Electronic Supplementary Information

Insight into the nature of M-C bonding in the lanthanide/actinide-biscarbene complexes: A theoretical perspective

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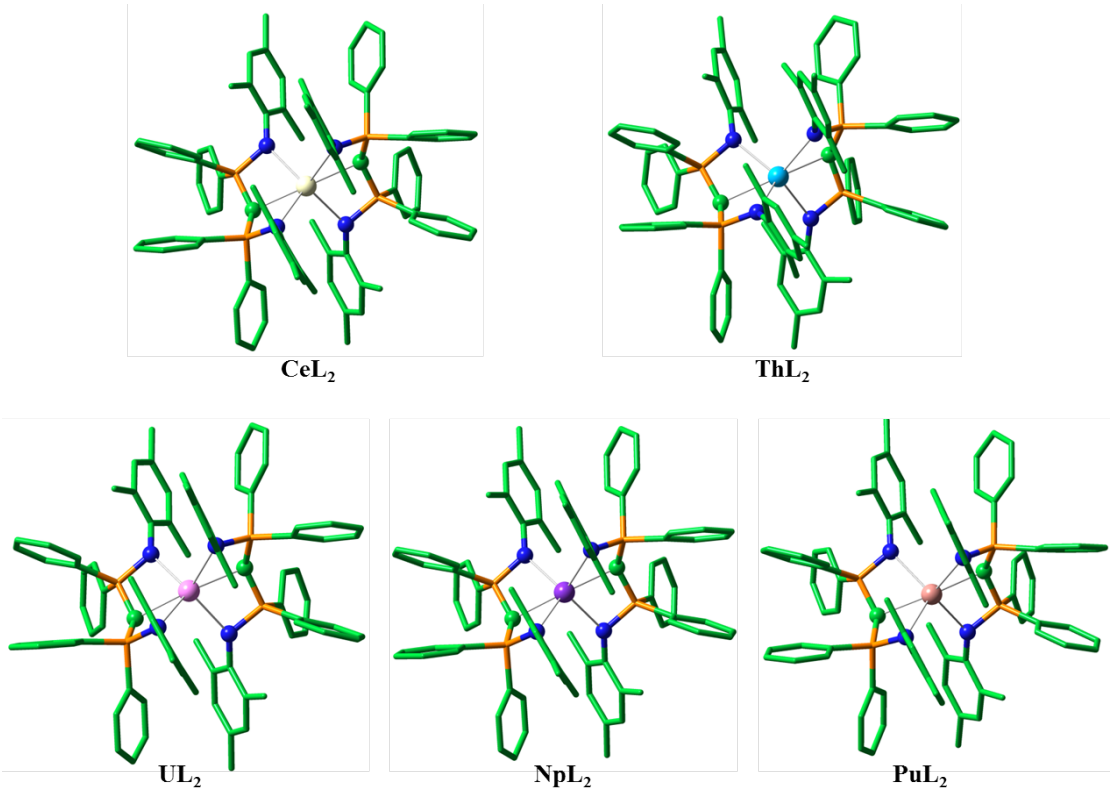

Figure S1. Structures of the ML_2 (M=Ce, Th, U, Np, Pu) complexes. Hydrogen atoms omitted for clarity.

