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Synthesis, Structures, and Solution Dynamics of Palladium Complexes of Quinoline-Functionalized N-Heterocyclic Carbenes

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A new type of quinoline-functionalized palladium N-heterocyclic carbene (NHC) complexes has been synthesized via silver transmetallation. The quinoline moiety was either directly attached to the imidazole ring or linked to it by a methylene group. NHCs with a methylene linker tend to form *trans* biscarbene complexes in the reaction of $Pd(COD)Cl_2$, while NHCs without any linker form chelating NHC-quinoline (NHC-N) complexes. These two types of carbenes also react with $[Pd(allyl)Cl]_2$ to give monodentate NHC palladium η^3-allyl chlorides [Pd(NHC)(allyl)Cl]. Fluxionality in the NMR time scale was observed for most complexes, and the origin of their dynamic behaviors was discussed for each type of structure. For [Pd(NHC)(allyl)Cl] with a relatively small wing tip group of the NHC, the fluxionality (selective line-broadening of ^{1}H NMR signals) is caused by selective η^3-η^1-η^3 allyl isomerization. For NHC with a bulkier ^{t}Bu group, a different line-broadening pattern was observed and was ascribed to partially hindered $Pd-C_{carbene}$ bond rotation. For cationic chelating complexes $[Pd(NHC\text{-}N)(allyl)]BF_4$, the dynamic exchange process likely originates from a dissociative boat-to-boat inversion of 7-membered palladacycles. Activation parameters were measured for this process. Crystal structures were reported for representative complexes in each category.

Introduction

N-Heterocyclic carbenes (NHCs) have been playing an important role as ligands in organometallic chemistry and in catalysis ever since their isolation in the free state by Arduengo and coworkers in 1991.[1] NHCs are known to have higher donor abilities than most of the phosphine ligands, and they tend to be less labile with the formation of strong metal-NHC bonds.[2−4] It is well recognized that replacement of phosphines can often provide enhanced catalytic activity and thermal stability.[2,5] While ligand lability is a key factor in the function of many efficient catalysts that rely on ligand dissociation in the catalytic cycle, this lability might also provide a route of catalyst decomposition. Hemilabile NHC ligands featuring labile donors and an NHC moiety have the advantages of both the strongly binding NHC ligands and the more labile heteroatoms. The chelation effect imparted on the metals offered extra stability desirable for the design of catalysts with both high stability and activity.[6−9] Reported examples of such complexes include those containing NHC-amine or NHC-imine,[8−12] NHC-alkoxyl/phenoxyl,[13] NHC-thioether,[14,15] and NHC-phosphine ligands.[9d,15−18] Applications of metal complexes with mixed donors are still limited, although examples have been reported in asymmetric hydrogenation,[11] transfer hydrogenation,[13b] hydrosilation,[13f]

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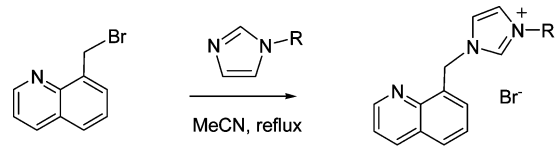
Heck-type reactions,[8,9a,17d] and olefin metathesis.[13d,19] Therefore, much effort has been devoted to the synthesis of complexes with functionalized NHC ligands.

Palladium complexes of N-heterocyclic carbenes have been widely used in catalysis owing to their easy accessibility, high thermal stability, and remarkable catalytic activities in various C−C coupling reactions.[2,5] Palladium complexes with mixed-donor ligands such as NHC-P or NHC-N ligands often show an increased catalytic activity. Examples of palladium complexes with NHC-nitrogen donor ligands are still limited although pyridine functionalized bidentate or multidentate NHC ligands have been frequently used.[8,20] We are interested in the functionalization of NHC ligands with new nitrogen donors and here we report the synthesis, structures, and solution dynamics of palladium complexes with new quinoline-tethered NHC ligands (NHCN).

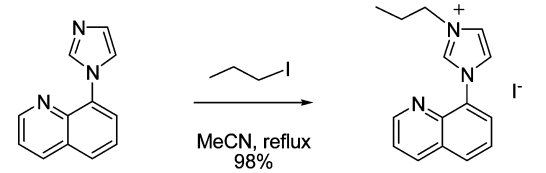
Results and Discussions

Ligand Synthesis. Imidazolium salts **1a-d** with a (8-quinolinyl)methyl group were synthesized with high yields by the quaternization of 8-(bromomethyl)quinoline with substituted imidazoles in MeCN (eq 1). Imidazolium salt **3** without any linker was synthesized by the quaternization of **2** using an excess amount of 1-iodopropane (eq 2). This quaternization is highly selective, and compound **3** was obtained as the only product. The quinoline nitrogen remained unalkylated on the basis of ^{1}H NMR spectroscopy ($CDCl_3$), and a low field signal at δ 10.40 (s, 1H) was assigned to the C(2)-*H* of **3**. The difference in the reactivity of the two nitrogen atoms likely originates from a combination of electronic and steric effects, with the imidazole nitrogen favored for both reasons.[20d]



(1)

1a: R = Mes, **1b**: R = ^{n}Bu
1c: R = ^{t}Bu, **1d**: R = ^{i}Pr



(2)

2 **3**

Neutral Palladium NHC Dichlorides. Compounds **1a-d** and **3** are precursors to NHCs, and their palladium complexes were synthesized using the silver transmetallation method.[21] Stirring of a mixture of **1a-d** and Ag_2O in CH_2Cl_2 gave a clear solution of silver carbene complexes **4a-d**, which were isolated with yields ranging from 84 to 92% (eq 3). Addition of an equal molar amount of $Pd(COD)Cl_2$ to a CH_2Cl_2 solution of **4b** immediately afforded a precipitate. NMR analysis showed that only half of the $Pd(COD)Cl_2$ was consumed, and hence, the ratio of the NHC to Pd is likely 2:1 in the product.[12] This stoichiometry was indeed confirmed by Electrospray Ionization mass spectrometry (ESI-MS), which also showed that the product was a mixture of palladium halides [$(NHC)_2PdCl_2$, $(NHC)_2PdClBr$, and $(NHC)_2PdBr_2$], instead of simply $(NHC)_2PdCl_2$. ^{1}H NMR spectroscopy also showed various overlapping peaks contributed from different halides. Although halide scrambling has been noted in the synthesis of rhodium and iridium NHC complexes via silver transmetallation,[22] there are few reports on halide scrambling in the synthesis of palladium NHC halide complexes. Therefore, it seemed advisable to use the same halide during the transmetallation. On the basis of these results, we optimized the conditions by using the silver carbene chloride to avoid any halide exchange (Scheme 1). Furthermore, the ratio of the silver carbene chloride and $Pd(COD)Cl_2$ was adjusted to 2:1. Thus palladium complexes **5b** and **5d** were synthesized, which could also be obtained from $Pd(MeCN)_2Cl_2$ or $Pd(PhCN)_2Cl_2$ in similar yields.

X-ray quality crystals of **5b** were obtained by slow diffusion of Et_2O into its CH_2Cl_2 solution. X-ray crystallographic analysis of **5b** revealed its *trans* square planar geometry of the palladium center

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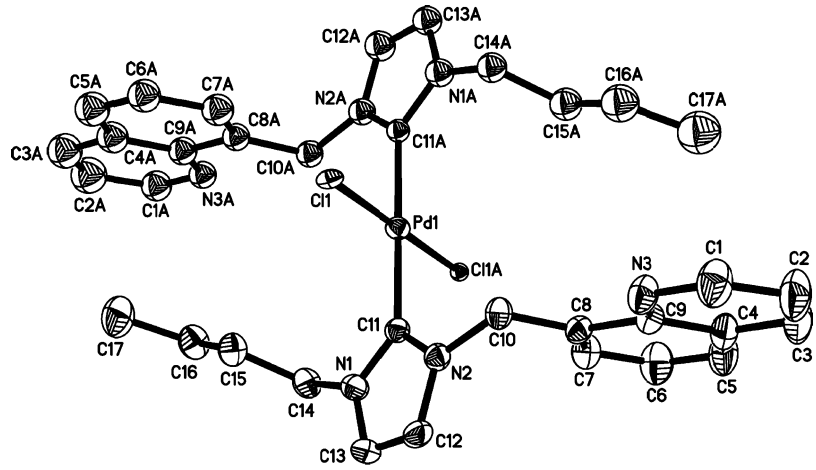
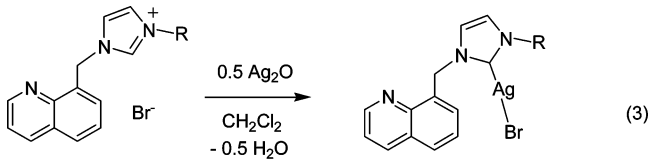


Figure 1. Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagram of the molecular structure of complex **5b** at 50% probability level. Selected lengths (Å) and angles (deg): Pd(1)−C(11) 2.020(4), Pd(1)−Cl(1) 2.3744(8), C(11)−Pd(1)−C(11A) 180.0(3), Cl(1)−Pd(1)−Cl(1A) 180.00(6), C(11)−Pd(1)−Cl(1) 90.71(12). Temperature 173(2) K, $F(000) = 728$, monoclinic, space group $P2(1)/n$, $a = 12.1693(5)$ Å, $b = 8.4018(4)$ Å, $c = 16.8050(7)$ Å, $\alpha = 90°$, $\beta = 106.463(3)°$, $\gamma = 90°$, $V = 1647.77(12)$ Å^3, $Z = 2$, $d = 1.427$ Mg/m^3, $\mu = 0.758$ mm^{-1}, Goodness-of-fit on $F^2 = 1.074$.



1a-d **4a**: R = Mes, **4b**: R = ^{n}Bu, **4c**: R = ^{t}Bu, **4d**: R = ^{i}Pr

(Figure 1). Complex **5b** is C_i symmetrical in the solid state, and the two imdazole rings are essentially perpendicular to the Pd coordination plane, giving an *anti* conformer. The Pd-carbene distances [2.020(4) Å] agree well with the distances found for similar biscarbene Pd complexes.[8a,9b,12,23]

Information on the solution structure of **5b** was obtained from the solution NMR spectra. Here two sets of signals were observed in the ^{1}H NMR spectrum with 1.0 to 0.97 ratio in $CDCl_3$. The presence of two sets of peaks was also evident in the ^{13}C NMR spectrum (acetone-d_6) with two characteristic Pd−$C_{carbene}$ signals (δ 171.6 and 171.3). In either set the methylene protons are equivalent and resonate as a singlet in the ^{1}H NMR spectrum, indicating that the imidazole plane represents a plane of symmetry on the time average. It follows that there is free rotation about the C(7)−C(10) bond to the quinoline substituent. While one set of signals is explained by the approximately C_{2h} symmetrical structure in solution evident from the X-ray analysis (anti conformer), the second set is attributed to the presence of a C_{2v} symmetrical isomer (syn conformer). Hence, the barrier of rotation about the Pd−$C_{carbene}$ bond must be high in the NMR time scale. Actually, while all lines are sharp at ambient temperature, they are broadened (but not coalesced) at 50 °C, so that a slow exchange between the anti and syn conformers proceeds by the Pd−$C_{carbene}$ rotation. The presence of any *cis*-$(NHC)_2PdCl_2$ structure is unlikely since here the methylene protons should be diastereotopic as long as the NHC planes are perpendicular to the coordination plane, a reasonable assumption based on closely related reports.[7,12] Similar spectra were also observed for **5d** (R = ^{i}Pr).

