Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Structure and Bonding of Lanthanoid(III) Carbonates.

Yannick Jeanvoine,[a] Pere Miró,[b] Fausto Martelli,[a] Christopher J. Cramer[b,*] and Riccardo Spezia[a,*]

[a]*Université d'Evry Val d'Essonne, CNRS UMR 8587 LAMBE, Bd F. Mitterrand, 91025 Evry Cedex, France.*

[b]*Department of Chemistry and Supercomputing Institute, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455-0431 USA.*

SUPPORTING INFORMATION

Contents

Table S16. Second-order perturbative estimates of donor-acceptor interactions in the NBO basis between carbonates and Ln(III). We specify the character of the acceptor orbital, while for the donor it always correspond to oxygen lone pair. Only energies above 10 kcal mol^{-1} are reported.

Table S17. Relative energy obtained with different functionals with B3LYP optimized geometries (fixed) and optimizing the geometry with the given functional. Energies are in kcal/mol.

Figure S1. La^{3+}-CO_3^{2-} energy curves for various basis set. Basis1 = 6-31+G(d,p); basis 2 = 6-311+G(d,p) ; basis 3 = 6-311++G(3df,2p) ; basis 4 = AUG-cc-pVTZ.

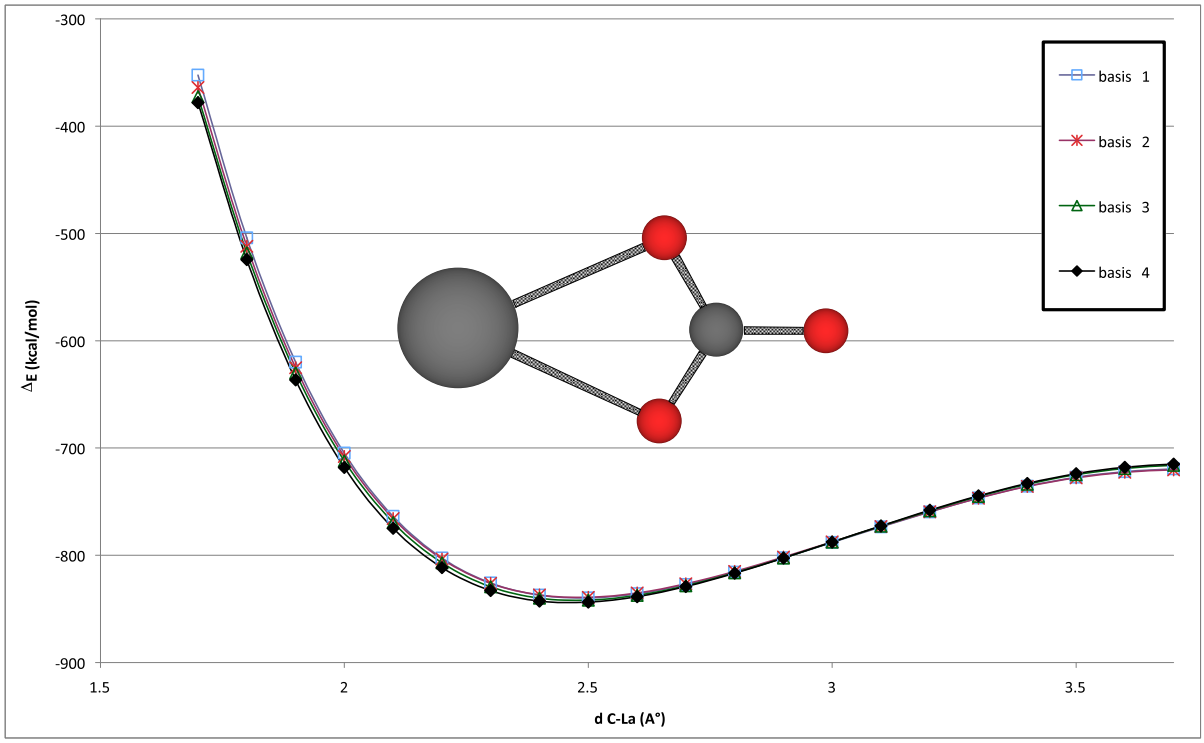

Table S1. Distances (in Å) between Ln, oxygen and carbon atoms in optimized geometries. O(1) is/are the oxygen(s) closer to Ln, O(2) the farest one(s). The carbonate coordination motifs are designated as number monodentate (m) or bidentate (b).

	$Ln\text{-}O^{(1)}$	$Ln\text{-}O^{(2)}$	Ln-C
LaC_3			
3m	2.20	4.29	3.60
2m1b	2.23/2.41	4.33/4.12	3.61/2.87
1m2b	2.44/2.25	4.16/4.36	2.90/3.62
3b	2.47	4.19	2.93
LaC_4			
4m	2.34	4.49	3.7
3m1b	2.38/2.60	4.49/4.30	3.72/3.01
2m2b	2.43/2.55	4.53/4.33	3.72/3.01
1m3b	2.59/2.47	4.58/4.38	3.81/3.09
4b	2.64	4.42	3.12
LuC_3			
3m	2.02	4.13	3.41
2m1b	2.04/2.20	4.15/3.89	2.64/3.42
1m2b	2.24/2.06	3.94/4.16	3.43/2.68
3b	2.27	3.97	2.71
LuC_4			
4m	2.13	4.21	3.48
3m1b	2.18/2.29	4.31/4.08	3.50/2.80
2m2b	2.21/2.43	4.31/4.10	3.54/2.82
1m3b	2.24/2.49	4.35/4.13	3.57/2.87
4b	2.48	4.2	2.9

Table S2. Energy decomposition analysis (EDA) in gas phase of the La-ligand interation. The metal centre (M^{3+}) was chosen as a fragment and the three/four ligands ($\{CO_3^{2-}\}_{3/4}$) as the other fragment. Energies in kcal·mol^{-1}. The carbonate coordination motifs are designated as number monodentate (m) or bidentate (b).

