Sensitized Photocatalytic CO2 Reduction With Earth Abundant 3d Metal Complexes Possessing Dipicolyl-Triazacyclononane Derivatives

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Complexes based on nitrogen and sulfur containing ligands involving 3d metal centers are known for the electrocatalytic reduction of CO2. However, photocatalytical activation has rarely been investigated. We herein present results on the light-driven CO2 reduction using either Ir(dFppy)3 \([\text{Ir, dFppy} = 2-(4,6\text{-difluorophenyl})\text{pyridine}]\) or \([\text{Cu(xant)(bcp)}]^+, \) (\text{Cu, xant = xantphos, bcp = bathocuproine}) as photosensitizer in combination with TEA (triethylamine) as sacrificial electron donor. The 3d metal catalysts have either dptacn (dipicolyl-triazacyclononane, \(\text{LN}_3\)) or dpdatcn (dipicolyl-diazathiocyclononane, \(\text{LN}_2\text{S}\)) as ligand framework and \(\text{Fe}^{3+}, \text{Co}^{3+} \text{or Ni}^{2+}\) as central metal ion. It turned out that the choice of ligand, metal center and solvent composition influences the selectivity for product formation, which means that the gaseous reduction products can be solely CO or H2 or a mixture of both. The ratio between these two products can be controlled by the right choice of reaction conditions. With using \text{Cu} as photosensitizer, we could introduce an intermolecular system that is based solely on 3d metal compounds being able to reduce CO2.

Keywords: photocatalysis, carbon dioxide reduction, 3d metal complexes, electron transfer, sulfur containing ligand

INTRODUCTION

Due to the fact that the global energy demand is projected to increase, there will still be a high necessity of usage of fossil fuels over the next couple of decades, as the development of renewable energy sources cannot adjust with the same speed (Sönnchen, 2020). This mismatch will not only cause problems due to an increase in the amount of greenhouse gases in the atmosphere, which are highly responsible for the climate change (e.g. methane, CO2), but also raises the need to search for other alternative energy resources (Aresta, 2010; Ringsmuth et al., 2016). Therefore one of the key answers to face both problems is the conversion of CO2 to liquid fuels (Benson et al., 2009; Ma et al., 2009). This process is forecast to have a positive impact on the global greenhouse gas balance by recycling prior emitted CO2. Due to the inertness of CO2 - both thermodynamically and kinetically - different strategies need to be developed to optimize the conversion to more useful C1 building blocks (Schrag, 2007). One option is using homogeneous catalysts instead of heterogeneous catalysts (Kumar et al., 2016) as often done by industry. One major advantage is the higher variety of
spectroscopic techniques that can be used to understand the mechanistic features and, hence, assist in finding the correlation between structure and catalytic activity (Francke et al., 2018). Significant progress has been made for the CO\textsubscript{2} to CO reduction with catalytic systems based on heavier transition metals such as rhenium or ruthenium (Tamaki et al., 2013; Tamaki et al., 2015; Gotico et al., 2018). However, these metals are expensive and rare, which leads to the need of finding complexes based on earth-abundant metals to perform the activation and conversion of CO\textsubscript{2} (Takeda et al., 2017; Dalle et al., 2019).

As often in modern chemistry, inspiration can be obtained from nature. 3d metal-based enzymes with complex frameworks are known to activate stable small molecules. One of the best studied enzymes is carbon dioxide dehydrogenase (CODH) – capable of oxidizing CO to CO\textsubscript{2} and vice versa. The catalytically active C-cluster is composed of a bimetallic Ni-Fe center in a nitrogen/sulfur rich environment (Lubitiz et al., 2014; Esselborn et al., 2016; Benvenuti et al., 2020; Ghosh et al., 2020). Beside molecular Ni and Fe complexes, systems containing Co were found to show high electro- as well as photo-catalytic activity towards CO\textsubscript{2} reduction by several groups (Tamaki and Ishitani, 2016; Benvenuti et al., 2020; Ghosh et al., 2020). Herein we present their photocatalytic activity in the presence of different photosensitizers, \textit{Ir} ([Ir(dFppy)\textsubscript{3}], dFppy = 2-(4,6-difluorophenyl)pyridine) and \textit{Cu} ([Cu(xant)(bcp)]PF\textsubscript{6}, xant = xanthphos, bcp = bathocuproine).

