

RESEARCH ARTICLE

View Article Online
View Journal | View Issue



Cite this: *Inorg. Chem. Front.*, 2020, 7, 4600

A computational study of the reactivity of rare-earth/phosphorus Lewis pairs toward polymerization of conjugated polar alkenes†

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The polymerization mechanism of methyl methacrylate (MMA) catalyzed by rare-earth/phosphorus (RE/P) Lewis pairs has been systematically studied through density functional theory (DFT) calculations. Having achieved an agreement between theory and experiment, it is found that the polymerization of MMA mediated by intermolecular RE/P Lewis pairs mainly follows the bimetallic mechanism, while the mono-metallic pathway could not be excluded in the case of a La analogue. In comparison with phenyl phosphorus as a Lewis base, the higher activity of cyclohexyl phosphorus toward MMA polymerization could be ascribed to the electron-donation ability, rendering more electron flow in the addition reaction. Besides, a computational modelling of analogous intramolecular RE/P systems indicates that the size of the central metal and the length of the chain connecting Lewis pairs play an important role in the catalytic activity.

Received 2nd September 2020,
Accepted 5th October 2020
DOI: 10.1039/d0qi01067g
rsc.li/frontiers-inorganic

Introduction

Polymers derived from conjugated polar monomers have attracted much attention because an unsaturated bond and a polar functional group remain in the polymer chain and thus are capable of meeting specific applications or undergoing further functionalization. Besides the radical and anionic polymerization methods,^{1,2} the catalytic coordination insertion³ and conjugate addition such as group-transfer polymerization (GTP)⁴ and Lewis pair polymerization (LPP)⁵ are also useful for the synthesis of such polymers. The former is usually problematic in controllability, and transition-metal catalyzed coordination insertion is known to suffer from poisoning by the functional group.³ In the context of conjugate

addition polymerization, LPP has attracted recent interest, thanks to the cooperation between the Lewis acid and base in chain initiation, propagation, and termination. In view of the cooperative behavior in LPP, the polymerization activity could be regulated by both the Lewis acid and Lewis base and thus showed rich chemistry, as demonstrated by previous works.⁶ Since the first LPP work reported by Chen and coworkers in 2010,^{5a} significant progress has been made in this field.^{5b–h} In Chen's primary work, Al(C₆F₅)₃-based Lewis pairs were demonstrated to catalyze the polymerization of conjugated polar alkenes and a high molecular weight polymerization product was obtained. Hong⁷ and Zhang^{6,8} reported a series of main-group FLP catalysts for the polymerization of a wide range of conjugated polar monomers, some of which showed living and controllable features. In spite of group 4 metal involved ion-pair polymerization,⁹ transition-metal containing LPP is not well established.^{10,11} Therefore, a highly active transition-metal containing LPP system is still a worthy challenge, which could be improved by modulation of Lewis acids and bases.

It is known that rare-earth metal complexes were reported to not only mediate the synthesis of small molecules^{12,13b} but also catalyze the polymerizations of non-polar or polar olefins.¹³ To regulate the acidity of Lewis acids in LPP, Xu *et al.* developed intramolecular and intermolecular rare-earth/phosphorus (RE/P) Lewis pairs (Chart 1) for polymerizing conjugated polar monomers such as methyl methacrylate (MMA).¹⁴ Their works demonstrated that the polymerization activity is significantly affected by rare-earth metals and Lewis bases. The authors observed that La complex **3** showed higher activity

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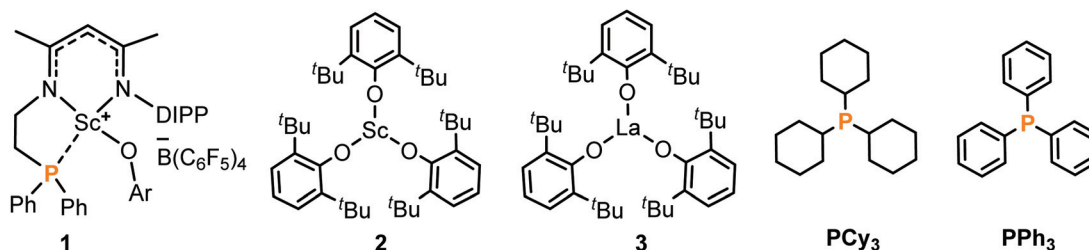
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†Electronic supplementary information (ESI) available: Computational details, figures showing the monometallic pathway and geometrical parameters of key stationary points, and optimized Cartesian coordinates of all stationary points together with their single-point energies (a.u.) in solution and the imaginary frequencies (cm⁻¹) of transition states (XYZ file). See DOI: 10.1039/d0qi01067g

Lewis Pairs

Experimentally observed reactivity trend: La (3) > Sc (2); PCy₃ > PPh₃Chart 1 Rare-earth metal Lewis pairs reported for LPP.¹⁴

than Sc analogue 2 and Lewis base PCy₃ exhibited higher activity compared with PPh₃. However, the origin of such activity discrepancy remained unclear.

