Table 1 Selected Distances, Angles, and Torsions for **2.1**

Bond	Distance (Å)	
	Experimental	Calculated
Re(1)-C(16)	1.89(1)	1.916
Re(1)-C(17)	1.934(8)	1.936
Re(1)-C(18)	1.90(1)	1.918
Re(1)-N(1)	2.162(6)	2.197
Re(1)-N(2)	2.236(9)	2.293
Re(1)-Cl(1)	2.496(2)	2.525
C(16)-O(1)	1.16(1)	1.15323
C(17)-O(2)	1.12(1)	1.15039
C(18)-O(3)	1.15(1)	1.15627
Angle	**Degrees (°)**	
	Experimental	Calculated
C(16)-Re(1)-C(17)	87.6(4)	86.877
C(16)-Re(1)-C(18)	88.3(4)	90.613
C(17)-Re(1)-C(18)	87.3(4)	89.557
C(16)-Re(1)-N(1)	96.4(3)	96.240
C(17)-Re(1)-N(1)	174.9(3)	175.600
C(18)-Re(1)-N(1)	95.9(3)	93.506
C(16)-Re(1)-N(2)	169.3(3)	170.368
C(17)-Re(1)-N(2)	101.1(3)	102.755
C(18)-Re(1)-N(2)	98.3(3)	89.415
N(2)-Re(1)-N(1)	74.5(3)	74.146
C(16)-Re(1)-Cl(1)	91.7(3)	91.453
C(17)-Re(1)-Cl(1)	91.7(3)	94.786
C(18)-Re(1)-Cl(1)	179.9(3)	175.286
N(1)-Re(1)-Cl(1)	84.0(2)	82.058
N(2)-Re(1)-Cl(1)	81.6(2)	87.840
O(1)-C(16)-Re(1)	179.6(9)	178.224
O(2)-C(17)-Re(1)	176.0(8)	176.907
O(3)-C(18)-Re(1)	177.3(9)	179.317
Torsion	**Degrees (°)**	
	Experimental	Calculated
N(1)-C(5)-C(6)-N(2)	16(1)	15
N(2)-C(10)-C(11)-N(3)	41(1)	139

Table 2 Selected Distances, Angles, and Torsions for **2.2**

Bond	Distance (Å)	
	Experimental	Calculated
Re(1)-C(16)	1.926(9)	1.92438
Re(1)-C(17)	1.975(10)	1.90687
Re(1)-N(1)	2.119(7)	2.13186
Re(1)-N(2)	2.080(7)	2.08705
Re(1)-N(3)	2.126(7)	2.13185
Re(1)-Cl(1)	2.489(3)	2.53337
N(1)-N(3)	4.14(1)	4.14772
C(16)-O(1)	1.14(1)	1.16042
C(17)-O(2)	1.05(1)	1.16341
Angle	Degrees (°)	
	Experimental	Calculated
C(16)-Re(1)-C(17)	91.5(4)	89.188
C(16)-Re(1)-N(2)	173.7(4)	172.050
C(17)-Re(1)-N(2)	94.6(3)	98.762
C(16)-Re(1)-N(1)	103.9(3)	102.980
C(17)-Re(1)-N(1)	92.7(3)	93.429
N(2)-Re(1)-N(1)	77.3(3)	76.684
C(16)-Re(1)-N(3)	101.8(3)	102.986
C(17)-Re(1)-N(3)	91.7(3)	93.419
N(2)-Re(1)-N(3)	76.6(3)	76.684
N(1)-Re(1)-N(3)	153.7(3)	153.210
C(16)-Re(1)-Cl(1)	91.8(3)	89.136
C(17)-Re(1)-Cl(1)	176.5(2)	178.324
N(2)-Re(1)-Cl(1)	82.1(2)	82.913
N(1)-Re(1)-Cl(1)	85.4(2)	86.953
N(3)-Re(1)-Cl(1)	88.7(2)	86.953
O(1)-C(16)-Re(1)	177.9(9)	179.079
O(2)-C(17)-Re(1)	173.2(8)	179.182
Selected Torsions (deg)		
N(1)-C(5)-C(6)-N(2)	1(1)	2
N(2)-C(10)-C(11)-N(3)	-4(1)	-2

