Spectroscopy and formation of lanthanum-hydrocarbon radicals formed by C-C bond cleavage and coupling of propene

Dilrukshi Hewage,[1] Wenjin Cao,[1] Sudesh Kumari,[1] Ruchira Silva,[1] Tao Hong Li,[2] and Dong-Sheng Yang[1,a]

[1]Department of Chemistry, University of Kentucky, Lexington, KY, 40506-0055

[2]Department of Chemistry, Southwest Forestry University, Kunming 650224, China

a) Corresponding authors: dyang0@uky.edu

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Table S1: Geometric parameters (Å or ^{o}) and relative energies (cm^{-1}) of the $La(CH_2)$ (C_s or C_{2v}), $La(CH_2CHCHCH_2)$ (C_s), and $La[(C(CH_2)_3)]$ (C_{3v} or Cs) complexes in different electronic states from DFT/B3LYP calculations. The atomic numbering is shown in Figure S1.

		$La(CH_2)$		
Parameter	$^2A'$	$^1A'$	$^4A_2$	$^3B_1$
Energy	0	43142	9842	52792
La-C	2.090	2.038	2.417	2.314
C-H1	1.122	1.120	1.099	1.097
C-H2	1.092	1.090	1.099	1.097
∠La-C-H2	90.5	92.5	125.7	125.2
∠La-C-H2	158.2	155.3	125.7	125.2
		$La(CH_2CHCHCH_2)$		
	$^2A'$	$^1A'$	$^4A''$	$^3A''$
Energy	0	40164	10128	49220
La-C1/C4	2.510	2.438	2.804	2.737
La-C2/C3	2.671	2.618	2.729	2.670
C1-C2/C3-C4	1.449	1.451	1.392	1.391
C2-C3	1.386	1.389	1.435	1.438
∠C1-La-C4	74.9	75.7	64.6	66.6
∠La-C1-C2	80.0	80.3	72.4	72.4
∠C1-C2-C3	125.1	123.5	124.2	124.3
		$La(C(CH_2)_3)$		
	$^2A_1$	$^1A_1$	$^4A''$	$^3A''$
Energy	0	41810	16364	54731
La-C1	2.476	2.446	2.712	2.559
La-C2	2.585	2.539	2.559	2.460
La-C3			3.117	2.942
C1-C2	1.431	1.429	1.446	1.453
C1-C3			1.413	1.416
∠La-C1-C2	77.8	76.9	68.3	69.5
∠La-C1-C3			92.8	90.8

Table S2: Total energies (E, hartree) and relative energies (E_{rel}, kcal mol^{-1}) without and with vibrational zero-point energy (ZPE) corrections of the intermediates (IMn) and transition states (TSn) and imaginary frequencies (cm^{-1}) of TSn from DFT/B3LYP calculations.

Species	IMG	E		E_{rel}	
		wo/ ZPE	w/ ZPE	wo/ ZPE	w/ ZPE
La + C_3H_6		-553.492859	-553.413548	0.0	0.0
IM1		-553.537346	-553.460838	-27.9	-29.7
IM2		-553.545788	-553.473801	-33.2	-37.8
IM3		-553.547632	-553.476142	-34.4	-39.3
IM4		-553.544664	-553.468539	-32.5	-34.5
IM5		-553.509884	-553.439249	-10.7	-16.1
TS1	904*i*	-553.522349	-553.449641	-18.5	-22.6
TS2	118*i*	-553.544988	-553.473616	-32.7	-37.7
TS3	929*i*	-553.520593	-553.447557	-17.4	-21.3
TS4	270*i*	-553.497875	-553.426561	-3.2	-8.2
$LaCH_2$ + C_2H_4		-553.492020	-553.420826	0.5	-4.6
La + $2C_3H_6$		-671.438391	-671.279887	0.0	0.0
$LaCH_2$ + C_2H_4 + C_3H_6		-671.437595	-671.287150	0.5	-4.6
IM6 + C_2H_4		-671.450046	-671.298047	-7.3	-11.4
IM7 + C_2H_4		-671.482614	-671.327402	-27.8	-29.8
IM8 + C_2H_4		-671.487724	-671.337613	-31.0	-36.2
IM9 + C_2H_4		-671.487116	-671.336103	-30.6	-35.3
IM10 + C_2H_4		-671.492538	-671.341476	-34.0	-38.6
IM11 + C_2H_4		-671.472927	-671.324520	-21.7	-28.0
IM12 + C_2H_4		-671.449720	-671.300664	-7.1	-13.0
IM13 + C_2H_4		-671.486019	-671.330963	-29.9	-32.0
IM14 + C_2H_4		-671.492377	-671.342259	-33.9	-39.1
IM15 + C_2H_4		-671.471140	-671.323278	-20.6	-27.2
TS5 + C_2H_4	107*i*	-671.449631	-671.297526	-7.1	-11.1
TS6 + C_2H_4	931*i*	-671.457859	-671.305940	-12.2	-16.3

TS7 + C_2H_4	148*i*	-671.485444	-671.335677	-29.5	-35.0
TS8 + C_2H_4	265*i*	-671.483814	-671.333278	-28.5	-33.5
TS9 + C_2H_4	1056*i*	-671.463373	-671.315293	-15.7	-22.2
TS10 + C_2H_4	102*i*	-671.444017	-671.293288	-3.5	-8.4
TS11 + C_2H_4	70*i*	-671.448070	-671.296923	-6.1	-10.7
TS12 + C_2H_4	828*i*	-671.463789	-671.312365	-15.9	-20.4
TS13 + C_2H_4	1099*i*	-671.461203	-671.313605	-14.3	-21.2
La($CH_2CHCHCH_2$) + H_2 + C_2H_4		-671.471836	-671.327804	-21.0	-30.1
La[$C(CH_2)_3$] + H_2 + C_2H_4		-671.472609	-671.328301	-21.5	-30.4

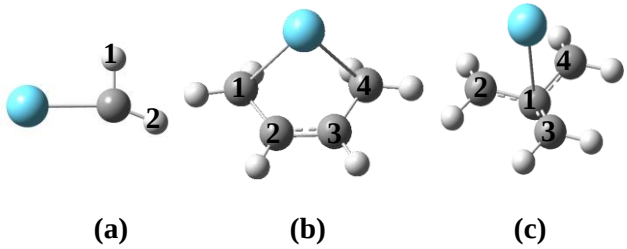

Figure S1. Structures and atomic numbering of La(CH_2) (a), La($CH_2CHCHCH_2$) (b), and La($C(CH_2)_3$) (c) from DFT/B3LPY calculations.