A few theoretical mechanistic works on the mechanism of MMA polymerization by main-group FLPs have been documented.^{15–17} Chen and Cavallo *et al.* reported the calculations on the formation of the zwitterionic active species in LPP of MMA and found that NHC-based zwitterions were more stable compared with PR₃-based analogues and the MMA addition favorably followed the bimetallic pathway.¹⁵ They also conducted mechanistic studies on the chain propagation and termination of LPP of conjugated polar monomers catalyzed by Al-based FLPs and found that intramolecular backbiting cyclization might account for the chain-termination,¹⁶ being in line with separate works by Lu *et al.*¹⁸ Taton and coworkers computationally demonstrated a cooperative mechanism in MMA polymerization catalyzed by a PR₃/Me₃SiNTf₂ Lewis pair.¹⁷ In spite of these mechanistic studies on the main-group LPP, the theoretical study of such 1,4-conjugate addition polymerization catalyzed by RE/P Lewis pairs, to the best of our knowledge, has not been reported to date.

Stimulated by our previous theoretical works on rare-earth metal catalyzed polymerizations,¹⁹ we are interested in the molecular-level factors governing the polymerization activity observed in the RE/P systems, with the purpose of elucidating the related reaction mechanism. It is generally considered that, in the LPP, stronger acidity of the Lewis acid could induce higher activity. Our primary calculation based on the HSAB (hard and soft acids/bases) principle and DFT indicates that 2 has higher chemical hardness and thus stronger Lewis acidity in comparison with 3 (0.20 vs. 0.16 eV).^{19c,20} However, as aforementioned, the activity of 3 is higher than that of 2,^{14b} which drove us to explore the origin of such activity discrepancy. In the present work, DFT calculations have been conducted for the intramolecular and intermolecular RE/P Lewis pairs (Chart 1) toward the polymerization of MMA, which is a commercially important and scientifically interesting commodity acrylic monomer. On the basis of the clarification of the related polymerization mechanism, the origin of different activity between Sc and La analogues and the effects of different Lewis bases have been elucidated, which could

provide a piece of information for the development of LPP systems.

Results and discussion

Polymerization mechanism

It is generally considered that FLP (frustrated Lewis pair) mediated polymerization of conjugated polar alkenes follows Michael addition to grow a polymer chain rather than coordination insertion or single electron transfer.^{15,16} In the case of intramolecular Lewis pairs such as 1⁺ (Chart 1), as shown in Fig. 1, the reaction starts with the coordination of monomer MMA and then 1,4-addition (1a_{coord} → 1a_{TS} → 1a) could occur to provide 1a with a newly formed P–C bond. While the incoming monomer approaches the metal center of the active species 1a, the 1,4-addition reaction repeatedly takes place to form C–C bonds and the polymerization could smoothly occur. Such a C–C formation process has a moderate energy barrier (19.6 kcal mol^{−1}) and is exergonic (Fig. 1), suggesting a feasible polymerization event.

In the case of the intermolecular RE/P Lewis pair (Chart 1), the monometallic and bimetallic mechanisms have been considered, respectively. As shown in Fig. 2, starting with 2C, the energy barrier for the monometallic mechanism (2TS_{de}, 34.9 kcal mol^{−1}, see Fig. S2 in the ESI† for the complete monometallic pathway) is significantly higher than that for the bimetallic pathway (2TS_{de}, 20.2 kcal mol^{−1}), showing a preference for the bimetallic reaction manner. Although the enchainment of the second MMA is slightly endergonic (conversion of 2C to 2F), the addition of the third MMA is exergonic (2F to 2H), suggesting an energetically favorable enchainment process.

To obtain better understanding of the priority of the bimetallic mechanism, the distortion/interaction analyses²¹ have been comparatively performed for the key transition states 2TS_{de} and 2TS_{de}. During such analyses, the energies of the monomer moiety and the remaining metal complex (two fragments) in the TS geometries were evaluated *via* single-point calculations. Such single-point energies of the fragments and the energy of the TS were used to estimate the interaction

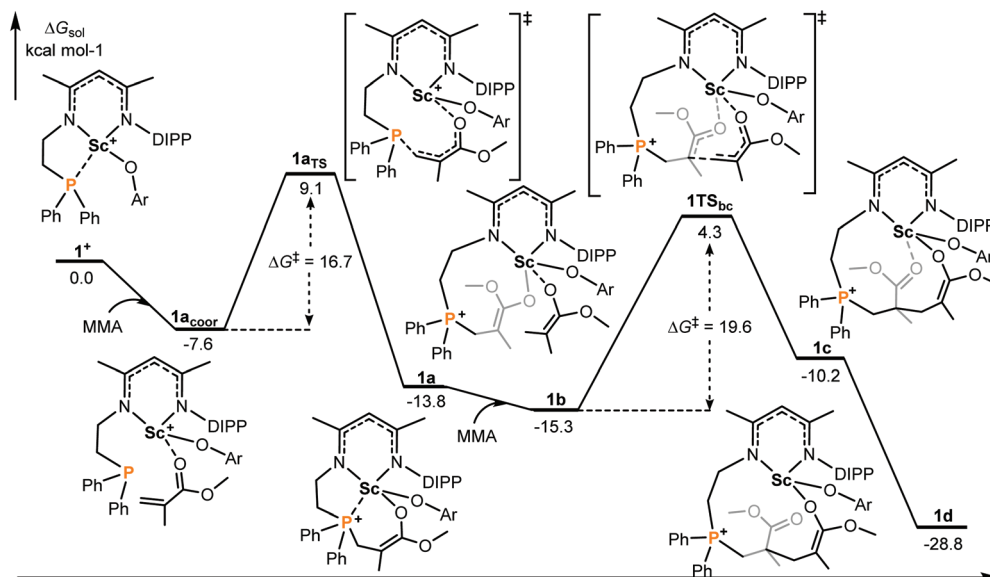


Fig. 1 Computed energy profiles (M06(SMD)/6-311G**nSDD//B3PW91/6-31G**nSDD, see the ESI† for more details for 1^+ mediated polymerization of MMA (intramolecular RE/P systems). Free energies (kcal mol⁻¹) are relative to isolated reactants.