Species	Pauli Repulsion	Orbitalic Interaction		Electrostatic Interaction	
3m	245.64	-344.33	(16.01%)	-1806.09	(84.99%)
2m1b	246.32	-329.93	(14.99%)	-1871.09	(85.01%)
1m2b	241.29	-314.75	(14.02%)	-1930.34	(85.98%)
3b	232.89	-299.36	(13.10%)	-1985.49	(86.90%)
4m	177.67	-337.96	(12.48%)	-2168.35	(86.52%)
3m1b	170.61	-323.56	(12.74%)	-2216.42	(87.26%)
2m2b	163.60	-309.65	(12.03%)	-2264.64	(87.97%)
1m3b	155.16	-297.99	(11.43%)	-2308.89	(88.57%)
4b	145.29	-286.47	(10.86%)	-2350.77	(89.14%)

Table S3. Energy decomposition analysis (EDA) in gas phase of the Lu-ligand interation. The metal centre (M^{3+}) was chosen as a fragment and the three/four ligands ($\{CO_3^{2-}\}_{3/4}$) as the other fragment. Energies in kcal·mol^{-1}. The carbonate coordination motifs are designated as number monodentate (m) or bidentate (b).

Species	Pauli Repulsion	Orbitalic Interaction		Electrostatic Interaction	
3m	237.37	-384.53	(16.88%)	-1892.91	(83.12%)
2m1b	244.41	-377.15	(16.07%)	-1969.96	(83.93%)
1m2b	238.74	-365.01	(15.21%)	-2034.24	(84.79%)
3b	229.29	-350.53	(14.34%)	-2094.31	(85.66%)
4m	181.19	-402.95	(15.06%)	-2272.17	(84.94%)
3m1b	171.83	-387.51	(14.30%)	-2322.35	(85.70%)
2m2b	163.95	-373.40	(13.59%)	-2374.79	(86.41%)
1m3b	153.19	-361.52	(13.00%)	-2420.44	(87.00%)
4b	141.33	-348.76	(12.40%)	-2464.02	(87.60%)

Table S4. Energy decomposition analysis (EDA) in gas phase of the La-ligand interation. The metal centre with 3 carbonates ($\{M(CO_3^{2-})_2\}^{-1}$) was chosen as a fragment and the remaining ligand (CO_3^{2-}) as the other fragment. Energies in kcal·mol^{-1}. The carbonate coordination motifs are designated as number monodentate (m) or bidentate (b).

Species	Ligand	Pauli Repulsion	Orbitalic Interaction		Electrostatic Interaction	
3m	mo	114.53	-90.10	(47.54%)	-99.41	(52.46%)
2m1b	mo	104.40	-81.04	(50.61%)	-79.10	(49.39%)
2m1b	bi	130.23	-95.94	(42.33%)	-130.71	(57.67%)
1m2b	mo	95.05	-73.77	(55.78%)	-58.48	(44.22%)
1m2b	bi	116.49	-85.67	(45.08%)	-104.36	(54.92%)
3b	bi	104.37	-77.73	(49.80%)	-78.36	(50.20%)

Table S5. Energy decomposition analysis (EDA) in gas phase of the Lu-ligand interation. The metal centre with 3 carbonates ($\{M(CO_3^{2-})_2\}^{-1}$) was chosen as a fragment and the remaining ligand (CO_3^{2-}) as the other fragment. Energies in kcal·mol^{-1}. The carbonate coordination motifs are designated as number monodentate (m) or bidentate (b).

Species	Ligand	Pauli Repulsion	Orbitalic Interaction		Electrostatic Interaction	
3m	m	126.26	-101.25	(46.63%)	-115.89	(53.37%)
2m1b	m	106.18	-79.47	(45.87%)	-93.79	(54.13%)
2m1b	b	149.5	-104.4	(38.83%)	-164.3	(54.13%)
1m2b	m	97.14	-72.11	(50.61%)	-70.38	(49.39%)
1m2b	b	125.03	-87.78	(41.23%)	-125.13	(58.77%)
3b	b	111.87	-78.96	(45.97%)	-92.80	(54.03%)

Table S6. Natural Orbitals for Chemical Valence in gas phase for in the fragments presented in Table 3 in La species with 3 carbonate ligands. Energy in kcal·mol^{-1} (only energies above 5kcal·mol^{-1} are presented). The carbonate coordination motifs are designated as number monodentate (m) or bidentate (b). Energies are highly dependent on the fragment choice.

Species	Ligand	Orbitals				Energy
3m	m	1st	O-2p	→	La-5d^0	-24.29959
		2nd	O-2p	→	La-5d^0	-31.35437
		3rd	O-2p	→	La-5d^0	-15.06170
2m1b	m	1st	O-2p	→	La-5d^0	-20.31610
		2nd	O-2p	→	La-5d^0	-29.32818
		3rd	O-2p	→	La-5d^0	-13.83859
2m1b	b	1st	O-2p	→	La-5d^0	-35.16901
		2nd	O-2p	→	La-5d^0	-21.51368
		3rd	O-2p	→	La-5d^0	-8.31394
1m2b	m	1st	O-2p	→	La-5d^0	-27.11360
		2nd	O-2p	→	La-5d^0	-17.50859
		3rd	O-2p	→	La-5d^0	-12.70027
1m2b	b	1st	O-2p	→	La-5d^0	-30.21364
		2nd	O-2p	→	La-5d^0	-20.60048
		3rd	O-2p	→	La-5d^0	-7.30717
3b	b	1st	O-2p	→	La-5d^0	-26.75174
		2nd	O-2p	→	La-5d^0	-19.45519
		3rd	O-2p	→	La-5d^0	-6.47782

Table S7. Natural Orbitals for Chemical Valence in gas phase for in the fragments presented in Table 4 in Lu species with 3 carbonate ligands. Energy in kcal·mol^{-1} (only energies above 5kcal·mol^{-1} are presented). The carbonate coordination motifs are designated as number monodentate (m) or bidentate (b). Energies are highly dependent on the fragment choice.

