

Cation-Controlled Olefin Isomerization Catalysis with Palladium Pincer Complexes

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ABSTRACT: Palladium(II) pincer complexes with varying amine donor substituents have been prepared and studied in olefin isomerization catalysis. Installing a macrocycle into the pincer ligand enables cation-switchable positional olefin isomerization: no reaction is observed with the catalyst alone, while in the presence of Li⁺ salts isomerization proceeds cleanly. Mechanistic studies implicate a key role of highly electrophilic Pd centers with accessible olefin binding sites in catalysis.

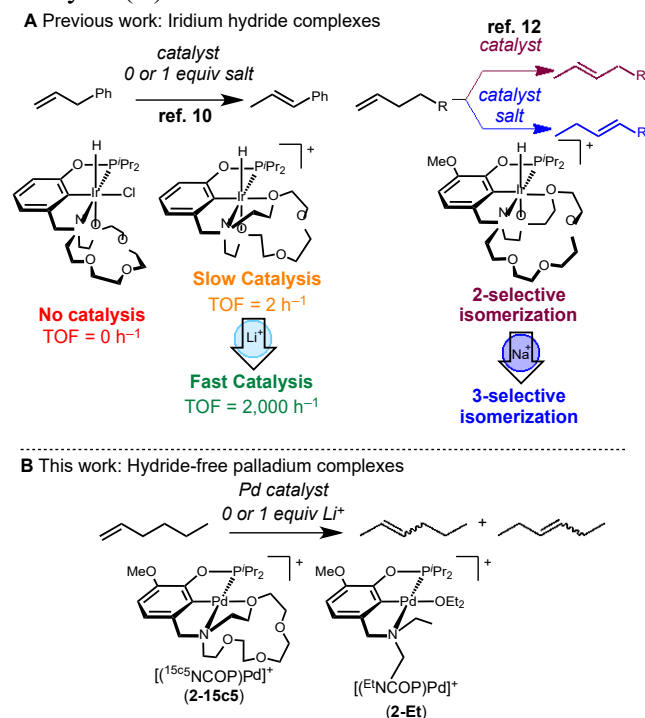
INTRODUCTION

The prevailing strategy for optimizing organometallic catalysts involves synthesizing new ligand–metal combinations with distinct structures until the desired reactivity is found. Just one elegant example of this approach comes from the development of palladium and nickel α -diimine catalysts by Brookhart and coworkers.^{1,2} Whereas phenanthroline Pd complexes oligomerize olefins, complexes with more sterically encumbered α -diimine supporting ligands give highly branched polymers.^{2,3} When even bulkier ligands are employed, internal olefins are released from the metal center, leading instead to selective positional isomerization to yield 2-alkenes.⁴

An alternative approach to optimizing catalysis involves designing *controllable catalysts*, with activity or selectivity modulated by external additives.^{5–7} Our group has been developing cation-responsive olefin isomerization catalysts.^{8,9} The iridium catalysts of Scheme 1 feature pincer-crown ether ligands that enable cation-controlled catalysis. An aza-crown ether macrocycle is incorporated into a phenylphosphinite chelate to enable ether oxygen interactions either with the catalytic active site or external cationic additives.^{8,9} The hemilabile ether donor acts as a “gate” of reactivity, preventing reactivity until cation-crown interactions disrupt the

equilibria to favor substrate binding. This approach has been leveraged to achieve on/off switchable and rate-tunable allylbenzene isomerization, wherein salts control rate by modulating the extent of substrate binding (Scheme 1A).^{10,11} The positional selectivity of olefin isomerization can also be controlled with similar catalysts, with 2-selective isomerization in the absence of Na⁺ salts, but 3-selective isomerization when Na⁺ salts are added.¹²

Scheme 1. Previous studies of iridium pincer-crown ether catalysts (A) and current studies of palladium catalysts (B) for olefin isomerization.



In a recent study of cation binding affinity to pincer-crown ether complexes, we found that Pd complexes bind Li⁺ ions tighter than Ni, Pt, and Ir complexes due to the low Allred-Rochow electronegativity of Pd.¹³ We were therefore interested in exploring

cation-controlled catalysis based on these strong cation-crown interactions. There is a rich history of catalysis and small molecule activation chemistry mediated by palladium pincer complexes,^{14–16} but surprisingly limited olefin isomerization reactivity. There is, however, extensive literature on alkene isomerization by palladium complexes, including simple salts.^{14,17} We wondered if such reactivity could be controlled through cation-crown interactions, despite expected differences in mechanism of isomerization between iridium complexes and palladium complexes.