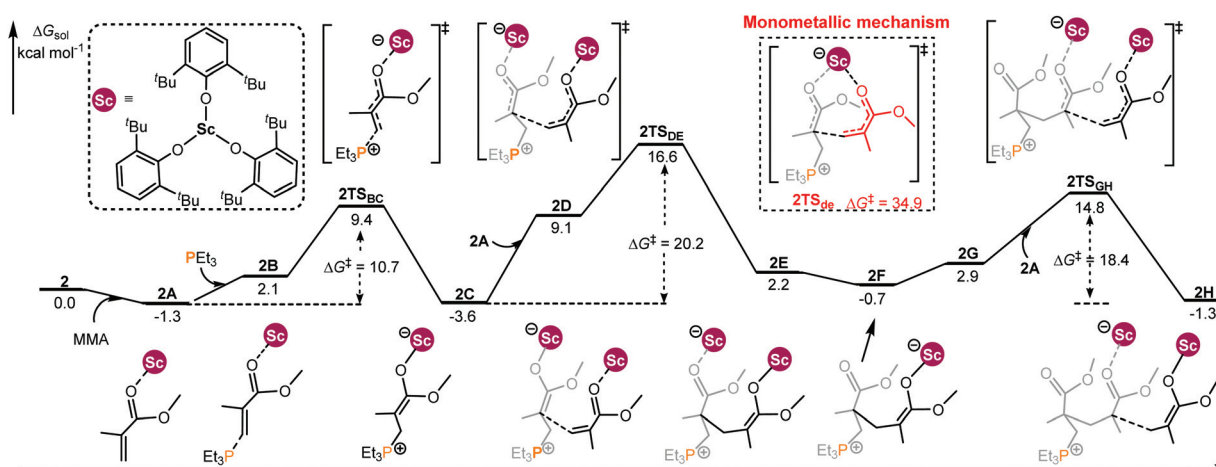


Fig. 2 Computed energy profiles for 2/ PET_3 mediated (intermolecular RE/P systems) bimetallic enchainment of MMA. Free energies (kcal mol⁻¹) are relative to isolated reactants.

energy ΔE_{int} . These energies, together with the energies of the respective fragments in their optimal geometry, allow for the estimation of the deformation energies of the two fragments, $\Delta E_{\text{def}}(\text{cat.})$ and $\Delta E_{\text{def}}(\text{mono.})$. As the energy of the TS, ΔE_{TS} , is evaluated with respect to the energy of the two separated fragments, the relation $\Delta E_{\text{TS}} = \Delta E_{\text{int}} + \Delta E_{\text{def}}(\text{cat.}) + \Delta E_{\text{def}}(\text{mono.})$ holds. As shown in Fig. 3, the total deformation energy ΔE_{def} in 2TS_{de} is 60.7 (12.8 + 47.9) kcal mol⁻¹, which could be hardly balanced out by its ΔE_{int} (−12.3 kcal mol⁻¹), leading to high ΔE_{TS} of 48.4 kcal mol⁻¹. However, the ΔE_{def} in 2TS_{DE} (31.9 kcal mol⁻¹) is compensated by an interaction energy of −9.2 kcal mol⁻¹, leading to ΔE_{TS} = 22.7 kcal mol⁻¹, which is lower than that for 2TS_{de} . As a consequence, the less steric hindrance inducing smaller deformations of the metal complexes could

account for the higher stability of 2TS_{DE} . A comparison of the structures of the two transition states indicates that the C1–C2 distance in 2TS_{de} is obviously shorter than that in 2TS_{DE} (2.09 vs. 2.17 Å, Fig. 3), suggesting a more crowded environment at the reaction center in 2TS_{de} . This is also consistent with the greater deformations in the 2TS_{de} case.

Metal effect on catalyst activity

It was reported that different metal centers led to a significant activity difference in the intermolecular FLP system.^{14b} This drove us to computationally compare the MMA addition mediated by an analogous complex such as 3 (La complex) with the same ligand as that in 2 (Sc complex, Chart 1). Like the 2/ PET_3 system, it is also found that, in the case of 3/ PET_3 ,

