Cation-Controlled Olefin Isomerization Catalysis with Palladium Pincer Complexes

Alexandra H. Farquhar,‡ Kristen E. Gardner,‡ Sebastian Acosta-Calle, Andrew M. Camp, Chun-Hsing Chen, and Alexander J. M. Miller*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

Supporting Information Placeholder

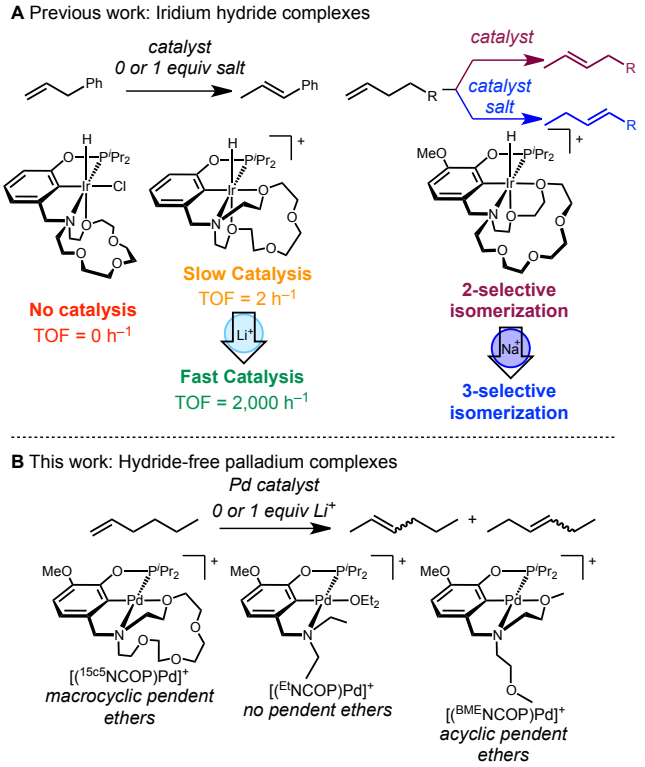
ABSTRACT: A series of palladium(II) pincer complexes with different substituents on the amine donor has been prepared and studied in olefin isomerization catalysis. Installing a macrocycle into the pincer ligand enables cation-switchable positional olefin isomerization: no reaction is observed with the 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] [8,9] Our group has been developing cation-responsive olefin isomerization catalysts. 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] 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 had higher affinity than Ni, Pt, and Ir, attributed to

the low Allred-Rochow electronegativity of Pd. 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,[13–15] but surprisingly limited olefin isomerization reactivity. There is, however, extensive literature on alkene isomerization by palladium complexes, including simple salts.[13,16] We wondered if such reactivity could be controlled through cation-crown interactions, particularly given the likely differences in mechanism of isomerization between iridium complexes and palladium complexes.

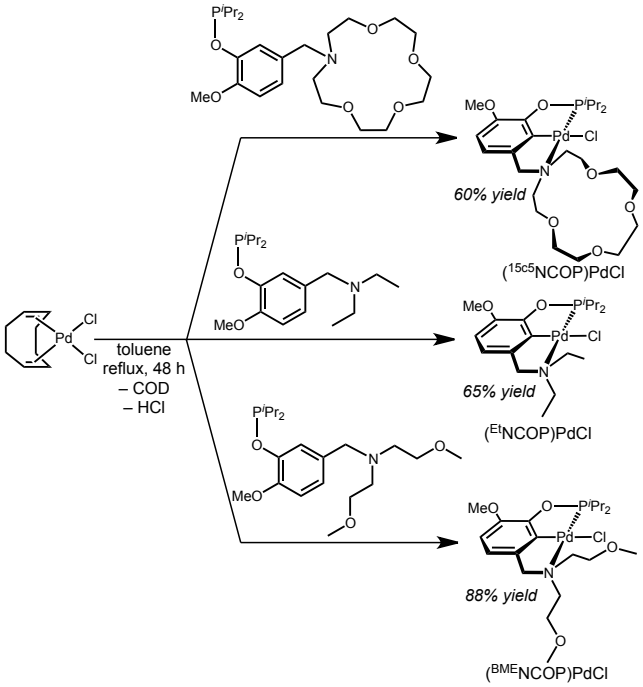
Herein we report the synthesis of palladium(II) complexes supported by three different aminophenylphosphinite pincer ligands (Scheme 1B). These complexes are catalysts for double bond positional olefin isomerization, with the crown ether group enabling on/off activity switching with Li^+ salts. Mechanistic 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 target palladium complexes were prepared according to Scheme 2. The three ligands were prepared according to recently reported procedures.[17,18] The methoxy group in the backbone was selected to prevent unwanted metalation at the site ortho to the phosphinite (para to the amine donor).[11,19] Refluxing $Pd(COD)Cl_2$ with the ligand produced square planar palladium(II) chloride complexes with tridentate NCOP pincer coordination. The structures are similar to other palladium NCP pincer complexes.[19,20,29,21–28]

