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CATALYTIC ACTIVITIES OF LANTHANIDE COMPOUNDS IN THE POLYMERIZATION OF ISOPRENE

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ABSTRACT

The differences in catalytic activities of the lanthanide compounds (from lanthanum to lutetium) toward the polymerization of isoprene are investigated. Two catalyst systems are studied, i.e. a binary system $LnCl_3\cdot(TBP)_3$—i—Bu_3Al and a ternary system $Ln(naph)_3$—i—Bu_3Al—$Et_3Al_2Cl_3$ (Ln-ion of rare earth element; TBP-trin-butylphosphate; naph-naphthenate). It turns out that $NdCl_3\cdot(TBP)_3$ shows the highest activity, while $LnCl_3\cdot(TBP)_3$ complexes of Eu, Sm, Tb, Dy, Er, Tu, Yb and Lu do not polymerize isoprene or show very low activities. Similar results are obtained when $Ln(naph)_3$ is used. Spectrophotometric studies show that in contrast to Eu and Sm, which are reduced from trivalent to divalent when mixed with the aluminum compounds such as Pr, Nd, Gd and Er in the catalytically active system $Ln(naph)_3$—i—Bu_3Al—$Et_3Al_2Cl_3$, all exist in a valence state of 3. In view of the same valence of 3, the difference in the catalytic activities in the polymerization of isoprene of these latter elements is still not explicable on the basis of the valence state of the elements. Infrared spectra of $LnCl_3\cdot(TBP)_3$ show that there is no correlation between the catalytic activities of these complexes and their $\nu_p=0$ values. Data of laser Raman spectroscopy reveal identical characteristic frequencies of Ln—Cl in $LnCl_3\cdot(TBP)_3$ which are quite different in the catalytic activities (for example, Ce, Nd, Pr, Sm, Eu, and Yb). It seems that there is no relationship at all between the catalytic activities and the bond energies of Ln—Cl.

Taking all the facts mentioned above into account, we believe that the difference in the catalytic activities of the present rare earth catalyst systems may be related to the number of electrons in 4*f*-orbitals. Perhaps, the 4*f*-orbitals of these trivalent rare earth ions take part in the bond formation to a certain degree. Hence, we venture to explain the difference in catalytic activities in terms of the molecular orbital theory.

We have reported previously[1] that the catalytic activities of naphthenates of seven light rare earth elements in cis-1, 4-polymerization of isoprene are in the following order: Nd > Pr > Ce > Gd > La ≫ Sm, while Eu does not polymerize isoprene. Similar results were obtained by Rafikov *et al.* recently[2]. Studies on the valence state of Sm and Eu in the catalyst systems have shown[1] that weak catalytic activities of these elements are probably due to their reduction to a valence state of 2; the difference in catalytic activities of the other rare earth elements still remains to be explained. We have studied the catalytic activities of other lanthanide compounds (from lanthanum to lutetium) in the dienes polymerization, and explained qualitatively the results in terms of molecular orbital theory.

I. Experimental

In this paper, two catalytic systems were studied: a binary system $LnCl_3$-$(TBP)_3$[1] + i − Bu_3Al and a ternary system $Ln(naph)_3$ + i-Bu_3Al + $Et_3Al_2Cl_3$, $LnCl_3$-$(TBP)_3$ was prepared by reacting $LnCl_3$ with TBP in aqueous solution, and $Ln(naph)_3$ was obtained by the extraction procedure. Hydrogenated gasoline used as the solvent for polymerization had a b.p. range of 60—90°C. Polymerization was carried out in 100 ml glass bottles at 50°C for 6 hr. Other polymerization procedure and the methods of polymer characterization were the same as before[3].

