Design of Cationic Mixed Phosphine/N-Heterocyclic Carbene Palladium(II) π-Allyl Complexes as Monoligated Phosphine Pd(0) Precatalysts: Synthesis, Structural Studies, Catalysis, and Reactivity

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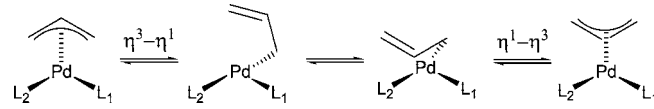
Compounds of general formula [Pd(L)(NHC)(L′)]BF_4 (where L = allyl or crotyl, NHC = tetramethylimidazolin-2-ylidene (tmiy) or 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (dipdmiy), and L′ = tertiary phosphine) have been prepared from the parent [Pd(L)Cl(NHC)(L′)] complexes and fully characterized. A perpendicular orientation of the NHC is observed in the solid state (X-ray) and in solution (NOESY). The crystal structures of these complexes reveal the double-bond character of the allyl *trans* to the phosphine ligand; for example, [Pd(η^3-C_3H_5)(tmiy)(PPh_3)]BF_4 (**4d**) displays C−C distances of 1.198 Å (*trans* to P) and 1.374 Å (*trans* to the NHC). The NHC-Pd-allyl precatalysts are thought to generate monoligated phosphine-Pd(0) active species by reductive elimination of 2-allylimidazolium following $\eta^3-\eta^1$ isomerization of the allyl group. This was observed in the case of [Pd(η^3-C_3H_5)(tmiy)(PCy_3)]BF_4 (**4b**), which successfully catalyzed the coupling of imidazolium salts with ethylene. The intriguing reactivity of **4b** with PhI, yielding 2-phenylimidazolium selectively, is also reported.

Introduction

Palladium(II) π-allyl complexes have attracted considerable attention over the years,[1−9] mainly due to their reactivity toward nucleophiles, which makes those complexes excellent catalysts for the so-called Tsuji−Trost allylic alkylation.[10−23] Transition metal allyl complexes can exist in two coordination modes, η^1 (anionic, 2*e* donor ligand) and η^3 (mixed, 4*e* ligand). An interesting feature of Pd-allyl complexes is their tendency to undergo $\eta^3-\eta^1-\eta^3$ rearrangements (Scheme 1):

Scheme 1. $\eta^3-\eta^1-\eta^3$ Rearrangement in Pd(II) Complexes



This behavior can be observed directly by NOESY spectroscopy.[9,15,18,24−28] Allyl decoordination occurs under steric or electronic control and may happen exclusively *trans* to either L_1 or L_2. It is then followed by rotation around either the Pd−C or the C−C bond of the allyl.[9,16,17,25,26]

Upon switching from η^3 to η^1 coordination, the allyl ligand is analogous to a σ-alkyl group, and the decomposition of Pd(II)-alkyl-NHC (NHC= N-heterocyclic carbene) complexes by reductive elimination is well documented.[29−36] Thus, it was anticipated that a Pd(II)-allyl-NHC complex (**1**, Scheme 2) containing a tertiary phosphine ligand could reductively eliminate 2-propenylimidazolium to yield **2**, a "monoligated"[37] phosphine-Pd(0) complex. Monoligated Pd(0) species are believed to be active catalysts in a number of Pd-catalyzed

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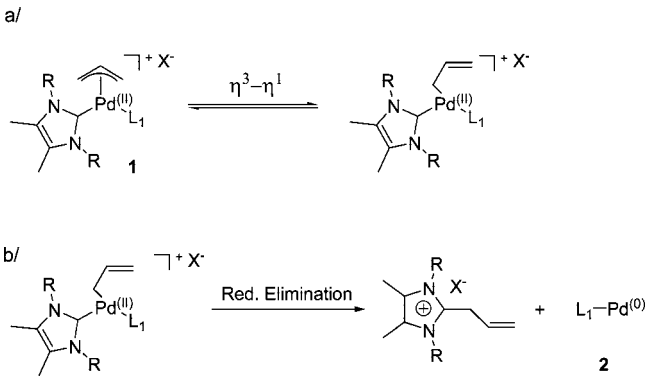
Scheme 2. Hypothetical Reductive Elimination of 2-Propenylimidazolium from a Pd-π-allyl Complex Following H^3-η^1 Rearrangement



reactions, and the design of precatalysts able to effectively generate "Pd(0)-L" is currently an active research area.[38−53]

NHC-containing Pd(II) π-allyl complexes have been known for some time. They have mainly been developed by Nolan as cross-coupling catalysts, showing excellent catalytic activity in Suzuki−Miyaura and Buchwald−Hartwig coupling.[47,48,54−58] Nolan and Beller also reported the use of such complexes in butadiene telomerization,[40,55] and a number of donor-functionalized NHC Pd-allyl compounds have been applied to allylic alkylation, either as preformed[59,60] or *in situ*[59,61,62] catalysts. Other examples have been reported by Porschke,[7,8] Pregosin,[9] and Li[63] (structural studies) and Wang (Suzuki coupling).[64] When we initiated our studies on compounds of type **1**, there was no reported example of mixed phosphine-NHC cationic Pd(II) complexes. Since then, Danopoulos,[65] Jarvo,[66] and Visentin[67] have reported related complexes in which the phosphine and the NHC form a chelate ring, thus preventing reductive elimination of 2-allylimidazolium.[33] In addition Roland[68] and Liu[69] have now reported *in situ* catalysts probably involving a complex of type **1**.

In this paper we present a general synthetic route for a new family of Pd-allyl complexes containing both a phosphine and a carbene ligand, and we report some aspects of their solid-state and solution structures investigated by X-ray diffraction and 2D NMR (HSQC and NOESY). A range of complexes with a variety of different phosphines, carbenes, and allylic groups have been investigated. Since all previously reported examples of Pd-NHC-π-allyl complexes were found to be stable toward reductive elimination of 2-allylimidazolium, a consequential target of this study was to attempt to determine if our compounds showed evidence of $\eta^3-\eta^1-\eta^3$ rearrangement. Preliminary investigations relating to the catalytic activity of mixed ligand complex [Pd(η^3-C_3H_5)(tmiy)(PCy_3)]BF_4 (**4b**) in the Pd-catalyzed coupling of azolium salts with olefins have demonstrated the formation of L-Pd(0) active species via the reductive elimination of 2-propenylimidazolium following ethylene-promoted $\eta^3-\eta^1$ allyl isomerization. Novel studies, aimed at trapping L-Pd(0) with PhI, yielded the clean formation of 2-phenylimidazolium, highlighting the interesting reactivity of these mixed-ligand systems.

Results and Discussion

Synthesis. The synthesis of the title compounds [Pd(π-allyl)(NHC)(L)]BF_4 was initially planned according to Scheme 3.

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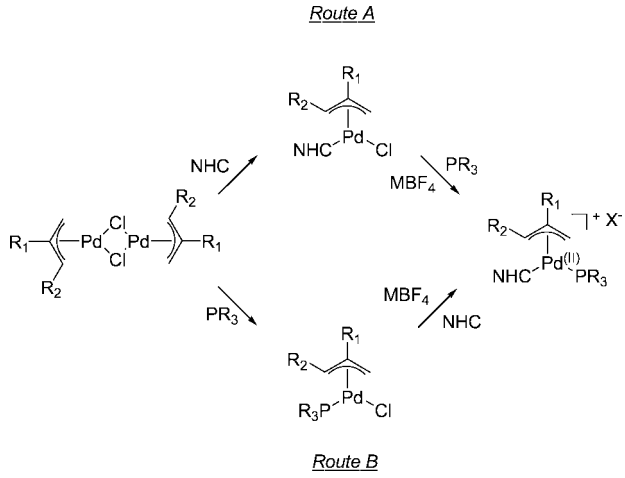
Scheme 3. Possible Routes for the Synthesis of Compounds of General Formula [Pd(π-allyl)(NHC)(L)]BF_4



The intermediate chloro complexes have previously been isolated as air-stable solids for a variety of phosphines and carbenes.[1,7,55,70] With this general scheme as a guide, a range of ligands (allyl, NHC, and phosphine) were identified (Figure 1).

The NHCs investigated in this study were selected because of their low steric bulk compared to IMes or IPr. This feature was expected to increase the propensity of the final Pd(II) π-allyl complexes to reductively eliminate 2-allylimidazolium salt.[34] A range of commercially available phosphines with a variety of stereoelectronic properties were also selected. Tolman's electronic (ν) and cone angle (θ) parameters for phosphines are useful descriptors of their properties.[71] From Tolman's parameters PEt_3 is the least bulky of the selected ligands, while PCy_3 is the bulkiest. The phosphines PPh_3 and PCy_3, which are widely used in catalysis,[38,72−75] are the least and the most electron-donating ligands, respectively.[76]

Following route A, compounds **4a**, **5a**, and **6a** were obtained as air-stable yellow solids slowly decomposing over time at room temperature (Scheme 4; **6a** and **5a** are stable over weeks in the solid state, whereas **4a** decomposes to Pd black in one week).

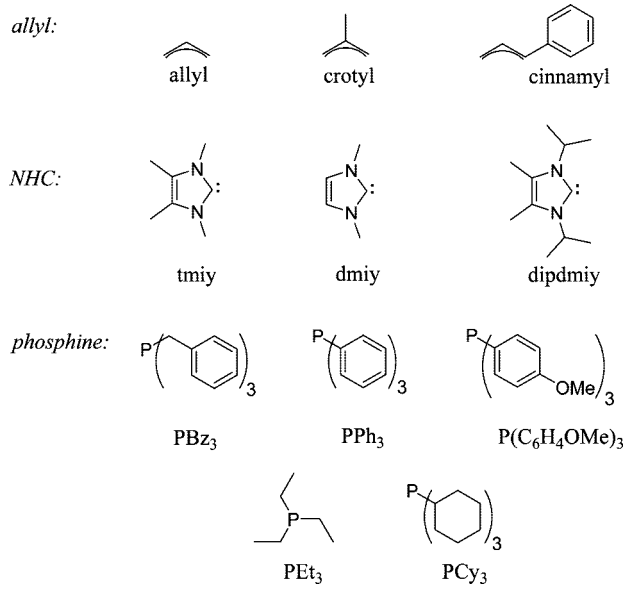
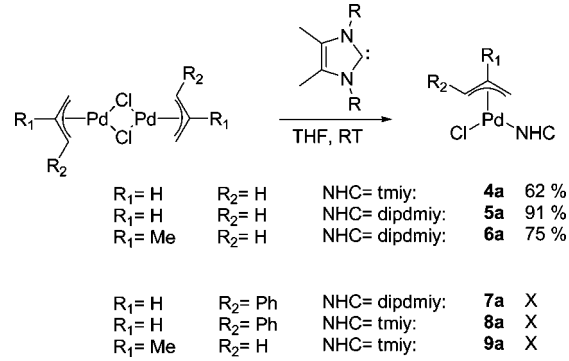
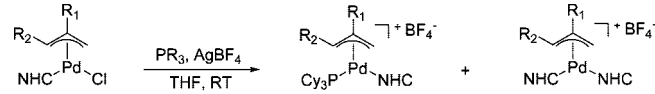


Figure 1. Selected ligands.

Scheme 4. Synthesis of [Pd(π-allyl)Cl(NHC)]



Scheme 5. Initial Attempted Synthesis of [Pd(π-allyl)(NHC)(L)]BF_4 from [Pd(π-allyl)Cl(NHC)]



Surprisingly, it was not possible to obtain complexes **7a**−**9a** pure, as the reactions invariably resulted in a mixture of products.[77] Nolan[47] and others[7,8,62] have used a similar procedure to prepare compounds with bulky NHCs. However, in our case, the NHCs are both less bulky and more basic, which might account for the multiple side reactions we observed.

The synthesis of the desired mixed-ligand, cationic complexes from complexes **4a**−**6a** was then attempted (Scheme 5).

Initial attempts to generate the desired compounds used $AgBF_4$ in the presence of the selected phosphine (Scheme 5). This led to ligand scrambling, generating unwanted bis-carbene cationic complexes[78] that could not be readily separated from the mixed phosphine-carbene complexes. A few reports have previously appeared in the literature on the unexpected reactivity of silver carbene transfer agents. Porschke reported the synthesis of NHC-Pd π-allyl complexes containing weakly coordinating ligands such as BF_4^- and TfO^- from the corresponding chloro precursors.[8] The authors also found that the NHC in the chloro complexes reacted with an excess of Ag(I) salt to give [Ag(NHC)(Y)] (where Y = BF_4). The steric bulk of the NHCs employed in their study apparently prevented the formation of cationic bis-carbene complexes, but it is likely that in the present work the formation of a silver-NHC complex would be followed by carbene transfer to Pd.

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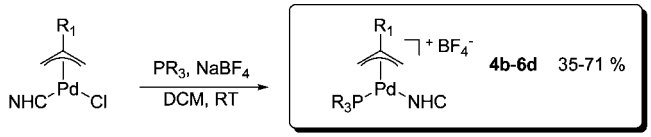
(76) A Tolman map of the ligands in this work can be found in the Supporting Information.
(77) However, an impure sample of **7a** was successfully recrystallized from DCM/hexane on a small scale, and crystals suitable for X-ray diffraction were obtained.
(78) Identified on the basis of ^1H and ^{31}P NMR spectroscopy and ESI-MS.