Species	Ligand	Orbitals				Energy
3m	m	1st	O-2p	→	Lu-6s	-14.62685*
		2nd	O-2p	→	Lu-5d^0	-21.20628
		3rd	O-2p	→	Lu-5d^0	-18.35011
		4th	O-2p	→	Lu-5d^0	-13.93904
2m1b	m	1st	O-2p	→	Lu-5d^0	-17.35802
		2nd	O-2p	→	Lu-5d^0	-22.82156
		3rd	O-2p	→	Lu-5d^0	-14.95281
2m1b	b	1st	O-2p	→	Lu-5d^0	-17.24372
		2nd	O-2p	→	Lu-5d^0	-22.93462
		3rd	O-2p	→	Lu-5d^0	-14.96220
1m2b	m	1st	O-2p	→	Lu-5d^0	-14.70391
		2nd	O-2p	→	Lu-5d^0	-21.94559
		3rd	O-2p	→	Lu-5d^0	-12.28322
1m2b	b	1st	O-2p	→	Lu-5d^0	-25.80296
		2nd	O-2p	→	Lu-5d^0	-20.22867
		3rd	O-2p	→	Lu-5d^0	-7.07274
3b	b	1st	O-2p	→	Lu-5d^0	-23.02938
		2nd	O-2p	→	Lu-5d^0	-17.82575
		3rd	O-2p	→	Lu-5d^0	-6.38278

* Inside fragment 1 with really small contribution of fragment 2.

Table S8. Topological analysis of the electron density of La species with 3 carbonate ligands. Gas phase calculations.

LaCar3_0bi3mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}	(3,-1)	0.0838	0.4091	0.1024	1.2224	-0.1025	-0.0001
La-O_{carb}	(3,-1)	0.0839	0.4090	0.1026	1.2235	-0.1030	-0.0003
La-O_{carb}	(3,-1)	0.0837	0.3987	0.1023	1.2219	-0.1049	-0.0026

LaCar3_1bi2mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}	(3,-1)	0.0794	0.3887	0.0964	1.2148	-0.0957	0.0008
La-O_{carb}	(3,-1)	0.0794	0.3887	0.0964	1.2148	-0.0957	0.0008
La-O_{carb}'	(3,-1)	0.0620	0.2395	0.0586	0.9453	-0.0574	0.0012
La-O_{carb}'	(3,-1)	0.0620	0.2395	0.0586	0.9453	-0.0574	0.0012
La-$(O_{carb})_2$	(3,+1)	0.0343	0.1844	0.0427	1.2460	-0.0393	0.0034

LaCar3_2bi1mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}	(3,-1)	0.0755	0.3710	0.0911	1.2066	-0.0895	0.0016
La-O_{carb}'	(3,-1)	0.0579	0.2267	0.0541	0.9344	-0.0515	0.0026
La-O_{carb}'	(3,-1)	0.0577	0.2264	0.0540	0.9359	-0.0514	0.0026
La-O_{carb}'	(3,-1)	0.0579	0.2269	0.0541	0.9344	-0.0515	0.0026
La-O_{carb}'	(3,-1)	0.0579	0.2268	0.0541	0.9344	-0.0515	0.0026
La-$(O_{carb})_2$	(3,+1)	0.0326	0.1753	0.0398	1.2209	-0.0358	0.0040
La-$(O_{carb})_2$	(3,+1)	0.0327	0.1756	0.0399	1.2202	-0.0359	0.0040

LaCar3_3bi0mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}'	(3,-1)	0.0542	0.2121	0.0501	0.9243	-0.0472	0.0029
La-O_{carb}'	(3,-1)	0.0542	0.2120	0.0501	0.9243	-0.0472	0.0029
La-O_{carb}'	(3,-1)	0.0541	0.2131	0.0500	0.9242	-0.0467	0.0033
La-O_{carb}'	(3,-1)	0.0543	0.2139	0.0502	0.9245	-0.0470	0.0033
La-O_{carb}'	(3,-1)	0.0542	0.2134	0.0501	0.9243	-0.0468	0.0033
La-O_{carb}'	(3,-1)	0.0542	0.2135	0.0501	0.9245	-0.0468	0.0033
La-$(O_{carb})_2$	(3,+1)	0.0312	0.1633	0.0373	1.1946	-0.0337	0.0035
La-$(O_{carb})_2$	(3,+1)	0.0312	0.1643	0.0374	1.1984	-0.0335	0.0039
La-$(O_{carb})_2$	(3,+1)	0.0312	0.1653	0.0373	1.1949	-0.0332	0.0041

Table S9. Topological analysis of the electron density of La species with 4 carbonate ligands. Gas phase calculations.

LaCar4_0bi4mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}	(3,-1)	0.0603	0.3058	0.0699	1.1588	-0.0633	0.0066
La-O_{carb}	(3,-1)	0.0602	0.3056	0.0698	1.1595	-0.0632	0.0066
La-O_{carb}	(3,-1)	0.0603	0.3058	0.0699	1.1585	-0.0633	0.0066
La-O_{carb}	(3,-1)	0.0604	0.3061	0.0699	1.1585	-0.0634	0.0066

LaCar4_1bi3mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}	(3,-1)	0.0546	0.2746	0.0621	1.1378	-0.0555	0.0066
La-O_{carb}	(3,-1)	0.0560	0.2843	0.0639	1.1411	-0.0567	0.0072
La-O_{carb}	(3,-1)	0.0560	0.2843	0.0639	1.1411	-0.0567	0.0072
La-O_{carb}	(3,-1)	0.0493	0.1599	0.0443	0.8995	-0.0487	-0.0043
La-O_{carb}	(3,-1)	0.0405	0.1601	0.0357	0.8809	-0.0313	0.0044
La-$(O_{carb})_2$	(3,+1)	0.0272	0.1349	0.0306	1.1215	-0.0274	0.0032

