Electronic Supplementary Information

Infrared Photodissociation Spectroscopic Investigation of $TMO(CO)_n^+$ (TM = Sc, Y, La): Testing 18-Electron Rule

Yinjuan Chen[a], Ke Xin[a], Jiaye Jin[b], Wei Li[b], Qiang Wang[c], Xuefeng Wang[a*] and Guanjun Wang[b*]

a School of Chemical Science and Engineering, Tongji University, 1239 Siping Road, Shanghai, 200092 China

b Department of Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433 China

c State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, PR China

E_mail: xfwang@tongji.edu.cn; gjwang@fudan.edu.cn

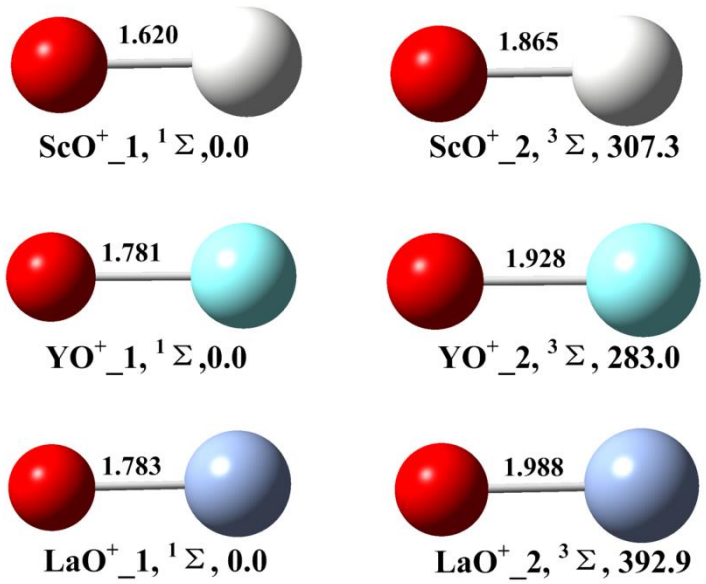


Fig. S1. Optimized minimum-energy structures of ScO^+, YO^+ and LaO^+ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

ScO^+_1 Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
21	0.000000	0.000000	0.446994
8	0.000000	0.000000	-1.173359

ScO^+_2 Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
21	0.000000	0.000000	0.514519
8	0.000000	0.000000	-1.350611

YO^+_1 Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
39	0.000000	0.000000	0.303484
8	0.000000	0.000000	-1.479482

YO^+_2 Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z

39	0.000000	0.000000	0.328149
8	0.000000	0.000000	-1.599724

LaO^+_1 Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
57	0.000000	0.000000	0.219169
8	0.000000	0.000000	-1.561580

LaO^+_2 Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
57	0.000000	0.000000	0.244684
8	0.000000	0.000000	-1.743376

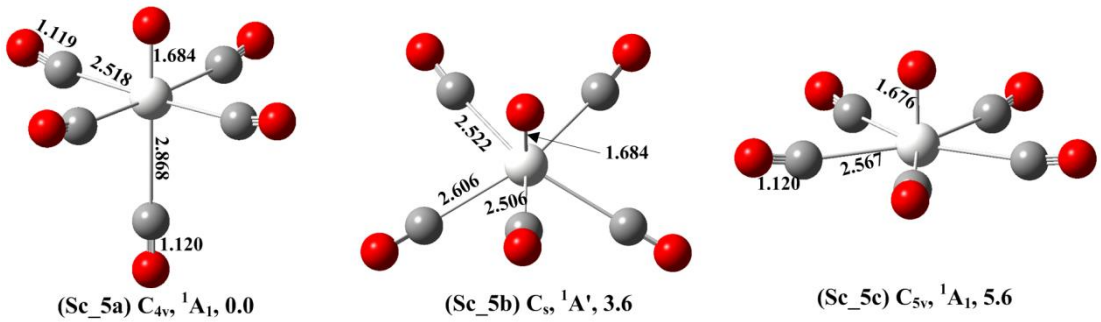


Fig. S2. Optimized structures of the minimum-energy isomers of the $ScO(CO)_5^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$ScO(CO)_5^+$ (Sc_5a) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
21	0.000000	0.000000	0.245468
6	0.000000	2.517044	0.304806
6	-2.517044	0.000000	0.304806
6	2.517044	0.000000	0.304806
6	0.000000	-2.517044	0.304806
6	0.000000	0.000000	-2.622487
8	-3.607753	0.000000	0.555305
8	0.000000	3.607753	0.555305

8	0.000000	0.000000	-3.742671
8	3.607753	0.000000	0.555305
8	0.000000	-3.607753	0.555305
8	0.000000	0.000000	1.929548

Frequencies	**IR intensity**
20.4400	1.8137
20.4400	1.8137
25.3343	0.0000
31.7183	1.1015
31.7183	1.1015
38.0939	0.0000
47.8811	0.1445
69.5270	39.9259
69.5271	39.9259
114.0937	4.0552
157.2026	0.0210
157.2026	0.0210
160.5550	0.0000
170.6103	0.2524
192.7161	0.0000
203.5890	3.1071
203.5890	3.1071
233.7241	0.0000
249.0156	10.2388
249.0156	10.2388
270.7959	0.0000
291.2427	38.0084
291.2427	38.0084
296.5048	2.5680
958.7078	135.9878
2275.7424	71.4833
2284.0513	0.0000
2284.1353	193.5023
2284.1353	193.5023
2289.6567	0.2772

$ScO(CO)_5^+$ (Sc_5b) Standard orientation

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z

21	0.035715	0.049400	0.000000
6	-0.924188	0.892919	2.271203
6	2.012475	0.055212	1.565392
6	2.012475	0.055212	-1.565392
6	-0.924188	0.892919	-2.271203
6	-2.341797	-0.743460	0.000000
8	0.228896	-1.623608	0.000000
8	-1.347859	1.207152	3.258184
8	-3.258168	-1.389063	0.000000
8	-1.347859	1.207152	-3.258184
8	2.877579	-0.197954	-2.229909
8	2.877579	-0.197954	2.229909

Frequencies	**IR intensity**
4.1743	0.0368
17.5027	0.0560
53.8055	0.3159
57.5689	2.0700
58.0560	1.1821
58.7968	0.0058
61.6660	0.1603
83.1700	24.3432
112.5030	37.1425
140.0528	0.9976
141.9559	1.2941
159.7269	0.1285
188.1515	0.0001
198.9220	5.7021
213.0630	0.9126
216.5568	3.8025
220.3664	8.2365
265.0351	6.0053
273.1223	0.0629
289.6423	6.5763
291.4011	26.3859
298.4594	16.8546
309.0329	5.7133
323.0887	45.4719
957.4709	115.3254
2264.7080	173.9930
2275.0041	70.4783
2278.4586	132.8011

2284.9310	129.0883
2287.0148	18.6114

$ScO(CO)_5^+$ (Sc_5c) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
21	0.000000	0.000000	0.160257
6	0.000000	2.565739	0.222812
6	-2.440163	0.792857	0.222812
6	-1.508104	-2.075727	0.222812
6	1.508104	-2.075727	0.222812
6	2.440163	0.792857	0.222812
8	0.000000	0.000000	-1.515439
8	0.000000	3.672313	0.051844
8	3.492577	1.134807	0.051844
8	2.158531	-2.970963	0.051844
8	-2.158531	-2.970963	0.051844
8	-3.492577	1.134807	0.051844

Frequencies	**IR intensity**
-16.7830	0.0000
-16.6711	0.0001
54.9548	0.3465
60.7299	0.8214
60.8418	0.8339
66.8247	0.0001
67.0022	0.0003
87.8843	29.4924
88.3284	29.3493
127.8961	0.0017
128.1021	0.0000
152.6905	0.0000
186.8796	0.0028
213.1447	14.1279
213.2622	13.8991
236.1905	0.0004
236.4421	0.0001
254.0169	0.1603
254.1771	0.2023
278.6668	5.6427
295.1650	46.9059

295.4286	46.9209
317.7825	0.0001
318.0337	0.0001
972.2613	108.1715
2275.9235	0.0391
2275.9577	0.0001
2278.2499	239.3639
2278.2516	239.3523
2284.1983	0.0189

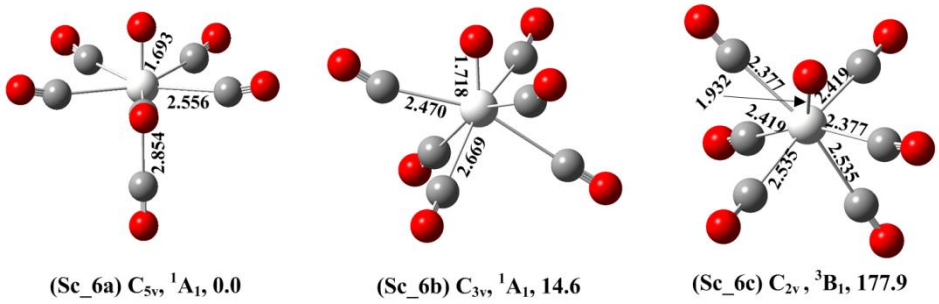


Fig. S3. Optimized structures of the minimum-energy isomers of the $ScO(CO)_6^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$ScO(CO)_6^+$ (Sc_6a) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
21	0.000000	0.000000	0.171266
6	0.000000	2.554548	0.250179
6	-2.429520	0.789399	0.250179
6	2.429520	0.789399	0.250179
6	-1.501526	-2.066673	0.250179
6	1.501526	-2.066673	0.250179
8	-3.465334	1.125955	0.512610
8	0.000000	3.643667	0.512610
8	2.141694	-2.947789	0.512610
8	3.465334	1.125955	0.512610
8	-2.141694	-2.947789	0.512610
8	0.000000	0.000000	1.864586
6	0.000000	0.000000	-2.682829
8	0.000000	0.000000	-3.803257

Frequencies	IR intensity
2.8307	0.0001
5.3056	0.0006
23.7953	1.5228
23.9805	1.4743
53.6454	0.1741
59.5348	2.2112
59.8578	2.1829
66.0910	0.0012
66.2952	0.0023
90.2782	35.0300
91.1115	35.0299
122.5887	2.8336
133.5425	0.0003
133.9279	0.0017
154.2702	0.0143
154.3272	0.0119
157.7500	0.5805
182.1511	0.0029
216.5654	11.5347
216.6895	11.7295
247.0622	0.0023
247.7925	0.0024
257.2822	0.0383
257.3792	0.0389
292.6843	4.4657
299.0486	42.1131
299.1612	42.2332
314.4527	0.0007
314.6843	0.0021
929.7439	112.0191
2242.8409	0.0986
2242.9266	0.4669
2244.8335	260.0325
2244.9547	259.5831
2248.5058	68.4416
2252.5932	3.8082