R_1= H, NHC= tmiy:

PR_3= PCy_3 :	**4b**
PR_3= $P(C_6H_4OMe)_3$:	**4c**
PR_3= PPh_3:	**4d**
PR_3= PBz_3:	**4e**
PR_3= PEt_3:	**4f**

R_1= H, NHC= dipdmiy:

PR_3=PCy_3:	**5b**
PR_3=$P(C_6H_4OMe)_3$:	**5c**
PR_3=PPh_3:	**5d**
PR_3= PEt_3:	**5e**

R_1= Me, NHC= dipdmiy:

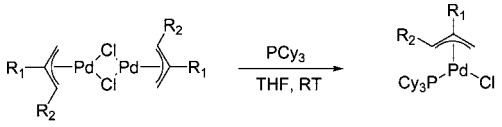
PR_3= PCy_3 :	**6b**
PR_3= $P(C_6H_4OMe)_3$:	**6c**
PR_3= PEt_3:	**6d**

R_1= Me, NHC= tmiy:

PR_3= PCy_3 :	**2b**

Figure 2. Compounds of general formula [Pd(π-allyl)(NHC)(PR_3)]BF_4 obtained in this study.

Scheme 6. Synthesis of [Pd(π-allyl)Cl(PCy_3)]



R_1= H	R_2= H	**1a**	81 %
R_1= Me	R_2= H	**2a**	81 %
R_1= H	R_2= Ph	**3a**	75 %

Subsequently, using $NaBF_4$ instead of $AgBF_4$ to abstract the halide afforded the desired cationic compounds **4b**−**6d** (Figure 2) in reasonable yields, without generating any of the biscarbene complex.[79]

Thus, route **A** is a robust synthetic procedure for a wide range of phosphine ligands. Route B, which would theoretically allow for more diversity in the NHC (once a particular phosphine has been introduced, e.g., PCy_3), turned out to be impractical for several reasons, notably the enhanced reactivity of NHCs toward [Pd(π-allyl)Cl(PCy_3)] complexes **1a**−**3a**, which were obtained by a modification of existing procedures,[70,80] Scheme 6, and the lower lability of the chloro ligand (necessitating the use of $AgBF_4$, which in turns lead to NHC scrambling). In all cases multiple side products were obtained, rendering the purification extremely difficult. We could obtain only complex **2b** (R_1= Me, R_2 = H, NHC = tmiy, PR_3 = PCy_3, Figure 2) using this route.

Atoms in the target cationic compounds are designated according to Figure 3. In the case of neutral compounds of general formula [Pd(η^3-C_3H_5)Cl(L)], the carbon atom trans to Cl is referred to as C_{Cl}, and the carbon atom trans to L is referred to as C_L.

X-ray Diffraction Studies. For the majority of neutral and cationic compounds, crystals suitable for X-ray diffraction were grown by slow evaporation of CH_2Cl_2 solutions of the complexes into hexane, or diffusion of Et_2O into THF solutions of the compounds.[81] The structures of these crystals were elucidated by single-crystal X-ray diffraction, and POV-Ray projections of representative compounds are presented in Figures 4 and 5. Selected bond lengths and angles are presented in Tables 1−4. (Most of the X-ray data, for neutral compounds **2a**−**7a**, are presented in the Supporting Information, in Tables S1−S8, where CIF files and POV-Ray projections can also be found.)

The more compact parent allyl group η^3-C_3H_5 is disordered (disorder was refined anisotropically), with the notable exception of **4a**. The crotyl ligand in **2a** is also disordered (refined anisotropically). The unit cells of two complexes bearing a tmiy ligand (**2b** and **4b**) contain two independent molecules. Least-square planes were calculated for the allyl ligand,[83] the mean

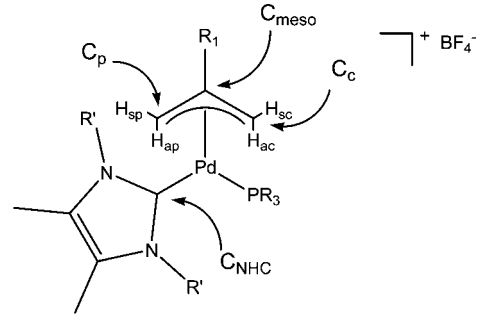


Figure 3. Designation of H and C atoms in compounds of general formula [Pd(π-allyl)(NHC)(PR_3)]BF_4.

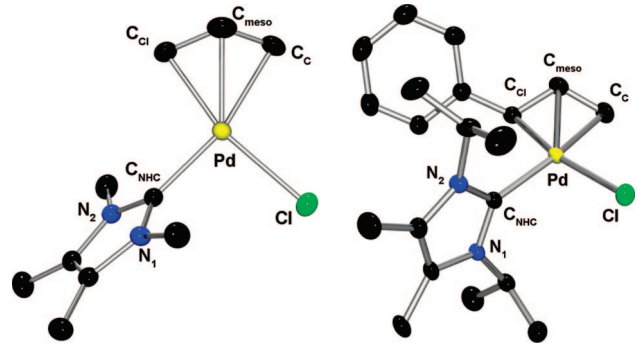


Figure 4. POV-Ray projections of neutral complexes **4a** and **7a**.[82]

(79) The synthesis of known [Pd(η^3-C_3H_5)(PCy_3)$_2$]BF_4 from **5a** was also attempted, but the reaction mainly yielded tricyclohexylphosphonium allyl cation and almost no desired compound. This is most probably the result of nucleophilic attack of free PCy_3 onto the allyl ligand and indicates that NHC ligands are probably far better at labilizing the chloro ligand (and slow down the nucleophilic attack on the allyl).

(80) Reference deleted in revision.

(81) Some compounds did not crystallize; others gave thin microcrystals unsuitable for X-ray crystallography.

(82) Solvent molecules as well as hydrogen atoms and, in the case of cationic complexes, BF_4 anions have been omitted from these projections for clarity. Thermal ellipsoids are drawn at the 50% probability level.

(83) Comprising the three carbon atoms coordinated to Pd.

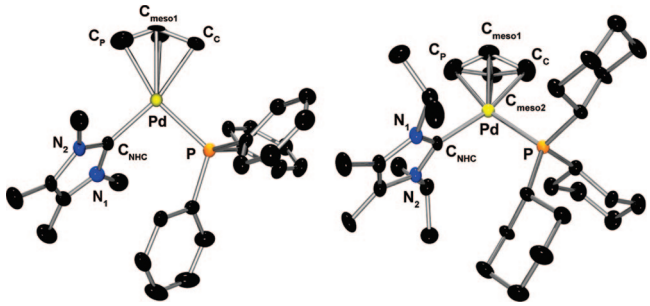


Figure 5. POV-Ray projections of cationic complexes **4d** and **5b**.

coordination plane,[84] and the NHC ring.[85] Interplanar angles Φ_1 (carbene twist angle) and Φ_2 between those planes were calculated, as shown in Figure 6.[86]

Neutral complexes generally display little variation in their geometries. The main structural features of these compounds are as follows:

• A pseudo-square-planar geometry with Cl−Pd−L angles around 90°. Only **7a** differs significantly from this arrangement, with a Cl−Pd−L angle of 105.2° (Table S3).

• A Φ_2 value of about 65° with respect to the coordination plane, and the plane of the three carbon atoms of the allyl group forming a $C_{Cl}-C_{meso}-C_L$ angle of 120° on average (Table S4, in the Supporting Information).

• A roughly perpendicular orientation of the NHC with respect to the coordination plane, most probably to minimize steric interactions. This tendency increases both with the size of the NHC and with that of the π-allyl. Thus, Φ_1 values range from 60.1(1)° (**4a**) to 89.2(1)° (**7a**) (Table S4).[87]

• Distances between Pd and the NHC ligands are much shorter than distances between Pd and the phosphines (on average 2.04 Å versu 2.30 Å, Table 1), reflecting the higher covalent radius of phosphorus (1.07 Å) compared to that of carbon (0.73 Å)[88] and the stronger metal−NHC bond.

• Distances between Pd and the carbon atom *trans* to the NHC or the phosphine ($Pd-C_L$ = 2.20 Å on average for NHCs and 2.19 Å for PCy_3) are longer than distances between Pd and the carbon atom *trans* to Cl ($Pd-C_X$), owing to the strong electron-donating ability of NHCs and PCy_3. Likewise, the allyl C−C bond *trans* to L (L= NHC or PCy_3) is shorter than the C−C bond *trans* to Cl in any given complex (Table 1). This can be rationalized by considering that the allyl H_2C-CH moiety *trans* to a strong σ-donor ligand such as PCy_3 or an NHC should be more olefin-like (i.e., better π acceptor) than an allyl *trans* to a weaker donor such as Cl.

• Finally, there is no significant variation in the C−N bond distance of NHCs, with an average value of 1.35 Å (Table S2). This parameter is expected to vary depending on the degree of back-donation from Pd to the NHC (more back-donation should decrease the "push" mesomeric effect in the NHC and lengthen the C−N distance); therefore, it seems that all complexes display a similar level of back-donation.

As expected, there are noticeable differences in the geometries of neutral [Pd(π-allyl)Cl(L)] complexes and their cationic [Pd(π-allyl)(L)(L′)] counterparts, although both families show a number of common features. For example, $Pd-C_{NHC}$ distances (2.04 Å on average, Tables 1 and 2), N_1-C_{NHC}, N_2-C_{NHC} (1.35 Å on average Tables 1 and 3) and angles $N_1-C_{NHC}-N_2$ (105.5° on average, Tables S4 and S8) are almost equal within standard deviation limits. On the other hand, $Pd-PR_3$ distances are shorter for cationic complexes—2.31 Å on average (Table 2), compared to 2.37 Å average for neutral complexes (Table 1)—indicating that phosphine coordination is predominantly affected by the nature (neutral or cationic) of the Pd complex, perhaps to compensate for the lower electronic density on Pd.

The main structural features of the cationic complexes are as follows:

• A pseudo-square-planar geometry, with a narrower C_p-Pd-C_c value (66° on average, Table S7) compared to the three other angles around Pd.

• A Φ_2 angle of just above 65° is generally observed (Table 4), with the notable exceptions of **5b** (59.8°) and **4d** (39.5°).

• As observed for neutral complexes, $C_X-C_{meso}-C_L$ angles are close to 120° on average (Table 4). Some structures (**4d**, 138.3°; **5b**, 131.3°; and **5c**, 127.8°) deviate significantly from this value. There is no apparent trend in these values (although the crotyl group displays a narrower angle than the allyl).

• Compared to neutral complexes, the perpendicular orientation of the NHC ligand is even more pronounced at 85° on average for Φ_1, most probably to accommodate the larger phosphine ligand. This geometry is likely to be the one adopted in solution, as indicated by NOESY studies (*vide infra*). Complex **4d** displays a reduced value for Φ_1, at 71.5°, probably a result of reduced congestion within the complex.

• In the cationic complexes C−C bonds *trans* to NHCs (C_C-C_{meso}) are longer than C−C bonds *trans* to phosphines (C_P-C_{meso}); see Table 3. This does not seem to be due to purely electronic reasons, since C_P-C_{meso} is shorter in **4d** (1.198 Å) than in **4e** (1.247 Å), despite PBz_3 being a stronger donor than PPh_3. A *cis* steric effect cannot be invoked either, since C_C-C_{meso} is longer in **4b** (1.426 Å) than in **4d** (1.374 Å), despite the bulkier nature of PCy_3 compared to PPh_3. A more subtle interplay of factors is probably responsible; nevertheless it is interesting to note that it confers a marked double-bond character to the part of the allyl *trans* to the phosphine ligand.

• Finally, $Pd-C_C$ distances appear to correlate well with the cone angle (θ) of the phosphine ligand, highlighting the steric influence of the phosphine. For example, $Pd-C_C$ distances decrease in the order PCy_3 (θ = 170°), PBz_3 (θ = 165°), and PPh_3 (θ = 145°) for complexes **4b** (2.220 Å), **4e** (2.181 Å), and **4d** (2.168 Å).

Solution Structure. The assignment of chemical shifts for [Pd(π-allyl)(NHC)(PR_3)]BF_4 complexes was obtained in part by the combination of 1D ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Relevant chemical shifts are presented in Tables 5 and 6. Atoms are designated according to Figure 3, as previously indicated.

The presence of a phosphine ligand leads to $^3J_{HP}$ and $^2J_{CP}$ coupling in ^{1}H and $\{^1H\}^{13}C$ spectra for hydrogen and carbon atoms *trans* to P. This feature of phosphine-containing Pd(II) π-allyl complexes has been reported previously.[1] In addition, $^3J_{HH}$ coupling between H_{meso} and H_{anti} allows the complete assignment of chemical shifts of carbon and hydrogen atoms in π-allyl ligands.

Overall, there is no clear-cut correlation between Tolman parameters (θ and ν) of the phosphine ligands and NMR chemical shifts in the cationic complexes. In particular, ^{13}C

(84) Comprising Pd and the four atoms sitting at the corners of the pseudo-square.

(85) Comprising the three carbon and two nitrogen atoms of the imidazolin-2-ylidene ring.

(86) These angles were calculated with the PLATON suite of programs using the LSPL and CALC GEOM commands.

(87) Cl is relatively small, but the fact that smaller NHCs significantly deviate from this orientation points to a steric rather than electronic preference.

(88) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.

