Spectroscopic Characterization of Lanthanum-Mediated Dehydrogenation and C-C bond Coupling of Ethylene

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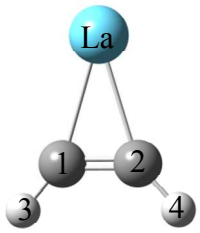
Table S1. Bond lengths (Å) and bond angles (°) of $La(C_2H_2)$ and $La(C_4H_6)$ complexes in various electronic states from DFT/B3LYP calculations. Doublet and quartet states are for neutral species and singlet and triplets for cations. Atomic labels are shown in Figure S1.

		LaC_2H_2		
Parameters	$^2A_1$	$^1A_1$	$^4B_1$	$^3B_1$
C1-C2	1.345	1.347	1.265	1.260
La-C1	2.306	2.253	2.542	2.511
H3-C1-C2	126.7	128.3	149.1	150.7
C1-La-C2	33.91	34.79	28.81	29.06
		$La(C_4H_6)$		
	$^2A'$	$^1A'$	$^4A''$	$^3A''$
C1-C2	1.449	1.451	1.391	1.392
C2-C3	1.385	1.389	1.435	1.426
C1-La	2.510	2.437	2.804	2.720
C2-La	2.671	2.617	2.728	2.670
H5-C1-C2	117.0	116.4	122.1	120.3
H5-C1-H6	111.7	111.4	115.5	114.8
H5-C1-C2-C3	-43.09	-46.20	-19.94	-22.8
H6-C1-C2-C3	-179.2	-178.9	-176.7	-178.8

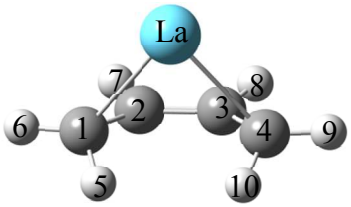
Table S2. Relative energies of stationary points and the imaginary frequencies of transition states along the reaction coordinates of $La(C_2H_2)$ and $La(C_4H_6)$ from CCSD(T)//B3LYP calculations.

Species	Energy (kcal/mol)	Frequency (cm^{-1})
$La(C_2H_2)$ formation		
$La + C_2H_4$	0.00	
IM1	-32.4	
TS1	-2.56	887*i*
IM2	-26.8	
IM2A	-15.1	
TS2	7.81	936*i*
IM3	-7.19	
$La(C_2H_2) + H_2$	-4.69	
$La(C_4H_6)$ formation[a]		
C_2H_4 + IM2	-26.8	
Adduct	-47.7	
TS3	8.0	238*i*
IM4	5.8	
TS4	8.1	346*i*
IM5	-27.2	
IM6 + H_2	-24.6	
TS5 + H_2	8.6	537*i*
$La(C_4H_6) + H_2$	-49.9	

[a] Energies of the stationary points for the formation of $La(C_4H_6)$ are referenced to that of La + 2 C_2H_4.



$La(C_2H_2)$



$La(C_4H_6)$

Figure S1. Structures of $La(C_2H_2)$ and $La(C_4H_6)$.

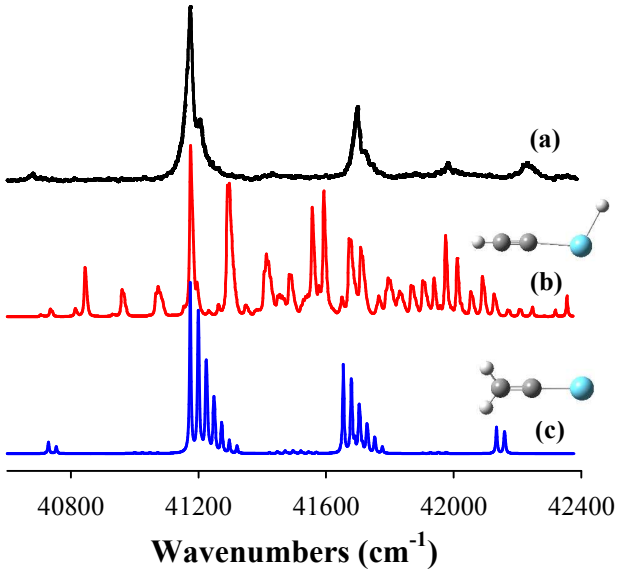


Figure S2. MATI spectrum of $La(C_2H_2)$ (a) and simulations of H-La-CCH ($^1A' \leftarrow {}^2A'$, 300 K) (b) and La-[η^1-(CCH_2)] (($^1A_1 \leftarrow {}^2A_1$, 300 K) (c).