$ScO(CO)_6^+$ (Sc_6b) Standard orientation

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z

21	0.000000	0.000000	0.220739
6	0.000000	2.374619	0.900305
6	2.056480	-1.187309	0.900305
6	-2.056480	-1.187309	0.900305
6	-1.859035	1.073315	-1.364649
6	1.859035	1.073315	-1.364649
6	0.000000	-2.146629	-1.364649
8	0.000000	3.313050	1.515418
8	-2.653750	1.532143	-2.006480
8	0.000000	0.000000	1.938518
8	-2.869185	-1.656525	1.515418
8	0.000000	-3.064287	-2.006480
8	2.869185	-1.656525	1.515418
8	2.653750	1.532143	-2.006480

Frequencies	**IR intensity**
11.1533	0.2368
12.7319	0.2451
38.8835	0.0711
51.1879	0.0005
53.1381	0.0051
53.2392	0.0014
61.7959	2.0317
62.0979	1.9490
68.3562	0.6638
110.5856	12.3137
110.6710	12.2406
135.0040	1.5437
138.5661	22.3060
138.9527	22.4025
171.5906	1.4841
180.9837	0.2335
181.5621	0.2500
185.6773	0.0000
210.4081	4.2856
210.5654	4.3987
214.0658	1.0358
266.1887	6.1828
266.6802	5.8784
279.2059	0.0046
288.7697	9.8548
288.7716	9.8919

347.4602	0.4092
353.8748	48.7566
354.1651	48.4333
902.7169	122.5255
2250.8068	232.3454
2250.9406	232.4312
2259.0966	70.9893
2276.8820	81.9853
2277.0782	81.8020
2279.9028	75.5262

$ScO(CO)_6^+$ (Sc_6c) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
21	0.000000	0.000000	0.189835
6	0.000000	1.657354	-1.727958
6	0.000000	2.208858	1.177058
6	2.363425	0.000000	-0.066683
6	0.000000	-1.657354	-1.727958
6	0.000000	-2.208858	1.177058
8	0.000000	2.433371	-2.537945
8	0.000000	3.151901	1.787884
8	0.000000	-3.151901	1.787884
8	3.487811	0.000000	-0.097072
8	0.000000	-2.433371	-2.537945
8	0.000000	0.000000	2.122324
6	-2.363425	0.000000	-0.066683
8	-3.487811	0.000000	-0.097072

Frequencies	**IR intensity**
23.9127	0.0000
36.0053	0.3502
44.2824	1.3281
45.5575	0.0322
51.5639	0.0000
55.9497	1.6626
57.9166	0.4758
66.7349	0.4234
67.6126	2.3074
80.9419	14.1949
84.9714	13.7141

148.6338	2.4765
167.5563	0.0350
185.5861	0.8951
212.7617	0.0010
214.9167	4.4589
227.1934	0.0000
237.9258	1.4899
245.5570	0.0000
248.4489	0.2818
262.3078	1.6509
268.7832	2.1311
286.2455	3.0267
288.7017	1.9706
289.2586	0.0000
316.6893	10.3330
330.1249	20.2546
340.0404	0.0000
343.8469	7.8120
612.2747	57.7573
2184.7210	1421.8175
2205.0240	75.4610
2209.3522	709.3556
2224.6884	378.8470
2226.9620	298.2939
2256.6074	89.3311

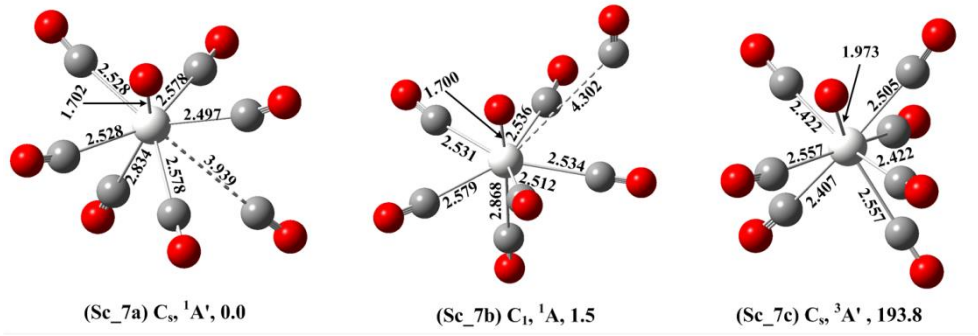


Fig. S4. Optimized structures of the minimum-energy isomers of the $ScO(CO)_7^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$ScO(CO)_7^+$ (Sc_7a) Standard orientation

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z

21	-0.343056	0.438151	0.000000
6	-0.306787	-0.577376	2.369738
6	0.278285	2.326581	1.560928
6	-2.097831	-1.337653	0.000000
6	0.278285	2.326581	-1.560928
6	-0.306787	-0.577376	-2.369738
8	0.257469	3.255581	2.188369
8	-0.370972	-0.989189	3.409177
8	-0.370972	-0.989189	-3.409177
8	-3.086698	-1.867872	0.000000
8	0.257469	3.255581	-2.188369
8	-1.794731	1.327564	0.000000
6	2.466006	0.065791	0.000000
8	3.578730	-0.069392	0.000000
6	1.071187	-3.238306	0.000000
8	1.393457	-4.314412	0.000000

Frequencies	**IR intensity**
14.5501	0.4269
16.7457	1.9134
23.1188	0.2929
24.3448	0.1064
28.8458	0.4123
37.0183	0.5436
41.5897	0.1227
56.8876	0.2899
57.4863	0.9578
59.8485	2.8536
61.3982	0.1413
62.6326	0.0425
83.6381	0.7226
93.1313	1.4810
94.5337	27.4216
102.5627	7.5818
128.6907	33.7291
134.5530	0.3928
140.3095	1.1852
157.7321	0.8608
166.9964	0.0341
179.2266	0.0046
186.6044	0.0010
209.8920	11.7921

212.2086	10.0763
228.1236	0.0005
232.9783	1.7139
268.7998	7.5728
281.2075	5.0870
294.1771	0.8938
303.6453	24.3331
306.2487	11.4092
322.3694	2.3340
335.6311	51.6706
925.7023	133.7393
2247.5146	69.5847
2252.8392	230.7608
2260.1099	89.6109
2264.5056	133.4196
2269.0464	75.5693
2276.8152	166.4987
2279.2307	14.6938

$ScO(CO)_7^+$ (Sc_7b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
21	-0.391388	0.056672	-0.034289
6	0.930653	-2.066390	0.387654
6	-1.543729	-1.762319	-1.364789
6	1.344304	0.606187	1.812927
6	-2.551924	1.074854	-1.008162
6	-0.071153	2.548526	-0.067809
8	-1.864415	-2.493056	-2.151778
8	1.617061	-2.951488	0.360211
8	0.239665	3.590794	-0.340349
8	2.129958	0.867793	2.566617
8	-3.416813	1.536997	-1.549127
8	0.542189	0.209078	-1.442806
6	-2.072085	-0.585700	2.199492
8	-2.730669	-0.846701	3.067690
6	3.874008	-0.045230	-0.586414
8	4.577862	0.110374	-1.450123

Frequencies	**IR intensity**
8.7706	0.4953

11.3035	0.1162
15.5943	0.1581
23.5169	0.5984
30.2121	0.2649
32.4951	0.4958
43.7822	2.5519
55.3805	0.2446
58.7922	1.0048
61.5947	2.1357
62.4052	0.8360
64.4600	0.1812
66.1210	0.2380
82.9536	27.4696
101.9286	22.6648
109.5287	17.2981
120.9350	4.1681
133.8166	0.4086
135.1821	0.8369
154.2193	0.0808
157.8984	0.4048
159.7220	0.1686
185.5637	0.0050
208.1270	13.4612
217.3193	10.1254
230.1800	0.6206
237.6204	0.5560
266.1450	1.8147
269.6363	0.5564
291.7560	31.7424
299.8290	13.1085
309.2820	3.6209
311.1946	1.9545
315.5227	43.0787
934.7842	129.8007
2234.3012	86.3738
2260.9567	192.5026
2265.8785	67.6775
2271.2286	131.5754
2272.3421	74.8313
2276.8664	150.8102
2280.7983	26.3929

$ScO(CO)_7^+$ (Sc_7c) Standard orientation

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
8	-1.940844	0.855714	0.000000
6	1.062776	-1.454489	1.673966
6	1.062776	-1.454489	-1.673966
6	-1.485268	-1.931240	0.000000
6	-0.974731	0.565977	2.215443
6	-0.974731	0.565977	-2.215443
8	-2.270758	-2.736689	0.000000
8	1.508239	-2.138666	-2.445019
8	1.508239	-2.138666	2.445019
8	-1.498830	0.864748	3.163817
8	-1.498830	0.864748	-3.163817
6	0.223405	2.541391	0.000000
8	0.141248	3.662612	0.000000
6	2.369071	0.653774	0.000000
8	3.443061	0.988073	0.000000
21	-0.134857	0.062077	0.000000

Frequencies	**IR intensity**
-11.9968	0.1699
33.8694	0.1301
48.4609	0.2948
48.6616	0.1886
54.5927	0.0372
61.1641	0.0450
62.6955	0.2861
66.9533	0.6480
68.9460	1.2489
70.1857	1.1442
72.0013	0.5278
87.5714	12.7540
99.0132	2.6564
128.7667	2.4196
136.9209	12.9007
148.5413	2.0575
156.9062	0.3865
177.1598	2.7758
203.2815	3.8188
209.7895	2.8000
210.0256	0.1335
232.2914	1.3028

241.3537	0.0365
245.3097	3.3759
271.2394	0.0653
275.7806	3.7114
305.1453	2.8949
311.4837	0.3195
312.2342	5.0406
322.6896	8.9223
336.9290	0.5738
338.6660	1.0057
342.3320	1.3568
370.1372	0.4670
557.0404	48.6611
2195.5019	997.5317
2200.2599	520.3318
2203.0239	904.4667
2213.4407	129.7872
2218.7467	213.3200
2220.1598	313.1435
2248.1639	27.8440

