Supporting Information for:

Olefin Insertion Reactivity of a (Phosphine-arenesulfonate)Palladium(II) Fluoride Complex

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I. Additional Experimental Details

Isomerization of 2 in Solution. A Teflon NMR tube liner was charged with **2** (19.1 mg, 0.036 mmol, 44:56 *cis-P,F:trans-P,F*) and CD₂Cl₂ (0.25 mL). The sample was maintained at room temperature and monitored by ¹H, ³¹P, and ¹⁹F NMR (Figures S5, 6, 7). The concentrations of *cis-P,F-***2** and *trans-P,F-***2** were obtained by comparison to an internal standard. Equilibrium was reached within 2.5 days.

Reaction of cis-P,F/trans-P,F-(PO-OMe)PdF(lut) (2) with [NBu4]Br to produce (PO-

OMe)PdBr(lut) (1). A Teflon NMR tube liner was charged with *cis/trans-P,F-***2** (8.9 mg, 0.014 mmol, 32:68 *cis-P,F:trans-P,F*), [NBu₄]Br (4.4 mg, 0.014 mmol), and CD₂Cl₂ (0.3 mL). The sample was tracked by ¹H, ³¹P{¹H}, and ¹⁹F{¹H} NMR (Figure S8). Quantitative conversion to (PO)PdBr(lut) **1** was complete by 24 h.

Reaction of 2 with vinyl bromide. A Teflon NMR tube liner was charged with **2** (6 mg, 0.008 mmol, 70:30 *cis-P,F:trans-P,F*) and CD₂Cl₂ (0.25 mL). VBr (80 μ L, 0.08 mmol, 1 M in THF) was added via microsyringe and the Teflon liner was sealed in an NMR tube. The tube was heated at 50 °C and monitored periodically by NMR. After 13 h at 50 °C, the sample contained **1** (73% by ³¹P NMR), **3** (11%), an unidentified compound (9%, ³¹P: δ 16), and *cis-P,F-***2** (7%).

Reaction of 2 with vinyl benzoate to produce 6. A Teflon NMR tube liner was charged with *cis/trans-P,F-*2 (17 mg, 0.026 mmol, 36:64 *cis-P,F:trans-P,F*) and CD₂Cl₂ (0.25 mL). VOBz (7.2 μ L, 0.052 mmol) was added via microsyringe and the Teflon liner was sealed in an NMR tube. The tube was heated at 60 °C. After 3 h, the ³¹P{¹H} NMR spectrum showed the presence of (PO)Pd{CH₂CHF(OBz)}(lut) (41%), 6 (6%), *trans-P,F-*2 (38%), and unidentified species. After an additional 22 h, the ³¹P{¹H} NMR spectrum contained only resonances for 6 (80%) and an unknown species (δ 0.1, 20%, likely a decomposition product of **6**). Figure S14 shows NMR monitoring of this reaction.

II. NMR Spectra of New Compounds





Figure S1. NMR spectra of 1 (CD₂Cl₂). • acetone impurity



(d) ${}^{13}C{}^{1}H$ NMR expansion from δ 110–165 (500 MHz)





(e) ${}^{31}P{}^{1}H$ NMR (202 MHz)



(f) ¹H-¹H COSY NMR (500 MHz)



(g) ¹H-¹H COSY expansion (500 MHz)



(h) 1 H- 13 C HMQC NMR (500 MHz)



(i) ¹H-¹³C HMQC expansion (500 MHz)



⁽j) ¹H-¹³C HMBC NMR (500 MHz)



(k) ¹H-¹³C HMBC expansion (500 MHz)



(l) ¹H-¹³C HMBC expansion (500 MHz)



Figure S2. NMR spectra of 2 (42:58 *cis-P*,*F*:*trans-P*,*F mixture*, CD₂Cl₂, with added CsF).







showing more resolved signals (CD₂Cl₂, no CsF added).



Figure S4. NMR spectra, including expansions, of **2** (40:60 *cis-P*,*F*:*trans-P*,*F*) before (bottom) and after (top) addition of CsF (CD₂Cl₂, 25 °C).