Herein we report the synthesis of palladium(II) complexes supported by aminophenylphosphinite pincer ligands (Scheme 1B). When an aza-crown ether donor is present, on/off switchable double bond positional olefin isomerization is possible using Li^+ salts. Mechanistic studies reveal a pathway that is distinct from prior iridium pincer catalysts, featuring highly electrophilic Pd centers that mediate isomerization.

RESULTS AND DISCUSSION

Synthesis of Palladium Complexes. The synthetic routes to the target palladium complexes are summarized in Scheme 2. Three ligands were prepared according to recently reported procedures.^{18,19} The methoxy group in the backbone was selected to prevent unwanted metalation at the site ortho to the phosphinite (para to the amine donor).^{11,20} Refluxing $\text{Pd}(\text{COD})\text{Cl}_2$ with the ligand produced square planar palladium(II) chloride complexes with tridentate NCOP pincer coordination. The products are similar to other palladium NCP pincer complexes.^{20,21,30,22–29}

The aza-crown-ether-containing chloride complex ($^{15\text{c5}}\text{NCOP}$) PdCl (**1-15c5**) is closely related to a previously published variant without a methoxy group in the backbone.¹³ The four macrocyclic ether oxygen atoms could interact with either the Pd center or cationic additives during catalysis, which might enable controlled catalysis. The diethylamine-containing complex ($^{\text{Et}}\text{NCOP}$) PdCl (**1-Et**) has no ethers near the Pd center, so no controlled catalysis would be expected. The bis(methoxyethyl)amine-containing complex ($^{\text{BME}}\text{NCOP}$) PdCl (**1-BME**) also has an acyclic amine but contains two ether groups that could potentially engage in cation interactions. The structure of **1-BME** derived from X-ray diffraction of crystals grown from hexanes at -35°C is shown in Figure 1.

Scheme 2. Synthesis of pincer-crown ether palladium chloride complexes.

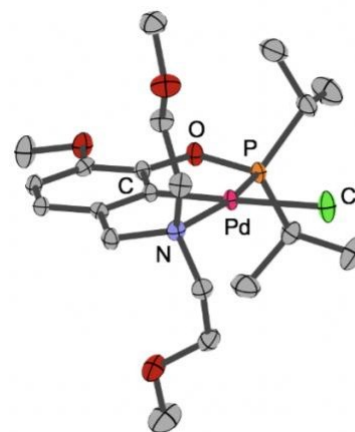
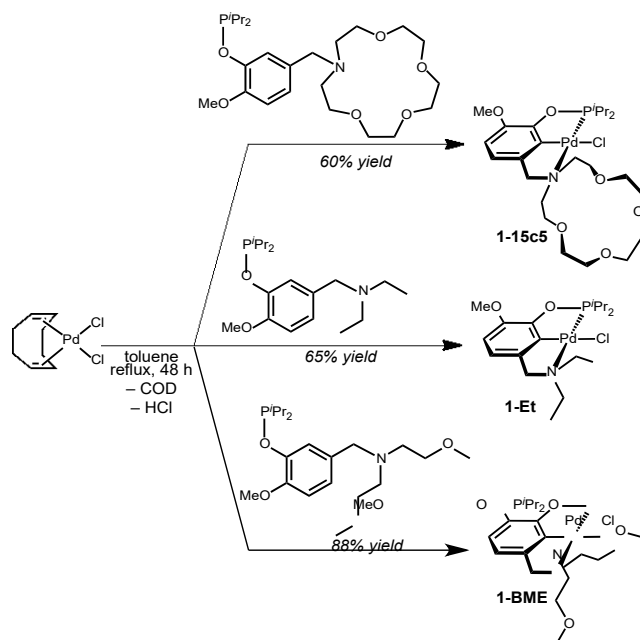


