Supporting Information

Computational Study of the Reactivity of Rare-Earth/Phosphorus Lewis

Pairs toward Polymerization of Conjugated Polar Alkenes

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Computational details

Considering relatively large molecular size of the intermolecular rare-earth/phosphorus (RE/P) Lewis pair system (2 and 3), the two-layer ONIOM (B3PW91:HF) approach,^{S1} as implanted in Gaussian 16 program,^{S2} was used for their geometrical optimizations and subsequent analytic frequency calculations. In the ONIOM(B3PW91:HF) calculations, the substituent 2,6-'Bu₂-C₆H₃ in the ancillary ligand is placed in the outside layer treated by the Hartree-Fock (HF) method for saving computational time and consideration of steric effects (Figure S1). The other atoms, including those in the monomer molecules, constitute the inner layer. The common method of calculating the ONIOM energy of whole system is given in the previous work.^{S3} In the HF calculation, the LANL2MB basis set was used for C and H atoms. In the B3PW91 calculation, S4-S6 the 6-31G* basis set was considered for C, H, O and P atoms. The Sc atoms were treated by the Stuttgart/Dresden effective core potential (ECP) and the associated basis sets.^{S7-S8} All optimizations were carried out in the gas phase without any symmetry constraint. The transition state structures are shown to connect the reactant and product on either side via intrinsic reaction coordinate (IRC) following. This basis set is denoted as "BSI". For the intramolecular rare-earth/phosphorus (RE/P) Lewis pair system (1, 4-9), the B3PW91 hybrid exchange-correlation functional was utilized for geometry optimization and the 6-31G* basis set was considered for C, H, O, N and P atoms. The Sc atoms were treated by the Stuttgart/Dresden effective core potential (ECP) and the associated basis sets. This basis set is denoted as "BSII". Such a computational strategy has been widely used for the study of organometallic systems.^{S9-} ^{S11} To obtain more reliable relative energies, the single-point calculations of optimized structures were carried out at the level of M06^{S12}/BSIII, taking into account solvation effect of toluene with the SMD^{S13} solvation model. In the BSIII, the 6-311G (d, p) basis set was used for nonmetal atoms, while the basis sets together with associated pseudopotentials for Sc atoms are the same as that in geometry optimization. Therefore, unless otherwise mentioned, the free energy (ΔG , 298.15 K, 1 atm) in solution, which was used for description of energy profiles, was obtained from the solvation single-point calculation and the gas-phase Gibbs free energy correction. Considering the overestimation of the entropy contribution, the free energies were corrected by +2.6 (or -2.6) kcal/mol for one-to-two (or two-to-one) molecular conversions, based on the freevolume theory.^{S14} The 3D molecular structures displayed in this paper were drawn by using CYLview.^{S15}

All the ETS-NOCV^{S16} calculations were performed by employing the B3LYP-D3/DZP ^{S17} level of theory as implemented in the Amsterdam density functional (ADF) package.^{S18} The relativistic effect of Sc atom was considered by the zero-order regular approximation (ZORA).^{S19} The extended transition state (ETS) method decomposes the total interaction energy (ΔE_{int}) into four chemically relevant components, that is, $\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{orbital} + \Delta E_{disp}$, in which ΔE_{Pauli} , ΔE_{elstat} , $\Delta E_{orbital}$, and ΔE_{disp} represent the Pauli repulsion, electrostatic interaction, orbital interaction, and dispersion interaction, respectively. Furthermore, the $\Delta E_{orbital}$ term could be attributed to the specific orbital interaction in terms of the natural orbital for chemical valence (NOCV) eigenvalues. The ETS-NOCV approach offers a technique to analyze the orbital interaction through the deformation density.



Ln = Sc(2), La(3)

Figure S1. Structure of Lewis acid investigated. The gray part is involved in the low-level calculation during the optimization.



Figure S2. Computed energy profiles for $2/PEt_3$ mediated monometallic pathway for the insertion of MMA. Free energies are relative to isolated reactants.



Figure S3. Computed energy profiles for $3/PEt_3$ mediated monometallic pathway for the insertion of MMA. Free energies are relative to isolated reactants.



Figure S4. Geometric parameters (distances in Å) of 2A, 2C, 3A, 3C, 2TS_{DE} and 3TS_{DE}.

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