

Advances in PNP-ligated rare-earth-metal complexes: reactivity and catalytic performances

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ABSTRACT

Due to the large ionic radius and high electro-positivity nature, rare earth metal complexes are difficult to stabilize and undergo pathways like ligand redistribution and intramolecular C-H activation. To solve such problems and retain reactive versatility, rare earth complexes supported by a variety of tridentate PNP pincer ligands have been explored. Such complexes can serve as perfect precursors for preparing ultra-active rare earth species containing two metal-carbon bonds, let alone Ln=N and Ln=P multiple bonds. In addition, the combined stability and activity of the cation rare earth mediates made them the best catalysts for the polymerization of olefins and other non-polar hydrocarbon monomers, especially conjugated dienes. The practical utilization of rare earth metal catalysts for new materials production have also extensively explored by experts from the academic and industries. **Polyolefins J (2023) 10: 89-99**

Keywords: PNP ligand; rare earth metals; lanthanides; reactivity; catalysis.

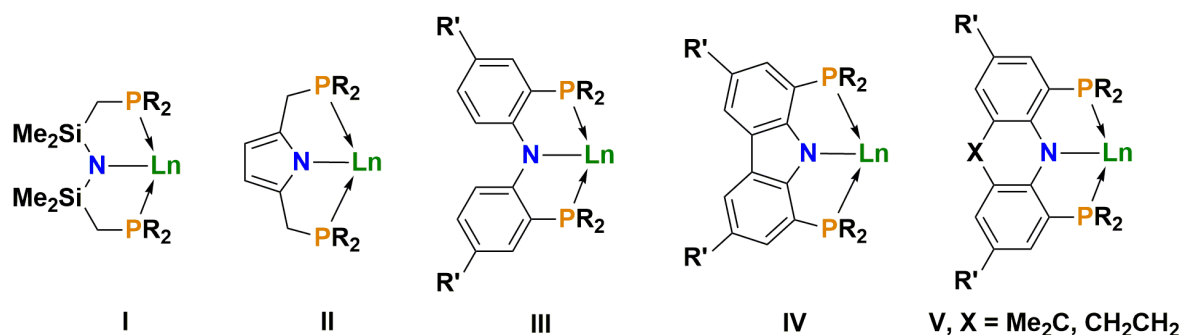
INTRODUCTION

Multi-dentate pincer ligands demonstrated to be excellent ancillary ligands for transition metals and main group elements. The tridentate PNP ligand, with two phosphine donor side arms and one anionic nitrogen donor, is one of the most representative categories. During the past few decades, the chemistry of PNP-ligated d-block transition metals [1-5] and main group elements [6] have been explored extensively, which has

drastically broadened the landscape of organometallic chemistry and homogeneous catalysis. On the other hand, PNP-ligated rare-earth metal complexes, though drawing less attention, have also made significant development during the past few years (Scheme 1).

Considering the extreme electropositive nature, the early rare earth metal complexes were predominantly stabilized by bis-cyclopentadienyl moiety [7-11] to

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Scheme 1. PNP ligated rare ear metal complexes.

prevent dimerization or ligand redistribution. Then, the electron-rich and steric bulk strategy allowed the outcome of half-sandwich type rare earth metal complexes [12], which gave rise to diverse reactive and catalytic behaviors, as a consequence of more reactive sites. Comparatively, rare earth complexes supported by anionic pincer ligands [13-14], let alone PNP-type ligands, have similar stability to half-sandwich categories. Such robustness facilitates the synthesis and isolation of some the extremely active species possessing rare earth nitrogen multiple bound. In addition, PNP-ligated rare earth complexes also show high activity toward regio- and stereo-selective polymerization of conjugated dienes and other non-polar hydrocarbon monomers. Here we present representative examples of the reported rare-earth complexes supported by anionic PNP ligands with their reactivity and catalytic behaviors.

