocatalytic CO₂ Reduction

In order to determine the formed reduction products and furthermore the amount as well as selectivity they are formed within the catalytic regions of the different rhenium complexes, additionally controlled potential colometry (CPC) experiments were carried out (Figure S18). These long-term electrolyses were performed at defined potentials for 24 h in a one-compartment cell using a three-electrode setup with glassy carbon as working electrode, a silver wire as pseudo-reference electrode and a platinum wire as counter electrode. After saturation of the 1 mM rhenium complex and 0.1 M ["Bu₄N]PF₆ containing acetonitrile/water (4:1) solution with CO₂, the cell was sealed tightly for the time of the experiment. The CPCs with the different rhenium complexes were carried out at the corresponding peak potentials of the catalytic currents observed in the presence of CO_2 (Figure 4 and Table 2). During electrolysis, the headspace composition of the cell was analyzed every 2 h within the first 8 h via GC-MS (Table 2) and after 24 h electrolysis, the composition of the headspace of the cell and additionally the composition of the liquid phase of the cell was analyzed via GC-MS (Figure 5). The selectivity of the product formation utilizing the different rhenium complexes is reflected by the Faradaic Efficiencies (FE) and in combination with the consumed charge the maximum amounts of formed products can be determined along with a statement about the activity.

complex	E _{CPC} ^[a] (V)	Time (h)	FE _{H2} (%)	FE _{co} (%)	Q (C)	TON ^[b]
blank	-2.68	2	78	2.1	0.12	
		4	69	0.2	0.35	
		6	89	0.5	1.5	-
		8	95	0.3	3.7	
		24	96	0.7	22.3	
Re{N₄}	-2.68	2	53	4.8	0.17	
		4	67	7.4	0.56	
		6	63	9.3	1.0	0.90
		8	69	11	1.4	
		24	57	11	3.9	
Re{N ₂ S ₂ }	-2.47	2	46	4.5	0.12	
		4	56	4.5	0.22	
		6	44	4.7	0.31	0.08
		8	53	4.9	0.43	
		24	41	4.9	1.56	
Re{ <i>i</i> -N₄}	-2.59	2	44	13	0.47	
		4	56	15	1.3	
		6	69	18	2.3	4.10
		8	70	17	3.6	
		24	75	6.9	22.4	
Re{ <i>i</i> -SN₃}	-2.35	2	89	2.9	0.10	
		4	83	7.0	0.40	
		6	76	7.3	0.75	0.62
		8	72	7.8	1.0	
		24	69	6.5	4.0	
Re{ <i>i</i> -ON₃}	-2.61	2	52	10	0.14	
		4	60	7.7	0.33	
		6	45	7.9	0.62	0.93
		8	44	11	0.90	
		24	49	21	3.1	

Table 2. Quantification of the gaseous electrolysis products by

In general, during all experiments utilizing the different rhenium complexes only H₂ and CO were obtained as gaseous products. The complexes generally herein suppress the H₂ formation which is the main reaction in the absence of any Re^I complex. In addition, after 24 h of electrolysis, none of the experiments showed the formation of a deposited species during rinse test analysis, which would be an indication for catalyst decomposition or at least render the catalytically active species to be a heterogeneous one.

Within the first 8 h of CPC with Re{N₄} as catalyst, the cumulated FEs for the production of H₂ and CO increased from 58% to 80% during electrolysis, whereby the CO/H₂ ratio shifted from 1:11 to 1:6 in favor of CO, resulting in a FE of 11% for CO after 8 h.

After 24 h of electrolysis, the FE for the generation of H₂ decreased to 57%, while the FE for the generation of CO was maintained at 11%, further improving the CO/H₂ ratio. Additionally, liquid phase analysis revealed formic acid with a FE of 7.2% as well as methanol with a notably FE of 12% as further CO_2RR products. Although the use of $Re\{N_4\}$ as electrocatalyst reveals a low selectivity for the CO_2RR with a total FE of ~30% for the sum of all CO₂ reduction products, the selectivity is



