ORGANOMETALLICS

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cis/*trans* Isomerization of *o*-Phosphino-Arenesulfonate Palladium Methyl Complexes

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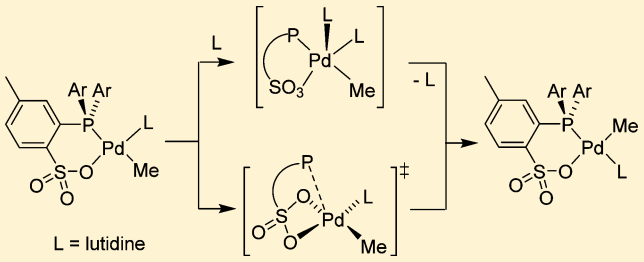
Supporting Information

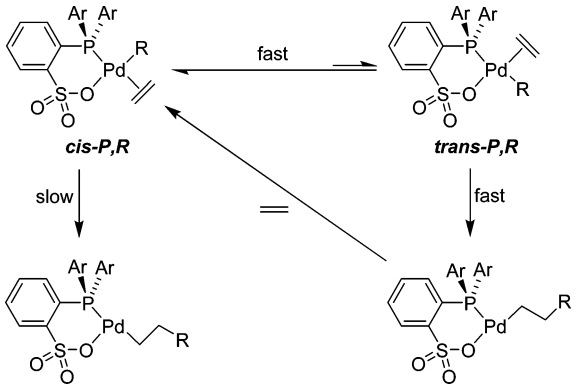
ABSTRACT: The *cis*/*trans* isomerization of (PO-OMe)PdMe(lut) ([PO-OMe]$^-$ = 2-{P(2-OMe-Ph)$_2$}-4-Me-benzenesulfonate) was studied to model the proposed isomerization in chain propagation in ethylene polymerization by (*o*-phosphinoarenesulfonate)PdR(ethylene) species. Nonequilibrium mixtures of *cis*-*P*,*C*- and *trans*-*P*,*C*-(PO-OMe)PdMe(2,6-lutidine) were generated by the reaction of Na[PO-OMe] and {Pd(μ-Cl)Me(2,6-lutidine)}$_2$ in CD_2Cl_2 at −25 °C. Kinetic studies revealed lutidine-catalyzed and noncatalyzed isomerization pathways. The lutidine-catalyzed pathway involves five-coordinate (PO-OMe)PdMe(lut)$_2$ intermediates that undergo Berry pseudorotation. Kinetic studies, structure−activity relationships, solvent effects, and density functional theory calculations for the noncatalyzed pathway are most consistent with a mechanism, originally proposed by Nozaki, Morokuma, and co-workers, which proceeds through a five-coordinate transition state with κ^3-*P*,*O*,*O* coordination of the [PO]$^-$ ligand.



INTRODUCTION

Palladium alkyl catalysts that contain *o*-phosphino-arenesulfonate ligands ([PO]$^-$, Scheme 1) have been studied intensively because of their ability to polymerize ethylene to linear polyethylene and copolymerize ethylene with polar vinyl monomers.[1,2] Because of the unsymmetrical structure of the PO$^-$ ligand, two modes of coordination and insertion of olefins are possible for (PO)PdR species, with the alkyl group either *cis* or *trans* to the phosphine (Scheme 1). Density functional theory (DFT) studies by Ziegler and co-workers[3] and by Nozaki, Morokuma, and co-workers[4] show that *cis*-*P*,*R*-(PO)Pd(R)(ethylene) species are more stable than the corresponding *trans*-*P*,*R* isomers, which are destabilized by the *trans* arrangement of the strong donor phosphine and alkyl ligands. Observable and isolable (PO)Pd(R)(L) complexes invariably have *cis*-*P*,*R* geometries.[1,2] The DFT studies show that the barrier to ethylene insertion of *cis*-*P*,*R*-(PO)Pd(R)(ethylene) is higher than those for isomerization of *cis*-*P*,*R*-(PO)Pd(R)(ethylene) to *trans*-*P*,*R*-(PO)Pd(R)(ethylene) and ethylene insertion of the *trans*-*P*,*R* isomer. These results imply that chain propagation occurs by isomerization of the *cis*-*P*,*R*-(PO)Pd(R)(ethylene) resting state to the *trans*-*P*,*R* isomer followed by insertion, as shown in Scheme 1. Analogous mechanisms were proposed for chain propagation by Ni catalysts that contain salicylaldiminato and anilinotropone ancillary ligands.[5]

