Supporting Information

for

Surprisingly facile CO_2 insertion into cobalt alkoxide bonds: A theoretical investigation

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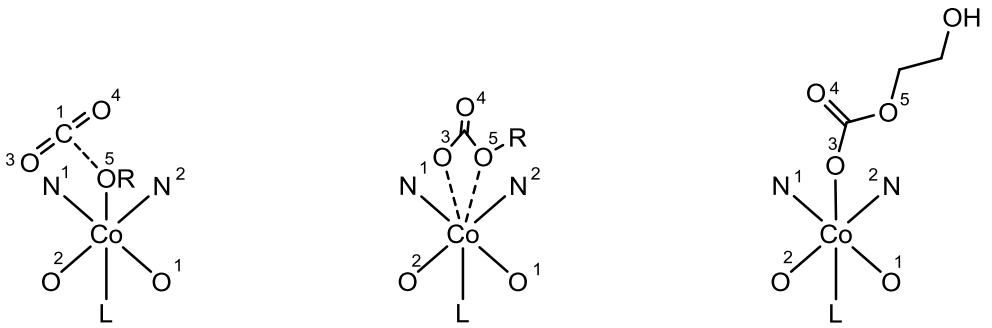
Atomic coordinates, calculated bond lengths and bond angles as well as calculated Mulliken charges for the reactant state, the precursor state, the transition state and the product state.



Reactant / precursor state Transition state Product state

Scheme S1: Numbering applied in the [Co(Salen)(L)] complexes.

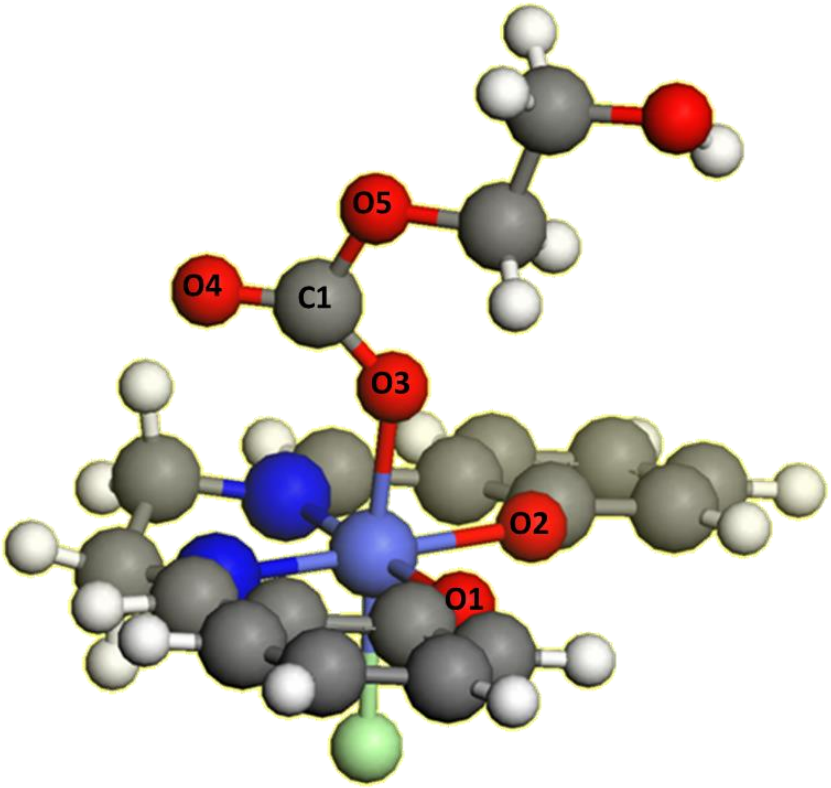


Figure S1: Graphical representation of the product state (**PS**).

Table S1: Calculated bond lengths and bond angles for selected bonds of the reactant state **RS** and calculated Mulliken charge on the cobalt center.

	Bond length [Å]						Angle [°]	Charge† [C]
Ligand	Co-L	Co-OR	Co-N^1	Co-N^2	Co-O^1	Co-O^2	O-Co-OC	Co
Chloride	2.345	1.942	1.912	1.913	1.938	1.932		0.639
CH_3COO^-	1.991	1.933	1.917	1.904	1.940	1.937		0.703
CH_3COO^- [a]	1.995	1.933	1.917	1.908	1.943	1.937		0.700
CH_3COO^- [b]	1.990	1.932	1.912	1.897	1.960	1.961	106.365	0.703
p-Methoxyphenolate	1.983	1.937	1.920	1.919	1.928	1.933	87.439	0.709
CCl_3COO^-	2.034	1.914	1.919	1.906	1.936	1.935	81.459	0.702
2,4-Dinitrophenolate	2.027	1.901	1.921	1.919	1.926	1.926	61.274	0.701
2,4,6-Trinitrophenolate	2.134	1.897	1.924	1.911	1.920	1.916	88.632	0.710
TBD [c]	2.046	1.896	1.923	1.919	1.934	1.957	68.717	0.723

† Mulliken charge

[a] Salen ligand **1a** with cyclohexyl backbone

[b] Salen ligand **1b** with cyclohexyl backbone and *t*-Bu-groups

[c] TBD = 1,5,7-Triazabicyclo[4.4.0]dec-5-ene

Table S2: Calculated bond lengths and bond angles for selected bonds of the precursor state **preS** and calculated Mulliken charge on the cobalt center.