The aza-crown-ether-containing chloride complex (^{15c5}NCOP)PdCl, which is closely related to a previously published variant without a methoxy group in the backbone,[30] features a crown ether. The four ether oxygen atoms in the macrocycle could interact with either the Pd center or cationic additives during catalysis, which might enable controlled catalysis. The diethylamine-containing complex has no ethers near the Pd center, so no controlled catalysis would be expected. The bis(methoxyethyl)amine-containing complex also has an acyclic amine but contains two ether groups that could potentially in engage in cation interactions. The structure of (^{BME}NCOP)PdCl derived from X-ray diffraction of crystals grown from hexanes at –35 °C is shown in Figure 1.

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



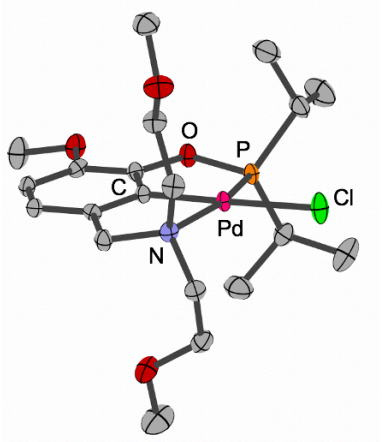


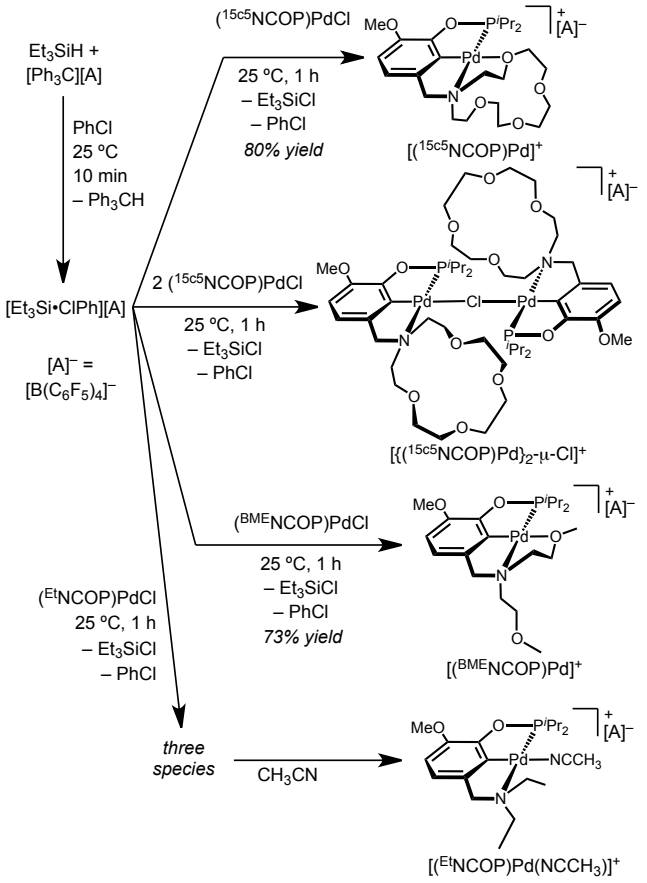
Figure 1. Molecular structure of one of the two unique (^{BME}NCOP)PdCl molecules in the asymmetric unit from single-crystal X-ray diffraction, with ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity. Distances (Å) and angles (°): Pd−P 2.1943(5), Pd−C(Ar) 1.954(2), Pd-N 2.189(2), 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 (^{15c5}NCOP)Pd(X) 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 [κ^4-(^{15c5}NCOP)Pd][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 (^{15c5}NCOP)PdCl with [Et_3Si][$B(C_6F_5)_4$][31–33] (generated *in situ* from Et_3SiH and [Ph_3C][$B(C_6F_5)_4$])[33] produced [κ^4-(^{15c5}NCOP)Pd][$B(C_6F_5)_4$] 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 [Et_3Si][$B(C_6F_5)_4$] resulted in formation of a distinct species with broad ^{1}H NMR signals. The same species was produced upon mixing equimolar amounts of neutral (^{15c5}NCOP)PdCl and the cationic [(^{15c5}NCOP)Pd][$B(C_6F_5)_4$] in CD_2Cl_2. Based on this result and comparisons with other pincer complexes in the literature,[29,34] we tentatively assign this species as the mono-halide-bridged dipalladium complex [{κ^3-(^{15c5}NCOP)Pd}$_2$-μ-Cl][$B(C_6F_5)_4$] (Scheme 3).