LaCar4_2bi2mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}	(3,-1)	0.0499	0.2527	0.0557	1.1182	-0.0483	0.0074
La-O_{carb}	(3,-1)	0.0499	0.2527	0.0557	1.1182	-0.0483	0.0074
La-O_{carb}	(3,-1)	0.0458	0.1783	0.0406	0.8858	-0.0366	0.0040
La-O_{carb}	(3,-1)	0.0386	0.1528	0.0336	0.8713	-0.0290	0.0046
La-O_{carb}	(3,-1)	0.0458	0.1783	0.0406	0.8858	-0.0366	0.0040
La-O_{carb}	(3,-1)	0.0386	0.1528	0.0336	0.8713	-0.0290	0.0046
La-$(O_{carb})_2$	(3,+1)	0.0259	0.1328	0.0286	1.1042	-0.0240	0.0046
La-$(O_{carb})_2$	(3,+1)	0.0259	0.1328	0.0286	1.1042	-0.0240	0.0046

LaCar4_3bi1mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}	(3,-1)	0.0339	0.1325	0.0289	0.8514	-0.0246	0.0043
La-O_{carb}	(3,-1)	0.0420	0.1619	0.0366	0.8696	-0.0326	0.0039
La-O_{carb}	(3,-1)	0.0379	0.1490	0.0328	0.8658	-0.0284	0.0044
La-O_{carb}	(3,-1)	0.0416	0.1522	0.0363	0.8706	-0.0345	0.0018
La-O_{carb}	(3,-1)	0.0420	0.1619	0.0366	0.8698	-0.0326	0.0039
La-O_{carb}	(3,-1)	0.0340	0.1329	0.0290	0.8516	-0.0247	0.0043
La-O_{carb}	(3,-1)	0.0447	0.2264	0.0490	1.0968	-0.0413	0.0076
La-$(O_{carb})_2$	(3,+1)	0.0238	0.1173	0.0256	1.0726	-0.0218	0.0038
La-$(O_{carb})_2$	(3,+1)	0.0248	0.1239	0.0270	1.0908	-0.0231	0.0039
La-$(O_{carb})_2$	(3,+1)	0.0239	0.1175	0.0256	1.0733	-0.0218	0.0038

LaCar4_4bi0mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
La-O_{carb}	(3,-1)	0.0327	0.1284	0.0276	0.8435	-0.0230	0.0046
La-O_{carb}	(3,-1)	0.0372	0.1438	0.0317	0.8518	-0.0274	0.0043
La-O_{carb}	(3,-1)	0.0327	0.1288	0.0276	0.8433	-0.0229	0.0047
La-O_{carb}	(3,-1)	0.0371	0.1436	0.0316	0.8516	-0.0274	0.0043
La-O_{carb}	(3,-1)	0.0371	0.1436	0.0316	0.8519	-0.0274	0.0043
La-O_{carb}	(3,-1)	0.0327	0.1291	0.0276	0.8436	-0.0230	0.0047
La-O_{carb}	(3,-1)	0.0327	0.1285	0.0276	0.8434	-0.0230	0.0046
La-O_{carb}	(3,-1)	0.0372	0.1437	0.0317	0.8518	-0.0274	0.0043
La-$(O_{carb})_2$	(3,+1)	0.0224	0.1096	0.0236	1.0508	-0.0197	0.0038
La-$(O_{carb})_2$	(3,+1)	0.0224	0.1096	0.0236	1.0508	-0.0197	0.0039
La-$(O_{carb})_2$	(3,+1)	0.0224	0.1098	0.0236	1.0512	-0.0197	0.0039
La-$(O_{carb})_2$	(3,+1)	0.0224	0.1096	0.0236	1.0513	-0.0198	0.0038

Table S10. Topological analysis of the electron density of Lu species with 3 carbonate ligands. Gas phase calculations.

LuCar3_0bi3mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.1011	0.6453	0.1613	1.5955	-0.1613	0.0000
Lu-O_{carb}	(3,-1)	0.1012	0.6438	0.1614	1.5949	-0.1619	-0.0005
Lu-O_{carb}	(3,-1)	0.1012	0.6394	0.1614	1.5949	-0.1630	-0.0016

LuCar3_1bi2mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.0957	0.6069	0.1505	1.5720	-0.1493	0.0012
Lu-O_{carb}	(3,-1)	0.0958	0.6069	0.1506	1.5725	-0.1495	0.0011
Lu-O_{carb}	(3,-1)	0.0754	0.3852	0.0954	1.2643	-0.0945	0.0009
Lu-O_{carb}	(3,-1)	0.0754	0.3851	0.0954	1.2644	-0.0944	0.0009
Lu-$(O_{carb})_2$	(3,+1)	0.0408	0.2427	0.0576	1.4112	-0.0544	0.0031

LuCar3_2bi1mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.0923	0.5851	0.1437	1.5572	-0.1411	0.0026
Lu-O_{carb}	(3,-1)	0.0684	0.3484	0.0844	1.2336	-0.0817	0.0027
Lu-O_{carb}	(3,-1)	0.0685	0.3489	0.0845	1.2339	-0.0818	0.0027
Lu-O_{carb}	(3,-1)	0.0685	0.3487	0.0845	1.2337	-0.0817	0.0027
Lu-O_{carb}	(3,-1)	0.0684	0.3485	0.0844	1.2337	-0.0817	0.0027
Lu-$(O_{carb})_2$	(3,+1)	0.0383	0.2242	0.0526	1.3726	-0.0491	0.0035
Lu-$(O_{carb})_2$	(3,+1)	0.0383	0.2242	0.0526	1.3727	-0.0491	0.0035

LuCar3_3bi0mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.0638	0.3193	0.0771	1.2089	-0.0744	0.0027
Lu-O_{carb}	(3,-1)	0.0638	0.3189	0.0771	1.2086	-0.0744	0.0027
Lu-O_{carb}	(3,-1)	0.0638	0.3242	0.0771	1.2088	-0.0732	0.0040
Lu-O_{carb}	(3,-1)	0.0637	0.3246	0.0771	1.2088	-0.0729	0.0041
Lu-O_{carb}	(3,-1)	0.0638	0.3248	0.0771	1.2089	-0.0730	0.0041
Lu-O_{carb}	(3,-1)	0.0638	0.3240	0.0771	1.2088	-0.0731	0.0039
Lu-$(O_{carb})_2$	(3,+1)	0.0365	0.2140	0.0490	1.3418	-0.0444	0.0046
Lu-$(O_{carb})_2$	(3,+1)	0.0365	0.2134	0.0490	1.3421	-0.0446	0.0044
Lu-$(O_{carb})_2$	(3,+1)	0.0365	0.2049	0.0490	1.3421	-0.0467	0.0023

Table S11. Topological analysis of the electron density of Lu species with 4 carbonate ligands. Gas phase calculations.

