

Alkyl Effects on the Chain Initiation Efficiency of Olefin Polymerization by Cationic Half-sandwich Scandium Catalysts: A DFT Study

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Table S1. Frontier molecular orbital energies and chemical hardness of cationic species **1**, **2**, and **3**.

Species	HOMO energy (eV)	LUMO energy (eV)	Chemical hardness (eV)
1	−9.632	−5.769	3.035
2	−9.142	−5.197	2.999
3	−9.959	−6.095	3.113

Table S2. HOMO and LUMO energies of ethylene (**e**), propene (**p**), 1-hexene (**h**), styrene (**s**), *trans*-butadiene (**b**), *cis*-butadiene (**b'**), *trans*-isoprene (**i**), and *cis*-isoprene (**i'**).

Olefin	HOMO (eV)	LUMO (eV)
e	−7.619	−0.190
p	−7.102	0.136
h	−7.075	0.109
s	−6.394	−1.306
b	−6.585	−1.116
b'	−6.666	−1.143
i	−6.476	−1.034
i'	−6.530	−0.929

Table S3. Computed relative free energies of the stationary points involved in the chain initiation of propylene polymerization catalyzed by species **1**, **2**, and **3**. Energies are relative to **1/2/3** and propylene.

Species	Insertion modes	ΔG (kcal/mol)		
		C	TS	P
1	1,2- <i>re</i>	-2.8 (\mathbf{C}^1_{12p})	7.7 (\mathbf{TS}^1_{12p})	-4.4 (\mathbf{P}^1_{12p})
	1,2- <i>si</i>	-2.8 ($\mathbf{C}^1_{12p'}$)	7.7 ($\mathbf{TS}^1_{12p'}$)	-4.4 ($\mathbf{P}^1_{12p'}$)
	2,1- <i>re</i>	-2.6 (\mathbf{C}^1_{21p})	9.8 (\mathbf{TS}^1_{21p})	-2.9 (\mathbf{P}^1_{21p})
	2,1- <i>si</i>	-2.6 ($\mathbf{C}^1_{21p'}$)	9.8 ($\mathbf{TS}^1_{21p'}$)	-2.9 ($\mathbf{P}^1_{21p'}$)
2	1,2- <i>re</i>	3.0 (\mathbf{C}^2_{12p})	19.1 (\mathbf{TS}^2_{12p})	3.8 (\mathbf{P}^2_{12p})
	1,2- <i>si</i>	3.1 ($\mathbf{C}^2_{12p'}$)	21.6 ($\mathbf{TS}^2_{12p'}$)	4.3 ($\mathbf{P}^2_{12p'}$)
	2,1- <i>re</i>	4.6 (\mathbf{C}^2_{21p})	22.0 (\mathbf{TS}^2_{21p})	9.9 (\mathbf{P}^2_{21p})
	2,1- <i>si</i>	3.1 ($\mathbf{C}^2_{21p'}$)	28.5 ($\mathbf{TS}^2_{21p'}$)	5.0 ($\mathbf{P}^2_{21p'}$)
3	1,2- <i>re</i>	-7.7 (\mathbf{C}^3_{12p})	7.9 (\mathbf{TS}^3_{12p})	-1.0 (\mathbf{P}^3_{12p})
	1,2- <i>si</i>	-7.6 ($\mathbf{C}^3_{12p'}$)	8.1 ($\mathbf{TS}^3_{12p'}$)	-4.3 ($\mathbf{P}^3_{12p'}$)
	2,1- <i>re</i>	-9.1 (\mathbf{C}^3_{21p})	11.7 (\mathbf{TS}^3_{21p})	-2.6 (\mathbf{P}^3_{21p})
	2,1- <i>si</i>	-8.2 ($\mathbf{C}^3_{21p'}$)	19.8 ($\mathbf{TS}^3_{21p'}$)	0.6 ($\mathbf{P}^3_{21p'}$)

Table S4. Computed relative free energies of the stationary points involved in the chain initiation of 1-hexene polymerization catalyzed by species **1**, **2**, and **3**. Energies are relative to **1/2/3** and 1-hexene.