Scheme 1



Three general mechanisms have been implicated in the *cis*/*trans* isomerization of square planar complexes of Pd(II) and other d^8 metals.[6] These include (i) associative processes catalyzed by exogeneous ligands or solvents involving consecutive ligand displacement steps or rearrangement of five-coordinate species via multiple Berry pseudorotations or turnstile processes,[7] (ii) dissociative processes involving configurationally labile three-coordinate intermediates,[8] and (iii) unimolecular rearrangement via a distorted tetrahedral transition state without ligand loss or gain.[9]

Ziegler's DFT analysis of the *cis*/*trans* isomerization of (2-P{2-OMe-Ph}$_2$-benzenesulfonate)Pd(Pr)(CH$_2$=CH$_2$) and related species implicated a unimolecular mechanism involving a distorted tetrahedral transition state (**TS-1**) in which the Pr group and the ethylene ligand are rotated by ∼90° from their position in the ground state structure (Scheme 2).[3] Morokuma

Received: October 3, 2014

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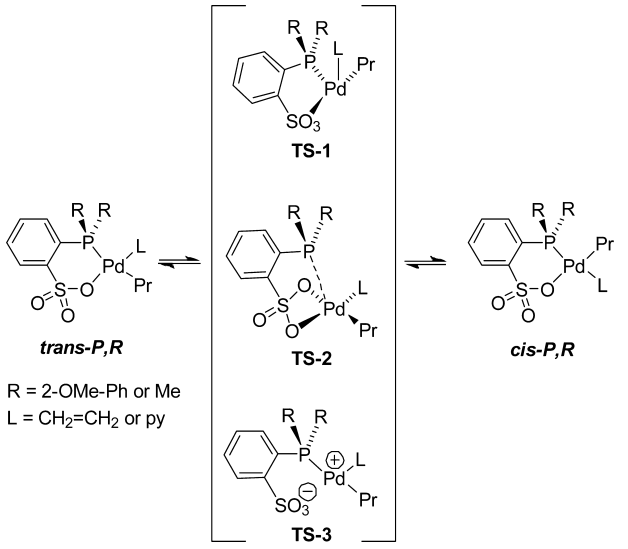
Scheme 2



and Nozaki's analysis of the isomerization of the model species *trans-P,C*-(2-PMe_2-benzenesulfonate)Pd(Pr)(CH_2=CH_2) to *cis-P,C*-(2-PMe_2-benzenesulfonate)Pd(Pr)(CH_2=CH_2) revealed an alternative mechanism involving coordination of a second sulfonate oxygen to Pd, leading to a square-pyramidal five-coordinate transition state (**TS-2**) with the phosphorus atom located at the apical position with a very long Pd–P contact (2.771 Å vs 2.352 Å in the ground state), and subsequent Berry pseudorotations.[4] **TS-2** was found to be 4.2 kcal/mol more stable than **TS-1** for this model system. The **TS-2** process proposed by Morokuma and Nozaki can be considered to be an intramolecular version of the classical ligand-catalyzed *cis/trans* isomerization.[10] Morokuma and Nozaki also found that isomerization of *trans-P,C*-(2-PMe_2-benzenesulfonate)Pd(Pr)(pyridine) to *cis-P,C*-(2-PMe_2-benzenesulfonate)Pd(Pr)(pyridine) via **TS-2** is favored over a sulfonate dissociation pathway (**TS-3**) by 9.1 kcal/mol.[4a] However, site-specific solvation effects that were not considered in the DFT analyses might stabilize **TS-3**.

In an initial study of *cis/trans* isomerization mechanisms of (PO)Pd complexes, we investigated the degenerate pyridine exchange in (PO-OMe)Pd$(py)_2^+$ ([PO-OMe]$^-$ = 2-{P(2-OMe-$Ph)_2$}-4-Me-benzenesulfonate) and the *cis/trans* isomerization of {2-P(^{i}Pr)$_2$-4-Me-benzenesulfonate}Pd(Cl){P(O-*o*-tolyl)$_3$}.[11] Kinetic studies of these model systems show that both processes occur via five-coordinate intermediates formed by the coordination of pyridine, P(O-*o*-tolyl)$_3$, or chloride. Noncatalyzed pathways were not observed in these cases. To date, it has not been possible to observe *cis/trans* isomerization of (PO)Pd(R)(L) alkyl species. Here we describe a method of generating nonequilibrium mixtures of *cis-P,C*- and *trans-P,C*-(PO-OMe)PdMe(2,6-lutidine) (**1a**) and related complexes with substituted 2,6-lutidine ligands, studies of their isomerization to the thermodynamically favored *cis-P,C*-(PO-OMe)-PdMe(2,6-lutidine) isomers, and observations related to the mechanism of this process.