Compound **3** can also react as a carbene precursor with Ag_2O and complex **6** was isolated in 88% yield. When Pd(COD)Cl_2 was treated with 1 equiv of **6** in CH_2Cl_2, the COD ligand was easily displaced by the carbene to afford cis-(NHC)$PdCl_2$ (**7**) in 77% yield, bearing a chelating NHC-quinoline ligand (Scheme 2). It should be noted that in this reaction, maintaining the *cis*-$PdCl_2$ entity, no halide exchange was observed. In the ^{13}C NMR spectrum of **7**, the carbene resonates at δ 149.2 and is thus more shielded than in complexes **5b** and **5d**. Treatment of **7** with 2 equiv of $AgBF_4$ in CH_3CN resulted in the formation of complex **8** in quantitative yield. In the ^{1}H and ^{13}C NMR spectra of **8** (CD_3CN), the signal of free CH_3CN [δ 1.90 (^{1}H) and 1.76 (^{13}C)] was found with the expected intensity, indicating exchange between the CH_3CN ligands and the CD_3CN solvent.

Cationic Palladium NHC-Qinoline Complexes. Complexes with chelating NHC-N ligands can be obtained by chloride abstraction of **5b** using 2 equiv of $AgPF_6$ in MeCN (eq 4). Dicationic palladium complex **9b** was obtained in 98% yield and was spectroscopically and crystallographically characterized. There is only one set of peaks in the ^{1}H NMR spectrum. The methylene linker protons are diasterotopic ($^2J_{HH} = 15.6$ Hz) and so are all methylene protons in the N−CH_2CH_2CH_2Me unit, indicating that the imidazole ring is no longer a plane of symmetry. X-ray crystallography further confirmed the identity of the C_i symmetrical **9b** (Figure 2). Each palladacycle adopts a rather unusual rigid seven-membered "boat-type" conformation. In each ring the square planar palladium (ideally 90°) and a tetrahedral C atom (ideally 109.5°) are connected via two links with two and three sp^2 hybridized atoms (ideally 120°). Because the adjacent sp^2 centers in the quinoline moiety are forced to be coplanar with their substituents, the palladacycle consists of two almost planar parts joined at the square planar palladium and the sp^3-hydridized C atom. This rigid boat-type conformation is the only one the ring can attain. While the individual palladacycle is chiral, a *meso* structure is obtained for the whole complex because of the C_i point group symmetry. Indicative of some ring strain, the two aromatic rings in the quinoline moiety are slightly twisted, and the palladium atom is not positioned exactly along the C(11)−N(3)−C(15) bisector, but it is oriented away from the NHC

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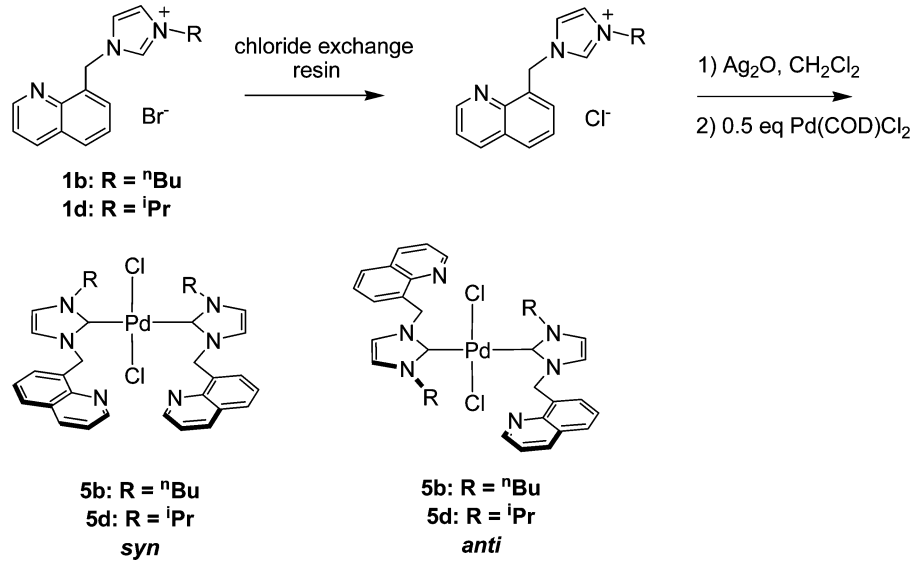
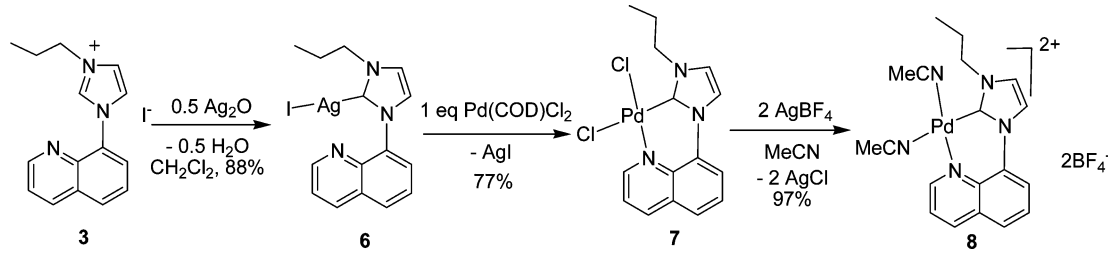
Scheme 1



Scheme 2



unit. Related 7-membered NHC-containing metallacycles have been reported for palladium and iridium.[24] Obviously, despite the supporting chelation effect, the resulting palladacycle is only formed in the absence of coordinating chloride ions which would compete for a coordination site during the formation of complex **5b**.

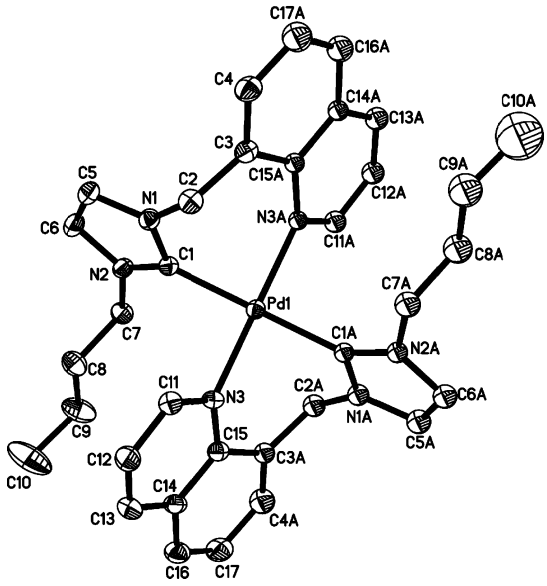
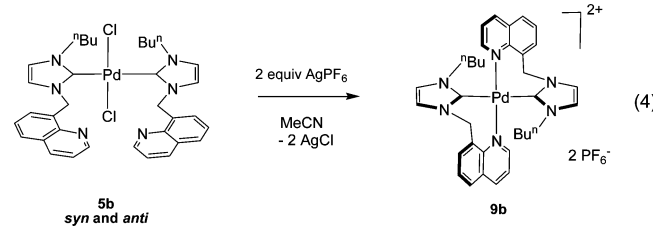


Figure 2. ORTEP diagram of the molecular structure of complex **9b** (cation only) at 50% probability level. Selected lengths (Å) and angles (deg): Pd(1)−C(1) 2.016(2), Pd(1)−N(3) 2.0634(19), N(3A)−Pd(1)−N(3) 180.000(1), C(1)−Pd(1)−C(1A) 180.000(1), N(1)−C(1)−N(2) 105.66(19), N(1)−C(1)−Pd(1) 118.71(16). Temperature 173(2) K, $F(000) = 468$, triclinic, space group $P\bar{1}$, $a = 10.0533(4)$ Å, $b = 10.6877(8)$ Å, $c = 10.7290(5)$ Å, $\alpha = 108.459(3)°$, $\beta = 108.014(2)°$, $\gamma = 107.082(2)°$, $V = 936.75(9)$ Å^3, $Z = 1$, $d = 1.643$ Mg/m^3, $\mu = 0.676$ mm^{-1}, Goodness-of-fit on $F^2 = 1.108$.



Synthesis and Molecular Structures of Neutral Palladium NHC η^3-Allyl Complexes. Imidazolium salts **1a-d** and **3** were also successfully applied as the carbene precursors for the synthesis of (NHC)Pd(η^3-allyl)Cl complexes using the silver transmetallation method (Scheme 3). Silver carbene complexes **4a-c** rapidly reacted with 0.5 equiv of [Pd(η^3-allyl)Cl]$_2$ in CH_2Cl_2 to give the Pd(NHC)(allyl)Cl complexes **10a-c**. Complex **12** was also synthesized by the same method (Scheme 3) and no halide scrambling was observed.

X-ray crystallography unambiguously confirmed the structures of complexes **10a** (Figure 3) and **10c** (Figure 4). For **10c**, two molecules with pseudo-enantiomeric relation co-crystallized, and only one of them is shown and discussed. The torsion angle defined by the Cl−Pd−$C_{carbene}$−N^{t}Bu is

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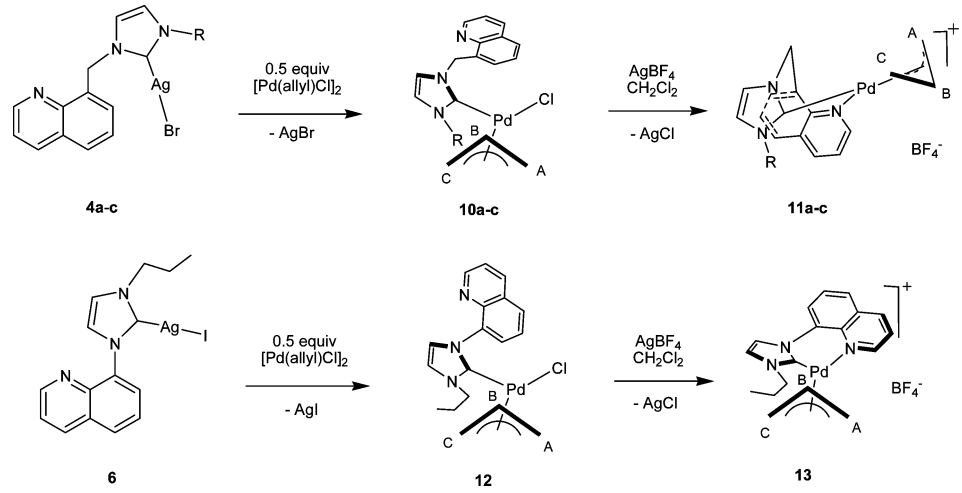
Scheme 3



72.37 for one molecule and 82.02° for the other (see the Supporting Information for the CIF file of **10c**). The Pd−$C_{carbene}$ distances in **10a** [2.054(5) Å] and **10c** [2.069(4) Å] are similar. The trihapticity of the allyl group follows from the three Pd−C(allyl) distances ranging from 2.116(6) to 2.202(5) Å for **10a** and from 2.121(5) to 2.198(5) Å for **10c**. The Pd(1)−C(3) bond in **10a** and the Pd(1)−C(3) bond in **10c** are slightly longer because of the imbalance of the donor strength of NHC and Cl, resulting in shortening of the Pd−C bond trans to Cl and lengthening of the bond *trans* to the NHC. In both structures C_B of the allyl group and the *tert*-Bu or Mes wing tip are oriented in an *anti* fashion with respect to the palladium coordination plane. Compared with palladium NHC allyl complexes with carbene possessing symmetric wing tips in the literature, the structures of **10a,c** are usual.[25,29]

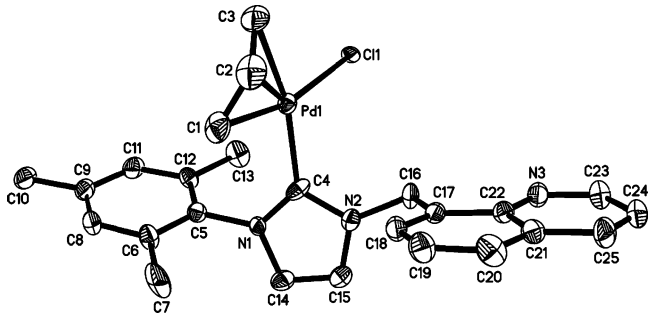


Figure 3. ORTEP diagram of the molecular structure of complex **10a** at 50% probability level. Selected lengths (Å) and angles (deg): Pd(1)−C(1) 2.116(6), Pd(1)−C(2) = 2.126(5), Pd(1)−C(3) = 2.202(5), Pd(1)−C(4) 2.054(5),Pd(1)−Cl(1)2.4163(10),N(1)−C(4)−Pd(1)129.7(3),N(2)−C(4)−Pd(1) 124.9(4). Temperature 173(2) K, $F(000) = 520$, monoclinic, space group $P2(1)$, $a = 7.9796(2)$ Å, $b = 12.7023(4)$ Å, $c = 11.7635(4)$ Å, $\alpha = 90°$, $\beta = 106.5800(10)°$, $\gamma = 90°$, $V = 1142.76(6)$ Å^3, $Z = 2$, $d = 1.483$ Mg/m^3, $\mu = 0.945$ mm^{-1}, Goodness-of-fit on $F^2 = 1.055$.