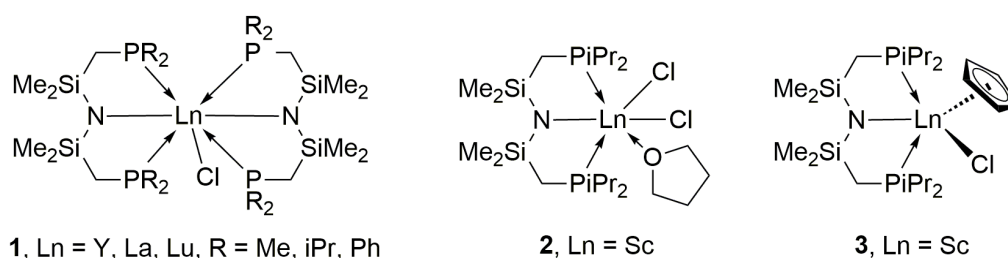
STABILIZATION OF LANTHANIDE DI-ALKYL AND OTHER COMPLEXES

Early efforts to stabilize lanthanide complexes with a SiMe₂-bridged PNP ligand

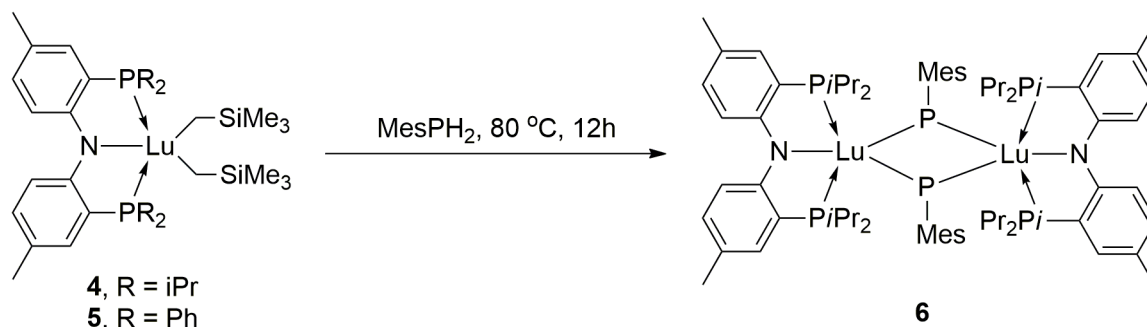
In 1988, Fryzuk et al. introduced the first PNP ligated rare earth complexes by the reaction of 2 equivalents

of lithium salt of the ligand $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2$ with anhydrous yttrium chloride [15]. In 1991, the group extended the scope to lanthanide metals. Thus, through the reaction of $\text{MN}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2$ ($\text{M} = \text{Li}, \text{K}$; $\text{R} = \text{Me}, \text{Ph}, \text{i-Pr}$) with anhydrous lanthanide (La and Lu) chloride, the remaining chloride can be substituted by hydrocarbyl ligand (Scheme 2). However, these hydrocarbyl complexes are thermally unstable and undergo a cyclo-metalation reaction to generate a new species after loss of RH [16].

In 1996, the Fryzuk group reported the mono-ligated PNP scandium complexes containing two hydrocarbyl groups. The complexes were prepared by reacting the lithium salt $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{PPri}_2)_2$ with $\text{ScCl}_3 \cdot 3\text{THF}$ and subsequent replacement of the chloride by alkyl groups. These bis(hydrocarbyl) species decomposed when reaction with small molecules like CO and H_2 while reaction with ethylene resulted in polyethylene as expected. These results indicated that such PNP ligand structures were insufficient in stabilizing highly reactive lanthanide di-alkyl complexes [17]. In 2000, follow-up research added another ancillary Cp ligand to generate a more coordinately saturated complex with only one alkyl group [18]. The strategy did offer more stability to the complexes, however the complexes lost the diversity of catalytic reactions and could only undergo some metathesis reactions.



Scheme 2. Fryzuk's PNP-ligated rare earth metal complexes.



Scheme 3. Kiplinger's PNP-ligated rare earth metal complexes.

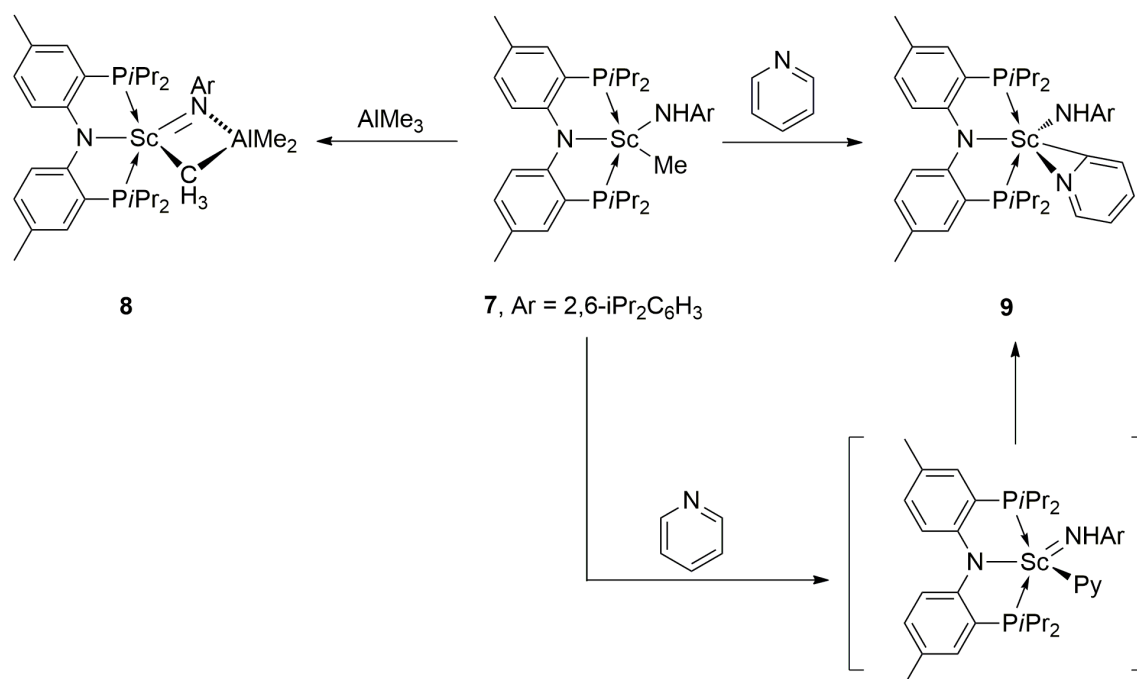
Stabilization of a Ln=PR moiety by PNP ligand with a PhNHPPh backbone

