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Supporting Information

Electrochemically Driven Reduction of Carbon Dioxide Mediated by Mono-Reduced Mo-Diimine Tetracarbonyl Complexes: Electrochemical, Spectroelectrochemical and Theoretical Studies

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1. Synthesis and spectroscopic characterization of complexes 1-3

Complexes **1-3** were synthesized according to reported procedures.^[1] As shown in Scheme S1, the general procedure consists of mixing $[Mo(CO)_6]$ with one equivalent of diimine ligand (bpy, phen or py-indz) in toluene under argon. The mixture is reacted under reflux. A colored (**1**: orange-red, **2**: red; **3**: yellow) precipitate is formed (see below) and washed with a 1:1 toluene/petroleum ether (15 mL) cold mixture.



Scheme S1. Synthetic pathway for complexes 1-3

Tetracarbonyl(2,2'-bipyridine)molybdenum(0) (Complex 1)



Molybdenum hexacarbonyl (0.69 g, 2.63 mmol) and 2,2'-bipyridine (0.41 g, 2.63 mmol) were refluxed in toluene for 90 minutes in dark conditions. The solution color changed from strong purple to red, forming a precipitate that was filtered and washed with cold toluene and diethyl ether, yielding an orange-red powder. Recrystallization in 1:1 diethyl ether / dichloromethane provided an orange-red crystalline solid. Yield: 0.77 g (81%). ¹H RMN (300 MHz, d8-THF): 9.11 (d, J=5 Hz, 2 H), 8.44 (d, J=8.2 Hz, 2H), 7.94 (td, J=8, 1.4 Hz, 2H), 7.52 (t, J=5.9 Hz, 2H). IR: see Table S1.

Tetracarbonyl(2,2'-phenanthroline)molybdenum(0) (Complex 2)



Molybdenum hexacarbonyl (1.00 g, 3.79 mmol) and 2,2⁻-phenanthroline (0.68 g, 3.79 mmol) were refluxed in 25 mL of toluene overnight at 90°C. The red solution was filtered. The solid was washed with cold toluene and diethyl ether. Recrystallization in 1:1 toluene / dichloromethane provided a red crystalline solid. Yield: 0.94 g (96%). ¹H RMN (300 MHz, d8-THF): 9.48 (dd, J=5,1.3 Hz, 2H), 8.63 (dd, J=8.1,1.3 Hz, 2H), 8.1 (s, 2H), 7.88 (dd, J=8.1,5 Hz, 2H). IR: See Table S1

Tetracarbonyl(2,2'-pyridyl-indazol)molybdenum(0) (Complex 3).



 $[Mo(CO)_6]$ (0.26 g, 1 mmol) and pyridylindolizine (0.19 g, 1 mmol) in toluene (20 mL) were stirred at reflux for 6 h. A yellow-orange solution was obtained. After evaporation of the toluene, the material was dissolved in dichloromethane and filtered. Hexane was then added to precipitate the complex. Recrystallization in a solution 1:1 hexane / dichloromethane gave a yellow crystalline solid. Yield = 0.356 g (88%). ¹H RMN (300 MHz, d8-THF): 9.14(d, J=5.2 Hz, 1H), 8.93 (d, J=7.1 Hz, 1H), 8.03 (dd, J=6.7,1.5 Hz, 1H), 7.96 (s, 1H), 7.81 (d, J=9 Hz, 1H), 7.36 (t, J=6.5,6.4 Hz, 1H), 7.15 (dd, J=8.8,6.7 Hz, 1H), 7.15 (dd, J=8.8,6.7 Hz, 1H), 7.07 (dd, J=10,3.8 Hz, 1H). IR: See Table S1.

Table S1. IR spectroscopic data of complex 1-3 at solid state and in THF.^[a]

Complex	1		2		3	
	Solid ^[b]	THF	Solid ^[b]	THF	Solid ^[b]	THF
<i>v</i> ₁ / cm ⁻¹	1805	1840	1818	1840	1801	1836
$v_2 / {\rm cm}^{-1}$	1859	1880	1857	1880	1857	1877
v_3 / cm ⁻¹	1912	1900	1909	1899	1908	1895
v_4 / cm ⁻¹	2007	2012	2004	2012	2008	2010

[a] Data restricted to the 1800-2050 cm⁻¹ energy range. [b] Measured by ATR IR spectroscopy.