II. Results and Discussion

It is evident from Fig. 1 that though lanthanide compounds are very similar in general chemical properties, they show quite a different catalytic activity toward isoprene polymerization. $NdCl_3 \cdot (TBP)_3$ shows the highest activity, while $LnCl_3 \cdot (TBP)_3$ complexes of Eu, Sm, Tb, Dy, Er, Tu, Yb and Lu do not polymerize isoprene or show very low activities. On the other hand, the above-mentioned order of the activities remains unchanged when $Ln(naph)_3$ is used (Fig. 2). A spectrophotometric study shows that in contrast to Eu, Sm, Pr, Nd, Gd, and Er in the catalytically active systems. $Ln(naph)_3$-i-Bu_3Al-$Et_3Al_2Cl_3$ all exist in a valence state of 3. Thus, the difference in the catalytic activity of these systems in the polymerization of isoprene is not explicable on the basis of the valence state of the rare earth elements. Infrared spectra of $LnCl_3 \cdot (TBP)_3$ (Table 1 and Fig. 3) show that the characteristic frequencies of $-P=O$ group ($\nu_{P=O}$) of $LaCl_3 \cdot (TBP)_3$ and $CeCl_3 \cdot (TBP)_3$ appear at 1220 cm^{-1} and that of the other 12 $LnCl_3 \cdot (TBP)_3$ at 1210 cm^{-1}.

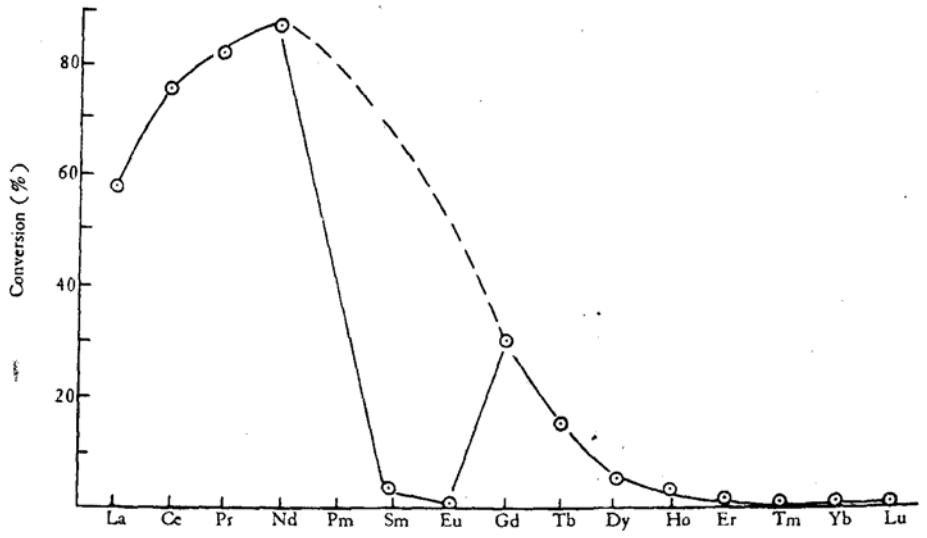

Fig. 1. Catalytic activities of various $LnCl_3 \cdot (TBP)$.
Other component: i-Bu_3Al.

1) Ln... ion of rare earth element; TBP... trin-butylphosphate; naph... naphthenate.

No doubt there is some energy difference between these two classes of rare earth complexes, yet there is no correlation between the catalytic activities of these complexes and their $\nu_p = 0$ values.

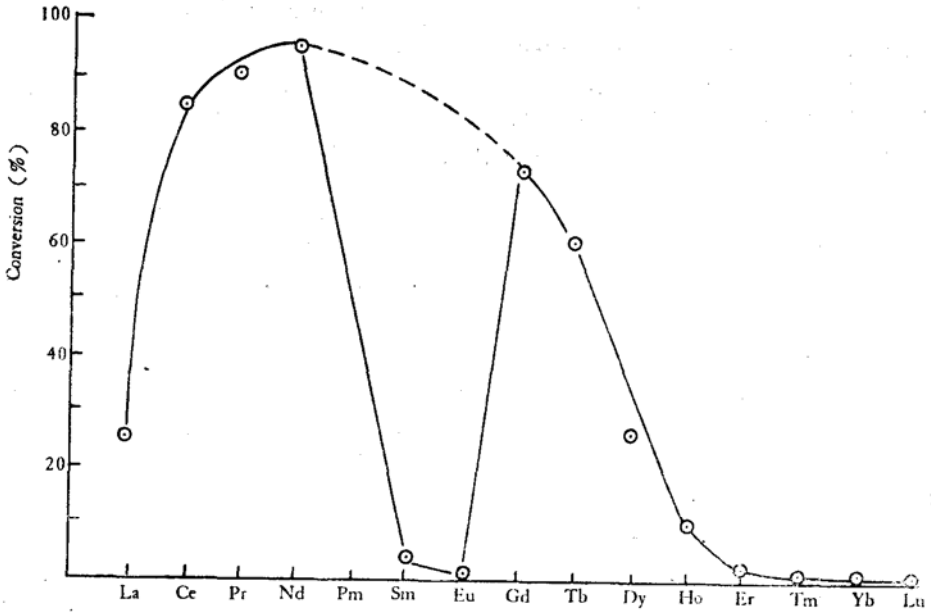

Fig. 2. Catalytic activitiy of various Ln(naph)$_3$.
Other components: i-Bu$_3$Al and Et$_3$Al$_2$Cl$_3$.