Table 1. Selected Bond Distances (Å) for Neutral Complexes of General Formula [Pd(π-allyl)Cl(L)]

	allyl = η^3-C_4H_7 L = PCy_3 **2a**	allyl = η^3-C_9H_9 L = PCy_3 **3a**	allyl = η^3-C_3H_5 L = tmiy **4a**	allyl = η^3-C_3H_5 L = dipdmiy **5a**	allyl = η^3-C_9H_9 L = dipdmiy **7a**
Pd−L	2.302(1)	2.299(1)	2.046(3)	2.042(4)	2.043(2)
Pd−Cl	2.362(1)	2.373(1)	2.399(1)	2.375(1)	2.370(1)
Pd−C_L	2.177(7)	2.320(2)	2.200(3)	2.199(5)	2.202(2)
Pd−C_{meso}	2.121(12)	2.161(2)	2.131(3)	2.140(8)	2.148(2)
Pd−C_{Cl}	2.110(7)	2.107(2)	2.107(3)	2.097(4)	2.130(2)
C_{Cl}−C_{meso}	1.404(14)	1.419(3)	1.401(5)	1.469(11)	1.429(3)
C_L−C_{meso}	1.367(14)	1.386(3)	1.349(5)	1.236(10)	1.386(3)

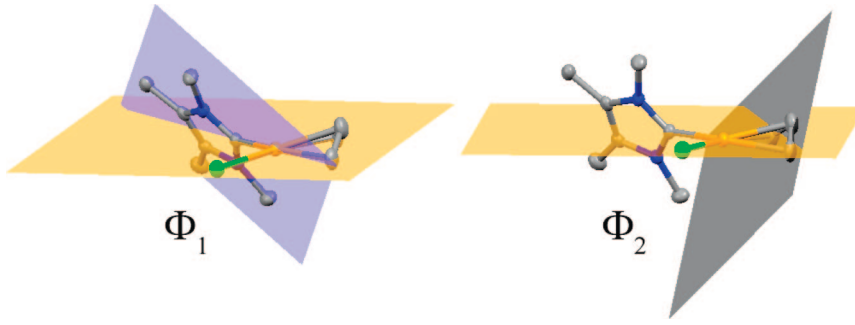


Figure 6. Least-squares planes calculated to determine acute angles Φ_1 and Φ_2 between the carbene ring (blue) or the allyl group (black) and the mean coordination plane (gold).

Table 2. Bond Distances (Å) around Pd for Complexes of General Formula [Pd(π-allyl)(NHC)(PR_3)]BF_4

compound	Pd−C_{NHC}	Pd−P	Pd−C_c	Pd−C_{meso}	Pd−C_P
[Pd(η^3-C_3H_5)(tmiy)(PCy_3)]$^+$**4b**	2.035(3)	2.328(1)	2.220(10)	2.163(6)	2.197(12)
[Pd(η^3-C_3H_5)(tmiy)(PPh_3)]$^+$ **4d**	2.056(3)	2.308(1)	2.168(4)	2.177(14)	2.167(6)
[Pdη^3-C_3H_5)(tmiy)(PBz_3)]$^+$ **4e**	2.057(3)	2.307(1)	2.181(4)	2.151(10)	2.181(4)
[Pd(η^3-C_3H_5)(dipdmiy)(PCy_3)]$^+$ **5b**	2.062(2)	2.317(1)	2.182(3)	2.131(7)	2.178(3)
[Pd(η^3-C_3H_5)(dipdmiy)P(Ar)$_3$]$^+$ **5c**[a]	2.050(5)	2.300(1)	2.165(6)	2.099(10)	2.147(6)
[Pd(η^3-C_4H_7)(tmiy)(PCy_3)]$^+$ **2b**	2.045(2)	2.315(1)	2.176(2)	2.180(2)	2.167(3)
[Pd(η^3-C_4H_7)(dipdmiy)(PCy_3)]$^+$ **6b**	2.054(6)	2.319(2)	2.185(6)	2.168(7)	2.155(7)
[Pd(η^3-C_4H_7)(dipdmiy)(PEt_3)]$^+$ **6d**	2.047(6)	2.297(2)	2.153(7)	2.141(7)	2.158(8)

[a] Ar = *p*-$C_6H_4OCH_3$.

Table 3. Other Bond Distance (Å) for Complexes of General Formula [Pd(π-allyl)(NHC)(PR_3)]BF_4

compound	C_P−C_{meso}	C_C−C_{meso}	N_1−C_{NHC}	N_2−C_{NHC}
[Pd(η^3-C_3H_5)(tmiy)(PCy_3)]$^+$ **4b**	1.403(11)	1.426(10)	1.353(4)	1.354(4)
[Pd(η^3-C_3H_5)(tmiy)(PPh_3)]$^+$ **4d**	1.198(16)	1.374(16)	1.351(5)	1.355(4)
[Pd(η^3-C_3H_5)(tmiy)(PBz_3)]$^+$ **4e**	1.247(13)	1.524(14)	1.336(5)	1.351(4)
[Pd(η^3-C_3H_5)(dipdmiy)(PCy_3)]$^+$ **5b**	1.297(8)	1.382(8)	1.349(3)	1.353(3)
[Pd(η^3-C_3H_5)(dipdmiy)P(Ar)$_3$]$^+$ **5c**[a]	1.275(14)	1.421(14)	1.346(6)	1.348(6)
[Pd(η^3-C_4H_7)(tmiy)(PCy_3)]$^+$ **2b**	1.405(4)	1.410(3)	1.356(3)	1.351(3)
[Pd(η^3-C_4H_7)(dipdmiy)(PCy_3)]$^+$ **6b**	1.385(10)	1.397(10)	1.363(9)	1.367(8)
[Pd(η^3-C_4H_7)(dipdmiy)(PEt_3)]$^+$ **6d**	1.394(10)	1.382(11)	1.379(8)	1.334(9)

[a] Ar = *p*-$C_6H_4OCH_3$.

Table 4. Other Angles (deg) for Complexes of General Formula [Pd(π-allyl)(NHC)(PR_3)]BF_4

compound	C_p−C_{meso}−C_c	N_1−C_{NHC}−N_2	Φ_1	Φ_2
[Pd(η^3-C_3H_5)(tmiy)(PCy_3)]$^+$ **4b**	121.3(1)	104.8(3)	89.6(2)	68.5(1)
[Pd(η^3-C_3H_5)(tmiy)(PPh_3)]$^+$ **4d**	138.3(1)	104.2(3)	71.5(2)	39.5(2)
[Pd(η^3-C_3H_5)(tmiy)(PBz_3)]$^+$ **4e**	120.7(9)	106.0(3)	83.3(2)	69.0(12)
[Pd(η^3-C_3H_5)(dipdmiy)(PCy_3)]$^+$ **5b**	131.3(6)	105.7(2)	80.0(1)	59.8(7)
[Pd(η^3-C_3H_5)(dipdmiy)P(Ar)$_3$]$^+$ **5c**[a]	127.8(1)	105.7(4)	84.2(2)	65.3(1)
[Pd(η^3-C_4H_7)(tmiy)(PCy_3)]$^+$ **2b**	117.1(2)	104.5(2)	83.3(1)	68.5(3)
[Pd(η^3-C_4H_7)(dipdmiy)(PCy_3)]$^+$ **6b**	118.2(6)	104.6(6)	80.6(3)	67.4(8)
[Pd(η^3-C_4H_7)(dipdmiy)(PEt_3)]$^+$ **6d**	118.2(7)	104.8(5)	84.3(3)	68.6(8)

[a] Ar = *p*-$C_6H_4OCH_3$.

NMR shifts of the coordinating carbon of the NHC are relatively insensitive to the nature of the phosphine, ranging from 170.8 ppm (**5c**) to 174.3 ppm (**6b**). Also, ^{31}P NMR shifts do not vary significantly with changes in the allyl or NHC ligands, although marked differences are observed between different phosphines (e.g., the chemical shifts for PCy_3 complexes range from 41.39 ppm (**5b**) to 43.17 ppm (**2b**), whereas those for PPh_3 complexes range from 19.99 ppm (**5d**) to 22.36 (**4d**)). Interestingly, however, the chemical shift of the π-allyl carbon atom *trans* to the NHC (Table 7) is quite sensitive to which phosphine is present, ranging from 60.8 ppm (**5b**) to 69.9 ppm (**5c**), while the chemical shifts of the carbon atom *trans* to PR_3 ranges only from 64.8 ppm (**6c**) to 67.1 ppm (**5e**), suggesting that the impact of the phosphine is largely steric rather than electronic. However,

Table 5. Selected ^{1}H NMR Shifts (δ in ppm) for [Pd(π-allyl)(NHC)(PR$_3$)]BF$_4$ Complexes (in d_2-DCM)

compound	R_1	H_{sp}	H_{sc}	H_{ap} (J_{HP} in Hz)	H_{ac}
2b	CH_3 1.77	3.84	3.87	2.59 (8.8)	2.49
4b	H 5.24	4.07	4.10	2.80 (8.9)	2.58
4c	H 5.58	4.29	3.99	3.06 (NA)	2.91
4d	H 5.52	4.22	3.92	3.00 (10.3)	2.85
4e	H 4.99	3.94	3.04−3.14[a]	2.65 (10.3)	2.08
4f	H 5.31	4.12	3.93	2.83 (9.4)	2.66
5b	H 5.20	4.09−4.15[a]	4.09−4.15[a]	2.72 (8.8)	2.58
5c	H 5.53	4.22−4.30[a]	3.76	2.98 (8.8)	2.87
5d	H 5.50	4.21	3.71	2.94 (9.9)	2.84
5e	H 5.28	4.13	3.90	2.75 (9.5)	2.65
6b	CH_3 1.74	3.87−3.91[a]	3.87−3.91[a]	2.62 (8.8)	2.47
6c	CH_3 1.87	3.86	3.43	2.77−2.85 (NA)[b]	2.77−2.85
6d	CH_3 1.75	3.90	3.63	2.63 (9.5)	2.52

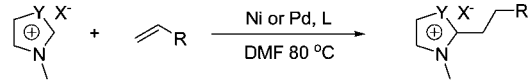
[a] Overlap with other peaks. [b] Overlap with H_{ac} prevented the determination of J_{HP}.

Table 6. Selected ^{13}C and ^{31}P NMR Shifts (δ in ppm) for [Pd(π-allyl)(NHC)(PR$_3$)]BF$_4$ Complexes (in d_2-DCM)

compound	C_{meso} (J_{CP} in Hz)	C_P (J_{CP} in Hz)	C_C	C_{NHC} (J_{CP} in Hz)	P
2b	134.1 (4.0)	66.1 (29.0)	61.2	174.2 (16.0)	43.17
4b	119.9 (4.5)	66.5 (28.0)	61.3[a]	173.2 (16.0)	42.01
4c	121.6 (5.5)	65.8 (31.0)	68.9	171.9 (17.0)	26.25
4d	121.4 (5.5)	65.2 (31.0)	68.1	172.8 (21.5)	22.36
4e	121.2 (6.0)	66.0 (30.0)	64.5	171.8 (2.0)	26.09
4f	121.1 (5.0)	66.1 (29.0)	61.7	172.4 (19.0)	20.41
5b	119.4 (4.0)	66.7 (28.0)	60.8	173.4 (15.0)	41.39
5c	121.0 (6.0)	66.2 (31.0)	69.9[a]	170.8 (19.0)	23.88
5d	120.8 (5.0)	65.7 (31.0)	69.1	171.3 (17.0)	19.99
5e	120.6 (5.0)	67.1 (30.0)	61.5	171.2 (19.0)	20.41
6b	133.7 (4.0)	66.8 (29.0)	60.9	174.3 (16.0)	42.40
6c	135.6 (5.0)	64.8 (32.0)	68.8	171.2 (18.0)	21.89
6d	135.0 (5.0)	66.5 (31.0)	61.3	172.2 (19.0)	21.59

[a] A very small P−C coupling was seen in the ^{13}C NMR spectrum.

Scheme 7. Direct Coupling of Azolium Salts with Olefins Using Ni or Pd Catalysts



Y= NR', O, S
X$^-$= Br$^-$, BF4$^-$

Ni: R= H, Ph, nC_4H_9
Pd: R= ?

the fact that **5b** (containing PCy_3) and **5e** (PEt_3) have very similar chemical shifts for C_c indicates that steric effects alone cannot explain the range of chemical shifts.

It has previously been suggested that the ^{13}C NMR chemical shift of π-allyl ligands is an indicator of electrophilicity, with downfield carbons being more electrophilic.[1] We find that for complexes with trialkylphosphines (**2b**, **4b**, **4e**, **4f**, **5b**, **5e**, **6b**, and **6d**), the C_C carbon *trans* to the NHC is upfield compared to the C_P carbon *trans* to the phosphine (61.0 ppm compared to 66.5 ppm on average, Table 6), indicating that C_P is the more electrophilic carbon. This pattern is reversed for phosphines with aromatic substituents (**4c**, **4d**, **5c**, **5d**, and **6c**), and C_C (69 ppm on average) is downfield compared to C_P (65.5 ppm on average). Complex **4e**, bearing benzyl groups, falls nicely between these extremes (64.5 ppm for C_C and 66.0 ppm for C_P). These observations could be important for ligand design in allylic alkylation, since enantioselectivity has been shown to arise from electronic discrimination in the case of P,N ligands.[21,23] It is also evident that trying to define phosphines by their Tolman parameters alone and relating these features to catalytic activity is not reliable. Studies by Orpen have previously shown discrepancies between observed and expected catalytic activity (based on Tolman parameters).[89]

We note that CH_3 groups on the N-^{i}Pr wingtips of dipdmiy (or those attached to the carbene ring) are nonequivalent, an observation that can be explained by the absence of free rotation around the Pd−C_{NHC} bond caused by the presence of phosphine *cis* to the carbene. Therefore, NOESY experiments were carried out in order to assign the chemical shifts of the nonequivalent carbene hydrogens. Work by Pregosin has shown that NOESY can be successfully applied to Pd(II) π-allyl complexes to gain structural information, and they observed chemical exchange occurring at the allyl ligand.[6,9,16,18,24−26,28] An elegant example of the application of NOESY to the observation of dynamic allyl exchange in a chiral bis-phosphine complex is shown in Figure 7. Diastereoisomers A and B are both present in solution, and negative-phase cross-peaks between these compounds reveal selective exchange between allyl hydrogens *trans* to PPh_2, (i.e., decoordination occurs under steric control exclusively *cis* to the bulky PCy_2 moiety).

X-ray diffraction studies (*vide supra*) show that NHCs adopt a roughly perpendicular orientation with respect to the coordination plane in the solid state. It was thus interesting to confirm this preference in solution. The NOESY spectra of complexes bearing either a phosphine with alkyl substituents or a more compact NHC (dmiy, tmiy) did not show any cross-peak between the phosphine and the NHC, thus precluding absolute assignment of NMR signals. However, complexes **5c**, **5d**, and **6c**, which bear a dipdmiy ligand and a phosphine ligand with aromatic substituents, were investigated. Atoms in **5c**, **5d**, and **6c** are designated as shown in Figure 8.