Figure S1. ¹H NMR spectrum of complex 1 in d8-THF.



Figure S2. ¹H NMR spectrum of complex 2 in d8-THF.



Figure S3. ¹H NMR spectrum of complex 3 in d8-THF.

2. X-ray diffraction data ^[1c, 2]



Scheme S2. Atom numbering for calculated structures of complexes 1-3 ($N^{(1)}$ is the N atom of the pyridyl group in complex 3)

Table S2. Bond distances (Å) for complexes 1, 2 and 3 from X-Ray data according to Scheme S2.

Atom 1	Atom 2	1	2	3
Мо	C ⁽¹⁾	2.056(4)	2.024	2.010(4)
Мо	C ⁽²⁾	1.952(4)	1.959	1.944(4)
Мо	C ⁽³⁾	1.962(3)	1.959	1.951(4)
Мо	C ⁽⁴⁾	2.022(4)	2.026	2.028(4)
Мо	N ⁽¹⁾	2.241(2)	2.243	2.271(3)
Мо	N ⁽²⁾	2.249(3)	2.243	2.200(3)
C ⁽¹⁾	O ⁽¹⁾	1.135(4)	1.141	1.134(5)
C ⁽²⁾	O ⁽²⁾	1.168(5)	1.154	1.159(5)
C ⁽³⁾	O ⁽³⁾	1.160(4)	1.154	1.160(5)
C ⁽⁴⁾	O ⁽⁴⁾	1.151(5)	1.146	1.139(5)
C ⁽⁵⁾	C ⁽⁶⁾	1.483(5)	1.439	1.456(5)

Table S3. Angle (°) values for complexes 1, 2 and 3 from X-Ray data.

Atom 1	Atom 2	Atom 3	1	2	3
C ⁽¹⁾	Мо	C ⁽²⁾	85.1(1)	85.9	84.0(1)
C ⁽¹⁾	Мо	C ⁽³⁾	88.4(1)	85.9	87.0(2)
C ⁽¹⁾	Мо	C ⁽⁴⁾	167.8(1)	167.6	168.6(2)
C ⁽¹⁾	Мо	N ⁽¹⁾	93.6(1)	95.4	92.3(1)
C ⁽¹⁾	Мо	N ⁽²⁾	93.8(1)	95.4	97.0(1)
C ⁽²⁾	Мо	C ⁽³⁾	90.1(1)	93.2	91.0(2)
C ⁽²⁾	Мо	C ⁽⁴⁾	84.3(1)	85.6	87.7(1)
C ⁽²⁾	Мо	N ⁽¹⁾	99.1(1)	96.6	96.5(1)
C ⁽²⁾	Мо	N ⁽²⁾	171.4(1)	170.2	168.3(1)
C ⁽³⁾	Мо	C ⁽⁴⁾	85.7(1)	85.6	85.4(2)
C ⁽³⁾	Мо	N ⁽¹⁾	170.7(1)	170.2	172.4(1)
C ⁽³⁾	Мо	N ⁽²⁾	98.4(1)	96.6	100.7(1)
C ⁽⁴⁾	Мо	N ⁽¹⁾	94.0(1)	94.5	96.3(1)
C ⁽⁴⁾	Мо	N ⁽²⁾	97.6(1)	94.5	92.7(1)
N ⁽¹⁾	Мо	N ⁽²⁾	72.34(9)	73.6	71.8(1)

3. UV-Vis spectroelectrochemistry



Figure S4. UV-Vis-SEC spectra of complexes **1** (Panel A), **2** (Panel B), and **3** (Panel C) in dry THF/NBu₄PF₆ 0.1 M before (black) and after reduction at $E_{1/2}(1)$ (red) and $E_{pc}(2)$ (green) under Ar.



Figure S5. UV-Vis-SEC spectra of complexes **1** (Panel A), **2** (Panel B), and **3** (Panel C) in dry THF/NBu₄PF₆ 0.1 M before (black) and after reduction at $E_{1/2}(1)$ (red) and $E_{pc}(2)$ (green) under CO₂.