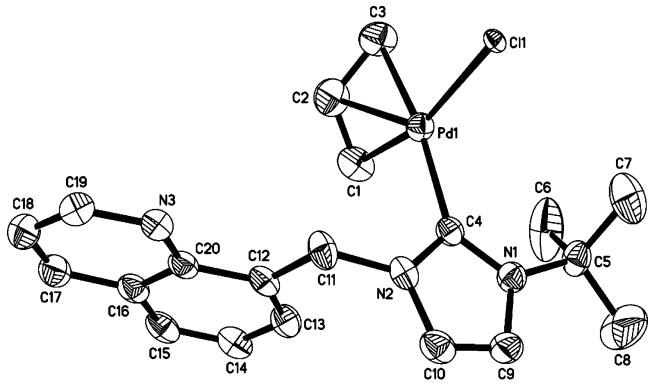


Figure 4. ORTEP diagram of the molecular structure of complex **10c** at 50% probability level. Selected lengths (Å) and angles (deg): Pd(1)−Cl(1) 2.4209(9), Pd(1)−C(1) 2.121(5), Pd(1)−C(2) 2.121(5), Pd(1)−C(3) 2.198(5), Pd(1)−C(4) 2.069(4), C(4)−Pd(1)−Cl(1) 98.59. Temperature 173(2) K, $F(000) = 912$, triclinic, space group $P\bar{1}$, $a = 11.3527(5)$ Å, $b = 11.5964(5)$ Å, $c = 17.1348(7)$ Å, $\alpha = 85.099(2)°$, $\beta = 77.932(2)°$, $\gamma = 63.716(2)°$, $V = 1977.81(15)$ Å^3, $Z = 4$, $d = 1.505$ Mg/m^3, $\mu = 1.080$ mm^{-1}, Goodness-of-fit on $F^2 = 1.062$.

Solution Dynamics of 10a,b. NMR spectroscopy shows that complexes **10a-c** all have fluxionality to different extents in the NMR time scale depending on the bulk of the R substituents (wing tip groups). The following common features were observed for the ^{1}H and ^{13}C spectra (room temperature, $CDCl_3$) of **10a** (R = Mes) and **10b** (R = ^{n}Bu): (1) there is simply one set of signals in both the ^{1}H and ^{13}C spectra; (2) the protons of the methylene linkers resonate as a singlet, which has been reported for other PdCl(allyl)(NHC) complexes;[25,26] and (3) three sharp signals and two broad signals are observed for the five allyl protons, with the broad signals attributed to the *syn* and *anti* protons at the allyl terminus trans to the chloride (C_c, see Scheme 3 for the labeling scheme and Table 1 for signal assignment). Exactly same pattern was also observed for complex **12** (see Figure 5 for the broadening of signals).

The broadening pattern of the allyl groups in complexes **10a,b** suggests that there is syn/anti exchange only between the protons on carbon C. This is consistent with a selective η^3 to η^1 rearrangement of the allyl ligand, possibly under electronic control. The η^1-allyl intermediate then undergoes C−C bond rotation followed by re-formation of the η^3 complex (Scheme 4). The fact that the CH_2 linker protons are equivalent in solution can be accounted for by this selective η^3 to η^1 rearrangement *together with* free Pd−$C_{carbene}$ rotation. If only the NHC ring rotates, the

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Table 1. ^{1}H and ^{13}C Characterization Data for Palladium Allyl Complexes ($CDCl_3$, 23 °C)

	allyl ^{1}H and ^{13}C										
complex	A_{syn}	A_{anti}	B	C_{syn}	C_{anti}	$^{13}C_A$	$^{13}C_B$	$^{13}C_C$	^{1}H (CH_2)	^{13}C (CH_2)	^{13}C (carbene)
10a	4.06	2.95	4.87	2.9 (br)	1.64 (br)	72.2	114.4	48.3	6.29	50.4	181.3
10b	4.26	3.24	5.24	3.30 (br)	2.23 (br)	72.7	114.6	48.1	6.07	51.0	179.6
10c (set a)	4.18	3.28	5.22	3.41	2.26	71.1[b]	113.8[b]	50.3	6.20, 6.30	58.1	179.0
10c (set b)	4.18	3.18	5.21	3.26 (br)	2.19	70.9[b]	113.4[b]	50.2	5.91, 6.53	58.0	178.7
11b[a]	4.48 (br)	3.73 (br)	5.84 (br)	3.70 (br)	2.89 (br)	78.1	119.3	46.2	6.88 (br)	52.4	174.8 (br)
11c (set a)	4.20	3.64	5.86	3.74	2.94	75.3[b]	118.9[b]	51.3[b]	[5.62 (endo) + 7.35 (exo)][b]	57.9[b]	173.8[b]
11c (set b)	4.42	3.55	5.70	3.91	2.83	74.7[b]	117.4[b]	50.7[b]	[5.40 (endo) + 7.00 (exo)][b]	54.1[b]	173.2[b]
12	4.07	2.98	4.83	2.67 (br)	1.51 (br)	71.6	114.3	49.0		52.8	180.7
13[c]	4.36	3.80	5.82	4.04	3.05	*d*	*d*	*d*		*d*	*d*
14[e]	4.22	3.65	5.69	3.93 (br)	2.94 (br)	76.6	121.5	48.2			174.6

[a] 55 °C. [b] Unable to assign to set a or set b. [c] In acetone-d_6. [d] Poor solubility in acetone for ^{13}C NMR analysis. [e] In CD_3CN.

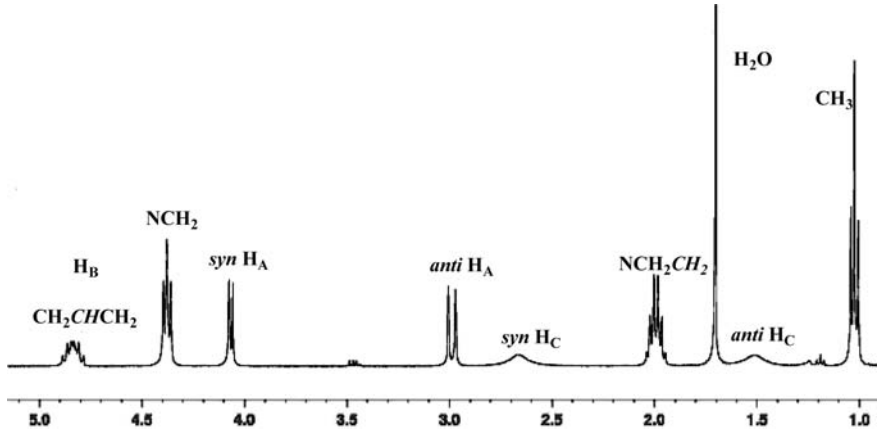
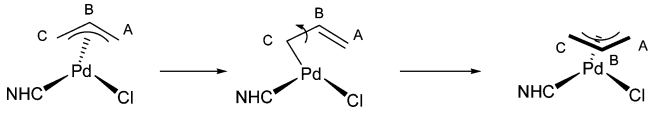


Figure 5. Part of the ^{1}H NMR spectrum of complex **12**.

Scheme 4



complex remains chiral and the CH_2 remain diastereotopic. However, the concurrent η^3-η^1-η^3 rearrangement process should lead to enantiomerization of this complex and to the equivalence of the CH_2 protons. This type of selective syn/anti exchange has been observed on many occasions and this process could be associative or dissociative in mechanism.[25−28] Pörschke recently reported selective line-broadening of allyl protons of Pd(allyl)(IPr)Cl [IPr = *N*,*N*-bis(2,6-diisopropylphenylimidazol-2-ylidene)] only in donor solvents such as THF, whereas no solvent dependence of the ^{1}H and ^{13}C NMR spectra was observed for Pd(allyl)(IPr)Me.[25] Here, the lability of the anionic ligand (Cl vs Me) plays an important role. Moreover, Albinati and Pregosin analyzed the selective syn/anti exchange of Pd(allyl)(IPr)Br using phase-sensitive ^{1}H NOESY spectroscopy and have concluded that the conversion is dissociative in CD_2Cl_2.[26] The rate constant of the allyl proton exchange was determined to be 0.8 ± 0.1 s^{-1} at 298 K, although all the allyl proton signals are seemingly sharp.[26]

Solution Dynamics of 10c. The solution dynamic behavior for **10c**, however, is different from that of **10a**,**b**. Both ^{1}H and ^{13}C NMR spectra at room temperature show two sets of peaks with a ratio of 1:1.13 ($CDCl_3$) based on proton signal integration. In either set of proton peaks, the linker CH_2 protons are diastereotopic. We note that while there are two independent molecules in the crystals comprising an enantiomeric pair, these are not distinguishable by solution NMR. However, solution NMR does show that two different C_1 symmetrical molecules are present, so they must have a different origin, most likely representing rotamers. These two rotamers are caused by hindered rotation of the NHC ligand about the Pd−$C_{carbene}$ bond, which puts the quinolinyl group of one rotamer closer to the syn proton at C_C (as in the molecule of the crystal), but away from it in the second rotamer. As a contrast, only the *syn* proton on C_C is broadened and this signal is attributed to the quinolinyl group in one isomer, but not in the other (Table 1). The selective broadening pattern here likely originates from a partially hindered rotation along the Pd−$C_{carbene}$ bond in this conformer, and only the chemical environment of this *syn* proton on C_C is more affected when the NHC ligand undergoes local motion.