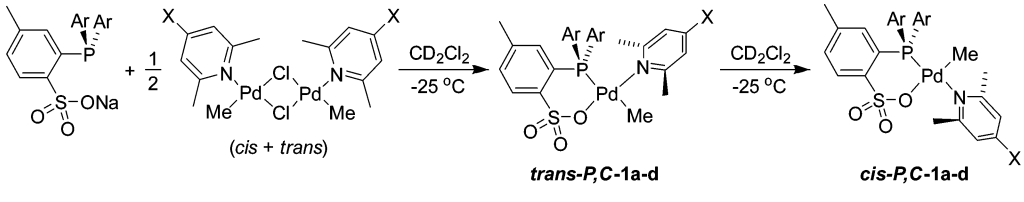
RESULTS

Generation of Mixtures of *cis-P,C*- and *trans-P,C*-(PO-OMe)PdMe(2,6-lutidine) Complexes. The reaction of Na[PO-OMe] and {Pd(μ-Cl)Me(2,6-lutidine)}$_2$ in CD_2Cl_2 at −25 °C for 30 min generates a 4/1 mixture of ***trans-P,C*-1a** and ***cis-P,C*-1a** in quantitative NMR yield (Scheme 3). The mixture is not stable at −25 °C, and the ***cis-P,C*-1a**/***trans-P,C*-1a** ratio increases over time until ***trans-P,C*-1a** is completely converted to ***cis-P,C*-1a**. The reaction temperature and time are critical for the successful generation of mixtures with high ***trans-P,C*-1a**/***cis-P,C*-1a** ratios. No reaction is observed below −40 °C, and mixtures with a large fraction of ***cis-P,C*-1a** are obtained above −25 °C. The use of shorter reaction times at −25 °C results in mixtures of ***trans-P,C*-1a**, ***cis-P,C*-1a**, and unreacted starting materials.

The structures of ***trans-P,C*-1a** and ***cis-P,C*-1a** are readily apparent from the NMR spectral data of these species. The ^{1}H (−25 °C) and ^{13}C (−60 °C) NMR spectra of ***trans-P,C*-1a** each contain a doublet for the Pd-CH_3 group with a large ^{31}P coupling constant ($^3J_{HP}$ = 8.5 Hz; $^2J_{CP}$ = 102 Hz), consistent with a *trans* arrangement of the methyl and phosphine ligands.[12] In contrast, the ^{1}H NMR spectrum of ***cis-P,C*-1a** (−25 °C) contains a doublet for the Pd-CH_3 group with a small $^3J_{HP}$ value (3.0 Hz) and the ^{13}C NMR spectrum (−60 °C) contains a singlet for the Pd-CH_3 group, as expected for a *cis-P,C* isomer. Two broad singlets are observed for the 2-O*Me*-Ph units in the ^{1}H NMR spectrum of ***trans-P,C*-1a** at −60 °C, which is indicative of restricted inversion of the puckered chelate ring and/or rotation around the P–C_{ipso} bonds.[13] Similar results were observed for ***cis-P,C*-1a** at −60 °C. Several analogues of ***trans-P,C*-1a** with different *para*-substituted 2,6-lutidine ligands (lut-X) were also prepared, as shown in Scheme 3 (initial ***trans-P,C*-1**/***cis-P,C*-1** ratios of 2.3 for **1b**, 1.9 for **1c**, and 1.0 for **1d**).