4. NIR-spectroelectrochemistry



Figure S6. NIR-SEC spectra of complexes **1** (Panel A), **2** (Panel B), and **3** (Panel C) in dry THF/NBu₄PF₆ 0.1 M before (black) and after reduction at $E_{1/2}(1)$ (red) and $E_{1/2}(1)$ (blue) under Ar.



Figure S7. NIR-SEC spectra of complexes **1** (Panel A), **2** (Panel B), and **3** (Panel C) in dry THF/NBu₄PF₆ 0.1 M before (black) and after reduction at $E_{1/2}(1)$ under Ar (red) or CO₂ (orange).

5. IR-spectroelectrochemistry



Figure S8. Schematic representation of the IR-SEC developed and used for the studies. WE: Working electrode, RE: Reference electrode; CE: Counter electrode.



Figure S9. IR-SEC spectra of complexes **1** (Panel A), **2** (Panel B), and **3** (Panel C) in dry THF/NBu₄PF₆ 0.1 M upon reduction at $E_{1/2}(1)$ (orange) and $E_{pc}(2)$ (purple) under CO₂. For comparison, IR spectra upon reduction at $E_{pc}(2)$ under Ar (green) are given.

6. IR spectroscopy of chemically mono-reduced species and related compounds



Figure S10. IR spectra of chemically-reduced complexes $1^{\bullet-}$, $2^{\bullet-}$ and $3^{\bullet-}$ in THF before (red) and after (pink) reaction with CO₂. Black curves correspond to IR spectra of neutral complexes 1-3. The cyan and grey curves in Panel A represent intermediates curves during reaction of $1^{\bullet-}$ with CO₂.



Figure S11. IR spectra of $(NH_4^+)(HCO_2^-)$ (red) and $(NH_4^+)_2(CO_3^{2^-})$ (blue) in THF.



Figure S12. IR spectra of CO₂-saturated solution of THF in presence of 0.1% H₂O wit (black) and without (blue) complex **2** (1 mM)

7. Electrochemistry



Figure S13. CVs ($E / V vs. Fc^+/Fc$) at a BDD working electrode of A) complex **1**, B) complex **2** and C) complex **3**, in dry THF/NBu₄PF₆ 0.1 M ($v = 0.1 V s^{-1}$) under argon (black) and CO₂ (red).



Figure S14. Plots of $I_{pc}(1)I v^{1/2}$ against v under Ar (black), under CO₂ (red) and under CO₂ + 0.55 M H₂O (blue) for (A) complex **1** and (B) complex **3**.



Figure S15. CVs (*E* / V vs. Fc⁺/Fc, v = 0.1 V s⁻¹) at a BDD (orange) and GC (purple) working electrode of complex **1** (1 mM), in THF/NBu₄PF₆ 0.1 M under argon.



Figure S16. CVs (*E* / V vs. Fc⁺/Fc, v = 0.01 V s⁻¹) at a BDD working electrode of complex **2** (1 mM), in dry THF/NBu₄PF₆ 0.1 M under argon for progressive addition of H₂O: 0 µL (black), 30 µL (orange), 60 µL (green).



Figure S17. CVs ($E / V vs. Fc^+/Fc$, $v = 0.1 V s^{-1}$) at a BDD working electrode of complex **2** (1 mM), in dry THF/NBu₄PF₆ 0.1 M under CO₂ for progressive addition of H₂O: 0 µL (black), 30 µL (red), 60 µL (blue), 90 µL (green).



Figure S18. Plots of $i_{pc}(1)$ vs. $v^{1/2}$ for CVs at a BDD working electrode of complexes **1-3** (1 mM) in THF/NBu₄PF₆ 0.1 M under Ar.

8. CV simulations

Voltammetric simulations were performed by using the Kissa 1D software (Amatore, C.; Klymenko, O.; Svir, I.; A new strategy for simulation of electrochemical mechanisms involving acute reaction fronts in solution: Principle, *Electrochem.Commun.* **2010**, *12*, 1170-1173).