**DISCUSSION AND RESULTS**

**Synthesis and Characterization**

The complexes were prepared by first synthesizing the corresponding ligands 1,4-di(picolyl)-1,4,7-triazacyclononane L\textsubscript{N3} and 1-thia-4,7-di(picolyl)-diazacyclononane L\textsubscript{NS2}. We followed published procedures with slight adjustments (see also the Supporting Information). Briefly, L\textsubscript{N3} was prepared beginning with the tosylation of diethylenetriamine and glycol (Friscourt et al., 2012). The next step was a Cs\textsubscript{2}CO\textsubscript{3} catalyzed macrocyclization using the tosylated compounds to form trityosyl-triazacyclononane (ts-tacn) (Cao et al., 2010). Partial detosylation of the formed macrocycle using HBr in acetic acid resulted in the formation of ts-tacn (Cao et al., 2010),
which was transformed into dipicolyl-tosyl-tacn using two equivalents of 2-picolylchloride hydrochloride in a base-catalyzed Sn2 reaction (Stavila et al., 2008). To obtain the desired ligand L\textsuperscript{N3} the remaining tosyl protecting group was cleaved using conc. H\textsubscript{2}SO\textsubscript{4} (Luk’yanyenko et al., 1990; Stavila et al., 2008). L\textsuperscript{N2S} was prepared in a similar fashion: First N,N’-bis-tosyl-bis-(2-aminoethyl)sulfide was synthesized via sodium ethoxide driven Sn2 reaction of cysteamine hydrochloride and 2-chloroethylamine hydrochloride (Wilson, 2007), followed by tosylation as described earlier for L\textsuperscript{N3} (Friscourt et al., 2012). The macrocyclization was started with LiOH (2.5% in water) in toluene and using NaBH\textsubscript{4}Br as phase-transfer catalyst (Wilson, 2007). To obtain L\textsuperscript{N2S} a detosylation and substitution with 2-picolylchloride hydrochloride was performed (Chak et al., 1994; Wilson, 2007). Both proligands were used immediately to obtain the complexes, due to sensitivity towards oxidation. Hence it was not possible to store the proligands for longer time periods. For both compounds, L\textsuperscript{N3} and L\textsuperscript{N2S}, the analytical data nonetheless agreed with those published earlier. Metal complexation could be achieved by reaction of the corresponding ligand with an equimolar amount of simple metal salt, e.g., metal triflates M(OTf)\textsubscript{2} (M = Fe, Co, Ni). Work-up of the reaction mixture was done under air atmosphere leading to oxidation of the iron and cobalt compounds. Purification of the crude product was obtained via washing with CH\textsubscript{2}Cl\textsubscript{2} to remove excess of ligand and washing with toluene (Fe(OTf)\textsubscript{2} and Co(OTf)\textsubscript{2}) or THF (Ni(OTf)\textsubscript{2}) to remove unreacted metal salt. The desired complexes were obtained as solids, which were redissolved in a small amount of MeCN and precipitated using Et\textsubscript{2}O. Since L\textsuperscript{N3} was synthesized as hydroxide salt (stemming from column chromatographic purification using dichloromethane), Fe-L\textsuperscript{N3} and Co-L\textsuperscript{N3} were obtained as complexes with one chloride ligand and two uncoordinated trflate counter anions, which could be verified by mass spectrometry and X-ray diffractometry. Ni-L\textsuperscript{N3} was isolated as a chloride free complex by precipitating AgCl using Ag(OTf). The complexes M-L\textsuperscript{N2S} were prepared in the same fashion giving yields in the range of 44–50%. All complexation reactions should be done soon after preparation of the proligands, due to sensitivity against oxidation of the compounds L\textsuperscript{N3} and L\textsuperscript{N2S}.