In 2008, Kiplinger et al. introduced another class of PNP ligand with a PhNHPPh backbone to stabilize the highly reactive lanthanide complexes. With the aid of the ligand, they isolated the first lanthanide phosphinidene complex with two bridging phosphinidene units between two (PNPiPr)Lu moieties, via the reaction of PNP-ligated Lu(III) bis(alkyl) complexes with one equivalent of MesPH₂ (Mes = 2,4,6-Me₃-C₆H₂) [19]. The lanthanide phosphinidene complex behaves similarly to the known nucleophilic phosphinidene systems of Ta and Zr, as a nucleophilic phosphinidene transfer reagent. However, stabilization a terminal lanthanide phosphinidene remained a challenge due mainly to the large ionic radii of the lanthanide ions. The failure to

isolate a terminal lanthanide phosphinidene complex may be due to the discrepancy in energy between the lanthanide and phosphine orbitals, and the formation of these highly polarized bonds is prohibited (Scheme 3).

Stabilization of a Ln=NR moiety by PNP ligand with a PhNHPPh backbone

The PNP moiety with PhNHPPh backbone demonstrated to be an ideal ancillary ligand for supporting the lanthanide phosphinidene complex. In 2008, by adopting the same ligand, Mindiola et al. observed the existence of complexes of group 3 transition-metal elements (including the lanthanides) with terminal imido groups [20]. PNP-ligated Sc di-chloride complex can readily undergo transmetalation reaction with LiN-HAr (Ar=2,6-iPr₂C₆H₃) to afford [(PNP)Sc-(NHAr)Cl] (Scheme 4). When methyl group was introduced



Scheme 4. Mindiola's PNP-ligated rare earth metal complexes.

as a leaving group for the deprotonation of the anilide, the complex [(PNP)Sc-(NHAr)Me] was chosen as the precursor. By applying a combination of isotopic labeling and reactivity studies of the precursor, it was found that intermolecular C-H activation of pyridine and benzene, as well as the complexation with AlMe₃, were promoted by the announced transient Sc=NR complex.

Mechanistic studies showed that the Sc(III) scaffold (PNP)Sc is sufficient to support a terminal imido group. However, the highly reactive of the imide intermediate facilitates the C-H bond activation of substrates such as pyridine [21]. The proposed pathway proceeds via an associative-type mechanism, in which, the formation of scandium imide moiety most likely involves a pre-equilibrium step between the precursor and the pyridine adduct, followed by the α -hydrogen abstraction step. In addition, rare earth complexes with unsaturated Sc-C bonds with a single trialkyl aluminum unit has also been successfully achieved by the same group [22].

Stabilization of a redox innocent metal center

In 2017, Schelter et al. reported the coordination of the anionic bis[2-(diisopropylphosphino)-4-methylphenyl]amido (PNP) ligand framework to the cerium(III) cation and the isolation of a series of {(PNP)Ce} and {(PNP)₂Ce} type complexes possessing the redox-active cerium ion [23]. Electrochemical and computational studies revealed the stabilization of the Ce³⁺ oxidation state by the PNP ligand framework (Scheme 5).

Stabilization of rare earth di-alkyl complexes by a pyrrole-based PNP ligand

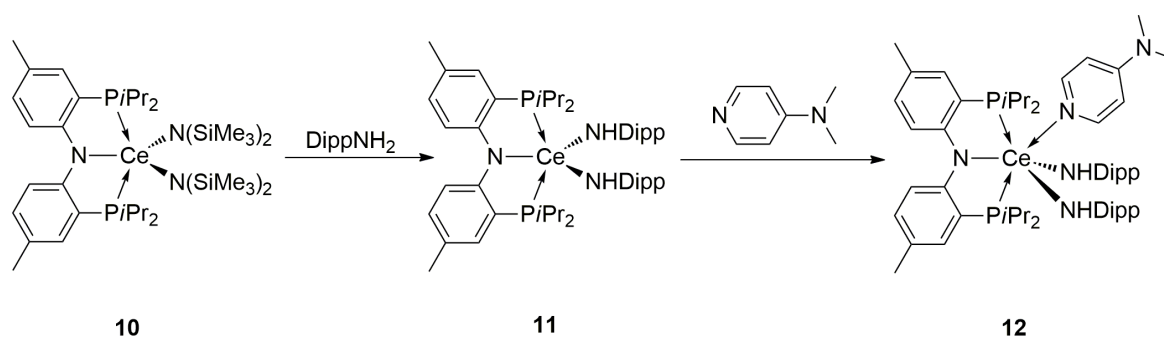
In 2015, Anderson et al. demonstrated the use of mono-anionic pyrrole-based PNP ligand with two PR₂

