

Catalysis

Switching the Reactivity of Palladium Diimines with “Ancillary” Ligand to Select between Olefin Polymerization, Branching Regulation, or Olefin Isomerization

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Abstract: Coordinating solvents are commonly employed as ancillary ligands to stabilize late transition metal complexes and are conventionally considered to have little effect on the reaction products. Our work identifies that the presence of ancillary ligand in Pd-diimine catalyzed polymerizations of α -olefins can drastically alter reactivity. The addition of different amounts of acetonitrile allows for switching between distinct reaction modes: isomerization–polymerization with high branching (0 equiv.), regular chain-walking polymerization (1 equiv.), and alkene isomerization with no polymerization (>20 equiv.). Optimization of the isomerization reaction mode led to a general set of conditions to switch a wide variety of diimine complexes into efficient alkene isomerization catalysts, with catalyst loading as low as 0.005 mol %.

Late transition metal catalysts for olefin polymerization are valued for their polar monomer tolerance and the ability to control branching through a “chain-walking” mechanism.^[1] Such catalysts are typically cationic or neutral palladium or nickel complexes employing bidentate or multidentate ligands bound to the active site. These ligands alter the electronic and steric environment and can be tuned to adjust the extent of β -hydride elimination and reinsertion, which are the key steps in branch formation through the “chain-walking” mechanism,^[2] and the electrophilicity of the active site (crucial for polar monomer tolerance.) Examples of this tuning can lead to high molecular weight polyethylene with low branching,^[3] regular branching structure,^[4] hyperbranched polyolefins,^[5] and, if hydride elimination is sufficiently favorable, catalysts capable of alkene isomerization without the propensity to undergo polymerization.^[6]

Ancillary ligands, commonly a coordinating solvent such as acetonitrile (NCMe), are often employed to stabilize late transition metal complexes. For example, nitriles are used with palladium diimines in order to yield a stable precatalyst complex (**1**, Scheme 1), where the ancillary ligand will occupy the vacant coordination site (prior to exposure to monomer) and prevent the formation of an unstable 14 electron



Scheme 1. Typical structures of late transition metal catalysts for olefin polymerization showing a bidentate ligand in blue and an ancillary ligand in red. Counterions for the cationic complexes **1** and **3** are not shown.

complex.^[7] Other examples of late transition metal complexes employing ancillary ligands are shown in Scheme 1, including a Drent-type neutral phosphine-sulfonato Pd^{II} complex^[1d,8] (**2**), a cationic biphosphine monoxide palladium(II) complex^[9] (**3**), and a neutral salicylaldiminato Ni^{II} complex^[3,10] (**4**).

Acetonitrile has previously been found to have a very similar coordination strength to ethylene^[4] ($K_{eq}(-85^\circ\text{C}) = (4.6 \pm 0.9) \times 10^{-2}$) when complexed with a palladium diimine catalyst,^[11] indicating that under typical polymerization conditions where monomer is in a large excess, a nitrile complex should have at most only a moderate inhibition on the rate of propagation. This decrease in turnover frequency (TOF) has also been reported for a higher α -olefin (1-hexene).^[12] Polymerizing 1-hexene in the presence of nitriles was found to decrease the TOF of the catalyst with a larger effect seen for more strongly donating nitriles. Similarly, using increasing concentrations of 3,5-bis(trifluoromethyl)benzonitrile gave decreasing molecular weights over a 3-hour reaction period. The dispersity of the obtained polymers was low (>1.10), indicating that nitriles do not promote chain transfer and a living polymerization can be maintained. No significant differences between polymer samples apart from the lower rate in the presence of ancillary ligands were reported, which was attributed to an active/dormant equilibrium whereby the acetonitrile adduct is not capable of undergoing polymerization.^[12]

Recent work has suggested that the absence of ancillary ligands could be key to internal alkene polymerizability; observed in a study which increased the branching of α -olefin polymerizations with a palladium diimine catalyst through a Lewis acid triggered isomerization of 1-alkenes to internal alkenes which can then polymerize with high branching (isomerization-polymerization).^[13] The proposed mechanism states that the Lewis acid undergoes a counterion swap to a complex which favors isomerization as well as forming an adduct with the ancillary nitrile ligand and thereby prevent competitive binding with internal alkenes. An ancillary ligand