Table 3 Selected Distances, Angles, and Torsions for **2.3**

Bond	Distance (Å)	
	Experimental	Calculated
Re(1)-C(16)	1.911(3)	1.91740
Re(1)-C(17)	1.890(3)	1.91814
Re(1)-C(18)	1.921(4)	1.93897
Re(1)-N(1)	2.173(3)	2.19687
Re(1)-N(2)	2.232(2)	2.28998
Re(1)-Br(1)	2.6410(4)	2.67953
C(16)-O(1)	1.150(4)	1.15290
C(17)-O(2)	1.157(4)	1.15012
C(18)-O(3)	1.155(5)	1.15591
Angle	Degrees (°)	
	Experimental	Calculated
C(16)-Re(1)-C(17)	89.1(1)	90.772
C(16)-Re(1)-C(18)	85.9(1)	86.823
C(16)-Re(1)-N(1)	97.9(1)	96.034
C(17)-Re(1)-N(1)	92.5(1)	93.597
C(18)-Re(1)-N(1)	175.4(1)	175.575
C(16)-Re(1)-N(2)	171.2(1)	170.290
C(17)-Re(1)-N(2)	96.0(1)	89.435
C(18)-Re(1)-N(2)	101.3(1)	102.886
N(1)-Re(1)-N(2)	74.7(1)	74.265
C(16)-Re(1)-Br(1)	92.7(1)	90.399
C(17)-Re(1)-Br(1)	177.6(1)	176.076
C(18)-Re(1)-Br(1)	91.6(1)	94.069
N(1)-Re(1)-Br(1)	85.74(7)	82.555
N(2)-Re(1)-Br(1)	82.07(7)	88.780
O(1)-C(16)-Re(1)	178.6(3)	178.270
O(2)-C(17)-Re(1)	179.5(3)	179.355
O(3)-C(18)-Re(1)	179.9(3)	176.781
Selected Torsions (deg)		
N(1)-C(6)-C(1)-N(2)	-15.4(4)	-14.749
N(2)-C(5)-C(11)-N(3)	141.1(3)	136.119

