Supporting Information

Instrumentation and measurement

The used rhenium complexes^[1] and [Ru(dmb)₃](PF₆)₂^[2] were synthesized as described in literature. NMR spectra were obtained using a Bruker AVIII-300 spectrometer at 298 K and referenced to residual solvent signals. GC analysis was performed using a Varian 490 gas chromatographer equipped with a 1-m COX column and a GC thermal conductivity detector. He (5.0) was used as the carrier gas. Irradiation experiments were performed in a 160 mL Schlenk tube (internal diameter = 3 cm) using a LED light source emitting at λ = (450±30) nm or (520±50) nm. Incident light intensities were determined using a K₃[Fe(C₂O₄)₃] actinometer.^[3] Reaction vessels were wrapped in an aluminium foil prior to sample preparation and unwrapped just before irradiation experiments. DMF/TEOA solutions containing the required rhenium catalyst and DBU in the desired concentration were saturated with CO₂ by bubbling for at least 15 min and sealed with a septum. The pressure was adjusted to 140 kPa. Irradiation experiments were performed in a dark room. For GC analysis, 100 µL samples were drawn from the headspace above the solution and injected directly into the micro gas chromatograph. TONs were determined from the point at which catalyst activity fully ceased or from the point measured last and were defined as TON = n(CO)/n(cat.), in which cat. represents the investigated catalytic system or mixture. TOFs were calculated from the linear slope of the initial catalytic activity.

Irradiation source

LED setups

TUM LED control unit:

I = constant

 \rightarrow Constant photon flux

- Power supply 220–240 V//50 Hz
- Eight LEDs (λ = 450 [4.14·10⁻⁶ Einstein s⁻¹] or 520 nm) independently switchable and tuneable
- Air cooling system
- Irradiation power tuneable via current



Figure S1. Left: TUM LED Control Unit. Right: Irradiation of Catalytic Mixture with 450 nm LEDs.

Stern-Volmer Plots



Figure S2. Stern-Volmer plots of deoxygenated DMF solutions of catalyst 1 (1.0 mM). TEOA (black; K_{SV} = 2.7 M⁻¹) or DBU (red; K_{SV} = 0 M⁻¹) was used as quencher. λ_{ex} = 365 nm.

Photocatalytic Experiments

Control experiments without light, CO_2 , catalyst, or TEOA do not show any CO formation. Analysis of the product solution by ¹H-NMR spectroscopy does not show any formation of formate, formaldehyde or methanol during both, experiments with or without DBU. Furthermore, no H₂ or methane was detected via GC during the photocatalytic experiments.

Table S1.TON and TOF values of photocatalytic CO2 reductionexperiments.Reaction conditions: Irradiation (λ =450 nm) of CO2-saturated DMF/TEOA solutions containing 0.1 mM catalyst 1.						
TEOA [M]	TON	TOF [h ⁻¹]				
0.00	0.00	0.0				
0.10	2.11	4.3				
0.20	2.25	5.5				
0.52	3.14	8.0				
0.69	3.80	9.8				
0.86	4.25	12				
1.20	4.35	12				
1.72	4.57	9.9				
2.00	4.00	6.6				
2.25	3.77	5.9				
2.50	3.59	5.6				

Table S2. TON and TOF values of photocatalytic CO_2 reduction experiments. Reaction conditions: Irradiation ($\lambda\text{=}450$ nm) of CO_2-saturated DMF solutions containing 0.1 mM catalyst 1.

DBU [mM]	TEOA [M]	TON	TOF [h ⁻¹]
0.00	0.00	0.0	0.0
12.5	0.00	0.0	0.0
0.00	0.10	2.11	4.3
2,50	0.10	4.16	8.9
5.00	0.10	5.61	10
12.5	0.10	7.48	14
25.0	0.10	5.27	11
50.0	0.10	5.11	11
100	0.10	4.37	11
200	0.10	4.54	11
500	0.10	0.67	1.4
0.00	1.72	5.03	9.3
12.5	1.72	4.39	7.9

Table S3. TON and TOF values of photocatalytic CO_2 reduction experiments. Reaction conditions: Irradiation (λ =450 nm) of CO₂-saturated DMF solutions containing 0.1 mM catalyst **2**.

DBU [mM]	TEOA [M]	TON	TOF [h⁻¹]
0.00	0.00	0.0	0.0
12.5	0.00	0.0	0.0
0.00	0.10	4.75	7.0
5.00	0.10	10.3	13
12.5	0.10	14.8	20
25.0	0.10	12.6	16
50.0	0.10	10.6	16
100	0.10	8.50	15
200	0.10	5.44	10
500	0.10	1.06	1.4
0.00	1.72	9.74	19
12.5	1.72	8.47	14

Table S4. TON and TOF values of photocatalytic CO_2 reduction experiments. Reaction conditions: Irradiation ($\lambda{=}450$ nm) of $CO_2{\text{-saturated DMF}}$ solutions containing 0.1 mM catalyst 3.

DBU [mM]	TEOA [M]	TON	TOF [h ⁻¹]
0.00	0.00	0.0	0.0
25.0	0.00	0.0	0.0
0.00	0.10	8.41	13
2.50	0.10	8.79	17
5.00	0.10	11.0	20
12.5	0.10	12.9	24
25.0	0.10	13.4	29
50.0	0.10	12.8	31
100	0.10	12.7	37
200	0.10	7.34	18
500	0.10	0.87	3.0
0.00	1.72	8.84	18
25.0	1.72	6.17	11

Additional content



Scheme S1. Simplified scheme of photocatalytic reduction of CO_2 with [Re(dmb)(CO_3)X]. Rhenium-based complexes are capable to act as both photosensitizer and CO_2 reducing catalyst. Thus, no additional photosensitizer is necessary. After photoexcitation of rhenium complexes to the ³MLCT state, an electron transfer from a sacrificial electron donor like triethanolamine (TEOA) can take place, which leads to the one electron reduced (OEleR) species of the catalyst. Subsequent loss of the halide ligand and coordination of CO_2 , followed by protonation, results in the protonated CO_2 adduct of the catalyst. Transfer of a second electron is necessary, which either can be delivered from TEOA or a second OEleR species. Dissociation of hydroxide and CO and coordination of halide completes the catalytic cycle and recovers the original catalyst. Alternatively, also solvent molecules can coordinate to the rhenium instead of halides ^[4]



Scheme S2. The transfer of one electron of a TEOA molecule to the ³MLCT state or to the protonated CO₂ adduct of the rhenium complex leads to the nitrogencentred radical TEOA⁺. Deprotonation of this radical-cation by another TEOA molecule generates a carbon-centred TEOA-radical, which represents a strong reducing agent. Hence, electron back hopping from the OEIeR species to the TEOA-radical is prevented, which is important for efficient quenching of the excited state of the rhenium catalyst. An electron transfer from the carbon-centred TEOA-radical to the ³MLCT state or to the protonated CO₂ adduct of the rhenium complex leads to 2,2¹-azanediylbis(ethan-1-ol) and 2-hydroxyacetaldehyde or to 2-(bis(2-hydroxyethyl)amino)acetaldehyde, depending on which carbon atom the radical is located.^[5] Similar processes take place using TEA as sacrificial electron donor.^[6]

Literature

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