LuCar4_0bi4mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.0759	0.4778	0.1115	1.4692	-0.1036	0.0079
Lu-O_{carb}	(3,-1)	0.0758	0.4779	0.1115	1.4704	-0.1035	0.0080
Lu-O_{carb}	(3,-1)	0.0758	0.4767	0.1113	1.4687	-0.1034	0.0079
Lu-O_{carb}	(3,-1)	0.0758	0.4770	0.1113	1.4685	-0.1033	0.0080

LuCar4_1bi3mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.0682	0.4202	0.0974	1.4279	-0.0898	0.0076
Lu-O_{carb}	(3,-1)	0.0606	0.2079	0.0722	1.1914	-0.0923	-0.0202
Lu-O_{carb}	(3,-1)	0.0449	0.2257	0.0509	1.1343	-0.0455	0.0055
Lu-O_{carb}	(3,-1)	0.0705	0.4470	0.1019	1.4454	-0.0921	0.0098
Lu-O_{carb}	(3,-1)	0.0705	0.4472	0.1019	1.4456	-0.0920	0.0099
Lu-$(O_{carb})_2$	(3,+1)	0.0319	0.1724	0.0401	1.2586	-0.0371	0.0030

LuCar4_2bi2mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.0631	0.3743	0.0885	1.4020	-0.0834	0.0051
Lu-O_{carb}	(3,-1)	0.0436	0.2071	0.0488	1.1194	-0.0458	0.0030
Lu-O_{carb}	(3,-1)	0.0556	0.2348	0.0643	1.1571	-0.0699	-0.0056
Lu-O_{carb}	(3,-1)	0.0631	0.3743	0.0885	1.4020	-0.0834	0.0051
Lu-O_{carb}	(3,-1)	0.0436	0.2071	0.0488	1.1194	-0.0457	0.0030
Lu-O_{carb}	(3,-1)	0.0556	0.2348	0.0643	1.1569	-0.0699	-0.0056
Lu-$(O_{carb})_2$	(3,+1)	0.0304	0.1696	0.0377	1.2411	-0.0331	0.0047
Lu-$(O_{carb})_2$	(3,+1)	0.0304	0.1696	0.0377	1.2408	-0.0330	0.0047

LuCar4_3bi1mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.0381	0.1817	0.0409	1.0730	-0.0364	0.0045
Lu-O_{carb}	(3,-1)	0.0502	0.2330	0.0565	1.1257	-0.0548	0.0017
Lu-O_{carb}	(3,-1)	0.0451	0.2196	0.0502	1.1145	-0.0455	0.0047
Lu-O_{carb}	(3,-1)	0.0381	0.1817	0.0409	1.0729	-0.0364	0.0045
Lu-O_{carb}	(3,-1)	0.0574	0.3557	0.0788	1.3710	-0.0686	0.0102
Lu-O_{carb}	(3,-1)	0.0484	0.2097	0.0542	1.1200	-0.0560	-0.0018
Lu-O_{carb}	(3,-1)	0.0502	0.2330	0.0565	1.1257	-0.0548	0.0017
Lu-$(O_{carb})_2$	(3,+1)	0.0279	0.1513	0.0334	1.1948	-0.0289	0.0045
Lu-$(O_{carb})_2$	(3,+1)	0.0279	0.1512	0.0334	1.1948	-0.0289	0.0045
Lu-$(O_{carb})_2$	(3,+1)	0.0292	0.1619	0.0360	1.2299	-0.0314	0.0045

LuCar4_4bi0mo							
	Type	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	V_b	E^e_b
Lu-O_{carb}	(3,-1)	0.0424	0.2025	0.0459	1.0838	-0.0412	0.0047
Lu-O_{carb}	(3,-1)	0.0392	0.1775	0.0418	1.0661	-0.0392	0.0026
Lu-O_{carb}	(3,-1)	0.0392	0.1775	0.0418	1.0658	-0.0392	0.0026
Lu-O_{carb}	(3,-1)	0.0422	0.2018	0.0457	1.0831	-0.0410	0.0047
Lu-O_{carb}	(3,-1)	0.0422	0.2016	0.0457	1.0830	-0.0410	0.0047
Lu-O_{carb}	(3,-1)	0.0392	0.1776	0.0418	1.0661	-0.0392	0.0026
Lu-O_{carb}	(3,-1)	0.0390	0.1767	0.0416	1.0651	-0.0389	0.0026
Lu-O_{carb}	(3,-1)	0.0422	0.2018	0.0457	1.0829	-0.0410	0.0047
Lu-$(O_{carb})_2$	(3,+1)	0.0266	0.1383	0.0312	1.1722	-0.0278	0.0034
Lu-$(O_{carb})_2$	(3,+1)	0.0266	0.1381	0.0311	1.1716	-0.0277	0.0034
Lu-$(O_{carb})_2$	(3,+1)	0.0266	0.1381	0.0311	1.1716	-0.0277	0.0034
Lu-$(O_{carb})_2$	(3,+1)	0.0265	0.1378	0.0311	1.1711	-0.0277	0.0034

Table S12. Cartesian coordinates of La species with 3 carbonate ligands.