Table 4 Selected Distances, Angles, and Torsions for **2.5**

Axial CN			Planar CN		
Bond	Distance (Å)		Bond	Distance (Å)	
	Exp.	Calc.		Exp.	Calc.
Re(2)-C(35)	2.148(7)	2.13963	Re(1)-C(19)	2.105(8)	1.98769
Re(2)-C(36)	1.926(6)	1.94011	Re(1)-C(16)	1.928(5)	2.09197
Re(2)-C(37)	1.954(7)	1.96758	Re(1)-C(18)	1.96(1)	2.00792
Re(2)-C(38)	1.902(9)	1.91853	Re(1)-C(17)	1.918(7)	1.90499
Re(2)-N(5)	2.242(7)	2.28998	Re(1)-N(1)	2.253(5)	2.32197
Re(2)-N(6)	2.168(5)	2.20279	Re(1)-N(2)	2.176(4)	2.18806
C(35)-N(8)	1.138(9)	1.16104	C(19)-O(3)	1.17(1)	1.14703
C(36)-O(4)	1.145(8)	1.15044	C(16)-N(4)	1.149(7)	1.16100
C(37)-O(5)	1.151(9)	1.15134	C(18)-O(2)	1.14(1)	1.14276
C(38)-O(6)	1.17(1)	1.15368	C(17)-O(1)	1.130(8)	1.15781
Angle	Degrees (°)		Angle	Degrees (°)	
	Exp.	Calc.		Exp.	Calc.
C(36)-Re(2)-C(38)	87.7(3)	87.273	C(16)-Re(1)-C(17)	87.8(3)	90.158
C(36)-Re(2)-C(37)	88.0(3)	89.890	C(16)-Re(1)-C(18)	87.0(3)	84.822
C(36)-Re(2)-C(35)	92.1(3)	93.356	C(16)-Re(1)-C(19)	92.5(3)	88.356
C(38)-Re(2)-C(37)	88.5(3)	90.973	C(17)-Re(1)-C(18)	88.7(3)	88.453
C(38)-Re(2)-C(35)	90.8(3)	91.628	C(17)-Re(1)-C(19)	90.5(3)	87.745
C(37)-Re(2)-C(35)	179.2(3)	175.933	C(18)-Re(1)-C(19)	179.1(3)	172.179
C(36)-Re(2)-N(5)	100.6(3)	102.576	C(16)-Re(1)-N(1)	102.2(2)	98.105
C(36)-Re(2)-N(6)	174.2(3)	175.708	C(16)-Re(1)-N(2)	175.9(2)	172.047
C(38)-Re(2)-N(5)	169.3(3)	170.146	C(17)-Re(1)-N(1)	168.3(3)	170.509
C(38)-Re(2)-N(6)	96.6(3)	96.171	C(17)-Re(1)-N(2)	95.9(3)	97.544
C(37)-Re(2)-N(5)	98.4(2)	89.360	C(18)-Re(1)-N(1)	97.7(3)	88.487
C(37)-Re(2)-N(6)	96.0(2)	92.605	C(18)-Re(1)-N(2)	94.8(3)	93.374
C(35)-Re(2)-N(5)	82.3(2)	87.543	C(19)-Re(1)-N(1)	83.2(2)	96.317
C(35)-Re(2)-N(6)	83.9(2)	84.008	C(19)-Re(1)-N(2)	85.7(2)	93.899
N(5)-Re(2)-N(6)	74.7(2)	73.977	N(1)-Re(1)-N(2)	73.9(2)	73.675
O(6)-C(38)-Re(2)	179.4(7)	178.027	O(1)-C(17)-Re(1)	178.2(7)	177.623
O(5)-C(37)-Re(2)	175.5(6)	179.414	O(2)-C(18)-Re(1)	172.0(7)	176.452
N(8)-C(35)-Re(2)	178.0(6)	176.457	O(3)-C(19)-Re(1)	178.0(6)	176.552
O(4)-C(36)-Re(2)	179.0(7)	177.313	N(4)-C(16)-Re(1)	178.7(6)	178.113
Torsion	Degrees (°)		Torsion	Degrees (°)	
	Exp.	Calc.		Exp.	Calc.
N(5)-C(20)-C(25)-N(6)	14.5(9)	13.735	N(1)-C(1)-C(6)-N(2)	12.5(8)	14.777
N(5)-C(24)-C(30)-N(7)	41(1)	135.774	N(1)-C(5)-C(11)-N(3)	43.7(9)	137.014

Table 5 Selected Distances, Angles and Torsions for Acetonitrile Adduct of **2.8**

Bond	Distance (Å)	
	Experimental	Calculated
Re(1)-C(16)	1.889(4)	1.93046
Re(1)-C(17)	1.885(3)	1.92844
Re(1)-N(1)	2.091(3)	2.10116
Re(1)-N(2)	2.135(3)	2.15397
Re(1)-N(3)	2.131(3)	2.15392
Re(1)-N(4)	2.160(3)	2.15202
N(2)-N(3)	4.138(4)	4.18483
C(16)-O(1)	1.170(4)	1.15749
C(17)-O(2)	1.171(4)	1.15244
Angle	Degrees (°)	
	Experimental	Calculated
C(16)-Re(1)-C(17)	87.69(16)	88.104
C(16)-Re(1)-N(1)	175.95(12)	176.094
C(17)-Re(1)-N(1)	96.35(12)	95.802
C(16)-Re(1)-N(3)	103.81(13)	103.594
C(17)-Re(1)-N(3)	94.03(12)	92.309
N(1)-Re(1)-N(3)	76.20(10)	76.306
C(16)-Re(1)-N(2)	103.58(13)	103.598
C(17)-Re(1)-N(2)	93.73(12)	92.307
N(1)-Re(1)-N(2)	75.99(10)	76.305
N(3)-Re(1)-N(2)	151.77(11)	152.544
C(16)-Re(1)-N(4)	90.50(14)	88.484
C(17)-Re(1)-N(4)	178.10(12)	176.587
N(1)-Re(1)-N(4)	85.46(10)	87.611
N(3)-Re(1)-N(4)	86.94(10)	88.504
N(2)-Re(1)-N(4)	86.15(10)	88.485
O(1)-C(16)-Re(1)	179.1(3)	178.807
O(2)-C(17)-Re(1)	178.0(3)	178.860
Torsion	Degrees (°)	
	Experimental	Calculated
N(1)-C(1)-C(6)-N(2)	1.7(4)	1.105
N(1)-C(5)-C(11)-N(3)	-1.8(4)	-1.110

Table 6 Selected Distances, Angles, and Torsions for κ^2(terpy)Mn(CO)$_3$Br from Compain et. al.