With a tractable halide abstraction strategy in hand, cationic complexes with varying amine donors were sought. Treating the diethylamino-substituted complex (^{Et}NCOP)PdCl with [Et_3Si][$B(C_6F_5)_4$] and Et_2O in PhCl produced a mixture of three species according to ^{1}H NMR and ^{31}P{^{1}H} NMR spectroscopy (Scheme 3). The major ion peak by ESI-MS was the three-coordinate cation [(^{Et}NCOP)Pd]$^+$, 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 [(^{Et}NCOP)Pd($NCCH_3$)]$^+$ as a single well-defined 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.

Treating (^{BME}NCOP)PdCl with [Et_3Si][$B(C_6F_5)_4$] produced the cationic complex [(^{BME}NCOP)Pd][$B(C_6F_5)_4$] in 73% yield, Scheme 3. The solution molecular symmetry of [(^{BME}NCOP)Pd]$^+$ is C_s, consistent with rapid exchange between the bound and free oxygen donors. The same behavior was observed for nickel pincer-crown ether complexes.[35]

Cation-Controlled Isomerization of 1-hexene. Positional isomerization of olefins was examined using the three cationic palladium complexes. Palladium complexes have long been recognized as active catalysts for olefin isomerization.[36] 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 ^{1}H NMR spectroscopy. Standard conditions called for 5 mM Pd (1.7 mol%), 5 mM

$LiBAr^F_4$•3Et_2O, 70 mM Et_2O, 300 mM 1-hexene, and 50 mM mesitylene internal standard at 25 ºC.