Cationic Palladium NHC Allyl Complexes. The chloride complexes **10b-c** and **12** readily underwent halide abstraction with $AgBF_4$ to afford ionic complexes **11b-c** and **13**, respectively (Scheme 3). The isolated products were char-

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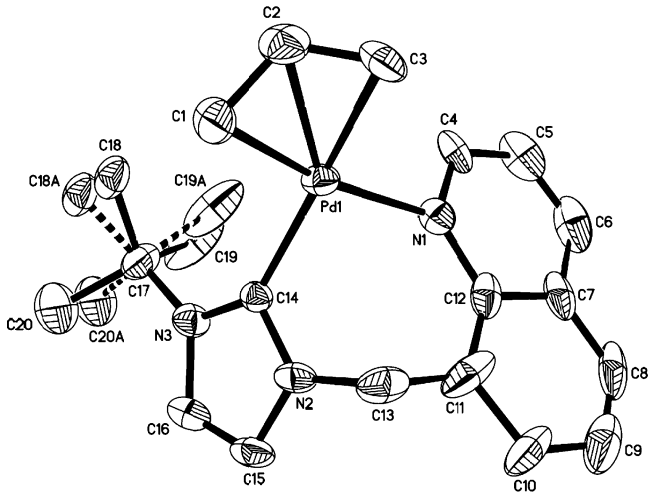

Figure 6. ORTEP diagram of the molecular structure of complex **11c** (cation only) at 50% probability level. Selected lengths (Å) and angles (deg): Pd(1)−C(14) 2.051(6), Pd(1)−N(1) 2.142(5), Pd(1)−C(1) 2.123(6), Pd(1)−C(2) 2.145(7), Pd(1)−C(3) 2.169(7), C(14)−Pd(1)−N(1) 88.8.(2), N(3)−C(14)−Pd(1) 142.0(5), N(2)−C(14)−Pd(1) 113.2(4). Temperature 173(2) K, $F(000) = 1008$, orthorhombic, space group $P2(1)2(1)2(1)$, $a = 10.9198(5)$ Å, $b = 12.8986(6)$ Å, $c = 14.6494(7)$ Å, $\alpha = \beta = \gamma = 90.0°$, $V = 2063.37(17)$ Å^3, $Z = 4$, $d = 1.608$ Mg/m^3, $\mu = 0.945$ mm^{-1}, Goodness-of-fit on $F^2 = 1.089$.

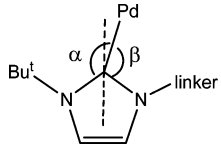

Figure 7. In-plane distortion of the carbene in complex **11c**.

acterized by elemental analysis and NMR spectroscopy, and furthermore the structure of complexes **11c** was confirmed by X-ray crystallography (Figure 6). The chelating NHC-N ligand and the η^3-allyl group make up the coordination sphere of the Pd(II). The Pd-NHC distance [2.024(4) Å] is in the normal range. The allyl ligand adopts an *endo* structure and the seven-membered palladacyle exhibits a rigid boat-type conformation analogous to that in **9b**. The Pd is in a plane with the NHC ring, and there is no out-of-plane distortion, with the summation of the three angles around $C_{carbene}$ being 360.0°. However, an in-plane distortion is quite obvious. This type of yaw distortion was recently described by Crabtree,[30] and the extent of distortion was defined by $\theta = 1/2(\alpha - \beta)$ (Figure 7). θ values ranging up to 15° have been observed for carbene complexes.[31] Here $\theta = 14.4°$ is close to the upper limit.

$CDCl_3$ solutions of **11b,c** show dynamic structures in the NMR time scale. For both complexes two sets of proton peaks in nearly 1:1 ratio were observed at ambient temperature (Table 1). The signals of **11b** showed significant line-broadening and poor resolution of virtually all signals. Coalescence of the allyl protons was achieved at 55 °C in the ^{1}H NMR spectrum (Table 1). ^{13}C{^{1}H} NMR spectrum of **11b** also showed two broad exchanging carbene signals (δ 174.9 and 174.3).

The dynamics of **11c** were studied in more detail. Here, the two sets of proton peaks were observed together with diasteretopic CH_2 linker protons in each conformer. They showed essentially no line-broadening at ambient temperature, but line-broadening occurred at elevated temperatures. Two sets of peaks were also observed in the ^{13}C NMR spectra. The identity of the solvents ($CDCl_3$, CD_2Cl_2, and DMSO-d_6) has no significant effect on the relative amounts of these two species. The lack of solvent effects suggests that the two species are probably not examples of κ^2-C,N (bidentate) versus κ^2-C (monodentate) isomers.[12] The five allyl protons and the methylene linker protons are all well resolved in ^{1}H NMR spectroscopy, and the kinetic parameters were measured by VT NMR line-width analysis. The Eyring plot gives $\Delta H^{\ddagger} = 19.0$ kcal/mol and $\Delta S^{\ddagger} = 3.2$ eu for this exchange process (average of two measurements, see the Supporting Information).

There are three possible mechanisms leading to the fluxionality in **11c** (Scheme 5). Path (1) is overall a boat-to-boat conversion of the palladacycle which will lead to an *anti* (set **a**) to *anti* (set **b**) exchange in the allyl group and also an exchange between endo (set **a**) and exo (set **b**) protons of the methylene linker. Path (2) involves the partially hindered π-allyl rotation with NHC-N ligand being a spectator.[32] This process will lead to an anti-anti exchange for the allyl protons but an *endo-endo* exchange for the methylene protons. Path (3) is the η^3-η^1-η^3 (π-σ-π) rearrangement process and will lead to an *syn-anti* exchange for the allyl protons together with an endo-endo exchange for the methylene protons.

The rotating-frame Overhauser enhancement spectroscopy (ROESY) spectrum of **11c** in $CDCl_3$ was obtained to elucidate the mechanism of this exchange. Correlations of signals (cross peaks) in ROESY can be exchange-derived (colored in red here) or Overhauser-derived (colored in black here) and they are distinguishable.[33] It clearly shows exchange-derived correlation of the *anti-anti* (and also *syn-syn* and *meso-meso*) allyl protons and also endo-exo exchange for the CH_2 linker protons in between these two sets of peaks (Figure 8 and Figure S4, Supporting Information). The conclusion that these exchanging signals are contributed by different molecules was safely drawn on the basis of the ^{1}H−^{1}H correlation spectroscopy (COSY) spectrum of **11c**. The fact that exchange between endo and exo protons of the CH_2 linker was observed suggests that pathways (2) and (3) are unlikely (see Figure S4, Supporting Information), therefore pathway (1) is the most likely mechanism. Modelling shows that this 7-membered metalacycle is highly rigid, and it is not very likely for it to undergo boat-to-boat ring flip with the 7-membered ring staying intact, although this type of ring flip has been known in 6-membered carbene

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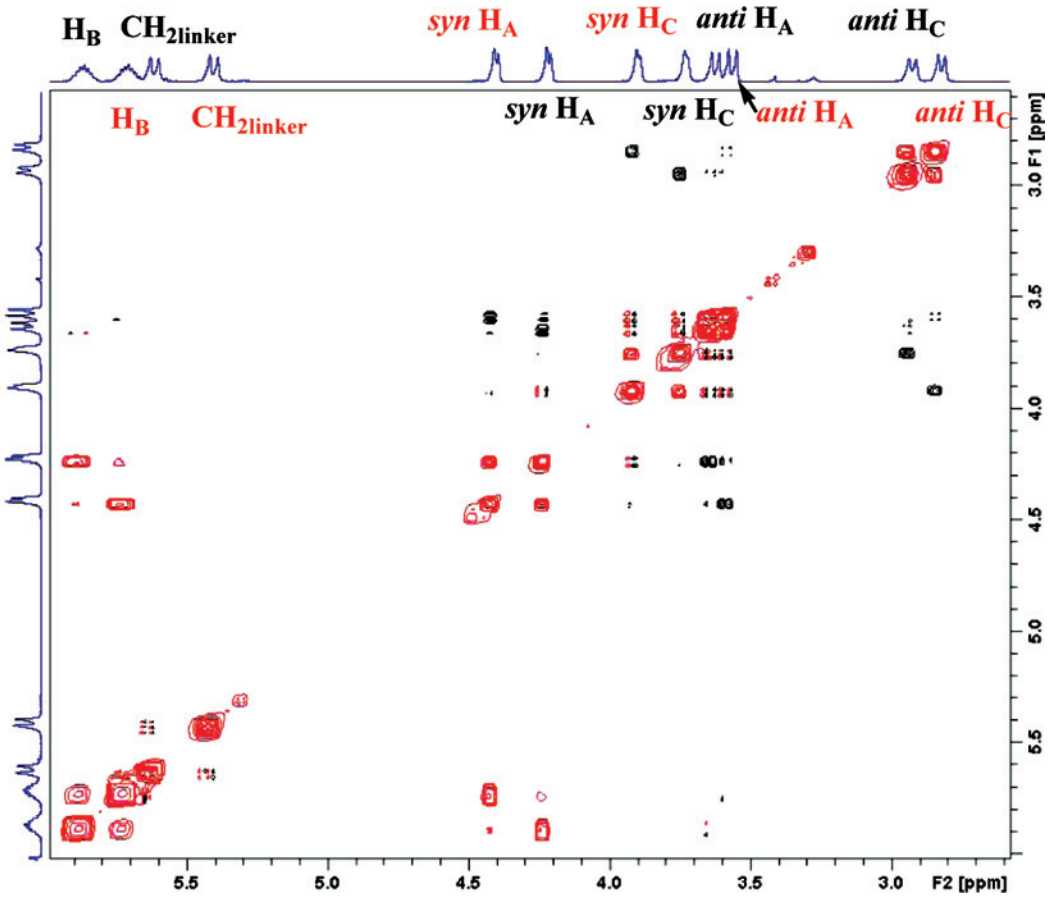
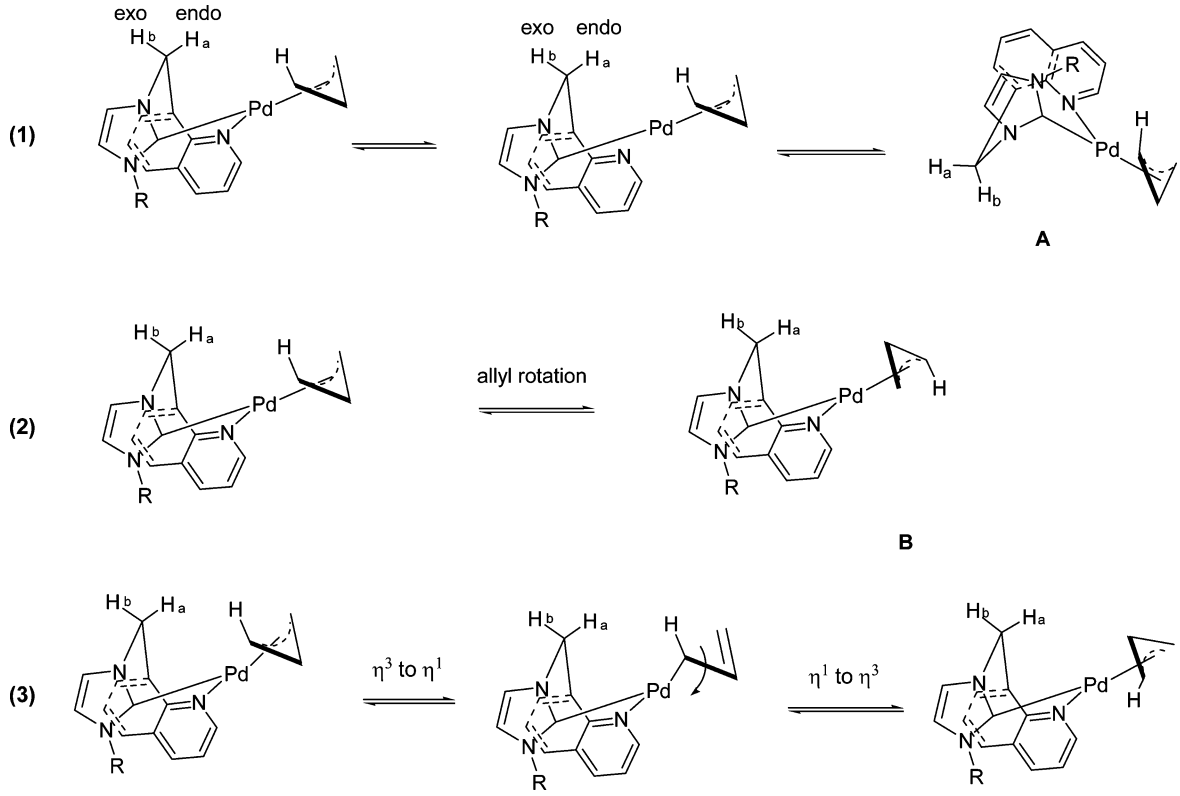


Figure 8. Part of the ROESY spectrum of **11c** in $CDCl_3$.