The successful complex formation was supported by high resolution MS revealing characteristic peaks at m/z 516.0974 (Fe-L\textsuperscript{N3}), 519.0975 (Co-L\textsuperscript{N3}), 518.1018 (Ni-L\textsuperscript{N3}), as well as 533.0584 (Fe-L\textsuperscript{N2S}), 536.0568 (Co-L\textsuperscript{N2S}) and 535.0590 (Ni-L\textsuperscript{N2S}) for the corresponding [M + OTf\textsuperscript{+}] fragments (Supplementary Figures S13–S18). To verify the oxidation state of +3 for both the Fe and the Co complexes, different approaches have been made. Since Co-L\textsuperscript{N3} and Co-L\textsuperscript{N2S} represent diamagnetic compounds, i.e., they are in the low-spin d\textsuperscript{6} form, NMR spectroscopy could be applied. Thereby, Co-L\textsuperscript{N3} gives a nicely resolved \textsuperscript{1}H NMR spectrum (Supplementary Figure S11) where all signals can be assigned. The ligand conformation leads to an asymmetry in the complex in contrast to the symmetric nature of the ligand itself (see also crystal structure in Figure 1). Thus, the pyridyl substituents give rise to eight individual signals in the aromatic region, ranging from 9.5 to 7.2 ppm. The methylene groups arise at 5.1, 4.6, and 4.5 ppm and the macrocyclic protons from 4.2 to 2.0 ppm. In case of Co-L\textsuperscript{N2S} the \textsuperscript{1}H NMR spectrum shows broad signals in the region from 2 to 9 ppm. It seems that the S-donor atom in the ligand macrocycle is less strongly bound leading to a higher mobility in the system and hence stronger dynamics.

On the other hand, Fe-L\textsuperscript{N3} and Fe-L\textsuperscript{N2S} are paramagnetic compounds, which give rise to non-interpretable \textsuperscript{1}H NMR spectra. The magnetic properties indicate a +3 oxidation state in octahedral environment with a strong ligand field, as for +2 oxidation state a d\textsuperscript{6} low-spin state, and thus a diamagnetic compound, would be expected. The +3 oxidation state was confirmed by using EPR spectroscopy for both compounds giving a Fe\textsuperscript{III} typical spectrum with signals having a g value of around 4.0 and 2.0 (Supplementary Figure S23) (Srinivasan and Gralla, 2002).

Electrochemical and spectroscopic properties were determined via cyclic voltammetry (CV) and UV/vis measurements. The UV/vis studies in DMF solution (Table 1; Supplementary Figures S19–S21) reveal a strong ligand-based absorption peaking at 268 nm for all compounds, which can be assigned to be situated at the aromatic picolyl substituents. These maxima are outside the visible spectrum and do not have an impact on the color of the complexes. For the two Fe complexes the dark brown color derives from a broad absorption feature ranging from 600 to 350 nm with a shoulder at around 432 nm (Fe-L\textsuperscript{N3}) or 502 nm (Fe-L\textsuperscript{N2S}). The Ni complex Ni-L\textsuperscript{N3} only has an additional absorption maximum at 308 nm and hence is colorless. As the Ni-L\textsuperscript{N2S} absorbs in a broader area from 500 to 300 nm it is isolated as light brown solid. The most striking difference is revealed for the Co complexes where d-d transitions are observed at 362 nm (ε = 320 dm\textsuperscript{3}/mol•cm) for Co-L\textsuperscript{N3} and 490 nm (ε = 390 dm\textsuperscript{3}/mol•cm) for Co-L\textsuperscript{N2S} leading to a light red/pink color.
In the CV measurements of the complexes Fe-L\textsuperscript{N3} and Fe-L\textsuperscript{N2S} a reversible redox event is observed at a half-wave potential of -0.09 and 0.20 V (referenced to Fe/Fe\textsuperscript{3+}), respectively, representing the Fe\textsuperscript{II}/Fe\textsuperscript{III} redox couple (Table 1; Supplementary Figure S22). In addition, there are irreversible reduction events at -2.50 V and -2.91 V for Fe-L\textsuperscript{N3} and -2.29 V and -2.77 V for Fe-L\textsuperscript{N2S}, which can tentatively be assigned to the Fe\textsuperscript{II}/Fe\textsuperscript{I} reduction and the formal Fe\textsuperscript{I}/Fe\textsuperscript{0} reduction. However, there is certainly the possibility that the true electronic distribution is different and ligand-based reduction cannot be neglected without further experiments.

