Supporting Information Dalton Trans.

Mono- and bimetallic Ir(III) based catalysts for the homogeneous photocatalytic reduction of CO_2 under visible light irradiation. New Insights regarding catalyst deactivation.

Richard O. Reithmeier,[a] Simon Meister,[a] Bernhard Rieger,[*a] Armin Siebel,[b] Martin Tschurl,[c] Ulrich Heiz[c] and Eberhardt Herdtweck[d]

[a] WACKER-Chair of Macromolecular Chemistry, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany, phone: (+)49 89 289 13571, fax: (+)49 89 289 13562; e-mail: rieger@tum.de

[b] Department of Technical Electrochemistry, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany.

[c] Chair of Physical Chemistry, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany.

[d] Chair of Inorganic Chemistry/Molecular Catalysis, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany.

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1. Detailed Crystallographic Information

Single Crystal X-Ray Structure Determination of Compound 1 (CCDC 982397).

General:

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II, κ–CCD) at the window of a fine-focused sealed tube with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator by using the SMART software package.[1] The measurement was performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a cactus prickle (Opuntia ficus-india) and transferred to the diffractometer. The crystal was frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[2] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX[7] based on SIR-92[3] in conjunction with SHELXL-97[5].Unless otherwise noticed, methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)}$ = 1.5·$U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with aromatic C–H distances of 0.95 Å, and $U_{iso(H)}$ = 1.2·$U_{eq(C)}$. If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97[5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[4] Images of the crystal structures were generated by PLATON.[6]

Special:

1: Full refinement was possible without running into problems.

Compound 1

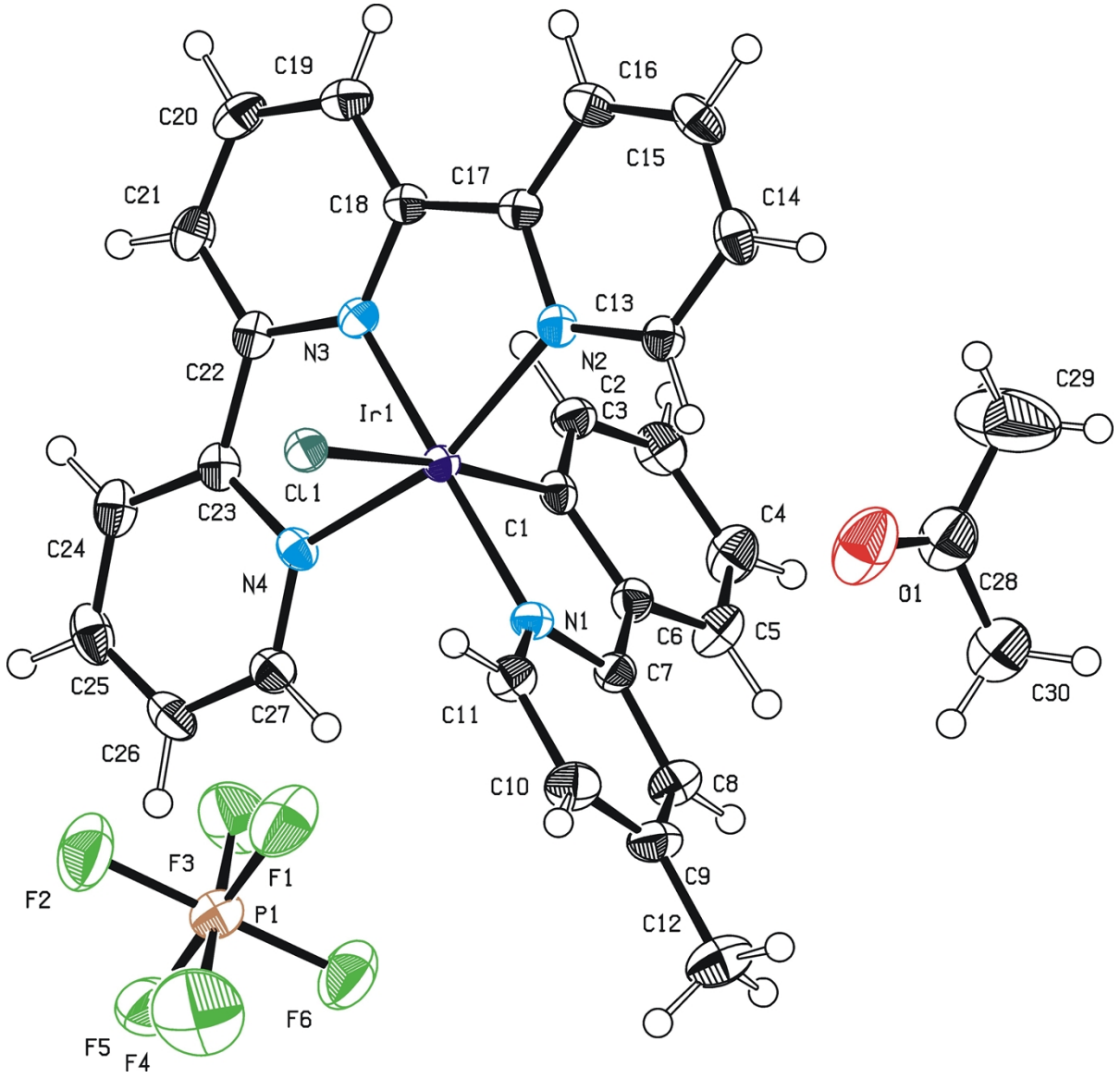


Fig. S1 – Ortep drawing with 50% ellipsoids for complex **1**.[6]