The mechanism and associated parameters are given as below. Two different concentrations (0.001 M and 0.55 M) for H^{+} were considered. The 0.001 M concentration accounts for residual water in the electrolytic solution. The 0.55 M concentration corresponds to the situation for which water was intentionally added:

ET steps: $[Mo(CO)_4(L)] + e^- = [Mo(CO)_4(L)]^ k^0, E^0$ Homogeneous reactions: $[Mo(CO)_4(L)]^- + CO_2 = [Mo(CO)_4(L)] + P1$ k_{f1}, k_{b1} $[Mo(CO)_4(L)]^- + CO_2 + H^+ = [Mo(CO)_4(L)] + P2$ k_{f2}, k_{b2}

Initial concentrations: $[[Mo(CO)_4(L)]] = 0.001 \text{ M}; \quad [[Mo(CO)_4(L)]^-] = 0 \text{ M}; \quad [CO_2] = 0 \text{ M or } 0.3 \text{ M}; \quad [H^+] = 0.001 \text{ M or } 0.55 \text{ M};$ $[P1] = 0 \text{ M}; \quad [P2] = 0 \text{ M}.$

Diffusion coefficients: $D([Mo(CO)_4(L)]) = 10^{-5} \text{ cm}^2/\text{s}; D([Mo(CO)_4(L)]^-) = 10^{-5} \text{ cm}^2/\text{s}; D(CO_2) = 2 \ 10^{-5} \text{ cm}^2/\text{s}; D(H^+) = 4 \ 10^{-5} \text{ cm}^2/\text{s}; D(P1) = D(P2) \ 10^{-5} \text{ cm}^2/\text{s};$

Electrode area = 0.07 cm²; k^0 = 0.005 cm s⁻¹, α = 0.5.

Table S4. Electrochemical data obtained for the complexes 1-3 by CV simulation

	E°/V	<i>k</i> _{f1} / M ⁻¹ s ⁻¹	<i>k</i> _{b1} / M ⁻¹ s ⁻¹	<i>k</i> _{f2} / M ⁻² s ⁻¹	$k_{\rm b2} /{\rm M}^{-1}{\rm s}^{-1}$
Complex 1	-2.00	0.2	400	1.3	400
Complex 2	-2.00	0.5	0.05	2.5	0.25



Figure S19. Experimental (A, B) and simulated (C, D) CVs of complexes **1** (left) and **2** (right) in dry THF/NBu₄PF₆ 0.1 M under argon (black), under CO₂ (red) and under CO₂ + H₂O (blue). v = 0.05 V s⁻¹. E / V vs. Fc⁺/Fc. Comparative CVs are for each complex are given in panels E and F. For detailed simulations, see above part.



Scheme S3. Atom numbering for calculated structures of complexes $[Mo(CO)_{3(}L)]$ and their CO_2 , CO_2H and H adducts.

Table S5. Calculated bond distances (Å) and angles (°) for the $CO_2^{\bullet-}$ and $COOH^{\bullet-}$ adducts and isolated CO_2 and $[CO_2]^{\bullet-}$ molecules according to numbering of Scheme S3.

	Mo–C(O) ₂	Mo–O(CO)	O–C(O)	(O)C–O	0-C-0	Mo-N ⁽¹⁾	Mo-N ⁽²⁾	$C^{(5)} - C^{(6)}$
[Mo(CO) ₃ (bpy)(CO ₂)] ^{•-}	2.348	2.434	1.240	1.21	142.5	2.221	2.221	1.437
$[Mo(CO)_3(phen)(CO_2)]^{\bullet-}$	2.348	2.439	1.241	1.21	142.4	2.227	2.227	1.411
$[Mo(CO)_3(py-indz)(CO_2)]^{\bullet-}$	2.364	2.487	1.242	1.214	141.2	2.235	2.198	1.426
[Mo(CO)₃(bpy)(COOH)] ^{●−}	2.278	3.169	1.238	1.400	115.6	2.331	2.331	1.467
[Mo(CO) ₃ (phen)(COOH)] ^{•-}	2.278	3.171	1.238	1.401	115.6	2.238	2.238	1.430
$[Mo(CO)_3(py-indz)(COOH)]^{\bullet-}$	2.280	3.180	1.239	1.403	115.3	2.259	2.222	1.445
CO ₂			1.171		180.0			
[CO ₂] ^{•-}			1.247		134.7			

Table S6. Calculated bond distances (Å) for the neutral and reduced tetracarbonyl complexes and the reduced tricarbonyl complexes according to numbering of Schemes S2 and S3.