Figure S5. Time dependence of the concentrations of *cis-P*,*F*-**2** (red) and *trans-P*,*F*-**2** (blue) in CD_2Cl_2 at room temperature.



Figure S6. Stacked ¹H NMR spectra showing isomerization of *cis-P,F-***2** and *trans-P,F-***2** in CD_2Cl_2 at room temperature. •H grease



Figure S7. ¹H NMR of equilibrium mixture of *cis-P,F-*2 and *trans-P,F-*2 in CD₂Cl₂; •H grease.



Figure S8. NMR monitoring of the reaction of **2** (32:68 *cis-P,F:trans-P,F* mixture) and [NBu₄]Br (CD₂Cl₂, 25 °C) to produce **1**. Reaction assay at (a) 30 min, (b) 24 h, and (c) an authentic sample of **1** for comparison. For full assignments of the $-OCH_3/-CH_3$ (H¹⁶, H¹⁷, and H¹⁸) of **2**, see the main text. *Cis-P,F-***2** and *trans-P,F-***2** are denoted by *c***2** and *t***2** in the figure.



Figure S9. NMR monitoring of the reaction of 2 and vinyl fluoride (CD₂Cl₂, sealed tube).



(c) ¹H NMR showing the peaks corresponding to PdC H_2 C HF_2 (500 MHz). VF: dq at δ 4.82.



(d) ${}^{31}P{}^{1}H$ NMR (202 MHz)



(e) ¹⁹F NMR (470 MHz) from δ -450 – -230. • Unassigned impurity.



(f) 19 F NMR (470 MHz). The VF signal appears at δ –117.



Figure S10. Time dependence of the concentrations of *cis-P,C-2* (red), *trans-P,C-2* (blue), and 3 (black) during the reaction of 2 and VF in CD_2Cl_2 at room temperature. The concentrations were determined by integration of the ¹H NMR OMe resonances.



(b) ¹H NMR spectrum expansion from δ 6.4–8.6 (500 MHz)

Figure S11. NMR spectra of 3 (>90% from the reaction between 2 and VF, CD_2Cl_2).



(d) ¹H NMR spectrum expansion showing PdC H_2 C HF_2 resonances (500 MHz). Note the overlapping VF resonance centered at δ 4.83.



(f) ${}^{19}F{}^{1}H$ NMR (470 MHz). The insert shows the ${}^{19}F$ signal for PdCH₂CF₂H. The resonance at δ –117. Is from VF.



(g) ${}^{13}C{}^{1}H$ NMR including inserts of the PdCH₂CHF₂ J_{CF} triplets (125 MHz)



(h) ${}^{13}C{}^{1}H$ NMR spectrum expansion from δ 90–165 (125 MHz)



(i) ¹H-¹H COSY NMR (500 MHz)



(j) ¹H-¹H COSY NMR spectrum expansion (500 MHz)



(k) ¹H-¹H NOESY NMR spectrum



(l) ¹H-¹H NOESY NMR spectrum (zoom out)



(a) ¹H NMR spectrum (500 MHz). VOAc: δ 7.25, 4.85, 4.54, and 2.09; CH₃(C=O)F: δ 2.26; signals for residual *trans-P,F-2* are marked in the expansions.





(b) ¹H NMR spectrum expansion from δ 6.4–8.6 (500 MHz); •*trans-P,F-2*.



(c) ¹H NMR spectrum expansion from δ 0.0–6.2 (500 MHz); CH₃(C=O)F: δ 2.26; • *trans-P,F-2*.



(d) ¹H NMR spectrum showing PdC H_2 CHF(OAc) signals (500 MHz)



(e) ¹³C{¹H} NMR spectrum, including expansions (125 MHz). VOAc δ 2.26.168.22, 141.70, 97.53, 20.76.





(g) ${}^{19}F{}^{1}H$ } NMR spectrum (470 MHz); unassigned impurities.