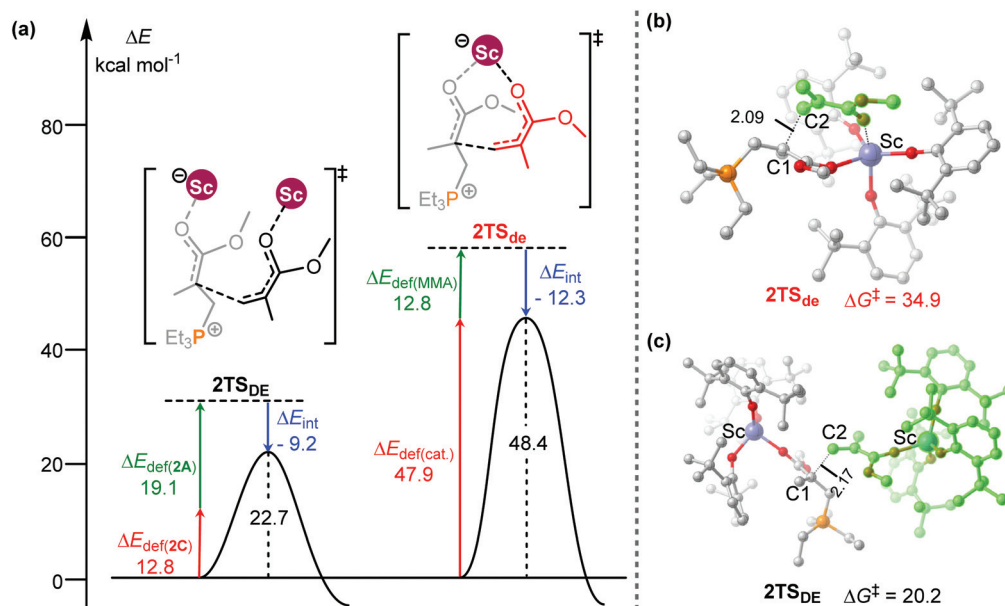


Fig. 3 (a) Distortion/interaction analyses (kcal mol^{-1}) and geometric parameters (distances in Å) of (b) 2TS_{DE} and (c) 2TS_{DE} .

the bimetallic mechanism is both kinetically and thermodynamically more favorable than the monometallic pathway (Fig. 4 and S3[†]). However, the overall energy barrier of the monometallic pathway is $16.1 \text{ kcal mol}^{-1}$, which is not totally insurmountable under experimental conditions (room temperature). Besides, the monometal-mediated insertion process of MMA tends to be exergonic in chain propagation ($3\text{f} \rightarrow 3\text{i}$, Fig. S3[†]). In view of this and the limited catalyst concentration, the monometallic mechanisms could not be excluded in the 3/ PEt_3 system. However, in the case of 2, the calculated energy

barrier for the monometallic mechanism is too high ($34.9 \text{ kcal mol}^{-1}$) to be overcome under the experimental conditions. Therefore, only the bimetallic mechanism works in the 2 involved system. On the other hand, in the favorable bimetallic pathway, the overall energy barrier in the 3 catalyzed system is significantly lower than that in the 2 mediated reaction (10.9 vs. $20.2 \text{ kcal mol}^{-1}$, Fig. 4 and 2). This is in line with the experimentally observed higher activity of 3 compared with 2.^{14b}

To gain deeper insights into this activity difference between 2 and 3 in the bimetal mediated chain propagations, the

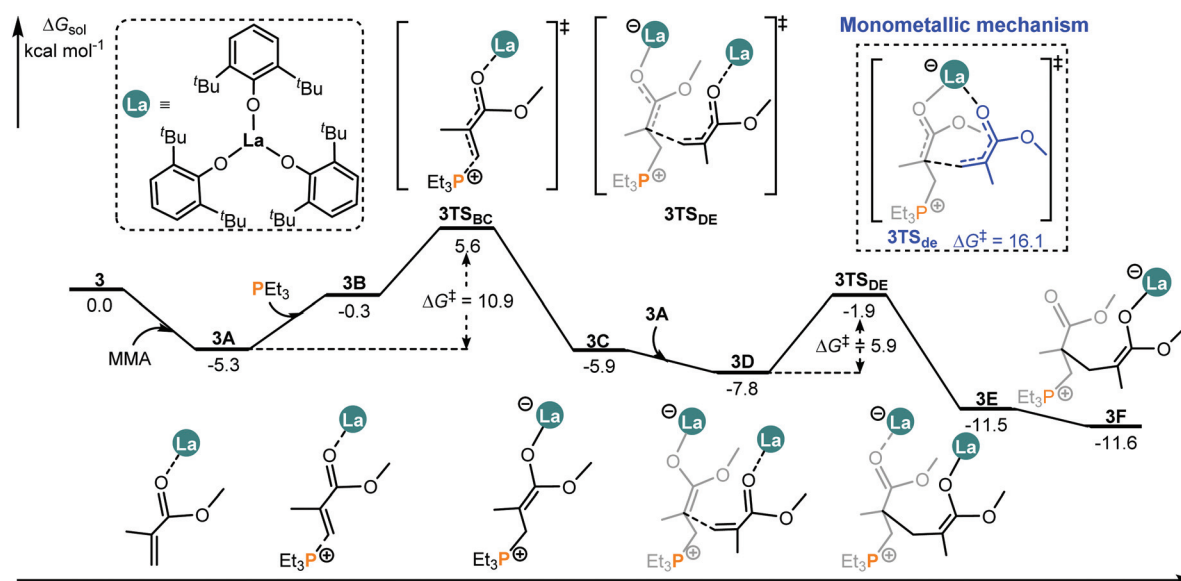


Fig. 4 Computed energy profiles for the 3/ PEt_3 mediated (intermolecular RE/P systems) bimetallic pathway for MMA enchainment. Free energies (kcal mol^{-1}) are relative to isolated reactants.