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Figure 5. Faradaic Efficiencies (FE, stacked bars) and total consumed charge (red lines) after 24 h long-term electrolysis of 1 mM rhenium complex solutions in CO₂ saturated acetonitrile/water (4:1) with 0.1 M ["Bu₄N]PF₆ at a defined potential. The potential during electrolysis was held at -2.68 V vs Fc/Fc⁺ for blank, at -2.68 V vs Fc/Fc⁺ for Re{N₄}, at -2.47 V vs Fc/Fc⁺ for Re{N₂S₂}, at -2.59 V vs Fc/Fc⁺ for Re{*i*-N₄}, at -2.35 V vs Fc/Fc⁺ for Re{*i*-SN₃} and at -2.61 V vs Fc/Fc⁺ for Re{*i*-ON₃}. Gray: hydrogen (H₂), blue: carbon monoxide (CO), green: formic acid (FA) yellow: methanol (MeOH) and red: acetaldehyde (C–CHO).

drastically increased compared to the blank measurement in absence of any catalyst (FE_{co} 0.7%). However, it must be taken into account that the charge consumed during electrolysis in presence of $Re\{N_4\}$ is almost six times lower compared to the measurement without catalyst, indicating a lower total catalytic activity for $Re\{N_4\}$.

Compared to Re{N₄}, the FEs of Re{N₂S₂} for the formation of the gaseous products within the first 8 h are lower and relatively constant with an averaged FE of 50% for H_2 and 4.7% for CO, resulting in an averaged CO/H₂ ratio of 1:11. Product quantification after 24 h electrolysis using Re{N₂S₂} as catalyst revealed a decrease in the FE for the H_2 production to 41%, while the FE for the CO production was maintained at 4.9%. Furthermore, liquid phase analysis showed the formation of acetaldehyde with a FE of 18%. However, this product originates from the hydrogenation of acetonitrile, rather than CO₂ reduction, as already observed in previous studies on similar nickel- and cobalt-containing complexes.[44,50] Moreover, besides the drastically lower CO₂RR selectivity of Re{N₂S₂} compared to $Re\{N_{4}\}$, the total consumed charge and the total FE of the electrolysis with $Re\{N_2S_2\}$ are significantly lower compared to that with $Re\{N_4\}$, indicating a comparatively lower catalytic activity for $Re\{N_2S_2\}$.

In case of **Re**{*i*-**N**₄} the FEs for the generation of both H₂ and CO increases gradually during the first 8 h of electrolysis, reaching a plateau with a FE of 70% for H₂ and 17% for CO. Although **Re**{*i*-**N**₄} revealed a higher FE for the production of CO after 8 h compared to **Re**{**N**₄}, the FE of **Re**{*i*-**N**₄} for CO formation dropped drastically to ~7% after 24 h electrolysis, while the FE for the generation of H₂ increased slightly to 75%. Additionally, formic acid with a FE of 10% and methanol with a FE of 2.3% were identified as further reduction products. Although **Re**{*i*-**N**₄} with a summed FE of ~19% shows a lower selectivity for the CO₂RR compared to **Re**{**N**₄}, the absolute amounts of CO₂ reduction products are significantly higher for **Re**{*i*-**N**₄}, since the total consumed charge and thus the activity is almost six times higher compared to **Re**{**N**₄}.

The averaged CO/H₂ ratio of **Re**{*i*-**SN**₃} is with 1:10 similar to that of **Re**{**N**₂**S**₂} during the first 8 h, except for the first 2 h. However, in contrast to **Re**{**N**₂**S**₂} the absolute FEs for **Re**{*i*-**SN**₃} are higher with an averaged FE of 77% for H₂ and 7.4% for CO. After 24 h electrolysis with **Re**{*i*-**SN**₃} as catalyst, the FEs for the gaseous products dropped to ~76% in total, while the previous CO/H₂ ratio of 1:10 was maintained. Again, the liquid phase analysis revealed formic acid and methanol as further CO₂RR products with FEs of 7.1% and 3.9% respectively. Compared to **Re**{**N**₂**S**₂} the CO₂RR selectivity of **Re**{*i*-**SN**₃} is significantly higher and comparable with that of **Re**{*i*-**N**₄}. However, the consumed charge and consequently the catalytic activity of **Re**{*i*-**SN**₃} is significantly lower compared to **Re**{*i*-**N**₄} and comparable with that of **Re**{**N**₄}.