Scheme 5

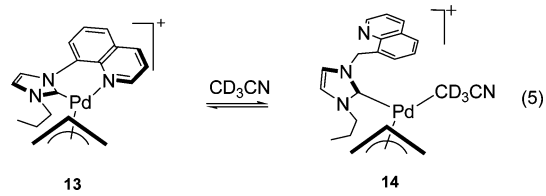


palladacycles.[10a,34−36] Instead, boat-to-boat conversion via the dissociation of the labile quinoline N atom seems more likely. A simple Pd−$C_{carbene}$ bond rotation is not likely here since the tethering effect of the quinoline nitrogen would

significantly raise the rotation barrier around the Pd−$C_{carbene}$ bond.

Complex **13** was synthesized by an analogous method (Scheme 3). The BF_4 salt is insoluble in chloroform, but it is sparingly soluble in acetone-d_6, where it shows well-resolved allyl proton signals with no indication of line-broadening at ambient temperature, in agreement with a stable chelate coordination of the NHC-quinoline ligand. No ^{13}C NMR spectrum could be obtained for **13** in either acetone-d_6 or CD_2Cl_2 because of poor solubility.

Complex **13** is much better soluble in acetonitrile and here the NMR spectra are significantly different. The ambient temperature ^1H NMR spectrum shows line-broadening for the syn and anti protons on C_C, reminiscent of the likewise monodentate complexes **10a-b** and **12** and suggesting that the species present in solution undergo selective η^3-η^1- allyl isomerization. In the ^{13}C NMR spectrum, in addition to the signal of solvent CD_3CN (δ 1.32, septet), a new signal is found (δ 1.18, septet) which is attributed to coordinated CD_3CN, so the exchange must be slow. We conclude that solvation of **13** with CD_3CN leads to the opening of the NHC-quinoline chelate ring so that the ligand becomes monodentate, affording the ionic complex **14** in solution (eq 5). Attempts to isolate **14** by removal of CH_3CN from the corresponding solutions have been unsuccessful, and only the starting material **13** was recovered, indicating that the κ^2(C,N) to κ^1(C) conversion is reversible.



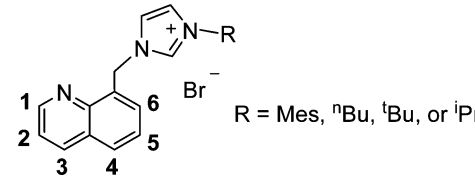
13 **14** (5)

Conclusions

We have described the synthesis a new type of neutral and cationic quinoline functionalized Pd NHC complexes via silver transmetallation. The quinoline moiety could be directly attached to the imidazole or linked by a methylene group. NHCs with a methylene linker tend to form *trans* biscarbene complexes with pendent quinoline groups in the reaction of $Pd(COD)Cl_2$, while NHCs without CH_2 linker form chelating palladium NHC-quinoline complexes. These two types of carbenes also react with $[Pd(allyl)Cl]_2$ to give monodentate NHC palladium η^3-allyl chlorides [Pd(NHC)(allyl)Cl]. Fluxionality in the NMR time scale was observed for most complexes, and the solution dynamics depend on the carbene wing tip and the coordination mode. For Pd(NHC)(allyl)Cl with a Mes or *n*-Bu wing tip, the fluxionality originates from selective η^3-η^1-η^3 rearrangement. While selective broadening was also observed for Pd(NHC)(allyl)Cl with a *tert*-Bu wing tip, the fluxionality is proposed to originate from the partially hindered Pd-carbene bond rotation. In cationic complex [Pd(NHC-N)(allyl)]BF_4, boat-to-boat conversion of the 7-membered ring via a dissociative mechanism is proposed as the mechanism of the solution dynamics on the basis of ROESY spectroscopy. Crystal structures were obtained for complexes in each category.

Experimental Section

General Descriptions. All the manipulations were performed under a positive flow of nitrogen although most of the products proved air stable. One-dimensional NMR spectra were recorded on a Bruker ACF 300 or a Bruker DPX 400 NMR spectrometer. ROESY spectrum was recorded on a Bruker AMX 500 NMR spectrometer. Unless otherwise indicated, NMR spectra were recorded at room temperature and were internally referenced relative to the residual protio-solvent (^1H) or the solvent (^{13}C). Chemical shifts were reported with respect to $\delta = 0$ for tetramethylsilane. Microanalyses were performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry, Nanyang Technological University. $Pd(PhCN)_2Cl_2$ and $[Pd(allyl)Cl]_2$ were purchased from the Strem Co. $Pd(COD)Cl_2$ was prepared following a published procedure.[37] Solvents and all remaining reagents were purchased from Aldrich and were used without further purification.



Synthesis of 8-(Bromomethyl)quinoline. 8-(Bromomethyl)quinoline was synthesized based on a literature report.[38] N-bromosuccinimide (2.94 g, 16.5 mmol) and benzoyl peroxide (182 mg, 0.752 mmol) were added to a cyclohexane solution (50 mL) of 8-methylquinoline (2.15 g, 15.0 mmol). The mixture was stirred under reflux and under light for 10 h. White precipitates were observed. The mixture was filtered, and the solution was washed with aq $NaHCO_3$ (2 × 8 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent gave a pale brown solid which was recrystallized from hot ethanol and water to give white crystals. Yield: 2.26 g (68%). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.02 (dd, 1H, $J = 3.9$ Hz and 1.5 Hz, N-$CH_{quinoline}$), 8.17 (dd, 1H, $J = 8.2$ and 1.4 Hz), 7.85−7.80 (m, 2H), 7.54−7.44 (m, 2H), 5.25 (s, 2H, CH_2). The NMR spectrum matches that in a literature report.[38]

General Procedure for Synthesis of Imidazolium Salts (1a−d). A substituted imidazole was added to a solution of 8-(bromomethyl)quinoline in acetonitrile. The solution was heated

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under reflux for 3−16 h. Removal of MeCN followed by addition of ether gave a solid or an oil, which was further washed with ether (2 × 5mL) and dried under vacuum.

Synthesis of 1a. 1-Mesitylimidazole (440 mg, 2.36 mmol) and 8-(bromomethyl)quinoline (500 mg, 2.25 mmol) were heated under reflux in MeCN (10 mL) for 16 h. A white solid was obtained following the workup, which was dried under vacuum to give an analytically pure white powder (912 mg, 99%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.40 (s, 1H, NCHN), 8.93 (dd, 1H, J = 4.2 and 1.5 Hz, H-1), 8.66 (d, 1H, J = 6.9 Hz), 8.22 (dd, 1H, J = 8.2 and 1.5 Hz, H-3), 8.16 (s, 1H, CH $_{imidazole}$), 7.89 (d, 1H, J = 8.0 Hz), 7.61 (t, 1H, J = 7.4 Hz, H-5), 7.50 (dd, 1H, J = 8.3 and 4.2 Hz, H-2), 6.99 (s, 1H, CH $_{imidazole}$), 6.95 (s, 2H, 2CH $_{mesityl}$), 6.53 (s, 2H, CH_2 $_{linker}$), 2.30 (s, 3H, CH_3 $_{mesityl}$), 1.98 (s, 6H, CH_3 $_{mesityl}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 150.2 (N−C $_{quinoline}$), 146.3 (N-CH $_{quinoline}$), 141.2, 138.0, 136.8, 134.3, 133.1, 131.7, 130.8, 130.0, 129.8, 128.5, 127.2, 124.1, 122.2 (imidazole), 121.7 (imidazole), 49.2 (CH_2 $_{linker}$), 21.1 (CH_3), 17.6 ($2CH_3$). Anal. Calc for $C_{22}H_{22}N_3Br$ (408.33): C, 64.71; H, 5.43; N, 10.29. Found: C, 64.46; H, 5.32; N, 10.37.

Synthesis of 1b. 1-*n*-Butylimidazole (409 mg, 3.30 mmol) and 8-(bromomethyl)quinoline (666 mg, 3.00 mmol) were heated under reflux in acetonitrile (10 mL) for 3 h. Product **1b** was obtained as an oil (1.00 g, 99%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.74 (s, 1H, NCHN), 8.98 (d, 1H, J = 2.8 Hz, H-**1**), 8.43 (d, 1H, J = 6.8 Hz), 8.21 (d, 1H, J = 8.1 Hz, H-**3**), 7.88 (d, 1H, J = 7.9 Hz), 7.78 (s, 1H, CH $_{imidazole}$), 7.60 (t, 1H, J = 7.6 Hz, H-**5**), 7.50 (dd, 1H, J = 8.1 and 4.2 Hz, H-**2**), 7.20 (s, 1H, CH $_{imidazole}$), 6.22 (s, 2H, CH_2 $_{linker}$), 4.28 (t, 2H, J = 7.4 Hz, NCH_2), 1.93−1.85 (m, 2H, NCH_2CH_2), 1.40−1.31 (m, 2H, $NCH_2CH_2CH_2$), 0.93 (t, 3H, J = 7.2 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 150.4 (N−C $_{quinoline}$), 146.1 (N-CH $_{quinoline}$), 137.4, 136.7, 132.5, 131.6, 130.0, 128.5, 127.0, 123.2, 121.8 (imidazole), 120.8 (imidazole), 49.8, 49.0 (CH_2 $_{linker}$), 32.1, 19.5, 13.4 (CH_3). Anal. Calcd for $C_{17}H_{20}N_3Br$ (346.26): C, 58.97; H, 5.82; N, 12.14. Found: C, 58.78; H, 5.72; N, 12.23. The chloride analogue of **1b** was obtained by chloride exchange between **1b** and Dowex®21K chloride exchange resin in methanol for 12 h.[22] ^{1}H NMR spectra of the chloride and the bromide salts are nearly the same except for slight difference of the resonance of the imidazolium C(2)-*H*.

Synthesis of 1c. 1-*tert*-Butylimidazole (273 mg, 2.20 mmol) and 8-(bromomethyl)quinoline (444 mg, 2.00 mmol) in acetonitrile (10 mL) were heated under reflux in MeCN (10 mL) for 3 h. **1c** was obtained as a white solid (680 mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.88 (s, 1H, NCHN), 8.97−8.95 (m, 1H, H-**1**), 8.60 (d, 1H, J = 6.9 Hz), 8.21 (d, 1H, J = 8.2 Hz, H-**3**), 7.88−7.86 (m, 2H, CH $_{imidazole}$+ CH $_{quinoline}$), 7.62 (t, 1H, J = 7.5 Hz, H-**5**), 7.50 (dd, 1H, J = 8.2 and 4.2 Hz, H-**2**), 7.29 (s, 1H, CH $_{imidazole}$), 6.31 (s, 2H, CH_2 $_{linker}$), 1.69 (s, 9H, $C(CH_3)_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 150.2 (N−C $_{quinoline}$), 146.0 (N-CH $_{quinoline}$), 136.6, 135.6, 132.7, 131.8, 129.7, 128.3, 126.9, 123.4, 121.6 (imidazole), 118.5 (imidazole), 60.1 ($C(CH_3)_3$), 48.5 (CH_2 $_{linker}$), 30.0 ($C(CH_3)_3$). Anal. Calcd for $C_{17}H_{20}N_3Br$ (346.26): C, 58.97; H, 5.82; N, 12.14. Found: C, 58.69; H, 5.94; N, 12.17.