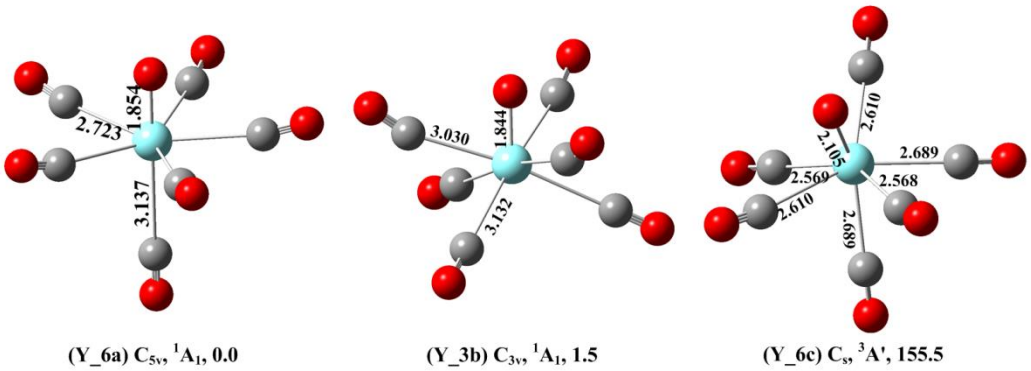


Fig. S5. Optimized structures of the minimum-energy isomers of the $YO(CO)_6^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$YO(CO)_6^+$ (Y_6a) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	2.716159	0.288757
6	2.583221	0.839339	0.288757
6	-1.596518	-2.197419	0.288757
6	1.596518	-2.197419	0.288757
8	0.000000	3.793709	0.595098
8	2.229886	-3.069175	0.595098
8	-2.229886	-3.069175	0.595098

8	3.608032	1.172321	0.595098
6	0.000000	0.000000	-3.045754
8	0.000000	0.000000	-4.166885
8	0.000000	0.000000	1.945974
6	-2.583221	0.839339	0.288757
8	-3.608032	1.172321	0.595098
39	0.000000	0.000000	0.091672

Frequencies	**IR intensity**
2.6486	0.0227
2.6921	2.3285
3.5901	0.7293
4.5302	2.8682
39.8994	0.0204
47.9711	1.4464
48.2455	1.5522
58.0120	0.0011
58.2024	0.0002
69.3528	38.6597
70.1120	38.7821
88.5785	2.8656
120.4504	0.2951
120.5167	0.3031
139.3685	0.0010
139.5557	0.0001
154.2791	0.1872
176.5675	0.0002
187.6050	11.1383
187.6532	11.1202
226.1689	3.6887
226.5365	3.5975
242.5555	0.0001
242.7340	0.0008
261.0915	16.7400
261.1650	16.6953
265.5992	0.0283
265.9139	0.3600
266.0469	2.5004
806.4045	124.5384
2267.0529	81.6387
2270.8786	0.4152
2270.9059	1.1649

2272.1053	293.1756
2272.2525	293.9954
2279.2290	1.4619

$YO(CO)_6^+$ (Y_6b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	2.507426	-0.852463
6	-2.171495	-1.253713	-0.852463
6	2.171495	-1.253713	-0.852463
6	2.178079	1.257514	1.295010
6	-2.178079	1.257514	1.295010
6	0.000000	-2.515029	1.295010
8	0.000000	3.403291	-1.528451
8	3.055250	1.763950	1.772678
8	0.000000	0.000000	-1.850575
8	2.947337	-1.701646	-1.528451
8	0.000000	-3.527899	1.772678
8	-2.947337	-1.701646	-1.528451
8	-3.055250	1.763950	1.772678
39	0.000000	0.000000	0.025059

Frequencies	**IR intensity**
15.4799	0.1041
16.6594	0.1212
29.9337	0.0032
49.9473	0.0209
50.1889	0.2558
50.4499	0.1890
51.1045	1.5250
51.1307	1.6976
55.1057	0.3900
109.8726	30.5174
110.4115	29.9717
132.1633	0.4302
135.9468	9.6773
136.5476	10.1418
162.5255	0.3200
178.8769	0.0951
179.6000	3.4116
179.8317	3.4818

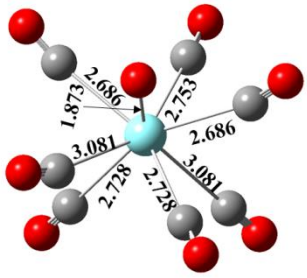
196.6089	6.5287
196.6867	6.0705
201.9910	2.1251
236.0573	11.9716
236.4757	11.8088
254.3000	2.3298
254.4332	2.4239
261.6378	0.0023
308.7069	0.2123
313.8349	27.2764
314.0277	27.0829
781.2505	107.6150
2248.2633	247.8193
2248.2987	247.6946
2256.1913	85.3094
2277.1690	105.8653
2277.2586	105.6964
2279.8570	56.9242

$YO(CO)_6^+$ (Y_6c) Standard orientation

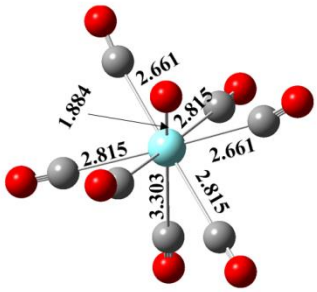
Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.018847	-1.753967	1.911942
6	-2.534559	-0.267932	0.000000
6	2.546630	-0.212919	0.000000
6	-0.013134	1.285506	-2.343342
8	0.022438	-2.505357	2.746415
8	-0.021866	1.925943	-3.266032
8	3.668427	-0.305090	0.000000
8	-3.654770	-0.377258	0.000000
6	0.018847	-1.753967	-1.911942
8	0.022438	-2.505357	-2.746415
8	-0.040990	2.240404	0.000000
6	-0.013134	1.285506	2.343342
8	-0.021866	1.925943	3.266032
39	0.001757	0.136226	0.000000

Frequencies	**IR intensity**
18.6627	0.0007
25.0336	0.5044
36.1083	0.0102

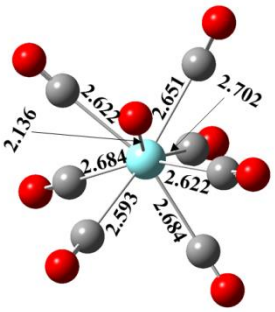
41.3714	0.2058
42.0403	0.0014
42.2532	0.3522
42.8447	3.3004
58.9372	4.4471
59.0477	3.6466
59.1343	4.3239
84.0100	19.9932
145.4213	0.1073
167.4453	0.7929
173.3527	1.7889
188.2333	9.2588
207.0239	0.1034
211.8274	17.2912
216.7101	0.0003
228.5113	2.3409
230.4052	0.6890
231.7629	1.5261
240.9001	0.0000
249.8537	1.0787
254.5511	1.0183
256.7070	0.0000
283.7851	14.2762
295.3947	2.8763
301.1147	0.0010
304.3103	15.3510
536.8386	50.7518
2168.4968	2019.6650
2194.1210	1.9265
2198.2574	831.8769
2214.2520	765.7590
2215.7318	620.7640
2254.0519	21.5913



(Y_7a) C_1, ^1A, 0.0



(Y_7b) C_{3v}, $^1A_1$, 3.0



(Y_7c) C_s, $^3A'$, 153.7

Fig. S6. Optimized structures of the minimum-energy isomers of the $YO(CO)_7^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$YO(CO)_7^+$ (Y_7a) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	-0.404468	-0.002498	-1.983991
6	-1.568610	0.000004	2.464531
6	0.915305	-2.588568	-0.089421
6	-2.114453	-1.705009	-0.549485
6	-2.122176	1.695413	-0.550335
6	2.222913	0.001740	-1.529194
8	-2.929223	-2.304007	-1.050144
8	1.294215	-3.645196	-0.183250
8	-2.150810	0.000985	3.429864
8	-2.940875	2.289492	-1.050425
8	2.938385	0.002193	-2.403296
6	0.904549	2.591598	-0.097040
8	1.278315	3.649657	-0.195284
6	2.117872	0.006691	2.091681
8	2.926953	0.010535	2.877213
39	-0.057239	-0.000526	-0.153075

Frequencies	IR intensity
9.2751	0.0160
19.3200	0.6048
27.4376	0.4211
32.6664	0.2157
32.8448	0.0932
37.1046	0.3361
45.2699	1.1674
48.8630	0.7949
49.8481	3.2264
52.9196	0.1341
53.6316	0.1079
74.6880	3.7622
91.7962	36.4065
93.5634	7.0541
107.2307	41.5323
129.7622	0.1903
134.7927	0.4325
134.9459	0.0002

147.4330	2.2001
155.2202	1.4607
158.1626	0.0287
164.5639	0.3159
174.1049	6.1396
178.1893	5.2073
180.3821	7.2492
213.7361	0.4204
215.5290	6.8543
232.8720	6.4018
242.5300	9.2045
248.9656	0.1023
254.4687	0.5905
285.0553	15.4265
297.6946	6.9672
312.9780	35.4799
786.4593	125.7071
2213.9926	246.1472
2224.4649	110.0144
2229.4600	153.6296
2237.5078	51.6334
2241.2138	82.3700
2247.3281	167.3273
2249.8356	15.3437

$YO(CO)_7^+$ (Y_7b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	0.000000	0.000000	2.085867
6	-2.153716	1.243449	1.149104
6	0.000000	2.662334	-0.713764
6	-2.305649	-1.331167	-0.713764
6	2.153716	1.243449	1.149104
6	0.000000	-2.486897	1.149104
6	2.305649	-1.331167	-0.713764
6	0.000000	0.000000	-3.100921
8	-2.907819	1.678830	1.858435
8	0.000000	3.738454	-1.025637
8	-3.237596	-1.869227	-1.025637
8	0.000000	0.000000	-4.222740
8	3.237596	-1.869227	-1.025637
8	0.000000	-3.357660	1.858435

8	2.907819	1.678830	1.858435
39	0.000000	0.000000	0.201981

Frequencies	**IR intensity**
17.0146	0.7920
17.3203	0.7730
34.6194	0.2471
34.7931	0.2504
36.7442	0.2255
54.5191	1.5554
54.7811	1.4438
56.9527	0.1153
57.6174	0.7007
57.9443	0.3439
57.9925	0.9889
63.5473	2.2057
112.8726	29.4038
113.1197	28.6268
122.3475	0.8321
122.4720	0.7017
126.3279	0.6437
133.6768	11.5702
133.9810	12.5694
159.9204	0.6021
179.8321	0.0001
186.4413	15.3073
186.5588	15.2190
202.7367	0.7611
203.3507	0.7502
217.8725	0.6012
244.8900	11.0886
245.1244	11.0056
270.8471	0.7279
271.1182	0.6929
284.2215	0.0001
314.3859	0.0565
320.3532	28.5322
320.6305	28.5768
771.6495	122.1057
2239.5426	265.5856
2239.6320	265.6385
2248.2878	103.2731