side arms in rare earth chemistry [24]. A series of novel PNP-supported scandium and lanthanide complexes have been prepared and characterized, and their reactivity with C-H bonds was examined (Scheme 6). The reactions with primary amines led to the formation of amido complexes that undergo cyclometalation via σ -bond metathesis. In addition, several class of C-H bonds, including sp-, sp²-, and sp³-C-H bonds can be activated. C-H activation of intermolecular sp² bonds has never observed for non-Cp-supported complexes of scandium or the lanthanides, suggesting that strongly donating, highly polarized ligands might be the key to generating reactive centers for σ -bond metathesis.

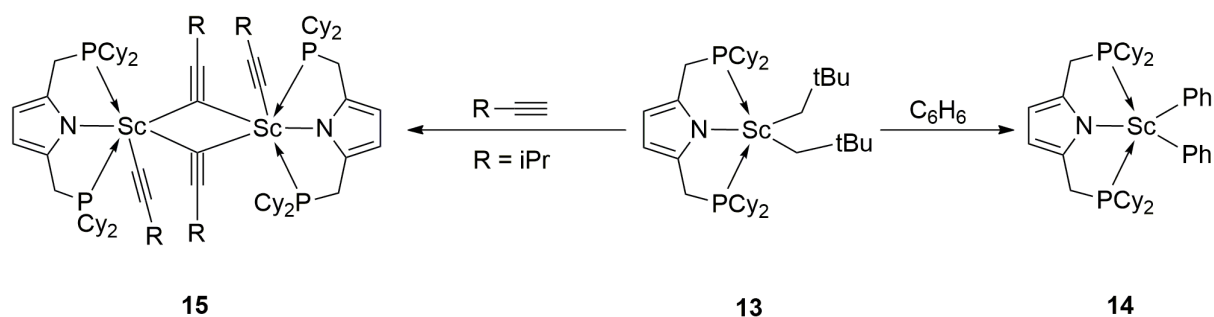
The same group then studied the catalytic performance of the scandium and yttrium congeneric complexes supported by the PNP ligand [25]. The catalytic alkene hydrogenation and hydrosilylation, alkyne selective partial-hydrogenation and partial-hydrosilylation, were studied with the complexes. It is found that the yttrium complex has the highest activity in all cases. However, the higher activity is accompanied with faster catalyst decomposition, so the total yield of some reactions with scandium catalyst is higher. Theory calculations showed that the reaction can form alkene/alkyne-inserted metal hydride intermediates via sigma-bond metathesis.

POLYMERIZATION CATALYSIS

As mentioned above, the anionic PNP ligand has been demonstrated to be an ideal ancillary ligand for supporting lanthanide complexes, even the ultra-active phosphinidene and imide species. Likewise, it is reasonable that lanthanide complexes supported by such



Scheme 5. Schelter's PNP-ligated rare earth metal complexes.



Scheme 6. Anderson's PNP-ligated rare earth metal complexes.

multi-dentate systems are ideal catalyst precursors for polymerization catalysts. New polymer materials with well-controlled microstructures and desired properties rely on developing new generations of polymerization catalysts, and rare earth catalysts with well-defined structures are among them. The active species of rare earth catalyst systems are commonly cationic, which are highly reactive, thus the selection of supporting ligands is of great importance. By adopting PNP ligands with extraordinary performance, the polymerization catalysis of rare earth complexes made its characteristic ways.

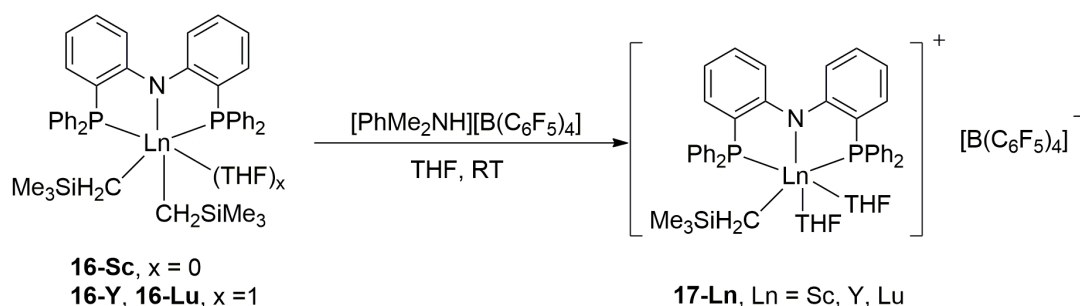
Polyisoprene (PIP) and polybutadiene (PBD) rubbers, which can be produced with rare earth metal catalysts, possessing high *cis*-1,4 units are among the most demanding elastomers used in tires industry, and other elastic materials applications. The current industrially used catalyst is a Z-N type multi-component system consisting typically of Nd carboxylate, alkyl aluminum, and chloride source [26]. The multi-component catalysts systems lack "livingness" and yield polymers with broad molecular weight distribution.