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effect has also been seen in ethylene polymerizations with neutral salicylaldiminato Ni^{II} complexes: the temperature dependence on the degree of branching changes according to the lability of the ancillary ligand (1.1 to 7.3/1000 carbons). Density functional theory (DFT) studies on a related complex suggested that the overall barrier to β -hydride elimination is lower for an ancillary ligand adduct compared to an ethylene adduct.^[14]

Herein we report that acetonitrile ancillary ligand can be used to drastically tune the reactivity of palladium diimines to select for distinct reaction modes. Polymerization in the absence of ancillary ligand yields rapid isomerization of α -olefins to internal alkenes which then polymerize to give a highly branched polymer. 1 equiv. of ancillary ligand with respect to palladium preferentially polymerizes α -olefin, with any isomers formed polymerizing at a much lower rate. Adding an excess of ancillary ligand (20 equiv. with respect to palladium) transforms the system into an alkene isomerization catalyst without any observable polymerization. Optimization of the isomerization pathway in the presence of excess acetonitrile leads to a general set of experimental conditions which can be employed to switch a wide range of palladium diimine polymerization precatalysts into effective isomerization catalysts.

Isomerization is a well-known side reaction when polymerizing α -olefins with Pd-diimine catalysts, occurring through β -hydride elimination and subsequent reinsertion.^[15] A typical reaction with catalyst **1** will yield around 71% polymer and 28% internal alkenes in 3 hours (1% 1-alkene left), with branching analysis by ^{13}C NMR (S10.3, Figure S3) showing methyl and butyl branching (S11.1, Scheme S4), indicative of chain-walking polymerization of 1-hexene.^[5,16] Allowing the reaction to proceed for an additional 18 hours shows a slight decrease in the internal olefin signals via ^1H NMR and the appearance of ethyl and propyl branches (characteristic of chain-walking polymerization of 2 and 3-hexenes) (S11.2, Scheme S5; S11.3, Scheme S6) by quantitative ^{13}C NMR (S10.3, Table S1, Figure S3).^[13,17]

Previous studies into the effect of ancillary ligands on Pd-diimine catalyzed reactions showed only an inhibition on the rate of polymerization.^[12] However, the removal of ancillary ligand through reaction with a Lewis acid has been implicated as being crucial to increasing the polymerizability of internal alkenes.^[13] We reasoned that the presence and concentration of a labile ligating species could play a crucial role in the reactivity of Pd-diimines.

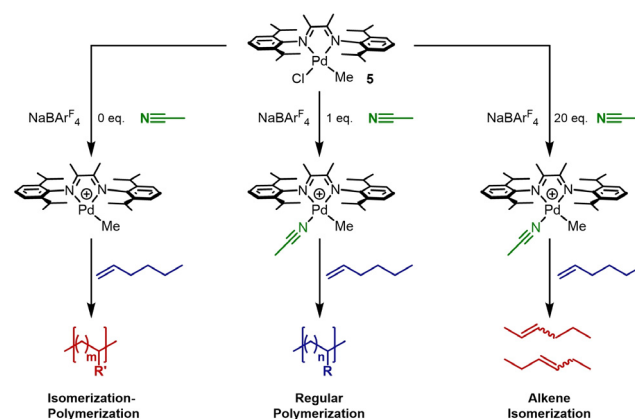
To test this hypothesis, we conducted a series of experiments with varying amounts of acetonitrile (Table 1), analyzing the extent of polymerization and isomerization in each case.

Polymerization of 1-hexene from the Pd methyl chloride **5**, activated with NaBARF_4 in the absence of acetonitrile proceeds with significant isomerization, Scheme 2, Table 1. Sampling after 5 minutes revealed that the reaction had achieved 46% conversion to polymer. Analysis of the sample shows that only 16% is the starting material, 1-hexene, with the rest having been isomerized to internal alkenes (32% 2-hexene and 6% 3-hexene). A conventional understanding of Pd-diimine catalysts would suggest that the internal alkenes

Table 1: Reaction of 1-hexene with palladium diimine catalyst (**5**), with varying concentration of ancillary ligand, NCMe.