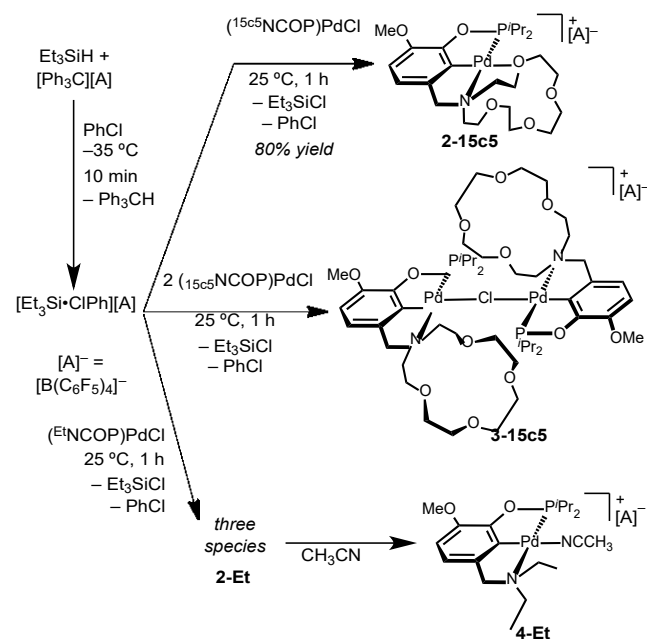
Figure 1. Molecular structure of one of the two unique ($^{\text{BME}}\text{NCOP}$) PdCl (**1-BME**) molecules in the asymmetric unit from single-crystal X-ray diffraction, with ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity. Distances ($\text{\AA}$) and angles ($^\circ$): Pd–P 2.1943(5), Pd–C(Ar) 1.954(2), Pd–N 2.189(2), Pd–Cl 2.3892(6); P–Pd–Cl 101.99(2), Cl–Pd–N 95.36(5), N–Pd–C(Ar) 82.30(8), C(Ar)–Pd–P 80.45(7)

Prospective catalysts for olefin isomerization were targeted next. Hypothesizing that an accessible olefin binding site would be needed, the chloride ligand was removed to produce a series of cationic

complexes with weakly bound ligands *trans* to the phenyl backbone.

When crown-ether-containing palladium halide complexes ($^{15}\text{C}_5\text{NCOP}$)PdX were treated with salts of sodium, potassium, thallium, or trityl cation in an attempt to abstract the halide, spectroscopic studies supported either partial conversion or salt interactions without halide abstraction. The use of AgPF_6 did lead to full conversion to a new species assigned as $[\kappa^4\text{-}(^{15}\text{C}_5\text{NCOP})\text{Pd}][\text{PF}_6]$ based on high-resolution mass spectrometry. However, persistent silver impurities hampered purification.

Scheme 3. Synthesis of cationic palladium complexes.



An alternative route to cationic palladium complexes was devised based on silylium salts as halide abstractors. As shown in Scheme 3, treating **1-15c5** with $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ ^{31–33} (generated *in situ* from Et_3SiH and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ³³) produced $[\kappa^4\text{-}(^{15}\text{C}_5\text{NCOP})\text{Pd}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2-15c5**) as a white powder in 80% yield, following pentane washes and passage through a short alumina column to remove Ph_3CH , Et_3SiCl , and other impurities.

The use of a slight excess of silylium proved critical. Utilization of less than one equivalent $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ resulted in formation of a distinct species with broad ^1H NMR signals. The same species was produced upon mixing equimolar amounts of neutral $(^{15}\text{C}_5\text{NCOP})\text{PdCl}$ and the cationic $[\kappa^4\text{-}(^{15}\text{C}_5\text{NCOP})\text{Pd}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 . Based on this result and comparisons with other pincer

complexes in the literature,^{30,34} we tentatively assign this species as the mono-halide-bridged dipalladium complex $[\{\kappa^3\text{-}(^{15}\text{C}_5\text{NCOP})\text{Pd}\}_2\text{-}\mu\text{-Cl}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3-15c5**, Scheme 3).

With a tractable halide abstraction strategy in hand, cationic complexes with varying amine donors were sought. Treating the diethylamino-substituted chloride complex **1-Et** with $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ and Et_2O in PhCl produced a mixture of three species according to ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Scheme 3). The major ion peak by ESI-MS was the three-coordinate cation $[(\text{Et}^1\text{NCOP})\text{Pd}]^+$ (**2-Et**), suggesting the presence of weakly coordinating ligands such as Et_2O or PhCl . Reactions with the strong donor ligand acetonitrile confirm the presence of labile ligands: addition of ca. 100 equiv acetonitrile converted the mixture to $[(\text{Et}^1\text{NCOP})\text{Pd}(\text{NCCH}_3)]^+$ (**4-Et**) as a single species assigned as the cationic acetonitrile complex. The mixture was therefore considered a suitable precatalyst based on the presence of easily displaced ligands, and was used without purification.