Kinetics of Isomerization of *trans-P,C*-1a to *cis-P,C*-1a. The kinetics of isomerization of ***trans-P,C*-1a** to ***cis-P,C*-1a** were probed by ^{1}H NMR in CD_2Cl_2 solution at −25 °C. The isomerization displays first-order behavior in ***trans-P,C*-1a** with a first-order rate constant k_0 of 1.60(4) × 10^{-4} s^{-1} at −25 °C. The isomerization is accelerated in the presence of free 2,6-lutidine. For example, the observed first-order rate constant (k_{obs}) in the presence of 1.67 M 2,6-lutidine is 43(3) × 10^{-4} s^{-1}. A plot of k_{obs} versus 2,6-lutidine concentration is linear with a non-zero intercept, indicating that the isomerization is also

Scheme 3



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first-order in 2,6-lutidine (Figure 1). These results are consistent with the rate law in eq 1 and the operation of two

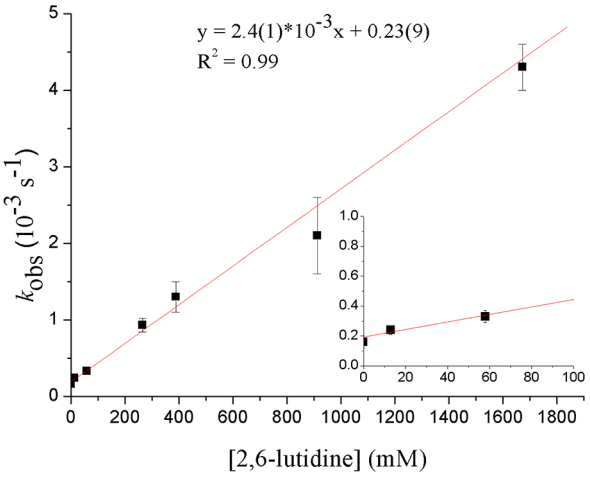

Figure 1. Plot of the observed first-order rate constant for the isomerization of ***trans-P,C*-1a** to ***cis-P,C*-1a** (k_{obs}) vs the concentration of free 2,6-lutidine. The inset is an expansion of the *y*-intercept region of the kinetic plot. Conditions: −25 °C, CD_2Cl_2 solution.

independent isomerization pathways: a 2,6-lutidine-catalyzed process (k_1[2,6-lutidine]) and a non-2,6-lutidine-catalyzed pathway (k_0).

$$\text{rate} = (k_0 + k_1[\text{2,6-lutidine}])[\textbf{\textit{trans-P,C}-1a}] \quad (1)$$

The isomerization of ***trans-P,C*-1a** to ***cis-P,C*-1a** was studied over the temperature range of −25 to −5 °C, and the resulting Eyring plot is shown in Figure 2. The activation parameters for the isomerization are as follows: $\Delta G^{\ddagger}(-25\ ^{\circ}C) = 19(1)$ kcal/mol; $\Delta H^{\ddagger} = 19(1)$ kcal/mol; $\Delta S^{\ddagger} = -0.97(8)$ eu.

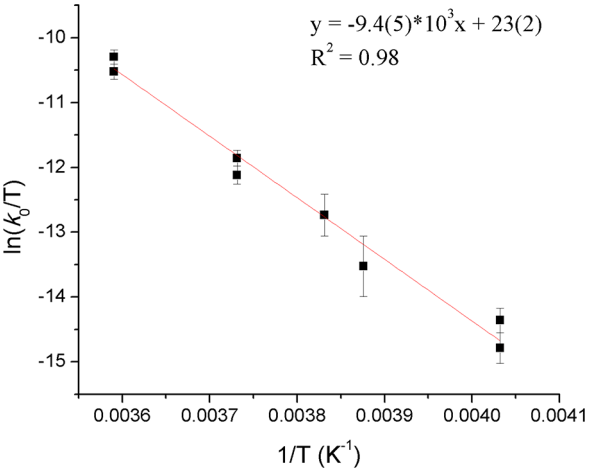

Figure 2. Eyring plot for the isomerization of ***trans-P,C*-1a** to ***cis-P,C*-1a** in CD_2Cl_2.