<i>t</i>		0 equiv. NCMe ^[a]	1 equiv. NCMe ^[a]	20 equiv. NCMe ^[a]
	Conv. ^[b]	46% Polymer	16% Polymer	0% Polymer
5 mins	Remaining monomer	16% 1-hex	75% 1-hex	82% 1-hex
		32% 2-hex	6% 2-hex	13% 2-hex
		6% 3-hex	3% 3-hex	5% 3-hex
	Conv. ^[b]	85% Polymer	52% Polymer	0% Polymer
1 hour	Remaining monomer	0% 1-hex	25% 1-hex	27% 1-hex
		14% 2-hex	19% 2-hex	60% 2-hex
		1% 3-hex	4% 3-hex	13% 3-hex
	Conv. ^[b]	97% Polymer	71% Polymer	0% Polymer
3 hours	Remaining monomer	0% 1-hex	1% 1-hex	5% 1-hex
		2% 2-hex	23% 2-hex	75% 2-hex
		1% 3-hex	5% 3-hex	20% 3-hex
	Branching ^[c]	128	84	N/A

[a] Room temperature, 2 mL of 1-hex in 6 mL of dichloromethane with 0.2 mol% palladium diimine catalyst, 0.2 mol% NaBARF_4 . Equivalencies of NCMe are calculated with respect to Pd catalyst. [b] Conversion calculated by ^1H NMR in CDCl_3 . [c] Branching is given per 1000 carbon atoms and was determined by quantitative ^{13}C NMR.



Scheme 2. Switching reactivity of a palladium diimine by activation with varying amounts of NCMe. 0 equiv. results in rapid isomerization of 1-hexene and polymerization of the resultant internal hexenes. 1 equiv. of NCMe gives polymerization with very low rates of internal alkene polymerization. 20 equiv. of NCMe gives rapid isomerization and no measurable polymerization.

generated in the isomerization side reaction are too weakly coordinating to polymerize at an appreciable rate.^[12,18] However, after 1 hour no 1-hexene remains in the reaction (85% polymer) and after 3 hours a significant amount of the internal alkenes have successfully been incorporated (97% polymer, $M_n = 48\,600$ Da, $\bar{D} = 1.18$, S10.5, Table S3), suggesting that the NCMe present in a typical polymerization significantly inhibits internal alkene coordination. Branching analysis of the precipitated polymer showed 128 branches per 1000 carbon atoms, with carbon NMR showing significant amounts of ethyl and propyl branches indicating that 2-hexene and 3-hexene have been polymerized (S10.4,

Table S2, Figure S4). Overall, monomer isomerization appears to be favored over polymerization, giving isomers which then polymerize to give a highly branched polymer. In-situ activation of a Pd-diimine precursor with $\text{NaBAr}^{\text{F}}_4$ for 1-hexene polymerization has previously been reported in the literature with similar ethyl and propyl branches found in the resultant polymer, however the authors attribute this branching to ligand electronic effects and do not report a crude NMR.^[19] Given our results, it seems likely that these branches are also due to isomerization of 1-hexene to internal alkenes followed by polymerization. Repeating the reaction of **5** activated with $\text{NaBAr}^{\text{F}}_4$ with the addition of 1 equivalent of acetonitrile (Table 1, Scheme 2) gives a drastically different result. Activation in the presence of acetonitrile gives the well-known isolable precatalyst **1**, and polymerization results agree with this, showing a typical polymerization of 1-hexene as previously reported in various publications.^[12,20] After 5 minutes 16% conversion to polymer is seen, with the remaining monomer being $\approx 75\%$ 1-hex and 9% isomers. The polymerization of 1-hexene proceeds to 71% ($M_n = 34200$, $\bar{D} = 1.06$, S10.5, Table S3) with only 1% 1-hex remaining after 3 hours, the rest having been converted to isomers. Branching analysis of this polymer shows ≈ 84 branches per 1000 carbons (S10.4, Table S2, Figure S4), and a branching distribution of methyl and butyl branches, consistent with 1,2 and 2,1 insertion and chain-walking of 1-hexene only.^[16b,21]