The FEs of Re{i-ON₃} for the formation of the gaseous products within the first 8 h of electrolysis are relatively constant with an averaged FE of 50% for H₂ and 9% for CO, resulting in an averaged CO/H₂ ratio of \sim 1:5. However, product analysis after 24 h of electrolysis with Re{i-ON₃} as catalyst revealed a significant shift of the CO/H₂ ratio in favor of CO to almost 1:2, resulting in FEs for H_2 and CO of 49% and 21% respectively. Furthermore, liquid phase analysis identified methanol as further reduction product with a remarkable FE of 24%. While generation of formate/formic acid during electrocatalytic CO₂ reduction is rather common,^[21,51,52] the formation of methanol is particularly noteworthy. Although experiments performed in CD₃CN show no incorporation of deuterium into methanol or formic acid, final proof for the formation of methanol from CO_2 must be obtained by utilization of ${}^{13}CO_2$. Consequently, an electrolysis experiment was carried out using ¹³CO₂ and **Re{***i***-ON₃**} as a proxy for all. Unfortunately, due to the lack of a suitable analytical method for these small amounts of methanol produced, we could not unequivocally identify CO₂ as the origin of methanol.

While the catalytic activity of $Re{i-ON_3}$ based on the consumed charge is comparable to that of $Re{N_4}$ and $Re{i-SN_3}$, the CO₂RR selectivity of $Re{i-ON_3}$ is highest within the series of rhenium complexes investigated herein with a total FE of 45%.

One explanation for the above average CO₂RR selectivity of complex **Re**{*i*-ON₃} compared to all other rhenium complexes investigated herein is the nature of the uncoordinated donor atom of the macrocyclic ligand. During the catalytic cycle a free binding site at the rhenium center of the [Re(κ^3 -{L})(CO)₃]⁺ complexes is expected, as in case of Re(bpy)(CO)₃Cl.^[23,24] While Re(bpy)(CO)₃Cl only binds CO₂ at this position, the [Re(κ^3 -{L})(CO)₃]⁺ complexes can also bind the uncoordinated donor atom of the macrocycle at this position and thus intrinsically inhibit catalysis.^[31] Since nitrogen donor atoms reveal a higher binding affinity to low-valent rhenium centers compared to oxygen donor atoms, the intrinsic inhibition in case of **Re**{N₄},

Re{N₂S₂}, Re{i-N₄} and Re{i-SN₃} is higher compared to Re{i-ON₃}.

Conclusions

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In summary, we herein describe the synthesis and characterization of hitherto unprecedented cyclam based rhenium complexes Re{N₄}, Re{N₂S₂}, Re{*i*-N₄}, Re{*i*-SN₃} and Re{*i*-ON₃} along with their performances in the electrocatalytic reduction of CO₂.

Within the series of the cyclam based rhenium complexes interesting trends are observed. Since the rhenium center selects three of the four donor atoms of the macrocyclic ligand for coordination, a ranking of the binding affinity of Re¹ to different donor atoms in the order of S > N > O was revealed. Moreover, it was shown that in case of the isocyclam derivatives the κ^3 -coordination mode, which leaves the donor atom between the propyl units uncoordinated, is preferred due to the minimized ring strains.

Regarding the electrocatalytic CO₂ reduction, all rhenium complexes reveal a significant increase in CO₂RR selectivity compared to the measurement in absence of any catalyst. However, H_2 remains the major reduction product in all cases. While $Re{i-N_4}$ shows the highest catalytic activity within the series, Re{i-ON₃} reveals the highest CO₂RR selectivity after 24 h with a total FE of 45%, which in turn is split into 21% CO and 24% methanol. The remaining complexes can be ranked according to their CO_2RR selectivity from $Re\{N_4\} > Re\{i-N_4\} > Re$ $\{i-SN_3\} > Re\{N_2S_2\}$, where $Re\{N_2S_2\}$ has only a FE of 4.9% for the production of CO.

Notably, in comparison to the literature known electrocatalyst Re(bpy)(CO)₃Cl, the reduction of CO₂ proceeds for all herein investigated rhenium complexes at comparatively higher overpotentials together with a lower CO₂RR selectivity.