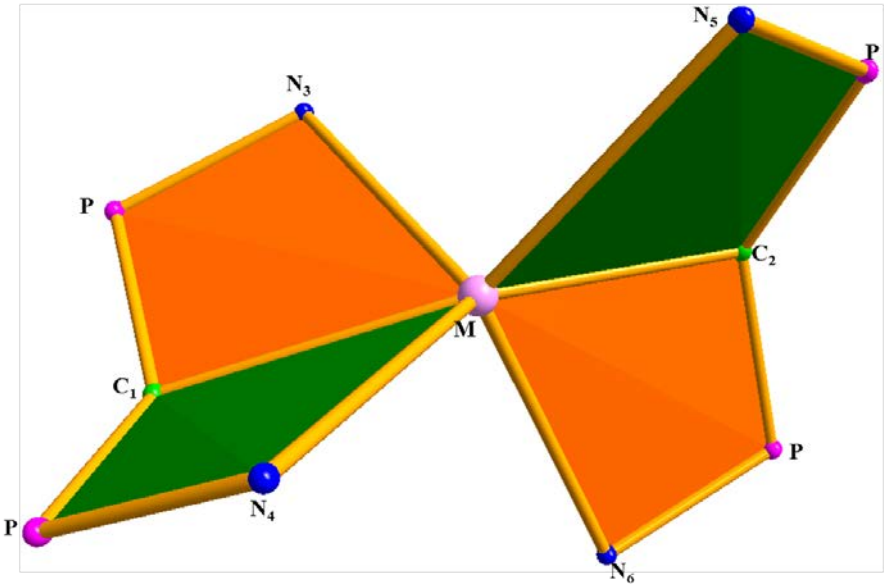

Figure S2. Simplified structure of the ML_2 complex.

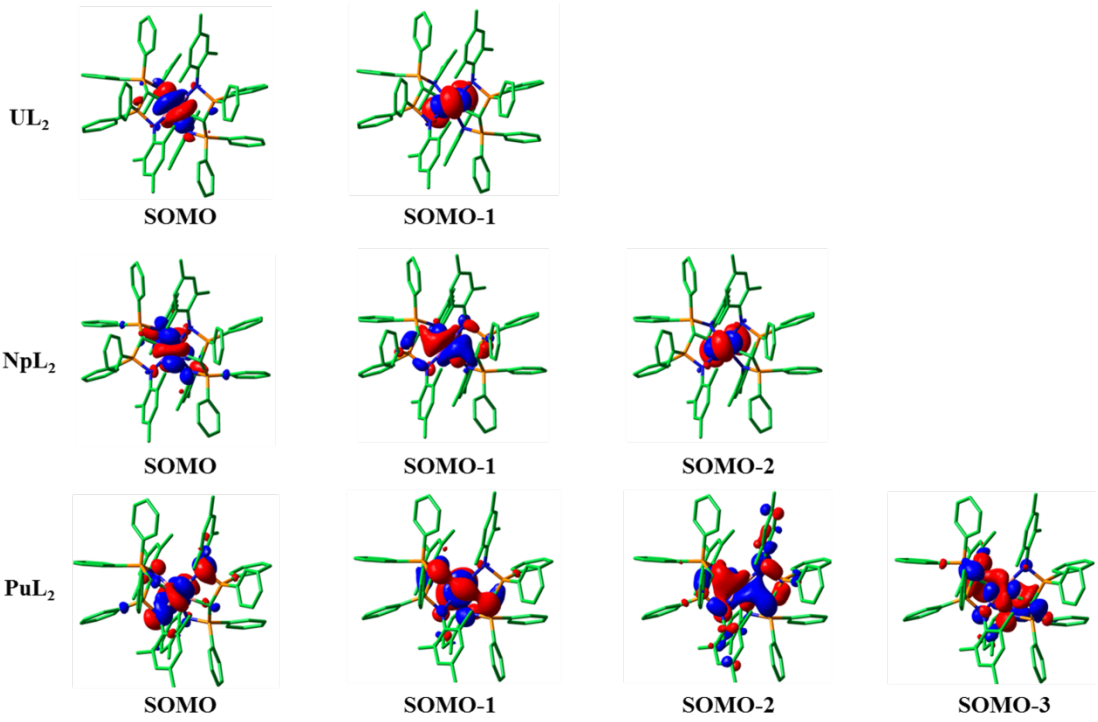

Figure S3. The singly occupied alpha-spin MOs (SOMOs) of the three ML_2 (M=U, Np, Pu) complexes in toluene solution at the BP86/ECP/cc-pVTZ level of theory. The isosurface value of the MOs is established as 0.02 au.