Table 1

Infrared and Laser Raman Spectra of LnCl$_3$ (TBP)$_3$

Complex	Characteristic Infrared Frequency of $-p=0$ ($\nu_p=0$) (cm^{-1})	Characteristic Laser Raman Frequency of Ln-Cl (cm^{-1})	Complex	Characteristic Infrared Frequency of $-p=0$ ($\nu_p=0$) (cm^{-1})	Characteristic Laser Raman Frequency of Ln-Cl (cm^{-1})
La	1220	45	Tb	1210	36
Ce	1220	60	Dy	1210	35
Pr	1210	40	Ho	1210	43
Nd	1210	60	Er	1210	47
Sm	1210	40	Tu	1210	50
Eu	1210	40	Yb	1210	40
Gd	1210	45	Lu	1210	46

Data of the laser Raman spectroscopy (Table 1) reveal identical characteristic frequencies of Ln-Cl in those LnCl$_3$·(TBP)$_3$ (for example, Ce and Nd; Pr, Sm, Eu and Yb) which are quite different in catalytic activities. It seems that there is no relationship at all between the catalytic activity and the bond energy of Ln-Cl.

Taking the above-mentioned facts into account, we believe that the difference in catalytic activity of the rare earth catalysts may be related to the number of electrons occupying 4*f*-orbitals. Perhaps the 4*f*-orbitals of those trivalent rare earth ions take part in bond formation to a certain degree in their environment.

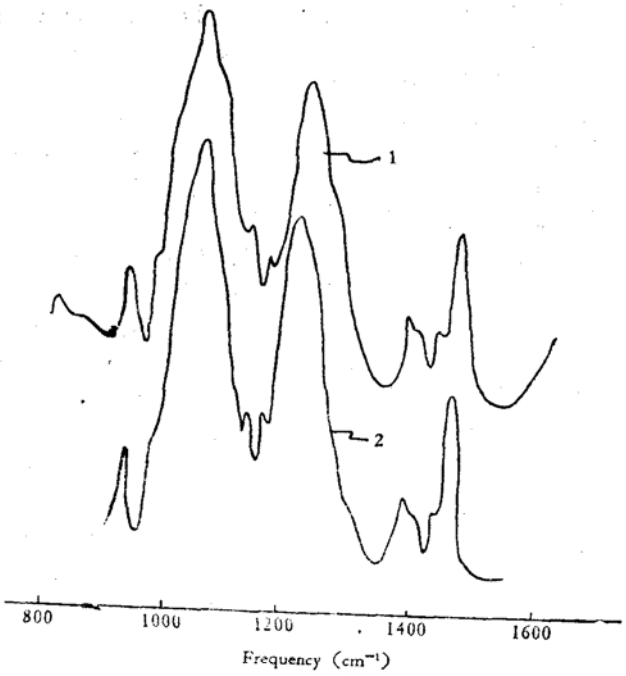

Fig. 3. Infrared spectra of various $LnCl_3 \cdot (TBP)_3$.
1—$LaCl_3 \cdot (TBP)_3$; 2—$PrCl_3 \cdot (TBP)_3$.