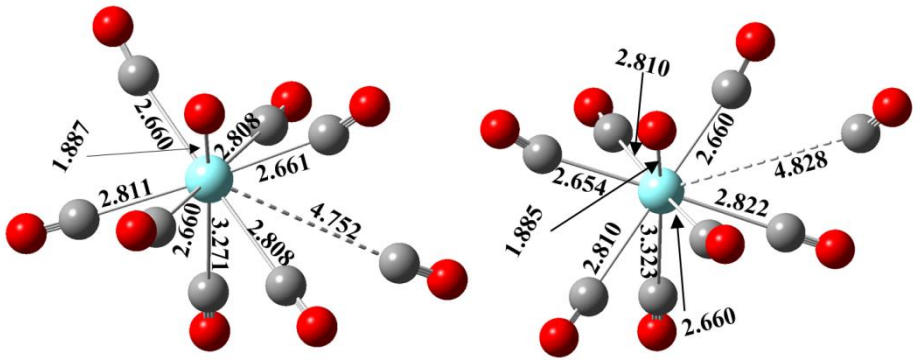
2260.4252	55.9474
2271.7702	132.7233
2271.8960	132.6342
2274.7173	35.4997

$YO(CO)_7^+$ (Y_7c) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	0.684263	2.128598	0.000000
6	-1.284921	-1.228236	1.941569
6	-1.284921	-1.228236	-1.941569
6	-2.351672	1.192089	0.000000
6	0.518800	1.185119	2.332144
6	0.518800	1.185119	-2.332144
8	-3.304848	1.789304	0.000000
8	-1.835120	-1.730635	-2.783394
8	-1.835120	-1.730635	2.783394
8	0.785979	1.791699	3.239155
8	0.785979	1.791699	-3.239155
6	2.647581	-0.073255	0.000000
8	3.765666	0.041447	0.000000
6	0.842504	-2.463604	0.000000
8	1.237581	-3.517759	0.000000
39	0.002255	0.104520	0.000000

Frequencies	**IR intensity**
17.0381	0.1098
25.5952	0.1764
41.0428	0.1453
42.9440	0.0357
48.2646	0.0213
49.8860	0.5830
55.2206	0.4722
56.4921	0.6733
60.2600	0.5160
61.7403	1.8712
63.8736	0.3824
87.1460	16.1237
95.0016	13.5313
139.5613	1.6192
140.4416	0.6823

161.1983	6.7311
165.2550	0.0255
175.7812	3.4366
179.9307	7.7992
198.2141	5.9366
208.1706	0.0420
225.7833	1.1673
226.7887	2.0596
240.1821	1.0253
245.8911	0.0710
247.8947	1.1964
269.3709	0.7372
279.0344	0.8391
280.3566	1.3255
288.2799	8.0335
289.6674	8.2852
301.3196	0.0345
303.8785	0.6270
320.9865	0.0563
503.5529	41.4641
2181.0599	1222.3838
2192.2597	969.3920
2197.0413	808.5596
2203.2027	656.9784
2213.8319	579.7901
2216.1535	134.4228
2251.1777	0.4893



(Y_8a) C_s, ^{1}A', 0.0 **(Y_8b) C_s, ^{1}A', 0.7**

Fig. S7. Optimized structures of the minimum-energy isomers of the $YO(CO)_8^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$YO(CO)_8^+$ (Y_8a) Standard orientation

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
8	1.825461	1.521557	0.000000
6	0.403879	2.086802	2.162157
6	-1.877670	2.432677	0.000000
6	0.088672	-1.078379	2.284800
6	0.403879	2.086802	-2.162157
6	2.306156	-1.087909	0.000000
6	0.088672	-1.078379	-2.284800
6	-2.680172	-0.984997	0.000000
8	0.800443	2.817434	2.917611
8	-2.668088	3.226929	0.000000
8	0.088672	-1.711482	3.209363
8	-3.655270	-1.539957	0.000000
8	0.088672	-1.711482	-3.209363
8	3.363566	-1.467161	0.000000
8	0.800443	2.817434	-2.917611
39	0.208763	0.549187	0.000000
6	-0.389820	-4.165336	0.000000
8	-0.419316	-5.289016	0.000000

Frequencies	**IR intensity**
13.6949	0.1977
14.2129	1.2685
15.9856	1.3693
17.3445	0.5923
26.0782	0.4907
34.0913	0.3565
36.7742	0.0635
37.9858	0.1744
54.8090	1.8498
54.8832	1.6681
56.9779	0.5464
57.0907	0.2551
58.3038	0.8293
58.4951	0.3244
65.6509	1.8014
73.6993	0.0373
78.3873	1.0463
111.0546	31.5455
113.5675	31.5610
119.4458	2.9470

127.4131	0.2385
128.0230	1.0953
134.0282	10.7204
134.7932	8.5339
159.5885	0.6145
180.1103	0.0011
185.6433	16.5192
186.8355	15.6476
201.8945	0.5897
205.2007	0.5276
219.4800	0.7790
245.5894	10.4450
245.8335	9.6540
270.3181	0.5697
271.7869	1.0095
284.8439	0.0005
315.4887	0.6401
321.2113	28.8942
322.0367	27.6733
765.3652	124.1013
2237.4132	264.0520
2237.5824	275.5284
2241.6121	92.5702
2246.4938	95.8734
2259.3935	56.4874
2270.5392	136.8862
2270.9828	128.5580
2273.7138	34.8883

$YO(CO)_8^+$ (Y_8b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	-1.816981	-0.541185	0.000000
6	-0.351042	-1.218878	2.127141
6	2.065724	-1.361090	0.000000
6	-0.054772	1.932705	2.330665
6	-0.351042	-1.218878	-2.127141
6	-2.200327	2.069606	0.000000
6	-0.054772	1.932705	-2.330665
6	2.629615	2.163782	0.000000
8	-0.742709	-1.957061	2.877525
8	2.951235	-2.047472	0.000000
8	-0.066396	2.539126	3.272769

8	3.573737	2.769856	0.000000
8	-0.066396	2.539126	-3.272769
8	-3.245549	2.481327	0.000000
8	-0.742709	-1.957061	-2.877525
39	-0.165113	0.366915	0.000000
6	0.067956	-4.455619	0.000000
8	-0.352808	-5.498614	0.000000

Frequencies	**IR intensity**
10.7605	0.8083
15.1249	0.3007
17.8331	0.7862
18.6113	0.2639
27.9628	0.7686
35.4604	0.3419
35.7446	0.2386
43.3621	1.0261
53.7546	0.8829
55.2740	1.4463
56.4856	0.1059
58.2218	0.5215
58.6423	1.0290
60.1398	0.5795
61.7381	2.1784
65.2832	0.4113
88.2388	3.8997
111.8941	28.7271
114.2278	29.0856
120.2548	2.8336
122.2928	0.2411
127.3449	0.7999
133.3332	12.7922
134.9146	9.8436
161.2661	0.6515
179.6807	0.0818
186.5337	13.9749
187.5140	15.0186
200.6964	1.5898
205.5573	0.4133
218.3347	0.9595
243.6077	10.6207
244.9385	10.8909

269.0973	0.9182
269.6269	0.1441
283.6760	0.0646
314.1700	0.8252
319.0103	26.6176
321.8668	29.1035
766.4586	120.8341
2236.6940	254.9432
2237.7912	115.8403
2239.9851	245.0915
2247.9100	109.7631
2259.7197	55.8396
2271.2207	139.5186
2272.0681	114.0879
2274.7160	43.5052

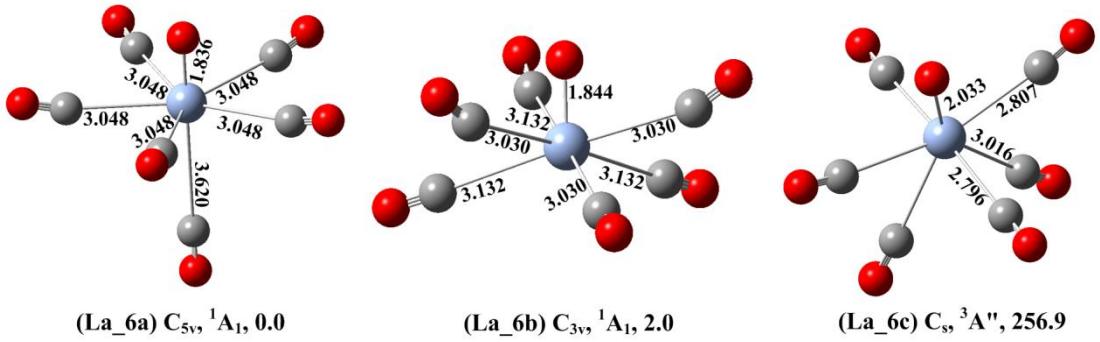


Fig. S8. Optimized structures of the minimum-energy isomers of the $LaO(CO)_6^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$LaO(CO)_6^+$ (La_6a) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	3.044271	0.312484
6	2.895274	0.940731	0.312484
6	-1.789377	-2.462867	0.312484
6	1.789377	-2.462867	0.312484
8	0.000000	4.135391	0.568880
8	2.430722	-3.345602	0.568880
8	-2.430722	-3.345602	0.568880
8	3.932991	1.277906	0.568880
6	0.000000	0.000000	-3.457769
8	0.000000	0.000000	-4.580261
8	0.000000	0.000000	1.998825
6	-2.895274	0.940731	0.312484

8	-3.932991	1.277906	0.568880
57	0.000000	0.000000	0.162604

Frequencies	**IR intensity**
-7.3203	2.1245
-7.1252	2.1591
10.9084	0.0036
12.3673	0.0145
22.8052	0.0141
28.2238	0.3301
28.5490	0.4015
36.9442	0.0026
37.0395	0.0001
53.4055	27.2205
53.4905	27.2111
63.4809	2.4139
97.2013	0.1525
97.2239	0.1528
106.9569	0.0006
107.2445	0.0002
112.2689	0.0077
131.4146	14.0533
131.4454	14.0001
141.1310	0.0059
164.9358	5.3769
165.2678	5.4766
180.6071	0.0008
180.7830	0.0024
183.5942	0.0045
184.2760	0.0292
191.5239	1.2635
193.6657	6.2966
193.9984	5.9609
791.4803	187.8875
2255.6790	75.3156
2268.9878	0.0552
2269.0417	0.7699
2270.2571	191.1319
2270.3535	191.8852
2273.3702	4.8502