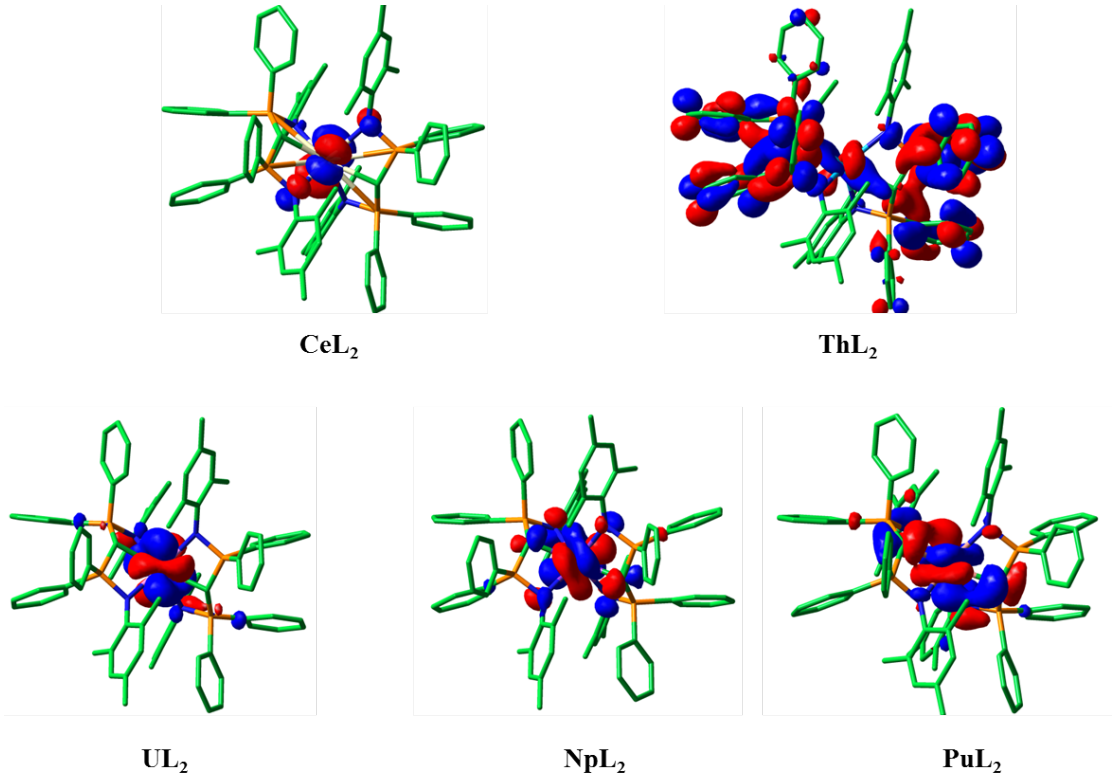

Figure S4. The lowest unoccupied MO (LUMO) of the five ML_2 (M=Ce, Th, U, Np, Pu) complexes in toluene solution at the BP86/ECP/cc-pVTZ level of theory. The isosurface value of the MOs is established as 0.02 au.