Operator:	*** Herdtweck ***
Molecular Formula:	C_{30} H_{27} Cl F_6 Ir N_4 O P $[(C_{27}$ H_{21} Cl Ir $N_4)^+]$, $[(P$ $F_6)^-]$, $(C_3$ H_6 O)
Crystal Color / Shape	Red plate
Crystal Size	Approximate size of crystal fragment used for data collection: 0.05 × 0.18 × 0.25 mm
Molecular Weight:	832.20 a.m.u.
F_{000}:	1624
Systematic Absences:	h0l: h+l≠2n; 0k0: k≠2n
Space Group:	Monoclinic $P\,2_1/n$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9872 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.75° < θ < 25.47°; Mo($K\overline{\alpha}$); λ = 0.71073 Å a = 8.4917(2) Å

	b =	27.4235(7) Å	β = 100.8879(10)°
	c =	13.0479(3) Å	

V = 2983.80(12) Å^3; Z = 4; D_{calc} = 1.852 g cm^{-3}; Mos. = 0.53

Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 50 kV; 30 mA; λ = 0.71073 Å; Mo(K$\overline{\alpha}$)
Temperature:	(-150±1) °C; (123±1) K
Measurement Range:	1.75° < θ < 25.47°; h: -10/10, k: -33/33, l: -15/15
Measurement Time:	2 × 15 s per film
Measurement Mode:	measured: 7 runs; 2641 films / scaled: 7 runs; 2641 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 40.0 mm
LP - Correction:	Yes [2]
Intensity Correction	No/Yes; during scaling [2]
Absorption Correction:	Multi-scan; during scaling; μ = 4.688 mm^{-1} [2] Correction Factors: T_{min} = 0.5634 T_{max} = 0.7452
Reflection Data:	70305 reflections were integrated and scaled 1066 reflections systematic absent and rejected 11 obvious wrong intensity and rejected (0 2 0) 69228 reflections to be merged 5502 independent reflections 0.033 R_{int}: (basis F_o^2) 5502 independent reflections (all) were used in refinements 5056 independent reflections with $I_o > 2\sigma(I_o)$ 99.3 % completeness of the data set 400 parameter full-matrix refinement 13.8 reflections per parameter
Solution:	Direct Methods [3, 7]; Difference Fourier syntheses
Refinement Parameters:	In the asymmetric unit: 44 Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 0.95, 0.98 Å). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4, 5, 7]
Extinction Correction:	no
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$ with a: 0.0165; b: 5.0754; P: [Maximum(0 or F_o^2)+2$*F_c^2$]/3
Shift/Err:	Less than 0.001 in the last cycle of refinement:
Resid. Electron Density:	+0.60 e**Error!**/Å^3; -0.92 e**Error!**/Å^3
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$
[$F_o > 4\sigma(F_o)$; N=5056]:	= 0.0204
[all reflctns; N=5502]:	= 0.0241
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$
[$F_o > 4\sigma(F_o)$; N=5056]:	= 0.0446
[all reflctns; N=5502]:	= 0.0458

Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.137
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)$	

2. Irradiation Setup

TUM LED setup:

I=const
-> constant light output

- Power Supply 220 - 240V / 50Hz
- 8 LEDs (K2 Luxeon high power LED's), independently switch- and tunable (see also Table S1)
- Air cooling system
- Irradiation power tunable via current