Unfortunately, reactions of bis(methoxyethyl)amine-containing chloride complex **1-BME** with $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ were not as reliable. The purity and spectroscopic signals of the putative cationic species varied from batch to batch, and the catalytic results were not sufficiently reproducible. Thus, we focused our catalysis studies on the complexes featuring aza-crown ether and diethylamine donors, **2-15c5** and **2-Et**.

Cation-Controlled Isomerization of 1-hexene.

Positional isomerization of olefins was examined using the two cationic palladium complexes **2-15c5** and **2-Et**. Palladium complexes have long been recognized as active catalysts for olefin isomerization.^{17,35–37} In many cases, no hydride ligand is needed in the precatalysts, in contrast to the NCOP iridium hydride catalysts we previously studied for cation-controlled isomerization. We hypothesized that cation-crown interactions could still gate substrate access to the Pd center, regardless of the specific mechanism of isomerization.

The double-bond positional isomerization of 1-hexene was monitored by ^1H NMR spectroscopy. Standard conditions called for 5 mM Pd (1.7 mol%), 5 mM $\text{LiBar}^{\text{F}}_4\cdot 3\text{Et}_2\text{O}$, 70 mM Et_2O , 300 mM 1-hexene, and 50 mM mesitylene internal standard at 25°C .

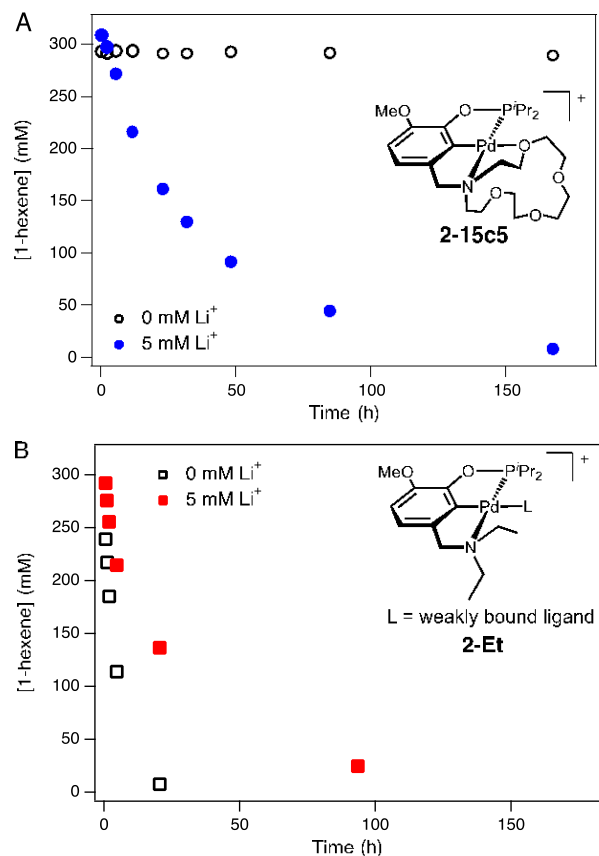
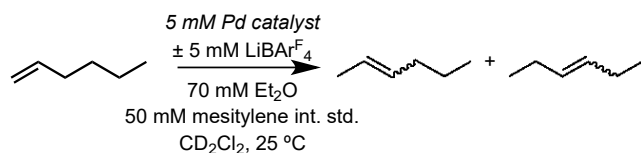


Figure 2. Isomerization of 300 mM 1-hexene catalyzed by $[(^{15}\text{c}5\text{NCOP})\text{Pd}][\text{B}(\text{C}_6\text{F}_5)_4]$ (A) and $[(^{\text{Et}}\text{NCOP})\text{Pd}][\text{B}(\text{C}_6\text{F}_5)_4]$ (B), with no salt additive (empty symbols) and with 5 mM $\text{LiBar}^{\text{F}}_4$ (filled symbols).