Bis(phosphino)phenyl amido ligated rare earth catalyst for diene polymerization

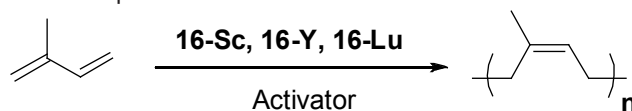
To improve the industrial catalyst system, Hou et al.

reported a new catalyst systems based on a cationic alkyl rare-earth metal complex bearing an ancillary [bis(2-dipheylphosphino)phenyl]amido (PNP) ligand (Scheme 7) [27]. Treatment with one equivalent of [PhMe₂NH][B(C₆F₅)₄] in C₆H₅Cl, the catalyst system provides extreme high activity, high *cis*-1,4 selectivity (99%) and excellent livingness ($M_w/M_n=1.05-1.13$) toward isoprene and butadiene polymerization, without the addition of aluminum additives (Table 1). The catalytic system can also apply to the copolymerization of isoprene and butadiene to produce highly *cis*-1,4 PIP-*co*-PB copolymers. Catalysts with central metal Y showed higher *cis*-1,4 selectivity than Sc and Lu analogs under various conditions. It is noticeable that the excellent "livingness" and the high *cis*-1,4 selectivity of the present polymerization system are maintained even at high temperatures.

In addition, they successfully isolated and characterized the structure of a related cationic alkyl lutetium complex assumed to be the active species [27], provided a suitable structural model and helped a better understanding of the polymerization process. However, the cationic complexes isolated from THF are not catalytic active toward isoprene and butadiene under identical polymerization conditions, which suggests that the true active species in the present catalyst



Scheme 7. Preparation of PNP-ligated rare earth metal complexes for polymerization.

Table 1. Living *cis*-1,4 polymerization of isoprene^[a].

Run	Catalyst	T _p / °C	t / min	Yield	M _n ^(b) / 10 ⁵	M _w /M _n ^(b)	<i>cis</i> -1,4 ^(c) / %	T _g ^(d) / °C	Eff. ^(e) / %
1	16-Sc/A ^(f)	RT	60	100	1.6	1.10	96.5	- 66	26
2	16-Y/A ^(f)	RT	60	100	2.3	1.10	99.3	- 69	18
3	16-Lu/A ^(f)	RT	60	100	1.9	1.09	97.1	- 67	22
4	16-Y/B ^(f)	RT	60	79	3.2	1.11	99.3	- 69	10
5	16-Y/C ^(f)	RT	60	0	-	-	-	-	-
6	16-Y/A ^(g)	RT	10	40	0.5	1.05	99.3	- 69	33
7	16-Y/A ^(g)	RT	15	90	1.0	1.05	99.3	- 69	37
8	16-Y/A ^(g)	RT	20	100	1.2	1.07	99.3	- 69	34
9	16-Y/A ^(g,h)	RT	40	150	1.8	1.08	99.3	- 69	34
10	16-Y/A ^(g,h)	RT	60	200	2.3	1.08	99.3	- 69	36
11	16-Y/A ^(g)	0	180	100	1.3	1.06	99.6	- 69	31
12	16-Y/A ⁽ⁱ⁾	50	10	90	0.7	1.05	98.7	- 68	53
13	16-Y/A ^(i,j)	50	20	188	1.4	1.05	98.7	- 68	55
14	16-Y/A ⁽ⁱ⁾	80	2	66	0.6	1.05	98.5	- 68	45
15	16-Y/A ⁽ⁱ⁾	80	5	100	0.8	1.05	98.5	- 68	51

^(a)Conditions: C₆H₅Cl (10 mL); Ln (25 mmol); [IP]₀/[Ln]₀=600; [Ln]₀/[activator]₀=1:1 (activator=[PhMe₂NH][B(C₆F₅)₄]⁻ (A), [Ph₃C][B(C₆F₅)₄]⁻ (B), B(C₆F₅)₃⁻ (C)), unless otherwise noted. ^(b)Determined by gel permeation chromatography (GPC) with respect to a polystyrene standard. ^(c)Determined by ¹H and ¹³C NMR spectroscopy. ^(d)Measured by differential scanning calorimetry (DSC). ^(e)Catalyst efficiency = M_n(calculated)/M_n(measured). ^(f)In runs 1–5, IP was added to a mixture of 16-Y and the activator. ^(g)In runs 6–11, a C₆H₅Cl solution of activator A was added to a solution of the neutral complex and IP. ^(h)After polymerization of 1.022 g (600 equiv.) of IP for 30 min, another 1.022 g of IP was added and the mixture was stirred for a further 10 (run 9) or 30 min (run 9). ⁽ⁱ⁾In runs 12–15, a mixture of 16-Y and IP in C₆H₅Cl (3 mL) was added to a preheated C₆H₅Cl solution (7 mL) of A. ^(j)[IP]₀/[16-Y]₀=1200.

systems should be cationic alkyl species with one or fewer THF ligands. The scope of center metal and ligand type has extended in some patents of the same group [28].