$LaO(CO)_6^+$ (La_6b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	0.000000	0.000000	-1.746008
6	0.000000	2.910870	-0.743527
6	-2.562539	1.479482	1.123456
6	2.562539	1.479482	1.123456
6	-2.520888	-1.455435	-0.743527
6	2.520888	-1.455435	-0.743527
6	0.000000	-2.958965	1.123456
8	0.000000	3.832647	-1.382693
8	-3.491859	2.016026	1.447546
8	3.491859	2.016026	1.447546
8	0.000000	-4.032051	1.447546
8	3.319170	-1.916323	-1.382693
8	-3.319170	-1.916323	-1.382693
57	0.000000	0.000000	0.097769

Frequencies	**IR intensity**
10.4419	0.0000
10.4781	0.0000
21.7424	0.0009
28.9760	0.1372
36.1040	0.3726
36.1260	0.3722
38.9234	0.0576
38.9335	0.0576
41.4315	0.0000
80.1550	16.0232
80.1837	16.0051
95.3969	0.5803
99.0026	1.0308
99.0045	1.0311
107.2751	0.0122
129.6682	23.7808
129.6757	23.8029
135.8683	0.0003
148.0034	0.0177
148.0555	0.0183
163.2253	0.7477
177.7467	9.2085
177.7973	9.1845

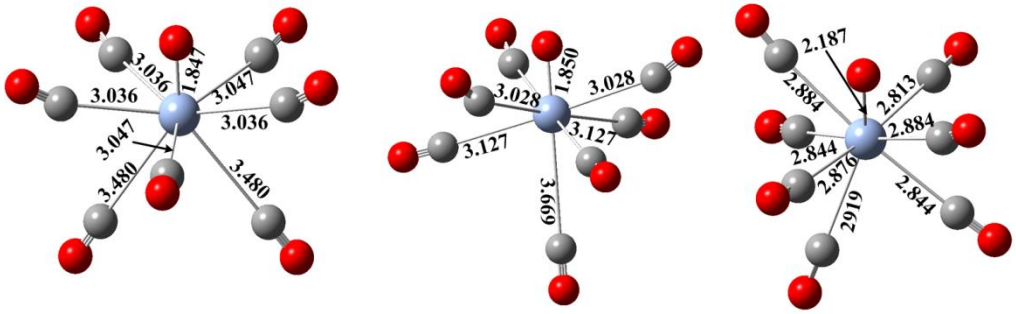
189.3398	0.0096
189.3630	0.0086
199.8177	0.0000
210.6238	0.2855
222.6225	12.2031
222.6230	12.2028
778.6613	170.2850
2260.5016	96.4038
2260.5018	96.4482
2261.9639	77.0713
2268.8047	113.2590
2268.8049	113.2826
2270.7210	9.1839

$LaO(CO)_6^+$ (La_6c) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-0.000346	-2.113318	1.752345
6	-2.790145	0.148507	0.000000
6	2.789355	0.147004	0.000000
6	0.000676	0.880980	-2.754621
8	-0.000346	-2.978910	2.466636
8	0.000877	1.241914	-3.820122
8	3.915229	0.146316	0.000000
8	-3.915999	0.148589	0.000000
6	-0.000346	-2.113318	-1.752345
8	-0.000346	-2.978910	-2.466636
8	0.000437	2.374634	0.000000
6	0.000676	0.880980	2.754621
8	0.000877	1.241914	3.820122
57	-0.000088	0.341239	0.000000

Frequencies	**IR intensity**
-24.3024	0.0000
17.5559	0.4684
19.6128	0.1436
28.5153	0.0378
29.8726	1.5933
30.8558	0.0000
36.0823	0.1313
42.0776	10.4836

51.6389	0.2192
57.9011	2.6738
87.4184	8.1239
116.8479	4.9566
119.3448	0.0000
136.2496	10.6813
148.3475	24.3269
151.5478	0.6507
173.4985	0.0000
175.5965	1.0703
184.6243	2.7945
186.5129	0.3351
191.6040	0.0000
198.2290	0.0843
201.7575	0.2016
206.6806	0.4996
226.1874	0.0000
252.1188	0.5984
257.6210	0.3057
259.0522	4.8681
273.3505	6.4812
554.0773	80.9909
2163.8578	2354.9719
2182.6818	27.0690
2184.7891	1736.5413
2215.2851	412.7632
2217.2443	317.3899
2248.9980	128.3669



(La_7a) C_s, $^1A'$, 0.0 (La_7b) C_{3v}, $^1A_1$, 2.5 (La_7c) C_s, $^3A'$, 234.4

Fig. S9. Optimized structures of the minimum-energy isomers of the $LaO(CO)_7^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$LaO(CO)_7^+$ (La_7a) Standard orientation

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	2.477034	-0.472033	1.776284
6	-0.995503	-0.996021	2.750365
6	2.477034	-0.472033	-1.776284
6	-0.995503	-0.996021	-2.750365
6	-3.046799	-0.183285	0.000000
8	-1.307024	-1.606156	3.638660
8	3.343758	-0.804963	2.404849
8	-4.158445	-0.326607	0.000000
8	3.343758	-0.804963	-2.404849
8	-1.307024	-1.606156	-3.638660
8	0.076603	-2.048323	0.000000
6	-0.005417	2.614418	-2.043277
8	-0.017646	3.527757	-2.695455
57	0.016083	-0.202166	0.000000
6	-0.005417	2.614418	2.043277
8	-0.017646	3.527757	2.695455

Frequencies	**IR intensity**
2.5927	0.0372
11.8330	0.2192
18.2792	0.6741
18.4615	0.0442
21.6063	0.1042
22.1709	0.2634
29.0327	0.1182
29.5234	0.3201
30.6041	0.4833
35.4469	0.0095
36.6364	0.0306
51.3975	4.1203
60.9802	27.1322
66.4975	4.0938
79.8925	21.0028
102.4313	0.0805
102.5218	0.1355
108.6420	0.0623
109.3690	0.0451
111.0628	0.0159
116.0048	0.0131
123.2367	1.0754
127.1480	11.2917

129.6506	15.0716
136.0865	2.9068
158.1583	5.4334
164.0508	13.1885
173.4444	0.1279
177.5424	2.7372
179.1075	0.0899
190.5490	1.1619
199.3365	5.3819
213.5528	1.7076
222.7136	13.0374
777.5116	192.8038
2256.2397	25.4038
2257.3581	126.8302
2260.2950	136.6701
2261.1991	32.3625
2265.6966	76.6994
2267.8989	149.5952
2270.7579	32.3659

$LaO(CO)_7^+$ (La_7b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	0.000000	0.000000	2.043510
6	-2.503470	1.445379	1.094214
6	0.000000	3.019146	-0.622464
6	-2.614657	-1.509573	-0.622464
6	2.503470	1.445379	1.094214
6	0.000000	-2.890758	1.094214
6	2.614657	-1.509573	-0.622464
6	0.000000	0.000000	-3.475222
8	-3.280701	1.894113	1.767591
8	0.000000	4.114820	-0.860619
8	-3.563539	-2.057410	-0.860619
8	0.000000	0.000000	-4.598011
8	3.563539	-2.057410	-0.860619
8	0.000000	-3.788227	1.767591
8	3.280701	1.894113	1.767591
57	0.000000	0.000000	0.193483

Frequencies	**IR intensity**
7.3371	0.5008

7.3463	0.5013
14.7687	0.2023
14.7729	0.2010
23.1154	0.0020
29.9210	0.1181
36.9662	0.4941
36.9704	0.4957
41.1824	0.1989
41.1846	0.1971
43.5492	0.0000
56.4778	1.8112
80.3635	17.3596
80.3720	17.3466
93.6109	0.7857
95.1206	0.9515
95.1451	0.9523
97.5605	1.1261
97.5620	1.1235
106.5492	0.0938
127.3126	24.3218
127.3159	24.3175
134.9814	0.0000
150.6569	0.0968
150.6635	0.0941
166.1351	0.2763
179.0935	8.1205
179.0941	8.1125
193.8805	0.0000
193.8885	0.0000
205.3996	0.0000
215.1298	0.1035
227.0110	12.6964
227.0128	12.6935
771.2107	190.9982
2252.8353	78.2824
2257.2153	101.0589
2257.2154	101.1044
2258.8851	74.4668
2265.8889	123.8465
2265.8889	123.8494
2267.9497	4.3965

$LaO(CO)_7^+$ (La_7c) Standard orientation

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
8	0.934603	-2.034715	0.000000
6	-0.002224	1.595805	2.345847
6	-0.002224	1.595805	-2.345847
6	2.621270	1.259875	0.000000
6	0.585044	-1.508670	2.416123
6	0.585044	-1.508670	-2.416123
8	3.656744	1.700854	0.000000
8	-0.002224	2.202765	-3.294193
8	-0.002224	2.202765	3.294193
8	0.837937	-2.233073	3.236261
8	0.837937	-2.233073	-3.236261
6	-2.219466	-1.696113	0.000000
8	-3.037175	-2.466899	0.000000
6	-2.408860	1.475092	0.000000
8	-3.393643	2.019999	0.000000
57	0.112156	-0.009609	0.000000

Frequencies	**IR intensity**
21.4016	0.0601
22.4623	0.1510
29.8991	0.2931
31.2302	0.0383
34.7553	1.3393
36.1950	0.6390
40.7886	1.0568
41.0237	0.6175
48.9535	0.9034
52.3802	0.0784
52.6513	0.9295
74.7738	14.1959
76.6138	10.2148
118.1067	5.3994
122.6707	0.9982
125.0494	0.4633
135.2533	10.2479
138.7464	5.9959
147.6938	2.4541
164.8742	3.2104
180.8396	0.0418
192.7654	0.4322
198.8148	0.0080

200.3938	0.2223
209.5866	0.0089
212.9955	0.4992
219.9220	1.5046
224.0843	0.5300
248.8650	0.1814
250.3487	3.9469
251.8518	0.6060
255.5137	3.4446
261.5751	1.1067
263.5123	0.8815
485.5042	66.6484
2166.3814	1554.7783
2176.5302	1353.1357
2185.3951	394.0902
2195.9070	1100.5181
2221.7431	195.3218
2224.7555	432.9880
2244.8492	20.9724