Interestingly, Fe-L\textsuperscript{N2S} is thus easier to reduce (by about 200 mV) than the sulfur free analogue. This result can be attributed to the electron donating property of the sulfur environment surrounded by similar ligand geometry, with Fe in an octahedral coordination sphere is completed by coordination with all five nitrogen atoms acting as donor atoms. The crystal structure shows a hydrogen octahedral coordination sphere is completed by coordination with all five nitrogen atoms acting as donor atoms. The crystal structure shows a hydrogen

### Crystallography

X-ray quality crystals of Co-L\textsuperscript{N3} and Fe-L\textsuperscript{N3} were obtained by slow vapor diffusion of Et\textsubscript{2}O to a high concentrated MeCN solution. Both complexes are isostructural (Figure 1; Supplementary Figure S24; Supplementary Tables S1, S2) with all five nitrogen atoms acting as donor atoms. The octahedral coordination sphere is completed by coordination of one chloride ion. The crystal structure shows a hydrogen atom at the secondary amine which confirms the +3 oxidation state (two trflate counter ions were also found per cation).

In case of Co-L\textsuperscript{N3} shorter Co-N bond lengths (1.94–1.97 Å) are observed, which is in line with Co\textsuperscript{3+} being smaller than Fe\textsuperscript{3+}. The Co-Cl bond distance, on the other hand, is almost identical to the Fe-Cl bond with -2.23 Å (Table 2; Supplementary Table S2). For Co-L\textsuperscript{N3} an isostructural complex [Co\textsuperscript{N3}(OH\textsubscript{2})\textsuperscript{+}][ClO\textsubscript{4}\textsuperscript{-}]•H\textsubscript{2}O was published earlier (McLachlan et al., 1995) having similar bond angles and distances, but a shorter Co-O bond since H\textsubscript{2}O is a smaller ligand than the chloride ion. Furthermore, there are a few crystal structures of similar Fe compounds with the L\textsuperscript{N3} ligand described in the literature. Two prominent examples are the complexes [Fe\textsuperscript{N3}(Cl)](PF\textsubscript{6})\textsuperscript{-} and [FeL\textsuperscript{N3}(NCS)](PF\textsubscript{6})\textsuperscript{-}, which were obtained via reaction under inert conditions and, hence, possess an oxidation state for Fe of +2 (Spiccia et al., 1998). Both complexes nonetheless show a similar ligand geometry, with Fe in an octahedral coordination environment surrounded by five nitrogen and one (pseudo-) halide donor atom.

In case of the L\textsuperscript{N2S} complexes we were not able to obtain crystals so far. Nonetheless, crystal structures have been reported for similar Fe\textsuperscript{II} and Ni\textsuperscript{II} complexes (Wasielewski and Mattes, 1993; Zhang et al., 1998).

### Photocatalysis

The photocatalytic activity of the prepared complexes was determined using Ir(dFppy)\textsubscript{3} and triethylenetetramine (TEA) as sacrificial electron donor. In earlier studies we successfully applied the following conditions (Giereth et al., 2021): 5 × 10\textsuperscript{-5} M catalyst concentration in 5 ml DMF with 5 × 10\textsuperscript{-3} M Ir as photosensitizer (PS) and 5 Vol\% TEA as sacrificial electron donor (SR). The catalysis mixture is placed in front of a 200 W Hg-lamp equipped with a 400 nm low-wavelength cut-off filter to exclude UV light. Ir was selected because of its ability to still absorb solar photons in the region of 400–460 nm (Becker et al., 2020) and its potentially well suited (excited state) redox properties (Table 1) (Koike and Akita, 2014; Lee and Han, 2020; Giereth et al., 2021). For this work we just focused on the gaseous reduction products formed and did not investigate the formation of liquid products. Further information is given in the supplementary data.

### Table 1 | Redox potentials [V], excited state redox potentials [V] (marked with *) and MLCT absorption maxima [nm] with corresponding molar attenuation coefficients $\epsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$) of the complexes. Peak potentials are given vs. Fe/Fe$^+$.

| Complex      | Irrev. $E_{red}$ | Revers. $E_{ox}$ | $\lambda_{max}$ (nm) |
|--------------|-----------------|-----------------|---------------------|
| Fe-L$^{N3}$  | -2.59           | -0.69           | 432 (1700)          |
| Co-L$^{N3}$  | -0.64           | -0.59           | 507 (3000$^{a}$)    |
| Fe-L$^{N2S}$ | -0.34           | 0.20            | 502 (700)           |
| Co-L$^{N2S}$ | -0.71           | -0.35           | 490 (900)           |

$^{a}$McLachlan et al. (1995).