These results show that the presence of an ancillary ligand has a large effect on Pd-diimine catalysts, enabling a switch in reactivity between an isomerization-polymerization (0 equiv., where monomer is isomerized to internal alkenes which can then polymerize) and a regular 1-hexene polymerization (1 equiv., 1-hexene is polymerized preferentially over internal alkenes.) Furthermore, what is thought of as typical reactivity of Pd-diimines with α -olefins (polymerization with isomerization as a side reaction) is shown to be largely a consequence of the “ancillary” ligand added to give a stable isolable catalyst. The difference in the polymeric products between reactions with 0 equiv. vs. 1 equiv. of ancillary ligand can be seen in the thermal properties of the polymer; the higher branching imparted by internal alkene polymerization gives a highly amorphous polymer ($T_g = -70^\circ\text{C}$), whereas exclusive 1-alkene polymerization allowed for “chain-straightening” to yield linear segments with some crystallinity ($T_m = 6^\circ\text{C}$).

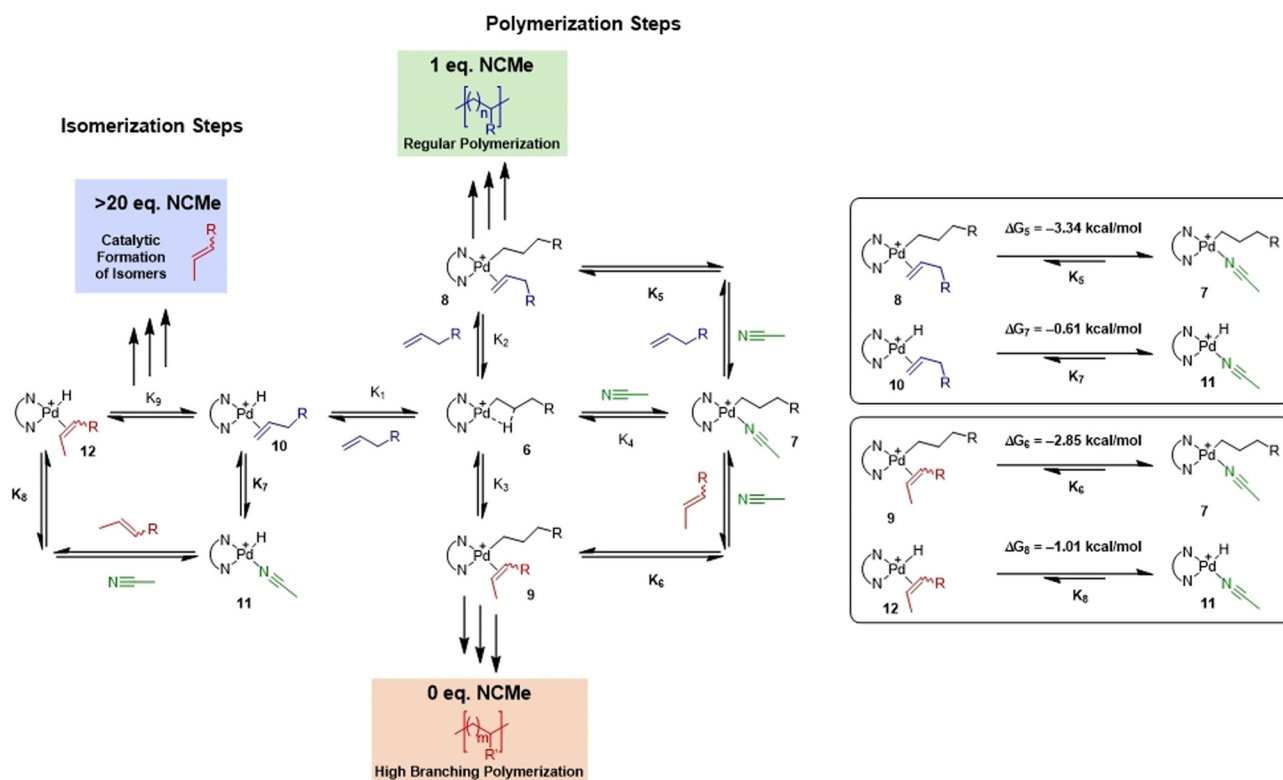
Further increasing the amount of acetonitrile gives a lower rate of polymerization, in agreement with a previous study into ancillary ligand concentration.^[12] However, the decreased rate of polymerization is only one effect of the increased ancillary ligand. Despite inhibiting polymerization, isomerization still occurs. For example, addition of 4 equiv. of acetonitrile with respect to Pd catalyst **5** gives just 9% polymer in three hours, with 54% of the remaining monomer isomerized to internal alkenes (S10.6, Table S4). Further increasing acetonitrile to 20 equiv. gives no observable polymerization in 3 hours, hence transforming the reaction into an alkene isomerization (95% conversion, Table 1). Under these conditions the ratio of product formed is 77:23 2-hexene-3-hexene with an *E:Z* ratio of 3:1 for the 2-hexene. This result is significant as previous attempts to utilize Pd-diimines as isomerization catalysts necessitated bulky “sand-