NHC ligands can be divided into four quadrants: above and under the coordination plane (*a* and *u*), toward or away from palladium (*in* and *out*). Hydrogens on the allyl are assigned as before, and phosphine hydrogens are designated according to their position relative to the phosphorus atom (*ortho*, o; *meta*, m; *para*, p).

Figure 9 shows the NOESY spectrum obtained for **6c**. The cross-peaks are circled and numbered from 1 to 23. Tables summarizing the data can be found in the Supporting Information together with the full spectra for **5c**, **5d**, and **6c**.

The relative *u/a* assignment of NMR signals for **6c** (Table S11) is given by cross-peaks 6, 7, 19, and 23 between *u* protons (H_u, H_{iu}, H_{outu}, H_{inu}). Absolute assignment stems from key interligand cross-peaks 1 (protons *in* and H_o), 9 (H_{sp}/H_{outa}), 14 (H_{ap}/H_{outu}), 21 (H_{outa}/crotyl CH_3), and 20 (H_{ina}/crotyl CH_3). H_o interacts with both *in* methyls, indicating that dipdmiy retains a roughly perpendicular orientation in solution.

Complexes **5c** and **5d** (Tables S9 and S10) have essentially the same NOESY pattern as **6c**. The only significant differences are the absence of cross-peaks between R_1 (H_{meso}) and H_{ina} and H_{outa}, as a consequence of replacing CH_3 by H, and the absence of cross-peaks between H_o and H_{ina} and between H_{sp} and H_{outa}. Finally, HSQC spectra (see Supporting Information) allow correlation of ^{1}H and ^{13}C NMR chemical shifts. Thus, the combination of HSQC and phase-sensitive NOESY allows complete ^{1}H and ^{13}C NMR assignments for **5c**, **5d**, and **6c**.

As mentioned above, NOESY can be applied to the observation of chemical exchange. However, only extremely weak cross-peaks for the allyl ligand are observed here; therefore, it is difficult to draw any definitive conclusions on possible allyl

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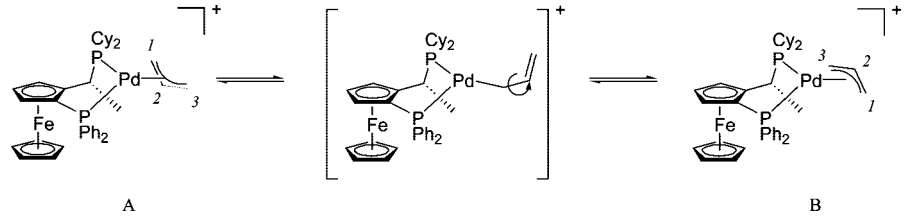

Figure 7. Dynamic behavior of a π-allyl bis-phosphine Pd(II) complex observed by NOESY.[25]

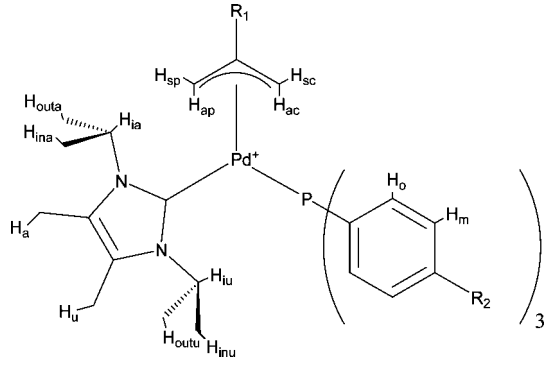

Figure 8. Naming of atoms for complexes studied by NOESY.

isomerization.[90] On the other hand, the absence of allyl exchange in these complexes would be contrary to recent findings by Pregosin et al. on [Pd(η^3-C_3H_5)(X)(IPr)] complexes (X = Cl, Br, I, NCO, SCN, CN, OAc, OTf), wherein (except where X = SCN or CN) allyl exchange was found to occur by selective decoordination *trans* to X (i.e., under electronic control). Compared to our experimental conditions (298 K, in CD_2Cl_2, 300 ms evolution time), Pregosin et al. used a substantially longer evolution period (800 ms), which may account for the different results. More detailed studies (e.g., investigating more coordinating solvents such as d_7-DMF or d_3-MeCN, using higher temperatures or longer evolution periods) are clearly warranted.

As physical measurements were inconclusive, indirect chemical methods were used to probe the likelihood of $\eta^3-\eta^1-\eta^3$ isomerization and, hence, the validity of our approach to generate monoligated Pd(0).

Catalysis and Reactivity. In the course of our studies on the Ni-catalyzed coupling of azolium salts with olefins (Scheme 7),[91−93] we also investigated a Pd-catalyzed version. It was anticipated that Pd catalysts would provide better functional group tolerance than their Ni counterparts, thus possibly broadening the scope of this reaction.[94]

Screening *in situ* catalysts using $Pd(dba)_2$ and various phosphine and NHC ligands revealed that PCy_3 was uniquely effective in the catalysis (Table S12). Importantly, the use of a 2.1 PCy_3/Pd ratio instead of 1.1 strongly inhibits catalyst activity, pointing to a monoligated PCy_3-Pd(0) catalyst. Therefore, the use of **4b** as a well-defined precatalyst was investigated.

The results in Table 7 clearly demonstrate that **4b** is a more effective catalyst than $Pd(dba)_2/PCy_3$ mixtures. Notably, complexes **1a** and **7a**, which lack an NHC ligand, do not show any activity. Thus, it appears that the activity of **4b** arises from its unique design, rather than its cationic nature or the specific presence of the allyl ligand. This, in turn, suggests that this complex may act as a source of monoligated PCy_3-Pd(0), possibly via reductive elimination of the NHC.

To probe this concept more thoroughly, and to shed more light on the activation of **4b**, we undertook a series of experiments aimed at detecting the possible products resulting from reductive elimination (i.e., 2-propenylimidazolium and the PCy_3-Pd(0) fragment). Thus, **4b** was heated to 80 °C in DMF for 5 h in the presence of phenyl iodide and ethylene and in the absence of additive (Scheme 8). Reaction mixtures were analyzed by ^{1}H and ^{31}P NMR and low-resolution ESI-MS.

ESI-MS analysis of the products from heating **4b** alone (without added reactants) confirmed the presence, albeit at trace levels, of 2-propenylimidazolium.[95] However, experiments conducted in the presence of ethylene and phenyl iodide lead to very different outcomes. In the presence of ethylene, the solution turned brown very quickly and some Pd black was observed. The ^{31}P NMR was unchanged, although there was significant background noise, but ^{1}H NMR revealed a new set of weak peaks (see Experimental Section), consistent with the presence of about 10−15% of 2-propenylimidazolium salt. ESI-MS showed two main sets of peaks corresponding to unreacted **4b** and 2-propenylimidazolium salt. A likely explanation for these observations is that ethylene coordination promoted the conversion of the η^3-allyl group into a η^1-bonding mode, leading to 2-propenylimidazolium salt elimination. Thus, the presence of an olefin appears to favor the activation of **4b**, indicating the potential of this family of complexes in Pd-catalyzed reactions, such as telomerization[40,96] or the Heck reaction.[97,98]

Finally, in an attempt to trap the PCy_3-Pd(0) fragment, generated by thermal activation of **4b**, we added PhI to the system. Unexpectedly, the reaction generated 2-phenylimidazolium and tricyclohexylphosphine palladium allyl iodide (**4g**) almost quantitatively. Complex **4g** was prepared separately and its identity confirmed by ^{1}H and ^{31}P NMR. The presence of previously reported 2-phenyltetramethylimidazolium[99] was also confirmed by ^{1}H NMR and ESI-MS (see Supporting Information). The reaction is very clean, and on first consideration appears to proceed via a Pd(II)/Pd(IV) sequence. However, preliminary studies indicate that reaction occurs through the activation of small amounts of **4b**, via reductive elimination, giving Pd(0), to which oxidative addition of PhI occurs; this is

(90) Some peaks are visible depending on the zoom applied to the spectra, but they disappear when all the circled peaks are visible.

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(94) Eventually, we did not find any benefit in using Pd catalysts. In particular, isomerizable and/or electron-withdrawing olefins did not react.

(95) ESI-MS of **4b** does not show the presence of 2-propenyltetramethylimidazolium in the absence of heating; therefore its presence cannot be attributed to MS-induced reductive elimination.

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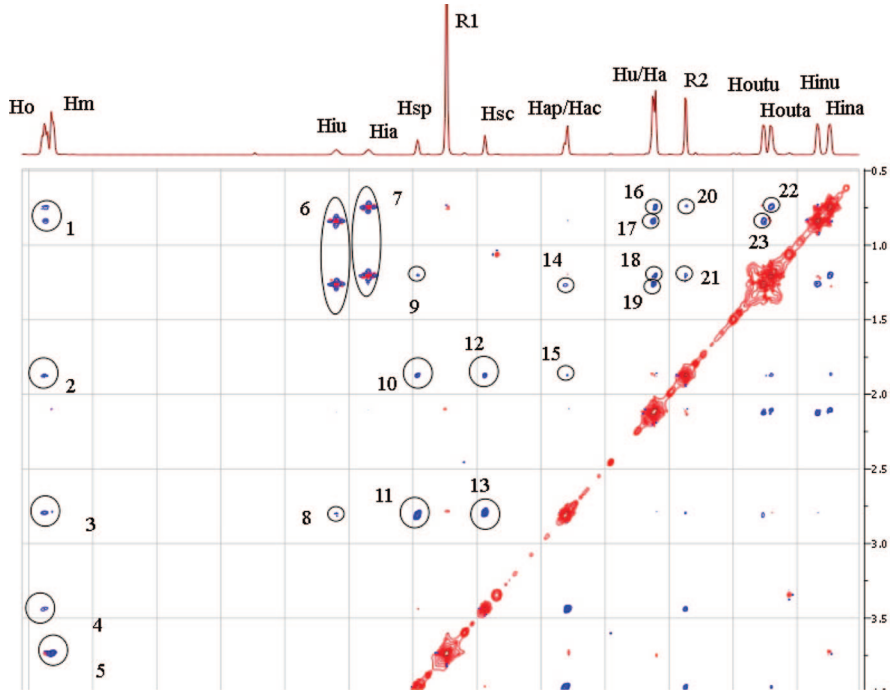
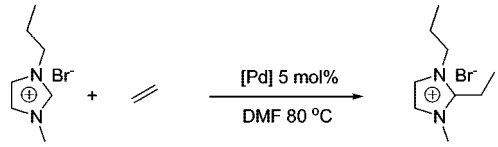


Figure 9. NOESY spectrum of **6c**.

Table 7. Selected Results for the Pd-Catalyzed Alkylation of [pmim]Br with Ethylene[a]



entry	catalyst	conv (%)
1	$Pd(dba)_2/PCy_3$ 1:1	26
2	$[Pd(\eta^3\text{-}C_3H_5)Cl(PCy_3)]$ **1a**	0
3	$[Pd(\eta^3\text{-}C_3H_5)(MeCN)(PCy_3)]BF_4$ **7a**	0
4	$[Pd(\eta^3\text{-}C_3H_5)(dmiy)(PCy_3)]BF_4$ **4b**	81

[a] Reagents and conditions: 1-propyl-3-methylimidazolium bromide, [pmim]Br, 0.73 mmol, [Pd] 5 mol %, DMF 3 mL, C_2H_4 1 bar, 80 °C, 24 h. Based on the average of two runs.

then followed by ligand exchange between the resulting Pd-aryl species and **4b**, yielding iodo complex **4g** and a Pd-NHC-aryl species that eventually undergoes reductive elimination to form phenylimidazolium and Pd(0). Such Pd-based ligand exchange processes are well documented,[36,99−101] although they are often overlooked in favor of mechanisms involving Pd(IV) intermediates.[102] The results of more detailed experimental and DFT investigations are ongoing and will be reported in a subsequent publication.

Conclusion

A new family of cationic $[Pd(\pi\text{-allyl})(NHC)(PR_3)]BF_4$ complexes containing an NHC, a π-bound allyl ligand, and a tertiary phosphine has been reported. The range of phosphines that can be incorporated into this type of complex appears to be virtually unlimited. By contrast, the choice of allyl and NHC ligands is quite restricted, owing to the variable stability of the $[Pd(\pi\text{-allyl})Cl(NHC)]$ templates. The structure of a number of these compounds was investigated by X-ray crystallography and NOESY, indicating that the carbene ligand adopts a roughly perpendicular orientation with respect to the coordination plane, both in solution and in the solid state. These compounds may generate monoligated phosphine-Pd(0), as demonstrated in the case of **4b**. This complex was found to undergo reductive elimination of 2-propenylimidazolium in the presence of ethylene, and this activation process appears to be responsible for the catalytic activity of **4b** in the coupling of imidazolium salts with ethylene. Finally, some intriguing reactivity was observed in the case of compound **4b**, notably its reaction with phenyl iodide. Reductive elimination yielded 2-phenylimidazolium, following a sequence probably involving monoligated Pd(0).