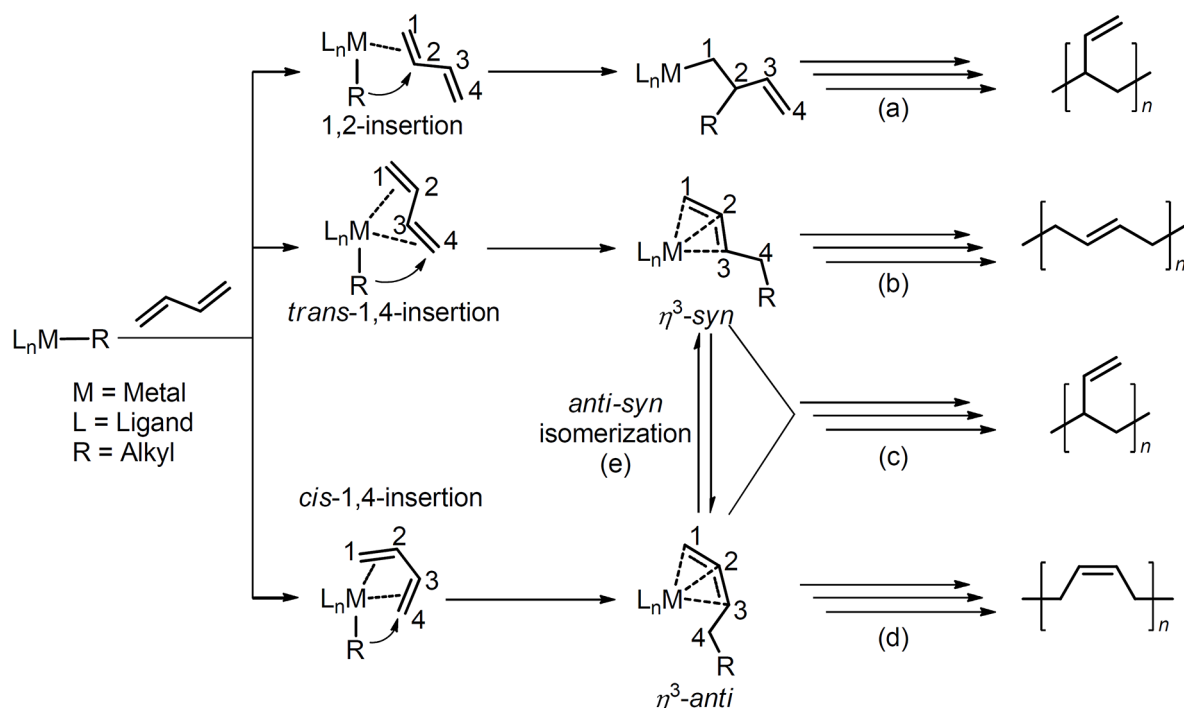
After that, Luo et al. carried out density functional theory (DFT) calculations for this highly selective *cis*-1,4-polymerization of butadiene catalyzed by a cationic rare-earth metal complex bearing an [bis(2-diphenylphosphino)phenyl]amido (PNP) ancillary ligand [29]. The result indicates that the chain initiation and propagation of butadiene polymerization occurs via the favorable *cis*-1,4-insertion route, while the *trans*-1,4 and 1,2-insertion are unfavorable both kinetically and thermodynamically. The regional selectivity (1,4 - and 1,2 - insertion) is mainly determined by the steric hindrance, while the electronic factor of the central metal has a decisive influence on the *cis* and *trans* insertion. Tetrahydrofuran (THF) coordination makes monomer insertion less favorable, which may suggest that the THF-coordinating cationic species might work at the chain initiation stage, and the THF-free cationic species could be the active species during the chain propagation process as observed ex-

perimentally (Scheme 8).

Bis(phosphino) carbazolidine-ligated rare earth catalyst for diene polymerization

As mentioned above, in the bis(phosphino) amido type of PNP-ligated rare earth metal complexes, the rotation of the two N-C(Phenyl) bonds can adjust the steric environment of central metal, thus the flexibility guaranteed coordination sphere and facilitated the high *cis*-1,4 selectivity. In 2011, Cui et al. reported similar bis(phosphino) carbazolidine rare earth metal complexes, in which the two phenyl rings of the backbone fused together to form a carbazole unit (Scheme 9) [30]. Using the amino-benzyl group, the complexes with THF-free seven-coordinate monomers were synthesized. The carbazolidine ligand binds to the Y ion via the two phosphine atoms and a nitrogen atom in a tridentate mode to form a planar pincer geometry with the Y ion deviates slightly out of the plane owing to the steric congestion arising from the phenyl phosphine groups.