Synthesis of 1d. 1-*iso*-Propylimidazole (363 mg, 3.30 mmol) and 8-(bromomethyl)quinoline (666 mg, 3.00 mmol) were heated under reflux in MeCN (10 mL) for 3 h. **1d** was obtained as a white solid (968 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.78 (s, 1H, NCHN), 8.96 (d, 1H, J = 4.0 Hz, H-**1**), 8.45 (d, 1H, J = 6.7 Hz), 8.20 (d, 1H, J = 8.0 Hz, H-**3**), 7.86 (d, 1H, J = 8.0 Hz), 7.80 (s, 1H, CH $_{imidazole}$), 7.58 (t, 1H, J = 7.2 Hz, H-**5**), 7.49 (dd, 1H, J = 8.2 and 4.2 Hz, H-**2**), 7.37 (s, 1H, CH $_{imidazole}$), 6.22 (s, 2H, CH_2 $_{linker}$), 4.82−4.78 (m, 1H, $CH(CH_3)_2$), 1.58 (d, 6H, J = 6.6 Hz, $2CH_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 150.3 (N−C $_{quinoline}$), 145.9 (N-CH $_{quinoline}$), 136.6, 135.8, 132.2, 131.6, 129.8, 128.3, 126.7, 123.2, 121.7 (imidazole), 119.4 (imidazole), 53.0 ($CH(CH_3)_2$), 48.6 (CH_2 $_{linker}$), 23.0 ($CH(CH_3)_2$). Anal. Calcd for $C_{16}H_{18}N_3Br$ (332.24): C, 57.84; H, 5.46; N, 12.65. Found: C, 57.50; H, 5.62; N, 12.77. The chloride analogue of **1d** was obtained by chloride exchange between **1d** and Dowex 21K chloride exchange resin in methanol for 12 h.[22] ^{1}H NMR spectra of the chloride and the bromide salts are nearly the same except for the resonance of the C(2)-*H* of the imidazolium.

Synthesis of Imidazole 2. Imidazole **2** was synthesized based on a literature report.[39] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.98 (dd, 1H, J = 5.6 and 2.3 Hz), 8.25 (dd, 1H, J = 11.1 and 2.3 Hz), 8.11 (s, 1H), 7.86 (dd, 1H, J = 10.8 and 2.0 Hz), 7.70 (dd, 1H, J = 9.9 and 2.0 Hz), 7.64−7.49 (m, 3H), 7.28 (s, 1H). The NMR spectrum of **2** matches that in a report.[39]

Synthesis of 3. Compound **2** (302 mg, 1.55 mmol) and 1-iodopropane (1.05 g, 6.18 mmol) were dissolved in acetonitrile (10 mL). The solution was heated under reflux for 24 h. All the volatiles were removed under reduced pressure, and dichloromethane (1 mL) was added to dissolve the residue. Diethyl ether (10 mL) was then added to the solution to give a yellow solid, which was filtered and washed with diethyl ether to give analytically pure **3** (556 mg, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.40 (s, 1H, NCHN), 8.99 (dd, 1H, J = 4.2 and 1.7 Hz, N-CH $_{quinoline}$), 8.43 (dd, 1H, J = 7.5 and 1.1 Hz), 8.37 (dd, 1H, J = 8.4 and 1.8 Hz), 8.09 (dd, 1H, J = 8.3 and 1.1 Hz), 7.98 (t, 1H, J =1.7 Hz, CH $_{imidazole}$), 7.81−7.75 (m, 1H), 7.67−7.59 (m, 2H, CH $_{imidazole}$+ CH $_{quinoline}$), 4.64 (t, 2H, J = 7.3 Hz, NCH_2), 2.19−2.09 (m, 2H, NCH_2CH_2), 1.12 (t, 3H, J = 7.4 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 151.8 (N-CH $_{quinoline}$), 140.7 (N−C $_{quinoline}$), 137.4, 136.8, 131.0, 130.8, 129.3, 126.8, 126.1, 124.4, 122.9, 121.5, 52.1(NCH_2), 23.7 (NCH_2CH_2), 10.8 (CH_3). Anal. Calcd for $C_{15}H_{16}IN_3$ (365.21): C, 49.33; H, 4.42; N, 11.51. Found: C, 49.21; H, 4.32; N, 11.67.

General Procedure for Synthesis of Silver Complexes 4a−d. Ag_2O was added to a CH_2Cl_2 solution of imidazolium salts, and the mixture was stirred for half an hour in the dark to essentially give a solution. If necessary, the mixture was then filtered to remove a small amount of insolubles. Removal of the solvent gave a white foamy solid. Occasionally, a loose solid could be obtained when further washed with ether.

Synthesis of Complex 4a. Ag_2O (86 mg, 0.37 mmol) was added to a CH_2Cl_2 solution of imidazolium **1a** (275 mg, 0.674 mmol). Compound **4a** was obtained as an analytically pure product (307 mg, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.98 (d, 1H, J = 2.5 Hz, H-**1**), 8.23 (dd, 1H, J = 8.3 and 1.7 Hz, H-**3**), 7.88 (d, 1H, J = 7.6 Hz), 7.78 (d, 1H, J = 5.6 Hz), 7.60−7.49 (m, 3H), 6.94 (s, 2H, 2CH $_{mesityl}$), 6.87 (d, 1H, J = 1.6 Hz, CH $_{imidazole}$), 6.00 (s, 2H, CH_2 $_{linker}$), 2.28 (s, 3H), 1.90 (s, 6H, $2CH_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 182.6 (carbene), 150.4, 146.0, 139.4, 136.4, 135.5, 134.7, 134.2, 129.8, 129.4, 129.1, 128.5, 126.6, 122.3, 122.1, 121.8, 51.6 (CH_2 $_{linker}$), 21.1 (CH_3), 17.8 ($2CH_3$). Anal. Calcd for $C_{22}H_{21}AgBrN_3$ (515.19): C, 51.29; H, 4.11; N, 8.16. Found: C, 51.01; H, 4.28; N, 8.05.

Synthesis of Complex 4b. Ag_2O (193 mg, 0.833 mmol) was added to a CH_2Cl_2 solution of **1b** (524 mg, 1.51 mmol). Compound **4b** was obtained as an analytically pure product (576 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.06 (d, 1H, J = 2.9 Hz, H-**1**), 8.20 (d, 1H, J = 8.3 Hz), 7.86 (d, 1H, J = 8.3 Hz), 7.78 (d, 1H, J = 7.0 Hz), 7.54 (t, 1H, J = 7.4 Hz, H-**5**), 7.48 (dd, 1H, J = 8.2 and 4.2 Hz, H-**2**), 7.36 (s, 1H, CH $_{imidazole}$), 6.92 (s, 1H, CH $_{imidazole}$), 5.95 (s, 2H, CH_2 $_{linker}$), 4.08 (t, 2H, J = 7.3 Hz, NCH_2), 1.76 (quintet,

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2H, $J = 7.2$ Hz, NCH_2CH_2), 1.35 (sextet, 2H, $J = 7.3$ Hz, CH_2CH_3), 0.94 (t, 3H, $J = 7.3$ Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 180.9 (carbene), 150.4, 145.7, 136.3, 134.0, 129.7, 128.9, 128.3, 126.3, 122.0, 121.6, 120.4, 51.7 (NCH_2), 51.2 (NCH_2), 33.3 ($CH_2CH_2CH_3$), 19.6 ($CH_2CH_2CH_3$), 13.5 (CH_3). Anal. Calcd for $C_{17}H_{19}AgBrN_3$ (453.13): C, 45.06; H, 4.23; N, 9.27. Found: C, 44.87; H, 3.95; N, 9.36.

Synthesis of Complex 4c. Ag_2O (77 mg, 0.33 mmol) was added to a CH_2Cl_2 solution of imidazolium **1c** (208 mg, 0.630 mmol). **4c** was obtained as a analytically pure product (251 mg, 92%). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.00 (dd, 1H, $J = 4.2$ and 1.7 Hz, H-**1**), 8.13 (dd, 1H, $J = 8.3$ and 1.7 Hz, H-**3**), 7.79−7.69 (m, 2H), 7.48 (t, 1H, $J = 7.2$ Hz, H-**5**), 7.42 (dd, 1H, $J = 8.2$ and 4.2 Hz, H-**2**), 7.29 (d, 1H, $J = 1.8$ Hz, CH $_{imidazole}$), 7.08 (s, 1H, $J = 1.7$ Hz, CH $_{imidazole}$), 5.94 (s, 2H, CH_2 $_{linker}$), 1.65 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 179.6 (carbene), 150.4, 145.8, 136.3, 134.1, 129.7, 128.9, 128.4, 126.4, 121.6, 120.5, 118.5, 57.6 ($C(CH_3)_3$), 52.4 (CH_2 $_{linker}$), 31.7 ($3CH_3$). Anal. Calcd for $C_{17}H_{19}AgBrN_3$ (453.13): C, 45.06; H, 4.23; N, 9.27. Found: C, 44.91; H, 4.31; N, 9.42.

Synthesis of Complex 4d. Ag_2O (192 mg, 0.829 mmol) was added to a CH_2Cl_2 solution of imidazolium **1d** (500 mg, 1.51 mmol). **4d** was obtained as an analytically pure product (612 mg, 92%). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.08 (dd, 1H, $J = 4.2$ and 1.7 Hz, H-**1**), 8.20 (dd, 1H, $J = 8.3$ and 1.7 Hz, H-**3**), 7.83 (d, 1H, $J = 8.2$ Hz), 7.77 (d, 1H, $J = 7.0$ Hz), 7.54 (t, 1H, $J = 7.4$ Hz, H-**5**), 7.47 (dd, 1H, $J = 8.2$ and 4.2 Hz, H-**2**), 7.38 (d, 1H, $J = 1.7$ Hz, CH $_{imidazole}$), 6.95 (d, 1H, $J = 1.7$ Hz, CH $_{imidazole}$), 5.93 (s, 2H, CH_2 $_{linker}$), 4.73 (septet, 1H, $J = 6.9$ Hz, $CH(CH_3)_2$), 1.44 (d, 6H, $J = 6.8$ Hz, $2CH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 180.2 (carbene), 150.6, 145.9, 136.4, 134.2, 130.0, 129.0, 128.5, 126.5, 122.3, 121.7, 116.8, 54.1 ($CH(CH_3)_2$), 51.5 (CH_2 $_{linker}$), 23.8 ($2CH_3$). Anal. Calcd for $C_{16}H_{17}AgBrN_3$ (439.10): C, 43.76; H, 3.90; N, 9.57. Found: C, 43.57; H, 3.82; N, 9.68.