Experimental Section

General Procedures. All manipulations involving air-sensitive compounds were performed under argon atmosphere, using standard Schlenk line techniques or in a nitrogen atmosphere MBraun UNILAB glovebox with less than 1 ppm water and O_2 (where free NHCs, phosphines, and Pd π-allyl dimers were stored). Solvents were dried using appropriate drying agents (CaH_2 for CH_2Cl_2, sodium/benzophenone for THF, Et_2O, and hexane). The following compounds were prepared according to literature procedures: $[Ag(dmiy)_2]_2Ag_4I_6$,[103] tmiy and dipdmiy.[104] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$, and $[Pd(\eta^3\text{-}C_3H_4C_6H_5)Cl]_2$ were prepared using a slight modification of known literature procedures (using non-degassed H_2O as solvent and no carbon monoxide).[4] NMR spectra were recorded at 298 K on a Bruker Avance 500 MHz with a multinuclear gradient probe. Chemical shift values are given relative to residual solvent peak,[105] i.e., for CD_2Cl_2 5.23 ppm for ^1H NMR and 54.00 ppm for ^{13}C NMR. ^{31}P chemical shifts are given relative to H_3PO_4 (capillary tube filled with an aqueous solution of H_3PO_4

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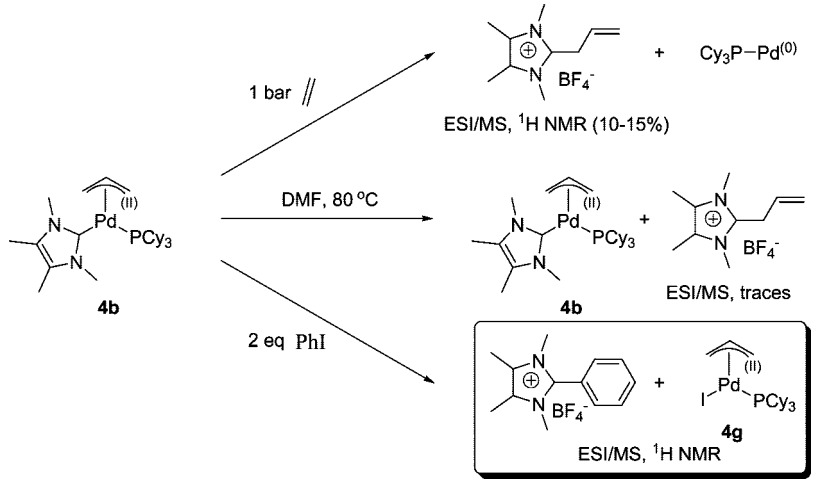
Scheme 8. Reactivity Studies on 4b



in CD_2Cl_2). NOESY spectra were recorded in degassed CD_2Cl_2 with a gradient duration of 300 ms. ESI-MS were perfomed on a Waters LCT Premier XE instrument, with a source temperature of 80 °C, a desolvation temperature of 200 °C, a capillary voltage of 3500 V, and a cone voltage of 100 V. X-ray diffraction data were obtained on a Kappa Nonius CCD diffractometer equipped with an Oxford cryogenic system to maintain the crystals at 150 K. Structure solution and refinement were performed by Dr. Andreas Stasch and Dr. Li-Ling Ooi at Cardiff University. Microanalyses were performed by Warwick Analytical Services.

Procedure for the Studies of the Activation of 4b. 4b (10 mg, 0.016 mmol) was dissolved in 1 mL of DMF. The appropriate reagent was added (e.g., phenyl iodide, 2 equiv), and the reaction mixture was heated to 80 °C under Ar or ethylene (1 bar). After 5 h, the solvent was removed *in vacuo*, and the crude reaction mixture was analyzed by ^{1}H and ^{31}P NMR spectroscopy and ESI-MS. The reaction with ethylene yielded 10−15% (2-propenyl)-tetramethylimidazolium tetrafluoroborate: ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.84 (m, 1H, C*H*CH_2), 5.15 (d, 1H, CHC*H*H (*Z*), ^3J = 12.5 Hz), 5.15 (d, 1H, CHCH*H* (*E*), ^3J = 17.2 Hz), 3.89 (m, 2H, CH_2), 3.71 (s, 6H, NCH_3), 2.23 (s, 6H, CCH_3). ESI_{pos}-MS (MeCN): $[M]^+$ found 165.1 (calc 165.14).

Procedure for the Pd-Catalyzed Coupling of Ethylene and [pmim]Br. A 60 mL Young's Schlenk tube was charged with the Pd catalyst (0.037 mmol, 5 mol %), or $Pd(dba)_2$ (0.037 mmol, 5 mol %) and PCy_3 (0.040 mmol, 5.5 mol %), and the substrate (0.73 mmol, 1 equiv) in a glovebox. DMF was then syringed under a flow of ethylene into the reaction vessel. and the orange-yellow solution was heated to 80 °C. The vessel was then pressurized with 1 bar of ethylene and closed. The solution was stirred for 24 h. The solvent was then removed *in vacuo* and the residue dissolved in d_6-DMSO and submitted for ^{1}H NMR spectroscopy.

Tricyclohexylphosphinepalladium Allyl Chloride, 1a. Tricyclohexylphosphine (PCy_3; 767 mg, 2.73 mmol, 1 equiv) was dissolved in 20 mL of DCM. This solution was canulated over 5 min to a solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (500 mg, 1.37 mmol, 0.5 equiv) in 20 mL of DCM. The solution became paler. When the addition was complete, the solution was stirred 30 min, evaporated under reduced pressure, and triturated with hexane to afford a yellow solid. The solid was rinsed with hexane. The collected mass was 1.02 g (81%). and found identical to literature.[70]

Tricyclohexylphosphinepalladium Crotyl Chloride, 2a. Tricyclohexylphosphine (PCy_3; 712 mg, 2.54 mmol, 1.0 equiv) was dissolved in 5 mL of DCM. This solution was canulated over 5 min to a solution of $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ (500 mg, 1.37 mmol, 0.5 equiv) in 5 mL of DCM. The solution became paler. When the addition was complete, the solution was stirred 10 min, evaporated under reduced pressure, and triturated with hexane to afford a yellow solid. The solid was rinsed with hexane. The collected mass was 986 mg (81%) and found identical to literature.[70]

Tricyclohexylphosphinepalladium cinnamyl chloride, 3a. Tricyclohexylphosphine (PCy_3; 832 mg, 2.97 mmol, 1.03 equiv) was dissolved in 10 mL of DCM. This solution was canulated over 5 min to a solution of $[Pd(\eta^3\text{-}C_4H_6C_6H_5)Cl]_2$ (750 mg, 1.45 mmol, 0.5 equiv) in 10 mL of DCM. The solution became paler. When the addition was complete, the solution was stirred 30 min, evaporated under reduced pressure, and triturated with hexane to afford a yellow solid. The solid was rinsed with hexane. The collected mass was 1186 mg (75%) and found identical to literature.[70]

Tetramethylimidazolin-2-ylidenepalladium Allyl Chloride, 4a. Tetramethylimidazolin-2-ylidene (tmiy; 182 mg, 1.47 mmol, 2.1 equiv) was dissolved in 5 mL of THF. This solution was syringed into a 5 mL THF suspension of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (256 mg, 0.70 mmol, 1 equiv) at −10 °C. The resulting brown solution was warmed to 0 °C for about 15 min. It was then cooled to −70 °C. A yellow precipitate formed, the solution was filtered out, and the solid was rinsed with 4 mL of a 1:1 mixture of THF and Et_2O. The collected mass was 280 mg (62%) and slowly degrades at room temperature, precluding microanalysis and ESI-MS. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.35 (m, 1H, H_{meso} overlapping with solvent signal), 4.13 (d, 1H, H_{syn} *trans* to Cl, $^3J_{HsynHmeso}$= 7.7 Hz), 3.66 (s, 6H, NCH_3), 3.37(d, 1H, H_{syn} trans to tmiy, $^3J_{HsynHmeso}$= 6.6 Hz), 3.20 (d, 1H, H_{anti} *trans* to Cl, $^3J_{HantiHmeso}$ = 13.6 Hz), 2.42 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 11.7 Hz), 2.10 (s, 6H, carbene CH_3). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 176.09 (s, PdC), 125.33 (s, NC), 114.61 (s, C_{meso}), 71.52 (s, C_{term} *anti* to Cl), 47.23 (s, C_{term} *anti* to tmiy), 35.18 (s, NCH_3), 8.91 (s, carbene CH_3).

1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Allyl Chloride, 5a. 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidene (dipdmiy; 260 mg, 1.40 mmol, 2.05 equiv) was dissolved in 2.5 mL of THF. This solution was syringed into a 2.5 mL THF suspension of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (250 mg, 0.68 mmol, 1 equiv) at −70 °C. The yellow solution was stirred for 25 min, then warmed to room temperature and evaporated. The residue was triturated with a 1:1 mixture of Et_2O and hexane, filtered through a sintered glass filter, and vaccuum-dried. The collected mass was 456 mg (91%), yellow solid, decomposes over time at room temperature (hence making microanalysis impossible). This compound was previously described in a patent but no analytical data were reported.[106] ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.25−5.35 (two overlapping m overlapping with residual solvent peak, 2H, isopropyl CH and H_{meso}), 4.85 (m, 1H, isopropyl CH),

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4.07 (d, H_{syn} *trans* to Cl, $^3J_{HsynHmeso}$= 7.5 Hz), 3.34 (d, 1H, H_{syn} *trans* to tmiy, $^3J_{HsynHmeso}$= 6.6 Hz), 3.18 (d, 1H, H_{anti} *trans* to Cl, $^3J_{HantiHmeso}$=13.6 Hz), 2.33 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$= 11.7 Hz), 2.12−2.20 (two overlapping s, 6H, carbene CH_3), 1.40−1.60 (two overlapping m, 12H, isopropyl CH_3). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 176.00 (s, PdC, 126.24 (s, NC), 125.62 (s, NC), 114.28 (s, C_{meso}), 70.83 (s, C_{term} *anti* to Cl), 54.32 (s, isopropyl CH), 53.07 (s, isopropyl CH), 48.23 (s, C_{term} *anti* to tmiy), 22.88 (s, isopropyl CH_3), 22.61 (s, isopropyl CH_3), 10.50 (s, carbene CH_3), 10.33 (s, carbene CH_3). Anal. Calcd for $C_{14}H_{25}N_2ClPd$ (MW = 363.24): C, 46.40; H, 6.96; N, 7.73. Found: C, 45.79; H, 6.82; N, 7.55.

1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Crotyl Chloride, 6a. 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidene (dipdmiy; 191 mg, 1.03 mmol, 2.05 equiv) was dissolved in 2 mL of THF. This solution was syringed into a 4 mL THF suspension of $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ (162 mg, 0.41 mmol, 1 equiv) at −55 °C. The yellow solution was stirred for 30 min, then warmed to room temperature and evaporated. The residue was triturated with a 1:1 mixture of Et_2O and hexane, filtered through a sintered glass filter, and vaccuum-dried. The collected mass was 237 mg (75%), yellow solid, slowly degrades at room temperature. ^1H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.26 (m, 1H, isopropyl CH), 5.00 (m, 1H, isopropyl CH), 3.87 (d, H_{syn} *trans* to Cl, $^4J_{HsynHsyn}$ = 2.9 Hz), 3.15 (m, 1H, H_{syn} *trans* to tmiy), 3.04 (s, 1H, H_{anti} *trans* to Cl), 2.26 (d, 1H, H_{anti} *trans* to tmiy, $^2J_{HantiHsyn}$ = 0.9 Hz), 2.18−2.17 (two overlapping s, 6H, carbene CH_3), 1.97 (s, 3H, crotyl CH_3), 1.40−1.60 (two overlapping m, 12H, isopropyl CH_3). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 176.89 (s, PdC), 126.07 (s, NC), 125.58 (s, NC), 113.16 (s, C_{meso}), 88.78 (s, C_{term} *anti* to Cl), 54.32 (s, isopropyl CH), 53.07 (s, isopropyl CH), 43.57 (s, C_{term} *anti* to tmiy), 23.16 (s, isopropyl CH_3), 22.86 (s, isopropyl CH_3), 22.63 (s, isopropyl CH_3), 22.40 (s, isopropyl CH_3), 17.31 (s, crotyl CH_3), 10.55 (s, carbene CH_3), 10.36 (s, carbene CH_3). High-resolution ESI_{pos}-MS (MeCN): $[M - Cl + MeCN]^+$ found 382.1479 (calc 382.1474, dev: 1.3 ppm). Anal. Calcd for $C_{15}H_{27}N_2ClPd$ (MW = 377.26): C, 48.53; H, 7.52; N, 7.99. Found: C, 47.86; H, 7.24 N, 7.45.

Tricyclohexylphosphine Tetramethylimidazolin-2-ylidene Palladium Crotyl Tetrafluoroborate, 2b. A mixture of tricyclohexylpalladium crotyl chloride **2a** (442 mg, 0.93 mmol, 1.0 equiv) and silver tetrafluoroborate (189 mg, 0.93 mmol, 1.0 equiv) was suspended in 4.0 mL of THF in a Schlenk tube under argon. Tetramethylimidazolin-2-ylidene (1115 mg, 0.93 mmol, 1.0 equiv) was added as a 4 mL solution in THF over 1 min. The reaction mixture was stirred at room temperature for 1 h, then evaporated, taken in DCM, filtered through Celite, evaporated, and triturated with Et_2O. The resulting powder was taken in hot THF and filtered, and the solution was evaporated and triturated with Et_2O to afford a white powder. The collected mass was 150 mg (25%). ^1H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 3.87 (m, 1H, H_{syn} *trans* to tmiy), 3.84 (m, 1H, H_{syn} *trans* to PCy_3), 3.46 (s, 3H, NCH_3), 3.32 (s, 3H, NCH_3), 2.59 (d, 1H, H_{anti} *trans* to PCy_3, J_{PHanti} = 8.8 Hz), 2.49 (s, 1H, H_{anti} *trans* to tmiy), 2.08 (s, 3H, carbene CH_3), 2.07 (s, 3H, carbene CH_3), 1.77 (overlapped s, 3H, crotyl CH_3), 1.59−1.83 (overlapped m, 18H, PCy_3 cyclohexyl), 1.47 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 1.41 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 1.00−1.24 (overlapped m, 15H, PCy_3 cyclohexyl). ^{13}C NMR (CD_2Cl_2, 125.03 MHz): δ (ppm) 174.18 (d, PdC, J_{PC} = 16.0 Hz), 134.11 (s, C_{meso}, J_{PC} = 4.0 Hz), 127.85 (s, NC), 127.74 (s, NC), 66.05 (d, C_{term} *trans* to PCy_3, J_{PC} = 28.9 Hz), 61.22 (s, C_{term} *trans* to tmiy), 36.71 (d, PCH, J_{PC} = 18.9 Hz), 36.31 (s, NCH_3), 36.29 (s, NCH_3), 31.06 (s, CH_2), 30.74 (s, CH_2), 27.99 (d, CH_2, J_{CP}= 2.0 Hz), 27.91 (d, CH_2, J_{CP} = 3.0 Hz), 26.72 (d, CH_2, J_{CP} = 2.0 Hz), 24.32 (s, crotyl CH_3), 9.44 (s, carbene CH_3), 9.41 (s, carbene CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 43.04. High-resolution ESI_{pos}-MS (MeCN): found 565.2912 (calcd 565.2903, dev: 1.6 ppm). Anal. Calcd for $C_{29}H_{52}N_2PPdBF_4$ (MW = 652.93): C, 53.35; H, 8.03; N, 4.29; P, 4.74. Found: C, 52.89; H, 7.95; N, 4.17; P, 5.00.