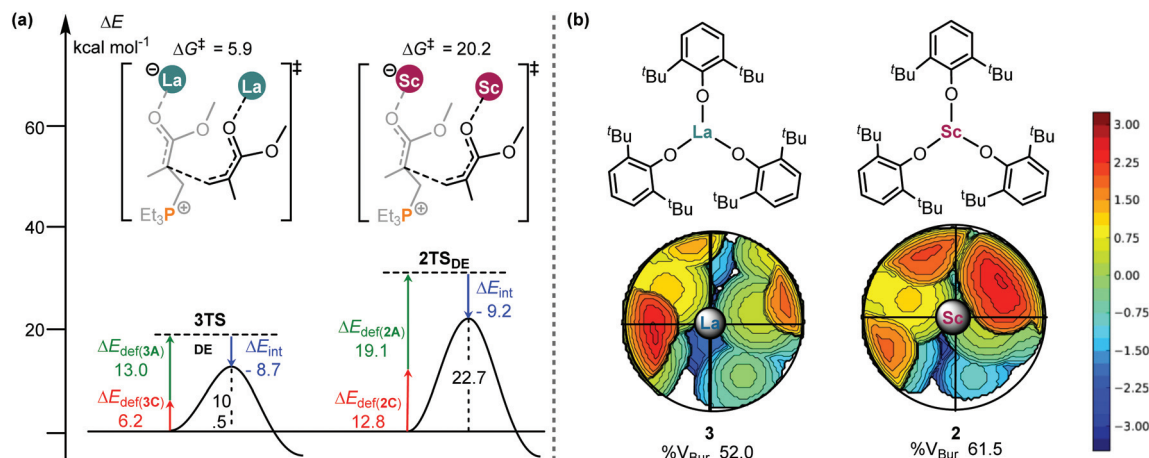


Fig. 5 (a) Distortion/interaction analyses (kcal mol^{-1}) of $3TS_{DE}$ and $2TS_{DE}$; (b) topographical steric maps of catalysts 3 and 2.

similar distortion/interaction analyses²¹ of the two C–C bond forming transition states ($2TS_{DE}$ and $3TS_{DE}$, Fig. 2 and 4) were performed. As shown in Fig. 5, although the interaction between the two fragments in $3TS_{DE}$ is weaker than that in $2TS_{DE}$ (-8.7 vs. -9.2 kcal mol⁻¹), the total deformation energy of the former ($13.0 + 6.2 = 19.2$ kcal mol⁻¹) is significantly smaller than that of the latter ($19.1 + 12.8 = 31.9$ kcal mol⁻¹), which compensates for the less negative interaction energy in $3TS_{DE}$, and eventually makes this TS more stable (free energy barrier of 5.9 vs. 20.2 kcal mol⁻¹). These results suggest that the steric factor (geometrical deformation) accounts for the lower stability of $2TS_{DE}$. In order to compare the sterics around the metal center in 2 and 3, the topographic steric maps were generated using the SambVca 2.0 web tool.²² When submitting an optimized structure on the web page of SambVca 2.0 and selecting the center site, the buried volume can be therefore calculated, simultaneously generating a topographic steric map. As expected, 3 had a lower percentage of buried volume in total (% V_{Bur} , 52.0 vs. 61.5, Fig. 5b) because of the larger radius of La; thus the relatively open enchainment environment in 3 could account for its higher activity. On the other hand, the torsion

angle difference $\Delta\angle C1C2C3P = 22.4^\circ$ and $\Delta\angle O5C6C5C4 = 14.2^\circ$ in $2TS_{DE}$ is significantly larger than those in $3TS_{DE}$ ($\Delta\angle C1C2C3P = 7.4^\circ$ and $\Delta\angle O5C6C5C4 = 2.1^\circ$, Fig. S4†). Such a greater geometrical deformation in $2TS_{DE}$ is also in line with the result of interaction/distortion analysis, resulting in a higher energy barrier and thus lower activity of the Sc complex.

Lewis base effect on polymerization activity

An experimental observation was noted that changing the substituents on the P atom in the Lewis base can also alter polymerization activities.^{14b} For instance, the replacement of PEt_3 with triphenylphosphine (PPh_3) noticeably decreased the activity. To understand the origin of such substituent effects, the energy profiles for MMA polymerization initiated by 2 and different bases R_3P ($\text{R} = \text{Cy}$ and Ph) were calculated. Following the bimetallic mechanism, the effect of the Lewis base on the polymerization activity is mainly reflected in the chain initiation step; thus only the chain initiation process is considered here.

The computational results indicate that PCy_3 as the Lewis base induced a lower energy barrier in comparison with PPh_3 (Fig. 6). In addition, PCy_3 involved zwitterionic species beyond

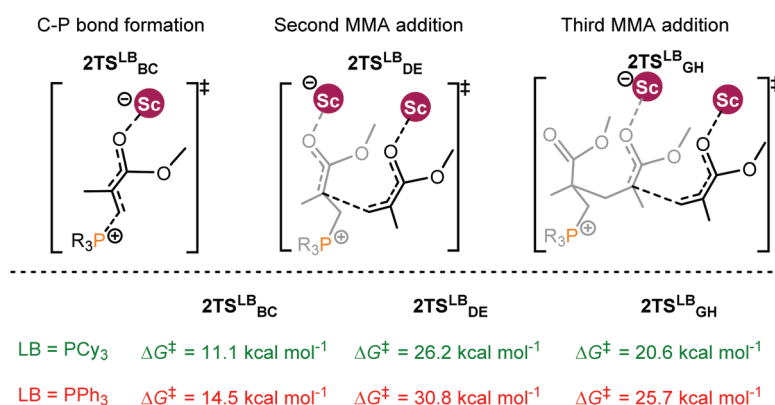


Fig. 6 Transition states for MMA polymerization initiated by the 2/ R_3P pair ($\text{R} = \text{Cy}$ and Ph). Free energies (kcal mol^{-1}) are relative to isolated reactants.

the C–P bond formation transition state is more stable than the case of PPh_3 (PCy_3 : $-5.3 \text{ kcal mol}^{-1}$ vs. PPh_3 : $1.8 \text{ kcal mol}^{-1}$). This result is in agreement with the activity trend experimentally observed. However, it remains a challenge to provide a chemically meaningful explanation for the origin of such a discrepancy in the activity. To obtain a piece of information on such differences, similar distortion/interaction analyses were performed for the key transition states TS2_{Cy} and TS2_{Ph} .

