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Pyridine-Assisted Chlorinations and Oxidations by Palladium(IV)

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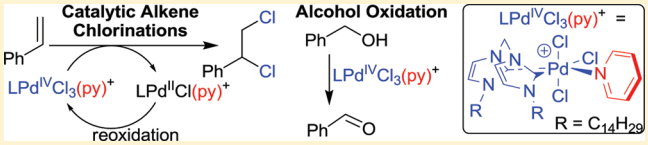
Supporting Information

ABSTRACT: The reactivity of the bis-NHC complex $LPd^{IV}Cl_4$ (L = κ^2-[R-NHCCH$_2$NHC-R] with R = $C_{14}H_{29}$) in chlorinations and oxidations of organic substrates was considerably increased in the presence of pyridine. For alkene chlorinations, this effect was due to the in situ formation of highly reactive $LPd^{IV}Cl_3(py)^+$, which was able to transfer Cl^+ to the C=C bond in a ligand-mediated process (devoid of π complexation), which did not require py dissociation. The enhanced reactivity in the presence of pyridine also extended to the oxidation of secondary and benzylic alcohols under mild conditions in a reaction where py served as a base, broadening the known scope of reactivity for Pd^{IV} complexes. $LPd^{IV}Cl_3(py)^+$ could be formed from Cl^-/py exchange or from the oxidation of $LPd^{II}Cl(py)^+$ by Cl_2. Taking advantage of the enhanced reactivities that pyridine coordination imparted on both Pd^{II} and Pd^{IV} complexes allowed for the catalytic chlorination of styrene with $LPd^{IV}Cl_4$ as a sacrificial oxidant, thereby establishing the principal feasibility of Pd^{II}/Pd^{IV} catalyses that obviates Pd^{II} activations of the substrate.



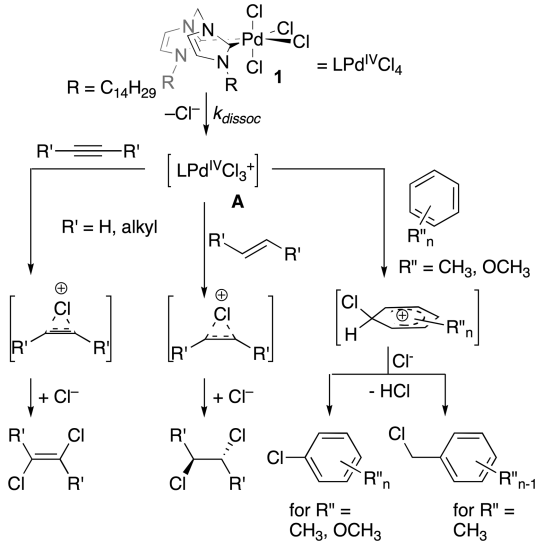
INTRODUCTION

Over the past 10 years the realm of palladium catalysis has been greatly expanded through the introduction of Pd^{II}/Pd^{IV} cycles in oxidative functionalizations of C−H and C=C bonds.[1] Despite some impressive advances, shortcomings in this field include (a) substrate activations by Pd^{II} that are sluggish and often require Lewis basic handles on the substrate to help overcome low intermolecular reactivity through chelation effects[1d,e,2−5] and (b) a narrowly defined role of Pd^{IV} intermediates that merely serve as a vehicle for reductive eliminations. A conceivably rich high-oxidation-state palladium chemistry that bypasses Pd^{II} activations and instead relies on sole interactions between organic substrates and Pd^{IV} is only in its infancy;[6] reports on intermolecular, non-chelation-controlled C−H bond activations by Pd^{IV} are sparse,[7] and interactions between alkenes and Pd^{IV} have not been studied before. Additionally, there have been no prior studies on oxidations of alcohols by Pd^{IV} complexes in any context. With these substrates in mind, a successful catalytic cycle would require that two key steps be established: (I) $Pd^{II} \rightarrow Pd^{IV}$ oxidation that does not affect the substrates present and (II) Pd^{IV}-mediated substrate functionalization with concomitant regeneration of Pd^{II}.

Previously, we have documented that isolated $LPd^{IV}Cl_4$ (**1**; L = R-NHCCH$_2$NHC-R, R = $C_{14}H_{29}$) is capable of dichlorinating alkenes and alkynes as well as monochlorinating arenes on aromatic and benzylic C−H bonds (Scheme 1),[8] thus conforming to the requirements of step II. Mechanistic studies on that system supported a stepwise ionic mechanism with the initial formation of cation $LPd^{IV}Cl_3^+$ (**A**) in the slow step; the latter subsequently transferred Cl^+ to the substrates in a ligand-mediated process devoid of π coordination.

In here we will explore avenues that allow for catalytic chlorinations of organic substrates by Pd^{IV} complexes. This includes the use of novel $LPd^{IV}Cl_3(py)^+X^-$ structures **2a** (X^- = Cl^-) and **2b** (X^- = TfO^-), which have reactivities significantly higher than that of **1**. We will also expound on the surprisingly expeditious formation of **2a,b** by way of Pd^{II}/Pd^{IV} oxidation. Furthermore, a facile Pd^{II}-catalyzed interconversion of **1** and pyridine into **2a** will be elucidated. Using these three effects in concert, we will demonstrate the principal feasibility of a Pd^{II}/Pd^{IV} catalysis that circumvents substrate activations by Pd^{II} altogether. In addition, we will expand the scope of Pd^{IV} chemistry into the arena of previously unexplored alcohol oxidations.

Scheme 1



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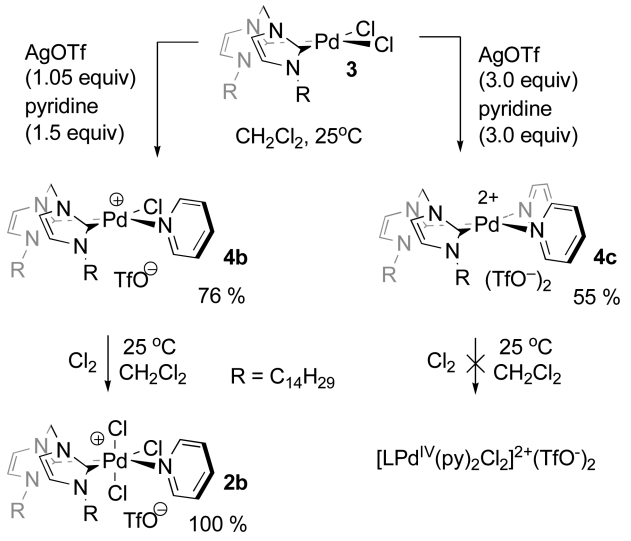
RESULTS AND DISCUSSION

Synthesis of LPd^{IV}Cl$_3$(py)$^+$TfO$^-$. Efforts to cleanly generate an isolable LPd^{IV}Cl$_3$(py)$^+$ salt were commenced by reacting tetrachloride **1** with AgOTf; the desired complex LPd^{IV}Cl$_3$(py)$^+$TfO$^-$ (**2b**) was produced; however, it was obtained only in 80% purity and the crude material could not be further refined. In contrast, we were more successful with a two-step procedure (Scheme 2). Cl$^-$/py substitution was

Scheme 2. Synthesis of 2b



accomplished from Pd^{II} complex **3** and a tightly controlled amount of AgOTf (1.05 equiv), which afforded LPd^{II}Cl(py)$^+$TfO$^-$ (**4b**) in ≥98% purity by ^{1}H NMR spectroscopy; a larger excess of silver triflate and pyridine gave rise to the formation of LPd^{II}(py)$_2^{2+}$(TfO$^-$)$_2$ (**4c**). Treatment of a CH_2Cl_2 solution of **4b** with a stream of Cl_2 gas quantitatively produced an orange-yellow solution of LPd^{IV}Cl$_3$(py)$^+$TfO$^-$ (**2b**), which was isolated in 97% purity by removing the solvent with a stream of N_2. In contrast, chlorination of dipyridine complex **4c** produced a complex product mixture with **2b** as the main component, while [LPd^{IV}(py)$_2$Cl$_2$]$^{2+}$(TfO$^-$)$_2$ could not be unequivocally identified.

NMR Chemical Shift Analysis of NHC Complexes. One- and two-dimensional ^{1}H NMR of the octahedral complex **2b** unveiled a κ^2(C,C),N-*mer* configuration with the py ligand *trans* to a carbene carbon, while no other geometric isomers were present. A ROESY experiment established a correlation between the side-chain protons H$^\alpha$/H$^\beta$ and pyridine protons H^o and H^m, while H$^{\alpha\prime}$/H$^{\beta\prime}$ did not show any cross peaks (Figure 1). Thus, starting from H$^\alpha$/H$^\beta$ a contiguous chain of vicinal

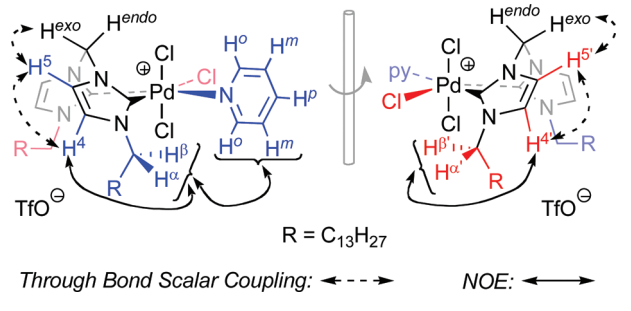
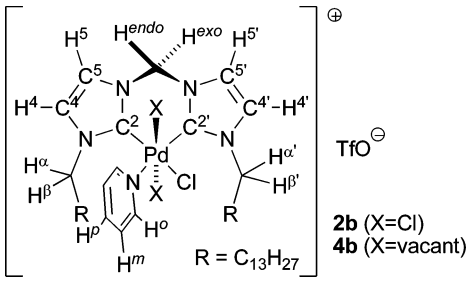


Figure 1. ROESY correlations in **2b**.

relationships across the ligand backbone was established for H^4, H^5, H^{exo}, H$^{5\prime}$, H$^{4\prime}$ all across to H$^{\alpha\prime}$/H$^{\beta\prime}$. No NOEs were observed between H^4/H$^{4\prime}$ and H^{endo}, consistent with a boat conformation.