Species	Insertion modes	ΔG (kcal/mol)		
		C	TS	P
1	1,2- <i>re</i>	-4.7 (\mathbf{C}^1_{12h})	7.6 (\mathbf{TS}^1_{12h})	-3.8 (\mathbf{P}^1_{12h})
	1,2- <i>si</i>	-4.7 ($\mathbf{C}^1_{12h'}$)	7.6 ($\mathbf{TS}^1_{12h'}$)	-3.8 ($\mathbf{P}^1_{12h'}$)
	2,1- <i>re</i>	-4.3 (\mathbf{C}^1_{21h})	8.5 (\mathbf{TS}^1_{21h})	-2.8 (\mathbf{P}^1_{21h})
	2,1- <i>si</i>	-4.0 ($\mathbf{C}^1_{21h'}$)	9.2 ($\mathbf{TS}^1_{21h'}$)	-1.9 ($\mathbf{P}^1_{21h'}$)
2	1,2- <i>re</i>	2.8 (\mathbf{C}^2_{12h})	18.9 (\mathbf{TS}^2_{12h})	4.6 (\mathbf{P}^2_{12h})
	1,2- <i>si</i>	2.6 ($\mathbf{C}^2_{12h'}$)	23.2 ($\mathbf{TS}^2_{12h'}$)	4.8 ($\mathbf{P}^2_{12h'}$)
	2,1- <i>re</i>	3.1 (\mathbf{C}^2_{21h})	22.6 (\mathbf{TS}^2_{21h})	12.2 (\mathbf{P}^2_{21h})
	2,1- <i>si</i>	2.2 ($\mathbf{C}^2_{21h'}$)	27.1 ($\mathbf{TS}^2_{21h'}$)	5.3 ($\mathbf{P}^2_{21h'}$)
3	1,2- <i>re</i>	-9.6 (\mathbf{C}^3_{12h})	7.3 (\mathbf{TS}^3_{12h})	-2.5 (\mathbf{P}^3_{12h})
	1,2- <i>si</i>	-9.2 ($\mathbf{C}^3_{12h'}$)	7.2 ($\mathbf{TS}^3_{12h'}$)	-2.9 ($\mathbf{P}^3_{12h'}$)
	2,1- <i>re</i>	-10.4 (\mathbf{C}^3_{21h})	12.7 (\mathbf{TS}^3_{21h})	-3.8 (\mathbf{P}^3_{21h})
	2,1- <i>si</i>	-10.2 ($\mathbf{C}^3_{21h'}$)	19.3 ($\mathbf{TS}^3_{21h'}$)	-0.3 ($\mathbf{P}^3_{21h'}$)

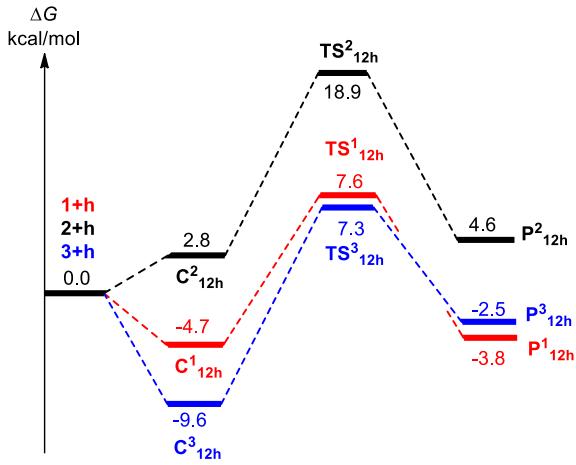


Figure S1. Computed free energy profiles for the chain initiation of 1-hexene polymerization catalyzed by cationic species **1**, **2**, and **3**. Free energies are relative to **1/2/3** and 1-hexene.

Table S5. Computed relative free energies of the stationary points involved in the chain initiation of styrene polymerization catalyzed by species **1**, **2**, and **3**. Energies are relative to **1/2/3** and styrene.