Tricyclohexylphosphine Tetramethylimidazolin-2-ylidenepalladium Allyl Tetrafluoroborate, 4b. A mixture of tetramethylimidazolin-2-ylidenepalladium allyl chloride (**4a**; 230 mg, 1.07 mmol, 1.0 equiv) and sodium tetrafluoroborate (334 mg, 3.21 mmol, 3.0 equiv) was suspended in 2.5 mL of DCM. Tricyclohexylphosphine (329 mg, 1.17 mmol, 1.1 equiv) was added as a 2.5 mL solution in DCM over 5 min. The reaction mixture was stirred at room temperature for 3 h, then filtered through Celite, and the solution was evaporated and triturated with Et_2O. The resulting brown-red powder was further purified by successive washes with small amounts of hot THF to yield a white powder. The collected mass was 230 mg. A further 115 mg was obtained from the THF liquors (combined yield 47%). ^1H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.24 (m overlapping with solvent signal, 1H, H_{meso}), 4.10 (overlapped m, 1H, H_{syn} *trans* to tmiy), 4.07 (overlapped m, 1H, H_{syn} *trans* to PCy_3), 3.47 (s, 3H, NCH_3), 3.30 (s, 3H, NCH_3), 2.80 (dd, 1H, H_{anti} *trans* to PCy_3, $^3J_{HantiHmeso}$ = 13.8 Hz, J_{PHanti} = 8.9 Hz), 2.58 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.2 Hz), 2.09 (s, 3H, carbene CH3), 2.07 (s, 3H, carbene CH3), 1.80 (m, 3H, PCH), 1.60−1.75 (m, 15H, PCy_3 cyclohexyl), 1.00−1.23 (m, 15H, PCy_3 cyclohexyl). Signals were assigned on the basis of a gs-HSQC experiment. A gs-COSY experiment showed coupling between H_{meso} and both H_{syn}, but it was impossible to resolve the spectrum in order to obtain coupling constants. ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 173.15 (d, PdC, J_{PC} = 16.3 Hz), 127.95 (s, NC), 127.74 (s, NC), 119.88 (d, C_{meso}, J_{PC}= 4.5 Hz), 66.50 (d, C_{term} *trans* to PCy_3, J_{PC} = 27.9 Hz), 61.28 (s, C_{term} *trans* to tmiy), 36.85 (d, PCH, J_{PC} = 18.9 Hz), 36.26 (s, NCH_3), 36.01 (s, NCH_3), 30.94 (s, CH_2), 30.64 (s, CH_2), 27.95 (s, CH_2), 27.86 (s, CH_2), 26.65 (s, CH_2), 9.43 (s, carbene CH_3), 9.37 (s, carbene CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 42.88. High-resolution ESI_{pos}-MS (MeCN): found 551.2729 (calcd 551.2746, dev: −3.2 ppm). Anal. Calcd for $C_{28}H_{50}N_2PPdBF_4$ (MW = 638.28): C, 52.64; H, 7.89; N, 4.39. Found: C, 52.78; H, 7.78; N, 4.15.

Triphenylphosphine Tetramethylimidazolin-2-ylidenepalladium Allyl Tetrafluoroborate, 4c. A mixture of tetramethylimidazolin-2-ylidenepalladium allyl chloride (**4a**; 125 mg, 0.41 mmol, 1.0 equiv) and sodium tetrafluoroborate (131 mg, 1.27 mmol, 3.0 equiv) was suspended in 2.5 mL of DCM. Triphenylphosphine (113 mg, 0.43 mmol, 1.1 equiv) was added as a 2.5 mL solution in DCM over 5 min. The reaction mixture turned from pink to yellow to orange. It was stirred at room temperature for 2.5 h, then filtered through Celite, evaporated, and purified by trituration with THF, followed by successive washes with small amounts of hot THF. The collected mass was 108 mg (42%), white powder. ^1H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 7.39−7.44 (m, 3H, H_{arom} *para* to P), 7.28−7.34 (m, 6H, H_{arom} *meta* to P), 7.06−7.12 (m, 6H, H_{arom} *ortho* to P), 5.58 (m, 1H, H_{meso}), 4.29 (m, 1H, H_{syn} *trans* to PPh_3), 3.99 (d, 1H, H_{syn} *trans* to tmiy, $^3J_{HsynHmeso}$ = 7.3 Hz), 3.09 (s, 3H, NCH_3), 3.06 (m overlapping with NCH_3 signal, 1H, H_{anti} *trans* to PPh_3), 2.95 (s, 3H, NCH_3), 2.91 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.2 Hz), 1.90 (s, 6H, carbene CH_3). Signals were assigned on the basis of gs-HSQC and gs-NOESY experiments (Supporting Information). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 171.90 (d, PdC, J_{PC} = 16.8 Hz), 133.79 (d, C_{arom} *ortho* to P, J_{PC} = 13.0 Hz), 132.12 (d, PC_{arom}, J_{PC} = 43.9 Hz), 131.67 (d, C_{arom} *para* to P, J_{PC} = 3.0 Hz), 129.52 (d, C_{arom} *meta* to P, J_{PC} = 11.0 Hz), 127.78 (s, NC), 127.62 (s, NC), 121.59 (d, C_{meso}, J_{PC} = 5.5 Hz), 68.88 (d, C_{term} *trans* to tmiy), 65.84 (s, C_{term} *trans* to PPh_3, J_{PC} = 30.9 Hz), 35.39 (s, NCH_3), 35.24 (s, NCH_3), 9.29 (s, carbene CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 26.12. High-resolution ESI_{pos}-MS (MeCN): found 531.1332 (calcd 531.1343 dev: −2.1 ppm). Anal. Calcd for $C_{28}H_{32}N_2PPdBF_4$ (MW = 620.14): C, 54.18; H, 5.20; N, 4.52. Found: C, 54.01; H, 5.11; N, 4.34.

Tris(4-methoxyphenyl)phosphine Tetramethylimidazolin-2-ylidenepalladium allyl Tetrafluoroborate, 4d. A mixture of tetramethylimidazolin-2-ylidenepalladium allyl chloride (**1a**; 125 mg, 0.41 mmol, 1.0 equiv) and sodium tetrafluoroborate (131 mg, 1.27 mmol, 3.0 equiv) was suspended in 2.5 mL of DCM. Tris(4-methoxyphenyl)phosphine (140 mg, 0.43 mmol, 1.1 equiv) was added as a 2.5 mL solution in DCM over 5 min. No change of color was observed. The reaction mixture was stirred at room temperature for 2.5 h, then filtered through Celite, evaporated, and purified by trituration with Et_2O, then 3:1 Et_2O/THF mixtures to give a yellow oil, turning back to a powder after drying and triturating with Et_2O. The collected mass was 145 mg (50%), yellow powder, soluble in THF. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 6.93−6.98 (m, 6H, H_{arom}), 6.77−6.81 (m, 6H, H_{arom}), 5.52 (m, 1H, H_{meso}), 4.22 (m, 1H, H_{syn} *trans* to $P(C_6H_4OMe)_3$), 3.92 (d, 1H, H_{syn} *trans* to tmiy, $^3J_{HsynHmeso}$ = 7.3 Hz), 3.72 (s, 9H, OCH_3), 3.10 (s, 3H, NCH_3), 3.00 (dd, 1H, H_{anti} *trans* to $P(C_6H_4OMe)_3$, $^3J_{HantiHmeso}$ = 13.5 Hz, J_{PHsyn} = 10.3 Hz), 2.95 (s, 3H, NCH_3), 2.85 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.4 Hz), 1.90 (s, 6H, carbene CH_3). Signals were assigned on the basis of gs-HSQC and gs-NOESY experiments (Supporting Information). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 172.84 (d, PdC, J_{PC} = 21.3 Hz), 162.40 (d, $C_{arom}O$, J_{PC} = 2.0 Hz), 135.21 (d, C_{arom}, J_{PC} = 15.0 Hz), 127.56 (s, NC), 127.40 (s, NC), 123.57 (d, PC, J_{PC} = 48.9 Hz), 121.35 (d, C_{meso}, J_{PC} = 5.5 Hz), 115.00 (d, C_{arom}, J_{PC} = 11.5 Hz), 68.08 (s, C_{term} *trans* to tmiy), 65.23 (d, C_{term} *trans* to $P(C_6H_4OMe)_3$, J_{PC} = 31.4 Hz), 56.05 (s, OCH_3), 35.44 (s, NCH_3), 35.27 (s, NCH_3), 9.33 (s, carbene CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 22.23. High-resolution ESI_{pos}-MS (MeCN): found 621.1632 (calcd 621.1660 dev: −4.5 ppm). Anal. Calcd for $C_{31}H_{38}N_2O_3PPdBF_4$ (MW = 710.17): C, 52.38; H, 5.39; N, 3.99. Found: C, 51.00; H, 5.27; N, 4.09. These values are not satisfactory due to the solubility of **4d** in THF, causing minor impurities to remain in the sample.

Tribenzylphosphine Tetramethylimidazolin-2-ylidenepalladium Allyl Tetrafluoroborate, 4e. A mixture of tetramethylimidazolin-2-ylidenepalladium allyl chloride (**4a**; 125 mg, 0.41 mmol, 1.0 equiv) and sodium tetrafluoroborate (131 mg, 1.27 mmol, 3.0 equiv) was suspended in 2.5 mL of DCM. Tribenzylphosphine (131 mg, 0.43 mmol, 1.1 equiv) was added as a 2.5 mL solution in DCM over 5 min. The reaction mixture turned from pink to yellow. It was stirred at room temperature for 2.5 h, then filtered through Celite, evaporated, and purified by trituration with THF, followed by successive washes with small amounts of hot THF. The collected mass was 167 mg (62%), white powder. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 7.21−7.25 (m, 9H, H_{arom}), 6.96−7.00 (m, 6H, H_{arom}), 4.99 (m, 1H, H_{meso}), 3.94 (m, 1H, H_{syn} *trans* to PBz_3), 3.04−3.14 (two overlapping m, 7H, PCH_2 and H_{syn} *trans* to tmiy), 3.02 (s, 3H, NCH_3), 2.82 (s, 3H, NCH_3), 2.65 (dd, H_{anti} *trans* to PBz_3, $^3J_{HantiHmeso}$ = 13.3 Hz, J_{PHanti} = 10.3 Hz), 2.08 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.4 Hz), 1.98 (s, 3H, CCH_3), 1.97 (s, 3H, CCH_3). Signals were assigned on the basis of gs-HSQC and gs-NOESY experiments (Supporting Information). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 171.83 (d, PdC, J_{PC} = 19.9 Hz), 134.59 (d, C_{arom}, J_{PC} = 3.0 Hz), 130.28 (d, C_{arom}, J_{PC} = 5.0 Hz), 129.46 (d, C_{arom}, J_{PC} = 2.0 Hz), 127.87 (d, C_{arom}, J_{PC} = 3.0 Hz), 127.77 (s, NC), 127.58 (s, NC), 121.21 (d, C_{meso}, J_{PCmeso} = 6.0 Hz), 66.01 (s, C_{term} *trans* to PBz_3, J_{PC} = 29.9 Hz), 64.45 (d, C_{term} *trans* to tmiy), 35.42 (d, PCH_2, J_{PC} = 17.0 Hz), 35.27 (s, NCH_3), 34.99 (s, NCH_3), 9.36 (s, carbene CH_3), 9.34 (s, carbene CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 25.96. High-resolution ESI_{pos}-MS (MeCN): found 575.1779 (calcd 575.1807 dev: −4.9 ppm) Anal. Calcd for $C_{31}H_{38}N_2PPdBF_4$ (MW = 662.18): C, 56.18; H, 5.78; N, 4.23. Found: C, 56.05; H, 5.76; N, 4.20.