Experimental Section

All reactions were performed under a dry Ar or N_2 atmosphere using standard Schlenk techniques or by working in a glovebox. Starting materials and chemicals were obtained from commercial suppliers and used without further purification. All solvents were dried and degassed according to standard methods.^[53] 1,8-Dithia-4,11-diazacyclotetradecane $\{N_2S_2\}$,^[48] 1,4,7,11-tetraazacyclotetradecane $\{i-N_4\}_{i}^{[44]}$ 1-thia-4,8,12-triazacyclotetradecane $\{i-SN_3\}_{i}^{[44]}$ and 1oxa-4,8,12-triazacyclotetradecane $\{i-ON_3\}^{[44]}$ were synthesized according to literature-known procedures. NMR spectra were recorded at room temperature from the dissolved crystalline samples with a Bruker AVIII-300 NMR spectrometer and are reported in parts per million (ppm). Unfortunately, the recorded ¹³C{¹H} NMR spectra did not show the quaternary carbon signals associated with the carbonyl ligands, and furthermore, assignment of the ¹H signals was not possible due to the high flexibility and anisotropy of the complexes (Figure S19-S23). Mass spectra were obtained with a Bruker Daltonics Esquire 6000 instrument. CHN analyses were measured with an Elementar vario MICRO cube. IR spectra were recorded with a Bruker Tensor 27 FT-IR instrument attached with a Pike Miracle ATR unit and are reported in cm⁻¹. UV/vis/NIR spectra were recorded with a JASCO V-670 instrument at 25 °C and are reported in nm.

General Procedure for the Syntheses of the Complexes [Re(κ^3 -{L})(CO)₃]Br: Ligand {N₄}, {N₂S₂}, {*i*-N₄}, {*i*-SN₃} or {*i*-ON₃} (1 equiv.) was dissolved in degassed acetone (48 mLmmol⁻¹) and Re(CO)₅Br (1 equiv.) was added to the macrocycle solution. The reaction mixtures were heated under reflux conditions for 12 h. In all cases a color change to light yellow/brown was observed. Subsequently, the reaction mixtures were cooled to room temperature, filtered, and concentrated. After recrystallization pure complexes Re{N₄}, Re $\{N_2S_2\}$, Re $\{i-N_4\}$, Re $\{i-SN_3\}$ and Re $\{i-ON_3\}$ were obtained.

 $[Re(\kappa^3-N,N,N-\{N_A\})(CO)_3]Br$ (**Re**{N_A}): The vellow solid obtained from reaction of $\{N_{4}\}$ (50 mg, 0.25 mmol) with Re(CO)₅Br (101 mg, 0.25 mmol) was recrystallized in hot acetone, yielding $Re\{N_{4}\}$ in 87% (120 mg, 0.22 mmol) as colorless solid. ¹³C{¹H} NMR (75 MHz, CD₃OD): δ = 24.6 (CH₂CH₂CH₂), 43.9, 47.6, 48.5, 51.7, 57.7, 58.3, 59.7, 60.7 (CH₂NH) ppm. **ESI-MS**: calcd. for [C₁₃H₂₄N₄O₃Re]⁺: *m*/*z*=471.1; found: 470.9. EA: C13H24BrN4O3Re: calcd. C, 28.37; H, 4.39; N, 10.18%; found: C, 28.47; H, 4.59; N, 10.35%. IR (ATR): v = 3395, 3059, 2907, 2872, 2826, 2014, 1898, 1880, 1468, 1055, 1024 cm⁻¹. UV/vis/NIR (CH₃CN): 317, 322 (sh) nm.

 $[Re(\kappa^3-S,S/N,N-\{N_2S_3\})(CO)_3]Br$ $(Re\{N_2S_3\})$: The yellow/brown solid obtained from reaction of $\{N_2S_2\}$ (50 mg, 0.21 mmol) with Re(CO)₅Br (87 mg, 0.21 mmol) was recrystallized using a mixture of acetone and methanol as solvent and diethyl ether as precipitant. Complex Re{N₂S₂} was obtained as colorless solid in 90% (110 mg, 0.19 mmol) yield. ¹³C{¹H} NMR (75 MHz, CD₃OD): δ = 24.5, 27.2, 27.5, 28.5 (CH₂CH₂CH₂), 28.8, 29.4, 29.7, 30.2, 30.7, 31.9, 32.5, 37.5 (CH₂S), 39.1, 47.4, 47.7, 51.0, 53.7, 54.4, 57.4, 62.3 (CH₂NH) ppm. ESI-MS: calcd. for $[C_{13}H_{22}N_2O_3ReS_2]^+$: m/z = 505.1; found: 504.8. EA: $C_{13}H_{22}BrN_2O_3ReS_2 + 0.33$ $CH_3OH + 0.67$ H_2O : calcd. C, 26.37; H, 4.09; N, 4.61%; found: C, 26.25; H, 4.00; N, 4.72%. IR (ATR): $\tilde{v} = 3400$, 2937, 2814, 2735, 2027, 1906, 1448, 1045, 1018 cm⁻¹. UV/vis/NIR (CH₃CN): 318, 324 nm.