Species	Insertion modes	ΔG (kcal/mol)		
		C	TS	P
1	1,2- <i>si</i>	-4.5 ($\mathbf{C}^1_{12s'}$)	10.8 ($\mathbf{TS}^1_{12s'}$)	-0.6 ($\mathbf{P}^1_{12s'}$)
	1,2- <i>re</i>	-4.7 (\mathbf{C}^1_{12s})	11.1 (\mathbf{TS}^1_{12s})	1.4 (\mathbf{P}^1_{12s})
	2,1- <i>si</i>	-0.6 ($\mathbf{C}^1_{21s'}$)	5.5 ($\mathbf{TS}^1_{21s'}$)	-10.1 ($\mathbf{P}^1_{21s'}$)
	2,1- <i>re</i>	-4.6 (\mathbf{C}^1_{21s})	14.7 (\mathbf{TS}^1_{21s})	-2.2 (\mathbf{P}^1_{21s})
2	1,2- <i>si</i>	2.6 ($\mathbf{C}^2_{12s'}$)	22.5 ($\mathbf{TS}^2_{12s'}$)	6.9 ($\mathbf{P}^2_{12s'}$)
	1,2- <i>re</i>	1.5 (\mathbf{C}^2_{12s})	24.3 (\mathbf{TS}^2_{12s})	8.0 (\mathbf{P}^2_{12s})
	2,1- <i>si</i>	1.7 ($\mathbf{C}^2_{21s'}$)	22.3 ($\mathbf{TS}^2_{21s'}$)	9.3 ($\mathbf{P}^2_{21s'}$)
	2,1- <i>re</i>	15 (\mathbf{C}^2_{21s})	28.5 (\mathbf{TS}^2_{21s})	10.6 (\mathbf{P}^2_{21s})
3	1,2- <i>si</i>	-9.2 ($\mathbf{C}^3_{12s'}$)	16.1 ($\mathbf{TS}^3_{12s'}$)	1.2 ($\mathbf{P}^3_{12s'}$)
	1,2- <i>re</i>	-11.4 (\mathbf{C}^3_{12s})	12.0 (\mathbf{TS}^3_{12s})	-7.2 (\mathbf{P}^3_{12s})
	2,1- <i>si</i>	-10.9 ($\mathbf{C}^3_{21s'}$)	4.9 ($\mathbf{TS}^3_{21s'}$)	-11.9 ($\mathbf{P}^3_{21s'}$)
	2,1- <i>re</i>	-9.2 (\mathbf{C}^3_{21s})	15.2 (\mathbf{TS}^3_{21s})	-6.8 (\mathbf{P}^3_{21s})

Table S6. Computed relative free energies of the stationary points involved in the chain initiation of butadiene polymerization catalyzed by species **1**, **2**, and **3**. Energies are relative to **1/2/3** and *trans*-butadiene. The symbol “/” means the failure to locate the stationary points.

Species	Insertion modes	ΔG (kcal/mol)		
		C	TS	P
1	<i>trans</i> -1,2- <i>si</i>	-3.7	8.9	-0.4
	<i>trans</i> -1,2- <i>re</i>	-3.7	12.1	1.0
	<i>trans</i> -1,4- <i>supine</i>	-2.2 (C ¹ _{14b})	4.6 (TS ¹ _{14b})	-19.6 (P ¹ _{14b})
	<i>trans</i> -1,4- <i>prone</i>	-3.9	13.1	-17.4
	<i>cis</i> -1,2- <i>si</i>	-1.1	11.4	1.1
	<i>cis</i> -1,2- <i>re</i>	-0.4	12.4	1.0
	<i>cis</i> -1,4- <i>supine</i>	1.7	13.9	-18.3
	<i>cis</i> -1,4- <i>prone</i>	-1.6 (C ¹ _{14b'})	2.4 (TS ¹ _{14b'})	-20.1 (P ¹ _{14b'})
2	<i>trans</i> -1,2- <i>si</i>	3.6	23.2	7.9
	<i>trans</i> -1,2- <i>re</i>	2.7	24.3	8.7
	<i>trans</i> -1,4- <i>supine</i>	6.5 (C ² _{14b})	19.2 (TS ² _{14b})	-5.2 (P ² _{14b})
	<i>trans</i> -1,4- <i>prone</i>	/	/	/
	<i>cis</i> -1,2- <i>si</i>	6.6	23.9	9.3
	<i>cis</i> -1,2- <i>re</i>	6.0	25.0	9.7
	<i>cis</i> -1,4- <i>supine</i>	7.2	28.7	3.3
	<i>cis</i> -1,4- <i>prone</i>	6.0 (C ² _{14b'})	17.4 (TS ² _{14b'})	-7.0 (P ² _{14b'})
3	<i>trans</i> -1,2- <i>si</i>	-8.8	17.3	1.8
	<i>trans</i> -1,2- <i>re</i>	-8.8	16.1	-5.9
	<i>trans</i> -1,4- <i>supine</i>	-8.8 (C ³ _{14b})	6.76 (TS ³ _{14b})	-21.66 (P ³ _{14b})
	<i>trans</i> -1,4- <i>prone</i>	-8.8	11.1	-20.9
	<i>cis</i> -1,2- <i>si</i>	-5.5	15.8	-8.5
	<i>cis</i> -1,2- <i>re</i>	-0.5	12.5	-7.8
	<i>cis</i> -1,4- <i>supine</i>	-5.5	6.5	-18.2
	<i>cis</i> -1,4- <i>prone</i>	-4.3 (C ³ _{14b'})	0.2 (TS ³ _{14b'})	-21.2 (P ³ _{14b'})