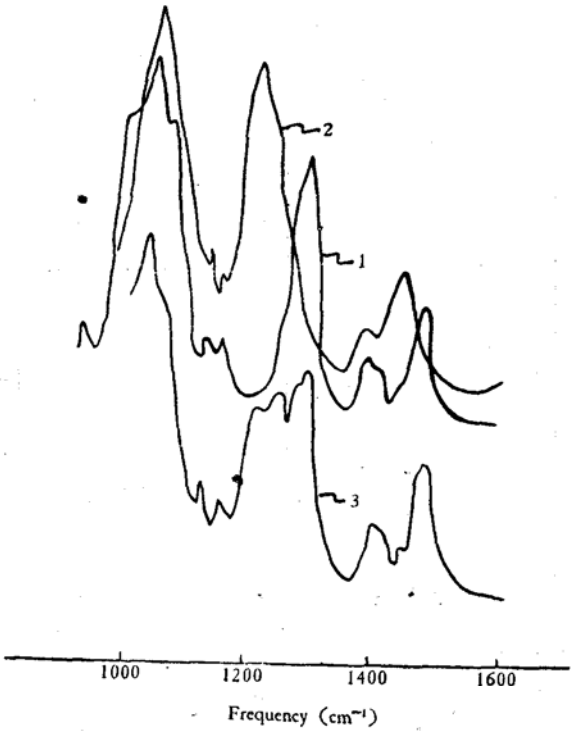

Fig. 4. Infrared spectra of TBP and complexes of $NdCl_3$ and TBP.
1—TBP; 2—$NdCl_3 \cdot (TBP)_3$; 3—$NdCl_3 \cdot (TBP)_8$.

Hence, we suggest the following proposals: (i) there is a chemical bond formation between the rare earth ion and the ligands (diene or other groups); (ii) the ligand field stabilization energy is higher than the spin pairing energy of 4*f*-orbitals. With regard to bond formation involving 4*f*-orbitals, there are various viewpoints in the literature. It has been shown that the chemical bond in the compounds of iodine, Sb and actinide may involve the component of *f*-orbital (for example, the hybridized orbital of 10_4^- may be represented as $Sp^{3-n-m}d^nf^m$). Using group theory, Tang Au-chin *et al.*[4] have analyzed the bond hybridization in lanthanide compounds involving 4*f*-orbitals. Results of infrared spectra of $NdCl_3 \cdot TBP$ complex and its phosphorus content reveal that the coordination number of rare earth ion in this complex is 6 (Table 2 and Fig. 4), and the complex may be represented as $NdCl_3 \cdot (TBP)_3$. For octahedral hexacoordination complex ion, if a σ-orbital belonging to each coordinating group forms a bond with the central metal ion, according to the symmetry principle[5] these six σ-orbitals belong to the symmetrical species a_{1g}, e_g and t_{1u}. Valence orbitals of the lanthanide metals are 4*f*, 5*d* and 6*s*, in which the seven *f*-orbitals belong to a_{2u}, t_{1u} and t_{2u}, d-orbitals e_g, t_{2g} and *s*-orbitals a_{1g}. Therefore, the orbitals matched with those of the ligands must be $a_{1g}(6s)$, $e_g(5d)$ and $t_{1u}(4f)$, i.e. a d^2sf^3 hybridization is realized. They form six bonding orbitals a_{1g}, e_g and t_{1u}, as well as six antibonding orbitals a_{1g}^*, e_g^* and t_{1u}^*. Besides, the other orbitals t_{2u} a_{2u} and t_{2g} remain in the non-bonding state. The energy-level diagram is shown schematically as follows:

Table 2

Infrared Spectra of Complexes $NdCl_3 \cdot (TBP)$ and Analysis of Phosphorus Therein

Compound or Complex	Characteristic Frequency ($\nu_p = 0$) (cm^{-1})	Amount of Phosphorus in Complex (%)	
		Theoretical	Experimental
TBP	1,290 (strong) 1,265 (weak)	11.65	11.90
$NdCl_3 \cdot (TBP)_3$	1,210	8.86	8.84
$NdCl_3 \cdot (TBP)_4$[a]	1,210 (strong) 1,265 (weak) 1,290 (weaker)		
$NdCl_3 \cdot (TBP)_6$[a]	1,210 (weak) 1,265 (strong) 1,290 (weak)		
$NdCl_3 \cdot (TBP)_8$[a]	1,210 (weaker) 1,265 (weak) 1,290 (strong)	10.41	10.34

a) It may be better written as $NdCl_3 \cdot (TBP)_3 + x$TBP, because free TBP exists in the present case as shown by infrared spectra.

The number of the bonding electrons of the ligand reaches 12, and the metal has *n* valence electrons. The six bonding orbitals a_{1g}, e_g and t_{1u} take twelve electrons, leaving *n* electrons to fill the non-bonding orbitals a_{2u} and t_{2u} and the antibonding orbital t_{1u}^*. Although the actual complex may be distorted somewhat from the octahedra

—— for example, the diene may be coordinated via three center-bond forms, but the phase relationship of orbitals remains the same. Hence, the order of energy-level in the above scheme should be unchanged qualitatively. The following discussion is based on this postulate.