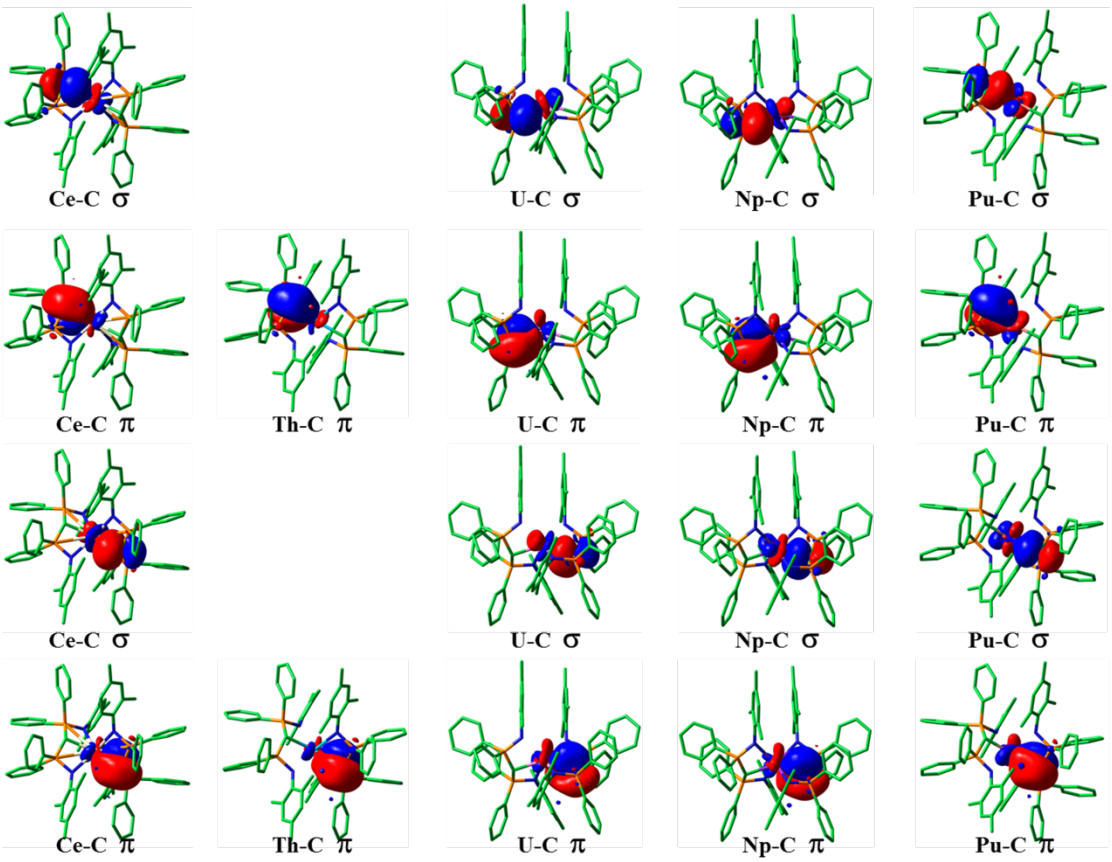

Figure S5. Natural bond orbitals between metal atom and carbon atom of carbene ligands in the ML_2 (M=Ce, Th, U, Np, Pu) complexes. Hydrogen atoms omitted for clarity. The isosurface value of the MOs is established as 0.02 au.

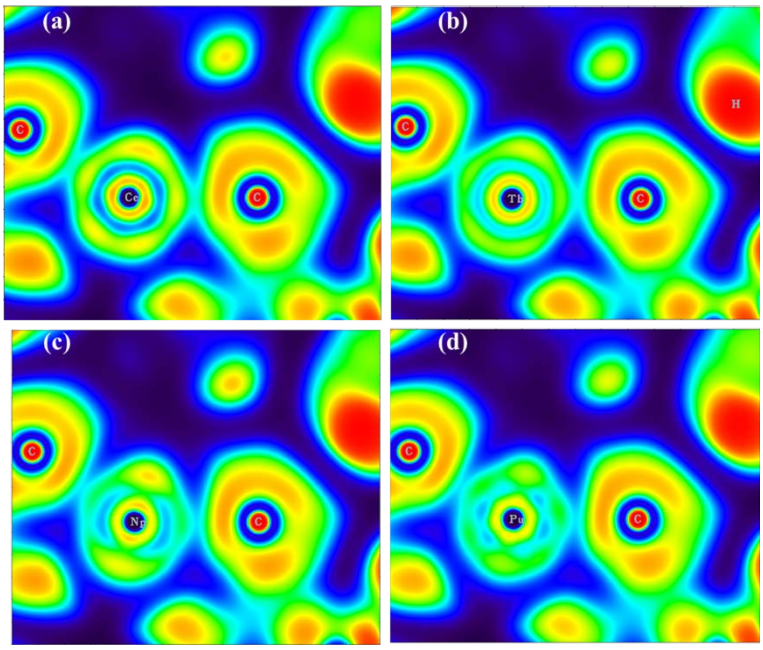

Figure S6. Two dimensional ELF contours of one C_1MC_2 plane containing the two M-C bonds for the complexes (a) CeL_2, (b) ThL_2, (c) NpL_2 and (d) PuL_2.

Table S1. The relative electronic energies (RE, kcal/mol) to each ground state for the UL_2, NpL_2 and PuL_2 complexes.

Complexes	Spin state	RE
UL_2	1	9.85
	3	0.0
NpL_2	2	17.62
	4	0.0
PuL_2	1	33.62
	3	25.01
	5	0.0

Table S2. U-C and U-N bond distances in UL_2 complex in toluene solution using BP86, B3LYP, M06 and M06L functionals with 6-31G(d) and 6-311G(d) basis set.[a]