As shown in Fig. 7a, the two fragments (2C and 2A) are highlighted in black and green, respectively. The activation energy of each transition state (ΔE_{TS}) is decomposed into the distortion energy (ΔE_{def}) of the two reactive fragments and the interaction energy (ΔE_{int}) between the deformed two fragments. In TS2_{Ph} , the total distortion energy ΔE_{def} is $54.6 \text{ kcal mol}^{-1}$, which could be partially balanced out by its ΔE_{int} ($-6.9 \text{ kcal mol}^{-1}$) resulting in a ΔE_{TS} of 47.7 ($54.6 - 6.9 = 47.7$) kcal mol^{-1} . However, the total distortion energy ($\Delta E_{\text{def}} = 55.9 \text{ kcal mol}^{-1}$) in TS2_{Cy} can be largely compensated by an interaction energy of $-9.2 \text{ kcal mol}^{-1}$, thus giving a lower ΔE_{TS} ($46.7 \text{ kcal mol}^{-1}$). The distortion/interaction model analysis indicates that higher interaction energy could account for the stability of TS2_{Cy} in comparison with TS2_{Ph} . To have a better understanding of such an interaction accounting for the relative stability of these two transition states, the ETS-NOCV²³ (extended transition state and natural orbitals for chemical valence) calculations were performed by using

the Amsterdam density functional (ADF) package²⁴ to dissect the interaction energy (Fig. 7b). The interaction energy ($\Delta E'_{\text{int}}$) between the deformed 2A and 2C_{Cy} can be further dissected into Pauli repulsion (ΔE_{Pauli}), electrostatic interactions (ΔE_{elstat}), orbital interactions ($\Delta E_{\text{orbital}}$), and dispersion interactions (ΔE_{disp}) (see computational methods in the ESI† for details). Of these interactions, the electrostatic (ΔE_{elstat}), orbital ($\Delta E_{\text{orbital}}$), and dispersion (ΔE_{disp}) interactions are the stabilizing factors, while the Pauli repulsion (ΔE_{Pauli}) is the destabilizing factor. As shown in Fig. 7b, although the TS2_{Cy} is disfavored by Pauli repulsion compared with 2TS_{Ph} ($\Delta \Delta E_{\text{Pauli}} = 112.3 - 98.9 = +13.4 \text{ kcal mol}^{-1}$), it has stronger attractive orbital interactions ($\Delta \Delta E_{\text{orbital}} = -7.9 \text{ kcal mol}^{-1}$) and electrostatic interaction ($\Delta \Delta E_{\text{elstat}} = -7.3 \text{ kcal mol}^{-1}$) between the 2A and 2C moieties. These results indicate that the electronic properties of the Lewis base (PPh_3 and PCy_3) can alter the electron-density of the C=C bond in the 2C_{Cy} and 2C_{Ph} , as also suggested by the CHelpG atomic charge²⁵ (charges from the electrostatic potential using a grid-based method). As shown in Fig. 8a, the unsigned values of charge on C1 and C3 in 2C_{Ph} are smaller than those in 2C_{Cy} , suggesting an inductive effect of the Ph groups in 2C_{Ph} . This could account for the lower reactivity of PPh_3 as a Lewis base because of the lower electron density on C1 atoms in comparison with PCy_3 (-0.19 vs. -0.45), rendering more electron flow during the 1,4-addition in the case of PCy_3 . On the other hand, to gain a deeper understanding of the orbital inter-