$^{b}$Giereth et al. (2021).

$^{c}$Reversible redox process.

$^{d}$Teegardin et al. (2016).

### Table 2 | Selected interatomic distances [Å] and bond angles (°) for Fe-L$^{N2S}$.

| Fe(1)-Cl(1)  | 2.223(5)       | N(2)-Fe(1)-Cl(1) | 174.90(5)  |
| Fe(1)-N(1)   | 1.972(18)      | N(3)-Fe(1)-N(4)  | 169.67(7)  |
| Fe(1)-N(2)   | 1.908(15)      | N(5)-Fe(1)-N(1)  | 169.64(6)  |
| Fe(1)-N(3)   | 1.972(18)      | N(2)-Fe(1)-N(5)  | 82.94(8)   |
| Fe(1)-N(4)   | 1.997(18)      | N(3)-Fe(1)-Cl(1) | 90.50(5)   |
| Fe(1)-N(5)   | 1.974(18)      | N(4)-Fe(1)-N(1)  | 83.37(8)   |
It can be observed, that not only the ligand but also the metal centre do have an impact on both the formed products and the catalytic activity (Figure 2; Table 3). While Fe-LN3 shows a slightly higher TON for H2 than for CO formation after 24 h reaction time, Co-LN3 shows no H2 formation and the highest TONCO for the here investigated complexes. This result might be due to the fact that Fe tends to form hydride intermediates (Drosou et al., 2020). When a sulfur atom is added to the ligand framework, considerable H2 formation is observed. It is thereby a shift to higher TONH2 is observable, while TONCO stays very similar to the one of Co-LN2S to a sulfur atom in the ligand system. Further evidence for molecular catalysis could be obtained by adding mercury to a catalysis solution with Co-LN3. Similar TONs were obtained indicating that Co colloids did not form. In case of Co-LN2S the ratio of CO:H2 changes to about 2:1 (i.e., 66% selectivity for CO formation) in comparison to no H2 formation for Co-LN3. In case of Fe-LN2S the CO:H2 ratio stays very similar to the one of Co-LN2S, but the activity drops by about one third, and about half in comparison to Fe-LN3. For the Ni complexes the electrochemical data predicted no (photo)catalytic activity, because they do not show a reduction process in the solvent window investigated. This could be confirmed for Ni-LN3, whereas Ni-LN2S shows a moderate TONH2, which again is probably induced by the sulfur atom in the ligand system.

In order to investigate if the product ratio or the activity can be adjusted by adding an additional proton source, water was added to a Co-LN2S catalytic mixture in different concentrations. Thereby a shift to higher TONH2 is observable, while TONCO is decreasing (Supplementary Table S4). When adding 1 Vol.% water a ratio of CO:H2 18:24 was observed, while the addition of 5 Vol.% water led to a ratio of CO:H2 5:54. This result strikingly demonstrates that the product selectivity can be manipulated to a large amount by the addition of a proton source.

To investigate the influence of the type of PS, catalytic experiments were performed using Cu. This PS was chosen due to its similar absorption and redox features as compared to Ir (Table 1) (Giereth et al., 2021). Unexpectedly, the combination of Cu and Co-LN3 shows only a TONCO of 13 after 24 h of illumination, i.e., only a seventh part compared to the reaction using Ir. The much lower overall TONCO can be attributed to the rather fast photodecomposition of Cu (Giereth et al., 2021). In the first 2 hours of illumination, Cu actually shows a better performance than Ir (Supplementary Figure S25; TONCO of 9 vs. 3). However, there is almost no further increase in CO evolution for Cu indicating that most of the photosensitizer is decomposed already after a few hours of reaction time. The initial better performance of Cu vs. Ir is tentatively assigned to the more suitable excited state oxidation potential of Cu (Table 1) and, hence, more efficient oxidative quenching of the excited state by the catalyst (see next section).