It is possible that, even in the absence of added 2,6-lutidine, a low concentration of free 2,6-lutidine could be present due to decomposition of **1a** and could catalyze the isomerization. However, addition of 6 mol % {(PO-3,5-^{t}Bu)PdMe}$_2$ ([PO-3,5-^{t}Bu]$^-$ = 2-{P(3,5-^{t}Bu$_2$-Ph)$_2$}-4-Me-benzenesulfonate) as a lutidine trap has no effect on the isomerization rate, which rules out this possibility.[2h]

Influence of the Electronic Properties of the 2,6-Lutidine Ligand on k_0. The first-order rate constants for the isomerization of ***trans-P,C*-1b−d** to ***cis-P,C*-1b−d** (k_0^X) were determined to probe the influence of electronic effects on the rate of the non-lutidine-catalyzed isomerization. The results of this study are summarized in Table 1. Using **1a** as a benchmark,

Table 1. First-Order Rate Constants (k_0^X) for the Unimolecular Isomerization of *trans-P,C*-1a−d to *cis-P,C*-1a−d Containing 4-X-2,6-Lutidine Ligands in CD_2Cl_2 Solution at −25 °C

X	k_0^X (×10^{-4} s^{-1})	σ_p^+
NO_2	1.13(5)	0.79
H	1.60(4)	0
OMe	3.38(3)	−0.78
NMe_2	7.4 (3)	−1.7

incorporating a 4-NO_2 group into the 2,6-lutidine decreases the isomerization rate, while the presence of a 4-OMe or 4-NMe_2 group increases the rate. A Hammett analysis of these data, using **1a** (k_0; X = H) as the reference, is shown in Figure 3. A

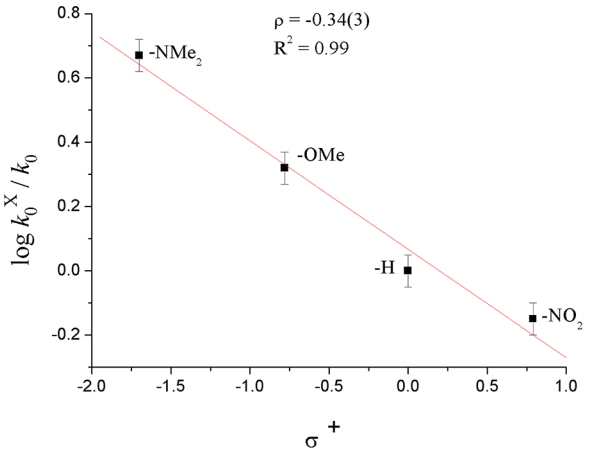

Figure 3. Hammett plot for the unimolecular isomerization of ***trans-P,C*-1a−d** to ***cis-P,C*-1a−d**. The X substituents are shown in the plot.

linear correlation between $\log(k_0^X/k_0)$ and σ_p^+, the Hammett constant for substituents that are conjugated with a reaction center and a delocalized positive charge,[14] is observed. The negative ρ value [−0.34(3)] implies a buildup of positive charge on the lutidine ligand and hence the Pd center in the transition state, though the effect is small.

Solvent Effects on k_0. The k_0 values for the isomerization of ***trans-P,C*-1a** in several solvent mixtures are listed in Table 2.

Table 2. First-Order Rate Constants (k_0) for the Unimolecular Isomerization of *trans-P,C*-1a to *cis-P,C*-1a in Different Solvent Mixtures at −25 °C

entry	solvent	k_0 (×10^{-4} s^{-1})
1	CD_2Cl_2	1.60(4)
2[a]	2.3 M[b] acetone-d_6 in CD_2Cl_2	2.15(2)
3[a]	2.2 M[b] ^{n}PrOH in CD_2Cl_2	4.7(1)
4[a]	4.1 M[b] CD_3OD in CD_2Cl_2	6.0(1)

[a]***trans-P,C*-1a** is insoluble in CD_3OD, ^{n}PrOH, and acetone-d_6. [b]Addition of >17 vol % cosolvent resulted in precipitation of ***trans-P,C*-1a** and ***cis-P,C*-1a**.