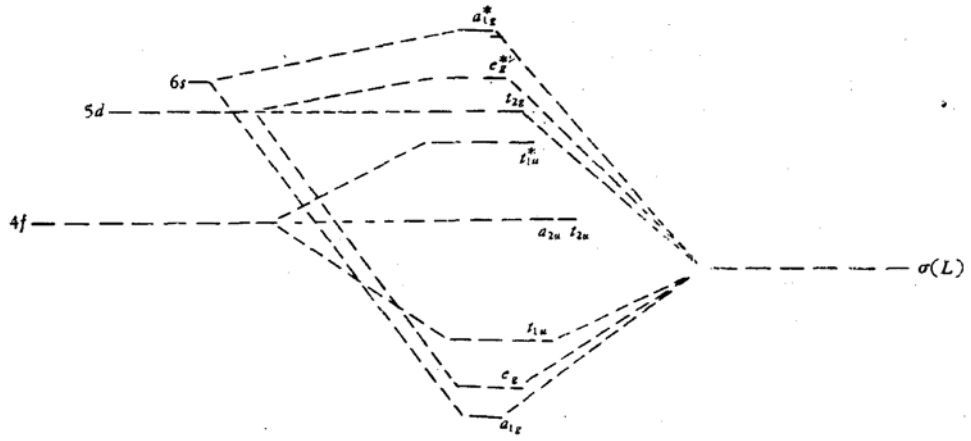

Fig. 5

Let us assume that the polymerization process of the dienes with rare earth metal catalyst is similar to that initiated by a transition metal catalyst system, i.e. polymerization takes place through the following steps: (i) coordination of dienes is made to the transition metal ion; (ii) in the meantime, the bond strength of the double bond is weakened, hence the reactivity increases; (iii) then the activated monomer is inserted into the bonds of Me-R (Me- metal, R- alkyl), or the activated diene takes cis-displacement reaction with R. It is known that whether the polymerization process takes place or not or whether the catalytic activity is large or small depends, first of all, on the nature of the catalyst, i.e. its capability to form the coordinating complex with the monomer, and the weakening of the double bond. We consider that there exists an energy change (ΔE) in the valence electrons during the complex formation, which is believed to be originated from the following two sources:

(1) After complexing with the metal ions, the 12 ligand valence electrons transit to new energy-levels, their energy change is

$$\Delta E_\sigma = 2e(a_{1g}) + 4e(e_g) + 6e(t_{1u}) - 12e(\sigma). \tag{1}$$

(2) The energy change arises from the redistribution of $4f^n$ electrons which is equal to ΔE_f. Thus, the total energy difference ΔE during the complex formation may be written as

$$\Delta E = \Delta E_\sigma + \Delta E_f. \tag{2}$$

With the postulate made above, we have studied the behavior of f^n-orbital of the whole series of the lanthanide elements. First, with $n = 1 - 4$ (Ce^{+3}, Pr^{+3}, Nd^{+3}, Pm^{+3}), their electron configurations are

$$(a_{1g})^2(e_g)^4(t_{1u})^6(a_{2u})^1(t_{2u})^3$$

and $\Delta E = n\epsilon(\text{compounds}) - n\epsilon(\text{atoms})$. Since the electrons are filled in the non-bonding orbitals, in the case of $n = 1-4$, ΔE_f is unchanged ($\Delta E_f = 0$), hence $\Delta E = \Delta E_\sigma$. ΔE depends merely on the energy difference of metal orbitals in complexing with the ligands. The above-mentioned results together with our previous work[1,7] have shown that the valence state of rare earth ions is 3 in the catalyst system with the exception of Sm and Eu. The orbital energy of metals decreases with the increase in atomic number, and the nearer it approaches the energy of the σ-orbital of the ligand the less it becomes. The energy change can be arranged in the following decreasing order:

$$\Delta E(Ce^{+3}) > \Delta E(Pr^{+3}) > \Delta E(Nd^{+3}) > \Delta E(Pm^{+3}), \tag{3}$$

and their catalytic activity increases correspondingly.