Synthesis of Complex 5b. The chloride analogue of silver complex **4b**(300 mg, 0.734 mmol) was dissolved in CH_2Cl_2 (10 mL), followed by addition of $Pd(COD)Cl_2$ (104 mg, 0.364 mmol) in one portion. White precipitates appeared immediately. This mixture was stirred at room temperature for 1 h. The mixture was filtered to give a solution and the solvent was quickly removed to afford a white solid, which was dried under vacuum. Recrystallization using CH_2Cl_2-ether gave analytically pure **5b** (235 mg, 91% yield). Two sets of peaks were observed in the ^1H NMR spectrum of **5b** and no attempt can be made to disentangle these two sets of signals since the ratio of these two species is 1.00:0.98. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.03 (dd, 1H, $J = 4.0$ and 1.4 Hz, N-CH $_{quinoline}$), 8.83 (dd, 1H, $J = 4.0$ and 1.4 Hz, N-CH $_{quinoline}$), 8.23 (d, 1H, $J = 7.0$ Hz), 8.10 (d, 1H, $J = 7.0$ Hz), 7.96 (d, 1H, $J = 8.1$ Hz), 7.82 (m, 2H), 7.46−7.62 (m, 3H), 7.35−7.25 (m, 2H), 6.94−6.97 (m, 2H), 6.82 (d, 1H, $J = 1.5$ Hz, CH $_{imidazole}$), 6.79 (d, 1H, $J = 1.6$ Hz, CH $_{imidazole}$), 6.61 (s, 2H, CH_2 $_{linker}$), 6.34 (s, 2H, CH_2 $_{linker}$), 4.62 (t, 2H, $J = 7.2$ Hz, $NCH_2CH_2CH_3$), 4.43 (t, 2H, $J = 7.3$ Hz, $NCH_2CH_2CH_3$), 2.18 (quintet, 2H, $J = 7.3$ Hz), 1.90 (quintet, 2H, $J = 7.4$ Hz), 1.50−1.59 (m, 2H), 1.02−1.10 (m, 5H, CH_2 + CH_3), 0.68 (t, 3H, $J = 7.4$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6, 75 MHz): δ 171.6 (carbene), 171.3 (carbene), 149.9, 149.5, 146.0, 145.6, 136.3, 135.9, 135.7, 135.1, 129.1, 128.9, 128.2, 127.7, 127.4, 127.2, 126.4, 126.1, 121.5, 121.44, 121.37, 121.25, 121.22, 121.0, 50.1 (CH_2 $_{linker}$), 50.0 (CH_2 $_{linker}$), 49.4 (NCH_2), 49.0 (NCH_2), 33.3 (CH_2), 33.1 (CH_2), 19.9 (CH_2), 19.4 (CH_2), 13.3 (CH_3), 13.0 (CH_3); Anal. Calcd for $C_{34}H_{38}PdCl_2N_6$ (708.03): C, 57.68; H, 5.41; N, 11.87. Found: C, 57.32; H, 5.49; N, 11.82.

Synthesis of Complex 5d. Complex **5d** was synthesized following the same method as for **5b**. Complex **5d** was obtained as a white solid (199 mg, 93%). Two sets of peaks were observed in the ^1H NMR spectrum of **5d** and no attempt was made to disentangle these two sets of resonance signals since the ratio of these two species is close to 1:1. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.99 (dd, 1H, $J = 4.1$ and 1.6 Hz, N-CH $_{quinoline}$), 8.80 (dd, 1H, $J = 4.1$ and 1.7 Hz, N-CH $_{quinoline}$), 8.20 (dd, 1H, $J = 8.1$ and 1.5 Hz), 8.10 (d, 1H, $J = 6.8$ Hz), 7.94−7.91 (m, 1H), 7.84−7.77 (m, 2H), 7.58−7.44 (m, 3H), 7.32−7.20 (m, 1H), 6.98 (d, 1H, $J = 1.7$ Hz, CH $_{imidazole}$), 6.94 (d, 1H, $J = 1.7$ Hz, CH $_{imidazole}$), 6.85 (d, 1H, $J = 1.8$ Hz, CH $_{imidazole}$), 6.80 (d, 1H, $J = 1.8$ Hz, CH $_{imidazole}$), 6.52 (s, 2H, CH_2 $_{linker}$), 6.31 (s, 2H, CH_2 $_{linker}$), 5.78 (septet, 1H, $J = 6.9$ Hz, $CH(CH_3)_2$), 5.54 (septet, 1H, $J = 6.9$ Hz, $CH(CH_3)_2$), 1.64 (d, 6H, $J = 6.8$ Hz, $2CH_3$), 1.31 (d, 6H, $J = 6.8$ Hz, $2CH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 169.8 (carbene), 169.7 (carbene), 149.7, 149.5, 146.2, 145.9, 136.2, 135.9, 135.1, 134.8, 130.5, 130.3, 128.1, 127.8, 127.6, 127.4, 126.9, 126.7, 121.74, 121.71, 121.2, 120.8, 116.32, 116.26, 52.00 (CH_2 $_{linker}$), 51.6 (CH_2 $_{linker}$), 49.5 (NCH_2), 49.3 (NCH_2), 23.6 (CH_3), 23.3 (CH_3); Anal. Calcd for $C_{32}H_{34}PdCl_2N_6$ (679.98): C, 56.52; H, 5.04; N, 12.36. Found: C, 56.34; H, 5.13; N, 12.43.

Synthesis of Complex 6. Ag_2O (105 mg, 0.453 mmol) was added to a dichloromethane (5 mL) solution of imidazolium salt **3** (300 mg, 0.822 mmol). The mixture was stirred for half hour in the dark. Following the same workup procedure for **4a**, **6** was obtained as a white or light yellow solid (339 mg, 88%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.89 (dd, 1H, $J = 4.0$ and 1.3 Hz, N-CH $_{quinoline}$), 8.29 (dd, 1H, $J = 8.4$ and 1.4 Hz), 7.98 (d, 1H, $J = 7.2$ Hz), 7.93 (d, 1H, $J = 8.4$ Hz), 7.62−7.58 (t, 1H, $J = 7.8$ Hz), 7.52−7.48 (m, 2H), 7.18 (d, 1H, $J = 1.6$ Hz, CH $_{imidazole}$), 4.13 (t, 2H, $J = 7.3$ Hz, NCH_2), 1.90 (sextet, 2H, $J = 7.2$ Hz, CH_2CH_3), 0.95 (t, 3H, $J = 7.4$ Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 183.9 (carbene), 151.3, 142.5, 136.7, 136.6, 129.5, 129.3, 127.2, 126.3, 124.7, 122.3, 120.2, 53.8 (NCH_2), 24.7 (NCH_2CH_2), 11.3 (CH_3). Anal. Calcd for $C_{15}H_{15}AgIN_3$ (472.07): C, 38.16; H, 3.20; N, 8.90. Found: C, 37.85; H, 3.25; N, 8.97.

Synthesis of Complex 7. To a CH_2Cl_2 (5 mL) solution of silver complex **6** (175 mg, 0.371 mmol) was added $Pd(COD)Cl_2$ (106 mg, 0.371 mmol). A solution was obtained after filtration and it was concentrated to 0.5 mL. Addition of ether (20 mL) to the solution gave a light yellow solid (118 mg, 77%). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.71 (d, 1H, $J = 4.1$ Hz, N-CH $_{quinoline}$), 8.49 (d, 1H, $J = 8.0$ Hz), 8.02 (d, 1H, $J = 7.6$ Hz), 7.92 (d, 1H, $J = 8.0$ Hz), 7.79−7.75 (m, 1H), 7.58−7.55 (m, 1H), 7.46 (d, 1H, $J = 2.1$ Hz, CH $_{imidazole}$), 7.21 (d, 1H, $J = 1.9$ Hz, CH $_{imidazole}$), 4.72 (br, 2H, NCH_2), 2.10−2.05 (m, 2H, CH_2CH_3), 1.07 (t, 3H, $J = 7.4$ Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 159.1, 149.2 (carbene), 140.4, 137.3, 133.5, 129.8, 128.3, 127.7, 124.7, 122.4, 121.9, 120.4, 53.2 (NCH_2), 24.7 (NCH_2CH_2), 11.1 (CH_3). Anal. Calcd for $C_{15}H_{15}Cl_2N_3Pd$ (414.63): C, 43.45; H, 3.65; N, 10.13. Found: C, 43.91; H, 3.76; N, 10.25.

Synthesis of Complex 8. To a MeCN (5 mL) solution of palladium complex **7** (75 mg, 0.18 mmol) was added $AgBF_4$ (71 mg, 0.36 mmol). The mixture was stirred for 3 h in the dark. The precipitate (AgCl) generated was removed by filtration to give a clear solution. Removal of all the volatiles afforded **8** as a white powder (105 mg, 97%). ^1H NMR (CD_3CN, 400 MHz): δ 9.12 (d, 1H, $J = 4.5$ Hz, N-CH $_{quinoline}$), 8.85 (d, 1H, $J = 7.9$ Hz), 8.36 (d, 1H, $J = 7.6$ Hz), 8.20 (d, 1H, $J = 8.1$ Hz), 7.98−7.92 (m, 2H), 7.85−7.83 (m, 1H), 7.61 (d, 1H, $J = 2.1$ Hz, CH $_{imidazole}$), 4.34 (t, 2H, $J = 7.3$ Hz, NCH_2), 2.09−2.00 (m, 2H, NCH_2CH_2), 1.96 (s, 6H, CH_3CN), 1.03 (t, 3H, $J = 7.3$ Hz, CH_3); $^{13}C\{^1H\}$ NMR

(CD_3CN, 100 MHz): δ 159.4 (carbene), 144.3, 136.8, 135.4, 133.4, 131.6, 130.5, 129.7, 127.1, 124.6, 124.4, 123.4, 118.3 (CH_3CN), 53.8 (NCH_2), 24.7 (NCH_2CH_2), 11.1 (CH_3), 1.76 (CH_3CN). The resonance of coordinated Me*C*N is masked by the solvent signal. Anal. Calcd for $C_{19}H_{21}B_2F_8N_5Pd$ (599.43): C, 38.07; H, 3.53; N, 11.68. Found: C, 37.88; H, 3.45; N, 11.79.

Complex 9b. $AgPF_6$ (23 mg, 0.091 mmol) was quickly weighted and added to a flask charged with CH_3CN (2 mL), to which was added palladium complex **5b** (32 mg, 0.045 mmol) in one portion. The mixture was stirred for 3 h in the dark. The workup procedure is the same as for complex **8.**

Yield: 41 mg (98%). ^1H NMR (CD_3CN, 500 MHz): δ 9.30 (dd, 1H, J = 5.4 and 1.6 Hz, N-CH $_{quinoline}$), 8.68 (dd, 1H, J = 8.2 and 1.4 Hz), 8.34−8.32 (m, 1H), 8.22 (d, 1H, J = 8.3 and 1.3 Hz), 8.10 (d, 1H, J = 15.6 Hz, CH_2 $_{linker}$), 7.91−7.88 (m, 1H), 7.60−7.57 (m, 1H), 7.41 (d, 1H, J = 1.8 Hz, CH $_{imidazole}$), 6.95 (d, 1H, J = 1.9 Hz, CH $_{imidazole}$), 5.81 (d, 1H, J = 15.7 Hz, CH_2 $_{linker}$), 3.87−3.81 (m, 1H, diastereotopic NCH_2), 3.65−3.59 (m, 1H, diastereotopic NCH_2), 1.31−1.24 (m, 1H, NCH_2CH_2), 0.62−0.58 (m, 1H, NCH_2CH_2), 0.57−0.52 (m, 2H, $NCH_2CH_2CH_2$), 0.41 (t, 3H, J = 7.1 Hz, CH_3); $^{13}C\{^1H\}$ NMR (CD_3CN, 125 MHz): δ 163.2 (carbene), 158.3, 144.9, 142.9, 136.1, 132.6, 132.0, 129.1, 128.1, 122.3, 122.2, 121.7, 52.2 (CH_2 $_{linker}$), 49.8 (NCH_2), 32.3 (CH_2), 19.0 (CH_2), 12.4 (CH_3). Anal. Calcd for $C_{34}H_{38}F_{12}N_6P_2Pd$ (927.05): C, 44.05; H, 4.13; N, 9.07. Found: C, 43.81; H, 4.33; N, 9.34.