**Photophysical Studies**

Luminescence quenching experiments were performed to obtain some insight into the reaction mechanism. The excited state of the (Ir) photosensitizer can be quenched oxidatively by the catalyst Co-LN3 (Supplementary Figure S26; Table 1). Specifically, Stern-Volmer luminescence quenching experiments in acetonitrile yield a quenching rate constant $k_q = 1.1 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ (for Ir), which is roughly a factor of seven (Montalti et al., 2006) below the diffusion limit. Under the catalytically relevant reaction conditions, $5 \times 10^{-5} \text{M}$ Co-LN3 was present, and given a rate constant of $1.1 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ for oxidative Ir luminescence quenching, this leads to a pseudo-first-order rate constant of $5.5 \times 10^5 \text{s}^{-1}$ for photoinduced electron transfer from Ir to Co-LN3. Given an inherent excited-state decay of $5 \times 10^5 \text{s}^{-1}$ (lifetime of Ir of about 2 μs) (Giereth et al., 2021) this implies that 11 in 100 photo-excitations ($5 \times 10^4 \text{s}^{-1}/5 \times 10^5 \text{s}^{-1} = 0.11$) will lead to electron transfer from Ir to Co-LN3 under the catalytically relevant conditions with $5 \times 10^{-5} \text{M}$ Co-LN3.

Similar bimolecular rate constants were determined by Chan and co-workers (Chan et al., 2015), who investigated

| Complex     | TONCO (24 h) | TONH2 (24 h) |
|-------------|--------------|--------------|
| Fe-LN3      | 27           | 35           |
| Co-LN3      | 90           | —            |
| Ni-LN3      | —            | —            |
| Fe-LN2S     | 20           | 13           |
| Co-LN2S     | 29           | 16           |
| Ni-LN2S     | —            | 35           |

**TABLE 3** Turn over number (TON) for CO and H2 formation for the respective complexes after 24 h of illumination. The catalytic reaction was performed with a catalyst concentration of $5 \times 10^{-5} \text{M}$ in DMF with 5% TEA as sacrificial electron donor applying a λ > 400 nm longpass filter and a 200 W Hg-lamp (–no product determined by GC).
the photocatalytic CO₂ reduction in acetonitrile with \([\text{Co}^{II}(\text{tpa})\text{Cl}]\text{Cl} \) (tpa = tris(2-pyridylmethyl)amine) and using \(\text{Ir}(\text{ppy})_3 \) (ppy = 2-phenylpyridine anion) as photocatalyst. Stern–Volmer analysis revealed quenching rate constants for the photosensitizer of \(5.29 \times 10^9 \text{M}^{-1}\text{s}^{-1}\) for \([\text{Co}^{II}(\text{tpa})\text{Cl}]\text{Cl} \) and \(4.14 \times 10^4 \text{M}^{-1}\text{s}^{-1}\) for TEA, respectively. It was further noted that reductive quenching of excited \(\text{Ir}(\text{ppy})_3 \) is not feasible from thermodynamic consideration (\(E_{1/2}^{\text{Ir}(\text{ppy})_3^{**}/\text{Ir}(\text{ppy})_3^-} = +0.31 \text{V vs. SCE}\)) and, hence, oxidative quenching of the PS is the more favourable reaction path. These findings are also in line with previous studies by some of us (Giereth et al., 2021), in which we used \(\text{Ir} \) in the presence of a large excess of TEA and a dirhenium catalyst. In the photocatalytic experiments, \(\text{Ir} \) (\(E_{1/2}^{\text{Ir}(\text{dFppy})_3^{**}/\text{Ir}(\text{dFppy})_3^-} = +0.36 \text{V vs. Fc/Fc}^+\)) (Teegardin et al., 2016) seemingly had no influence on the catalytic performance, because the dirhenium compound was itself an efficient photocatalyst and because of very inefficient reductive quenching of \(\text{Ir} \) by TEA. It is interesting to note that smaller quantities of a stronger reductant (such as BIH, 1,3-dimethyl-2-phenylbenzimidazoline) gave significantly greater turnover numbers and led to very fast CO₂ transformation.