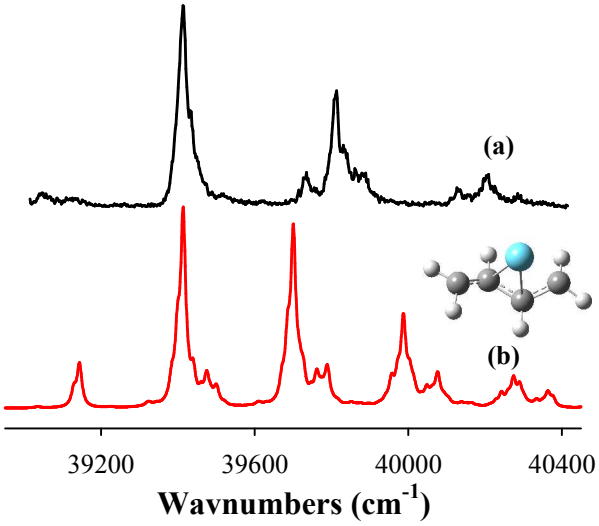


Figure S3. MATI spectrum of $La(C_4H_6)$ (a) and simulation of La-[η^2-(trans-$H_2CCHCHCH_2$) ($^1A \leftarrow {}^2A$, 300 K) (b).

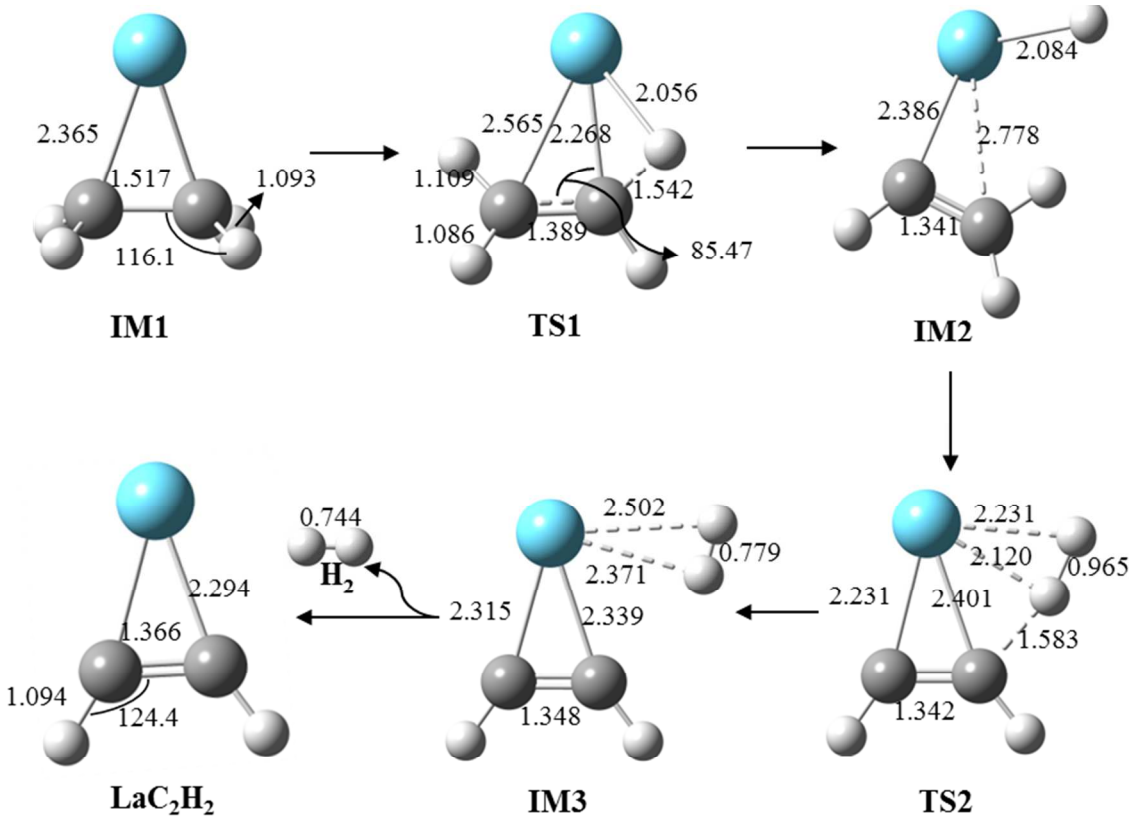


Figure S4. Geometries (Å or degree) of the stationary points along the coordinates of the La + ethylene reaction from DFT/B3LYP calculations. IMn: intermediates, TSn: transitions states.