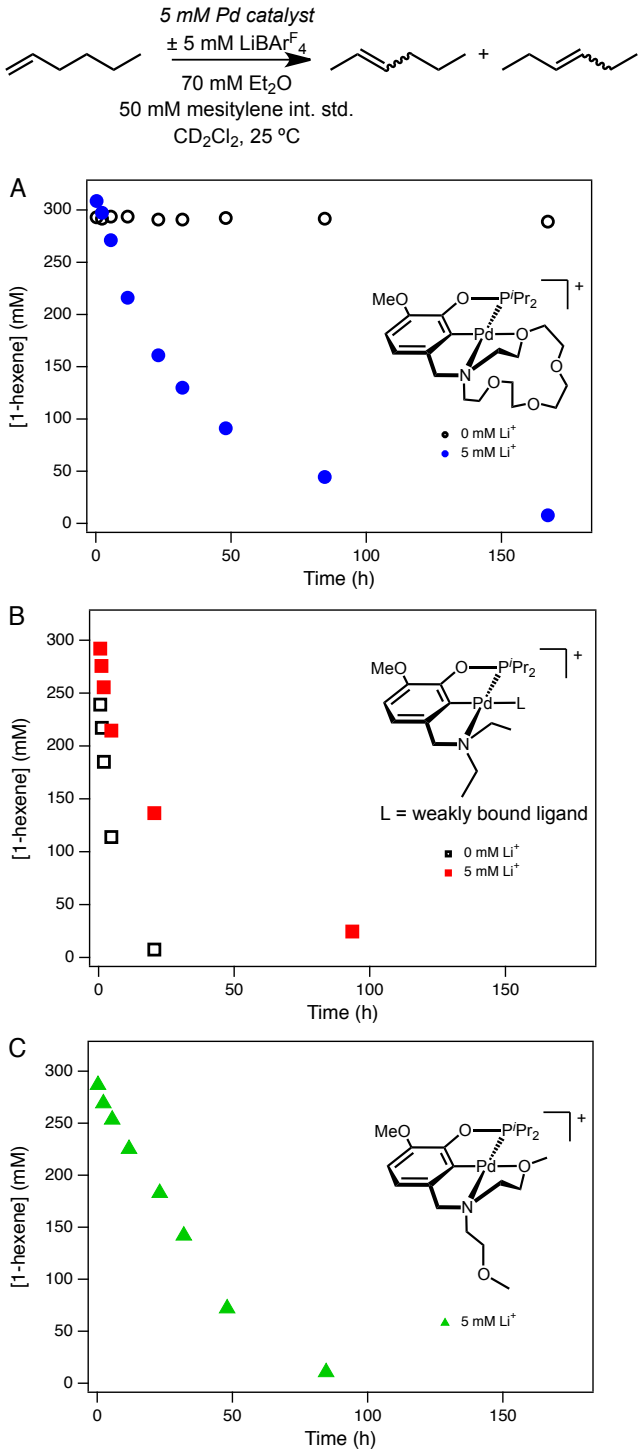


Figure 2. Isomerization of 300 mM 1-hexene catalyzed by [(^{15c5}NCOP)Pd][$B(C_6F_5)_4$] (A), [(^{Et}NCOP)Pd][$B(C_6F_5)_4$] (B), and [(^{BME}NCOP)Pd][$B(C_6F_5)_4$] (C) with no salt additive (empty symbols) and with 5 mM $LiBAr^F_4$ (filled symbols).

The crown-ether-containing complex [κ^4-(^{15c5}NCOP)Pd][$B(C_6F_5)_4$] was first treated with 1-hexene in dichloromethane. No isomerization of 1-hexene was observed by ^{1}H NMR spectroscopy, even after one week at room temperature (Figure 2A). Further, no changes were observed in the ^{1}H NMR spectrum to indicate any change in catalyst concentration, structure, or olefin binding in the presence of 1-hexene.

When the same complex was treated with 1-hexene under analogous reaction conditions *but with 1 equiv $LiBAr^F_4$ 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 (TOF = 1.37±0.60 h^{-1} for 5 data sets under identical conditions). Time-normalized kinetic analysis showed good overlays, however, consistent with a robust catalyst (Figure S25).

These results demonstrate cation control over isomerization. No activity is apparent except when $LiBAr^F_4$ 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 catalyst [(^{Et}NCOP)Pd][$B(C_6F_5)_4$] 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 (TOF 8.1 h^{-1}). In the presence of one equivalent of $LiBAr^F_4$, isomerization of 1-hexene proceeded slightly slower (TOF 5.7 h^{-1}). The rates of isomerization by [(^{Et}NCOP)Pd]$^+$ and [(^{15c5}NCOP)Pd]$^+$ in the presence of $LiBAr^F_4$ are very similar. It is not clear why $LiBAr^F_4$ 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 S28).

