Homogeneous Catalysis

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cis/trans Isomerization of Phosphinesulfonate Palladium(II) Complexes**

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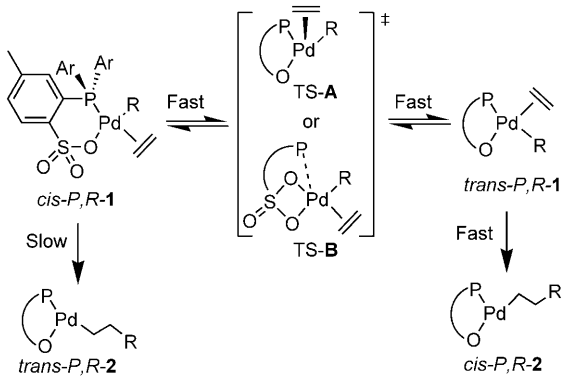
The copolymerization of ethylene with polar vinyl monomers by insertion processes enables the direct synthesis of functionalized plastics.[1] [{2-phosphinoarenesulfonate}PdR] species ([{PO}PdR]) copolymerize ethylene with a wide range of polar monomers to linear copolymers.[2] The {PO$^-$} ligand incorporates strong-*trans*-influence phosphine and weak-*trans*-influence sulfonate ligands in a *cis* arrangement in the {PO}Pd complex.[3] Owing to this "electronic asymmetry," the two open coordination sites of a {PO}Pd^{II} unit are quite different, which may contribute to the reactivity of these catalysts.

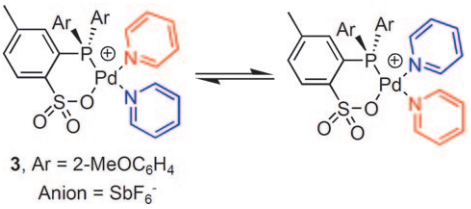
Two isomers and insertion (i.e., chain-growth) modes are possible for [{PO}PdR(ethylene)] complexes (**1**), as shown in Scheme 1. The species *cis-P,R*-**1** is more stable than *trans-P,R*-**1** owing to the unfavorable *trans* arrangement of the strong-



Scheme 1. Proposed chain-growth mechanism for [{PO}PdR] catalysts.

trans-influence alkyl and phosphine ligands in the latter species. Migratory insertion of *cis-P,R*-**1** is expected to yield *trans-P,R*-**2**, in which the Pd–C bond is *trans* to the phosphine ligand, while insertion of *trans-P,R*-**1** is expected to yield *cis-P,R*-**2**, in which the Pd–C bond is *cis* to the phosphine ligand. DFT studies predict that the barrier to ethylene insertion of *cis-P,R*-**1** is approximately 11 kcal mol^{-1} higher than that of *trans-P,R*-**1**.[4] The calculations also suggest that *cis-P,R*-**1** and *trans-P,R*-**1** are in fast equilibrium and that chain growth occurs by insertion of *trans-P,R*-**1**. The *cis-P,R*-**1**/*trans-P,R*-**1** isomerization was proposed to proceed via transition state TS-**A**,[4b] in which the geometry at palladium center may be described as square-pyramidal with one basal vacancy, or TS-**B**,[4a] in which a terminal sulfonate oxygen atom coordinates to palladium to form a five-coordinate species that undergoes Berry pseudorotation. It has not yet been possible to observe the isomerization of a *cis-P,R*-[{PO}PdR(L)] species to the *trans-P,R* isomer. Therefore, we have examined two model {PO}Pd^{II} systems to probe how *cis*/*trans* isomerization occurs.

We first prepared [{PO-OMe}Pd(py)$_2$]$^+$ [**3**, {PO-OMe} = 2-P(*o*-MeOC$_6$H$_4$)$_2$-*p*-toluenesulfonate, py = pyridine, Eq. (1)]



(1)

and investigated the mechanism of exchange of the pyridine ligands between the sites *cis* and *trans* to the phosphorus donor (*cis*-P and *trans*-P, respectively). Complex **3** was prepared by the reaction of [{PO-OMe}PdCl(py)][5] with Ag[SbF$_6$] in the presence of pyridine and characterized by NMR spectroscopy, ESI-MS, elemental analysis, and X-ray diffraction.[6]

Crystallization of **3** from pyridine yields [{κ^1-PO-OMe}Pd(py)$_3$][SbF$_6$] (**4**). X-ray analysis of **4** shows that the Pd center is bound by three pyridine ligands and the phosphine moiety of the {PO-OMe} ligand in a square-planar arrangement (Figure 1). The distance from the Pd atom to the nearest sulfonate oxygen atom (O(3)) is 3.066(5) Å, which is near the sum of the van der Waals radii of Pd and O (3.12 Å). These results show that the sulfonate has been nearly completely displaced by pyridine. NMR spectroscopy studies showed that **4** is in equilibrium with **3** and free pyridine in CD_2Cl_2 ($K_{eq} = [\mathbf{4}][\mathbf{3}]^{-1}[py]^{-1} = 0.28\,M^{-1}$ at 20 °C).