Selected Distances (Å)	
Mn(1)-N(1)	2.045(1)
Mn(1)-N(2)	2.105(2)
N(1)-N(2)	2.636(2)
Selected Angles (deg)	
N(1)-Mn(1)-N(2)	78.84(6)
Selected Torsions (deg)	
N(1)-C(8)-C(9)-N(2)	-16.5(2)
N(2)-C(13)-C(14)-N(3)	143.2(2)

Table 7 Crystal data and structure refinement for compounds **1**, **3**, **5**, and **7**

Compound	**1**	**3**	**5**	**7**
Empirical formula	$C_{19}H_{11}N_3O_3ReCl$	$C_{19}H_{11}N_3O_3ReBr$	$C_{20}H_{11}N_4O_3Re$	$C_{22}H_{14}N_4O_6F_3SRe$
Formula weight (g/mol)	538.96	583.41	530.04	693.63
Temperature (K)	200(2)	200	200	200
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal System	Triclinic	Monoclinic	Triclinic	
Space Group	P-1	C2/c	P-1	
a (Å)	9.8736(4)	31.1537(7)	9.9196(9)	
b (Å)	14.8202(4)	7.1176(2)	14.9902(14)	
c (Å)	16.3472(4)	16.8519(4)	16.5187(15)	
α (deg)	69.2890(10)	90.000	68.363(2)	
β (deg)	80.801(2)	111.0230(10)	80.929(2)	
γ (deg)	79.836(2)	90.000	79.975(2)	
Volume ($Å^3$)	2190.00(12)	3488.00	2236.6(4)	
Z, r (calc) (Mg/m^3)	2, 1.997	8, 2.222	2, 1.927	
Absorption coefficient (mm^{-1})	6.063	9.282	5.821	
Absorption correction		Semi-empirical from equivalents		
Final R indices [I≥2σ(I)]	R1 = 0.0397, wR2 = 0.0839	R1 = 0.0232, wR2 = 0.0614	R1 = 0.0390, wR2 = 0.0921	
R indices (all data)	R1 = 0.0604, wR2 = 0.0951	R1 = 0.0285, wR2 = 0.0642	R1 = 0.0500, wR2 = 0.0961	

Table 8 Crystal data and structure refinement for compounds **2**, **4**, **6**, and **8**

Compound	**2**	**4**	**6**	**8**
Empirical formula	$C_{18}H_{11}N_3O_2ReCl$	$C_{18}H_{11}N_3O_2ReBr$	$C_{19}H_{11}N_4O_2Re$	$C_{21}H_{14}N_4O_5F_3SRe$
Formula weight (g/mol)	510.95	530.04	502.04	665.61
Temperature (K)	200(2)	200	200	200
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal System	Triclinic			Triclinic
Space Group	P-1			P-1
a (Å)	8.5275(3)			8.5745(4)
b (Å)	14.2421(5)			11.9805(5)
c (Å)	17.4637(6)			13.0970(5)
α (deg)	77.948(2)			79.748(2)
β (deg)	85.684(2)			81.106(2)
γ (deg)	79.890			88.091(2)
Volume ($Å^3$)	2041.79(12)			1307.99(10)
Z, r (calc) (Mg/m^3)	4, 2.050			2, 1.993
Absorption coefficient (mm^{-1})	6.494			5.094
Absorption correction		Semi-empirical from equivalents		
Final R indices [I≥2σ(I)]	R1 = 0.0636, wR2 = 0.1018			R1 = 0.0294, wR2 = 0.0673
R indices (all data)	R1 = 0.0985, wR2 = 0.1110			R1 = 0.0366, wR2 = 0.0700

Table 9 Solvated and Gas Phase Energies of Axial & Trans $\kappa^{x}-(terpy)-Re(CO)_{5-x}CN$ (x=2,3)

Geometry	Bidentate		Terdentate	
	E(gas)[a]	E(solution)[b]	E(gas)[a]	E(solution)[b]
Axial	-1254.96132	-1254.99059	-1141.57255	-1141.60827
Trans	-1254.93788	-1254.97168	-1141.54660	-1141.58209
Difference	0.02343	0.01891	0.02595	0.02612
Difference (kcal/mol)	14.70	11.87	16.28	16.43

[a] B3LYP SCF energy in hartrees.
[b] B3LYP SCF energy in hartrees with PCM solvation in acetonitrile.