		(0)	(0)		(0) (0)		(0)	(5) (0)
	Mo–C ⁽¹⁾	Mo–C ⁽²⁾	$Mo-C^{(3)}$	$C^{(1)} - O^{(1)}$	$C^{(2)} - O^{(2)}$	Mo–N ⁽¹⁾	Mo–N ⁽²⁾	$C^{(5)} - C^{(6)}$
Complex 1	2.047	1.976	1.976	1.164	1.175	2.260	2.260	1.475
Complex 2	2.047	1.975	1.975	1.164	1.175	2.268	2.268	1.434
Complex 3	2.046	1.973	1.976	1.165	1.175	2.285	2.238	1.448
Complex 1 ^{•-}	2.044	1.974	1.974	1.169	1.181	2.254	2.254	1.430
Complex 2 ^{•-}	2.045	1.972	1.972	1.169	1.181	2.261	2.261	1.407
Complex 3 ^{•-}	2.044	1.972	1.974	1.169	1.181	2.270	2.231	1.418
[Mo(CO) ₃ (bpy)] ^{●−}	1.906	1.955	1.955	1.192	1.189	2.229	2.229	1.438
[Mo(CO)₃(phen)] ^{•-}	1.907	1.954	1.954	1.192	1.189	2.236	2.236	1.411
$\left[Mo(CO)_3(py\text{-}indz)\right]^{\bullet-}$	1.909	1.952	1.956	1.192	1.190	2.243	2.207	1.425

Table S7. Calculated angles (°) for the neutral and reduced tetracarbonyl complexes and the reduced tricarbonyl complexes according to numbering of Schemes S2 and S3.

	N ⁽¹⁾ –Mo–C ⁽¹⁾	N ⁽²⁾ -Mo-C ⁽¹⁾
Complex 1	93.2	93.2
Complex 2	93.2	93.2
Complex 3	93.1	93.6
Complex 1 ^{•-}	93.4	93.4
Complex 2 ^{•-}	93.4	93.4
Complex 3 ^{•-}	93.3	94.3
[Mo(CO)₃(bpy)] ^{•–}	107.2	107.2
[Mo(CO)₃(phen)] ^{•-}	107.3	107.3
[Mo(CO) ₃ (py-indz)] ^{●−}	109.2	106.9

Table S8. Calculated CO stretching energies for complexes 1, 1⁻⁻, 2, 2⁻⁻, 3 and 3⁻⁻.

	v _{1 (CO)} / cm ⁻¹
Complex 1	1911, 1940, 2016
Complex 1	1868, 1901, 1987
Complex 2	1913, 1942, 2018
Complex 2	1865, 1898, 1992
Complex 3	1912, 1939, 2012
Complex 3	1871, 1903, 1990

Table S9. Calculated bond distances (Å) for the reduced hydride species according to numbering of Scheme S3.

	Mo–H	Mo–N ⁽¹⁾	Mo–N ⁽²⁾	C ⁽⁵⁾ –C ⁽⁶⁾
[Mo(bpy)(CO) ₃ (H)] ^{•–}	1.844	2.227	2.227	1.460
[Mo(phen)(CO) ₃ (H)] ^{•-}	1.843	2.330	2.330	1.425
[Mo(py-indz)(CO) ₃ (H)] ^{•-}	1.849	2.258	2.220	1.441

Table S10. Mulliken charges of Mo, $(CO)_3$, Mo $(CO)_3$, L and X = CO, CO₂, COOH or H moieties of selected catalytic intermediates (L = bpy, phen, py-indz).