Triethylphosphine Tetramethylimidazolin-2-ylidenepalladium Allyl Tetrafluoroborate, 4f. A mixture of tetramethylimidazolin-2-ylidenepalladium allyl chloride (**4a**; 140 mg, 0.46 mmol, 1.0 equiv) and sodium tetrafluoroborate (142 mg, 1.37 mmol, 3.0 equiv) was suspended in 3.0 mL of DCM. Triethylphosphine (d = 0.81, 70 μL, 0.48 mmol, 1.05 equiv) was added neat by microsyringe over 2 min. The reaction mixture was stirred at room temperature for 3 h, then filtered through Celite, evaporated, and purified by trituration with hexane, followed by trituration in 1:3 mixtures of THF/Et_2O (forms an oil, which turned back into powdery material after drying and triturating with hexane). The product is a yellow-green powder, soluble in THF, and forms an oil when washed with Et_2O. The collected mass was 111 mg (51%). ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.31 (m, 1H, H_{meso}), 4.12 (m, 1H, H_{syn} *trans* to PEt_3), 3.93 (d, 1H, H_{syn} *trans* to tmiy, $^3J_{HsynHmeso}$ = 7.5 Hz), 3.46 (s, 3H, NCH_3), 3.29 (s, 3H, NCH_3), 2.83 (dd, H_{anti} *trans* to PEt_3, $^3J_{HantiHmeso}$ = 13.7 Hz, J_{PHanti} = 9.4 Hz), 2.66 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.4 Hz), 2.08 (s, 3H, CCH_3), 2.06 (s, 3H, carbene CH_3), 1.61 (m, 6H, PCH_2), 0.94 (m, 9H, CH_3). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 172.39 (d, PdC, J_{PC} = 18.9 Hz), 127.73 (s, NC), 127.54 (s, NC), 121.13 (d, C_{meso}, J_{PCmeso} = 5.0 Hz), 66.13 (s, C_{term} *trans* to PEt_3, J_{PC} = 28.9 Hz), 61.72 (d, C_{term} *trans* to tmiy), 35.82 (s, NCH_3), 35.59 (s, NCH_3), 19.10 (d, PCH_2, J_{PC} = 24.9 Hz), 9.37 (s, carbene CH_3), 8.53 (s, CH3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 21.38. High-resolution ESI_{pos}-MS (MeCN): found 389.1328 (calcd 389.1338 dev: −2.6 ppm). Anal. Calcd for $C_{16}H_{32}N_2PPdBF_4$ (MW = 476.14): C, 40.32; H, 6.77; N, 5.88; P, 6.51. Found: C, 39.91; H, 6.70; N, 5.91; P, 6.25.

Tricyclohexylphosphine 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Allyl Tetrafluoroborate, 5b. A mixture of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium allyl chloride (**5a**, 249 mg, 0.67 mmol, 1.0 equiv) and sodium tetrafluoroborate (214 mg, 2.06 mmol, 3.0 equiv) was suspended in 3 mL of DCM. Tricyclohexylphosphine (212 mg, 0.75 mmol, 1.1 equiv) was added as a 3 mL solution in DCM over 5 min. The reaction mixture was stirred at room temperature for 4.5 h, then filtered through Celite, evaporated, and triturated with Et_2O. The resulting powder was taken in hot THF and cooled to −80 °C for 30 min. The resulting precipitate was filtered, rinsed with Et_2O, and dried under vacuum. The collected mass was 160 mg (35%), white powder. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.20 (m overlapping with solvent signal, 1H, H_{meso}), 4.61 (m, 1H, isopropyl CH), 4.36 (m, 1H, isopropyl CH), 4.09−4.15 (two overlapped m, 2H, H_{syn} *trans* to dipdmiy and PCy_3), 2.72 (dd, 1H, H_{anti} *trans* to PCy_3, $^3J_{HantiHmeso}$ = 13.5 Hz, J_{PHanti} = 8.8 Hz), 2.58 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.2 Hz), 2.18 (s, 3H, carbene CH_3), 2.15 (s, 3H, carbene CH_3), 1.86 (m, 3H, PCH), 1.61−1.75 (m, 15H, PCy_3 cyclohexyl), 1.49 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 1.39 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 1.30 (d, 3H, isopropyl CH_3, ^{3} J_{HH} = 7.0 Hz), 1.24 (overlapped d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz), 1.02−1.30 (overlapped m, 9H, PCy_3 cyclohexyl). Signals were assigned on the basis of gs-NOESY and gs-HSQC experiments (Supporting Information). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 173.35 (d, PdC, J_{PC} = 15.0 Hz), 128.37 (s, NC), 128.02 (s, NC), 119.37 (d, C_{meso}, J_{PC} = 4.0 Hz), 66.72 (d, C_{term} *trans* to PCy_3, J_{PC} = 27.9 Hz), 60.79 (s, C_{term} *trans* to tmiy), 55.16 (s, isopropyl CH), 54.71 (s, isopropyl CH), 36.57 (d, PCH, J_{PC} = 18.9 Hz), 30.81 (s, CH_2), 30.64 (s, CH_2), 30.56 (s, CH_2), 27.94 (s, CH_2), 27.92 (s, CH_2),), 27.85 (s, CH_2), 27.84 (s, CH_2), 26.58 (s, CH_2), 23.23 (s, isopropyl CH_3), 22.82 (s, isopropyl CH_3), 21.71 (s, isopropyl CH_3), 21.51 (s, isopropyl CH_3), 10.92 (s, carbene CH_3), 10.90 (s, carbene CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 41.26. High-resolution ESI_{pos}-MS (MeCN): found 605.3354 (calcd 605.3378, dev: −4.0 ppm). Anal. Calcd for $C_{32}H_{58}N_2PPdBF_4$ (MW = 638.28): C, 55.30; H, 8.41; N, 4.03. Found: C, 55.10; H, 8.30; N, 3.94.

Triphenylphosphine 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Allyl Tetrafluoroborate, 5c. A mixture of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium allyl chlo-

ride (**5a**, 200 mg, 0.54 mmol, 1.0 equiv) and sodium tetrafluoroborate (169 mg, 1.63 mmol, 3.0 equiv) was suspended in 3 mL of DCM. Triphenylphosphine (150 mg, 0.57 mmol, 1.1 equiv) was added as a 3.0 mL solution in DCM over 3 min. The reaction mixture was stirred at room temperature for 2.5 h, then filtered through Celite, evaporated, and purified by trituration with Et_2O, a 3:1 mixture of Et_2O/THF, and finally with THF. The collected mass was 262 mg (71%), white powder. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 7.39−7.44 (m, 3H, H_{arom} *para* to P), 7.28−7.34 (m, 6H, H_{arom} *meta* to P), 6.94−7.00 (m, 6H, H_{arom} *ortho* to P), 5.53 (m, 1H, H_{meso}), 4.57 (m, 1H, isopropyl CH), 4.22−4.30 (two overlapped m, 2H, isopropyl CH and H_{syn} *trans* to PPh_3), 3.76 (dm, 1H, H_{syn} *trans* to tmiy, $^3J_{HsynHmeso}$ = 7.3 Hz), 2.98 (dd, 1H, H_{anti} *trans* to PPh_3, $^3J_{HantiHmeso}$ = 13.4 Hz, J_{PHanti} = 9.9 Hz), 2.87 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.4 Hz), 2.10 (s, 3H, CCH_3), 2.09 (s, 3H, CCH_3), 1.25 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz), 1.13 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz), 0.74 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 0.72 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz). Signals were assigned on the basis of gs-NOESY and gsHSQC experiments (Supporting Information). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 170.75 (d, PdC, J_{PC} = 18.9 Hz), 133.81 (d, C_{arom}, J_{PC} = 13.0 Hz), 132.10 (d, PC_{arom}, J_{PC} = 42.9 Hz), 131.72 (d, C_{arom}, J_{PC} = 2.0 Hz), 129.66 (d, C_{arom}, J_{PC} = 11.0 Hz), 128.50 (s, NC), 127.95 (s, NC), 121.02 (d, C_{meso}, J_{PC} = 6.0 Hz), 69.87 (d, C_{term} *trans* to dipdmiy, J_{PC} = 2.0 Hz), 66.17 (d, C_{term} *trans* to PPh_3, J_{PC} = 30.9 Hz), 55.47 (s, isopropyl CH), 54.46 (s, isopropyl CH), 22.84 (s, isopropyl CH_3), 22.59 (s, isopropyl CH_3), 21.09 (s, isopropyl CH_3), 20.90 (s, isopropyl CH_3), 10.62 (s, carbene CH_3), 10.52 (s, carbene CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 23.75. High-resolution ESI_{pos}-MS (MeCN): found 587.1948 (calcd 587.1969 dev: −3.6 ppm). Anal. Calcd for $C_{32}H_{40}N_2PPdBF_4$ (MW = 676.20): C, 56.79; H, 5.96; N, 4.14; P, 4.58. Found: C, 55.89; H, 6.03; N, 3.78; P, 4.36.

Tris(4-methoxyphenyl)phosphine 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Allyl Tetrafluoroborate, 5d. A mixture of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium allyl chloride (**5a**, 250 mg, 0.69 mmol, 1.0 equiv) and sodium tetrafluoroborate (214 mg, 2.06 mmol, 3.0 equiv) was suspended in 5 mL of DCM. Tris(4-methoxyphenyl)phosphine (255 mg, 0.78 mmol, 1.05 equiv) was added as a 5 mL solution in DCM over 1 min. The reaction mixture turned from yellow to colorless and finally to orange (after 30 min). It was stirred at room temperature for 5 h, then filtered through Celite, evaporated, and purified by trituration with Et_2O, followed by washing with hot THF. The collected mass was 290 mg (56%), white powder. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 6.83−6.90 (m, 6H, H_{arom} *ortho* to P), 6.79−6.83 (m, 6H, H_{arom} *meta* to P), 5.50 (m, 1H, H_{meso}), 4.60 (m, 1H, isopropyl CH), 4.30 (m, 2H, isopropyl CH), 4.21 (m, 1H, H_{syn} *trans* to $P(C_6H_4OMe)_3$), 3.74 (s, 9H, OCH_3), 3.71 (overlapped m, 1H, H_{syn} *trans* to dipdmiy), 2.94 (dd, 1H, H_{anti} *trans* to $P(C_6H_4OMe)_3$, $^3J_{HantiHmeso}$ = 13.5 Hz, J_{PHanti} = 9.9 Hz), 2.84 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.4 Hz), 2.12 (s, 3H, carbene CH_3), 2.10 (s, 3H, carbene CH_3), 1.27 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 1.15 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz), 0.82 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 0.78 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz). Signals were assigned on the basis of gs-HSQC and gNOESY experiments (Supporting Information). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 171.32 (d, PdC, J_{PC} = 17.0 Hz), 162.40 (bs, $C_{arom}O$), 135.23 (d, C_{arom} ortho to P, J_{PC} = 15.0 Hz), 128.39 (s, NC), 127.81 (s, NC), 123.65 (d, PC, J_{PC} = 48.9 Hz), 120.78 (d, C_{meso}, J_{PC} = 5.0 Hz), 115.16 (d, C_{arom} meta to P, J_{PC} = 11.0 Hz), 69.08 (s, C_{term} *trans* to tmiy), 65.68 (d, C_{term} *trans* to $P(C_6H_4OMe)_3$, J_{PC} = 30.9 Hz), 56.05 (s, OCH_3), 55.43 (s, isopropyl CH), 54.38 (s, isopropyl CH), 22.86 (s, isopropyl CH_3), 22.63 (s, isopropyl CH_3), 21.24 (s, isopropyl CH_3), 21.06 (s, isopropyl CH_3), 10.68 (s, carbene CH_3), 10.59 (s, carbene CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 19.86. High-resolution ESI_{pos}-MS (MeCN): found 679.2287 (calcd 679.2281 dev: 0.9 ppm). Anal. Calcd for $C_{35}H_{46}N_2O_3PPdBF_4$ (MW = 738.23): C, 54.81; H, 6.05; N, 3.66; P, 4.04. Found: C, 54.66; H, 6.00; N, 3.60; P, 3.97.

Triethylphosphine 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Allyl Tetrafluoroborate, 5e. A mixture of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium allyl chloride (**5a**; 250 mg, 0.69 mmol, 1.0 equiv) and sodium tetrafluoroborate (214 mg, 2.06 mmol, 3.0 equiv) was suspended in 5 mL of DCM. Triethylphosphine (d = 0.81, 105 μL, 0.72 mmol, 1.05 equiv) was added neat by microsyringe over 2 min. The reaction mixture was stirred at room temperature for 3 h, then filtered through Celite, evaporated, and purified by trituration with Et_2O. The collected mass was 193 mg (53%), yellow-green powder. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.28 (m, 1H, H_{meso}), 4.58 (m, 1H, isopropyl CH), 4.31 (m, 1H, isopropyl CH), 4.13 (m, 1H, H_{syn} *trans* to PEt_3), 3.90 (d, 1H, H_{syn} *trans* to dipdmiy, $^3J_{HsynHmeso}$ = 6.9 Hz), 2.75 (dd, H_{anti} *trans* to PEt_3, $^3J_{HantiHmeso}$ = 13.0 Hz, J_{PHanti} = 9.5 Hz), 2.65 (d, 1H, H_{anti} *trans* to tmiy, $^3J_{HantiHmeso}$ = 13.2 Hz), 2.17 (s, 3H, carbene CH_3), 2.14 (s, 3H, carbene CH_3), 1.65 (m, 6H, PCH_2), 1.45 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.3 Hz), 1.34 (overlapped d, 3H, isopropyl CH_3, $^3J_{HH}$ = 6.9 Hz), 1.33 (overlapped d, 3H, isopropyl CH_3, $^3J_{HH}$ = 6.9 Hz), 1.25 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.3 Hz) 0.95 (m, 9H, PEt_3 CH_3). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 171.24 (d, PdC, J_{PC} = 18.9 Hz), 128.22 (s, NC), 127.58 (s, NC), 120.64 (d, C_{meso}, J_{PCmeso} = 5.0 Hz), 67.09 (s, C_{term} *trans* to PEt_3, J_{PC} = 29.9 Hz), 61.49 (d, C_{term} *trans* to dipdmiy), 55.13 (s, isopropyl CH), 54.16 (s, isopropyl CH), 22.76 (s, isopropyl CH_3), 22.55 (s, isopropyl CH_3), 22.16 (s, isopropyl CH_3), 19.41 (d, PCH_2, J_{PC} = 24.9 Hz), 10.75 (s, carbene CH_3), 10.66 (s, carbene CH_3), 8.57 (s, PEt_3 CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 20.28. High-resolution ESI_{pos}-MS (MeCN): found 445.1945 (calcd 445.1964 dev: −4.3 ppm). Anal. Calcd for $C_{20}H_{40}N_2PPdBF_4$ (MW = 532.20): C, 45.10; H, 7.57; N, 5.26; P, 5.82. Found: C, 44.77; H, 7.56; N, 5.19; P, 6.10.