A comparison of one-dimensional ^{1}H NMR spectra of LPd^{II}Cl$_2$ (**3**) and LPd^{II}Cl(py)$^+$TfO$^-$ (**4b**) shows downfield shifts $\Delta\delta^{3,4b}$ for all NHC aromatic protons and bridge hydrogens in the range of 0.08−0.18 ppm (Table 1), consistent with a reduction of

Table 1



proton	δ(**3**)[a]	δ(**4b**)	δ(**2b**)	$\Delta\delta^{3,4b,c}$	$\Delta\delta^{2b,4b,d}$
H^4	6.83	6.98	7.37	+0.10	+0.39
H^5	7.61	7.80	8.15	+0.19	+0.35
H$^{4\prime}$	6.83[b]	6.94	7.29	+0.11	+0.35
H$^{5\prime}$	7.61[b]	7.69	8.04	+0.08	+0.35
H^{endo}	6.22	6.37	7.12	+0.15	+0.75
H^{exo}	6.56	6.74	7.25	+0.18	+0.51
H$^\alpha$/H$^\beta$	4.87, 4.09	3.46, 3.18	3.45, 3.17	−1.14[e]	−0.01[e]
H$^{\alpha\prime}$/H$^{\beta\prime}$	4.87, 4.09[b]	4.83, 4.21	4.95, 4.71	+0.04[f]	+0.31[f]
H^o		8.71	9.22		+0.51
H^m		7.47	7.68		+0.21
H^p		7.92	8.10		+0.18

[a]Chemical shifts are reported for a $CDCl_3$ solution that contains **4b** (0.1 M) in order to account for salt effects on **3** (when its chemical shifts are compared to those of **4b**). [b]In compound **3** chemical shifts δ(H$^{4\prime}$), δ(H$^{5\prime}$), and H$^{\alpha\prime}$/H$^{\beta\prime}$ are equivalent by symmetry with chemical shifts δ(H^4), δ(H^5), and H$^\alpha$/H$^\beta$. [c]$\Delta\delta^{3,4b} = \delta$(**4b**) − δ(**3**). [d]$\Delta\delta^{2b,4b} = \delta$(**2b**) − δ(**4b**). [e]Difference $\Delta\delta$ of averaged values of H$^\alpha$/H$^\beta$. [f]Difference $\Delta\delta$ of average values of H$^{\alpha\prime}$/H$^{\beta\prime}$.

electron density on the NHC ligands in the LPd^{II}Cl(py)$^+$ cation. Pyridine resonances for H^o, H^m, and H^p were in the typical range for a cationic Pd^{II}-py complex.[9] Whereas "remote" side-chain protons H$^{\alpha\prime}$/H$^{\beta\prime}$ also experienced a 0.04 ppm downfield shift in **4b**, the signals for H$^\alpha$/H$^\beta$ were shifted upfield by −1.14 ppm caused by the diatropic ring current of the nearby py ligand.[10] By further decreasing the electron density on palladium in **4c**, resonances for H^{exo} and H^{endo} were shifted downfield by 0.81 and 0.64 ppm relative to those for **4b**.

Equally, effects from reduced NHC electron density were manifested in the ^{13}C NMR spectrum of **4b**, which features small average downfield shifts for the remote aromatic carbons C^4, C$^{4\prime}$, C^5, and C$^{5\prime}$ together with an *upfield* shift on C$^{2\prime}$ relative to those for **3** (Table 2).[11] Huynh and co-workers have correlated such upfield shifts for carbene carbons in NHC-Pd^{II} complexes with a reduction of donor strengths of ligands *trans* to the NHC moiety, thus causing a decrease of electron density on the carbene.[12,13] A side by side comparison of **3** and Herrmann's bis-NHC complex LPd^{II}(N≡CCH$_3$)$_2^{2+}$(BF$_4^-$)$_2$ (L = CH$_3$−NHC−CH$_2$−NHC−CH$_3$)[14] further underscores these trends with a −9.77 ppm upfield shift for C^2 and 2.3 ppm (averaged) downfield shifts for C^4 and C^5 on the electron-deficient dication.

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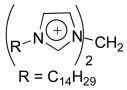
Table 2

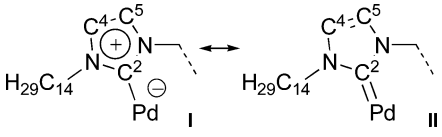
Entry	Compound	δ ^{13}C NMR nucleus: δ C^2 ($C^{2'}$)	δ C^4, δ C^5 ($C^{4'}$, $C^{5'}$)
1	$LPd^{IV}Cl_4$ (**1**) [a]	139.10	123.74, 122.83 average = 123.29
2	$LPd^{IV}Cl_3(py)^+$ TfO^- (**2b**)	139.48, 129.87	125.27, 125.10, 124.16, 123.62 average = 124.54
3	($LPd^{II}Cl_2$) (**3**)	156.17	122.25, 120.60 average = 121.43
4	$LPd^{II}Cl(py)^+$ TfO^- (**4b**)	156.66, 152.76	122.97, 122.59, 121.79, 121.51 average = 122.22
5	$[LPd^{II}(py)_2]^{2+}$ $(TfO^-)_2$ (**4c**)	154.07	122.91, 121.09 average = 122.00
6	 R = $C_{14}H_{29}$ (**5**) [a]	137.94	124.29, 122.15 average = 123.22

[a]From ref 8.

The oxidation of **4b** to **2b** caused 0.35−0.75 ppm downfield shifts for NHC backbone, bridge, and side-chain protons (Table 2). Downfield shifts (0.18−0.51 ppm) were also seen for H^o, H^m, and H^p, as expected for a Pd^{IV} pyridine complex.[15,16] A comparison of ^{13}C NMR chemical shifts (Table 2) for **1** and **2b** (entries 1 and 2) and for **3** and **4b** (entries 3 and 4) revealed Pd^{IV} upfield shifts for C^2 and $C^{2'}$ in the range of −17 to −23 ppm relative to the respective Pd^{II} complex. At the same time, small downfield shifts (1.9−2.3 ppm) were observed for the remote ring carbons C^4, C^5, $C^{4'}$, and $C^{5'}$ in **1** and **2b** in comparison to **3** and **4b**. This reinforces the idea that the pattern of significant upfield shifts on carbene carbons paired with small downfield shifts on "remote" aromatic carbons expresses the degree of electron deficiency on NHC ligands. Notably, these ^{13}C NMR chemical shift tendencies followed trends reported in imidazolium cations, with upfield shifts on C^2 and downfield shifts on $C^{4,5}$ in the presence of electron-withdrawing groups on C^2.[17,18] In fact, ^{13}C NMR chemical shifts of C^2 in both **1** and **2b** were very similar to those in the free imidazolium salt **5**; the signal for $C^{2'}$ in the NHC ring in **2b** *trans* to pyridine was shifted even further upfield from **5** (by −8.07 ppm), underscoring the electron-deficient character of the $Pd^{IV}Cl_3(py)^+$ moiety.

On the basis of these trends, we suggest that that the NHC portion in LPd^{IV} complexes **1** and **2b** is best described with resonance structure I (Scheme 3), while Pd^{II} structures **3** and

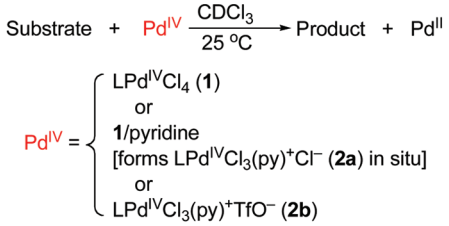
Scheme 3

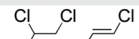
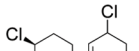
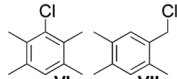


4b may be described with partial contributions from resonance structure II as well ("back bonding").[19] The absence of an organometallic double-bond character in Pd^{IV} complexes is consistent with the previously observed bond lengthening of C^2−$Pd^{II/IV}$ by 0.047 Å in **1** relative to **3**.[8] Of note are existing literature accounts on M^{II}/M^{IV} oxidations (M = Pd, Pt) of isolable NHC complexes that also report significant oxidation-induced upfield shifts on carbene carbons.[20−22]

Alkene Chlorinations with Pd^{IV} and Mechanistic Investigations. The reaction of olefin with Pd^{IV} chloride complexes produced alkene chlorination products at 25 °C (Table 3). We found that the yield in the reaction between **1** and styrene (87.4% after 2 h, entry 1) was improved to 93.2% at a dramatically reduced reaction time (4 min) when 10 equiv