These rare earth complexes, when activated with [Ph₃C][B(C₆F₅)₄]⁻, exhibited high *cis*-1,4-selectivity and excellent polymerization activity towards iso-

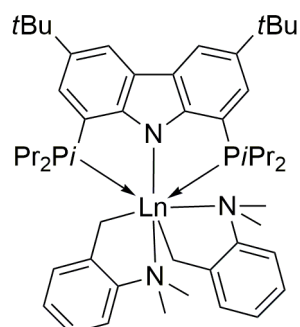


Scheme 8. Mechanism for Rare Earth Metal Catalyzed Diene Polymerization.

prene and butadiene in a wide range of polymerization temperatures, and the yttrium complex showed the best catalytic performance. Remarkably, upon copolymerization with butadiene, the cationic yttrium-active species could also initiate the ROP of e-CL to afford di-block PB-co-CL copolymers with desirable molecular weight. This rare earth polymerization catalyst system was also applied to 3-methylenecyclopentene [31] and 1-phenyl-1,3-butadiene [32] polymerization, but with limited success.

Acridane-based and iminodibenzyl-based PNP ligated rare earth catalyst for diene polymerization

Inspired by the catalytic performance of bis(phosphino)



18-Ln, Ln = Y, Sc, Er

Scheme 9. Cui's PNP-ligated rare earth metal complexes.

amido PNP ligated rare earth complexes of Hou's group and the similar bis(phosphino) carbazolidone rare earth metal complexes of Cui's group, Shi et al. reported the analogous acridane-based PNP-pincer ligands and iminodibenzyl-based PNP pincer ligands and their further complexations to a series of rare-earth metals (Scheme 10) [33]. These two PNP-rare earth systems can also be considered as the modification of bis(phosphino) amido PNP system. A convenient and efficient synthetic approach for preparation of acridane-based PNP ligands has developed. The new acridane-based PNP ligands are characteristic of the phenyl group of the backbone bounded by a Me₂C moiety (Scheme 10). In treatment with appropriate borate reagents, the isopropyl-substituted Y complex and phenyl-substituted Lu complex could catalyze the polymerization of isoprene and β-myrcene with high catalytic activity and relatively high *cis*-1,4-selectivity in a living manner. The Y/borate catalyst could also facilitate the copolymerization of isoprene and butadiene to provide copolymers with high *cis*-1,4-selectivity and well-defined sequence distribution.

While for the iminodibenzyl-based PNP cases, almost all of the PNP rare earth metal complexes promote the polymerization of isoprene and myrcene in a 3,4-selective manner [34], which is in sharp contrast to previous



19-Ln, R = *i*Pr, n = 0, Ln = Y, Lu

20-Ln, R = Ph, n = 0, Ln = Y, Lu

21-Ln, R = *i*Pr, n = 0, Ln = Y, Lu

22-Ln, R = Ph, n = 0, Ln = Sc, Y, Dy, Ho, Er, Tm, Lu

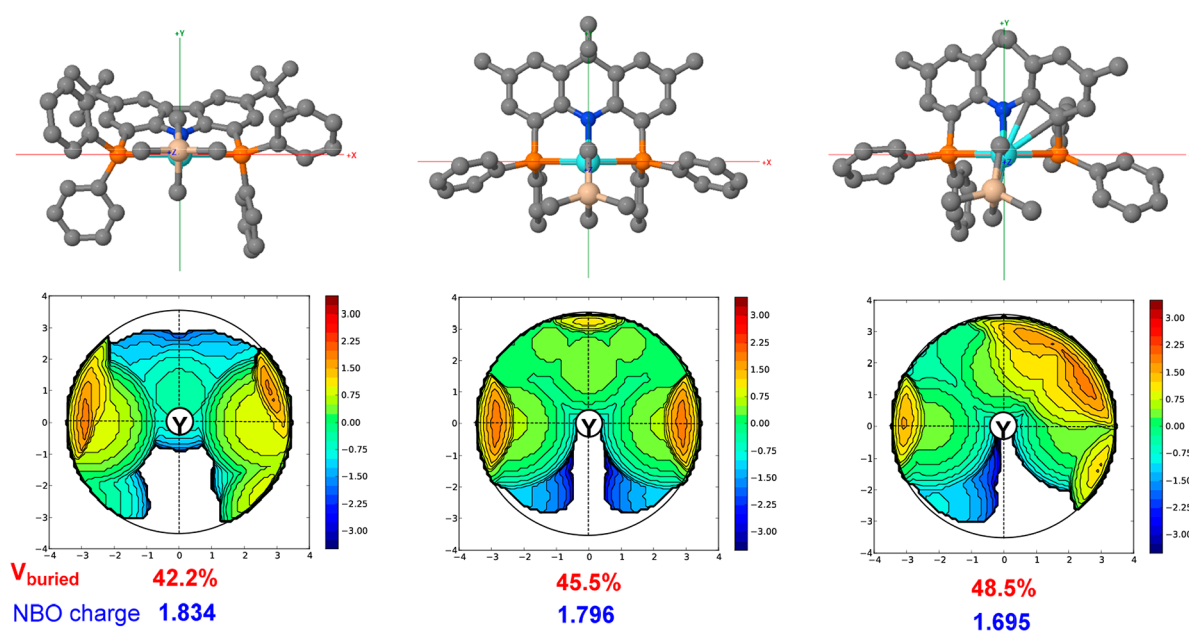
Scheme 10. Shi's PNP-ligated rare earth metal complexes.