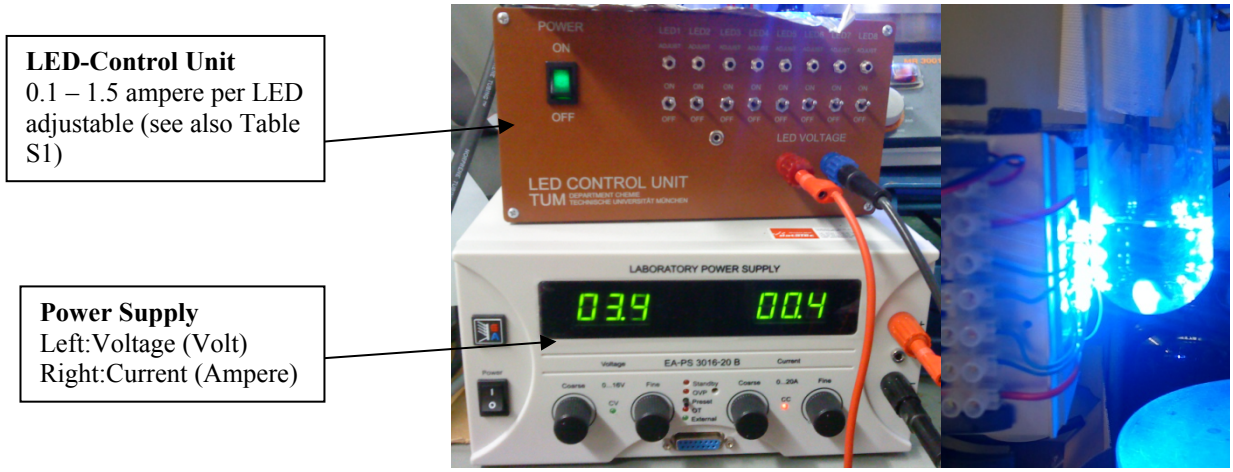
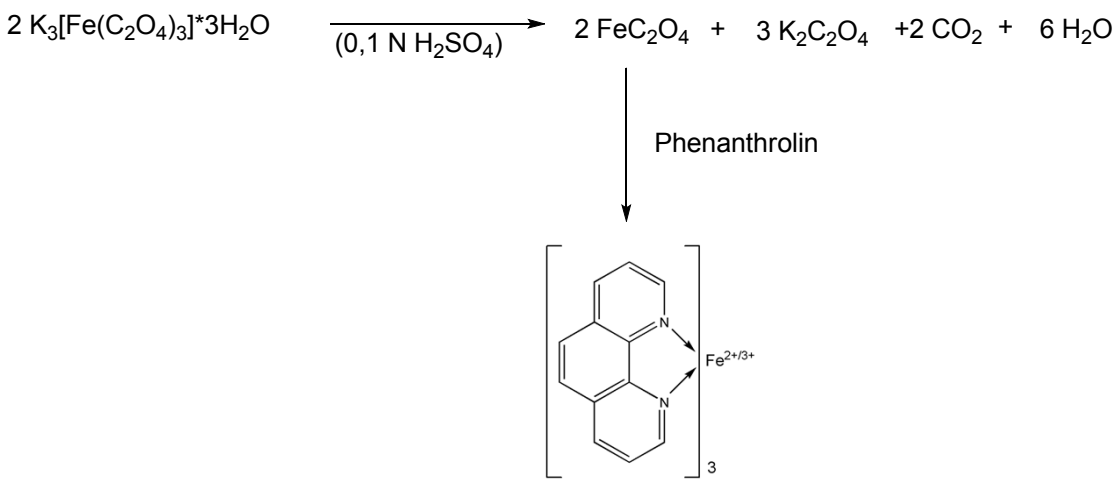


Fig. S2: LED-setup.

Actinometry[8-10]:



Scheme S1: Photolytic Reduction of Fe(III) to Fe(II).

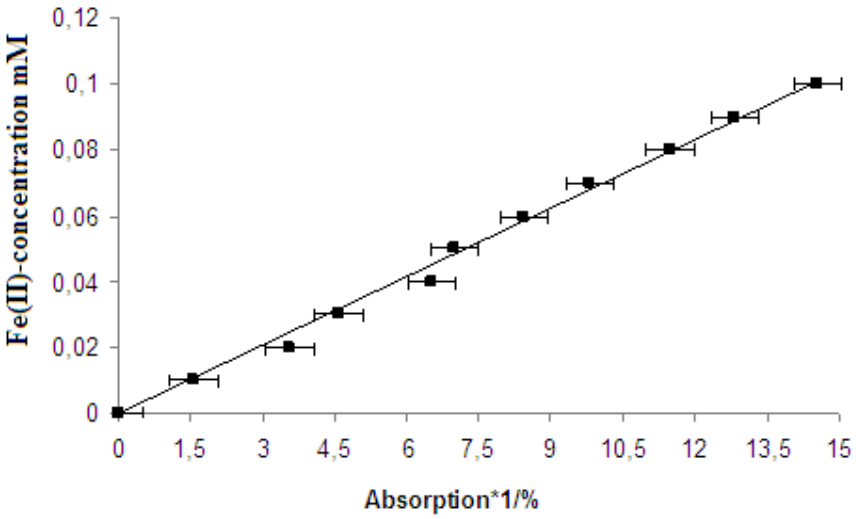


Fig. S3: Calibration curve for the actinometry.

Table S1: Light intensity for one LED depending on the power supply (current).

Current [A]	Absorption [%]	Concentration Fe(II) [µmol/l]	m Fe(II) [µmol]	Quants/sec [10^{16}/s]
0.1	1.11	7.67	0.614	4.10
0.2	1.39	9.61	0.769	5.14
0.3	1.74	12.0	0.962	6.43
0.4	2.51	17.4	1.39	9.28
0.5	2.72	18.7	1.50	10.0
0.6	2.63	18.1	1.45	9.72
0.7	3.80	26.3	2.10	14.1
0.8	4.42	30.6	2.44	16.3
0.9	4.89	33.8	2.70	18.1
1.0	5.47	37.8	3.03	20.2
1.1	5.97	41.3	3.30	22.1
1.2	6.52	45.1	3.60	24.1
1.3	7.06	48.8	3.90	26.1
1.4	7.60	52.6	4.20	28.1
1.5	8.15	56.3	4.51	30.1

References:

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

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[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

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