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New catalyst design for polymerization of norbornene esters by reducing intramolecular interaction

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Abstract We have used density functional theory to study palladium-based catalysts commonly used for the polymerization of norbornene derivatives with an ester group. *Exo–exo*, *exo–endo*, and *endo–endo* isomers of catalyst complexes were investigated; the *endo–endo* isomer was the most stable and inactive due to an intramolecular interaction between Pd and O of the carbonyl group. Phosphine groups are effective in minimizing the Pd–O interaction in the *endo–endo* isomer and $P(C_6H_{11})_3$ was found to be the most efficient reagent. The intramolecular Pd–O interactions were estimated using model complexes, and it was demonstrated that they play a crucial role in stabilizing the *endo–endo* isomer.

Keywords Catalyst · Norbornene derivatives · Density functional theory · Intramolecular interaction

Introduction

The metal-catalyzed polymerization of olefins is of outstanding industrial importance. As well as classical polymers such as polyethylene and polypropylene, polynorbornene, a polyolefin containing cyclic subunits, has attracted increasing interest. Polynorbornene possesses interesting properties, e.g., high glass transition temperature, optical transparency, and low birefringence. Norbornene is known to be polymerized in three different ways: ring-opening metathesis polymerization (ROMP), [1, 2,3, 4] cationic or radical polymerization, [5] and vinyl addition polymerization. [6, 7, 8, 9, 10] Each route leads to its own polymer type, which differs in structure and properties from the others. Our current interest is the vinyl- addition polymerization of norbornene derivatives with pendant functional groups.

Transition metal complexes have been used as catalysts to prepare polyolefins containing functional groups, which make up a substantial proportion of the commercially available thermoplastics. [11, 12] The functional group incorporated into polymer chains can provide enhanced intra- and intermolecular interactions, which may modify specific properties of materials, such as the glass transition temperature and dielectric properties. Most transition metal catalysts rapidly interact with the olefin's functional groups, particularly those containing oxygen functionalities, and become inactive for polymerization. This is true for the *endo*-functionalized norbornenes, which are usually accessible by Diels–Alder reactions, [13] and constitute the vast majority of available functional norbornenes. [9, 14, 15, 16] It has been presumed that the lower reactivity of *endo* derivatives is due to catalyst inhibition by coordination of the functional group to the metal center. [17] Hennis et al. [17] reported the stereochemistry of catalyst coordination to the *endo* ethyl ester norbornene by using a norbornene-complex-containing Pt catalyst. The authors suggested that, even though the olefin is initially coordinated through the *exo* face, the insertion of Pt occurs at the *endo* face because of the coordination of the carbonyl oxygen.

In this work, three isomers of the catalyst complex (Fig. 1a–c), *exo* face coordination of the Pd atom to the *exo* monomer (*exo–exo*), *exo* face coordination to the *endo* monomer (*exo–endo*), and *endo* face coordination to the *endo* monomer (*endo–endo*), were analyzed by density functional theory (DFT). Three phosphine groups were employed for L ligands to design an active catalyst. Their relative energies were also compared to estimate their thermodynamic stability. The binding energies between the Pd metal and the O atom of the carbonyl group in the *endo–endo* isomer were estimated from calculations for model compounds.

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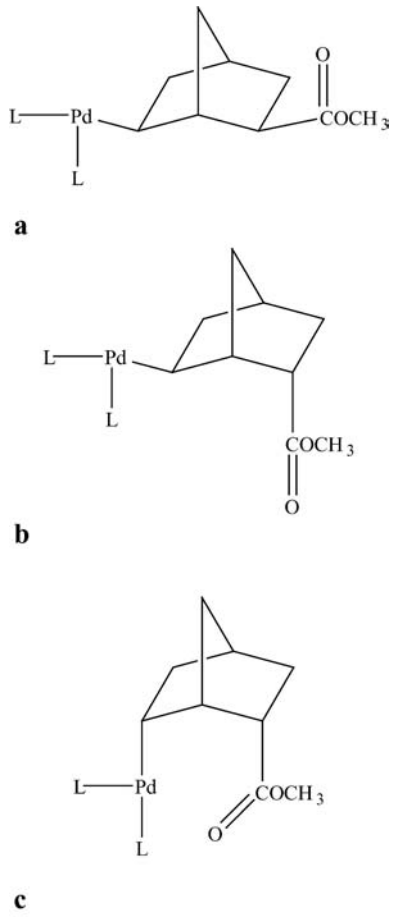

Fig. 1a–c Three isomers for ethyl ester norbornene: (**a**) *exo–exo*; (**b**) *exo–endo*; (**c**) *endo–endo*