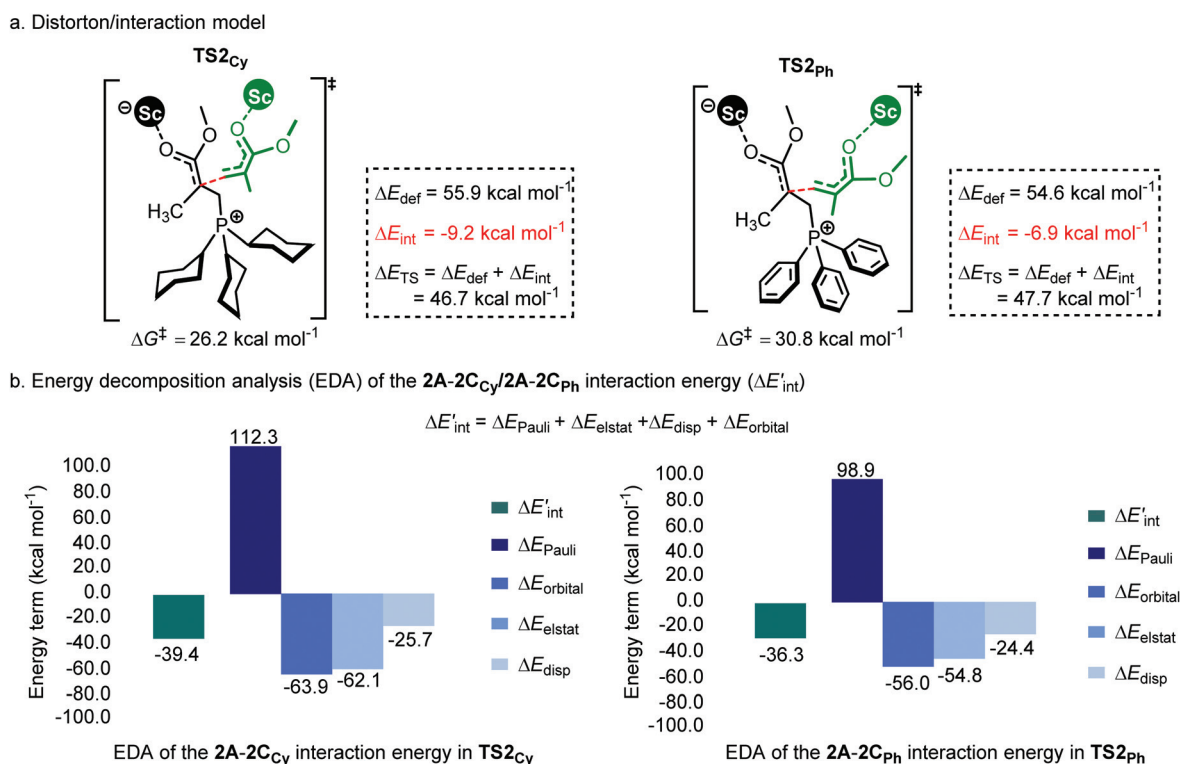


Fig. 7 (a) Distortion/interaction model (kcal mol^{-1}) and (b) energy decomposition analysis of TS2_{Cy} and 2TS_{Ph} . $\Delta G^\ddagger$ and ΔE_{TS} is calculated at the level of B3PW91/6-31G(d) planted in the Gaussian 16 program.²⁶ $\Delta E'_{\text{int}}$ is dissected into chemically meaningful terms according to the ETS-NOCV calculations at the level of B3LYP-D3/DZP planted in the Amsterdam density functional (ADF) package.²⁴

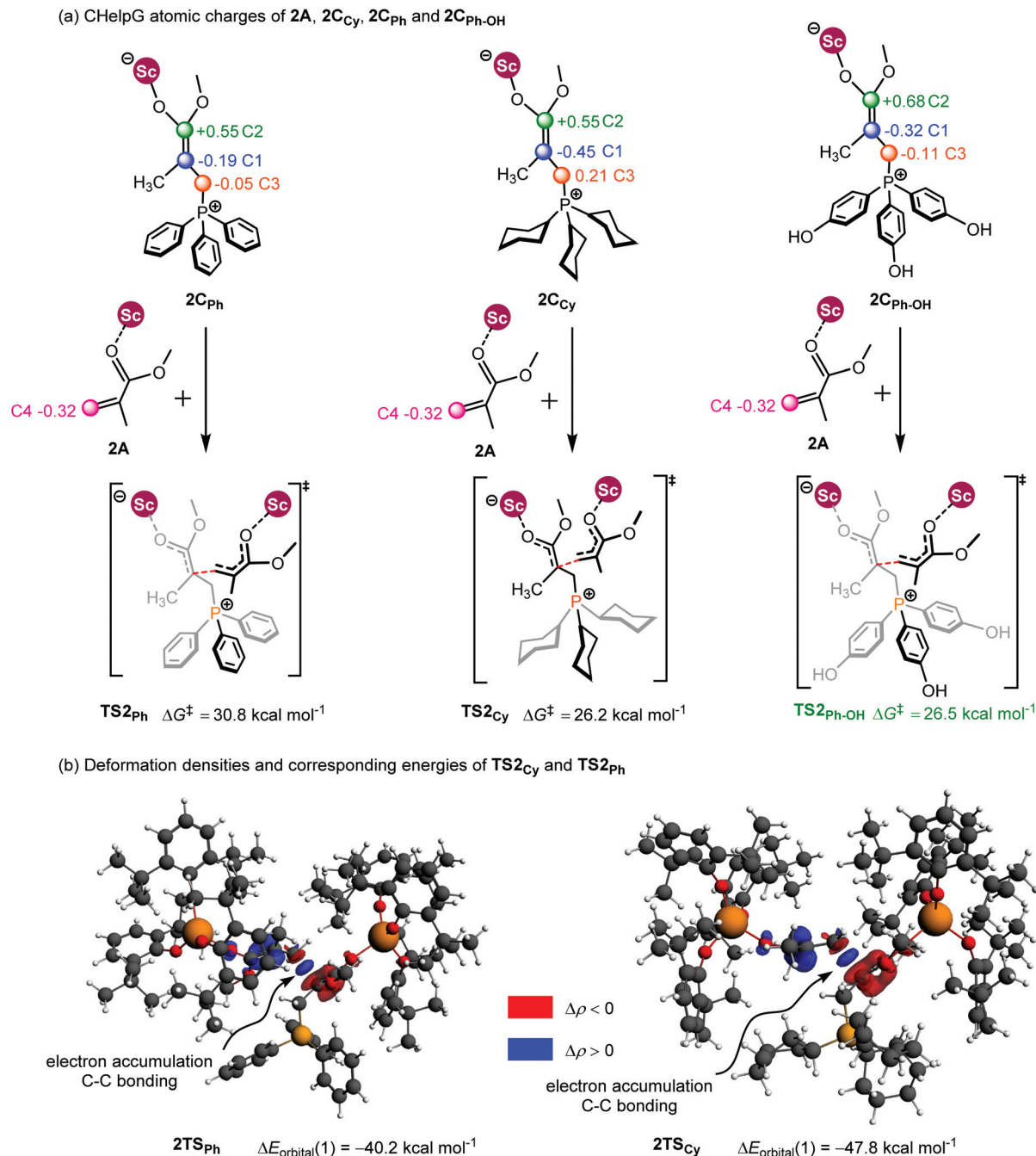


Fig. 8 (a) CHelpG atomic charge²⁵ in **2A**, **2C_{Ph}**, **2C_{Cy}** and **2C_{Ph-OH}**; (b) leading deformation densities and corresponding energies for **TS2_{Ph}** and **TS2_{Cy}**. The red color denotes charge depletion and the blue color represents charge accumulation ($|\Delta\rho| = 0.004$ a.u. for all the density surfaces).