 $[Re(\kappa^3-N,N,N-\{i-N_4\})(CO)_3]Br$ (**Re{i-N_4**): The yellow solid obtained from reaction of $\{i-N_4\}$ (58 mg, 0.29 mmol) with Re(CO)₅Br (117 mg, 0.29 mmol) was recrystallized using a mixture of acetone and methanol as solvent and diethyl ether as precipitant. Complex Re{i-N₄} was obtained as colorless solid in 74% (118 mg, 0.21 mmol) yield. ¹³C{¹H} NMR (75 MHz, CD₃OD): $\delta = 28.2$ (CH₂CH₂CH₂), 50.4, 52.7, 56.5, 61.6 (CH₂NH) ppm. **ESI-MS**: calcd. for [C₁₃H₂₄N₄O₃Re]⁺: *m*/ z = 471.1; found: 470.9. **EA**: C₁₃H₂₄BrN₄O₃Re + 0.33 CH₃OH + 0.33 H₂O: calcd. C, 28.24; H, 4.62; N, 9.88%; found: C, 28.27; H, 4.53; N, 9.77 %. IR (ATR): \tilde{v} = 3069, 2926, 2858, 2014, 1873, 1460, 1074, 1053, 1028 cm⁻¹. UV/vis/NIR (CH₃CN): 318, 323 (sh) nm.

 $[Re(\kappa^3-S,N,N-\{i-SN_3\})(CO)_3]Br$ (**Re{i-SN_3**): The yellow/brown solid obtained from reaction of {i-SN₃} (50 mg, 0.23 mmol) with Re(CO)₅Br (93 mg, 0.23 mmol) was recrystallized using a mixture of acetone and methanol as solvent and diethyl ether as precipitant. Complex Re{i-SN₃} was obtained as light brown solid in 92% (120 mg, 0.21 mmol) yield. ¹³C{¹H} NMR (75 MHz, CD₃OD): $\delta = 28.3$ (CH₂CH₂CH₂), 39.7 (CH₂S), 50.3, 59.6, 62.8 (CH₂NH) ppm. ESI-MS: calcd. for $[C_{13}H_{23}N_3O_3ReS_1]^+$: m/z = 488.1; found: 487.9. EA: C₁₃H₂₃BrN₃O₃ReS + 0.25 CH₃OH + 0.5 H₂O: calcd. C, 27.23; H, 4.31; N, 7.19%; found: C, 27.20; H, 4.09; N, 6.89%. **IR** (ATR): \tilde{v} = 3425, 3055, 2924, 2849, 2019, 1886, 1460, 1061, 1028 cm⁻¹. UV/vis/NIR (CH₃C–N): 318, 324 nm.

 $[Re(\kappa^3-N,N,N-\{i-ON_3\})(CO)_3]Br$ (**Re{i-ON_3}**): The yellow solid obtained from reaction of {i-ON₃} (50 mg, 0.25 mmol) with Re(CO)₅Br (101 mg, 0.25 mmol) was recrystallized using a mixture of acetone and methanol as solvent and methanol as precipitant. Complex Re {*i*-ON₃} was obtained as colorless solid in 98% (135 mg, 0.24 mmol) yield. ¹³C{¹H} NMR (75 MHz, CD₃OD): $\delta = 26.6$ (CH₂CH₂CH₂), 50.4,



56.4, 62.6 (CH₂NH), 71.0 (CH₂O) ppm. ESI-MS: calcd. for $[C_{13}H_{23}N_3O_4Re]^+$: m/z = 472.1; found: 471.9. EA: $C_{13}H_{23}BrN_3O_4Re +$ 0.45 C₃H₆O: calcd. C, 29.84; H, 4.49; N, 7.28%; found: C, 29.99; H, 4.59; N, 7.57%. **IR** (ATR): $\tilde{v} = 3117$, 3074, 2958, 2932, 2874, 2015, 1894, 1875, 1853, 1468, 1130, 1057 cm⁻¹. UV/vis/NIR (CH₃CN): 318, 323 (sh) nm.