Finally, isomerization was also examined with the bis(methoxyethyl)amine-based catalyst [κ^4-(^{BME}NCOP)Pd]$^+$. The run-to-run variations in kinetic profile were more pronounced with this catalyst in the absence of salts, so those conditions are omitted. The catalyst was better behaved when $LiBAr^F_4$ was present, with uncertainty in TOF derived from initial rates in the presence of salts gave TOF = 0.59±0.28 h^{-1} (Figure S27). It is striking that the rate is almost

within error of the crown-containing complex, despite the expectation of weak interactions between Li^+ and the methoxyethyl groups. In the relatively nonpolar and noncoordinating chlorinated solvent, however, some degree of ion-dipole interactions must still be present. In support of this notion, treating [κ^3-(^{BME}NCOP)Pd(NCCH$_3$)]$^+$ LiBAr$^F_4$ resulted in NMR changes consistent with a host-guest interaction in CD_2Cl_2 (Figure S31).

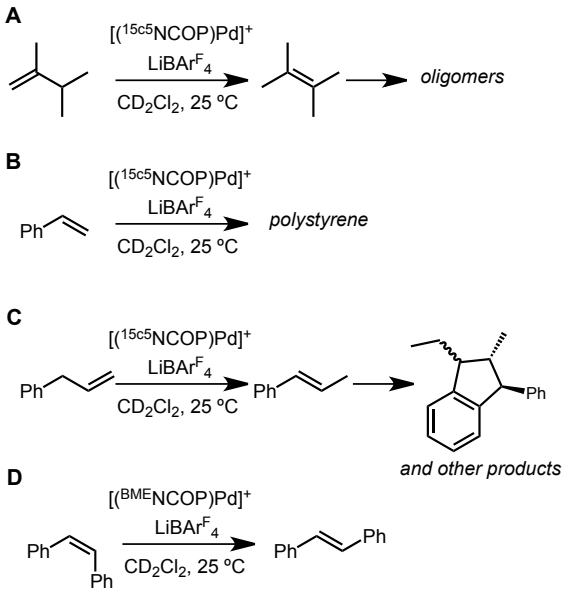
The catalytic studies show that the catalyst with a crown ether group is the only one capable of switchable behavior, with two different states of different activity. The diethylamino-based catalyst was highly active but not controllable, as expected.

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. 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.[37,38]

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

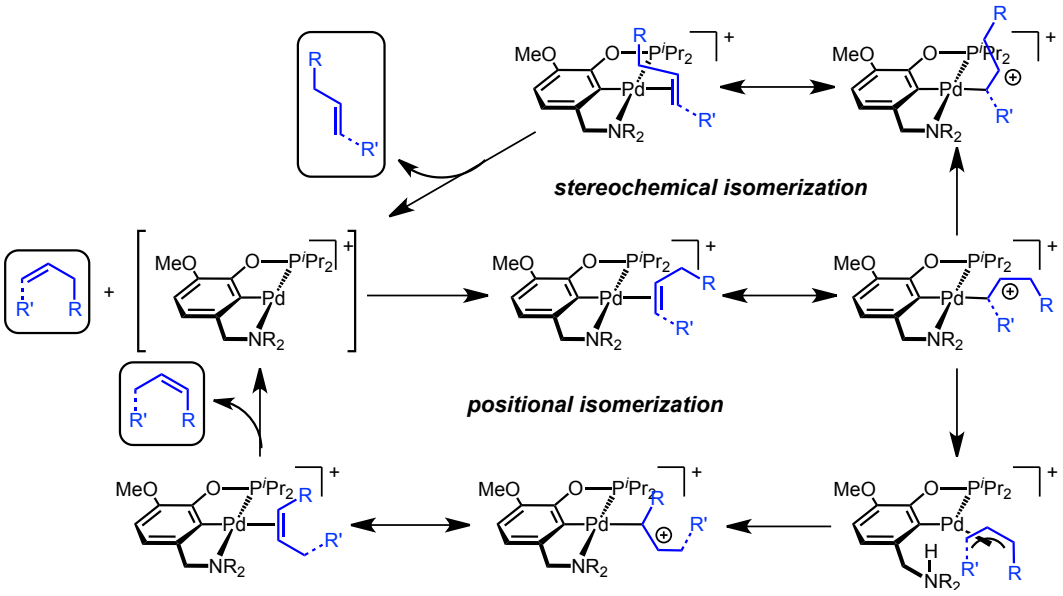
Initial evidence for an electrophilic carbocation mechanism for olefin isomerization came from the reaction of 2,3-dimethyl-1-butene (Scheme 4A). This substrate isomerizes within 1 h, much more quickly than 1-hexene, in the presence of [κ^4-(^{15c5}NCOP)Pd][B(C_6F_5)$_4$] and Li^+ salts (Figure S29). In fact, after the internal olefin formed from initial positional isomerization 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). Isomerization of