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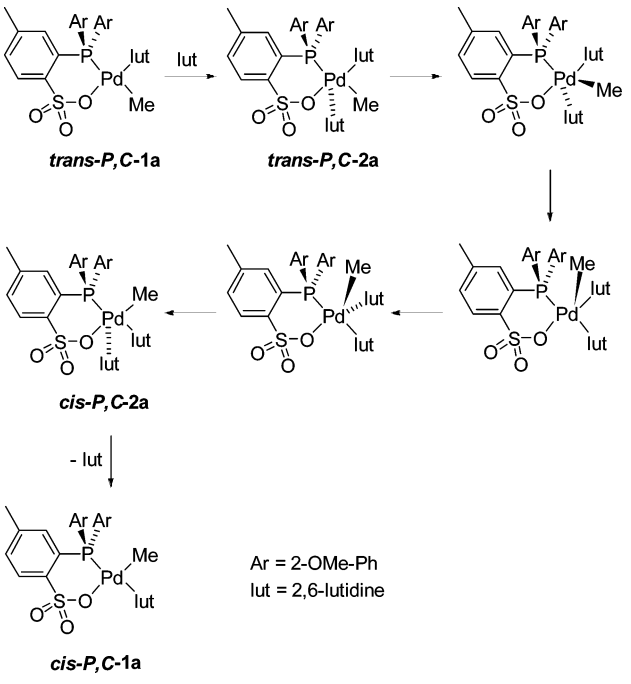
The addition of 17 vol % (2.3 M) acetone-d_6 (ε = 20.7; Gutmann donor number DN = 21) to the benchmark solvent CD_2Cl_2 (ε = 8.9; DN = 1) has a minimal effect on k_0 (entry 2).[15] The addition of 17 vol % (2.2 M) ^{n}PrOH (ε = 20.1; DN = 21) or 17 vol % (4.1 M) CD_3OD (ε = 33; DN = 19) increases the isomerization rate by a factor of 3−4 (entries 3 and 4). These results show that the polarity, donor ability, and hydrogen bonding ability of the solvent have only a minor effect on the isomerization rate.

Changes in Calculated Atomic Charges. As noted above, Morokuma and Nozaki found by DFT calculations that isomerization of *trans-P,C*-(2-PMe_2-benzenesulfonate)Pd(Pr)(pyridine) to *cis-P,C*-(2-PMe_2-benzenesulfonate)Pd(Pr)(pyridine) via **TS-2** is favored over a sulfonate dissociation pathway (**TS-3**) by 9.1 kcal/mol. Our own DFT calculations confirm this result and also show that the **TS-2** pathway is favored over the **TS-1** pathway by 11 kcal/mol for this system (B3LYP/6-31G* and LANL2DZ).[11] We also calculated NBO atomic charges of the Pd and P atoms along the **TS-1** and **TS-2** pathways. In **TS-1**, the Pd gains positive charge (+0.03 unit) and the P gains negative charge (−0.08 unit) relative to *trans-P,C*-(2-PMe_2-benzenesulfonate)Pd(Pr)(pyridine). In **TS-2**, even though the Pd is formally five-coordinate, Pd gains substantial positive charge (+0.129 unit) while P gains negative charge (−0.118 unit) compared to *trans-P,C*-(2-PMe_2-benzenesulfonate)Pd(Pr)(pyridine). This result is consistent with the long Pd−P distance and nearly complete displacement of the stronger donor P atom by the weaker donor sulfonate O atom in **TS-2**.

Mechanism of Isomerization of *trans-P,C*-1a to *cis-P,C*-1a. The 2,6-lutidine-catalyzed pathway can be explained by the classical ligand-catalyzed *cis/trans* isomerization mechanism, as shown in Scheme 4. In this process, 2,6-lutidine binds ot ***trans-P,C*-1a** to form the five-coordinate intermediate ***trans-P,C*-2a**, which undergoes two consecutive Berry pseudorotations to form ***cis-P,C*-2a**. Subsequent dissociation of 2,6-lutidine affords ***cis-P,C*-1a**. This process results in exchange of free and coordinated 2,6-lutidine.[16]

Scheme 4



Five possible mechanisms may be considered for the non-lutidine-catalyzed pathway, as summarized in Schemes 5 and 6. Mechanism A proceeds via a distorted tetrahedral transition state analogous to **TS-1**. Mechanism B proceeds via a five-coordinate transition state with κ^3-*P,O,O* coordination of the $[PO]^-$ ligand analogous to **TS-2**. Mechanism C proceeds by dissociation of the sulfonate to form a configurationally labile three-coordinate, zwitterionic species analogous to **TS-3**. Mechanism D is a classical solvent-catalyzed pathway involving initial coordination of solvent followed by three consecutive Berry pseudorotations to effect isomerization and solvent loss, as detailed in Scheme 6. Mechanism E proceeds by dissociation of the lutidine ligand to form a configurationally labile three-coordinate intermediate.