LaCar3_0bi3mo

La	-0.001100	-0.001317	-0.003841
C	0.979727	3.460611	0.003216
O	0.598942	2.120032	-0.019993
O	-2.138067	-0.541039	0.000191
C	-3.488988	-0.882287	0.002871
O	-4.029372	-1.017313	1.140121
O	1.534870	-1.582998	-0.039540
C	2.511531	-2.575103	0.003984
O	2.929735	-2.999922	-1.113025
O	1.133407	4.018540	-1.122739
O	1.131726	3.978245	1.148888
O	-4.033327	-1.021122	-1.131908
O	2.878225	-2.947456	1.157820

LaCar3_1bi2mo

La	-0.000008	0.142728	-0.000170
C	-3.136147	-1.645988	0.000316
O	-3.630973	-1.921231	1.136948
O	-3.635757	-1.925052	-1.133273
O	-1.927668	-0.969971	-0.003309
O	0.001160	2.283239	-1.116700
C	0.000883	3.011529	-0.000064
O	0.000127	2.283125	1.116595
O	1.927113	-0.970722	0.003121
C	3.135285	-1.647303	0.000088
O	3.629700	-1.924258	-1.136323
O	3.635051	-1.925137	1.133887
O	0.001290	4.264391	0.000010

LaCar3_2bi1mo

La	0.152569	-0.000095	0.000359
C	-3.470357	-0.012056	-0.000357
C	1.597478	-2.515003	-0.000306
C	1.573539	2.527740	0.000293
O	-4.042988	-0.015288	1.136622
O	-2.092720	-0.012015	-0.006612
O	-4.053353	-0.009669	-1.132067
O	2.233334	-3.600764	-0.001370
O	1.230775	-1.890853	1.114971
O	1.234375	-1.887309	-1.114875
O	2.199971	3.618833	0.000186
O	1.215358	1.897674	-1.114429
O	1.212701	1.899554	1.115297

LaCar3_3bi0mo

La	-0.000012	-0.000657	-0.000988
C	-0.026028	2.928162	0.001077
C	-2.524303	-1.485849	-0.000184

C	2.550304	-1.441060	0.001157
O	-0.035387	4.191379	0.001967
O	-0.015864	2.207972	-1.113003
O	-0.025084	2.206473	1.114245
O	-3.614594	-2.123842	-0.000995
O	-1.902533	-1.122054	1.113570
O	-1.901802	-1.120938	-1.113697
O	3.650856	-2.061203	0.001922
O	1.919973	-1.089748	1.114375
O	1.924542	-1.084294	-1.112883

Table S13. Cartesian coordinates of La species with 4 carbonate ligands.

LaCar4_0bi4mo

La	-0.000516	0.001711	-0.001189
C	-2.737083	1.587003	-1.917339
O	-1.717417	0.996100	-1.249069
O	1.014107	1.723451	1.224435
C	1.618883	2.713283	1.924308
O	2.162596	3.678652	1.270950
O	-0.978470	-1.690898	1.292244
C	-1.569258	-2.706786	1.966980
O	-1.551502	-2.679002	3.253318
O	-3.680217	2.133616	-1.235314
O	-2.714918	1.575127	-3.203709
O	1.621441	2.643984	3.208423
O	-2.119970	-3.651754	1.291322
C	2.688305	-1.598709	-1.970501
O	3.640823	-2.143159	-1.300148
O	2.645081	-1.595303	-3.256530
O	1.681485	-0.999096	-1.290039

LaCar4_1bi3mo

La	-0.000135	-0.076341	0.105193
C	0.002912	3.644753	0.423309
O	0.004810	4.372127	-0.642357
O	0.002402	4.155648	1.609172
O	0.001420	2.303856	0.292373
O	-0.000049	-0.498080	2.586750
C	-0.001413	-1.820751	2.562614
O	-0.002239	-2.354237	1.366980
C	-3.222823	-0.842133	-1.590620
O	2.037951	-0.540895	-1.023739
C	3.221589	-0.846695	-1.590434
O	4.298727	-0.698075	-0.896665
O	3.233927	-1.276664	-2.807264
O	-0.001873	-2.519166	3.639884
O	-3.235596	-1.273526	-2.806954
O	-4.299863	-0.691092	-0.897224
O	-2.038853	-0.537343	-1.024106

LaCar4_2bi2mo

La	0.000001	-0.160829	0.000000
C	2.817815	2.179798	-0.873384
C	1.306908	-2.035161	2.001710
C	-2.817850	2.179759	0.873376
C	-1.306871	-2.035192	-2.001702
O	3.181985	2.281684	-2.111987
O	1.792504	1.375861	-0.558116
O	3.416819	2.834123	0.069155
O	1.810255	-2.834708	2.878354

O	1.650518	-2.063747	0.739309
O	0.403442	-1.128607	2.323814
O	-3.182003	2.281678	2.111981
O	-1.792549	1.375807	0.558115
O	-3.416868	2.834056	-0.069173
O	-1.810208	-2.834747	-2.878344
O	-1.650479	-2.063779	-0.739301
O	-0.403427	-1.128617	-2.323812

LaCar4_3bi1mo

La	0.129567	0.000093	-0.047544
C	0.360783	2.791950	-1.344692
C	2.571382	0.001500	1.797404
C	-3.534530	-0.003657	0.987575
C	0.367471	-2.789979	-1.345563
O	0.494164	3.936170	-1.937119
O	0.238037	2.682321	-0.048804
O	0.343035	1.662273	-2.020518
O	3.589399	0.001790	2.596200
O	2.705320	0.001737	0.494378
O	1.335954	0.000768	2.246735
O	0.503830	-3.933944	-1.937628
O	0.351300	-1.660202	-2.021205
O	0.239945	-2.680551	-0.050048
O	-3.829551	-0.001028	2.252554
O	-4.464190	-0.007738	0.080773
O	-2.254234	-0.002123	0.612388

LaCar4_4bi0mo

La	0.000129	0.000048	-0.000078
C	-0.860512	2.705671	1.298532
C	-2.706065	-0.860585	-1.298130
C	2.705597	0.860430	-1.298730
C	0.860755	-2.705600	1.298421
O	-1.214694	3.819488	1.869597
O	-0.524606	1.648749	1.998381
O	-0.818600	2.574546	-0.001613
O	-3.820172	-1.215100	-1.868493
O	-2.574293	-0.818486	0.001936
O	-1.649632	-0.524602	-1.998580
O	3.819696	1.215096	-1.868894
O	1.649023	0.524946	-1.999210
O	2.573870	0.817685	0.001398
O	1.215275	-3.819491	1.869124
O	0.817819	-2.574425	-0.001700
O	0.525566	-1.648688	1.998542

Table S14. Cartesian coordinates of Lu species with 3 carbonate ligands.