works of acridane-based PNP rare-earth metal complexes that mediated exclusively the *cis*-1,4-selective polymerization of 1,3-dienes. It is generally accepted that the more open environment of the metal center, the more favorable it is for *cis*-1,4 selectivity of conjugated diene polymerization. The DFT and NBO calculations suggested that the steric hindrance around the metal center of the iminodibenzyl-based PNP ligand plays an indispensable role in the near exclusive 3,4-selectivity compared with their carbazolide-PNP and acridane-PNP analogs (Scheme 11).

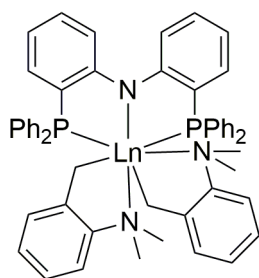
Optimization of bis(phosphino)phenyl amido-ligated rare earth catalyst for industrial application attempts

Xin and co-workers are fascinated by the excellent catalytic performance of PNP-ligated rare earth catalytic systems for the controlled polymerization of

conjugated dienes, and it is expected to be a further step towards industrial application. They optimized one of the best catalyst systems aiming to overcome the weaknesses on thermostability and sensitive to trace Lewis basic impurities of the cationic species. By adopting the [bis(2-dipheylphosphino)phenyl] amido (PNP) ligand system, Xin's group extended the scope of central metal (Y, Nd, and Gd) and further optimized the catalyst system to meet the industrial requirements of practical application (Scheme 12) [35]. with the treatment of {[bis(2-dipheylphosphino)phenyl]amido}LnR₂, (Ln=Y, Nd, Gd; R=-CH₂C₆H₄-2-NMe₂, -CH₂SiMe₃) with borate activation reagent [PhMe₂NH][B(C₆F₅)₄], all the catalysts exhibited excellent catalytic efficiency in an aromatic solvent, produced very-high to ultra-high molecular weight poly-isoprene rubber (PIR), and the obtained PIR con-



Scheme 11. Shi's PNP-ligated rare earth metal complexes structural characterization (From left to right 18-Y, 20-Y, 22-Y).



23-Ln, Ln = Y, Nd, Gd

Scheme 12. Xin's PNP-ligated rare earth metal complexes.

tained over 98% *cis*-1,4 head-to-tail repeating units. In most cases, the borate-activated polymerization reaction proceeded in a quasi-living pattern (PDI=1.2-1.5) with controlled monomer conversions. On the other hand, when treated with the commercially available modified methylaluminoxane (MMAO), all catalysts showed high catalytic efficiency, and produced high molecular weight PIR with narrow molecular weight distribution (PDI < 2.0) and high *cis*-1,4 head-to-tail repeating units in the range of 91–95%, and most importantly, in an aliphatic hydrocarbon solvent. This research makes single-site rare earth catalysts with well-defined structures a step beyond current industrial polybutadiene rubber (PBR) and PIR production processes.

CONCLUSION

The PNP type pincer ligands have significantly enriched the chemistry of rare earth metals. Comparable to cyclopentadienyl ligands, the tridentate systems play an increasingly significant role in stabilization of electropositive rare earth centers. Through the modification of the PNP backbone frameworks of the anionic PNP ligands, researchers have successfully prepared and isolated active complexes of scandium, yttrium, and lanthanide elements. Complexes containing ultra-high active Ln=X (X = N, P) units have also been successfully synthesized, isolated, and structurally characterized. The catalytic performance of the PNP-ligated rare earth metal catalysts systems has been explored in the polymerization of various unsaturated hydrocarbons, especially the catalytic polymerization of conjugated dienes (butadiene and isoprene) has

rapidly progressed in recent years. The high *cis*-1,4 selectivity and high catalytic activity of the PNP-ligated rare earth metal catalysts systems outperformed other lanthanides catalysts systems currently used in the production of high *cis*-PBD and PIP. The living or quasi-living characters of the PNP-ligated rare earth metal catalysts systems, which are considered as a disadvantage factor in industrial processes due to economic reasons, can be altered through the addition of chain-transfer reagent into the catalytic systems.

Several analogs of PNP-ligated rare earth metal catalysts systems developed for olefin and dienes polymerization demonstrated great potential for these types catalysts systems to be utilized in practical synthetic rubber production, along with advances in ligand structure modification that facilitate the creation of PNP-ligated rare earth catalyst system in the academic research fields, moreover the newly developed catalytic systems can speed up the practical application in synthetic PBD and PIP rubber production processes.

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