With $5 \leqslant n \leqslant 7$ (Sm^{+3}, E^{+3}, Gd^{+3}), the electron configurations can be described as follows respectively:

$$f^5 \quad (a_{1g})^2(e_g)^4(t_{1u})^6(a_{2u})^2(t_{2u})^3,$$

$$f^6 \quad (a_{1g})^2(e_g)^4(t_{1u})^6(a_{2u})^2(t_{2u})^4,$$

$$f^7 \quad (a_{1g})^2(e_g)^4(t_{1u})^6(a_{2u})^2(t_{2u})^5.$$

In this case the f-electrons are being filled into the non-bonding orbitals in pairs, and ΔE_f equals $(n\text{-}4)P$, where P is the spin pairing energy. The total energy change of the valence electrons is

$$\Delta E = \Delta E_\sigma + \Delta E_f = \Delta E_\sigma + (n-4)P. \tag{4}$$

According to Nugent's results[6], P is a positive value, larger than 0.55 ev (for rare earth elements below Sm, the P values are larger than 0.68 ev). Similar to the case of $n = 1$—4, there is a decrease of orbital energy of the metal with its increase in the atomic number. The magnitude may be approximated qualitatively by the first ionization potential of the metal. From Pm to Gd, the average variation in the ionization potential is less than 0.3 ev, i.e. the value of the orbital energy decreasing with the increase in atomic number should not be greater than this. The value of spin pairing energy $P(> 0.6$ ev) is greater than that of metal orbital energy decrease (0.3 ev). The result is that ΔE begins to increase from Sm to Gd,

$$\Delta E(Pm^{+3}) < \Delta E(Sm^{+3}) < \Delta E(Eu^{+3}) < \Delta E(Gd^{+3}), \tag{5}$$

and their catalytic activity decreases correspondingly.

With $n = 8$, the electron configuration is

$$f^8 \quad (a_{1g})^2(e_g)^4(t_{1u})^6(a_{2u})^2(t_{2u})^6$$

with ΔE_σ unchanged, $\Delta E_f = (n-4)P - P^*$, where P^* is the spin pairing energy of electrons in the atom. According to the same reason the energy difference should increase further and its catalytic activity decreases accordingly.

For $n = 9$—11, the f-electrons begin to fill in the antibonding orbital t_{1u}^*, $\Delta E_f = (4p - p^*) + (n-8)Q$, where Q is the energy difference between the anti-

bonding energy and spin pairing energy of an electron in the atom. Q is > 0. In this case, the energy difference after complex formation increases as follows:

$$\Delta E(Dy^{+3}) < \Delta E(Ho^{+3}) < \Delta E(Er^{+3}), \tag{6}$$

and their catalytic activity decreases correspondingly.

Similarly, for $n = 12$—14, the order of energy difference is

$$\Delta E(Tu^{+3}) < \Delta E(Yb^{+3}) < \Delta E(Lu^{+3}), \tag{7}$$

and the catalytic activity is in an inversed order.

From the calculated results obtained above, it is obvious that when the complex is formed by combining trivalent rare earth ions with the diene or other ligands, the energy differences are changed, the order of which is shown as follows:

$$\begin{aligned}&\Delta E(Ce^{+3}) > \Delta E(Pr^{+3}) > \Delta E(Nd^{+3}) > \Delta E(Pm^{+3}) < \Delta E(Sm^{+3})\\ &< \Delta E(Eu^{+3}) < \Delta E(Gd^{+3}) < \Delta E(Tb^{+3}) < \Delta E(Dy^{+3}) < \Delta E(Ho^{+3})\\ &< \Delta E(Er^{+3}) < \Delta E(Tu^{+3}) < \Delta E(Yb^{+3}) < \Delta E(Lu^{+3}).\end{aligned} \tag{8}$$

Comparing the catalytic activities shown in Figs. 1 and 2, we believe that there exists a relationship between them. The order of the catalytic activity is just the reverse of the former in general with the exception of that of Pm, Sm and Eu. It is a pity that we could not provide any direct proof to explain the contradiction for Pm, because Pm is not available in our laboratory, and Sm and Eu are reduced to divalent[11].

Thus, different catalytic activities of the catalyst systems composed of different rare earth metals could be explained satisfactorily by the above postulate. The catalytic activity is related to energy difference resulting from the complexing rare earth with dienes or other ligands.

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