	Bond length [Å]									Angle [°]	Charge† [C]
Ligand	Co-L	Co-OR	Co-N^1	Co-N^2	Co-O^1	Co-O^2	O^5-CO_2	C-O^3	C-O^4	∠(CO_2)	Co†
Chloride	2.278	2.084	1.903	1.922	1.934	1.922	1.678	1.224	1.222	140.054	0.645
CH_3COO^-	1.988	1.942	1.914	1.904	1.941	1.937	2.730	1.176	1.179	172.829	0.708
CH_3COO^- [a]	1.991	1.938	1.919	1.908	1.939	1.937	2.761	1.175	1.179	173.374	0.703
CH_3COO^- [b]	1.986	1.938	1.915	1.902	1.957	1.957	2.783	1.175	1.179	173.838	---
p-Methoxy-phenolate	1.981	1.948	1.918	1.917	1.931	1.932	2.721	1.175	1.179	172.653	0.713
CCl_3COO^-	2.025	1.925	1.918	1.907	1.936	1.936	2.801	1.175	1.178	174.099	0.707
2,4-Dinitro-phenolate	2.020	1.917	1.918	1.920	1.930	1.925	2.801	1.175	1.179	173.704	0.707
2,4,6-Trinitro-phenolate	2.132	1.902	1.922	1.911	1.915	1.923	2.876	1.175	1.178	175.324	0.712
TBD-PL	2.049	1.904	1.921	1.917	1.936	1.955	3.593	1.174	1.176	178.158	0.723
None	---	1.870	1.913	1.898	1.895	1.897	3.034	1.174	1.177	177.663	0.663

† Mulliken charge

[a] Salen ligand 1a with cyclohexyl backbone

[b] Salen ligand 1b with cyclohexyl backbone and *t*-Bu-groups

Table S3: Calculated bond lengths and bond angles for selected bonds of the transition state **TS** and calculated Mulliken charge on the cobalt center.

	Bond length [Å]										Angle [°]	Charge† [C]
Ligand	Co-L	Co-O^5R	Co-O^3	Co-N^1	Co-N^2	Co-O^1	Co-O^2	O^5-CO_2	C-O^3	C-O^4	∠(CO_2)	Co†
Chloride	2.235	2.927	3.019	1.899	1.908	1.912	1.907	1.434	1.263	1.246	110.206	
CH_3COO^-	1.905	2.860	2.980	1.904	1.894	1.926	1.917	1.441	1.264	1.243	109.909	0.724
CH_3COO^- [a]	1.903	2.950	3.027	1.907	1.903	1.923	1.914	1.438	1.265	1.243	110.090	0.719
CH_3COO^- [b]	1.905	3.471	3.367	1.898	1.888	1.923	1.921	1.446	1.261	1.246	111.184	0.708
p-Methoxy-phenolate	1.930	2.478	2.846	1.918	1.915	1.932	1.923	1.428	1.261	1.242	111.145	
CCl_3COO^-	1.967	3.469	3.196	1.903	1.899	1.912	1.908	1.419	1.263	1.250	112.261	
2,4-Dinitro-phenolate	1.930	2.677	2.880	1.911	1.917	1.915	1.914	1.431	1.265	1.241	109.410	0.729
2,4,6-Trinitro-phenolate	1.984	2.822	2.994	1.912	1.909	1.909	1.900	1.421	1.265	1.245	110.685	0.723
TBD-PL	1.943	2.592	2.850	1.917	1.910	1.939	1.931	1.451	1.261	1.238	109.054	
None	---	2.478	2.846	1.890	1.888	1.890	1.886	1.428	1.261	1.242	111.145	0.640

† Mulliken charge

[a] Salen ligand **1a** with cyclohexyl backbone

[b] Salen ligand **1b** with cyclohexyl backbone and *t*-Bu-groups

Table S4: Calculated bond lengths and bond angles for selected bonds of the product state **PS** and calculated Mulliken charge on the cobalt center.

	Bond length [Å]									Angle [°]	Charge† [C]
Ligand	Co-L	Co-O^3	Co-N^1	Co-N^2	Co-O^1	Co-O^2	C-O^5	C-O^3	C-O^4	∠ (CO_2)	Co†
Chloride	2.286	1.978	1.907	1.915	1.939	1.932	1.411	1.286	1.235	112.371	0.624
CH_3COO^-	1.954	1.977	1.923	1.912	1.936	1.932	1.390	1.292	1.238	113.775	0.706
CH_3COO^- [a]	1.951	1.978	1.915	1.926	1.933	1.932	1.390	1.292	1.238	113.766	0.703
CH_3COO^- [b]	1.954	1.978	1.919	1.909	1.945	1.944	1.396	1.289	1.238	114.216	0.707
p-Methoxyphenolate	1.949	1.985	1.929	1.927	1.917	1.926	1.393	1.291	1.238	113.612	0.715
CCl_3COO^-	1.989	1.954	1.926	1.914	1.928	1.926	1.383	1.298	1.236	113.917	0.704
2,4-Dinitrophenolate	1.973	1.937	1.908	1.920	1.934	1.924	1.401	1.294	1.231	112.119	0.699
2,4,6-Trinitro-phenolate	2.082	1.931	1.931	1.919	1.908	1.913	1.372	1.304	1.234	114.338	0.710
TBD-PL	1.999	1.941	1.932	1.927	1.930	1.948	1.390	1.298	1.233	114.283	0.727
None	---	1.895	1.918	1.903	1.891	1.893	1.365	1.315	1.228	113.944	0.668

† Mulliken charge

[a] Salen ligand **1a** with cyclohexyl backbone

[b] Salen ligand **1b** with cyclohexyl backbone and *t*-Bu-groups