(h) ¹H-¹H COSY NMR spectrum (500 MHz)



(i) ¹H-¹H COSY NMR spectrum expansion showing PdCH₂CHF(OAc) signals (500 MHz)



(a) 1 H NMR spectrum; • grease and minor unassigned species in bulk



(b) ¹H NMR spectrum expansion from δ 1.0–3.9 (500 MHz)

Figure S13. NMR spectra of 6 (CD₂Cl₂)



(c) ¹H NMR spectrum expansion from δ 6.4–8.6 (500 MHz)



(d) $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz)



(e) ${}^{13}C{}^{1}H$ NMR spectrum, including expansion of δ 105–165 region (125 MHz)



Figure S14. ³¹P{¹H} NMR monitoring of *cis:trans-P,F-***2** (36:64 *cis-P,F:trans-P,F*) and VOBz (CD₂Cl₂). The major product is **6**; • minor unassigned species.

III. X-ray Diffraction Data

	(PO-	$(PO-OMe)Pd(CH_2C(=O)H)(lut) \bullet CH_2Cl_2,$	
	OMe)PdBr(lut)•CH ₂ Cl ₂ ,	6 •1.5CH ₂ Cl ₂	
	$1 \cdot CH_2Cl_2$		
Identification code	0492_black	tw4	
Empirical formula	C ₂₉ H ₃₁ BrCl ₂ NO ₅ PPdS	C _{31.5} H ₃₅ Cl ₃ NO ₆ PPdS	
Formula weight	793.79	799.38	
Temperature (K)	100(2)	100(2)	
Crystal system	monoclinic	triclinic	
Space group	$P2_{1}/c$	P-1	
a (Å)	16.0520(9)	11.4841(6)	
b (Å)	12.0213(7)	12.3043(7)	
c (Å)	17.3935(10)	13.3303(8)	
α (°)	90	85.405(2)	
β (°)	111.076(2)	68.589(2)	
γ(°)	90	88.673(2)	
Volume (Å ³)	3131.8(3)	1747.95(17)	
Ζ	4	2	
Density (calculated)	1.004	1.519	
(Mg/m3)	1.684		
Absorption coefficient	2.100	0.908	
(mm^{-1})	2.196		
F(000)	1592.0	814.0	
Crystal size (mm ³)	$0.25 \times 0.09 \times 0.05$	$0.31 \times 0.16 \times 0.12$	
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	
Theta range for data	1 211 to 51 262	4.854 to 52.756	
collection (°)	4.544 10 54.502		
Index ranges	-20 \leq h \leq 20, -15 \leq k \leq	$-13 \le h \le 14$ $-14 \le k \le 14$ $0 \le l \le 16$	
	$14, -18 \le l \le 20$		
Reflections collected	42822	6647	
Independent reflections	$6751 [R_{int} = 0.0733,$	6647 [$R_{int} = 0.0611$, $R_{sigma} = 0.0708$]	
	$R_{sigma} = 0.0688]$		
Data / restraints /	6751/0/375	6647/0/421	
parameters	0701707070	0047/0/421	
Goodness-of-fit on F ²	1.013	1.058	
Final R indices	$R_1 = 0.0386, WR_2 =$	$R_1 = 0.0637, wR_2 = 0.1233$	
[I>2sigma(I)]	0.0724		
	$R_1 = 0.0764, WR_2 =$	$R_1 = 0.0962, wR_2 = 0.1363$	
R indices (all data)	0.0822		
Largest diff. peak and	0.99/-0.80	1 21/-0 88	
hole $(e.Å^{-3})$		1.21/ 0.00	