The intra- and intermolecular pyridine exchange properties of **3** were probed by NMR spectroscopy. The ^{1}H NMR spectrum of **3** in CD_2Cl_2 at 20 °C contains sharp *trans*-P pyridine and *cis*-P pyridine signals in a 1:1 integral ratio. The excess line widths of the *trans*-P and *cis*-P pyridine resonances are below the detection limit (ca. 0.5 Hz), thus indicating that intramolecular pyridine exchange does not occur on the timescale of NMR spectroscopy (T_2). The EXSY spectrum of

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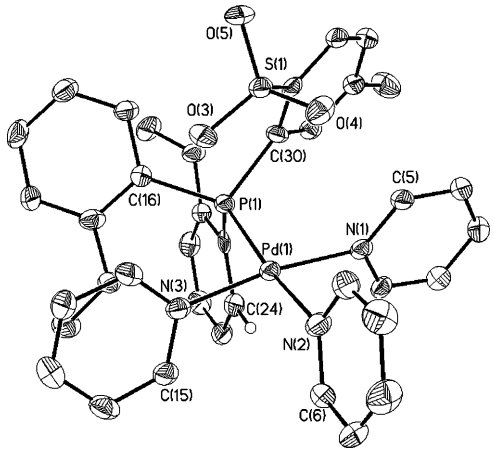


Figure 1. Molecular structure of the cation of [{PO-OMe}Pd(py)$_3$][SbF$_6$] (**4**). Hydrogen atoms except H(24) are omitted. Bond lengths [Å]: Pd(1)–N(1) 2.051(6), Pd(1)–N(2) 2.096(6), Pd(1)–N(3) 2.028(6), Pd(1)–P(1) 2.291(1), Pd(1)–O(3) 3.066(5), Pd(1)–H(24) 2.83.

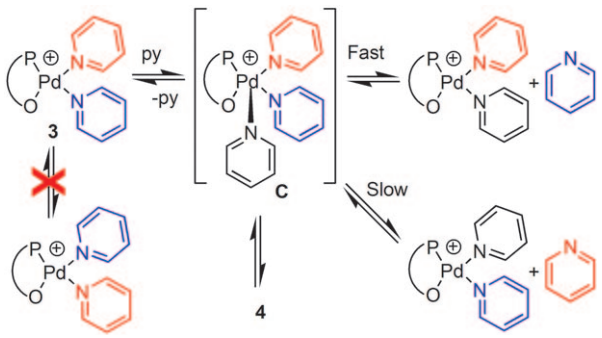
3 (CD_2Cl_2, 20 °C) does not contain crosspeaks between corresponding *trans*-P and *cis*-P pyridine resonances, thus indicating that the exchange is slower than the EXSY timescale. These results show that the barrier to intramolecular pyridine exchange is above 20 kcal mol^{-1}.[7]

In the presence of a low concentration of pyridine (9 mM) at 20 °C, the *trans*-P pyridine resonances of **3** in the ^{1}H NMR spectrum are coalesced with the free pyridine signals, consistent with fast intermolecular associative exchange of the *trans*-P pyridine with free pyridine. In contrast, the *cis*-P pyridine signals of **3** maintain their original chemical shifts and display little line broadening under these conditions. As the concentration of free pyridine is increased, moderate broadening of the *cis*-P pyridine signals is observed, consistent with slow associative exchange of the *cis*-P pyridine with free pyridine. The difference in rates of exchange of the *trans*-P and *cis*-P pyridine with free pyridine is expected, since phosphines are better *trans* directors than sulfonates.[8]

In the presence of free pyridine, the variable-temperature ^{1}H NMR spectra of **4** contain sharp resonances for coordinated and free pyridine, and the EXSY spectra do not contain crosspeaks between **4** and free pyridine. Therefore, **4** does not play a role in the pyridine exchange of **3** and free pyridine.