Table 10 Gas phase and solvated energies of compounds, transition states and intermediates in the 'carbonate' mechanism

Molecule	Label	E (gas)[a]	E (solution)[b]	E (solvation)[c]
CO_2 Linked Dimer	4.11	-2017.373132	-2017.412314	24.59
CO_2 Addition TS	4.12	-2206.120721	-2206.165017	27.80
C_2O_4 Linked Dimer	4.13	-2206.047558	-2206.097328	31.23
5 Member Ringed Dimer TS	4.14	-2206.013925	-2206.061531	29.87
CO_3 Linked Dimer	4.15	-2092.678255	-2092.725669	29.75
Bicarbonate Catalyst Cation	4.16	-1178.065153	-1178.119717	34.24
Bicarbonate Anion	4.17	-264.4852375	-264.4967144	7.20
Dimer Formation TS	4.18	-2017.434125	-2017.47423151664	25.17
Bicarbonate Dianion	4.19	-263.7946209	-264.1983931	253.37
Open Site Cation	4.27	-914.1064097	-914.1872844	50.75

[a] TPSS SCF energy in hartrees. [b] TPSS SCF energy in hartrees with COSMO solvation in DMF. [c] TPSS solvation energy in kcal/mol (E(gas) - E(solution)).

Table 11 Energies for the reaction steps in the 'carbonate' pathway

Description	Steps	Energy(gas)[a]	Energy(dmf)[b]
	4.01 $\longrightarrow$ 4.01^{3MLCT}	42.81191677	53.40083976
	4.01^{3MLCT} + 4.05 $\longrightarrow$ 4.02 + 4.06	81.44966532	-5.80393275
	4.02 $\longrightarrow$ 4.03 + 4.04	50.816912	15.440887
	4.06 + 4.05 $\longrightarrow$ 4.07 + 4.08	-1.077024	-2.915901
Addition of CO2 to open site	3, 35 $\longrightarrow$ 9 (4.4)	-0.2501423	6.37310903
Addition of second cat to CO2	9, 3 $\longrightarrow$ 19 (4.5)	-69.83107184	-81.24636949
relaxation of co2 insertion	19 $\longrightarrow$ 20 (4.7)	38.2733639	38.85353914
rearrange to 4ring dimer	20, 35 $\longrightarrow$ 21 (4.8)	-33.27085332	-34.66302954
relax to long	21 $\longrightarrow$ 22 (4.9)	45.9097102	42.47483127
rearrangement to 5ring dimer	22 $\longrightarrow$ 23 (4.1)	21.10519679	22.4628711
relax to final	23 $\longrightarrow$ 24, 34 (4.11)	-24.36281122	-24.83955672
break apart	24 $\longrightarrow$ 25, 8 (4.12)	317.9510511	262.7148121
return to ground states	8, 25, 31, 31 $\longrightarrow$ 1, 1, 33 (4.13)	-180.5526572	-239.626194

[a] TPSS SCF energy in kcal/mol. [b] TPSS SCF energy in kcal/mol with COSMO solvation in DMF.

Table 12 Gas phase and solvated energies of compounds, transition states and intermediates in the 'formate' mechanism

Molecule	Label	E (gas)[a]	E (solution)[b]	E (solvation)[c]
Proton Transfer TS	4.21	-1206.302997	-1206.32707	15.10
Catalyst Hydride	4.22	-914.9204746	-914.9448354	15.29
CO_2 Insertion TS	4.23	-1103.581201	-1103.619960	24.32
Catalyst Formate	4.24	-1103.635283	-1103.665628	19.04
Formate Anion	4.25	-189.3051464	-189.4151284	69.01
Open Site Cation	4.27	-914.1064097	-914.1872844	50.75

[a] TPSS SCF energy in hartrees.
[b] TPSS SCF energy in hartrees with COSMO solvation in DMF.
[c] TPSS solvation energy in kcal/mol (E(gas) - E(solution)).