Table 3. Chlorinations and Oxidations by 1 and 2a,b



Entry	Pd^{IV}	Substrate [c]	Product	% Yield (% Conversion)
1	**1** [a,c] (2 h)		 IV V	87.4 % (87.5 %) (**IV**:**V** = 2.2:1)
2	**1**/py [b] (4 min)		**IV** + **V**	93.2 % (100 %) (**IV**:**V** = 1.3:1)
3	**2b**		**IV** + **V**	90.5 % (93.1 %) (**IV**:**V** = 5.6:1)
4	**2b** +10 equiv py		**IV** + **V**	97.8 % (100 %) (**IV**:**V** = 1.1:1)
5	**1** [a,c]		 I	88.8% (96.4%)
6	**2b**		**I**	92.4 % (100 %)
7	**1** [a,c]		 II III	87.0 % (87.0 %) (**II**:**III** = 4.3:1)
8	**2b**		**II** + **III**	91.9 % (100 %) (**II**:**III** = 3.1:1)
9	**1** [a,c]		 VI VII	54.5 % (54.9 %) (**VI**:**VII** = 3.5:1)
10	**1** [c]		 VIII	62.2% (67.4%)
11	**1** [d]	$PhCH_2OH$	PhCHO (**IX**)	
	a (12 h)			2.0 % (3.5 %)
	b (72 h)			8.6 % (10.5 %)
	c (60 °C, 2 h)			9.7 % (17.3 %)
12	**1**/lutidine [d]	$PhCH_2OH$	**IX**	
	a (3 h)			4.8 % (5.2 %)
	b (24 h)			19.8 % (20.6 %)
13	**1**/py [b]	$PhCH_2OH$	**IX**	
	a (12 h)			7.2 % (8.1 %)
	b (60 °C, 2 h)			59.9 % (76.9 %)
14	**1** [c] (24 h)		 X	4.9 % (39.1 %)
15	**1**/py [b]		**X**	
	a (24 h)			53.6 % (54.2 %)
	b (42 h)			66.0 % (72.8 %)
16	**1** [b]	*n*-BuOH	*n*-PrCHO	
	a (12 h)			–
	b (60 °C, 2 h)			–

[a]From ref 8. [b]Formed in situ from **1** and py. [c][substrate] = 10−20 mM, 1.05 equiv of Pd^{IV} reagent. [e]Added Bu_4NCl (5 equiv). [d]Added Bu_4NBF_4 (5 equiv).

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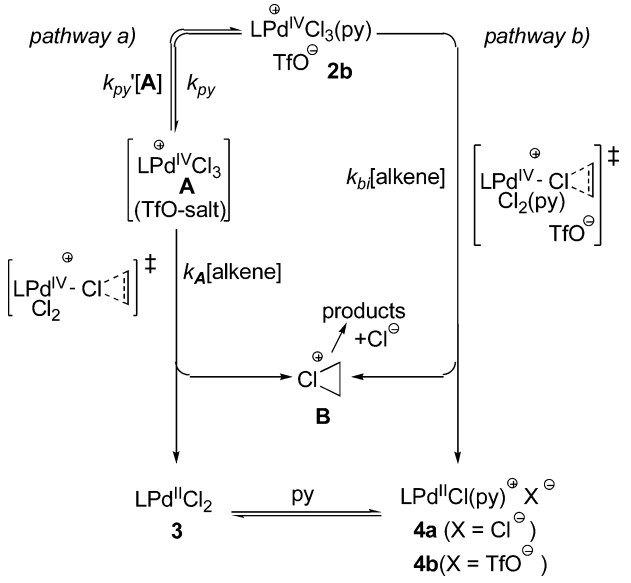
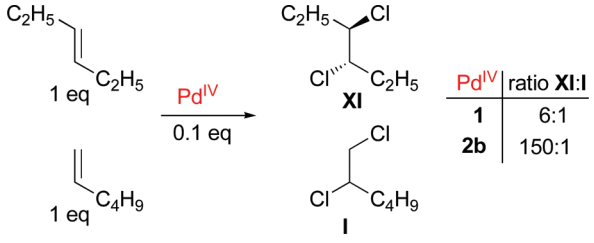
pyridine was added (entry 2). In situ ^{1}H NMR monitoring of the reaction (vide infra) revealed the presence of $LPd^{IV}Cl_3(py)^+Cl^-$ (**2a**). Furthermore, the isolated triflate analogue $LPd^{IV}Cl_3(py)^+TfO^-$ (**2b**) also produced higher yields and conversions than did **1** (entries 3, 4, 6, and 8). Cyclohexene produced a 3.1:1 mixture of 1,2-dichlorocyclohexane (**II**, *trans* only) and 3-chlorocyclohexene (**III**) (entry 8) following the second-order rate law $d[\mathbf{2b}]/dt = -k_2[\mathbf{2b}][cy]$ (k_2 = (7.1 ± 0.1) × 10^{-3} $M^{-1}s^{-1}$). Analogously, the reaction of **2b** and styrene produced a bimolecular rate constant of 3.35 × 10^{-3} M^{-1} s^{-1}. In combination, the exclusive *trans* geometry in **II**, the particular 3.1:1 ratio of **II** to **III** in entry 8, and the absence of 4-chlorocyclohexene in the reaction mixture were indicative of an ionic mechanism[23] that proceeds via the formation of an organic cyclic chloronium species of type **B** in the stereo-determining step (Scheme 4). The steric and electronic

Scheme 4. Mechanistic Considerations for Cl^+ Transfer from 2b



demands on the olefin during this stepwise chlorination were interrogated by a competition experiment involving a mixture of 1-hexene and *trans*-3-hexene being subjected to a substoichiometric amount of **2b** (Scheme 5). We found that

Scheme 5. Chlorination Competition Experiment Probing the Bias of 1 and 2b toward *trans*-3-Hexene/1-Hexene Mixtures

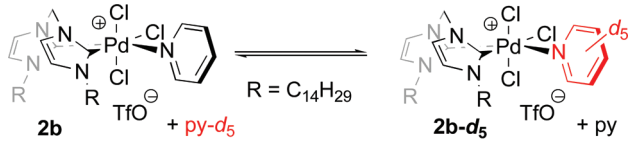


Pd^{IV}	ratio **XI**:**I**
1	6:1
2b	150:1

the preferred chlorination took place at the internal alkene over the terminal alkene with a bias of 150:1. The preference for the electron rich, yet sterically more encumbered *trans*-3-hexene is indicative of a ligand-mediated, "S_N2-type" transition state (with the C═C bond acting as a nucleophile) that does not involve the intermediacy of $LPd^{IV}Cl_3(\eta^2$-alkene)$^+$ π complexes.[24] The analogous 1-hexene/*trans*-3-hexene competition experiment in the presence of complex **1** (acting as a precursor for the active chlorinator **A**) was also biased toward the internal alkene; however, to a significantly lesser extent (6:1 ratio). We conclude from this divergence in chemoselectivity that the two species **2b** and **A** react with alkenes in similar but not identical transition states. In other words, pathway a does not pertain to the reactivity of **2b**. The fact that the addition of 10 equiv of pyridine did not slow down the reaction between **2b** and styrene (and even caused a rate acceleration; vide infra) further discredits the possibility of a pre-equilibrium between **2b** and **A** in pathway a (in which case one would expect the proportionality $k_2 \propto 1/[py]$).[25] At this point, we gravitate toward pathway b with a direct Cl^+ transfer from hexacoordinated complex **2b**[26] and conclude that alkene chlorinations by LPd^{IV} chlorides are responsive to the presence of positively charged metal centers rather than to the presence of pentacoordinated ligand environments.

Despite the irrelevance of pyridine dissociation in alkene chlorinations, complex **2b** underwent a facile py/py-d_5 exchange on a time scale of seconds when 10 equiv of py-d_5 was added (Scheme 6). Since small amounts of the reduced species

Scheme 6



K_{eq}(**2b**,**2b-d_5**) = 1.05 (in $CDCl_3$)
equilibrium established within seconds

$LPd^{II}(py)Cl^+$ were observed after py-d_5 addition, the ligand substitution is likely a Pd^{II}-catalyzed process analogous to the Cl^-/py exchange in $LPd^{IV}Cl_4$ (vide infra).[27] An intriguing facet of the equilibrium in Scheme 6 is the absence of potential *fac* isomers of **2b-d_5** even after a period of 1 h of continued ligand exchange. As pentacoordinated (and presumably fluxional)[28] species are likely intermediates in this process,[29] we are inclined toward a thermodynamic explanation for the exclusive formation of the *mer* isomer. Such a bias may be driven by steric effects, due to clashes of py with the bridge hydrogen H^{endo} or alternatively with side-chain methylene groups CH^{α}/H^{β} and $CH^{\alpha'}/H^{\beta'}$ if pyridine were forced to adopt an axial substitution. On the other hand, a possible stereoelectronic cause of the equatorial py substitution may be rooted in Pearson's antisymbiosis principle[30] with a harder nitrogen ligand *trans* to a soft carbene ligand as opposed to being aligned *trans* to a chloride ligand in a *fac* isomer. Recently, Ritter has reported an octahedral Pd^{IV} complex in which py ligands would also align themselves *trans* to a (soft) carbon ligand rather than *trans* to nitrogen.[15]

Alcohol Oxidations with Pd^{IV}. Various alcohols were mixed with $LPd^{IV}Cl_4$ (1.05 equiv) in $CDCl_3$, and reactions were followed by ^{1}H NMR spectroscopy at 25 °C (Table 3). After 24 h borneol had been converted to camphor (**VIII**) in 62.2% yield (entry 10), primarily limited by incomplete borneol conversion (67.4%). In comparison, benzyl alcohol produced benzaldehyde (**IX**) in very low yield (entries 11a,b). Improvements were found when oxidations were conducted in the presence of pyridine (entry 12a) or 2,6-lutidine (entries 13a,b) at 25 °C. This base effect increased in size at elevated

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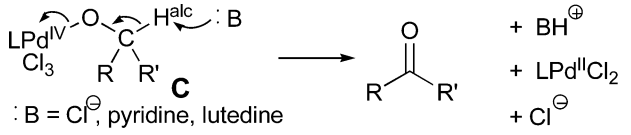
temperatures; for example, chlorinator **1** produced only a 9.7% yield of **IX** after 2 h 60 °C (entry 11c), while a mixture of **1** and pyridine afforded 62.1% (entry 12b). This result was mirrored by the behavior of 2-butanol, whose poor 4.9% oxidation yield by **1** (25 °C, 24 h, entry 14) was improved to 53.6% yield after 24 h (66.0% after 48 h) merely through the addition of pyridine (entries 15a,b). 1-Butanol was unreactive toward **1** even upon heating (entries 16a,b). Although no Pd^{IV}–O intermediates were spectroscopically detected during the experiments, we propose the in situ formation of Pd^{IV} alkoxides **C** (Scheme 7).