 Table S1. Crystal data and structure refinement for 1•CH₂Cl₂ and 6•1.5CH₂Cl₂

IV. Computational Methods.

All structures were calculated and optimized using the ORCA (v. 3.0.3) computational package.¹ Structures were optimized using the B3LYP density functional as implemented in ORCA² and included corrections for the zero order relativistic approximation for palladium (ZORA).³ Optimizations were performed using the triple zeta basis set implemented for ZORA in ORCA and included an effective core potential for Pd.^{4,5} Geometry optimizations were performed in CH₂Cl₂ using the COSMO solvent model as implemented in ORCA.⁶ Unless otherwise noted, all reaction intermediates were found to be minima by numerical frequency analysis in solvent confirming there were no negative frequencies present. All transition states were confirmed to be of the appropriate reaction coordinate by animating the single negative frequency and confirming it is chemically consistent with the reaction being studied. Transition states (TSs) were located using the quasi-newton method implemented in ORCA.⁷ Some TS structures were found by first optimizing using the BP86 functional and double zeta basis sets.^{8,9}

Since we were initially differentiating between inner sphere and outer-sphere mechanisms, VF calculations were performed including solvent corrections. Method validation and studies of the reactions of vinyl bromide were performed without solvent corrections. Notably the addition of solvent corrections did not appear to change the potential energy surfaces of the reactions studied (most changes were on the order of ~0.5 kcal/mol). Since there is disagreement within the literature about what the meaning of numerical frequency calculations in a polarizable continuum solvent model¹⁰ we rely on the solvent corrected energies calculated to analyze our reactions. Corrections for free energy calculations in the solvent model are included in the results for completeness and to confirm the structures are minima or transition states.

Method and Model Validation.

As previously found computationally by Nozaki and co-workers, linear growth of polyethylene is shown to be favored to proceed through insertion of ethylene into the *trans-P-C* isomer of (PH₂O)PdR(CH₂=CH₂), where the Pd-*R* group is *trans* to the phosphine. Insertion of ethylene by the *trans-O-C* isomer has been shown to either be endergonic or only modestly exergonic (see ref 21b,c in text). Nozaki and co-workers have shown that the transition states for *trans-P-C* pathways are lower in energy by 7-10 kcal/mol. Therefore, these computations imply that insertion of ethylene into the *trans-P-C* isomer is favored. Figure S15 summarizes our calculations using the simple model discussed in the main text. Our results qualitatively agree with the work of Nozaki. The calculated ground state free energies for ethylene insertion and propagation pathways for the two isomers, *trans P-C* and *trans-O-C*) are clearly differentiated by DFT (insertion into *trans-P-C* is favored by 18 kcal/mol). These results are well outside the error of the methods used¹¹ and are in agreement with other previous studies.^{12,13}

Finally, Nozaki and coworkers performed an expansive survey of the influence of ligand steric bulk on the barriers to ethylene insertion and propagation.¹⁴ Nozaki's work demonstrated that although there were some variations in transition state energies (1-5 kcal mol) using different P-R substituent groups, the energetically preferred pathway did not change with variation in the size and identity of the phosphine substituents, Additionally, the overall magnitudes of the transition states were not impacted by the identity of the phosphine substituents. The qualitative results of previous studies clearly demonstrate the lack of importance of the size of the phosphine ligand substituents on the initial steps in ethylene insertion and polymer chain propagation. Since our results are in good qualitative agreement with previous studies, we conclude that the relative bond energies of the insertion reaction are

more important than the steric environment of the reaction; therefore, our simple ligand model is adequate for evaluating the possible and feasible mechanisms for alkene insertion.



Figure S15. Free energy scheme for the insertion of ethylene into Pd-alkyl bonds of (PH₂O)PdMe species.

Insertion of ethylene into the Pd-F bond

Figure S16 shows the free energy surfaces for the insertion of ethylene into the Pd-F bond of the *cis-P,F* and *trans-P,F* isomers of $(PH_2O)PdF(CH_2=CH_2)$. The *trans-P-F* isomer was found to be 4 kcal/mol higher in energy than the *cis-P-F* isomer. Re-arrangement or exchange of these isomers can be achieved either by intramolecular-5-coordinate rearrangement, as proposed by Nozaki, or by associative 5-coordinate rearrangement with solvent. Intramolecular rearrangement is expected to be high in energy analogous to the results for VF (See main text). Insertion of ethylene into the Pd–F bond of the *trans-P-F* isomer is modestly endergonic (2 kcal/mol) and has a reasonably accessible free energy barrier of 14 kcal/mol. In contrast, insertion of ethylene into the Pd–F bond of the *cis-P-F* isomer is highly endergonic (+21 kcal/mol). The free energy barrier for this insertion is 24 kcal/mol, making the barrier for the back reaction (β -F elimination) a mere 3 kcal/mol. The large difference in free energy barriers to insertion combined with the drastically different energetics of the reaction clearly show insertion into the *trans-P-F* isomer to be preferred upon formation of the ethylene adduct. However, formation of the ethylene adduct may be rate limiting as is proposed for reactions with VF.