Table 13 Energies for the reaction steps in the 'formate' pathway

Description	Steps	Energy(gas)[a]	Energy(dmf)[b]
	$4.01 \longrightarrow 4.01^{3MLCT}$	42.81191677	53.40083976
	$4.01^{3MLCT} + 4.05 \longrightarrow 4.02 + 4.06$	81.44966532	-5.80393275
	$4.02 \longrightarrow 4.03 + 4.04$	50.816912	15.440887
	$4.06 + 4.05 \longrightarrow 4.07 + 4.08$	-1.077024	-2.915901
Hydride Extraction	3, 28 $\longrightarrow$ 4 (1.4)	-44.98519792	-48.45780366
Removal of TEA	4 $\longrightarrow$ 5, 30 (1.5)	22.43071182	18.60434411
Insertion of CO2	5, 35 $\longrightarrow$ 6 (1.6)	21.23560964	14.01772231
recoordination	6 $\longrightarrow$ 7 (1.7)	-33.93653504	-28.65739435
dissasotiation of HCO2-	7 $\longrightarrow$ 8, 32 (1.8)	140.3890516	39.66807547
Reformation of Catalyst	8, 31 $\longrightarrow$ 1 (1.9)	-141.7699459	-36.36774459

[a] TPSS SCF energy in kcal/mol. [b] TPSS SCF energy in kcal/mol with COSMO solvation in DMF.

Table 14 Energies for the reaction steps in the 'equatorial' geometry

Description	Steps	Energy(gas)[a]	Energy(dmf)[b]
	4.01 $\longrightarrow$ 4.01^{3MLCT}	42.81191677	53.40083976
	4.01^{3MLCT} + 4.05 $\longrightarrow$ 4.02 + 4.06	81.44966532	-5.80393275
	4.02 $\longrightarrow$ 4.03 + 4.04	50.816912	15.440887
	4.06 + 4.05 $\longrightarrow$ 4.07 + 4.08	-1.077024	-2.915901
Migration of Open Site	3 $\longrightarrow$ 38 (3.4)	23.36742627	19.7662463
Addition of CO_2 to open site	38, 35 $\longrightarrow$ 14 (3.4)	4.789871838	1.562073338
H transfer to CO_2	14, 28 $\longrightarrow$ 15 (3.5)	-36.36053213	-49.1348917
CO_2H equatorial relaxation	15 $\longrightarrow$ 16, 30 (3.6)	-3.388580017	8.343976667
$COOH_2$ ts	16, 29 $\longrightarrow$ 17, 26 (3.7)	-18.2531325	0.641599428
CO_4 + and H_2O	17 $\longrightarrow$ 13, 36 (3.8)	3.732973932	-0.992257078
dissassotiation of CO	13 $\longrightarrow$ 34, 8 (3.9)	40.89377695	35.56739959
Reformation of Catalyst	8, 31 $\longrightarrow$ 1 (3.10)	-141.7699459	-36.36774459

[a] TPSS SCF energy in kcal/mol.
[b] TPSS SCF energy in kcal/mol with COSMO solvation in DMF.

Table 15 Gas phase and solvated energies of mechanism reactants and products.

Molecule	Label	E (gas)[a]	E (solution)[b]	E (solvation)[c]
Ground State	4.01	-1374.621419	-1374.651099	18.62
3MLCT Complex	4.01^{3MLCT}	-1374.553193	-1374.565998	8.04
Radical Anion	4.02	-1374.684002	-1374.759190	47.18
Open Site Excimer	4.03	-914.3139376	-914.3287245	9.28
Chlorine Anion	4.04	-460.2890817	-460.4058583	73.28
Triethylamine (TEA)	4.05	-292.3051496	-292.3854033	50.36
Radical Cation TEA	4.06	-292.3051496	-292.3854033	50.36
Deprotonated TEA Radical	4.07	-291.9173706	-291.9211226	2.35
Triethylammonia	4.08	-292.9552538	-293.0382729	52.09
Carbon Dioxide	4.09	-188.6945676	-188.6974631	1.82
Carbon Monoxide	4.10	-113.3744946	-113.3754466	0.60
Diethylaminoethene	4.26	-291.3467768	-291.3525868	3.64

[a] TPSS SCF energy in hartrees.
[b] TPSS SCF energy in hartrees with COSMO solvation in DMF.
[c] TPSS solvation energy in kcal/mol (E(gas) - E(solution)).