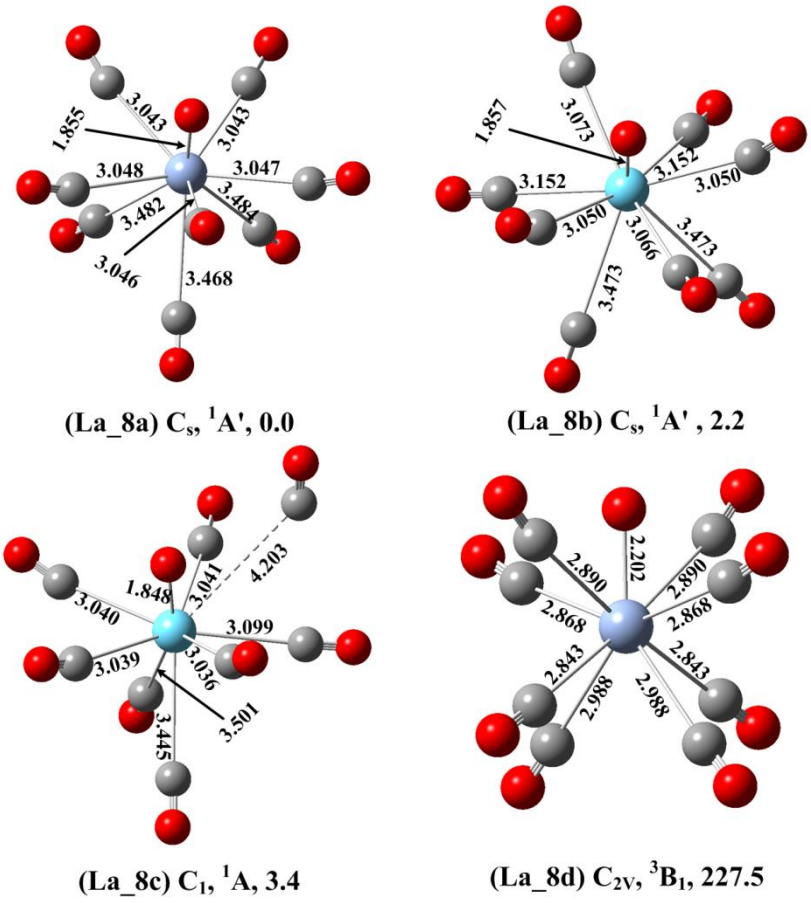


Fig. S10. Optimized structures of the minimum-energy isomers of the $LaO(CO)_8^+$

complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$LaO(CO)_8^+$ (La_8a) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-1.456805	-2.555853	-1.076950
6	-2.933605	0.665334	-0.705953
6	1.953784	-2.261130	-0.913309
6	2.737216	1.250346	-0.758030
6	-0.269388	2.863132	-1.238625
8	-3.954937	0.894683	-1.108421
8	-1.923053	-3.364613	-1.699542
8	-0.350171	3.736091	-1.939348
8	2.606574	-2.998143	-1.451110
8	3.678221	1.672887	-1.198400
8	0.024751	-0.034679	-2.127607
6	2.117372	-0.691894	2.414893
8	2.792665	-0.922337	3.281581
57	0.006481	-0.012338	-0.272795
6	-1.732164	-1.446849	2.380777
8	-2.280487	-1.938609	3.227968
6	-0.461443	2.239034	2.322995
8	-0.605966	2.996039	3.139198

Frequencies	IR intensity
0.4725	0.0046
12.5733	0.2441
14.6066	0.0679
20.9187	0.2831
22.8928	0.1231
25.0569	0.0182
25.6219	0.2381
29.3174	0.0250
30.5111	0.0447
31.9570	0.1447
32.9807	0.2710
38.5062	0.0776
38.9630	0.2768
46.5084	4.7527
52.6621	0.8816
65.9393	3.9000
72.2974	21.1541

84.3932	21.7204
97.1773	0.0420
97.7534	0.2336
100.9385	0.1869
105.7210	0.1477
107.1408	0.1261
115.0651	1.3374
118.5391	2.6948
121.4922	0.4238
122.7999	10.1055
130.5126	11.3971
131.8009	8.5483
135.2998	0.7640
160.7341	14.9128
162.0699	8.5738
171.8328	0.4118
173.2243	0.5296
194.1462	1.5787
199.7044	2.0200
213.0778	8.0295
219.5551	2.2436
233.8260	18.2513
768.1349	202.8219
2253.5138	24.1229
2253.7126	3.3516
2254.6730	163.2917
2255.9711	158.8529
2257.0684	49.1092
2260.0449	102.3437
2263.0798	171.4770
2265.5738	19.9561

$LaO(CO)_8^+$ (La_8b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	-0.766930	-1.886620	0.000000
6	-3.268200	-0.272589	0.000000
6	-1.570132	1.399983	2.398017
6	-1.570132	1.399983	-2.398017
6	0.448298	-1.443359	2.669867
6	0.448298	-1.443359	-2.669867
6	2.566811	-1.442162	0.000000
6	2.001076	1.846708	1.831580

8	-4.278507	-0.762150	0.000000
8	-2.084571	1.895258	3.262839
8	-2.084571	1.895258	-3.262839
8	2.715990	2.463632	2.438680
8	3.449131	-2.134836	0.000000
8	0.479514	-2.253229	-3.446739
8	0.479514	-2.253229	3.446739
6	2.001076	1.846708	-1.831580
8	2.715990	2.463632	-2.438680
57	-0.199071	-0.118828	0.000000

Frequencies	**IR intensity**
8.8721	0.0059
11.9269	0.0690
21.9232	0.0082
22.8152	0.0564
24.0251	0.1041
26.2262	0.4121
28.8371	0.1445
34.0355	0.2933
36.6013	0.5749
38.0014	0.4553
39.7419	0.2170
39.8683	0.1515
42.0411	0.0432
49.0649	0.2140
56.0467	2.1061
81.8433	9.1110
85.7362	1.2651
86.9340	14.9487
91.7400	4.7447
93.2905	0.0473
99.2828	1.6667
104.7312	0.2703
110.9710	3.7935
114.4148	4.1172
122.6057	18.4358
126.8252	13.1751
132.0680	7.8739
136.5737	1.3796
140.7527	4.6662
148.8683	5.5021
173.0575	3.7175

174.8633	9.7439
183.3668	0.1861
188.6389	0.3865
196.2740	3.5577
202.5456	0.0328
221.9095	0.5242
234.4124	16.6595
240.5525	19.5861
762.2788	196.0464
2250.5493	69.6137
2250.5605	99.3715
2252.4484	154.6911
2253.1111	60.4426
2254.9524	53.6651
2261.7590	152.4160
2263.3418	107.1954
2265.0586	17.8946

$LaO(CO)_8^+$ (La_8c) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	2.113127	-1.277142	-2.039183
6	-0.581639	-2.940006	-0.117653
6	1.358748	2.116536	-1.916505
6	-1.518371	2.509917	0.257689
6	-1.711523	-0.492128	2.327485
8	-1.035677	-3.922835	-0.411603
8	2.598392	-1.750824	-2.932466
8	-2.431835	-0.680365	3.165653
8	1.588856	2.807494	-2.769430
8	-2.255175	3.350170	0.164122
8	-0.908808	-0.183080	-1.576897
6	1.994973	2.245271	1.885413
8	2.594506	2.947247	2.523909
57	0.168013	0.002239	-0.086076
6	2.523735	-1.756834	1.709281
8	3.294689	-2.326231	2.293238
6	-4.021794	-0.219914	-0.338794
8	-4.759984	-0.396802	-1.169036

Frequencies	**IR intensity**
5.0369	0.3021

10.3718	0.1294
14.2093	0.4367
15.9830	2.0884
18.5271	0.2239
20.2284	0.2775
23.4760	0.8511
23.9031	0.4813
27.0413	0.3744
28.4123	0.3731
29.8688	0.1703
32.3207	0.0642
36.2729	0.1339
39.8283	7.5120
44.6395	2.7590
57.2537	0.8096
61.8749	9.0250
69.9710	11.9750
80.9937	19.4428
101.4905	0.0418
102.1183	0.1272
107.7912	0.1608
109.1192	0.1351
111.3182	0.0815
115.0279	0.1141
121.8865	0.0554
123.6090	5.2861
128.7394	10.3050
131.8792	15.5999
136.2776	3.0213
157.4351	7.1099
163.5719	11.7778
170.9395	0.0708
175.1517	0.2616
181.3222	3.3074
196.6258	0.5131
202.9494	3.5253
210.8931	7.8367
218.3619	11.4560
780.7228	202.4635
2234.4244	84.2397
2255.5811	40.1842
2257.1410	109.3746
2260.0656	82.4660
2262.0885	52.5724

2263.6572	150.8489
2265.7681	97.3492
2269.3080	40.6950

$LaO(CO)_8^+$ (La_8d) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	2.358254	1.753608
6	-2.746500	0.000000	0.909346
6	2.746500	0.000000	0.909346
6	0.000000	-2.455271	-1.349806
6	0.000000	-2.358254	1.753608
8	-3.751192	0.000000	1.413917
8	0.000000	3.135497	2.565259
8	0.000000	-3.135497	2.565259
8	3.751192	0.000000	1.413917
8	0.000000	-3.446436	-1.885649
8	0.000000	0.000000	2.285504
6	2.007994	0.000000	-2.129416
8	2.807163	0.000000	-2.920541
57	0.000000	0.000000	0.083218
6	0.000000	2.455271	-1.349806
8	0.000000	3.446436	-1.885649
6	-2.007994	0.000000	-2.129416
8	-2.807163	0.000000	-2.920541

Frequencies	**IR intensity**
17.5177	0.0000
21.1540	0.0297
27.8377	0.1779
30.6964	0.0000
31.0142	0.5036
39.3337	4.8369
42.5357	0.8024
43.8115	0.4491
44.2513	6.6919
46.4110	0.0000
50.6239	0.2657
51.4621	1.4812
56.1042	0.2706
57.1288	1.9227
83.1948	11.4883

101.5307	0.1956
112.0134	4.4503
116.0179	2.3008
119.1316	2.6445
132.3655	5.5025
133.2493	1.6529
136.2293	10.9088
156.1549	0.0478
176.1322	0.0000
186.3909	0.4390
194.1411	0.0010
194.5170	2.4078
198.0580	0.0000
217.6474	0.0000
218.3294	0.0003
224.6298	0.0534
229.2269	0.0309
235.3689	4.1244
255.7741	0.0000
256.6407	5.0136
262.9995	0.5333
263.7377	0.0314
266.8270	0.5179
272.2455	0.1764
464.7059	61.7288
2160.3689	1685.3721
2178.8655	659.2196
2198.4125	1038.2175
2205.0067	676.7457
2207.2864	604.9197
2217.5571	86.9685
2218.2616	401.8779
2242.6908	1.3831