Computation details

The Becke–Lee–Yang–Parr (BLYP) gradient corrected density functional [18, 19, 20] was employed to optimize all of the molecules, using the Dmol^3 [21, 22] program. Frequency calculations were performed for the complexes without phosphine groups to make sure that they are local minima. The energy adjusted effective core potential (ECP) [23, 24] was used for the Pd atom. A double numerical plus *d*-functions (DND) basis set was used for C, H, O, and P atoms, and the valence electrons for Pd were also expanded with the DND basis set. The real-space cutoff is 5.5 Å and the medium grid was chosen for numerical integration. The charges on the catalyst complexes are +1 and they have singlet multiplicities. Large ligands, particularly $P(C_6H_{11})_3$, may pose problems concerning local minima due to the existence of several stable conformations. Since it takes too much time to access many conformers of catalyst systems, conformational space was studied for $P(C_6H_{11})_3$ ligand using the COMPASS force field. Eighteen conformers with low energy were selected to be reoptimized using the BLYP functional. We found that the conformers of $P(C_6H_{11})_3$ have similar stabilities with energy differences being less than 1.5 kcal mol^{-1}, which implies that the conformation of $P(C_6H_{11})_3$ would little affect our results and discussion. The counteranions, which would be weakly coordinated to the catalyst complexes, are ignored in this work.

Table 1 Relative energies (in kcal mol^{-1}) of norbornene methyl ester isomers

	Without PX_3	PH_3	$P(C_6H_5)_3$	$P(C_6H_{11})_3$
exo–exo	20.0	9.5	1.5	–5.4
exo–endo	18.5	8.5	1.2	–3.5
endo–endo	0.0	0.0	0.0	0.0

Results and discussion

The optimized geometry of the *endo–endo* Pd(II)–norbornene methyl ester isomer and the relative energies of three isomers are shown in Fig. 2a and Table 1, respectively. The distance between Pd(II) and the oxygen of the carbonyl group (*r*[Pd–O]) is 2.11 Å for the *endo–endo* isomer, which implies that the oxygen of the carbonyl group is coordinated to the Pd(II) metal and that norbornene acts as a chelating ligand with the ester group. The relative energies of the *exo–exo* ($\Delta E_{exo-exo}$) and *exo–endo* ($\Delta E_{exo-endo}$) isomers compared with the *endo–endo* isomer are 20.0 kcal mol^{-1} and 18.5 kcal mol^{-1}, respectively, indicating that the *exo–exo* and *exo–endo* isomers are present in negligible amounts.

We have tried to modify the catalyst complex to increase the fraction of active isomers by employing phosphine groups. To investigate the electrostatic effect of the phosphine, the simplest phosphine (PH_3) was used to coordinate to the Pd(II) metal. The geometry of the *endo–endo* isomer with a PH_3 group and the relative energies of three isomers are given in Fig. 2b and Table 1, respectively. $\Delta E_{exo-exo}$ (9.5 kcal mol^{-1}) and $\Delta E_{exo-endo}$ (8.5 kcal mol^{-1}) become much smaller, although the *endo–endo* isomer is more stable than the other isomers. Part of the lone pair of phosphine seems to be transferred to the Pd(II) metal and alleviates the electron deficiency of the metal, which weakens the Pd–O coordination in the *endo–endo* isomer, and elongates *r*[Pd–O] from 2.11 Å to 2.18 Å.

We substituted the H atom of PH_3 with a bulky ligand such as phenyl (C_6H_5) and cyclohexyl groups (C_6H_{11}), expecting the bulky ligand to interrupt the coordination of the oxygen atom to the Pd(II) metal. The *endo–endo* isomers with $P(C_6H_5)_3$ and $P(C_6H_{11})_3$ coordination are drawn in Fig. 2c and d, respectively, and their relative energies are included in Table 1. For the $P(C_6H_5)_3$ coordination, $\Delta E_{exo-exo}$ (1.5 kcal mol^{-1}) and $\Delta E_{exo-endo}$ (1.2 kcal mol^{-1}) become smaller than those with PH_3 coordination, and *r*[Pd–O] is stretched from 2.18 Å to 2.20 Å. For the $P(C_6H_{11})_3$ coordination, the stabilities of three isomers are reversed, i.e. the *endo–endo* isomer is less stable than the *exo–exo* and *exo–endo* isomers, and *r*[Pd–O] is considerably elongated from 2.18 Å to 2.93 Å.