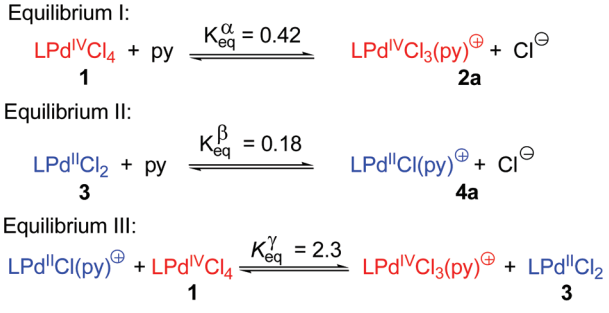
Scheme 7



The order of reactivity borneol > 2-butanol > 1-butanol suggests that abstraction of H^{alc} from complex **C** likely constitutes the slow step of the reaction. This is reminiscent of the relative ease of previously reported borneol oxidations by Cr^{VI} relative to 2-propanol that was attributed to the release of internal strain in the scission of the H^{alc}–$CRR'OCr^{VI}$ bond in the chromium borneolate.[31] The octahedral 18-VE complex **C** is unlikely to undergo a β-hydride elimination in the absence of a vacant site, and the prevalent reluctance of reported Pd^{IV} complexes[1c,32]—in particular Pd^{IV} alkoxides[33]—to engage in such a process attests to that. Our findings that the addition of bases such as pyridine and 2,6-lutidine accelerated conversions and improved yields is consistent with an E_2 process in the slow step of the reaction. Even though small amounts of $LPd^{IV}Cl_3(py)^+Cl^-$ (**2a**) were formed in situ from **1** and pyridine during these reactions, its presence appeared to have no particular benefit on the progress of the reaction (as it did in the case of alkene chlorinations), since the addition of 2,6-lutidine equally improved oxidation yields without forming spectroscopically detectable quantities of the analogous complex $LPd^{IV}Cl_3$(2,6-lutidine)$^+Cl^-$.

In Situ Generation of 2a, 2a-d_5, and 4a and Equilibria in Cl^-/py Exchanges for Pd^{IV} and Pd^{II}. After spectroscopically detecting the C_1-symmetrical cation $LPd^{IV}Cl_3(py)^+$ in entries 2, 13, and 15 (Table 1), we monitored the reactions of **1** and pyridine in the absence of organic substrates and found an equilibrium between **1** and $LPd^{IV}Cl_3(py)^+Cl^-$ (**2a**) with K^{α}_{eq} = $[LPd^{IV}Cl_3(py)^+][Cl^-]/([\mathbf{1}][py])$ = 0.42 that was fully established within hours (Scheme 8, equilibrium I) (analogously,

Scheme 8



the deuterated version **2a-d_5** was generated from **1** and py-d_5). The addition of Bu_4NCl shifted the equilibrium back to the side of **1**. Interestingly, mixtures of **1** and 2,6-lutidine did not form the respective lutidine complex. A Cl^-/py substitution also occurred (within seconds) in $LPd^{II}Cl_2$ (**3**) (equilibrium II) with K^{β}_{eq} = $[LPd^{II}Cl(py)^+]_{eq}[Cl^-]_{eq}/[\mathbf{3}]_{eq}[py]_{eq}$ = 0.18. With values for K^{α}_{eq} and K^{β}_{eq} in hand, the redox equilibrium constant K^{γ}_{eq} for the reaction **1** + $LPd^{II}Cl(py)^+$ ⇔ **3** + $LPd^{IV}Cl_3(py)^+$ can be estimated (K^{γ}_{eq} = $K^{\alpha}_{eq}/K^{\beta}_{eq}$ = 2.3). A thermodynamic preference for the right-hand side of equilibrium III implies that the neutral couple **1**/**3** has a greater reduction potential than the cationic counterpart $LPd^{IV}Cl_3(py)^+/LPd^{II}Cl(py)^+$.

Following the Cl^-/py exchange rates for **1** ($CDCl_3$/Bu_4NBF_4, 25 °C) via ^1H NMR spectroscopy, we discovered that the reaction proceeded through an initial induction period, after which velocities d[**1**]/dt reached a plateau (when plotted versus time) followed by a decline in rates in approaching equilibrium.[34] Time-independent velocities are a consequence of a rate law that is zero order in [**1**]; accordingly, respective d[**1**]/dt vs [**1**] plots feature identical [**1**]-independent plateaus (Figure 2). Interestingly, plateau heights were positively

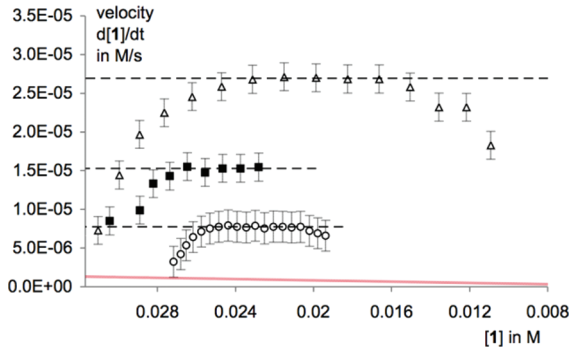


Figure 2. Velocity d[**1**]/dt versus [**1**] plots. Initial concentrations $[\mathbf{1}]_0$, $[py]_0$, and $[\mathbf{3}]_0$ for the three independent experiments are as follows: (I) $[\mathbf{1}]_0$ = 27.4 mM, $[py]_0$ = 274 mM, $[\mathbf{3}]_0$ = 0.11 mM (–○–); (II) $[\mathbf{1}]_0$ = 31.7 mM, $[py]_0$ = 317 mM, $[\mathbf{3}]_0$ = 0.24 mM (–■–); (III) $[\mathbf{1}]_0$ = 31.7 mM, $[py]_0$ = 634 mM, $[\mathbf{3}]_0$ = 0.24 mM (–△–). The contiguous red line at the bottom represents the calculated addend $k_{dissoc}[\mathbf{1}]$ in eq 1.

affected by concentrations [py] and [**3**]. A quantitative analysis[35] provided a two-term rate law with k_{assoc} = 0.192 ± 0.022 M^{-1} s^{-1} for an associative pyridine substitution on **3** (eqs 1 and 2).[36]

$$d[\mathbf{1}]/dt = -k_{dissoc}[\mathbf{1}] - k_{assoc}[\mathbf{3}][py] \quad (1)$$

$$k_{assoc} = (-k_{dissoc}[\mathbf{1}] - d[\mathbf{1}]/dt)/[\mathbf{3}][py] \quad (2)$$

In chemically rationalizing the bimodal kinetics, a hypothetical pyridine association to the octahedral 18-VE complex **1** was excluded from consideration.[37] Our dual-track model (Scheme 9) includes a slow dissociative route involving Pd^{IV}–Cl heterolysis (pathway c); this is supplemented by a competing two-step associative pathway d, in which Cl^-/py exchange occurs on Pd^{II} in the first step followed by an inner-sphere Cl^+ transfer[38] between $LPd^{II}Cl(py)^+$ and **1**, similar to documented cases for Pt^{II}/Pt^{IV}[39] and Pd^{II}/Pd^{IV} systems.[40] Since the associative term in eq 1 ($-k_{assoc}[\mathbf{3}][py]$) is independent of [**1**], the rate-determining step in pathway d cannot be the Cl^+ transfer between **1** and $LPd^{II}Cl(py)^+$ and must therefore be the Cl^-/py substitution in **3**. Few such exchanges on Pd^{II} have been kinetically studied in the past, presumably due to the rapid nature of the process. Basolo provided data that translate into