The crown-ether-containing cationic complex **2-15c5** was first treated with 1-hexene in dichloromethane. No isomerization of 1-hexene was observed by ^1H NMR spectroscopy, even after one week at room temperature (Figure 2A). Further, no changes were observed in the ^1H NMR spectrum to indicate any change in catalyst concentration, structure, or olefin binding in the presence of 1-hexene.

When **2-15c5** and 1-hexene were allowed to react under analogous reaction conditions *but with 1 equiv $\text{LiBar}^{\text{F}}_4$ as an additive* (Ar^{F} is 3,5-bis(trifluoromethyl)phenyl), isomerization of 1-hexene to the *E* and *Z* isomers of 2-hexene and 3-hexene proceeded over the course of five days. This reactivity corresponded to a turnover frequency

(TOF) of 1.7 h^{-1} . Reaction monitoring using different batches of catalyst revealed moderate variance in rates ($\text{TOF} = 1.37 \pm 0.60 \text{ h}^{-1}$ for 5 data sets under identical conditions). Time-normalized kinetic analysis showed good overlays, however, consistent with a robust catalyst (Figure S22).

These results demonstrate cation control over isomerization. No activity is apparent except when $\text{LiBar}^{\text{F}}_4$ is included as an additive. In comparison to the previously studied NCOP iridium catalysts, the Pd catalyst is slower in the absence of Li^+ (no detectable activity), but also in the presence of Li^+ .

The diethylamine-substituted cationic complex **2-Et** was explored next. With no oxygen donors on the amine group capable of binding to the Pd center, we expected the catalyst to be active for isomerization even in the absence of salts. Indeed, isomerization of 1-hexene proceeded smoothly over 15 h without salt additives ($\text{TOF} 8.1 \text{ h}^{-1}$). In the presence of one equivalent of $\text{LiBar}^{\text{F}}_4$, isomerization of 1-hexene proceeded slightly slower ($\text{TOF} 5.7 \text{ h}^{-1}$). The rates of isomerization by **2-Et** and **2-15c5** in the presence of $\text{LiBar}^{\text{F}}_4$ are similar. It is not clear why $\text{LiBar}^{\text{F}}_4$ addition modestly decelerates the isomerization reaction. Although the Li^+ salt contains Et_2O , experiments with additional Et_2O did not show signs of inhibition (Figure S24).

The qualitative comparisons are consistent with the concept of “gating” reactivity: the role of the Li^+ promoter in catalysis by **2-15c5** is proposed to be facilitation of substrate access to the Pd center, so the fastest possible rate would be expected to be similar to **2-Et** (which contains no “gating” hemilabile ligand).

Only the catalyst with a crown ether group has two significantly different activity states, suggesting that **2-15c5** could be capable of switchable olefin isomerization. We therefore sought to demonstrate control over catalytic activity, toggling between “on” and “off” states *in situ* using additives. No isomerization of 1-hexene is observed when **2-15c5** is added — the catalyst is in an “off” state over 19 h (Figure 3). Upon the addition of $\text{LiBar}^{\text{F}}_4 \cdot 3\text{Et}_2\text{O}$ (1 equiv relative to Pd), isomerization turns “on”, proceeding to 32% conversion after several hours. Addition of 2 equiv 12-crown-4 ether stopped the reaction, reverting **2-15c5** back to the “off” state. This switching behavior is consistent with our prior studies showing that 12-crown-4 ether has higher Li^+ affinity than $^{15}\text{c}5\text{NCOP}$ complexes.^{13,38} Addition of

another 2 equiv Li^+ restored the “on” state and isomerization proceeded towards completion.