Scheme 5. Proposed mechanism of olefin isomerization.



allylbenzene produced β-methylstyrene initially, followed by formation of a range of products that included cyclodimerized indenes (Scheme 4C).

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, nearly complete conversion to *trans*-stilbene was observed when pure *cis*-stilbene contacted $[(^{BME}NCOP)Pd]^+$. 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 summarizes the proposed mechanisms for stereochemical and positional isomerization. These align with earlier proposals for dicationic Pd salts.[37,38] The presence of carbocation intermediates may explain the sensitivity of these reactions to impurities or other run-to-run differences. Control reactions containing $LiBAr^F{}_4$ but omitting the Pd complex resulted in no detectable reaction after one week at room temperature, supporting the notion that Pd and Li^+ work synergistically.

CONCLUSIONS

The cationic palladium pincer-crown ether complex $[(^{15c5}NCOP)Pd]^+$ 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.

ASSOCIATED CONTENT

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

AUTHOR INFORMATION

Corresponding Author

*E-mail: ajmm@email.unc.edu

Notes

No competing financial interests have been declared.

ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation under CAREER awards CHE-1553802 and CHE-2102244. We thank Brandie M. Ehrmann and the University of North Carolina at Chapel Hill Department of Chemistry Mass Spectrometry Core Laboratory, acknowledging support from the National Science Foundation under Grant No. CHE-1726291.

REFERENCES

(1) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-Metal Catalysts for Ethylene Homo- and Copolymerization. *Chem. Rev.* **2000**, *100*, 1169–1204.

(2) Daugulis, O.; MacArthur, A. H. R.; Rix, F. C.; Templeton, J. L. A Career in Catalysis: Maurice Brookhart. *ACS Catal.* **2016**, 1518–1532.

(3) Wang, F.; Chen, C. A Continuing Legend: The Brookhart-Type α-Diimine Nickel and Palladium Catalysts. *Polym. Chem.* **2019**, *10*, 2354–2369.

(4) Kocen, A. L.; Klimovica, K.; Brookhart, M.; Daugulis, O. Alkene Isomerization by "Sandwich" Diimine-Palladium Catalysts. *Organometallics* **2017**, *36*, 787–790.

(5) Blanco, V.; Leigh, D. A.; Marcos, V. Artificial Switchable Catalysts. *Chem. Soc. Rev.* **2015**, *44*, 5341–5370.

(6) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Supramolecular Catalysis. Part 1: Non-Covalent Interactions as a Tool for Building and Modifying Homogeneous Catalysts.

Chem. Soc. Rev. **2014**, *43*, 1660.

(7) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Supramolecular Catalysis. Part 2: Artificial Enzyme Mimics. *Chem. Soc. Rev.* **2014**, *43*, 1734–1787.

(8) Yoo, C.; Dodge, H. M.; Miller, A. J. M. Cation-Controlled Catalysis with Crown Ether-Containing Transition Metal Complexes. *Chem. Commun.* **2019**, *55*, 5047–5059.

(9) Miller, A. J. M. Controlling Ligand Binding for Tunable and Switchable Catalysis: Cation-Modulated Hemilability in Pincer-Crown Ether Ligands. *Dalton Trans.* **2017**, *46*, 11987–12000.

(10) Kita, M. R.; Miller, A. J. M. An Ion-Responsive Pincer-Crown Ether Catalyst System for Rapid and Switchable Olefin Isomerization. *Angew. Chem. Int. Ed.* **2017**, *56*, 5498–5502.