			M. (00)		
	IVIO	(CO) ₃	$MO(CO)_3$	L	CO/CO ₂ /CO ₂ H/H
Complex 1	0.95	-0.94	-0.01	0.22	-0.23
Complex 2	0.94	-0.95	-0.01	0.24	-0.23
Complex 3	1.00	-1.01	-0.01	0.26	-0.25
Complex 1 ^{•-}	1.02	-1.16	-0.14	-0.57	-0.29
Complex 2 ^{•-}	1.01	-1.14	-0.14	-0.57	-0.29
Complex 3 ^{•-}	1.07	-1.18	-0.12	-0.57	-0.31
[Mo(CO) ₃ (bpy)] ^{•–}	1.10	-1.51	-0.41	-0.59	
[Mo(CO) ₃ (phen)] ^{•-}	1.09	-1.50	-0.41	-0.59	
[Mo(CO) ₃ (py-indz)] ^{•-}	1.09	-1.54	-0.45	-0.55	
[Mo(CO) ₃ (bpy)(CO ₂)] ^{•-}	0.91	-1.16	-0.24	-0.45	-0.30
[Mo(CO) ₃ (phen)(CO ₂)] ^{•-}	0.90	-1.14	-0.24	-0.45	-0.31
[Mo(CO) ₃ (py-indz)(CO ₂)] ^{•-}	0.96	-1.21	-0.25	-0.39	-0.36
[Mo(CO) ₃ (bpy)(COOH)] ^{•-}	1.06	-1.58	-0.52	-0.04	-0.44
[Mo(CO) ₃ (phen)(COOH)] ^{•-}	1.06	-1.57	-0.51	-0.06	-0.43
[Mo(CO) ₃ (py-indz)(COOH)] ^{•-}	1.12	-1.66	-0.54	0.01	-0.47
[Mo(CO) ₃ (bpy)(H)] ^{•–}	0.98	-1.60	-0.61	-0.13	-0.25
[Mo(CO) ₃ (phen)(H)] ^{•-}	0.97	-1.59	-0.61	-0.14	-0.25
[Mo(CO) ₃ (py-indz)(H)] ^{•-}	1.02	-1.67	-0.64	-0.06	-0.25



Figure S20. Comparative calculated IR spectra of (A) complexes 1 (black) and 1^{•-}(red), (B) complexes 2 (black) and 2^{•-}(red) and (C) complexes 3 (black) and 3^{•-}(red).



Figure S21. Calculated structure of $[Mo(CO)_3(phen)(COO-COOH)]^{\bullet-}$. Atom colors: H (white), C (grey), N (blue), O (red) and Mo (green).

Table S11. Calculated free energ	/ changes for the	reaction pathway:
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(a)
$$[Mo(CO)_3(L)(CO_2)]^{\bullet-} + CO_2 + H_2O \rightarrow [Mo(CO)_3(L)(CO_2H)] + HCO_3^{-}$$

(b) $[Mo(CO)_3(L)(CO_2H)] + e^- \Leftrightarrow [M_1]$	o(CO) ₃ (L)(CO ₂ H)] [•]
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L	$\Delta G(a) / kcal mol^{-1}$	$\Delta G(a+b) / \text{kcal mol}^{-1} $
bpy	+12.8	-13.5
phen	+12.4	-14.3
py-indz	+7.4	-23.8

* $\Delta G(b)$ was calculated from the redox potential difference $E^0(1) - E^0(5)$ (Table 3)

Table S12. Calculated free energy changes for the reaction pathwa	ay:
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(c)
$$[Mo(CO)_{3}(L)]^{\bullet-} + CO_{2} + H_{2}O \rightarrow [Mo(CO)_{3}(L)(H)] + HCO_{3}^{-}$$

(d)

$$[Mo(CO)_3(L)(H)] + e^- \Leftrightarrow [Mo(CO)_3(L)(CO_2H)]^{\bullet-}$$

 L
 $\Delta G(c) / kcal mol^{-1}$
 $\Delta G(c+d) / kcal mol^{-1(^{\circ})}$

 bpy
 +13.1
 -8.6

 phen
 +12.8
 -9.5

 py-indz
 +8.2
 -18.8

* $\Delta G(d)$ was calculated from the redox potential difference $E^0(1) - E^0(3)$ (Table 3)

10. References

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