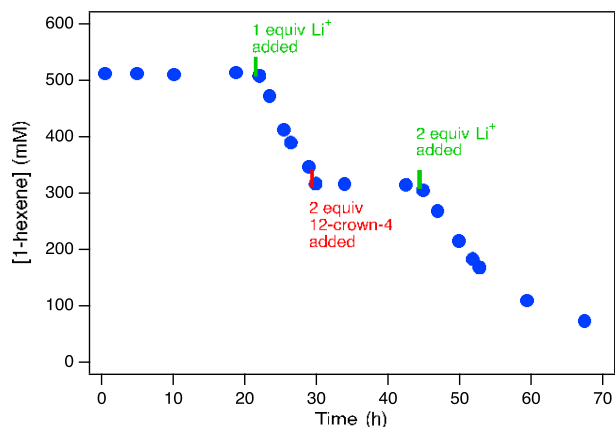


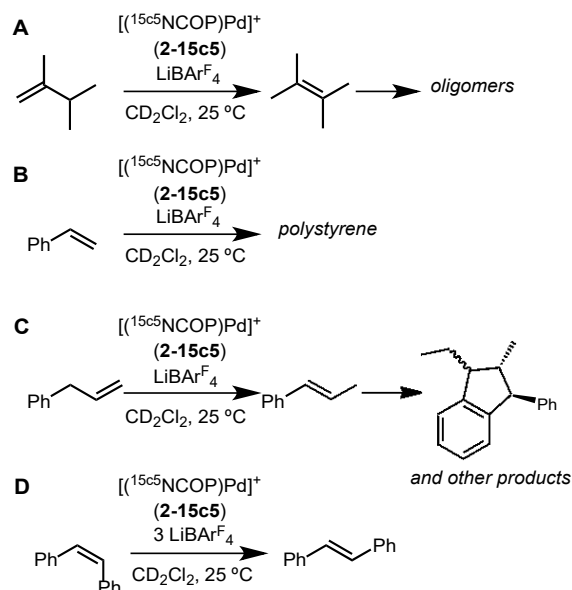
Figure 3. Cation-controlled 1-hexene isomerization by **2-15c5**. Conditions: 5 mM **2-15c5**, 510 mM 1-hexene, 57 mM mesitylene internal standard, CD_2Cl_2 , 25 °C. The vertical lines mark the time at which equivalents (relative to catalyst concentration) of $\text{LiBAr}^{\text{F}_4} \cdot 3\text{Et}_2\text{O}$ or 12-crown-4 ether were added to start or stop the reaction.

Probing the Mechanism of Isomerization. The two primary mechanisms of positional isomerization of olefins are (A) the “ π -allyl” mechanism, in which an allylic C–H bond is activated to form an η^3 -allyl π -complex; and (B) the “insertion-elimination” mechanism, in which a Pd–H intermediate facilitates olefin 1,2-insertion and β -hydrogen elimination.^{17,39,40} Electrophilic cationic palladium salts have been proposed to isomerize via formation of a bound carbocation that is readily deprotonated to enter the π -allyl pathway.^{36,41}

In situ monitoring revealed no evidence for a palladium(II) hydride intermediate, and there is no obvious way for a hydride complex to form. Thus, the insertion-elimination pathway was considered unlikely. Instead, an electrophilic mechanism is consistent with a variety of experimental observations.

Initial evidence for an electrophilic carbocation mechanism for olefin isomerization came from the reaction of 2,3-dimethyl-1-butene (Scheme 4A). This substrate isomerizes within 1 h in the presence of $[\kappa^4\text{-(}^{15}\text{c5NCOP)Pd}][\text{B}(\text{C}_6\text{F}_5)_4]$ and Li^+ salts (Figure S25), in a much faster reaction than 1-hexene. In fact, the internal olefin formed from initial positional isomerization eventually reacts further to form oligomers.

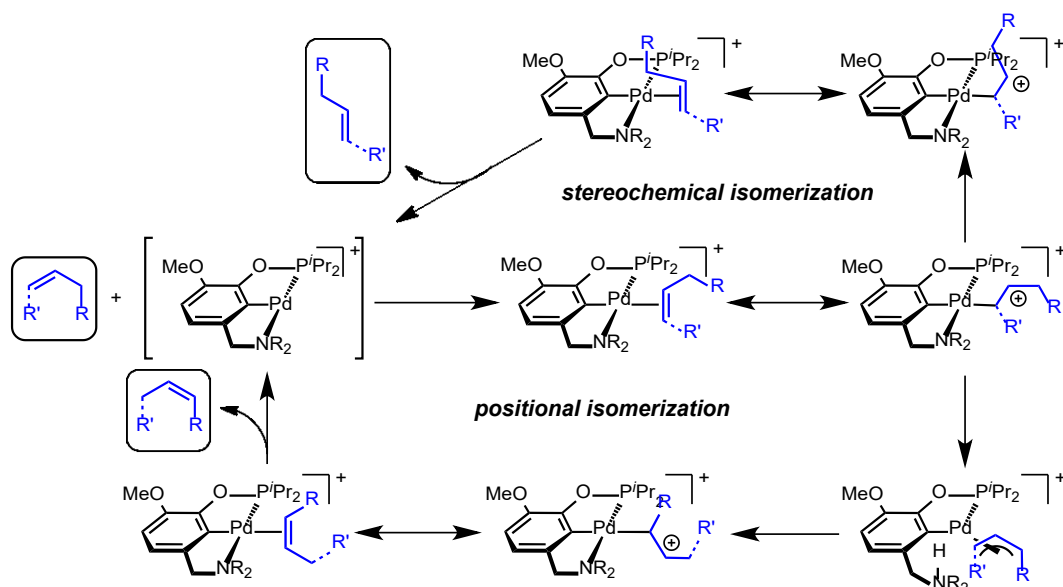
Scheme 4. Reactivity of palladium complexes with other alkenes.