These results are consistent with the mechanism of pyridine exchange for **3** shown in Scheme 2. Trigonal-bipyramidal intermediates are omitted from Scheme 2; a more complete mechanism is given in the Supporting Information. Complex **3** binds pyridine to form the unobserved five-coordinate intermediate (or transition state) **C**, leading to associative pyridine exchange. The formation of **4** also occurs through **C**.

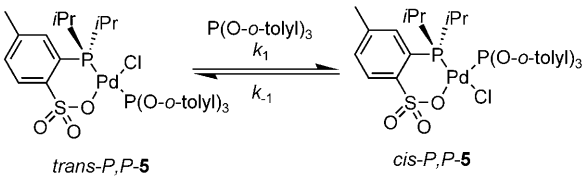
Complex **3** differs from [{PO}PdR(olefin)] complexes in that it is cationic rather than neutral and contains identical pyridine ligands instead of electronically different alkyl and olefin ligands. [{PO}PdCl(PR$_3$)] complexes are better models, because they have a neutral charge and contain electronically different chloride and phosphine ligands. We generated a small library of [{PO}PdCl(PR$_3$)] complexes to access a



Scheme 2. Pyridine exchange mechanism for **3**. $\widehat{PO}$ = {PO-OMe}.

system in which the *cis*-*P*,*P* and *trans*-*P*,*P* isomers can be both observed and their interconversion directly probed.[6] This work led to the discovery of [{PO-*i*Pr}PdCl{P(O-*o*-tolyl)$_3$}] (**5**, {PO-*i*Pr} = 2-P*i*Pr$_2$-*p*-toluenesulfonate), which has these properties.

The reaction of [{PO-*i*Pr}PdCl(py)] with P(O-*o*-tolyl)$_3$ in the presence of B(C$_6$F$_5$)$_3$ affords a 1:9 mixture of *cis*-*P*,*P*-[{PO-*i*Pr}PdCl(P(O-*o*-tolyl)$_3$)] [*cis*-*P*,*P*-**5**, Eq. (2)] and *trans*-*P*,*P*-[{PO-*i*Pr}PdCl(P(O-*o*-tolyl)$_3$)] (*trans*-*P*,*P*-**5**) in 94 % yield. No



(2)

change in the *cis*-*P*,*P*/*trans*-*P*,*P*-**5** ratio is observed by ^{1}H NMR spectroscopy when CD_2Cl_2, [D$_8$]THF, or [D$_6$]acetone solutions of *cis*-*P*,*P*/*trans*-*P*,*P*-**5** are heated at 35 °C over two days. In contrast, addition of P(O-*o*-tolyl)$_3$ to a solution of *cis*-*P*,*P*/*trans*-*P*,*P*-**5** in CD_2Cl_2 at 35 °C results in clean conversion of the initial 1:9 *cis*-*P*,*P*/*trans*-*P*,*P*-**5** mixture to an equilibrium 1.4:1 *cis*-*P*,*P*/*trans*-*P*,*P*-**5** mixture [Eq. (2)]. The ^{31}P{^{1}H} and ^{1}H NMR spectra of *cis*-*P*,*P*/*trans*-*P*,*P*-**5** in CD_2Cl_2 at 35 °C in the presence of added P(O-*o*-tolyl)$_3$ contain sharp resonances for *cis*-*P*,*P*-**5**, *trans*-*P*,*P*-**5**, and free P(O-*o*-tolyl)$_3$ but no resonances for new species, thus indicating that exchange of free and coordinated P(O-*o*-tolyl)$_3$ is slow on the time scale of NMR spectroscopy and that significant quantities of new species are not formed. These results show that the barrier to direct isomerization of *cis*-*P*,*P*/*trans*-*P*,*P*-**5** is high but that this isomerization is catalyzed by P(O-*o*-tolyl)$_3$.

The *cis*-*P*,*P*-**5**/*trans*-*P*,*P*-**5** isomerization in the presence of P(O-*o*-tolyl)$_3$ in CD_2Cl_2 obeys first-order approach-to-equilibrium kinetics [Eq. (3)]. k_{obs} is the sum of the forward (k_1, *trans* to *cis*) and reverse (k_{-1}, *cis* to *trans*) rate constants, and $K_{eq} = k_1/k_{-1}$. A plot of k_{obs} versus [P(O-*o*-tolyl)$_3$] is linear

$$\ln\left(\frac{[\textit{trans-P,P-}\mathbf{5}] - [\textit{trans-P,P-}\mathbf{5}]_{inf}}{[\textit{trans-P,P-}\mathbf{5}]_0 - [\textit{trans-P,P-}\mathbf{5}]_{inf}}\right) = -k_{obs}t \qquad (3)$$