LuCar3_0bi3mo

Lu	-0.001930	-0.000284	-0.004052
C	1.651621	2.986134	0.003740
O	0.976815	1.769458	-0.013888
O	-2.023685	-0.040078	0.000987
C	-3.414778	-0.067458	0.004455
O	-3.968437	-0.083533	1.141734
O	1.038031	-1.734357	-0.032766
C	1.768606	-2.917582	0.004129
O	2.070188	-3.422027	-1.116047
O	1.926123	3.487275	-1.124895
O	1.916811	3.458692	1.146775
O	-3.974449	-0.073021	-1.130045
O	2.051643	-3.360710	1.154862

LuCar3_1bi2mo

Lu	0.000013	0.137072	-0.000071
C	2.978452	-1.550138	0.000150
O	3.479734	-1.820360	-1.134287
O	3.478095	-1.821094	1.135109
O	1.764282	-0.891236	-0.000516
O	-0.000642	2.038013	1.115016
C	-0.001279	2.774464	0.000041
O	-0.001109	2.038204	-1.115014
O	-1.763191	-0.892883	0.000409
C	-2.977304	-1.551947	-0.000006
O	-3.478388	-1.822100	1.134502
O	-3.476986	-1.823190	-1.134891
O	-0.001813	4.023851	0.000166

LuCar3_2bi1mo

Lu	0.156156	-0.000009	-0.000177
C	-3.273410	-0.000620	0.000088
C	1.448960	-2.349499	0.000136
C	1.447890	2.350143	0.000312
O	-3.850131	-0.000918	1.134521
O	-1.898956	-0.000944	-0.001477
O	-3.852677	-0.000018	-1.133054
O	2.064505	-3.444802	-0.000029
O	1.092634	-1.709672	1.111023
O	1.093723	-1.708827	-1.110657
O	2.062824	3.445759	0.000397
O	1.092531	1.709719	-1.110664
O	1.092080	1.709764	1.111107

LuCar3_3bi0mo

Lu	-0.000078	-0.000073	-0.000304
C	1.908346	-1.927427	0.000378

C	0.715519	2.616212	0.000161
C	-2.623655	-0.688536	0.000203
O	2.796554	-2.824036	0.000465
O	1.184344	-1.618906	-1.067994
O	1.606455	-1.200415	1.068503
O	1.048386	3.833488	0.000576
O	0.236100	1.991281	1.068208
O	0.810330	1.834896	-1.068159
O	-3.844336	-1.008925	0.000479
O	-1.843038	-0.790603	1.068360
O	-1.994263	-0.216320	-1.068298

Table S15. Cartesian coordinates of Lu species with 4 carbonate ligands.

LuCar4_0bi4mo

Lu	0.000082	0.001010	-0.001717
C	-2.625237	1.369378	-1.834030
O	-1.583798	0.823944	-1.167803
O	0.842602	1.592058	1.140685
C	1.385798	2.632549	1.810298
O	1.903195	3.594595	1.132079
O	-0.835284	-1.571674	1.171906
C	-1.387737	-2.608409	1.839732
O	-1.391714	-2.576913	3.126040
O	-3.578970	1.898023	-1.153166
O	-2.617003	1.333938	-3.120199
O	1.360571	2.614600	3.096339
O	-1.884820	-3.579897	1.160293
C	2.627046	-1.395028	-1.811507
O	3.580095	-1.913951	-1.121544
O	2.620729	-1.380773	-3.097915
O	1.583764	-0.841781	-1.154845

LuCar4_1bi3mo

Lu	-0.000711	-0.074706	0.099650
C	0.023605	3.424926	0.445484
O	0.026493	4.177685	-0.603522
O	0.029834	3.913107	1.641900
O	0.013676	2.092305	0.285759
O	-0.006575	-0.460505	2.361905
C	-0.014010	-1.784515	2.311559
O	-0.014723	-2.274211	1.101657
C	-3.050312	-0.721827	-1.493363
O	1.856506	-0.466127	-0.932989
C	3.042268	-0.758718	-1.491072
O	4.110007	-0.655733	-0.773830
O	3.073159	-1.132065	-2.726556
O	-0.019852	-2.507580	3.372479
O	-3.086050	-1.098115	-2.727866
O	-4.116451	-0.604028	-0.776147
O	-1.860879	-0.441614	-0.936640

LuCar4_2bi2mo

Lu	-0.000022	-0.150943	0.000002
C	2.632697	2.063162	-0.833902
C	1.297667	-1.897545	1.786799
C	-2.632571	2.063416	0.833723
C	-1.297747	-1.897776	-1.786599
O	2.964453	2.189840	-2.080272
O	1.614504	1.263355	-0.506441
O	3.264772	2.696097	0.103152
O	1.832719	-2.696767	2.646122

O	1.570911	-1.932778	0.510446
O	0.422300	-0.974214	2.138004
O	-2.963960	2.190121	2.080175
O	-1.614581	1.263493	0.505912
O	-3.264783	2.696498	-0.103155
O	-1.832838	-2.697098	-2.645812
O	-1.571055	-1.932780	-0.510251
O	-0.422285	-0.974589	-2.137916