Though the fluorinated \(\text{Ir} \) complex is a somewhat stronger photo-oxidant than \(\text{Ir}(\text{ppy})_3 \) (+0.36 V vs SCE compared to +0.31 V vs SCE, see above) one may assume that the rate constant for bimolecular quenching of photoexcited \(\text{Ir} \) by TEA is on a similar order of magnitude, roughly \(4.14 \times 10^4 \text{M}^{-1}\text{s}^{-1}\) (see above). Under the catalytically relevant reaction conditions in which 0.36 M TEA is present, this leads to a pseudo-first order rate constant of \(1.5 \times 10^4 \text{s}^{-1}\). \(\text{Co-L}^{\text{N}3} \) is present at \(5 \times 10^{-5} \text{M} \) concentration under the catalytically relevant conditions, and given a rate constant of \(1.1 \times 10^9 \text{M}^{-1}\text{s}^{-1}\) for bimolecular electron transfer from photoexcited \(\text{Ir} \) to \(\text{Co-L}^{\text{N}3} \) (see above), one obtains a pseudo-first order rate constant of \(5.5 \times 10^4 \text{s}^{-1}\). Thus, under the assumption that reductive excited-state quenching of \(\text{Ir} \) by TEA is not more rapid than reductive quenching of \(\text{Ir}(\text{ppy})_3 \) despite its 0.05 V higher oxidative power (see above), oxidative quenching of \(\text{Ir} \) by \(\text{Co-L}^{\text{N}3} \) is a factor of 3.6 (\(= 5.5 \times 10^4 \text{s}^{-1}/1.5 \times 10^4 \text{s}^{-1}\)) faster than reductive quenching by TEA.

Therefore we speculate that the reaction mechanism is as illustrated in Scheme 2. Following the absorption of light by the photosensitizer, the excited \(\text{PS}^* \) transfers an electron to the catalyst. Subsequently, \(\text{PS}^- \) is reduced by TEA to reform \(\text{PS} \), which then restarts the cycle (Pellegrin and Odobel, 2017). The reduced catalyst \(\text{cat}^- \) is probably only able to interact with protons, derived from TEA decomposition, to form a hydride intermediate. Consecutive electron and proton transfer results in hydrogen formation (Dempsey et al., 2009; Darmon et al., 2014; Wiedner and Bullock, 2016). In order to be able to reduce CO₂ to CO, the catalyst very likely needs to be present in the double reduced form \(\text{cat}^{2-} \). The double reduced species could form in a dark reaction by further reduction of \(\text{cat}^- \) by the radical cation TEA⁺, which is a potent reductant (Shimoda et al., 2018). Alternatively, \(\text{cat}^{2-} \) could result from a disproportionation reaction (indicated in Scheme 2) as has been proposed for other 3d transition metal compounds (Takeda et al., 2017; Dalle et al., 2019). Such disproportionation reactions have likewise been demonstrated to play a key role in photoinduced charge accumulation (Skaisgirski et al., 2017). In another alternative, the attack of two single reduced catalyst species on CO₂ could be a possible reaction path, as has been suggested for rhenium complexes (Morris et al., 2009), though this requires the formation of a ternary encounter complex in solution. Further investigations to elucidate the reaction mechanism by characterization and isolation of intermediates are currently performed.

![Scheme 2](image-url)
**EXPERIMENTAL**

General procedure for the synthesis of complexes Fe-L\(^{N3}\) and Co-L\(^{N3}\). Macrocycle L\(^{N3}\) (1 eq.) was dissolved in MeCN (5 ml) and M(OTf)\(_2\) (1 eq.) was added. After stirring for 3 days at room temperature, the solvent was removed. The resulting oil was washed with CH\(_2\)Cl\(_2\) and toluene, dissolved in MeCN and precipitated using Et\(_2\)O.

**Synthesis of Fe-L\(^{N3}\)**

After purification Fe-L\(^{N3}\) was obtained as brownish red solid (38 mg, 54%).

ESI-MS: \(m/z\): calc. for [M + OTf\(^+\)], 516.0974; found, 516.0974. UV/vis: \(\lambda\) 268, 312, 432 nm.

**Synthesis of Co-L\(^{N3}\)**

After purification Co-L\(^{N3}\) was obtained as pink solid (49 mg, 38%).