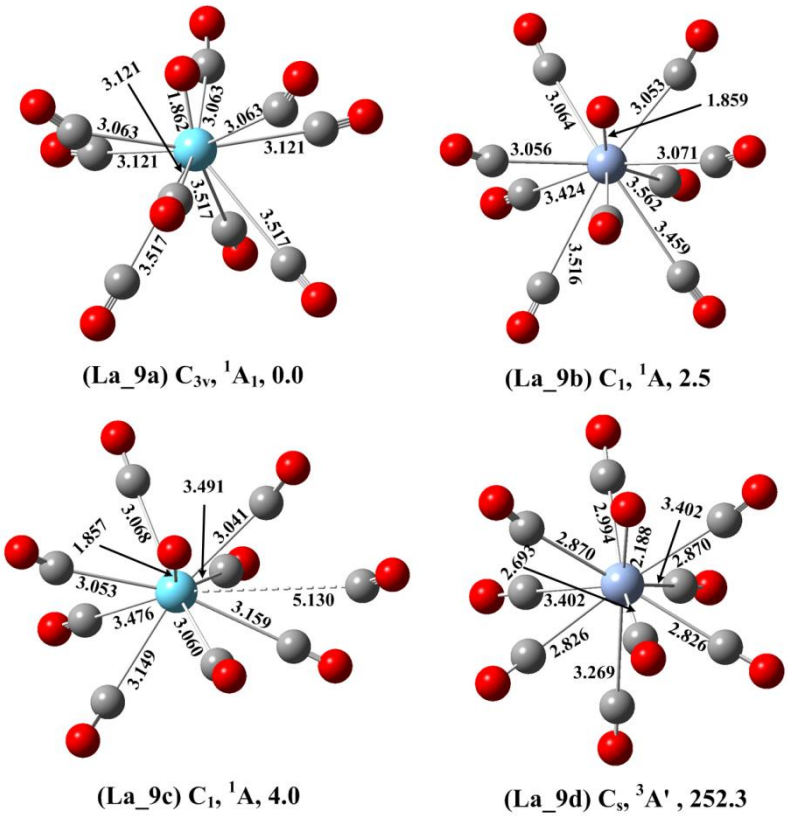


Fig. S11. Optimized structures of the minimum-energy isomers of the $LaO(CO)_9^+$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$LaO(CO)_9^+$ (La_9a) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	0.000000	0.000000	2.180155
6	-2.458543	1.419441	1.468097
6	0.000000	3.109001	0.039460
6	-2.692473	-1.554500	0.039460
6	2.458543	1.419441	1.468097
6	0.000000	-2.838881	1.468097
6	2.692473	-1.554500	0.039460
6	1.982722	1.144725	-2.351203
8	-3.135533	1.810301	2.274566
8	0.000000	4.230778	0.056520
8	-3.663961	-2.115389	0.056520
8	2.638677	1.523441	-3.180119
8	3.663961	-2.115389	0.056520
8	0.000000	-3.620602	2.274566
8	3.135533	1.810301	2.274566
6	0.000000	-2.289450	-2.351203

8	0.000000	-3.046882	-3.180119
57	0.000000	0.000000	0.317915
6	-1.982722	1.144725	-2.351203
8	-2.638677	1.523441	-3.180119

Frequencies	**IR intensity**
15.2156	0.0593
15.2245	0.0588
21.0846	0.0753
21.0915	0.0757
22.7917	0.0001
23.1181	0.2116
27.3639	0.0320
28.8583	0.1778
28.8838	0.1778
35.3043	0.5041
38.9345	1.1534
38.9385	1.1487
42.7343	0.0462
42.7356	0.0457
46.9862	0.0000
48.0337	0.0017
48.0389	0.0017
57.1049	2.3709
83.6038	0.7883
87.1424	2.3110
87.1488	2.2900
90.2088	8.5028
90.2183	8.5043
95.3129	0.0014
100.0212	0.0004
102.4820	2.2377
102.5809	2.3078
115.2729	0.8161
115.3231	0.8245
126.0040	29.0684
126.0234	29.1346
126.2410	0.0412
130.5165	0.0001
152.7948	5.6259
152.7999	5.6311
173.1134	0.0745
184.8343	5.5574

184.8373	5.5607
200.8666	0.0007
200.8692	0.0008
213.1952	0.0000
223.6654	0.1972
241.4180	20.4108
241.4223	20.4071
758.7962	207.4835
2245.3838	97.1635
2245.3839	97.1740
2247.6702	139.7326
2251.1133	45.9535
2251.1177	45.8984
2252.9065	95.9425
2259.6767	149.2509
2259.6770	149.3165
2262.0305	1.1011

$LaO(CO)_9^+$ (La_9b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-1.853995	-1.852757	-1.695889
6	-2.063112	1.820799	-1.491287
6	1.542361	-2.562974	-1.040150
6	3.122449	0.294209	-0.527431
6	1.103951	2.882462	-0.762534
8	-2.677790	2.378398	-2.247030
8	-2.399003	-2.387202	-2.518898
8	1.467431	3.808810	-1.281587
8	2.042463	-3.349524	-1.665706
8	4.149221	0.396898	-0.969110
8	0.447313	0.134955	-2.094361
6	1.896960	-0.197546	2.790357
8	2.511629	-0.276396	3.726838
57	0.092254	0.025113	-0.272616
6	-3.060642	-0.213457	1.266045
8	-4.067512	-0.289646	1.757414
6	-0.720566	2.317781	2.186223
8	-0.942201	3.086236	2.974283
6	-0.551313	-2.656909	1.756112
8	-0.750934	-3.555163	2.399459

Frequencies	IR intensity
-5.8235	0.4554
4.1722	0.1880
18.6012	0.4154
20.9230	0.3252
21.3904	0.0638
24.6937	0.2384
26.9530	0.4303
27.7832	0.5560
32.3996	0.1091
32.9135	0.1795
34.2980	0.1996
35.2315	0.1218
36.9703	0.9615
37.7922	2.3745
41.4069	1.3759
44.3158	0.2781
45.7245	1.3285
50.6383	1.7550
62.0590	7.8836
67.2863	21.0202
77.3482	19.2890
88.5529	0.1826
91.3912	0.3052
93.0693	0.0871
100.2122	0.3257
109.5644	2.5256
110.2217	2.7676
111.0045	3.6728
116.2461	7.6511
118.6163	11.9163
125.5334	0.4573
132.7704	0.2839
139.9406	4.3783
143.4613	7.0525
149.9371	4.6745
161.5973	7.3944
164.8190	9.8504
170.1409	0.2871
185.3612	0.2693
208.7547	0.1031
214.1532	0.0061
222.5017	0.1612

233.0520	16.7580
234.4644	19.4015
767.9501	205.5246
2249.5690	8.9311
2250.4597	24.1043
2251.5959	2.6552
2252.0083	14.1028
2252.4647	10.1003
2253.1420	211.4302
2253.8976	260.6122
2254.3413	261.9690
2259.4826	14.8509

$LaO(CO)_9^+$ (La_9c) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	0.431193	0.634509	-1.708344
6	1.717546	2.453465	0.276485
6	-1.491251	2.722363	1.273510
6	1.981730	-0.429049	2.089642
6	-2.424807	1.405208	-1.808796
6	1.596704	-2.041608	-1.056760
6	-1.744979	-1.924123	-1.770396
6	-3.414720	-0.361701	1.318456
8	2.461119	3.234309	-0.036477
8	-1.912554	3.670108	1.700394
8	2.784504	-0.619678	2.849396
8	-4.444133	-0.516013	1.739020
8	-2.160776	-2.573541	-2.585147
8	2.327823	-2.568205	-1.726524
8	-2.866776	1.907175	-2.710648
6	-0.737617	-2.801579	1.752165
8	-0.878319	-3.761937	2.316462
57	-0.263713	0.146086	-0.057199
6	4.860432	0.098768	-0.299159
8	5.879599	0.211102	-0.761947

Frequencies	**IR intensity**
6.3609	0.0503
10.5772	0.1668
14.5695	0.0084
16.7888	0.1138

21.2897	0.0966
23.4019	0.4005
23.6345	0.1371
24.8130	0.3151
29.4321	0.1092
32.2969	1.0252
33.9748	0.2964
36.0615	0.5786
38.7878	0.3689
40.0622	0.3476
42.5026	0.0397
42.9920	0.2026
47.7428	0.4900
54.0784	2.8439
62.5821	0.8392
75.4202	10.3959
78.7562	12.7643
85.8406	5.5246
87.7271	2.0322
91.1266	4.5062
94.2939	0.3160
99.5993	0.6894
105.1258	0.2245
110.9606	2.9567
114.0025	2.8607
122.7985	17.0956
126.8835	18.7795
132.2101	6.2759
136.9699	1.3678
142.4066	2.2690
148.9585	4.2594
172.3798	3.8463
173.5089	9.4076
182.7586	0.1063
186.4771	0.7465
195.6463	3.4904
201.9484	0.0104
221.7853	0.4851
232.2367	14.4339
240.0010	19.2276
769.7025	194.2350
2234.8905	89.6048
2249.6193	90.1266
2250.4084	74.8384

2251.9504	132.4176
2252.4738	90.4947
2254.3474	48.1898
2261.0410	150.4281
2262.9769	101.9748
2264.6478	22.6092

$LaO(CO)_9^+$ (La_9d) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	2.124237	1.185540	0.000000
6	2.022345	-2.038388	0.000000
6	-0.064364	-1.545642	2.333151
6	-0.064364	-1.545642	-2.333151
6	1.615895	1.004963	2.336005
6	1.615895	1.004963	-2.336005
6	-0.347218	2.940252	0.000000
6	-2.447270	0.919743	1.823281
8	2.841166	-2.819416	0.000000
8	-0.004888	-2.210301	3.244283
8	-0.004888	-2.210301	-3.244283
8	-3.210286	1.131203	2.619996
8	-0.345223	4.063037	0.000000
8	2.318621	1.414731	-3.112483
8	2.318621	1.414731	3.112483
6	-2.447270	0.919743	-1.823281
8	-3.210286	1.131203	-2.619996
57	0.277159	0.011870	0.000000
6	-2.202348	-2.118897	0.000000
8	-3.062808	-2.840821	0.000000