Table S7. Computed relative free energies of the stationary points involved in the chain initiation of isoprene polymerization catalyzed by species **1**, **2**, and **3**. Energies are relative to **1/2/3** and *trans*-isoprene. The symbol “/” means the failure to locate the stationary points.

species	Insertion modes	ΔG (kcal/mol)		
		C	TS	P
1	<i>trans</i> -4,3- <i>si</i>	-3.9	12.1	2.1
	<i>trans</i> -1,2- <i>re</i>	-3.5	13.6	4.2
	<i>trans</i> -1,4- <i>supine</i>	-1.5 (C ¹ _{14i})	5.8 (TS ¹ _{14i})	-20.2 (P ¹ _{14i})
	<i>trans</i> -1,4- <i>prone</i>	-5.2	16.2	-18.0
	<i>cis</i> -4,3- <i>si</i>	-0.7	13.2	2.01
	<i>cis</i> -4,3- <i>re</i>	-0.8	14.0	-2.2
	<i>cis</i> -1,4- <i>supine</i>	0.5	12.1	-20.2
	<i>cis</i> -1,4- <i>prone</i>	-1.2 (C ¹ _{14i'})	3.7 (TS ¹ _{14i'})	-19.1 (P ¹ _{14i'})
2	<i>trans</i> -4,3- <i>si</i>	3.8	24.0	8.8
	<i>trans</i> -4,3- <i>re</i>	3.4	25.1	8.6
	<i>trans</i> -1,4- <i>supine</i>	7.6 (C ² _{14i})	21.0 (TS ² _{14i})	-2.3 (P ² _{14i})
	<i>trans</i> -1,4- <i>prone</i>	/	/	/
	<i>cis</i> -4,3- <i>si</i>	6.5	24.3	9.3
	<i>cis</i> -4,3- <i>re</i>	5.5	26.4	9.6
	<i>cis</i> -1,4- <i>supine</i>	5.3	27.4	2.9
	<i>cis</i> -1,4- <i>prone</i>	8.0 (C ² _{14i'})	20.4 (TS ² _{14i'})	-3.4 (P ² _{14i'})
3	<i>trans</i> -4,3- <i>si</i>	-9.6	17.4	2.3
	<i>trans</i> -4,3- <i>re</i>	-9.9	11.9	1.9
	<i>trans</i> -1,4- <i>supine</i>	-8.8 (C ³ _{14i})	7.7 (TS ³ _{14i})	-20.6 (P ³ _{14i})
	<i>trans</i> -1,4- <i>prone</i>	-5.5	13.0	-20.8
	<i>cis</i> -4,3- <i>si</i>	-8.3	15.2	-7.7
	<i>cis</i> -4,3- <i>re</i>	-8.3	11.3	-8.5
	<i>cis</i> -1,4- <i>supine</i>	-8.3	4.5	-19.4
	<i>cis</i> -1,4- <i>prone</i>	-4.4 (C ³ _{14i'})	1.9 (TS ³ _{14i'})	-19.6 (P ³ _{14i'})

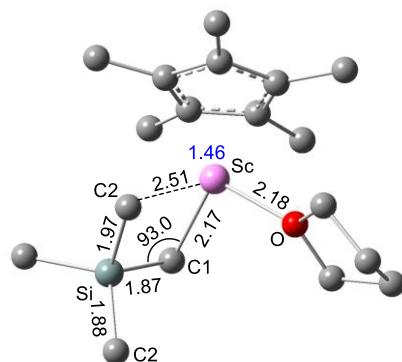


Figure S2. Geometric structures (distances in Å and angles in degree) of cationic half-sandwich scandium alkyl species **1'**.

Table S8. Computed relative free energies of the stationary points involved in the chain initiations of olefin polymerization by species **1'**. Energies are relative to the energy sum of **1'** and related monomer.

Monomers	ΔG (kcal/mol)		
	C	TS	P
ethylene	8.2	15.4	-7.4
propylene	8.2	20.9	1.2
1-hexene	8.5	19.6	1.4
styrene	6.1	17.5	-7.6
<i>cis</i> -butadiene	15.7	18.0	-13.3
<i>cis</i> -isoprene	14.2	18.1	-10.1