Bonds	Expt.[b]	BP86[c]	B3LYP[c]	M06[c]	M06L[c]	BP86[d]
U-C_1	2.448(9)	2.438(-0.4%)	2.427(-0.9%)	2.403(-1.9%)	2.434(-0.6%)	2.450(0.1%)
U-C_2	2.427(8)	2.426(0)	2.420(-0.3%)	2.416(-0.5%)	2.423(-0.2%)	2.436(0.4%)
U-N_3	2.501(8)	2.510(0.4%)	2.564(2.5%)	2.527(1.0 %)	2.479(-0.9%)	2.502(0)
U-N_4	2.449(7)	2.472(0.9%)	2.490(1.7%)	2.454(0.2%)	2.453(0.2%)	2.467(0.8%)
U-N_5	2.431(7)	2.492(2.5%)	2.504(3.0%)	2.432(0)	2.441(0.4%)	2.489(2.4%)
U-N_6	2.485(7)	2.511(1.0%)	2.562(3.1%)	2.500(0.6%)	2.567(3.3%)	2.510(1.0%)

[a]The values in parentheses are the relative errors of the calculated bond distances compared to the experimental ones, [b]The data are from ref. 11,[c]Using 6-31G(d) basis set, [d]Using 6-311G(d) basis set.

Table S3. Calculated compositions (%) of metal atom for the singly occupied alpha-spin MOs (SOMOs) of the three ML_2 (M=U, Np, Pu) complexes in toluene solution using BP86, PBE, PBE0 and B3LYP methods.

		BP86	PBE	PBE0	B3LYP
UL_2	SOMO	94.1	94.7	17.4	82.0
	SOMO-1	96.2	96.4	24.1	76.6
NpL_2	SOMO	89.2	89.3	5.9	6.8
	SOMO-1	89.5	90.0	14.5	16.8
	SOMO-2	95.9	96.0	13.7	17.9
PuL_2	SOMO	83.4	83.3	5.9	7.9
	SOMO-1	80.5	80.8	9.2	11.3

Table S4. Calculated compositions (%) of Kohn Sham frontier MOs for the five ML_2 complexes at the BP86/ECP/cc-pVTZ level of theory.

ML_2	MOs	M	C_1	C_2	N_3	N_4	N_5	N_6
	LUMO	94.7			1.1		1.3	
CeL_2	HOMO	17.2	19.8	20.4	2.5	1.2	1.0	3.0
	HOMO-1	5.8	20.1	23.6	7.0	4.2	5.8	8.8
	HOMO-2	9.3	20.5	14.7	7.9	6.0	5.5	6.0
	LUMO	4.7						
ThL_2	HOMO	7.7	24.5	24.2	2.5	1.3	1.1	2.7
	HOMO-1	3.0	21.0	26.8	5.9	3.9	5.8	7.9
	HOMO-2	5.1	24.7	17.6	7.5	5.3	4.6	5.6
	LUMO	93.2						
	SOMO	94.1(5f:93.4)						
	SOMO-1	96.2(5f:93.2)						
UL_2	HOMO	13.1	18.6	22.6	2.7	1.2	0.9	4.0
	HOMO-1	4.5	23.6	20.9	7.1	5.6	6.6	7.5
	HOMO-2	9.9	18.3	15.1	7.4	6.0	6.1	6.4
	LUMO	87.8	1.6	2.0	1.6			1.7
	SOMO	89.2(5f:88.4)			2.2			2.0
	SOMO-1	89.5(5f:87.6)						
NpL_2	SOMO-2	95.9(5f:94.0)						
	HOMO	8.3	16.0	27.1	4.8	5.7	6.7	8.5
	HOMO-1	19.5	21.9	12.6	4.7		1.0	3.0
	HOMO-2	13.4	16.0	12.5	7.7	6.4	6.5	6.4
	LUMO	80.1	3.6	3.6	2.4			2.9
	SOMO	83.4(5f:83.4)		1.2	3.7	4.5		
	SOMO-1	80.5(5f:79.7)	3.4	3.3	1.5	1.1		2.3
PuL_2	SOMO-2	72.6(5f:71.6)	3.7	4.3		2.2	3.3	
	SOMO-3	74.4(5f:73.0)	2.8	2.7	4.6	1.2		5.0
	HOMO	28.4	16.0	18.6	3.4	5.3	6.1	4.2
	HOMO-1	30.5	13.4	10.1	5.2		0.4	4.9
	HOMO-2	28.0	7.7	7.4	7.0	4.7	5.8	6.7