Electrochemistry: Electrochemical studies were performed using a PalmSens4 potentiostat in a standard three-electrode setup in a one-compartment cell. A glassy-carbon electrode was used as working electrode (WE), a Ag wire in a Luggin capillary as the pseudo-reference electrode (PRE), and a Pt wire as the counter electrode (CE). The working electrode was prepared by successive polishing with 1.0, 0.3 and 0.1 µm sandpaper and subsequent sonication in acetonitrile for 10 min. Tetrabutylammonium hexafluorophosphate (["Bu₄N]PF₆, 0.1 M) was used as the electrolyte in all electrochemical measurements either in anhydrous acetonitrile or an acetonitrile/water mixture (4:1). Prior to each experiment, the electrochemical cell was degassed with Ar for 10 min. The electrolyte solution was purged for 10 min either with Ar or CO₂ and an Ar or CO₂ atmosphere was maintained throughout the measurement. All cyclic voltammograms were recorded at a scan rate of 100 ${\rm mV}\,{\rm s}^{-1}$ if not stated otherwise, and after every experiment all pseudo-referenced potentials were referenced against the ferrocene/ferrocenium couple (Fc/Fc⁺). Controlled-potential coulometry (CPC) was performed for 24 h at defined potentials in a sealed onecompartment cell under conditions otherwise identical with those reported above. The electrochemical cell for long-term electrolysis contained 5 mL of electrolyte and a headspace of 57 mL.

Quantification of Electrolysis Products: Quantification of the headspace gas composition and liquid phase composition of the electrochemical cell was performed using a Shimadzu GCMS-QP2020 system equipped with two capillary columns and a MS detector. Gas separation was performed via hand injection using a Carboxen 1010 PLOT fused silica capillary GC column (L X I.D. $30 \text{ m} \times 0.32 \text{ mm}$, average thickness $15 \mu \text{m}$) and liquid phase separation was performed via headspace analysis using a SH-Rtx-200 ms fused silica capillary GC column (L X I.D. 30 m×0.25 mm, average thickness 1 µm). Helium was used as carrier gas and the product amount was determined by calibration curves. The following gaseous and liquid products/components were assayed via the GCMS system: H₂, O₂, N₂, CO, CH₄, C₂H₄, C₂H₆, methanol, ethanol, propanol, formic acid (formate), acetic acid (acetate), propionic acid (propionate), acetaldehyde and propionaldehyde. Liquid samples were acidified with concentrated sulfuric acid (10:1) prior injection.

X-ray Data Collection and Structure Solution Refinement: Single crystals suitable for X-ray structure analysis were handled in perfluorinated oil, mounted on a fiber loop, and placed in a cold N₂ stream (Oxford Cryostream) throughout the measurement. X-ray diffraction data were collected using either an Oxford Xcalibur-2 equipped with a Sapphire 2 CCD detector (Mo- K_{a} , $\lambda = 0.71073$ Å), a Rigaku Oxford diffraction XtaLAB SuperNova equipped with an Atlas CCD detector (Cu- $K_{\alpha'}$, λ = 1.54184 Å) or a Rigaku Oxford diffraction XtaLAB Synergy-S with a HyPix-6000HE detector (Cu- $K_{\alpha'}$ $\lambda =$ 1.54184 Å). The obtained data were analyzed with the program packages CrysAlis^{Pro} and Platon.^[54] The structures were solved by intrinsic phasing using ShelXT^[55] and refined against F^2 (ShelXL^[56]). Hydrogen atoms were added in calculated positions and refined using a rigid model. The program package OLEX^{2[57]} served as a graphical user interface. Crystallographic data and refinement parameters are presented in Table S2 in the Supporting Information.

Supporting Information (see footnote on the first page of this article): The Supporting Information contains bond length and bond angle analysis, NMR spectra, UV/vis/NIR spectra, cyclic voltammograms, controlled potential coulometries, as well as crystal structure refinements.