Table 16 Energies for the reaction steps in the excimer formation pathway

Reaction Steps	Energy(gas)[a]	Energy(dmf)[b]
$4.01 \longrightarrow 4.01^{3MLCT}$	42.81191677	53.40083976
$4.01^{3MLCT} + 4.05 \longrightarrow 4.02 + 4.06$	81.44966532	-5.80393275
$4.02 \longrightarrow 4.03 + 4.04$	50.816912	15.440887
$4.06 + 4.05 \longrightarrow 4.07 + 4.08$	-1.077024	-2.915901

[a] TPSS SCF energy in kcal/mol.
[b] TPSS SCF energy in kcal/mol with COSMO solvation in DMF.

Table 17 Gas phase and solvated energies of compounds, transition states and intermediates in the 'water-gas shift' mechanism

Molecule	Label	E (gas)[a]	E (solution)[b]	E (solvation)[c]
Catalyst-CO_2 (Axial)	4.31	-1103.008904	-1103.016031	4.47
Catalyst-CO_2H (Axial)	4.32	-1103.610331	-1103.640451	18.90
H_2O Dissociation (Axial) TS	4.33	-1104.018352	-1104.093313	47.04
Catalyst-CO_2 (Equatorial)	4.34	-1102.963633	-1102.992198	17.92
Catalyst-CO_2H (Equatorial)	4.35	-1103.597572	-1103.625739	17.68
H_2O Dissociation (Equatorial) TS	4.36	-1104.016156	-1104.093644	48.62
Water	4.37	-76.46413339	-76.47581393	7.33
Tetracarbonyl Catalyst Cation	4.38	-1027.546073	-1027.619412	46.02
H Transfer to Axial CO_2 TS	4.39	-1394.981543	-1395.011603	18.86
H Transfer to Equatorial CO_2 TS	4.40	-1394.938949	-1394.991623	33.05
Catalyst with Migrated Open Site	4.41	-914.2766988	-914.2972247	12.88

[a] TPSS SCF energy in hartrees. [b] TPSS SCF energy in hartrees with COSMO solvation in DMF. [c] TPSS solvation energy in kcal/mol (E(gas) - E(solution)).

Table 18 Energies for the reaction steps in the 'water-gas shift' mechanism

Description	Steps	Energy(gas)[a]	Energy(dmf)[b]
	4.01 $\longrightarrow$ 4.01^{3MLCT}	42.81191677	53.40083976
	4.01^{3MLCT} + 4.05 $\longrightarrow$ 4.02 + 4.06	81.44966532	-5.80393275
	4.02 $\longrightarrow$ 4.03 + 4.04	50.816912	15.440887
	4.06 + 4.05 $\longrightarrow$ 4.07 + 4.08	-1.077024	-2.915901
Addition of CO_2 to open site	3, 35 $\longrightarrow$ 9 (2.5)	-0.250142337	6.373109033
H transfer to CO_2 TS	9, 28 $\longrightarrow$ 10 (2.6)	-34.68146588	-46.71680199
CO_2H axial relaxation	10 $\longrightarrow$ 11, 30 (2.7)	15.33334974	11.64963925
$COOH_2$ ts	11, 29 $\longrightarrow$ 12, 26 (2.8)	-11.62501284	10.08113151
CO_4 + and H_2O	12 $\longrightarrow$ 13, 36 (2.9)	5.111298704	-1.20033086
dissassotiation of CO	13 $\longrightarrow$ 8, 34 (2.10)	40.89377695	35.56739959
Reformation of Catalyst	8, 31 $\longrightarrow$ 1 (2.11)	-141.7699459	-36.36774459

[a] TPSS SCF energy in kcal/mol.
[b] TPSS SCF energy in kcal/mol with COSMO solvation in DMF.