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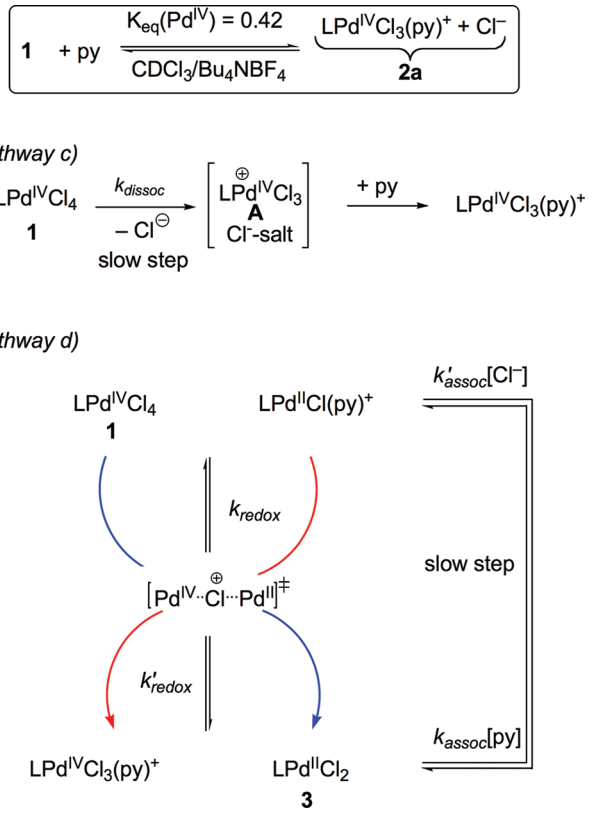
Scheme 9. Dissociative Pathway c and Redox Pathway d for the Cl^-/py Exchange in 1[a]

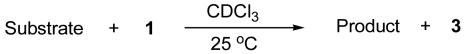


[a]Pathway d is the predominant route according to experimental data.

baseline values of $k_2 > 4.3\ M^{-1}\ s^{-1}$ for cationic Pd^{II} complexes in water.[41] Our value of k_{assoc} is at least 1 order of magnitude lower, which is likely due to the low solvent polarity in our $CDCl_3$ experiments as well as the absence of a positive charge in **3**.

Attempts To Synthesize Other Pd^{IV} Complexes Containing N,P,S Ligands. A few potential ligand candidates, including PPh_3, $BnNH_2$, and DMSO (Table 4), were tested for their compatibility in Cl^-/ligand substitutions on $LPd^{IV}Cl_4$ (**1**);

Table 4. Reaction of 1 with Heteroatom-Containing Substrates

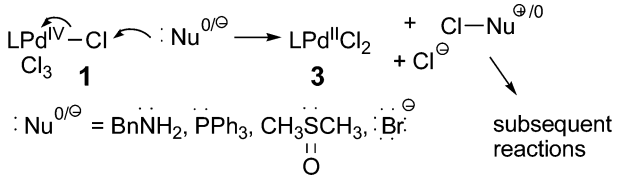


Entry	Substrate [a]	Product [b]	% Yield [c] (% Conversion)
1	PPh_3	Ph_3PCl_2	99.2 % (100%)
2	$BnNH_2$	$BnNHCl \cdot HCl$ [d]	51.9 % [e] (100 %)
3			93.1 % (100 %)
4	Bu_4NBr [f]	BrCl	95.1% (100 %)

[a][substrate] = 10–20 mM; 150 mM $Bu_4NCl/CDCl_3$; 1.05 equiv of (freshly prepared) **1** unless otherwise noted. [b]Identified via ^1H NMR spectroscopy chemical shift analysis and comparison to either authentic samples or published spectra. [c]Determined via ^1H NMR integration using 1,1,2,2-tetrachloroethane as an internal standard. [d]^1H NMR was recorded in D_2O. [e]Precipitated from $CHCl_3$ upon reaction of benzylamine with **1**; washed white solid with $CHCl_3$; yield was determined gravimetrically; loss of yield was primarily due to partial product solubility in chloroform. [f]5 equiv of Bu_4NBr was reacted with **1**.

however, instead of forming $LPd^{IV}Cl_3(ligand)^+$ complexes these compounds were chlorinated by **1** to Cl_2PPh_3, BnNHCl·HCl, and $ClCH_2S(O)CH_3$ (entries 1–3). Complex **3** was formed quantitatively as the sole organometallic product in all cases. The facile oxidation of heteroatom-containing substrates matches our previous observation of Br^- oxidation to BrCl by **1** (entry 4).[8] The reactions in entries 1, 2, and 4 were virtually instantaneous (on the basis of decolorations of yellow solutions of **1**), while the chlorination of DMSO (entry 3) proceeded with $t_{1/2} \approx 480$ s (presumably via initial S chlorination).[42] The rapid pace of heteroatom chlorinations is in contrast to relatively slow Cl^- dissociation from **1** ($t_{1/2}$ = 275 min) (Scheme 1),[8] which precludes the intermediacy of **A** in these reactions. A reasonable mechanism may instead entail a *direct* S_N2-type attack at a Cl^- ligand of **1** with concomitant Pd^{IV}/Pd^{II} reduction (Scheme 10).

Scheme 10



This proposal would be reminiscent of the inner-sphere Cl^+ transfer between **1** and **4a** (Scheme 9, pathway d). Alternatively, an outer-sphere electron transfer to form $LPd^{III}Cl_4^-X^{\bullet+}$ (X = N, P, S, Br^-) may precede the Cl transfer step. Our observation that a suspension of **1** in CH_2Cl_2 instantaneously oxidizes Cp_2Fe to Cp_2Fe^+ supports the principal viability of Pd^{III} intermediates. Various mononuclear[43] and binuclear[44] Pd^{III} systems have been reported recently.[45]

Relative Reactivity of Pd^{II} Complexes 3 and 4b toward Cl_2. In order to address the issue of facile Pd^{II} reoxidation in the context of catalytic Pd^{II}/Pd^{IV} functionalizations (requirement I in the Introduction), we needed to evaluate the respective propensities of **3** and **4b** toward chlorination. A direct competition experiment between **3** and **4b** and a chlorinator was not feasible, since the initially established product ratio of **1** and **2b** would be rapidly altered in the presence of unreacted starting material **3** and **4b** via channels outlined in Scheme 9 and thermodynamically driven by equilibrium III. Therefore, we resorted to an indirect comparison in which **3** and **4b** were individually pegged against a common substrate (cyclohexene) in separate competition experiments.[46] We found that Cl_2 reacted with **3** more slowly than with cyclohexene by a factor of 15 ± 2 (Table 5, entry 1a), while the reactivities of **4b** and cyclohexene were virtually identical (k_{rel} = 1.1 ± 0.2). Using these two ratios, we were able to indirectly estimate that **4b** is 13.6 times more reactive toward Cl_2 than **3**. Even though mixtures of cyclohexene and **3** (or **4b**) did not give rise to discrete new signals or to changes in chemical shifts, a concern was the potential relevance of endothermic π complexes that may have formed in a rapid pre-equilibrium,[47] in which case respective product ratios would be a consequence of the abundance of that π complex. To probe for this unsettling scenario, we conducted separate competition experiments with altered initial concentrations $[3]_0$ (or $[\mathbf{4b}]_0$) and $[cy]_0$ (entries 1b and 2b). Within error margins the relative rates were not affected, which therefore precludes the relevance of potential π complex intermediates.[48]

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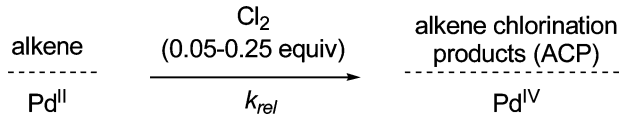
Table 5. Competition Experiment To Determine Relative Rates (k_{rel}) for Alkenes and Pd^{II} Complexes toward Chlorination with Cl_2

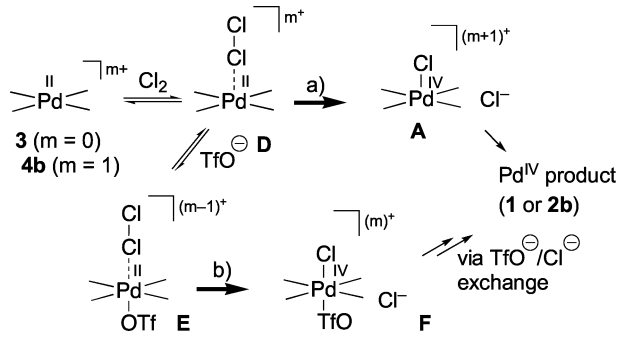


entry[a]	alkene → ACP	Pd^{II} → Pd^{IV}	k_{rel}[i]
1a[b]	cyclohexene → **II** + **III**	**1** → **3**	15 ± 2
1b[c]	cyclohexene → **II** + **III**	**1** → **3**	14 ± 2
2a[d]	cyclohexene → **II** + **III**	**4b** → **2b**	1.1 ± 0.2
2b[e]	cyclohexene → **II** + **III**	**4b** → **2b**	1.3 ± 0.3
3[f]	3-hexene → **XI**[h]	**4b** → **2b**	7 ± 1
4[g]	1-hexene → **I**	**4b** → **2b**	0.34 ± 0.04

[a]Mixtures of Pd^{II} and the alkene were treated with a solution of Cl_2 in $CDCl_3$, and a ^1H NMR spectrum of the product mixture was acquired immediately. [b]From $[cy]_0$ = 20.6 mM (0.667 equiv) and $[\mathbf{3}]_0$ = 30.9 mM (1.00 equiv). [c]From $[cy]_0$ = 5.7 mM (0.087 equiv) and $[\mathbf{3}]_0$ = 65.3 mM (1.0 equiv). [d]From $[cy]_0$ = 67.6 mM (1.10 equiv) and $[\mathbf{4b}]_0$ = 61.3 mM (1.00 equiv). [e]From $[cy]_0$ = 100.1 mM (4.3 equiv) and $[\mathbf{4b}]_0$ = 23.4 mM (1.0 equiv). [f]From [*trans*-3-hexene]$_0$ = 14.9 mM (1.10 equiv) and $[\mathbf{4b}]_0$ = 13.5 mM (1.00 equiv). [g]From [1-hexene]$_0$ = 10.4 mM (0.770 equiv) and $[\mathbf{4b}]_0$ = 13.5 mM (1.00 equiv). [h]**XI** = *meso*-3,4-dichlorohexane. [i]$k_{rel} = ([ACP]/[Pd^{IV}]) \times ([Pd^{II}]_0/[alkene]_0)$.