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- [1] M. Aresta, Ed., Carbon Dioxide as Chemical Feedstock. Wilev-VCH Verlag GmbH&Co. KGaA, Weinheim, Germany, 2010.
- [2] J. Qiao, Y. Liu, J. Zhang, Electrochemical Reduction of Carbon Dioxide: Fundamentals and Technologies, CRC Press, Boca Raton, 2016.
- [3] T. Stocker, The Physical Science Basis: Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Climate Change 2013: Cambridge University Press, New York, 2014.
- [4] J. H. Butler, S. A. Montzka, "The NOAA Annual Greenhouse Gas Index (AGGI)," can be found under https://www.esrl.noaa.gov/ gmd/aggi/aggi.html, 2019.
- [5] R. A. Eggleton, A Short Introduction to Climate Change, Cambridge University Press, Cambridge; Port Melbourne, Vic, 2012.
- [6] M. Aresta, F. Nocito, A. Dibenedetto, Adv. Catal. 2018, pp. 49-111
- [7] T. R. Karl, Science 2003, 302, 1719–1723.
- [8] A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, Chem. Rev. 2013, 113, 6621-6658.
- [9] R. M. Cuéllar-Franca, A. Azapagic, J. CO2 Util. 2015, 9, 82-102.
- [10] C. Panzone, R. Philippe, A. Chappaz, P. Fongarland, A. Bengaouer, J. CO2 Util. 2020, 38, 314-347.
- [11] E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, Chem. Soc. Rev. 2009, 38, 89-99.
- [12] D. R. Kauffman, J. Thakkar, R. Siva, C. Matranga, P. R. Ohodnicki, C. Zeng, R. Jin, ACS Appl. Mater. Interfaces 2015, 7, 15626-15632.
- [13] J. Qiao, Y. Liu, F. Hong, J. Zhang, Chem. Soc. Rev. 2014, 43, 631-675.
- [14] C. Long, X. Li, J. Guo, Y. Shi, S. Liu, Z. Tang, Small Methods 2018, 1800369.
- [15] M. Rakowski Dubois, D. L. Dubois, Acc. Chem. Res. 2009, 42, 1974-1982.
- [16] H. A. Hansen, J. B. Varley, A. A. Peterson, J. K. Nørskov, J. Phys. Chem. Lett. 2013, 4, 388-392.
- [17] A. A. Peterson, ECS Trans. 2015, 66, 41-52.
- [18] F. Möller, S. Piontek, R. G. Miller, U.-P. Apfel, Chem. Eur. J. 2018, 24, 1471-1493.
- [19] D.-M. Feng, Y.-P. Zhu, P. Chen, T.-Y. Ma, Catalysts 2017, 7, 373.

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[20] J. Hawecker, J.-M. Lehn, R. Ziessel, J. Chem. Soc. Chem. Commun. 1984, 328–330.

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- [21] J. Hawecker, J.-M. Lehn, R. Ziessel, *Helv. Chim. Acta* **1986**, *69*, 1990–2012.
- [22] B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining, T. J. Meyer, J. Chem. Soc. Chem. Commun. 1985, 1414–1416.
- [23] K. A. Grice, C. P. Kubiak, Adv. Inorg. Chem., Elsevier, 2014, pp. 163–188.
- [24] A. W. Nichols, C. W. Machan, Front. Chem. 2019, 7, 397.
- [25] J. M. Smieja, C. P. Kubiak, Inorg. Chem. 2010, 49, 9283-9289.
- [26] S. Sung, D. Kumar, M. Gil-Sepulcre, M. Nippe, J. Am. Chem. Soc. 2017, 139, 13993–13996.
- [27] A. Nakada, O. Ishitani, ACS Catal. 2018, 8, 354–363.
- [28] M. L. Clark, P. L. Cheung, M. Lessio, E. A. Carter, C. P. Kubiak, ACS Catal. 2018, 8, 2021–2029.
- [29] A. N. Hellman, R. Haiges, S. C. Marinescu, Dalton Trans. 2019, 48, 14251–14255.
- [30] M. R. Madsen, J. B. Jakobsen, M. H. Rønne, H. Liang, H. C. D. Hammershøj, P. Nørby, S. U. Pedersen, T. Skrydstrup, K. Daasbjerg, Organometallics 2020, 39, 1480–1490.
- [31] K. Talukdar, S. Sinha Roy, E. Amatya, E. A. Sleeper, P. Le Magueres, J. W. Jurss, *Inorg. Chem.* 2020, *59*, 6087–6099.
- [32] J. Mukherjee, I. Siewert, Eur. J. Inorg. Chem. 2020, 2020, 4319– 4333.
- [33] H. Shirley, T. M. Sexton, N. P. Liyanage, M. A. Perkins, S. A. Autry, L. E. McNamara, N. I. Hammer, S. R. Parkin, G. S. Tschumper, J. H. Delcamp, *ChemPhotoChem* 2021, cptc.202000296.
- [34] B. Merillas, E. Cuéllar, A. Diez-Varga, T. Torroba, G. García-Herbosa, S. Fernández, J. Lloret-Fillol, J. M. Martín-Alvarez, D. Miguel, F. Villafañe, *Inorg. Chem.* 2020, *59*, 11152–11165.
- [35] L. Suntrup, F. Stein, J. Klein, A. Wilting, F. G. L. Parlane, C. M. Brown, J. Fiedler, C. P. Berlinguette, I. Siewert, B. Sarkar, *Inorg. Chem.* 2020, *59*, 4215–4227.
- [36] J. Du, A. Wilting, I. Siewert, Chem. Eur. J. 2019, 25, 5555-5564.
- [37] J. K. Nganga, L. M. Wolf, K. Mullick, E. Reinheimer, C. Saucedo, M. E. Wilson, K. A. Grice, M. Z. Ertem, A. M. Angeles-Boza, *Inorg. Chem.* 2021, *60*, 3572–3584.
- [38] M. Beley, J.-P. Collin, R. Ruppert, J.-P. Sauvage, J. Chem. Soc. Chem. Commun. 1984, 1315.
- [39] Marc. Beley, J. Paul Collin, Romain. Ruppert, J. Pierre Sauvage, J. Am. Chem. Soc. 1986, 108, 7461–7467.