(11) Dodge, H. M.; Kita, M. R.; Chen, C.-H.; Miller, A. J. M. Identifying and Evading Olefin Isomerization Catalyst Deactivation Pathways Resulting from Ion-Tunable Hemilability. *ACS Catal.* **2020**, *10*, 13019–13030.

(12) Camp, A. M.; Kita, M. R.; Blackburn, P. T.; Dodge, H. M.; Chen, C.-H.; Miller, A. J. M. Selecting Double Bond Positions with a Single Cation-Responsive Iridium Olefin Isomerization Catalyst. *J. Am. Chem. Soc.* **2021**, *143*, 2792–2800.

(13) Selander, N.; Szabó, K. J. Catalysis by Palladium Pincer Complexes. *Chem. Rev.* **2011**, *111*, 2048–2076.

(14) González-Sebastián, L.; Morales-Morales, D. Cross-Coupling Reactions Catalysed by Palladium Pincer Complexes. A Review of Recent Advances. *J. Organomet. Chem.* **2019**, *893*, 39–51.

(15) Liu, J.-K.; Gong, J.-F.; Song, M.-P. Chiral Palladium Pincer Complexes for Asymmetric Catalytic Reactions. *Org. Biomol. Chem.* **2019**, *17*, 6069–6098.

(16) Hassam, M.; Taher, A.; Arnott, G. E.; Green, I. R.; van Otterlo, W. A. L. Isomerization of Allylbenzenes. *Chem. Rev.* **2015**, *115*, 5462–5569.

(17) Gregor, L. C.; Grajeda, J.; Kita, M. R.; White, P. S.; Vetter, A. J.; Miller, A. J. M. Modulating the Elementary Steps of Methanol Carbonylation by Bridging the Primary and Secondary Coordination Spheres. *Organometallics* **2016**, *35*, 3074–3086.

(18) Yoo, C.; Dodge, H. M.; Farquhar, A. H.; Gardner, K. E.; Miller, A. J. M. Decarbonylative Ether Dissection by Iridium Pincer Complexes. *Chem. Sci.* **2020**, *11*, 12130–12138.

(19) Pandey, D. K.; Khake, S. M.; Gonnade, R. G.; Punji, B. Mono- and Binuclear Palladacycles via Regioselective C–H Bond Activation: Syntheses, Mechanistic Insights and Catalytic Activity in Direct Arylation of Azoles. *RSC Adv.* **2015**, *5*, 81502–81514.

(20) Motoyama, Y.; Shimozono, K.; Nishiyama, H. Novel (Oxazolinyl) Phenyl Phosphinite Pincer Ligand : Development of the First Non-Symmetrical , PCN Type Chiral Palladium and Platinum Complexes. **2006**, *359*, 1725–1730.

(21) Niu, J. L.; Chen, Q. T.; Hao, X. Q.; Zhao, Q. X.; Gong, J. F.; Song, M. P. Diphenylprolinol-Derived Symmetrical and Unsymmetrical Chiral Pincer Palladium(II) and Nickel(II) Complexes: Synthesis via One-Pot Phosphorylation/Metalation Reaction and C-H Activation. *Organometallics* **2010**, *29*, 2148–2156.

(22) Ine, B.; Sanmartin, R.; Domı, E.; Urtiaga, M. K.; Arriortua, I. A Nonsymmetric Pincer-Type Palladium Catalyst In Suzuki , Sonogashira , and Hiyama Couplings in Neat Water. *Organometallics* **2008**, No. 9, 2833–2839.

(23) Li, J.; Siegler, M.; Lutz, M.; Spek, A. L.; Klein Gebbink, R. J. M.; van Koten, G. PCN- and PCS-Pincer Palladium Complexes as Tandem Catalysts in Homoallylation Reactions. *Adv. Synth. Catal.* **2010**, *352*, 2474–2488.

(24) Gong, J.-F.; Zhang, Y.-H.; Song, M.-P.; Xu, C. New PCN and PCP Pincer Palladium(II) Complexes:~ Convenient Synthesis via Facile One-Pot Phosphorylation/Palladation Reaction and Structural Characterization. *Organometallics* **2007**, *26*, 6487–6492.