wich” ligands to increase steric hindrance at the reactive center to result in weaker binding affinity of internal olefins and an external hydride source to form a Pd-H species.^[6a] A similar polymerization inhibition can be seen when more strongly binding ancillary ligands are used. Addition of 1 equiv. of dimethyl sulfide or pyridine exhibits no polymerization over 3 hours but still shows some isomerization (28% and 7%, respectively). Increasing the amounts of these ligands to 20 equiv. showed no polymerization or isomerization for pyridine, and 9% isomerization for dimethyl sulfide.

Mechanistically we propose that higher concentrations of acetonitrile will favor isomerization over polymerization through displacement of coordinated alkenes (**K**₅, **K**₆, **K**₇, **K**₈), as shown in Scheme 3. The agostic complex **6** can either undergo β -hydride elimination, coordination of an alkene, or coordination of acetonitrile. High concentrations of acetonitrile would shift the equilibrium **K**₄ to the right, slowing polymerization and isomerization which is in agreement with the data in Table 1 showing fast isomerization and polymerization when no ancillary ligand is used, and slower isomerization when 20 equiv. are added. However, displacement from the alkyl palladium complexes **8** and **9** (yielding complex **7**) is expected to be more favorable than from hydride complexes **10** and **12** (yielding **11**) to due steric factors. Therefore, polymerization would be inhibited more than isomerization when [NCMe] is high, accounting for the observation that isomerization is the sole pathway for reactions employing 20 equiv. of ancillary ligand. Computed Gibbs free energies, performed at PCM-B3LYP-D3/6-31+G(d)-LANL2DZ(Pd) in implicit dichloromethane solvent (Scheme 3, right), suggest that it is easier to displace alkenes from alkyl rather than hydride complexes.

1 equivalent of ancillary ligand is enough to greatly inhibit internal alkene polymerization, meaning that only 1-hexene can efficiently coordinate and insert to yield a polymer, hence the characteristic methyl and butyl branching distribution (see supporting information for an explanation of branch formation from 1-alkenes vs. internal alkenes S11.1, Scheme S4; S11.2, Scheme S5; S11.3, Scheme S6). Any internal alkene that is generated will polymerize but at a greatly reduced rate. In the absence of ancillary ligand any isomer generated is more readily polymerized. We postulate that this would drive the isomerization equilibrium to form more isomer, hence the branching structure of the polymer contains higher branching overall because internal alkenes cannot form linear segments, instead forming a higher number of ethyl and propyl branches (S10.4, Table S2, Figure S4). The higher rate of polymerization observed in the case of 0 equiv. vs. 1 equiv. can again be explained through the active/dormant equilibrium (**K**₄) in Scheme 3.

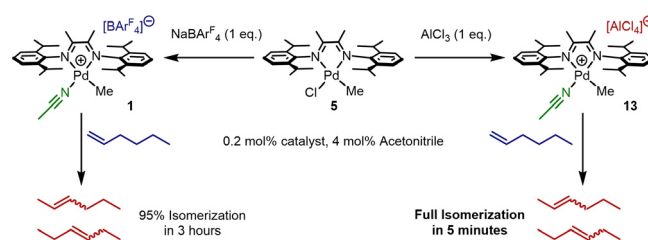
Reacting 1-hexene with precursor **5** in the absence of ancillary ligand yields fast isomerization to internal alkenes which can be polymerized to give a highly branched polymer. This system is similar to the previously reported system using a Lewis acid, AlCl_3 , to alter the reactivity of palladium diimine catalysts to isomerize then polymerize internal olefins.^[13] However, the reaction without aluminium chloride shows slightly lower branching (128 vs. 150 branches/1000C).