Other olefins reacted in diverse ways. Styrene undergoes Li^+ -promoted, Pd-catalyzed polymerization to polystyrene (Scheme 4B).³⁶ Isomerization of allylbenzene produced β -methylstyrene initially, followed by formation of a range of products that included cyclodimerized indenenes (Scheme 4C).^{42–44}

The olefin *cis*-stilbene was employed as a mechanistic probe (Scheme 4D). Because it has no allyl C–H bonds, it cannot form a η^3 -allyl complex. Yet, conversion to *trans*-stilbene was observed when pure *cis*-stilbene contacted **2-15c5** (albeit at a slower rate than 1-hexene isomerization). We propose that stilbene coordination leads to a significant contribution from the carbocation resonance form, leading to free rotation and *cis/trans* isomerization. Indeed, the mechanisms for stereochemical and positional isomerization may well be different, with an η^3 -allyl involved in the latter but not the former. Positional isomerizations would commence from the same coordination step, which would render allylic protons acidic enough for facile deprotonation to form the key η^3 -allyl complex intermediate.

Scheme 5. Proposed mechanism of olefin isomerization.



Scheme 5 summarizes the proposed mechanisms for stereochemical and positional isomerization. These align with earlier proposals for dicationic Pd salts.^{36,41} Control reactions containing LiBarF_4 but omitting the Pd complex resulted in no detectable reaction after 24 h at room temperature, supporting the notion that Pd and Li^+ work synergistically.

CONCLUSIONS

The cationic palladium pincer-crown ether complex $[(^{15}\text{C}_5\text{NCOP})\text{Pd}]^+$ (**2-15c5**) exhibits cation-controlled reactivity with alkenes. In the absence of Li^+ , no reaction is observed, while isomerization of 1-hexene to internal olefins occurs upon addition of a Li^+ salt. Other alkenes react in a manner indicative of carbocation intermediates, producing oligomers, polymers, or Friedel-Crafts-type cyclization products. The cationic palladium centers with weakly bound ligands are proposed to be sufficiently electrophilic to build up carbocation character. The amine ligand may also serve to facilitate proton transfer reactions.

Comparisons can be made between the new palladium catalysts and previously studied pincer-crown ether iridium catalysts. The iridium catalyst contains a hydride ligand and proceeds via an insertion/elimination mechanism for positional isomerization. In contrast, the palladium catalyst appears to proceed via an electrophilic π -allyl mechanism. Substrate binding to the metal center is essential in each catalyst, however, and the pincer-crown ether ligand enables cation control over

substrate binding in each system. A key difference is that the palladium catalyst shows no activity without salts, whereas the iridium catalyst slowly isomerizes olefins even without additives. This could be due to stronger binding of the crown ether oxygens by the more electrophilic Pd center.

Although slower than earlier electrophilic Pd catalysts for isomerization, the present system is a rare example of palladium pincer catalyst capable of olefin isomerization. Incorporating a crown ether into the supporting ligand enables true “on/off” switchable behavior that is important for applications in catalytic cascades where different catalysts must operate with temporal independence. The ability to “turn on” electrophilic reactivity with Li^+ addition, despite the multiple strong donor ligands, is striking.

ASSOCIATED CONTENT

Supporting Information

Experimental details, NMR spectra and crystallographic details (PDF).

Crystal data has been uploaded to the CCDC 2181813.

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

No competing financial interests have been declared.

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