Figure S16. Free energy surface for the insertion of ethylene into the Pd–F bonds of the stereoisomers of (PH₂O)PdF. Dotted lines show estimated reaction barriers based on other calculations.

Details of VF insertion into Pd-F bonds.

Below is the full potential energy surface for the insertion of VF into the Pd-F bonds of the stereoisomers of (PH₂O)PdF (Figure S17). This diagram includes the post-insertion rearrangement of products and all *cis/trans* isomerization pathways. All values are reported in kcal/mol and the values in parentheses are for the calculated free energies in a polarizable continuum solvent model. These values are the subject of significant debate in the literature¹⁰ and are provided for completeness only. Schemes S1 and S2 provide an alternate method of interpreting these results showing each intermediate structure and transition state and their energies relative to the reference complex (PH₂O)PdF(py).



Figure S17. Complete potential energy surface of the reaction of VF with (PH_2O)PdF including solvent corrections. The orange path shows possible inner-sphere insertion mechanisms and the blue path shows exo attack mechanisms. The yellow path shows the possible *cis/trans* isomerization of (PH_2O)PdF(VF) complexes and the gray path shows the *cis/trans* isomerization of (PH_2O)PdF(VF) complexes. Dotted lines show estimated transition state energies for associative displacement of fluoride by VF. Several rotamers can be found for structure **C1**. The rotamer chosen has a structure closest to that of the lutidine complex characterized by X-ray crystallography.



Scheme S1. Reaction profile of *cis-P-F-*(PH₂O)Pd(F)(py) with vinyl fluoride

Scheme S2. Reaction profile of trans-P-F-(PH₂O)Pd(F)(py) with vinyl fluoride



V. Mass Spectra of New Compounds



(a) Full HRMS Spectrum



(b) Expansion of HRMS to show $C_{28}H_{30}BrNO_5PPdS^+ [M+H]^+$

Figure S18. Mass spectrum of 1.



(c) Calculated Mass Spectrum for $C_{28}H_{30}BrNO_5PPdS^+ [M+H]^+$

Figure S18, cont. Mass spectrum of 1.



(a) Full HRMS Spectrum

Figure S19. Mass spectrum of 2.



(b) Expansion of HRMS to show $C_{28}H_{29}NO_5PPdS^+$ [M-F]⁺



(c) Calculated Mass Spectrum for $C_{28}H_{29}NO_5PPdS^+$ $[M-F]^+$

Figure S19, cont. Mass spectrum of 2.



(a) Full HRMS Spectrum



(b) Expansion of HRMS to show $C_{53}H_{56}F_4NO_{10}P_2Pd_2S_2^+$ [2M–lutidine+H]⁺

Figure S20. Mass spectrum of 3.



(c) Calculated Mass Spectrum for $C_{53}H_{56}F_4NO_{10}P_2Pd_2S_2^+$ [2M–lutidine+H]⁺

Figure S20, cont. Mass spectrum of 3.



(a) Full HRMS Spectrum

Figure S21. Mass spectrum of 6.



(b) Expansion of HRMS to show $C_{30}H_{33}NO_6PPdS^+ [M+H]^+$. The signal centered at m/z = 666 overlaps with the $[M+H]^+$ signal.



(c) Calculated Mass Spectrum for $C_{30}H_{33}NO_6PPdS^+ [M+H]^+$

Figure S21, cont. Mass spectrum of 6.

V. References

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