Scheme 3. Left: Proposed mechanistic details of the switch in reactivity of palladium diimines in the presence of varying amounts of ancillary ligand, NCMe. Right: Calculated free energies of alkene displacement with acetonitrile from Pd-alkyl and Pd-hydride complexes computed at the PCM-B3LYP-D3/6-31 + G(d)-LANL2DZ(Pd) level, in implicit dichloromethane solvent.

The reaction with 0 equiv. of NCMe is slower to isomerize than an AlCl_3 reaction, meaning that some 1-hexene could be incorporated in the early stages of the reaction and therefore lowering the branching. Coordination disproportionation, a well-studied reaction of AlCl_3 with NCMe in dilute solutions, yields cationic $[\text{AlCl}_2(\text{NCMe})_4]^+$ and $[\text{AlCl}_4]^-$ (S10.7, Scheme S3).^[22] The reaction of AlCl_3 with NCMe can be observed visually, where AlCl_3 coagulates in dilute solutions of NCMe (S10.7, Figure S11). An upfield shift of the NCMe protons can also be seen in ^1H NMR, suggesting complexation. This process serves to sequester NCMe (giving conditions similar to 0 equiv. NCMe, Table 1), but also generates anionic $[\text{AlCl}_4]^-$ capable of salt metathesis with the $[\text{BAR}^F_4]^-$ anion. To test if an $[\text{AlCl}_4]^-$ counterion complex gives a higher rate of isomerization we conducted an experiment where precatalyst **5** was activated with the Lewis acid, AlCl_3 , to directly obtain an $[\text{AlCl}_4]^-$ counterion derivative, **13**, of complex **1** (Scheme 4). Addition of 1-hexene and 20 equiv. of acetonitrile to this complex gave a sharp increase in the rate of isomerization compared to the reaction with complex **1**, with quantitative conversion to internal alkenes observed in just 5 minutes at 0.2 mol% catalyst loading. The higher isomerization rate of complex **13** implicates counterion ion exchange from $[\text{BAR}^F_4]^-$ to $[\text{AlCl}_4]^-$ as a key mechanistic step in AlCl_3 triggered branching regulation.^[13]

The quantitative conversion observed with complex **13** in 5 minutes suggests that the complex is highly active and that much lower catalyst concentrations could be employed. To



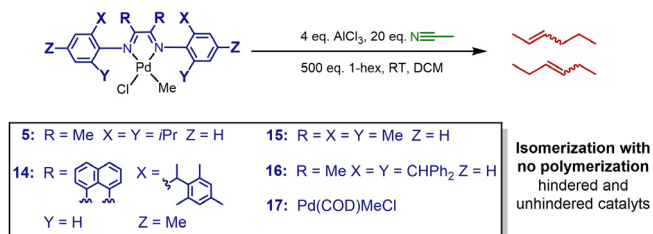
Scheme 4. Activation of **5** with NaBAR^F_4 or AlCl_3 . The tetrachloroaluminate counterion gives a higher rate of isomerization: quantitative conversion in just 5 minutes (0.2 mol% catalyst loading) with no observable polymer peaks by ^1H NMR.

test this we reduced the catalyst loading, with entries 1–3 in Table 2 showing that quantitative isomerization can be obtained in 18 hours with catalyst loadings as low as 0.005 mol%, corresponding to a turnover frequency (TOF) of over 1100h^{-1} . Attempts to lower the catalyst loading further resulted in an incomplete reaction. However, removing solvent and product by distillation followed by addition of fresh solvent, 1-hexene, and ancillary ligand allowed for reactivation of the catalyst. As well as providing further evidence of the dual action of AlCl_3 in branching regulation (removing NCMe and forming a new counterion via a disproportionation reaction), the fast isomerization seen from the $[\text{AlCl}_4]^-$ counterion complex also shows potential as a general method for transforming palladium diimine cata-

Table 2: Isomerization including catalyst scope and loading.