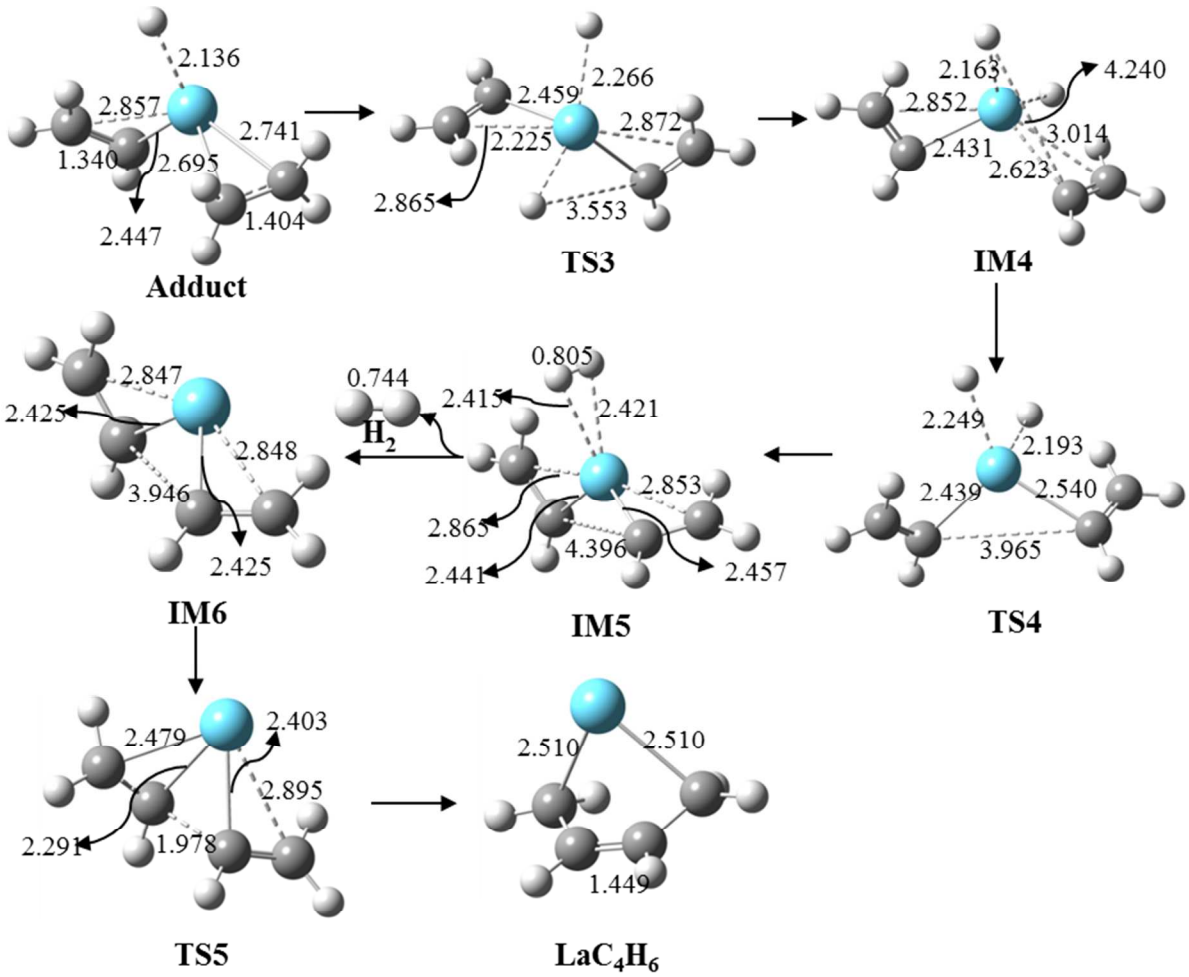


Figure S5. Bond lengths (Å) of the stationary points along the coordinates of the HLa(C_2H_3) (IM2 in Figure S4) + ethylene reaction from DFT/B3LYP calculations. IMn: intermediates, TSn: transitions states.