To account for the surprisingly[49] higher reactivity of the electron-deficient cation **4b** relative to **3**, we assumed the initial formation of pentacoordinated intermediates $LPd^{II}Cl_2(\eta^1\text{-}Cl_2)$ and $[LPd^{II}Cl(py)(\eta^1\text{-}Cl_2)]^+$ (**D** in Scheme 11), similar to van

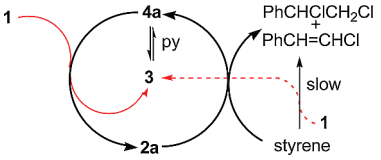
Scheme 11



Koten's end-on $(\eta^1\text{-}I_2)Pt^{II}$[50] and $(\eta^1\text{-}Cl_2)Pd^{II}$ complexes.[51] In the absence of counteranions, scission of the Cl–Cl bond would then produce the pentacoordinated 16-VE cation $LPd^{IV}Cl_3^+$ (**A**) (step a) followed by a collapse to **1**. In contrast, Cl–Cl bond breaking in $LPd^{II}Cl(py)(\eta^1\text{-}Cl_2)^+$ may be assisted by triflate ions[52] via the formation of the octahedral complex **E** and collapse to **F**.[53] Precedence for this proposal can be found in the oxidative additions of Cl_2 and Br_2 to $Pt(CN)_4^{2-}$ that were catalyzed by H_2O acting as an axial ligand to an octahedral $(\eta^1\text{-}X_2)Pt^{II}$ intermediate.[54,55] Interestingly, Lewis base promoted accelerations of S_N2-type oxidative additions have been documented for square-planar d^8 complexes of Rh[56] and Ir.[57] Regardless of the cause for the unexpected reactivity of **4b**, its rate of chlorination was comparable to that of cyclohexene and even exceeded that of 1-hexene (entry 4). For the development of novel Pd^{II}/Pd^{IV} catalyses the relatively easy oxidizability of **4b** (relative to **3**) in conjunction with the enhanced reactivity of **2b** (relative to **1**) underscores the dual benefit of py ligands in both oxidation states.

Pd^{II}/Pd^{IV}/Pyridine Catalysis on the Chlorination of Styrene by Pd^{IV}. In our studies on alkene chlorinations, we elucidated that (I) $LPd^{II}Cl(py)^+Cl^-$ (**4a**) is reversibly and swiftly formed from $LPd^{II}Cl_2$ (**3**) and pyridine, (II) complex **1** can rapidly oxidize **4a** to $LPd^{IV}Cl_3(py)^+Cl^-$ (**2a**), and (III) $LPd^{IV}Cl_3(py)^+$ ions displayed a reactivity toward alkenes significantly higher than that of $LPd^{IV}Cl_4$. On the basis of these parameters, it was plausible that otherwise slowly reacting mixtures of **1** and an alkene such as styrene would experience dramatic rate acceleration by simply adding pyridine to the reaction mixture; key to our hypothesis was the fact that noncatalyzed direct alkene chlorinations by **1** inadvertently produce **3**, which in turn reacts with pyridine to form **4a**, which ultimately allows for the catalytic cascade outlined in Scheme 12.

Scheme 12. Catalytic Pd^{II}/Pd^{IV} Styrene Chlorination Cycle Based on the Couple 4a/2a[a]



[a]While compound **1** functionalizes the alkene sluggishly (right), its main function is to reoxidize **4a** to **2a** and to feed the catalytic cycle (left) with additional supplies of **3**.

Once the reaction is "jump-started" (dashed line), [**3**] would build up continuously and so would the sum [**4a**] + [**2b**]. At this point, **1** would adopt the dual role of a terminal oxidant for **4a** (left circle) and a source of additional **3**; the system would become autocatalytic in the Pd^{II}/Pd^{IV} couple **4a**/**2a**.

Experimentally, the impact of pyridine on the reaction of various Pd^{IV} compounds (27.1 mM solutions in $CDCl_3$) with styrene (10-fold excess) is outlined in Figure 3. In the absence of pyridine the reaction of styrene and **1** proceeded slowly with $t_{1/2} \approx 275$ min (–○–). However, the addition of pyridine (10 equiv) caused a quantitative conversion of **1** to **3** and **4a** within 4 min (–△–) (with concomitant formation of styrene chlorination products **IV** and **V**). On the basis of our ^1H NMR detection limit, we were confident of a minimum of 97% conversion of Pd^{IV} (at least 5 half-lives; $t_{1/2} \leq 48$ s) amounting to a rate acceleration ≥344-fold relative to the pyridine-free reaction. This finding supports the notion that separately manifested individual steps can indeed operate in concert, as postulated in Scheme 12. Interestingly, the overall pace of Pd^{IV} disappearance from the mixture of **1**/py (forming chloride salt **2a** in situ) exceeded not merely the reaction rate of **1** alone but also the rate of disappearance of triflate salt **2b** in its reaction with styrene (–×–). The elevated reactivity of **2a** over **2b** is remarkable but not unexpected, considering our previous finding that the chloride salt of cation **A** is about 1500 times more reactive in Cl^+ transfer reactions to cyclohexene than the respective BF_4^- salt of **A**.[8]

Equally, we found that the addition of 10 equiv of pyridine enhances the performance of **2b** as well (–□–);[58] in this case excess pyridine presumably prevented Cl^- ions (formed as a byproduct in the formation of β-chlorostyrene(**V**)) to coordinatively displace py ligands in $LPd^{IV}Cl_3(py)^+$ and $LPd^{II}Cl(py)^+$. As a consequence of rising levels of chloride ions, the ratio [**2a**]/[**2b**] continuously soared upon styrene conversion, thus boosting the overall reactivity.[59] Therefore,

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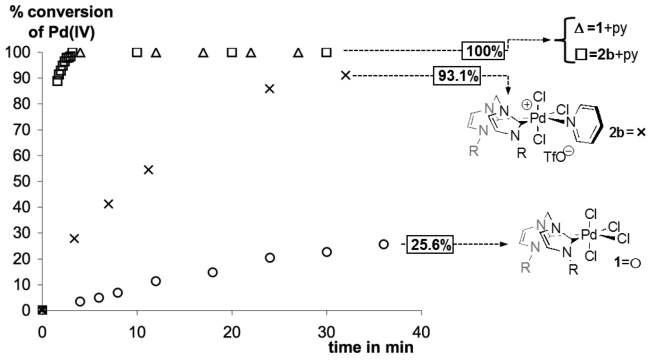
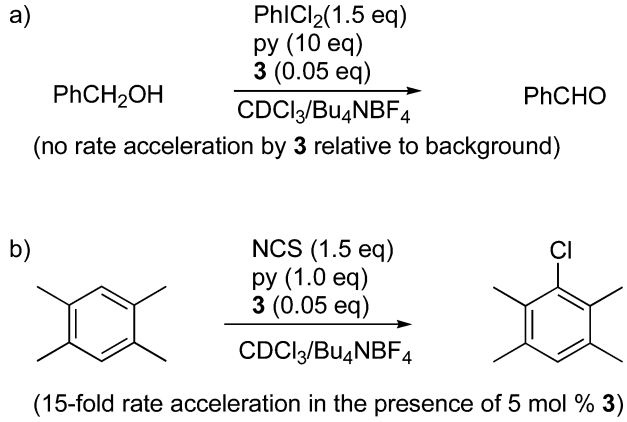


Figure 3. Reaction of Pd^{IV} (27.1 mM) with a 10-fold excess of styrene (271 mM) in $CDCl_3$. Conversions to Pd^{II} complexes **3** and **4b** were monitored by ^1H NMR spectroscopy with $CHCl_2CHCl_2$ as an internal standard. (A) Use of $LPd^{IV}Cl_4$ (**1**) as a chlorinating agent (5 equiv of Bu_4NBF_4 was added to increase the solubility of **1**): after 36 min the conversion of **1** (−○−) was 25.6% while the combined product yield of 1,2-dichloroethylbenzene (**IV**) and *β*-chlorostyrene (**V**) (ratio **IV**:**V** = 2.2:1) was 25.5% after 36 min; after 24 h (not shown) the conversion of **1** was 87.5% % with a 87.4% combined yield of products. (B) Use of $LPd^{IV}Cl_3(py)^+TfO^-$ (**2b**) as a chlorinating agent: after 32 min the conversion of **2b** (−×−) was 93.1% while the combined product yield of **IV** and **V** was 90.5% (ratio **IV**:**V** = 5.6:1). (C) Use of **1** and 10 equiv of pyridine as a chlorinating agent (forming a mixture of rapidly equilibrating $LPd^{IV}Cl_3(py)^+Cl^-$ (**2a**) and **1** in situ): after 4 min the conversion of all Pd^{IV} (−△−) including **2a** and **1** was 100% with a combined product yield of **IV** and **V** of 93.2% (ratio **IV**:**V** = 1.3:1). (D) Use of $LPd^{IV}Cl_3(py)^+TfO^-$ (**2b**) + py (10 equiv) as a chlorinating agent: after 89 s the conversion of **2b** (−□−) was 100% with a combined product yield of **IV** and **V** of 97.8% (ratio **IV**:**V** = 1.1:1).