Tricyclohexylphosphine 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Crotyl Tetrafluoroborate, 6b. A mixture of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium crotyl chloride (**6a**; 136 mg, 0.36 mmol, 1.0 equiv) and sodium tetrafluoroborate (112 mg, 1.08 mmol, 3.0 equiv) was suspended in 2.5 mL of DCM. Tricyclohexylphosphine (106 mg, 0.38 mmol, 1.08 equiv) was added as a 2.5 mL solution in DCM over 15 min. The yellow reaction mixture turned pale. It was stirred at room temperature for 2.5 h, then filtered through Celite, evaporated, and purified by trituration with Et_2O, then a 3:1 mixture of Et_2O/THF. The collected mass was 140 mg (60%), white powder. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 4.64 (m, 1H, isopropyl CH), 4.38 (m, 1H, isopropyl CH), 3.87−3.91 (two overlapped m, 2H, H_{syn} *trans* to dipdmiy and PCy_3), 2.62 (d, 1H, H_{anti} *trans* to PCy_3, J_{PHanti}= 8.8 Hz), 2.47 (s, 1H, H_{anti} *trans* to tmiy), 2.17 (s, 3H, carbene CH_3), 2.16 (s, 3H, carbene CH_3), 1.83 (m, 3H, PCH), 1.74 (overlapped s, 3H, crotyl CH_3), 1.60−1.79 (overlapped m, 15H, PCy_3 cyclohexyl), 1.47 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 1.41 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.2 Hz), 1.29 (overlapped d, 3H, isopropyl CH_3, $^3J_{HH}$ = 5.5 Hz), 1.27 (overlapped d, 3H, isopropyl CH_3, $^3J_{HH}$ = 5.5 Hz), 1.02−1.32 (overlapped m, 9H, PCy_3 cyclohexyl). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 174.27 (d, PdC, J_{PC} = 16.0 Hz), 133.66 (d, C_{meso}, J_{PC} = 4.0 Hz), 128.10 (s, NC), 128.03 (s, NC), 66.83 (d, C_{term} *trans* to PCy_3, J_{PC} = 28.9 Hz), 60.91 (s, C_{term} *trans* to tmiy), 55.08 (s, isopropyl CH), 54.77 (s, isopropyl CH), 36.37 (d, PCH, J_{PC} = 18.0 Hz), 30.79 (s, CH_2), 30.58 (s, CH_2), 27.92 (d, CH_2, J_{CP} = 3.0 Hz), 27.83 (d, CH_2, J_{CP} = 3.0 Hz), 26.61 (s, CH_2), 23.63 (s, crotyl CH_3), 23.14 (s, isopropyl CH_3), 22.94 (s, isopropyl CH_3), 21.60 (s, isopropyl CH_3), 21.44 (s, isopropyl CH_3), 10.93 (s, carbene CH_3), 10.87 (s, carbene CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 42.27. High-resolution ESI_{pos}-MS (MeCN): found 619.3504

(calcd 619.3534, dev: −4.8 ppm). Anal. Calcd for $C_{33}H_{60}N_2PPdBF_4$ (MW = 709.04): C, 55.90; H, 8.53; N, 3.95; P, 4.37. Found: C, 55.64; H, 8.57; N, 3.88; P, 4.46.

Tris(4-methoxyphenyl)phosphine 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Crotyl Tetrafluoroborate, 6c. A mixture of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium crotyl chloride (**6a**; 190 mg, 0.50 mmol, 1.0 equiv) and sodium tetrafluoroborate (165 mg, 1.57 mmol, 3.0 equiv) was suspended in 5 mL of DCM. Tris(4-methoxyphenyl)phosphine (172 mg, 0.53 mmol, 1.05 equiv) was added as a 2 mL solution in DCM over 5 min. The reaction mixture gradually turned from a paler to a darker yellow. It was stirred at room temperature for 3 h, then filtered through Celite, evaporated, and purified by trituration with Et_2O, followed by a 2:1 mixture of Et_2O/THF. The collected mass was 258 mg (65%), white powder. ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 6.78−6.85 (m, 6H, H_{arom} *meta* to P), 6.85−6.92 (m, 6H, H_{arom} *ortho* to P), 4.60 (m, 1H, isopropyl CH), 4.35 (m, 2H, isopropyl CH), 3.96 (m, 1H, H_{syn} *trans* to P($C_6H_4OMe)_3$), 3.74 (s, 9H, OCH_3), 3.43 (bs, 1H, H_{syn} *trans* to dipdmiy), 2.77−2.85 (overlapped dd and s, 2H, H_{anti} *trans* to P($C_6H_4OMe)_3$ and dipdmiy), 2.13 (s, 3H, carbene CH_3), 2.11 (s, 3H, carbene CH_3), 1.87 (s, 3H, crotyl CH_3), 1.26 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 6.9 Hz), 1.20 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 6.9 Hz), 0.84 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 6.9 Hz), 0.75 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.3 Hz). Signals were assigned on the basis of gs-HSQC and gs-NOESY experiments (Supporting Information). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 171.21 (d, PdC, J_{PC} = 18.0 Hz), 162.37 (s, $C_{arom}O$), 135.62 (d, C_{meso}, J_{PC} = 5.0 Hz), 135.18 (d, C_{arom}, J_{PC} = 15.0 Hz), 128.06 (s, NC), 127.96 (s, NC), 123.65 (d, PC, J_{PC} = 46.9 Hz), 115.10 (d, C_{arom}, J_{PC} = 11.0 Hz), 68.76 (s, C_{term} *trans* to dipdmiy), 64.83 (d, C_{term} *trans* to P($C_6H_4OMe)_3$, J_{PC} = 31.9 Hz), 56.04 (s, OCH_3), 55.21 (s, isopropyl CH), 54.91 (s, isopropyl CH), 24.07 (s, crotyl CH_3), 22.75 (s, isopropyl CH_3), 22.57 (s, isopropyl CH_3), 21.07 (s, isopropyl CH_3), 20.88 (s, isopropyl CH_3), 10.69 (s, carbene CH_3), 10.64 (s, carbene CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 21.76. High-resolution ESI_{pos}-MS (MeCN): found 693.2451 (calcd 693.2437 dev: 2.0 ppm). Anal. Calcd for $C_{35}H_{46}N_2O_3PPdBF_4$ (MW = 738.23): C, 55.37; H, 6.20; N, 3.59. Found: C, 54.94; H, 6.34; N, 3.55.

Triethylphosphine 1,3-Diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium Crotyl Tetrafluoroborate, 6d. A mixture of 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenepalladium crotyl chloride (**6a**; 200 mg, 0.53 mmol, 1.0 equiv) and sodium tetrafluoroborate (165 mg, 1.57 mmol, 3.0 equiv) was suspended in 5 mL of DCM. Triethylphosphine (d = 0.81, 81 μL, 0.56 mmol, 1.05 equiv) was added neat by microsyringe over 5 min. The color of the yellow reaction mixture gradually faded away. It was stirred at room temperature for 3 h, then filtered through Celite, evaporated, and purified by trituration with Et_2O. A solution of the compound in hot THF was layered with hexane followed by cooling to −80 °C. The collected mass was 197 mg (68%), gray powder. ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ (ppm) 4.57 (m, 1H, isopropyl CH), 4.32 (m, 1H, isopropyl CH), 3.90 (m, 1H, H_{syn} *trans* to PEt_3), 3.63 (m, 1H, H_{syn} *trans* to dipdmiy), 2.63 (d, H_{anti} *trans* to PEt_3, J_{PHanti} = 9.5 Hz), 2.52 (s, 1H, H_{anti} *trans* to tmiy), 2.16 (s, 3H, carbene CH_3), 2.15 (s, 3H, carbene CH_3), 1.75 (s, 3H, crotyl CH_3), 1.63 (m, 6H, PCH_2), 1.43 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz), 1.37 (overlapped d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz), 1.32 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz), 1.28 (d, 3H, isopropyl CH_3, $^3J_{HH}$ = 7.0 Hz) 0.95 (m, 9H, PEt_3 CH_3). ^{13}C NMR (CD_2Cl_2, 125.03 MHz): δ (ppm) 172.21 (d, PdC, J_{PC} = 18.9 Hz), 134.99 (d, C_{meso}, J_{PCmeso} = 5.0 Hz), 127.96 (s, NC), 127.76 (s, NC), 66.47 (s, C_{term} *trans* to PEt_3, J_{PC} = 30.9 Hz), 61.34 (d, C_{term} *trans* to dipdmiy), 55.05(s, isopropyl CH), 54.59 (s, isopropyl CH), 24.19 (s, crotyl CH_3), 22.70 (s, isopropyl CH_3), 22.52 (s, isopropyl CH_3), 22.15 (s, isopropyl CH_3), 22.06 (s, isopropyl CH_3), 19.36 (d, PCH_2, J_{PC} = 24.9 Hz), 10.81 (s, carbene CH_3), 10.77 (s, carbene CH_3), 8.66 (s, PEt_3 CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 21.46. High-resolution ESI_{pos}-MS (MeCN): found 457.2110 (calcd 457.2126 dev: −3.5 ppm). Anal. Calcd for $C_{21}H_{42}N_2PPdBF_4$ (MW = 546.21): C, 46.13; H, 7.74; N, 5.12; P, 5.66. Found: C, 45.99; H, 7.76; N, 4.97; P, 5.66.

Tricyclohexylphosphinepalladium Allyl Iodide, 4g. Tricyclohexylphosphinepalladium allyl chloride (**1a**; 144 mg, 0.31 mmol, 1.0 equiv) and sodium iodide (466 mg, 3.11 mmol, 10 equiv) were suspended in 5 mL of DCM for 18 h. The reaction mixture was filtered through Celite and evaporated, and the residue was triturated in hexane to afford the title compound as a yellow powder (112 mg 65%). This compound was reported in a patent but no analytical data were given.[107] ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.16 (m, 1H, H_{meso}), 4.53 (m, 1H, H_{syn} *trans* to PCy_3, 3.91 (m, 1H, H_{syn} *trans* to I), 3.12 (dd, 1H, H_{anti} trans to PCy_3, $^3J_{HantiHmeso}$ = 13.5 Hz, J_{PHanti} = 9.0 Hz), 2.75 (d, 1H, H_{anti} *trans* to I, $^3J_{HantiHmeso}$ = 12.3 Hz), 2.15 (m, 3H, PCH), 1.13−1.87 (m, 30H, PCy_3 cyclohexyl). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 115.27 (d, C_{meso}, J_{PC} = 5.0 Hz), 75.66 (d, C_{term} *trans* to PCy_3, J_{PC} = 29.9 Hz), 60.64 (d, C_{term} trans to I, J_{PC} = 2.0 Hz), 36.01 (d, PCH, J_{PC} = 18.9 Hz), 30.87 (s, CH_2), 28.10 (d, CH_2, J_{PC} = 3.0 Hz), 28.01 (d, CH_2, J_{PC} = 3.0 Hz), 26.93 (s, CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.46 MHz, 298 K): δ (ppm) 39.68. High-resolution ESI_{pos}-MS (MeCN): $[M - I + MeCN]^+$ found 466.1994 (calcd 466.2017, dev: −4.9 ppm). Anal. Calcd for $C_{21}H_{38}PPdI$ (MW = 554.82): C, 45.46; H, 6.90; P, 5.58. Found: C, 45.21; H, 6.85; P, 5.86.

Tricycloxexylphosphine Acetonitrilepalladium Allyl Tetrafluoroborate, 7a. $AgBF_4$ (42 mg, 0.22 mmol, 1 equiv) and [Pd(η^3-C_3H_5)(Cl)(PCy_3)] (**1a**; 100 mg, 0.22 mmol, 1 equiv) were stirred in dry acetonitrile (5 mL) under argon for 1 h. The suspension was then filtered through Celite, and the filtrate was concentrated to about 1 mL by evaporation. Dry Et_2O was then added to precipitate the product, and the resulting powder was dried under vacuum. The collected mass was 111 mg (91%). ^{1}H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ (ppm) 5.51 (m, 1H, H_{meso}), 4.95 (m, 1H, H_{syn} *trans* to PCy_3), 3.70 (dd, 1H, H_{anti} *trans* to PCy_3, $^3J_{HantiHmeso}$ = 14.4 Hz, J_{PHanti} = 8.4 Hz), 3.48 (m, 1H, H_{syn} *trans* to MeCN), 2.69 (d, 1H, H_{anti} *trans* to MeCN, $^3J_{HantiHmeso}$ = 11.8 Hz), 2.34 (s, 3H, MeCN), 1.86−1.96 (m, 3H, PCH), 1.12−1.85 (m, 30H, PCy_3 cyclohexyl). ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K): δ (ppm) 120.51 (bs, C_{meso}), 84.71 (d, C_{term} *trans* to PCy_3, J_{PC} = 21.9 Hz), 52.36 (s, C_{term} *trans* to MeCN), 35.32 (d,, PCH, J_{PC} = 18.9 Hz), 30.85(s, CH_2), 30.70 (s, CH_2), 28.07 (d, CH_2, J_{PC} = 2.0 Hz), 27.99 (d, CH_2, J_{PC} = 2.0 Hz), 26.72 (s, CH_2), 3.57 (s, MeCN CH_3). The signal for the carbon atom of CN in acetonitrile was not seen.

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Supporting Information Available: Tables of X-ray data collection information, atom coordinates and thermal parameters, bond lengths and angles, together with CIF data, for **2a**, **2b**, **3a**, **4a**−**e**, **4g**, **5a**−**c**, **6b**, **6d**, and **7a**. NOESY and HSQC spectra and summary tables for **5b**, **5c**, and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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