action, orbital analysis based on the NOCV approach was performed, which could give useful information about the reorganization of the electronic density in the transition states through the electronic deformation density. Fig. 8b shows the leading electronic deformation densities and the corresponding energies for **TS2_{Cy}** and **TS2_{Ph}**. It is indicated that the $\Delta E_{\text{orbital}}$ energy of **TS2_{Cy}** ($-47.8 \text{ kcal mol}^{-1}$) is more negative than that of **TS2_{Ph}** ($-40.2 \text{ kcal mol}^{-1}$). The charge flow from **2C_{Cy}** (red region) to **2A** (blue region) in **TS2_{Cy}** is also more

evident than that in **TS2_{Ph}**. Therefore, different Lewis bases could influence the electronic population in the intermediate such as **2C** and further affect the stability of the addition reaction transition state. In order to further explore the regulation effect of the Lewis base, the hydroxyl (electron-donating group) substituted phenyls have been modelled (Fig. 8a). As expected, the calculated CHelpG charge on C1 changed from -0.19 to -0.32 and the addition reaction energy barrier reduced from 30.8 to $26.5 \text{ kcal mol}^{-1}$.

the intermolecular RE/P system. Meanwhile, given the same Lewis acid, the observed activity difference of various PR₃ Lewis bases (R = Cy and Ph) could be ascribed to the electronic induction effect of the R group. Namely, the R group with stronger electron donation ability could increase the electron density on the reactive vinyl group and render more electron flow during the Michael addition, resulting in higher activity in comparison with the electron withdrawing group, which is in line with the experimentally observed activity trend. Besides, further computational modellings on a series of intramolecular RE/P catalysts indicate that increasing the radius of the central metal or the flexibility of the bridge connecting Lewis pair in the catalyst is beneficial to improving catalytic activity. These theoretical results are expected to be useful for the design of a more efficient RE/P polymerization system.

Reaction scheme showing the catalytic cycle for the polymerization of α -olefins. The catalyst $[Cat]$ is a Ln complex with a macrocyclic ligand containing a phosphorus atom (R^1-P-R^1) and a nitrogen atom ($N-R^2$). The ligand R^2 can be DMM (2,4,6-trimethylphenyl) or DIPP (2,4,6-triisopropylphenyl). The cycle proceeds through a transition state $[TS_{bc}]$ to form the polymer and regenerate the catalyst.

Catalyst modification

Inspired by the aforementioned calculation results, we speculated that it should be possible to improve the activity by modifying ligands in the intramolecular RE/P system.^{14a} As aforementioned, the P–C bond formation is not the rate determining step (Fig. 1), which was not considered here. As shown in Table 1, on the basis of original catalyst **1**, appropriate substituent alteration has no significant effect on the MMA enchainment energy barrier ($\Delta G_{\text{TsbC}}^{\ddagger}$, cat. **1**, 4–7). Interestingly, when the number of bridging methylenes increased to 2, the energy barrier decreased ($\Delta G_1^{\ddagger} = 19.6$ vs. $\Delta G_8^{\ddagger} = 17.2$ kcal mol^{−1}). Besides, when the metal Sc is changed to La, the energy barrier obviously decreased by 6.3 kcal mol^{−1} ($\Delta G_1^{\ddagger} = 19.6$ vs. $\Delta G_9^{\ddagger} = 13.3$ kcal mol^{−1}). These results suggest that the proper flexibility of the arm bridging intramolecular Lewis pair and larger-sized metal could be beneficial to the addition of MMA.

Conclusions

In summary, the origin of activity difference in the polymerization of methyl methacrylate (MMA) catalyzed by various rare-earth/phosphorus Lewis pairs (RE/P), *via* Michael addition, has been computationally elucidated. The calculated energy landscapes indicate that the intramolecular RE/P mediated MMA polymerization is a significant exergonic process and features a moderate energy barrier. In the case of intermolecular RE/P, the bimetallic mechanism is kinetically preferable over the monometallic pathway. Unlike the $\text{Sc}(\text{OAr})_3/\text{PET}_3$ ($\text{Ar} = 2,6\text{-}^t\text{Bu}_2\text{-C}_6\text{H}_3$) Lewis pair, however, the La analogue may also follow a monometallic mechanism in view of limited catalyst concentration and surmountable enchainment energy barrier. The detailed structure and energy analyses disclosed that geometrical deformation required for achieving the enchainment transition state mainly accounts for the activity discrepancy of the rare-earth metal complex as a Lewis acid in

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was partly supported by the NSFC (U1862115 and 21674014). The authors also thank the RICC (RIKEN Integrated Cluster of Clusters) and the Network and Information Center of the Dalian University of Technology for part of the computational resources. G. L. thanks the Innovation and Entrepreneurship Project of Overseas Returnees in Anhui Province (2020LCX006).

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