- [40] J. Song, E. L. Klein, F. Neese, S. Ye, *Inorg. Chem.* 2014, 53, 7500– 7507.
- [41] G. B. Balazs, F. C. Anson, J. Electroanal. Chem. 1993, 361, 149– 157.
- [42] J. D. Froehlich, C. P. Kubiak, Inorg. Chem. 2012, 51, 3932–3934.
- [43] P. Gerschel, K. Warm, E. R. Farquhar, U. Englert, M. L. Reback, D. Siegmund, K. Ray, U.-P. Apfel, *Dalton Trans.* 2019, 48, 5923– 5932.
- [44] P. Gerschel, B. Battistella, D. Siegmund, K. Ray, U.-P. Apfel, Organometallics 2020, 39, 1497–1510.
- [45] K. Wieghardt, C. Pomp, B. Nuber, J. Weiss, Inorg. Chem. 1986, 25, 1659–1661.
- [46] C. Pomp, S. Drüeke, H.-J. Küppers, K. Wieghardt, Z. Naturforsch. B 1988, 43, 299–305.
- [47] P. Hoffmann, A. Steinhoff, R. Mattes, Z. Naturforsch. B 1987, 42, 867–873.
- [48] T. L. Walker, W. Malasi, S. Bhide, T. Parker, D. Zhang, A. Freedman, J. M. Modarelli, J. T. Engle, C. J. Ziegler, P. Custer, W. J. Youngs, M. J. Taschner, *Tetrahedron Lett.* **2012**, *53*, 6548– 6551.
- [49] J. D. Froehlich, C. P. Kubiak, J. Am. Chem. Soc. 2015, 137, 3565– 3573.
- [50] L. Iffland, D. Siegmund, U. Apfel, Z. Anorg. Allg. Chem. 2020, 646, 746–753.
- [51] F. P. A. Johnson, M. W. George, F. Hartl, J. J. Turner, Organometallics 1996, 15, 3374–3387.
- [52] D. R. Case, A. Spear, A. F. Henwood, M. Nanao, S. Dampf, T. M. Korter, T. Gunnlaugsson, J. Zubieta, R. P. Doyle, *Dalton Trans.* 2021, *50*, 3479–3486.
- [53] D. D. Perrin, W. L. F. Armarego, Purification of Laboratory Chemicals, Pergamon Press, Oxford; New York, 1988.
- [54] A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7-13.
- [55] G. M. Sheldrick, Acta Crystallogr. Sect. A 2015, 71, 3-8.
- [56] G. M. Sheldrick, Acta Crystallogr. Sect. C 2015, 71, 3-8.
- [57] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.

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