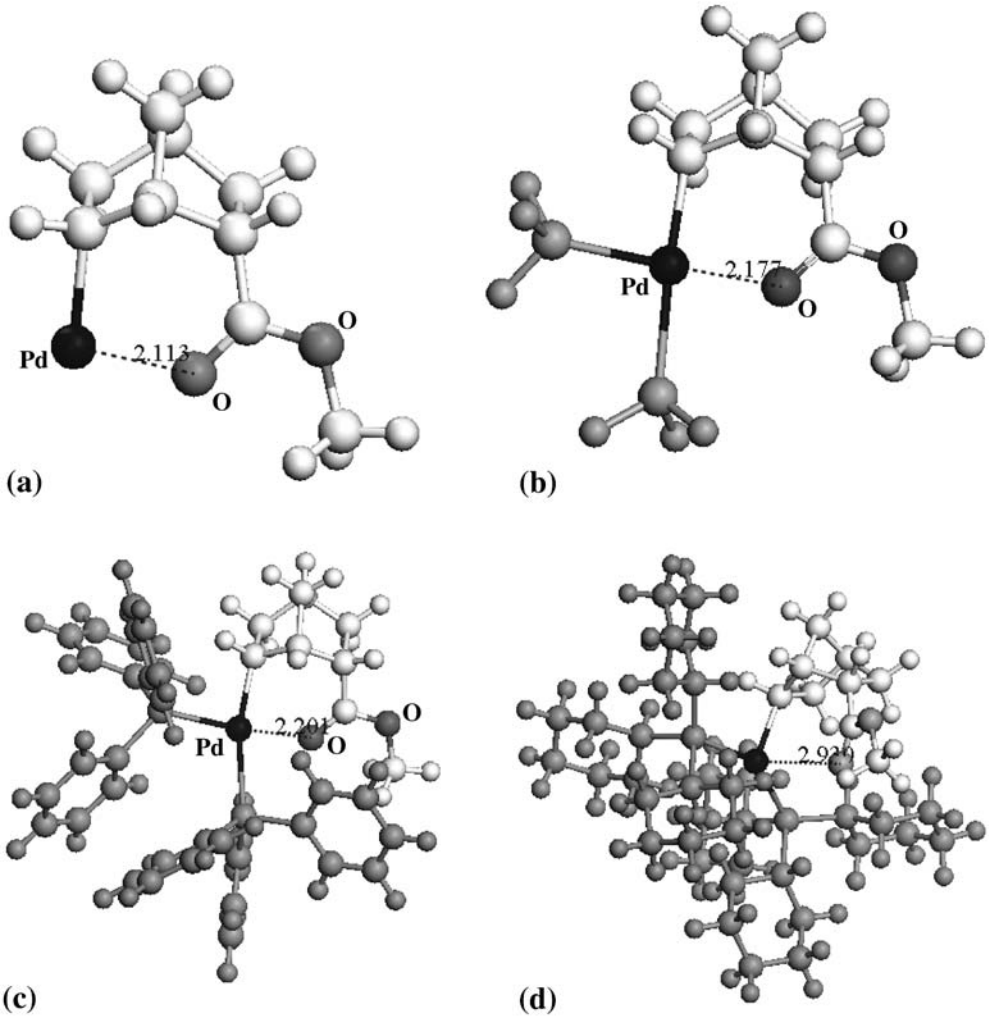

Fig. 2a–d The optimized geometries of methyl ester norbornene complex for *endo–endo* isomers: (**a**) without phosphine group; (**b**) with PH_3; (**c**) with $P(C_6H_5)_3$; (**d**) with $P(C_6H_{11})_3$. Bond lengths in Å

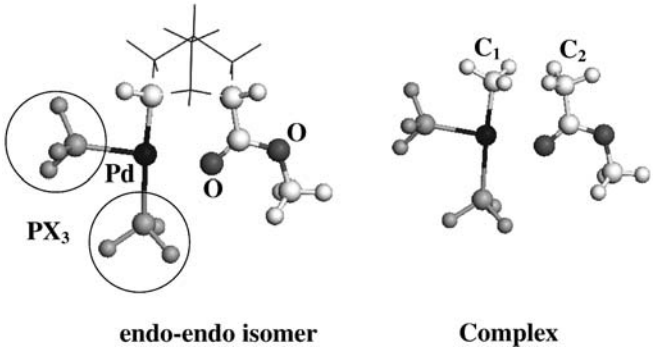

Fig. 3 Model complex for *endo–endo* isomer (no PX_3, X=H, C_6H_5, and C_6H_{11})

Our results show that the coordination of the $P(C_6H_{11})_3$ group is more effective than that of the $P(C_6H_5)_3$ group in preventing Pd–O coordination. Although the phenyl groups are bulky, three phenyl groups can avoid each other, i.e., the steric effect of $P(C_6H_5)_3$ on the stability of the *endo–endo* isomer is not as large as expected. The $P(C_6H_{11})_3$ group is too bulky for the Pd atom to be coordinated to the O atom of the carbonyl group, and makes the *endo–endo* isomer less stable, which causes $\Delta E_{exo-exo}$ and $\Delta E_{exo-endo}$ to decrease.