LuCar4_3bi1mo

Lu	0.123192	0.000045	-0.052615
C	0.289875	2.635065	-1.171953
C	2.457377	-0.000120	1.553795
C	-3.313989	-0.000496	0.920848
C	0.289928	-2.634756	-1.172266
O	0.401769	3.795857	-1.740641
O	0.231336	2.479665	0.120484
O	0.229456	1.521244	-1.868854
O	3.515719	-0.000012	2.302236
O	2.520723	0.000050	0.245721
O	1.245202	-0.000108	2.052632
O	0.403150	-3.795375	-1.741016
O	0.230703	-1.520763	-1.869010
O	0.231159	-2.479503	0.120186
O	-3.611744	-0.000157	2.185908
O	-4.245539	-0.001198	0.014683
O	-2.037654	0.000132	0.546812

LuCar4_4bi0mo

Lu	-0.000070	-0.000094	-0.000025
C	1.922144	1.850768	1.125516
C	-1.851275	1.923250	-1.125210
C	1.853473	-1.921325	-1.125060
C	-1.924035	-1.852315	1.124770
O	2.781671	2.678205	1.650057
O	1.141859	1.099200	1.856454
O	1.780660	1.714396	-0.166320
O	-2.677638	2.784409	-1.648822
O	-1.710862	1.784107	0.166403
O	-1.102887	1.140731	-1.857006
O	2.681543	-2.781047	-1.648339
O	1.098009	-1.145902	-1.857105
O	1.717881	-1.777096	0.166525
O	-2.783783	-2.679809	1.649070
O	-1.782129	-1.715743	-0.166869
O	-1.143930	-1.100902	1.856156

Table S16. Second-order perturbative estimates of donor-acceptor interactions in the NBO basis between carbonates and Ln(III). We specify the character of the acceptor orbital, while for the donor it always correspond to oxygen lone pair. Only energies above 10 kcal mol^{-1} are reported.

donor → acceptor	Character of empty Ln orbital	E(2) / kcal mol^{-1}
	$[La(\eta^1\text{-}CO_3)_2(\eta^2\text{-}CO_3)]^{3-}$	
O8 (η^2) → La	d (86%)	26.05
O6 (η^2) → La	d (86%)	25.62
O5 (η^1) → La	s (35%), d (34%), f (34%)	24.34
O9 (η^1) → La	s (35%), d (34%), f (34%)	24.34
O5 (η^1) → La	d (96%)	24.07
O9 (η^1) → La	d (96%)	23.76
O9 (η^1) → La	d (94%)	14.80
O5 (η^1) → La	d (94%)	14.78
O9 (η^1) → La	d (99%)	14.72
O5 (η^1) → La	d (99%)	14.36
	$[Lu(\eta^1\text{-}CO_3)_2(\eta^2\text{-}CO_3)]^{3-}$	
O9 (η^1) → Lu	s (90%)	24.28
O5 (η^1) → Lu	s (90%)	24.27
O8 (η^2) → Lu	d (100%)	23.05
O6 (η^2) → Lu	d (100%)	22.99
O5 (η^1) → Lu	d (100%)	22.55
O9 (η^1) → Lu	d (100%)	22.39
O5 (η^1) → Lu	d (100%)	14.28
O9 (η^1) → Lu	d (100%)	14.27
O5 (η^1) → Lu	d (100%)	12.84
O9 (η^1) → Lu	d (100%)	12.80
O9 (η^1) → Lu	d (100%)	12.32
O5 (η^1) → Lu	d (100%)	12.17
O6 (η^2) → Lu	s (90%)	10.47
O8 (η^2) → Lu	s (90%)	10.47
	$[La(\eta^1\text{-}CO_3)_3(\eta^2\text{-}CO_3)]^{5-}$	
O6 (η^2) → La	d (96%)	22.65
O5 (η^1) → La	d (96%)	21.37
O10 (η^1) → La	d (77%), f (22%)	16.64
O17 (η^1) → La	d (77%), f (22%)	16.57
O10 (η^1) → La	s (77%), f (23%)	16.28
O17 (η^1) → La	s (77%), f (23%)	16.25
O8 (η^2) → La	d (96%)	15.36
O17 (η^1) → La	d (96%)	14.44
O10 (η^1) → La	d (96%)	14.30
O8 (η^2) → La	d (96%)	11.68
O5 (η^1) → La	s (77%), f (23%)	11.47
	$[Lu(\eta^1\text{-}CO_3)_3(\eta^2\text{-}CO_3)]^{5-}$	
O5 (η^1) → Lu	d (84%)	36.35
O8 (η^2) → Lu	d (84%)	25.96

O6 (η^2) → Lu	s (52%), d (48%)	23.80
O10 (η^1) → Lu	s (52%), d (48%)	19.34
O10 (η^1) → Lu	d (69%), s (31%)	13.94
O10 (η^1) → Lu	d (94%)	13.92
O17 (η^1) → Lu	d (94%)	13.60
O5 (η^1) → Lu	d (69%), s (31%)	13.22

Table S17. Relative energy obtained with different functionals with B3LYP optimized geometries (fixed) and optimizing the geometry with the given functional. Energies are in kcal/mol.

	B3LYP	BLYP		M05		M05-2X		VSXC	
LaC_4	optimised	fixed[a]	optimised	fixed[a]	optimised	fixed[a]	optimised	fixed[a]	optimised
4m	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.10	8.03
3m1b	2.83	3.88	3.90	1.63	1.64	0.04	0.01	3.89	4.73
2m2b	6.93	8.95	8.98	4.50	4.53	1.45	1.36	1.26	1.32
1m3b	14.53	17.41	17.42	10.78	10.84	6.37	6.16	0.00	0.00
4b	23.86	27.41	27.40	18.75	18.82	13.54	13.21	0.77	1.39

LaC_3	optimised	fixed[a]	optimised	fixed[a]	optimised	fixed[a]	optimised	fixed[a]	optimised
3m	43.82	37.90	37.85	45.99	46.07	54.69	54.74	54.27	54.12
2m1b	24.60	21.01	20.97	26.32	26.33	31.42	31.49	32.30	32.18
1m2b	10.22	8.58	8.57	11.20	11.20	13.51	13.54	14.38	14.27
3b	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

[a]fixed to B3LYP geometry