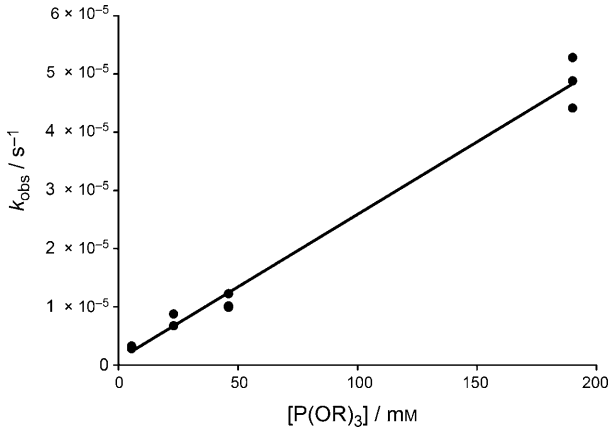
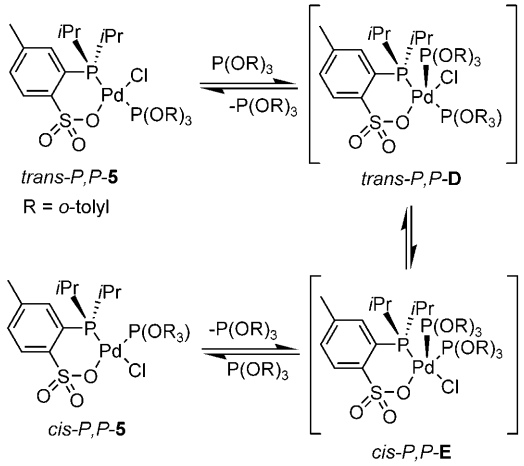


Figure 2. Plot of k_{obs} (s^{-1}) for approach to equilibrium of *cis*/*trans*-*P*,*P*-**5** versus [P(O-*o*-tolyl)$_3$] from three separate experiments. For [P(O-*o*-tolyl)$_3$] = 5.6, 23, and 46 mM, the data points for the separate experiments overlap.

(Figure 2). These data establish that *trans*-*P*,*P*-**5**/*cis*-*P*,*P*-**5** isomerization is first-order in palladium and P(O-*o*-tolyl)$_3$.

The equilibration of the 1:9 *cis*-*P*,*P*/*trans*-*P*,*P*-**5** mixture in the presence of P(O-*o*-tolyl)$_3$ (46 mM) is only slightly faster in [D$_6$]acetone ($k_{obs} = 1.4(1) \times 10^{-5}\ s^{-1}$) than in CD_2Cl_2 ($k_{obs} = 1.1(1) \times 10^{-5}\ s^{-1}$), thus suggesting that ionization of the Pd–Cl bond does not play a role in the isomerization of **5**.

A plausible mechanism for P(O-*o*-tolyl)$_3$-catalyzed *cis*-*P*,*P*-/*trans*-*P*,*P*-**5** isomerization is shown in Scheme 3. P(O-*o*-tolyl)$_3$ reacts with *trans*-*P*,*P*-**5** to generate the five-coordinate



Scheme 3. Proposed mechanism for the P(O-*o*-tolyl)$_3$-catalyzed isomerization of **5**.

intermediate *trans*-*P*,*P*-**D**. This intermediate isomerizes by Berry pseudorotation to *cis*-*P*,*P*-**E** and then dissociates P(O-*o*-tolyl)$_3$ to form *cis*-*P*,*P*-**5**. A complete mechanism with trigonal-bipyramidal intermediates is shown in the Supporting Information.

These studies establish that the *cis*/*trans* isomerization of inorganic {PO}Pd complexes proceeds through five-coordinate intermediates and not by a unimolecular mechanism.[9] Similar process may be important for [{PO}Pd(R)(ethylene)] catalysts in the presence of excess monomer. However, the presence of an alkyl ligand may open up isomerization pathways that are not available to the inorganic systems studied here.[10]

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[7] The lower limit to k_{exch} detectable by EXSY is $1/T_1$, where k_{exch} is the first order rate constant for exchange and T_1 is the relaxation time of the proton used for the determination of k_{exch}. The T_1 value of the *ortho*-pyridine hydrogen in **3** at 20 °C is 3.2 s, so $k_{exch} < 0.31\ s^{-1}$. See: C. L. Perrin, T. J. Dwyer, *Chem. Rev.* **1990**, *90*, 935.
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