Frequencies	**IR intensity**
-50.5235	0.0510
-16.6696	10.1972
16.9356	0.3230
23.8035	0.1126
28.0339	2.8307
28.6871	0.5021
29.3426	1.5282
32.8175	0.0889
33.9333	1.4550
34.7447	1.2792

38.8153	7.5882
43.2982	2.5327
44.7748	0.8622
45.9316	0.6613
55.5871	0.3561
57.2327	0.4360
59.7220	0.6462
64.4772	15.4670
66.3813	2.0337
80.2419	14.6851
92.8717	12.6270
97.9700	2.5348
106.5002	7.9384
114.3749	2.3223
118.1791	4.6519
118.7833	0.6915
137.8795	0.5927
148.7157	3.8936
157.3514	2.9055
164.8653	8.1038
166.7380	0.5045
178.1189	0.1431
194.5136	0.0800
199.7457	1.7204
210.4055	2.7243
219.7251	0.1757
227.9870	2.7152
243.5674	0.6237
252.2027	3.2870
256.4775	0.2681
261.4544	2.1238
268.3497	1.7950
282.8787	0.6015
290.1583	2.5711
477.8849	71.5795
2109.9549	845.6105
2112.4621	2504.9790
2158.8010	1183.4962
2200.3674	607.6109
2218.2903	349.4134
2233.7184	249.7387
2236.9702	149.6088
2238.8241	86.9573
2247.5568	150.1763

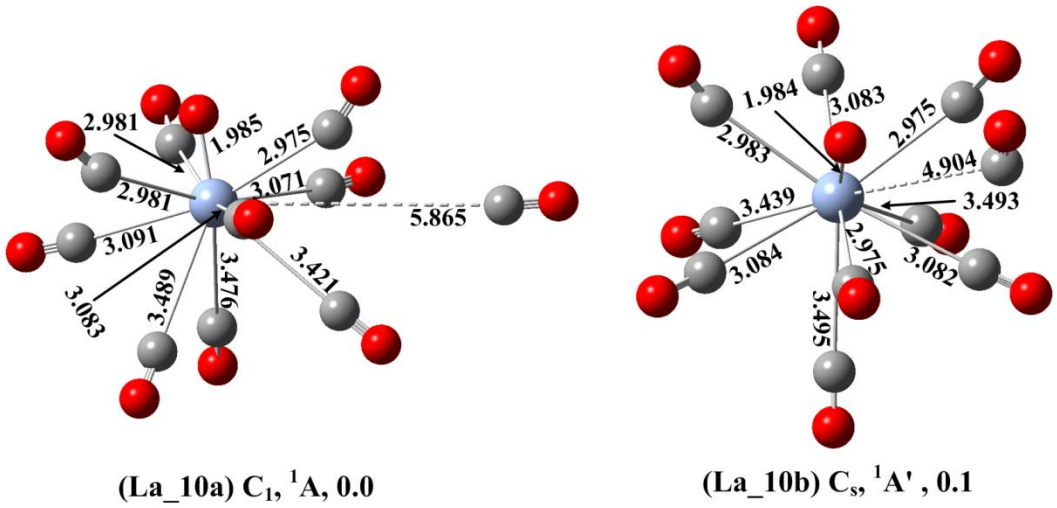


Fig. S12. Optimized structures of the minimum-energy isomers of the $LaO(CO)_{10}^{+}$ complexes. Relative energies (with ZPE correction) are given in kJ/mol.

$LaO(CO)_{10}^{+}$ (La_10a) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
8	0.642288	-0.056679	-2.189699
6	2.754249	-1.853458	-1.234460
6	3.367620	1.020277	0.298717
6	-0.100270	-3.066867	-0.084328
6	1.162359	2.737796	-1.495965
6	-2.074110	-0.977015	-1.697075
6	-1.857245	2.033537	-0.369904
6	0.610240	2.319808	2.333181
8	3.430729	-2.371449	-1.966268
8	4.418691	1.389600	0.431427
8	-0.299656	-4.170519	-0.116457
8	0.657327	3.083088	3.155537
8	-2.689350	2.773954	-0.504272
8	-2.736729	-1.250970	-2.561717
8	1.396220	3.482702	-2.303399
6	-1.931059	-0.685825	2.065878
8	-2.729191	-0.912369	2.822598
57	0.482459	-0.011878	-0.335392
6	1.889064	-1.470322	2.570418
8	2.335190	-1.932524	3.491582
6	-5.487814	0.012419	0.190590
8	-6.612817	-0.002967	0.197549

Frequencies	IR intensity
6.4704	0.0631
10.3505	0.1611
13.9808	0.4413
16.6951	0.1359
19.8356	0.3910
20.9332	0.2491
22.6918	0.1486
23.0350	0.0619
27.3723	0.1866
27.8168	0.1869
29.0732	0.2972
31.5733	0.1823
36.5567	0.4550
37.7873	2.0291
39.1998	1.5577
42.2177	0.0102
43.9165	0.0384
46.7039	0.0039
47.8921	0.0008
48.6341	0.2835
58.4687	2.1073
63.3438	0.0610
66.1349	0.1837
81.8371	18.5680
84.6827	1.0665
85.8090	8.1396
89.4502	1.7665
90.4137	4.5011
96.5865	0.1606
100.8773	0.0761
103.0223	2.0210
104.5358	1.9809
115.7511	1.4965
116.9956	0.8213
122.0666	24.7785
124.6189	23.1611
131.1040	1.5367
131.6855	2.1731
151.9369	4.9348
154.4136	4.1299
173.6280	0.2666
184.9387	5.2427

185.4787	4.6590
201.4736	0.0083
201.5957	0.0236
213.8843	0.0242
225.3613	0.2732
239.9732	17.7544
244.0767	19.9405
762.4496	206.4477
2233.0737	97.7381
2244.7508	97.5553
2245.2924	93.5666
2247.3920	144.6972
2249.8567	48.1021
2250.4032	47.6001
2252.1476	88.9849
2259.1716	147.5544
2259.6434	144.0799
2261.8332	4.0970

$LaO(CO)_{10}^{+}$ (La_10b) Standard orientation

Atomic Number	Coordinates (Angstroms) X	Y	Z
57	0.113833	-0.000645	-0.181982
8	-1.147866	-0.004773	-1.550404
6	-1.656249	-2.482220	0.015188
6	-1.649341	2.488583	-0.017238
6	-1.908590	0.018683	2.185916
6	1.174058	1.986286	2.558671
6	1.473468	2.678283	-1.051769
6	3.618185	-0.009565	0.188526
6	1.402146	-0.013798	-2.963340
6	1.457993	-2.691180	-1.035332
6	1.164974	-1.965106	2.573374
8	1.480632	-2.600351	3.443926
8	1.869547	-3.658457	-1.427514
8	-2.472007	-3.202063	-0.263442
8	-2.686025	0.027105	2.994631
8	-2.463850	3.204910	-0.308393
8	1.493129	2.629300	3.422254
8	1.891429	3.640402	-1.449825
8	4.737933	-0.014351	0.272686
8	1.413558	-0.017631	-4.086551

6	-4.569527	-0.006811	-0.423914
8	-5.307880	-0.001865	-1.273304

Frequencies	**IR intensity**
11.3273	0.1615
13.4616	0.0630
18.8420	0.1875
18.9903	0.1377
21.5407	0.2095
22.5149	0.0087
24.0765	0.2390
24.7752	0.0356
26.2483	0.3555
28.1815	0.2641
29.5665	0.0568
33.3205	0.9899
35.7203	0.6999
39.6472	1.0622
40.1130	0.5036
40.6537	0.3697
42.8623	0.0121
44.2028	0.0561
47.2267	0.0338
48.5437	0.0550
49.0149	0.0820
55.1550	2.3946
79.1476	17.3721
83.2194	0.8117
86.8500	5.0232
89.1210	0.2045
89.6328	4.1266
96.3821	0.5211
98.5745	0.0024
101.5546	1.1483
102.5852	1.2457
104.4391	0.0439
115.1918	0.2658
115.3307	1.0187
125.6424	29.2790
126.9416	0.3295
129.0153	26.8748
131.2986	2.0305
153.7240	5.1506

154.1747	3.8129
173.3741	0.1972
184.7020	5.2801
185.3107	5.5532
200.2580	0.0303
202.7272	0.0148
214.2534	0.0173
221.5761	0.3776
236.5353	19.3928
240.0268	18.3700
771.3930	215.3975
2230.3139	84.9784
2244.6433	103.7592
2246.4704	86.8550
2248.2101	139.1335
2250.3007	49.8193
2250.4865	48.9360
2252.3056	88.5583
2259.3000	149.7070
2260.0856	131.0658
2262.2574	12.2107

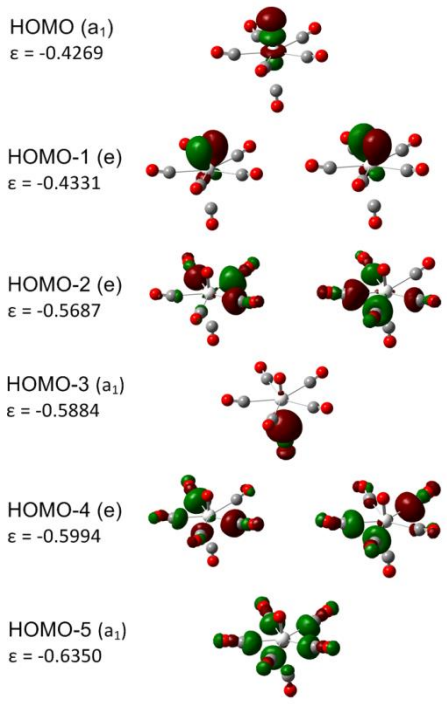


Fig. S13. Occupied valence molecular orbits (isovalue=0.02) of $ScO(CO)_6^+$ which display σ and π interactions of Sc-O and Sc-CO. The orbital energy eigenvalues are given in eV.

Natural Electron Configuration via NBO Analysis

ScO^+	Sc	[core]4S(0.06)3d(1.07)4p(0.01)
YO^+	Y	[core]5S(0.04)4d(0.89)5p(0.02)
LaO^+	La	[core]6S(0.01)4f(0.13)5d(0.81)6p(0.02)
$LaO(CO)_9^+$	La	[core]6S(0.30)4f(0.21)5d(1.18)6p(0.64)5f(0.02)6d(0.11)