the presence of pyridine amplified the reactivity of Pd^{IV} both by imposing a positive charge on the metal in $LPd^{IV}Cl_3(py)^+$ and by enabling a chloride-rich counteranion environment. In comparison, a recent literature report on Pd^{II}/Pd^{IV}-catalyzed aromatic C−H acetoxylations in the presence of $PhI(OAc)_2$/$Pd(OAc)_2$/py highlighted dramatic "pyridine effects" on reaction rates and yields as well (presumably through the action of $(py)Pd(OAc)_2$).[60]

An appealing extension from Scheme 12 would be the replacement of **1** with a more economical terminal oxidant. To this end, we selected benzyl alcohol and durene as substrate targets, since their oxidations were comparatively slow relative those of the other substrates given in Table 3 and the distinction between catalyzed reaction and noncatalyzed background reaction would be easier to make. Monitoring the oxidation of benzyl alcohol (1.00 equiv) to benzaldehyde ($CDCl_3/Bu_4NBF_4$, 25 °C) with $PhICl_2$ (1.5 equiv) in the presence of a catalytic amount of **3** (0.05 equiv, 13.2 mM) as well as pyridine (10 equiv) by ^1H NMR showed the formation of **4a** (6% yield from **3**) as well as **2a** (91% yield from **3**) and **1** (3% yield from **3**) within 4 min, while the concentration of residual **3** was below the detection limit. The high yield of Pd^{IV} confirmed that $PhICl_2$ is capable of Pd^{II}/Pd^{IV} oxidation at a faster rate than alcohol oxidation. Subsequently, benzaldehyde was indeed gradually formed (50.2% yield after 31 min; 51.7% conversion of benzyl alcohol); however, the control experiment in the absence of palladium produced a nearly identical result (54.9% yield after 31 min, 57.5% conversion of benzyl alcohol) (Scheme 13a). Clearly, the background reaction between the substrate and the terminal oxidant was much faster than the attempted catalytic Pd^{IV} oxidation. Next we explored if the chlorination of durene (entry 9, Table 3) would be conducive to catalysis, given the

Scheme 13



lower reactivity of the terminal oxidant and its previous use in NHC Pd^{IV} oxidation.[61] A mixture of the arene, *N*-chlorosuccinimide (1.5 equiv), **3** (0.05 equiv), and pyridine (1 equiv) (60 °C, $CDCl_3$) was followed at low conversions (0−5%), and the production of 1-chlorodurene (5% yield) (Scheme 13b) was 15 times faster in the presence of **3**/py in comparison to the background reaction (0.4% yield). Accounting for a catalyst loading of 5 mol %, the rate acceleration on a per catalyst basis was therefore 300-fold, even though only one turnover of catalyst could be accomplished prior to significant decomposition after 10 h at elevated temperature. Despite the demonstration of a principal extension of Scheme 12 to an economical terminal oxidant in lieu of **1**, a challenge that needs to be addressed more forcefully in the future is the balance that a terminal oxidant has to strike in being mild enough to not directly attack a substrate yet being powerful enough to bring about Pd^{II}/Pd^{IV} oxidation.

CONCLUSIONS

This body of work describes the synthesis and structural elucidation of novel cationic bis-NHC Pd^{IV} complexes $LPd^{IV}Cl_3(py)^+X^-$ (X = Cl^-, TfO^-) with equatorially bound pyridine. The chloride salt could be generated from $LPd^{IV}Cl_4$ and pyridine in situ. Octahedral $LPd^{IV}Cl_3(py)^+$ smoothly dichlorinated alkenes via an ionic mechanism involving direct ligand-mediated Cl^+ transfer without the need for *π*-alkene intermediates. Mixtures of $LPd^{IV}Cl_4$ and pyridine constituted the first reported Pd^{IV} system capable of alcohol oxidation, likely via E_2 elimination from in situ formed Pd^{IV} alkoxides. A total of five features could be imparted by pyridine on the reactivity profile of bis-NHC palladium systems by acting as a ligand or as a base. (I) $LPd^{IV}Cl_3(py)^+$ is more reactive toward alkenes than $LPd^{IV}Cl_4$, due to its positive charge and its ability to react as an octahedral complex. (II) $LPd^{II}Cl(py)^+$ underwent faster Pd^{II}/Pd^{IV} oxidation than $LPd^{II}Cl_2$, possibly due to the assistance of triflate coordination to reactive intermediates. (III) Cl^-/py substitution in $LPd^{IV}Cl_4$ is effectively promoted by traces of $LPd^{II}Cl(py)^+$ (formed in situ from $LPd^{II}Cl_2$). (IV) In the presence of excess pyridine in the reaction mixture coordinative Cl^- sequestration by $LPd^{IV}Cl_3(py)^+$ and $LPd^{II}Cl(py)^+$ ions was effectively diminished. As a consequence, the presence of Cl^- counterions further enhanced rates of alkene chlorination by $LPd^{IV}Cl_3(py)^+$. (V) In alcohol oxidations pyridine acted as a base (rather than a ligand) in slow E_2-type *β* eliminations. Exploiting features I−IV, we were able to devise a catalytic chlorination platform for styrene with $LPd^{II}Cl(py)^+/LPd^{IV}Cl_3(py)^+$ as a catalytic Pd^{II}/Pd^{IV} couple and $LPd^{IV}Cl_4$ as a sacrificial oxidant. Furthermore, an

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$LPdCl_2$/py/NCS mixture was able to monochlorinate durene, albeit with only one turnover. Taken together, this work demonstrates novel cationic Pd^{IV} pyridine complexes engaged in direct intermolecular catalytic reactions with organic substrates and breaks from the existing paradigm for common Pd^{II}/Pd^{IV} catalyses that require (slow) Pd^{II} activation steps.

EXPERIMENTAL SECTION

General Considerations: Materials and Methods. All reactions were carried out under atmospheric conditions unless otherwise noted. Inert gas experiments were performed using standard Schlenk techniques or in an inert-gas glovebox (MBRAUN) with extra-dry solvents (<2 ppm of H_2O) stored over heat-activated 4 Å molecular sieves. NMR spectra were obtained on a Varian Unity/INOVA 400 spectrometer that operates at 400 MHz for ^1H and 100 MHz for ^{13}C acquisitions. VnmrJ software (Varian) was used in NMR data acquisition, and ACD/Laboratories NMR processor software was used for data analysis. High-resolution mass spectra were acquired on an MDS SCIEX/Applied Biosystems QStar Elite hybrid quadrupole/TOF mass spectrometer. Solvents and specialty chemicals were purchased from Fisher Scientific or from Acros. All chemicals were used without further purification.

Synthesis of (1,1′-Ditetradecyl-3,3′-methylene-4-diimidazoline-2,2′-diylidene)trichloro(pyridine)palladium(IV) Triflate (2b). Pd^{II} complex **4b** (0.014 g, 0.015 mmol, 1.0 equiv) was dissolved in 0.75 mL of CH_2Cl_2 in a glass test tube under a blanket of N_2, and chlorine gas was bubbled through the solution until the solution turned bright orange. Solvent was removed using a stream of dry N_2, and the orange solid of **2b** was dried in vacuo for 2 h (yield: 0.015 g, 0.015 mmol, 100%). Compound **2b**, which is moderately stable toward air and moisture at room temperature, can be stored at −20 °C under air without degradation for at least 2 months. Detailed structural assignments of **2b** were obtained from a 2D ROESY NMR spectra as described in the Supporting Information. ^1H NMR (400 MHz, $CDCl_3$; proton assignments are based on Figure 1): δ 9.22 (br s, 2 H, H^o) 8.15 (br s, 1 H, H^S), 8.10 (br t, J = 7.4 Hz, 1 H, H^p), 8.04 (d, J = 1.95 Hz, 1 H, $H^{S'}$), 7.68 (br t, J = 5.7 Hz, 2 H, H^m), 7.37 (br s, 1 H, H^4), 7.29 (d, J = 2.0 Hz, 1 H, $H^{4'}$), 7.25 (d, J = 13.7 Hz, 1 H, H^{exo}), 7.12 (d, J = 13.3 Hz, 1 H, H^{endo}), 4.95 (ddd, J = 13.6, 11.4, 5.0 Hz, 1 H, $H^{\alpha'}$ *or* $H^{\beta'}$), 4.71 (ddd, J = 13.6, 11.5, 5.3 Hz, 1 H, $H^{\alpha'}$ *or* $H^{\beta'}$), 3.45 (ddd, J = 13.0, 11.6, 5.5 Hz, 1 H, H^{α} *or* H^{β}), 3.17 (ddd, J = 13.0, 11.4, 4.7 Hz, 1 H, H^{α} *or* H^{β}), 1.96−2.12 (m, 1 H), 1.80−1.94 (m, 1 H), 1.58−1.73 (m, 1 H), 1.43−1.57 (m, 3 H), 1.34−1.43 (m, 3 H), 1.19−1.34 (m, 34 H), 1.00−1.10 (m, 2 H), 0.91−1.00 (m, 2 H), 0.88 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.83, 140.68, 139.48, 129.87, 126.39, 125.27, 125.10, 124.16, 123.62, 120.60 (q, CF_3), 62.42, 53.34, 50.63, 31.91, 31.25, 30.01, 29.58−29.75 (multiple overlapping signals), 29.55, 29.52, 29.45, 29.34, 29.27, 29.19, 28.72, 26.48, 26.20, 14.11. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{40}H_{69}N_5Cl_3Pd^+$ 832.3642, found 832.3681 (+4.7 ppm).