\(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 9.24 (d, \(J = 5.8\) Hz, 1H), 8.33 (td, \(J = 1.5, 7.8\) Hz, 1H), 8.13 (td, \(J = 1.5, 7.8\) Hz, 1H\(_{\text{pico}}\)), 7.86 (m, 2H\(_{\text{pico}}\)), 7.72 (d, \(J = 7.9\) Hz, 1H\(_{\text{pico}}\)), 7.47 (t, \(J = 7.4\) Hz, 1H\(_{\text{pico}}\)), 7.21 (d, \(J = 5.9\) Hz, 1H\(_{\text{pico}}\)), 6.67 (s, NH), 5.09 (d, \(J = 16.5\) Hz, 1H\(_{\text{alkyl}}\)), 4.64 (d, \(J = 16.5\) Hz, 1H\(_{\text{alkyl}}\)), 4.46 (m, 2H\(_{\text{alkyl}}\)), 4.10 (m, 2H\(_{\text{macro}}\)), 3.79 (m, 3H\(_{\text{macro}}\)), 3.31 (dd, \(J = 6.6, 15.2\) Hz, 1H\(_{\text{macro}}\)), 3.23 (dd, 5.8, 12.5 Hz, 1H)), 3.01 (ddd, 5.3, 13.7 Hz, 1H\(_{\text{macro}}\)), 2.77 (td, 5.9, 13.7 Hz, 1H\(_{\text{macro}}\)), 2.54 (ddd, 5.9, 13.7 Hz, 1H\(_{\text{macro}}\)), 2.01 (m, 1H\(_{\text{macro}}\)).

\(^{13}\)C NMR (400 MHz, CD\(_3\)CN): \(\delta\) 164.83 (C\(_{\text{quart}}\)), 162.48 (C\(_{\text{quart}}\)), 153.65 (C\(_{\text{pico}}\)), 149.45 (C\(_{\text{pico}}\)), 141.83 (C\(_{\text{pico}}\)), 140.83 (C\(_{\text{pico}}\)), 126.69 (C\(_{\text{pico}}\)), 126.61 (C\(_{\text{pico}}\)), 125.51 (C\(_{\text{pico}}\)), 129.94 (C\(_{\text{pico}}\)), 69.43 (C\(_{\text{alkyl}}\)), 67.27 (C\(_{\text{alkyl}}\)), 63.92 (C\(_{\text{macro}}\)), 62.37 (C\(_{\text{macro}}\)), 61.53 (C\(_{\text{macro}}\)), 60.16 (C\(_{\text{macro}}\)), 54.23 (C\(_{\text{macro}}\)), 52.93 (C\(_{\text{macro}}\)).

UV/vis: 268, 312, 432 nm.

ESI-MS: \(m/z\): calc. for [M + OTf\(^+\)], 536.0571; found, 536.0568. UV/vis: 268, 490 nm.

**Synthesis of Ni-L\(^{N3}\)**

After purification Ni-L\(^{N3}\) was obtained as light brown solid (28 mg, 44%).

ESI-MS: \(m/z\): calc. for [M + OTf\(^+\)], 535.0590; found, 535.0590. UV/vis: 268 nm.

**SYNTHESIS OF CO-L\(^{N2S}\)**

First mechanistic investigations confirmed that an oxidative quenching mechanism is more likely than a reductive quenching process. Further experiments are on the way to confirm possible intermediates involved, such as a hydride species, and the influence of further reaction parameters on the outcome of the photocatalytic reaction, such as changing the sacrificial electron donor. The latter might also influence the quenching process and thus the overall TON and product selectivity.

**DATA AVAILABILITY STATEMENT**

The raw data supporting the conclusion of this article are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

**AUTHOR CONTRIBUTIONS**

MO was carrying out the synthetic and experimental work and wrote the manuscript, FB was measuring and solving the crystallographic data, RSS was executing the photophysical quenching studies with OSW supervising the photophysical experiments and editing the manuscript, MS was supervising the work and editing the manuscript.
**FUNDING**

This work was supported by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) via the priority program 2102 Light-controlled reactivity of metal complexes (DFG SCHW1454/9-1).

**ACKNOWLEDGMENTS**

The authors would like to thank the Humboldt Universität zu Berlin for the generous support of this project. We further thank the SPP 2102 (see Funding) for financial support. Furthermore, the authors want to thank Beatrice Cula for supervising the X-ray diffractometric analysis and Beatrice Battistella for performing the EPR measurements.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2021.751716/full#supplementary-material
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