Mechanism D, which involves a bimolecular solvent coordination step, is inconsistent with the near-zero $\Delta S^{\ddagger}$, the observed (though small) accelerating effect of electron-donating substituents on the lutidine ligand, and the small influence of solvent donor ability on the isomerization rate. Mechanism E, which involves dissociation of a lutidine ligand, is inconsistent with the near-zero $\Delta S^{\ddagger}$ and the observed rate law for the isomerization (see the Supporting Information). While the experimental results do not rule out mechanism A, this mechanism may be discounted by the DFT results for the model complex (2-PMe_2-benzenesulfonate)Pd(Pr)(pyridine), which show that **TS-1** is disfavored by 11 kcal/mol relative to **TS-2**.

Distinguishing between mechanisms **B** and **C** is more challenging. Both of these unimolecular mechanisms are consistent with the observed near-zero $\Delta S^{\ddagger}$ and the positive charge buildup on Pd in the transition state implied by the Hammett analysis. However, solvent effects on mechanism B should be minimal, while mechanism C should be strongly favored by polar, coordinating, and especially hydrogen-bonding solvents, which would stabilize the zwitterionic species **TS-3**. For comparison, the anchimerically assisted ionization of 4-methoxyneophyl tosylate, shown in Scheme 7, is 10 times faster in acetone but ∼2000 times faster in MeOH than in THF (ε = 7.5). Methanol stabilizes the departing tosylate anion through hydrogen bonding.[17] The relatively small solvent effects on the isomerization rate of ***trans-P,C*-1a** and the similarity of the effects of non-hydrogen-bonding (acetone) and hydrogen-bonding additives (^{n}PrOH and CD_3OD) argue against mechanism C. Furthermore, sulfonate dissociation is rarely observed for (*o*-phosphino-arenesulfonate)Pd species and is disfavored by the rigid phenylene linker. An unusual example of this process is the reaction of [{PO-OMe}Pd(py)$_2$][SbF_6] and pyridine to generate [κ^1-*P*-{PO-OMe}Pd(py)$_3$][SbF_6]; however, this process is reversible (K_{eq} = 0.28 M^{-1} at 20 °C), and the latter species could be isolated only from neat pyridine.[11]

CONCLUSIONS

The isomerization of *trans-P,C*-(PO-OMe)PdMe(lut) species to the thermodynamically favored *cis-P,C* isomers occurs by two independent pathways, a lutidine-catalyzed pathway and a unimolecular pathway. The lutidine-catalyzed pathway proceeds through five-coordinate (PO)PdMe(lut)$_2$ intermediates that undergo Berry pseudorotations. The non-lutidine-catalyzed pathway exhibits a near-zero $\Delta S^{\ddagger}$, is slightly accelerated by electron-donating substituents on the lutidine, and is only