Entry	Cat.	Alkene	Product ^[a]	Yield ^[b]	Cat. loading (mol%)
1	5	1-hexene	2-hexene	77	0.2
2 ^[c]	5	1-hexene	2-hexene	77	0.01
3 ^[c]	5	1-hexene	2-hexene	81	0.005
4	14	1-hexene	2-hexene	76	0.2
5	15	1-hexene	2-hexene	75	0.2
6	16	1-hexene	2-hexene	76	0.2
7	17	1-hexene	2-hexene	80	0.2
8 ^[d,e]	5	1-decene	2-decene	62.5	0.2
9 ^[d,e]	5	1-octadecene	2-octadecene	53	0.2
10	5	Allyl benzene	Methylstyrene	95	0.2
11 ^[e]	5	4-pentene-OTBS	3-pentene-OTBS	90	0.2

[a] Reactions carried out at room temperature; 2 mL of monomer in 6 mL of dichloromethane with Pd-diimine catalyst, 4 equiv AlCl_3 , 20 equiv of NCMe with respect to Pd catalyst, 3 hours standard reaction time. Product shown is the major component found in the reaction. [b] Yield calculated from ^1H NMR. [c] 18 Hour reaction time, 20 mL monomer in 60 mL of dichloromethane used. [d] Reactions in chlorobenzene. [e] 4 Equiv. $\text{NaBAR}_4^{\text{F}}$ used as activator.

**Scheme 5.** Isomerization of α -olefin with a variety of Pd complexes including sterically hindered and unhindered Pd-diimines and Pd-(COD)MeCl.

lysts into highly efficient alkene isomerization catalysts without the need for specialist ligand design or an external hydride source to form the Pd-H species. To investigate this hypothesis further we utilized four other palladium diimine complexes with different ligand structures (Scheme 5) and subjected them to conditions under which polymerization should be inhibited and isomerization enhanced (activation with AlCl_3 to form the $[\text{AlCl}_4]^-$ counterion in the presence of excess ancillary ligand (20 equiv. of NCMe with respect to Pd cat.)). Complex **15** contains methyl substituents, meaning there is very little steric hindrance around the palladium center, whereas compound **14** contains a naphthalene backbone and large aryl substituents.^[23] complex **16** is the highly robust phenyl substituted catalyst first reported by Chen for polymerization of ethylene at elevated temperatures.^[24] The precursor complexes were first activated with AlCl_3 prior to addition of ancillary ligand to prevent coordination disproportionation. Results show that all catalysts, despite the differences in sterics and electronics, fully isomerize 1-hexene to internal alkenes with no detectable polymerization (entries 4–7, table 2). Isomerization under similar conditions was also achieved for chloro(1,5-cyclooctadiene)methylpalladium(II), **17**, the precursor used to synthesize the Pd-diimines used in this study. The general

conditions for alkene isomerization are also shown to give 2-alkenes as the major product for reactions with higher olefins; 1-decene and 1-octadecene (entries 8 and 9, Table 2). Allyl benzene is converted to β -methylstyrene in good yield (entry 10, Table 2). Isomerization of a silyl ether protected alcohol (tert-butyldimethyl(pent-4-en-1-yloxy)silane) was selectively isomerized to tert-butyldimethyl(pent-3-en-1-yloxy)silane (entry 11, Table 2) although required $\text{NaBAR}_4^{\text{F}}$ as the activating agent.

Conclusion

We have shown that ancillary ligands commonly believed to be benign actually have a profound effect on the reactivity of Pd-diimine catalysts, revealing that the reactivity associated with nitrile adduct Brookhart catalysts can be largely attributed to the presence of this ligand. Varying the amount of ancillary ligand added was found to switch reactions between fast isomerization and polymerization, polymerization of α -olefins only, or exclusive isomerization by simply varying the amount of ligand added. The presence of NCMe disfavors polymerization of internal alkenes through competition for open coordination sites. Computed Gibbs free energies for key mechanistic steps show that acetonitrile displacement is favored for Pd-alkyl complexes over Pd-hydride species, meaning that high $[\text{NCMe}]$ will drive the reaction to form isomers in the absence of polymerization. Optimization and investigation into counterion effects on the alkene isomerization pathway also lead to the discovery that isomerization can be further favored by employing an $[\text{AlCl}_4]^-$ counterion, yielding efficient isomerization even with catalyst loading as low as 0.005 mol%. Furthermore, activation with AlCl_3 and 20 equivalents of NCMe is shown to yield isomerization (free of polymerization) for a wide range of both sterically hindered and unhindered Pd-diimines and Pd(COD)MeCl, without an external hydride source.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: ancillary ligand · chain-walking · isomerization · olefins · polymerization

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