The binding energy between Pd and O of the carbonyl group (E_{bind}) seems to be important for the stability of the *endo–endo* isomer. Since it is difficult to estimate E_{bind} within the *endo–endo* complexes, model molecules were employed in Fig. 3. The E_{bind} values for the model molecules were obtained by the two procedures. (a) Only hydrogen atoms connected to C_1 and C_2 were optimized, and the other atoms were fixed to their positions in the *endo–endo* isomers (procedure 1). (b) All atoms of the model molecules were optimized without any constraint (procedure 2). Procedure 1 provides a lower limit of the binding energy, because there are repulsions between the hydrogen atoms of C_1 and C_2 in the model system that do not exist in the real system. E_{bind} using procedure 2 could be overestimated (an upper limit), since the geometry parameters are fully optimized and the steric repulsions are minimized.

The binding energies obtained by procedure 1 and procedure 2, E_{bind1} and E_{bind2}, respectively, are plotted in Fig. 4, and $\Delta E_{exo-exo}$ values are also included in Fig. 4 to

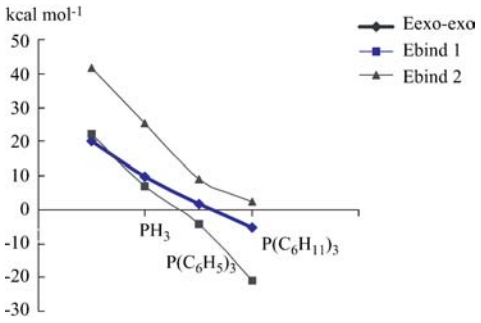

Fig. 4 $\Delta E_{exo-exo}$ and E_{bind} of model complexes using procedure 1 and 2

compare the influences of the phosphine group on $\Delta E_{exo-exo}$ and binding energies. The binding energies are a maximum when no phosphine group is coordinated for both procedure 1 and procedure 2, and the *endo–endo* isomer is stabilized by these binding energies to produce the maximum $\Delta E_{exo-exo}$ value. The coordination of PH_3 decreases E_{bind}, and makes the *endo–endo* isomer less stable, producing a smaller $\Delta E_{exo-exo}$ value. $P(C_6H_5)_3$ and $P(C_6H_{11})_3$ are better reagents than PH_3 for interrupting the coordination of the oxygen atom to the Pd(II) metal.

The influence of the phosphine group on E_{bind1} and E_{bind2} is similar; this implies that the Pd–O interaction is important not only for norbornene catalyst complexes but for other catalyst complexes, such as ethylene or propylene with a polar group, not having cyclic subunits. Comparison of E_{bind1}, E_{bind2} and $\Delta E_{exo-exo}$ shows that their behavior with phosphine groups is similar, and that the interaction between Pd and O plays a major role in stabilizing the *endo–endo* isomer. When no phosphine group is coordinated, interactions between the Pd atom and the O atom are a maximum, generating large $\Delta E_{exo-exo}$. The coordination of a phosphine group, especially $P(C_6H_{11})_3$, is an effective reagent in weakening the interaction between the Pd atom and the O atom, and produces a smaller $\Delta E_{exo-exo}$, implying that the fraction of the inactive *endo–endo* isomer decreases. The binding energies(ΔE_{Pd-P}) between palladium and phosphine groups($2PX_3$) were also calculated for *endo–endo* isomers. The ΔE_{Pd-P} values are calculated to be 57.2 kcal mol^{-1}, 65.2 kcal mol^{-1}, 57.2 kcal mol^{-1} for PH_3, $P(C_6H_5)_3$, and $P(C_6H_{11})_3$, respectively. Phosphine coordination may also influence the activity of the catalyst, although its effects are not discussed here. Instead, one of the authors (S.H.C.) [25] confirmed experimentally that the use of $P(C_6H_{11})_3$ increased the activity of the catalyst for ester norbornene polymerization more than 50 times, which implies that the effect of intermolecular ligand coordination may be different from that of intramolecular chelate coordination for our catalyst system. We expect further studies such as activation energy calculations for the reaction of the catalyst and a norbornene monomer to explain the effects of ligand or chelate coordination for the activity of catalyst system.

Conclusions

A palladium-based catalyst was studied for efficient norbornene methyl ester polymerization. The relative energies of catalyst complexes, molecular geometries, and binding energy analysis using model molecules show that there are strong interactions between the Pd atom and the O atom of the carbonyl group in the *endo–endo* isomer, which becomes very stable and inactive. A phosphine group, especially $P(C_6H_{11})_3$, is shown to be an effective reagent in preventing the oxygen atom from coordinating to the Pd(II) metal, and increases the fraction of active catalyst. However, we are still far away from the complete comprehension for the activity of catalyst, which invites more quantum chemical calculations considering counter anion effects, solvent effect, and so on in the future.

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