Synthesis of (1,1′-Ditetradecyl-3,3′-methylene-4-diimidazoline-2,2′-diylidene)trichloro(pyridine-d_5)palladium(IV) Triflate (2b-d_5). The deuterated analogue **2b-d_5** was synthesized according to the procedure outlined for **2b**. ^1H NMR (400 MHz, $CDCl_3$; proton assignments are based in Figure 1): δ 8.08 (d, J = 2.0 Hz, 1 H), 7.99 (d, J = 2.0 Hz, 1 H), 7.41 (d, J = 2.0 Hz, 1 H), 7.30 (d, J = 2.0 Hz, 1 H), 7.18 (d, J = 13.3 Hz, 1 H), 7.11 (d, J = 13.3 Hz, 1 H), 4.94 (ddd, J = 13.6, 11.4, 5.1 Hz, 1 H), 4.71 (ddd, J = 13.7, 11.5, 5.3 Hz, 1 H), 3.42 (ddd, J = 13.0, 11.6, 5.5 Hz, 1 H), 3.17 (ddd, J = 13.0, 11.4, 4.9 Hz, 1 H), 1.96−2.10 (m, 1 H), 1.79−1.94 (m, 1 H), 1.59−1.71 (m, J = 3.1 Hz, 1 H), 0.91−1.57 (m, 45 H), 0.88 (t, J = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.39, 129.98, 125.13, 124.88, 124.20, 123.79, 120.60 (q, J = 319.5 Hz), 62.32, 53.32, 50.61, 31.89, 31.23, 29.99, 29.63 (multiple overlapping signals), 29.54, 29.51, 29.44, 29.33, 29.26, 29.17, 28.70, 26.46, 26.18, 22.66, 14.10.

Synthesis of (1,1′-Ditetradecyl-3,3′-methylene-4-diimidazoline-2,2′-diylidene)chloro(pyridine)palladium(II) Triflate (4b). In 1.0 mL of CH_2Cl_2 compound **3** (0.148 g, 0.206 mmol, 1.00 equiv) and pyridine (0.0244 g, 0.310 mmol, 1.50 equiv) were mixed at room temperature. A solution of $AgSO_3CF_3$ (0.0535 g, 0.208 mmol, 1.01 equiv) in 0.1 mL of dry CH_2Cl_2 was then added, and the immediately formed precipitate of AgCl was removed via centrifugation. A stream of dry N_2 was used to reduce the volume of the supernatant to 0.1 mL, followed by the addition of hexanes (0.9 mL). The slightly gelatinous solid was collected by centrifugation and carefully dried under vacuum to afford **4b** (yield: 0.110 g, 0.120 mmol, 58.2%). The supernatant was subjected to further fractional precipitation via careful addition of diethyl ether to obtain another 0.0340 g of product (combined yield of **4b**: 0.144 g, 0.157 mmol, 76.1%). Both fractions were >97% pure by ^1H NMR spectroscopy. Compound **4b** does not show signs of decomposition when stored under air at −20 °C for greater than 2 months. ^1H NMR (400 MHz, dry $CDCl_3$): δ 8.71 (dt, J = 5.08, 1.56 Hz, 2 H), 7.92 (tt, J = 7.6, 1.6 Hz, 1 H), 7.80 (d, J = 2.0 Hz, 1 H), 7.69 (d, J = 2.0 Hz, 1 H), 7.47 (ddd, J = 7.7, 5.0, 1.4 Hz, 2 H), 6.98 (d, J = 2.0 Hz, 1 H), 6.94 (d, J = 2.0 Hz, 1 H), 6.74 (d, J = 13.3 Hz, 1 H), 6.37 (d, J = 13.3 Hz, 1 H), 4.83 (ddd, J = 13.7, 8.6, 6.7 Hz, 1 H), 4.21 (ddd, J = 13.7, 8.6, 6.3 Hz, 1 H), 3.46 (ddd, J = 13.6, 9.3, 5.7 Hz, 1 H), 3.18 (ddd, J = 13.4, 9.3, 6.3 Hz, 1 H), 1.79−2.01 (m, 2 H), 1.56−1.78 (m, 1 H), 1.07−1.48 (m, 43 H), 0.91−1.06 (m, 2 H), 0.87 (t, J = 6.7 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.66, 152.76, 152.20, 139.33, 125.84, 122.97, 122.59, 121.79, 121.51, 120.68 (q, J = 320.3 Hz, CF_3), 62.51, 50.99, 50.03, 31.85, 31.43, 30.79, 29.64, 29.60, 29.51, 29.35, 29.29, 29.20, 28.98, 26.53, 26.42, 22.61, 14.04. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{40}H_{69}N_5ClPd$, 760.4282, found 760.4262 (−2.1 ppm).

Synthesis of (1,1′-Ditetradecyl-3,3′-methylene-4-diimidazoline-2,2′-diylidene)bis(pyridine)palladium(II) Ditriflate, $[LPd(py)_2]^{2+}(TfO^-)_2$ (4c). In 1.0 mL of CH_2Cl_2 compound **3** (0.111 g, 0.145 mmol, 1.00 equiv) and pyridine (0.0368 g, 0.464 mmol, 3.00 equiv) were mixed in a centrifuge tube at room temperature. A solution of $AgSO_3CF_3$ (0.0836 g, 0.0.325 mmol, 2.10 equiv) in 0.1 mL of dry CH_2Cl_2 was then added, and the immediately formed precipitate of AgCl was removed via centrifugation. The solvent was removed with a stream of dry N_2, and the oily residue was dissolved in 0.2 mL of diethyl ether and filtered over a cotton ball within a Pasteur pipet. Addition of 1.5 mL of hexane caused precipitation of an oily residue. After decanting of the supernatant solution the oil was dissolved in a small amount of CH_2Cl_2 and this solution was filtered over approximately 50 mg of charcoal over a cotton ball within a Pasteur pipet. The filtrate was transferred into a centrifuge tube and layered with 0.7 mL of hexane. Gradually a colorless gelatinous precipitate formed. After 2 h, the supernatant solution was carefully decanted and the residue was washed with hexane. After centrifugation, the supernatant solution was discarded and the residue was washed two more times in this fashion. After careful drying under high vacuum a white powder of **4c** was obtained (yield: 0.171 g, 0.0665 mmol, 42.9%). ^1H NMR (400 MHz, dry $CDCl_3$): δ 9.34 (broad doublet, J = 6.2 Hz, 4 H), 7.80 (broad t, J = 7.8, 1.6 Hz, 2 H), 7.69 (d, J = 2.0 Hz, 2 H), 7.48 (ddd, J = 7.7, 6.1 Hz, 4 H), 7.33 (d, J = 13.0 Hz, 1 H), 6.87 (d, J = 2.0 Hz, 2 H), 6.37 (d, J = 13.1 Hz, 1 H), 4.16 (ddd, J = 13.8, 10.5, 5.5 Hz, 2 H), 3.87 (ddd, J = 13.8, 10.2, 5.8 Hz, 1 H), 0.92−1.45 (m, 52 H), 0.86 (t, J = 6.7 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.07, 152.01, 139.14, 126.35, 122.91, 121.09, 120.68 (q, J = 320.3 Hz, only the two central prongs of the quartet were resolved within the experimental signal-to-noise ratio), 62.90, 50.55, 31.89, 30.43, 29.67, 29.63, 29.51, 29.33, 29.30, 29.15, 26.11, 22.65, 14.09.

ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables giving 2-D NMR spectra and analysis for **2b**, detailed reaction protocols for kinetics experiments and their analyses, equilibration experiments, competition experiments, compound characterization by high-resolution Mass spectrometry and NMR spectroscopy, and a detailed derivation of eqs 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(26) A conceivable reaction sequence may also entail reductive elimination of Cl_2 from **2b**, in which case chlorine would be the actual alkene chlorinator. Reductive eliminations of dihalogens X_2 from Pd^{IV} complexes have been previously invoked by Webster (X = Cl, Br)[26a] and spectroscopically studied by Vicente (X = I).[26b] However, the *trans*-3-hexene/1-hexene chlorination bias for Cl_2 as the chlorinating agent was found to be 40.1:1,[8] which evidently does not match with the 150:1 bias of **2b**. (a) Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1983**, 133−141. (b) Vicente, J.; Arcas, A.; Julia-Hernandez, F.; Bautista, D. *Inorg. Chem.* **2011**, *50*, 5339−5341.
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(59) All of our styrene chlorinations produce HCl in the formation of the byproduct β-chlorostyrene. In the case of **2b** as the chlorinator (no pyridine added), virtually all of these newly formed chloride ions are coordinatively sequestered by the abundance of **2b** and Pd^{II} product **4b**, a process that is manifested in the ^1H NMR detection of **1** and **3** in the course of the reaction. The action of "chloride sponges" **4b** and **2b** can be easily counteracted by the addition of excess pyridine to the reaction mixture, thus allowing for a gradual buildup of free Cl^- ions and accordingly for the conversion of **2b** into the more reactive **2a**.
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