(25) Zhang, B.; Wang, W.; Shao, D.; Hao, X.; Gong, J.; Song, M. Unsymmetrical Chiral PCN Pincer Palladium(II) and Nickel(II) Complexes of (Imidazolinyl)Aryl Phosphinite Ligands: Synthesis via Ligand C−H Activation, Crystal Structures, and Catalytic Studies. *Organometallics* **2010**, *29*, 2579–2587.

(26) Yang, M.; Liu, Y.; Gong, J.; Song, M. Unsymmetrical Chiral PCN Pincer Palladium (II) and Nickel (II) Complexes with Aryl-Based Aminophosphine À Imidazoline Ligands : Synthesis via Aryl C À H Activation and Asymmetric Addition of Diarylphosphines to Enones. *Organometallics* **2011**, *30*, 3793–3803.

(27) Khake, S. M.; Soni, V.; Gonnade, R. G.; Punji, B. Design and Development of POCN-Pincer Palladium Catalysts for C–H Bond Arylation of Azoles with Aryl Iodides. *Dalton Trans.* **2014**, *43*, 16084–16096.

(28) Hou, A.; Liu, Y.; Hao, X.; Gong, J.; Song, M. Synthesis and Characterization of New (Pyrazolyl) Aryl Phosphinite PCN Pincer Palladium (II) Complexes. *J. Organomet. Chem.* **2011**, *696*, 2857–2862.

(29) Herbert, D. E.; Ozerov, O. V. Binuclear Palladium Complexes Supported by Bridged Pincer Ligands.

Organometallics **2011**, *30*, 6641–6654.

(30) Smith, J. B.; Camp, A. M.; Farquhar, A. H.; Kerr, S. H.; Chen, C.-H.; Miller, A. J. M. Organometallic Elaboration as a Strategy for Tuning the Supramolecular Characteristics of Aza-Crown Ethers. *Organometallics* **2019**, *38*, 4392–4398.

(31) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. Crystal Structure of a Silyl Cation with No Coordination to Anion and Distant Coordination to Solvent. *Science* **1993**, *260*, 1917–1918.

(32) Connelly, S. J.; Kaminsky, W.; Heinekey, D. M. Structure and Solution Reactivity of (Triethylsilylium)Triethylsilane Cations. *Organometallics* **2013**, *32*, 7478–7481.

(33) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. Homogeneous CO Hydrogenation: Ligand Effects on the Lewis Acid-Assisted Reductive Coupling of Carbon Monoxide. *Organometallics* **2010**, *29*, 4499–4516.

(34) Bailey, W. D.; Luconi, L.; Rossin, A.; Yakhvarov, D.; Flowers, S. E.; Kaminsky, W.; Kemp, R. A.; Giambastiani, G.; Goldberg, K. I. Pyrazole-Based PCN Pincer Complexes of Palladium(II): Mono- and Dinuclear Hydroxide Complexes and Ligand Rollover C − H Activation. *Organometallics* **2015**, *34*, 3998–4010.

(35) Smith, J. B.; Kerr, S. H.; White, P. S.; Miller, A. J. M. Thermodynamic Studies of Cation–Macrocycle Interactions in Nickel Pincer–Crown Ether Complexes Enable Switchable Ligation. *Organometallics* **2017**, *36*, 3094–3103.

(36) DAVIES, N. R. Palladium-Catalysed Olefine Isomerization. *Nature* **1964**, *201*, 490–491.

(37) Sen, A. Organometallic Chemistry of Electrophilic Transition and Lanthanide Metal Ions. The Dominant Pathways for Reactions Involving Carbon-Carbon Double and Single Bonds and Carbon-Hydrogen Bonds. *Acc. Chem. Res.* **1988**, *21*, 421–428.

(38) Sen, A.; Lai, T. W. Mechanism of Palladium(II)-Catalyzed Carbon-Carbon Double Bond Isomerization in Olefins. *Inorg. Chem.* **1984**, *23*, 3257–3258.

Table of Contents artwork