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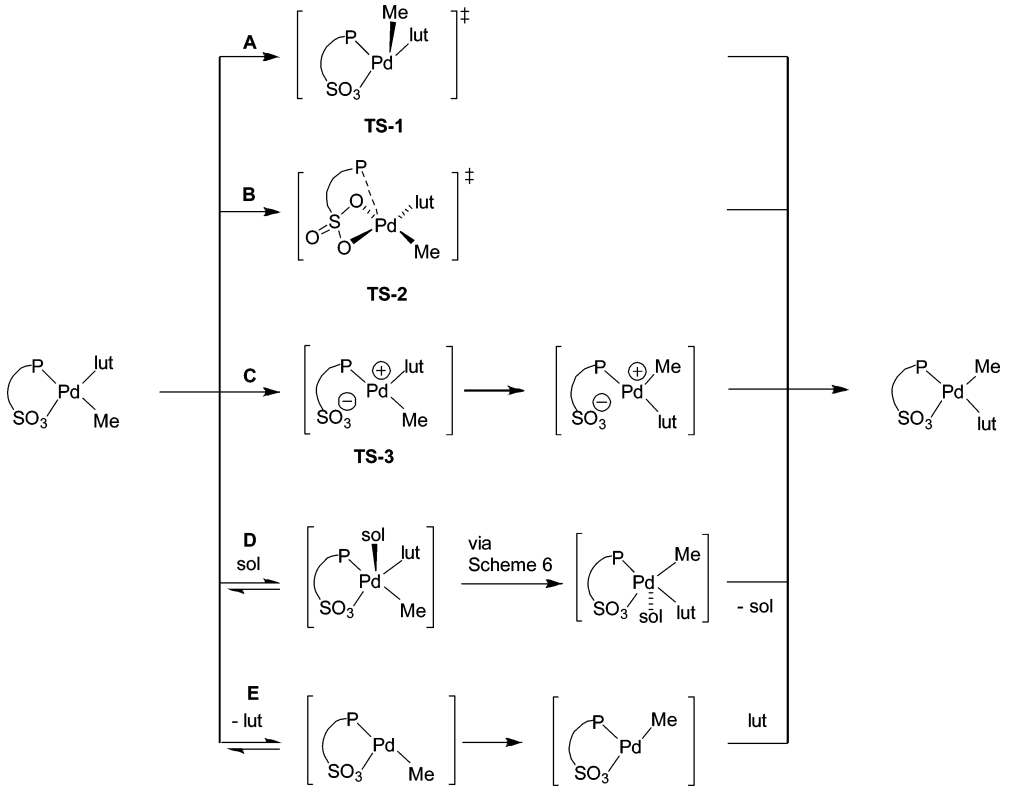
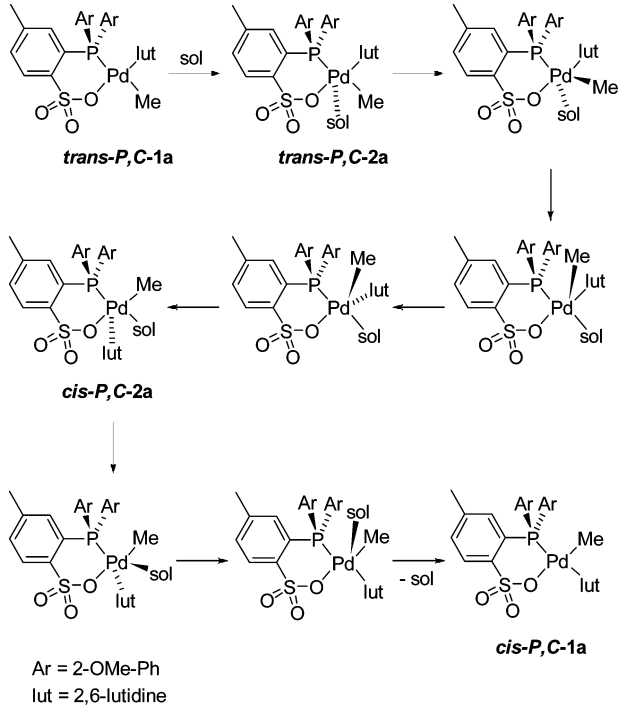
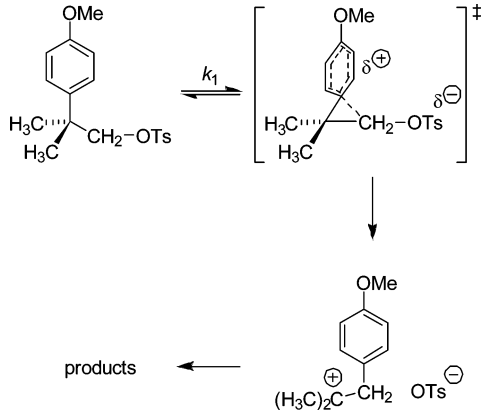
Scheme 5



Scheme 6



Scheme 7



slightly accelerated by addition of polar, coordinating, and hydrogen-bonding solvents. These results favor a mechanism originally proposed by Nozaki, Morokuma, and co-workers that proceeds through a five-coordinate transition state with κ^3-*P,O,O* coordination of the $[PO]^-$ ligand (**TS-2**).[4a] The experimental results are also consistent with a mechanism involving a distorted tetrahedral transition state (**TS-1**), but DFT results for related species show that **TS-1** is significantly disfavored relative to **TS-2**. The experimental results argue against mechanisms involving configurationally labile three-coordinate species generated by dissociation of the sulfonate or lutidine ligands, or five-coordinate species formed by coordination of a solvent molecule. These results also suggest that under catalytic polymerization conditions, where ethylene is present in large excess relative to (PO)PdR species, an ethylene-catalyzed *cis/trans* isomerization pathway via five-coordinate (PO)PdR(ethylene)$_2$ intermediates may outcompete the unimolecular pathway.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of compounds, experimental and computational details, figures, and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/om501007q | *Organometallics* XXXX, XXX, XXX−XXX

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (Grants CHE-0911180 and CHE-1048528).

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