General Procedure for Synthesis of Palladium Allyl complexes 10a−c. In a glove box filled with nitrogen, silver carbene complexes were dissolved in dichloromethane, to which was added $[Pd(allyl)Cl]_2$ in one portion. The mixture was stirred at room temperature for 1 h. The precipitates generated were removed by filtration. Removal of all the solvent gave a white solid as an analytically product.

Complex 10a. $[Pd(allyl)Cl]_2$ (103 mg, 0.280 mmol) was added to a CH_2Cl_2 solution of silver complex **4a** (290 mg, 0.563 mmol). Product **10a** was obtained as a white solid (272 mg, 95%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.95−8.94 (m, 1H, N-CH $_{quinoline}$), 8.16 (dd, 1H, J = 8.2 and 1.4 Hz), 8.07 (d, 1H, J = 5.7 Hz), 7.80 (d, 1H, J = 8.0 Hz), 7.53−7.44 (m, 2H), 7.35 (d, 1H, J = 1.6 Hz, CH $_{imidazole}$), 6.92 (s, 1H), 6.88 (s, 1H), 6.81 (d, 1H, J = 1.4 Hz, CH $_{imidazole}$), 6.27 (s, 2H, CH_2 $_{linker}$), 4.88 (m, 1H, H_B), 4.06 (d, 1H, J = 7.0 Hz, syn H_A), 2.95 (d, 1H, J = 13.1 Hz, anti H_A), 2.93 (br s, 1H, syn H_C), 2.30 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.64 (br d, 1H, J = 11.4 Hz, anti H_C); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 181.3 (carbene), 149.9, 146.5, 138.6, 136.5, 136.3, 135.8, 135.3, 135.2, 131.0, 129.0, 128.7, 128.3, 126.4, 122.9, 121.6, 121.3, 114.4 (C_B), 72.2 (br, C_A), 50.4 (CH_2 $_{linker}$), 48.3 (br, C_C), 21.1 (CH_3), 18.5 (CH_3), 18.1 (CH_3). Anal. Calcd for $C_{25}H_{26}ClN_3Pd$ (510.37): C, 58.83; H, 5.13; N, 8.23. Found: C, 58.56; H, 5.16; N, 8.16.

Complex 10b. $[Pd(allyl)Cl]_2$ (128 mg, 0.348 mmol) was added to a CH_2Cl_2 solution of silver complex **4b** (316 mg, 0.698 mmol). Complex **10b** was obtained as a white foamy solid (283 mg, 91%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.94−8.92 (m, 1H, N-CH $_{quinoline}$), 8.18−8.16 (m, 1H), 7.80−7.76 (m, 2H), 7.52−7.43 (m, 2H), 7.13 (d, 1H, J = 1.5 Hz, CH $_{imidazole}$), 6.88 (d, 1H, J = 1.5 Hz, CH $_{imidazole}$), 6.07 (s, 2H, CH_2 $_{linker}$), 5.24 (m, 1H, H_B), 4.26 (d, 1H, J = 7.5 Hz, syn H_A), 4.20−4.16 (br m, 2H, NCH_2), 3.30 (br s, 1H, syn H_C), 3.24 (d, 1H, J = 13.6 Hz, anti H_A), 2.23 (br d, 1H, J = 11.6 Hz, anti H_C), 1.81 (m, 2H, NCH_2CH_2), 1.36 (m, 2H, CH_2CH_3), 0.94 (t, 3H, J = 7.3 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 179.6 (carbene), 149.9, 146.1, 136.4, 134.9, 130.1, 128.2, 128.1, 126.4, 122.2, 121.4, 120.5, 114.6 (C_B), 72.7 (br, C_A), 51.0 (CH_2 $_{linker}$), 50.4 (NCH_2), 48.1 (br, C_C), 33.1 (NCH_2CH_2), 19.9 ($NCH_2CH_2CH_2$), 13.8 (CH_3). Anal. Calcd for $C_{20}H_{24}ClN_3Pd$ (448.30): C, 53.58; H, 5.40; N, 9.37. Found: C, 53.32; H, 5.33; N, 9.52.

Complex 10c. $[Pd(allyl)Cl]_2$ (100 mg, 0.272 mmol) was added to a CH_2Cl_2 solution of silver complex **4c** (247 mg, 0.545 mmol). Complex **10c** was obtained as a white foamy solid (231 mg, 96%). Two sets of peaks (set a and set b in 1.12 to 1.00 ratio) were observed in the ^1H NMR spectrum. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.94−8.93 (m, 2H, set a and set b, N-CH $_{quinoline}$), 8.16 (d, 2H, J = 8.1 Hz, set a and set b), 7.81−7.75 (m, 3H, set a and set b), 7.67 (d, 1H, J = 7.0 Hz, set a or b), 7.53−7.45 (m, 4H, set a and set b), 7.10 (d, 1H, J = 1.5 Hz, CH $_{imidazole}$), 7.07 (d, 1H, J = 1.5 Hz, CH $_{imidazole}$), 7.04−7.01 (m, 2H, 2CH $_{imidazole}$), 6.53 (d, 1H, J = 14.9 Hz, CH_2 $_{linker}$), 6.30 (d, 1H, J = 14.9 Hz, CH_2 $_{linker}$), 6.20 (d, 1H, J = 15.3 Hz, CH_2 $_{linker}$), 5.91 (d, 1H, J = 15.3 Hz, CH_2 $_{linker}$), 5.25−5.18 (m, 2H, H_B set a and H_B set b), 4.18 (m, 2H, syn H_A set a and set b), 3.41 (br, 1H, syn H_C set a), 3.28 (d, 1H, J = 13.1 Hz, anti H_A set a), 3.26 (br s, 1H, syn H_C set b), 3.18 (d, 1H, J = 13.4 Hz, anti H_A set b), 2.26 (d, 1H, J = 11.5 Hz, anti H_C set a), 2.19 (d, 1H, J = 12.0 Hz, anti H_C set b), 1.86 (s, 9H, set a or set b), 1.70 (s, 9H, set a or b); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 179.0 (carbene), 178.7 (carbene), 149.9, 149.8, 146.2, 146.0, 136.37, 136.35, 134.8, 134.7, 130.5, 130.1, 128.2, 128.1, 126.6, 126.5, 121.35, 121.33, 120.9, 120.8, 119.1, 119.0, 113.8 (C_B set a), 113.4 (C_B set b), 71.1 (br, C_A set a and set b), 58.1 ($C(CH_3)_3$, set a), 58.0 ($C(CH_3)_3$, set b), 51.7 (CH_2 $_{linker}$, set a), 51.3 (CH_2 $_{linker}$, set b), 50.3 (br, C_C set a and set b), 31.7 ($3CH_3$), 31.6 ($3CH_3$). Anal. Calcd for $C_{20}H_{24}ClN_3Pd$ (448.30): C, 53.58; H, 5.40; N, 9.37. Found: C, 53.17; H, 5.62; N, 9.49.

Complex 11b. The synthetic procedure is the same as for **9b** using palladium complex **10b** (66 mg, 0.15 mmol) and $AgBF_4$ (29 mg, 0.15 mmol). Complex **11b** was obtained as a white solid (72 mg, 96%). ^1H NMR ($CDCl_3$, 300 MHz, 328 K): δ 9.49 (br, 1H, N-CH $_{quinoline}$), 8.37 (dd, 1H, J = 8.3 and 1.6 Hz), 8.14 (d, 1H, J = 6.5 Hz), 7.92 (dd, 1H, J = 8.2 and 1.4 Hz), 7.61−7.56 (m, 2H), 7.41 (d, 1H, J = 1.6 Hz, CH $_{imidazole}$), 6.90 (br s, 2H, CH_2 $_{linker}$), 6.88 (d, 1H, J = 1.9 Hz, CH $_{imidazole}$), 5.84 (br, 1H, H_B), 4.48 (br d, 1H, J = 7.0 Hz, syn H_A), 4.00−3.96 (br m, 2H, NCH_2CH_2), 3.73 (br s, 1H, anti H_A), 3.70 (br, 1H, syn H_C), 2.89 (br, 1H, anti H_C), 1.75−1.65 (m, 2H, NCH_2CH_2), 1.28−1.19 (m, 2H, $NCH_2CH_2CH_2$), 0.84 (t, 3H, J = 7.3 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 328 K): δ 174.8 (br, carbene), 156.7, 145.7, 140.5, 134.8, 131.4, 131.3, 130.7, 127.5, 121.8, 121.3, 121.2, 119.3 (C_B), 78.1 (br, C_A), 52.4 (CH_2 $_{linker}$), 50.4 (NCH_2), 46.2 (br, C_C), 33.0 (CH_2), 19.5 (CH_2), 13.4 (CH_3). Anal. Calcd for $C_{20}H_{24}N_3BF_4Pd$ (499.65): C, 48.08; H, 4.84; N, 8.41. Found: C, 47.70; H, 4.92; N, 8.52.

Complex 11c. The synthetic procedure of **11c** is the same as that for **9b** using palladium complex **10c** (145 mg, 0.324 mmol) and $AgBF_4$ (64 mg, 0.33 mmol). Complex **11c** was obtained as a white solid (158 mg, 96%). The ^1H NMR spectrum of **11c** shows two sets of peaks in a ratio of 1.00:0.98 and they were disentangled by the $^1H-^1H$ COSY (see Table 1 and the Supporting Information). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.48−9.46 (m, 1H, set a or set b, N-CH $_{quinoline}$), 9.25 (dd, 1H, J = 4.8 and 1.0 Hz, set a or set b, N-CH $_{quinoline}$), 8.39−8.37 (m, 2H, set a and set b), 8.17 (d, 1H, J = 6.7 Hz, set a or set b), 8.11 (d, 1H, J = 6.7 Hz, set a or set b), 7.96−7.92 (m, 2H, set a and set b), 7.68−7.56 (m, 4H, set a and set b), 7.40 (d, 1H, J = 1.4 Hz, CH $_{imidazole}$), 7.35 (d, 1H, J = 15.0 Hz, set a or set b, exo diastereotopic CH_2 $_{linker}$), 7.32 (d, 1H, J = 1.4 Hz, CH $_{imidazole}$), 7.01−6.97 (m, 3H, 2 imidazole CH + 1 exo diastereotopic CH_2 $_{linker}$), 5.86 (m, 1H, H_B set a), 5.70 (m, 1H, H_B set b), 5.62 (d, 1H, J = 14.9 Hz, endo diastereotopic CH_2 $_{linker}$,

coupled with the signal at 7.35), 5.40 (d, 1H, $J = 15.0$ Hz, endo diastereotopic $CH_{2\ linker}$, coupled with a signal in 7.01−6.97), 4.42 (d, 1H, $J = 7.4$ Hz, syn H_A set b), 4.20 (d, 1H, $J = 7.6$ Hz, syn H_A set a), 3.91 (d, 1H, $J = 6.6$ Hz, syn H_C set b), 3.74 (d, 1H, $J = 6.6$ Hz, syn H_C set a), 3.64 (d, 1H, $J = 13.6$ Hz, anti H_A set a), 3.55 (d, 1H, $J = 13.5$ Hz, anti H_A set b), 2.94 (d, 1H, $J = 12.3$ Hz, anti H_C set a), 2.83 (d, 1H, $J = 11.8$ Hz, d, 1H, anti H_C set b), 1.69 (s, 9H, $3CH_3$), 1.57 (s, 9H, $3CH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 173.8 (carbene), 173.2 (carbene), 155.9, 155.4, 145.7, 145.6, 140.35, 140.31, 135.0, 134.9, 131.4, 131.3, 131.0, 130.9, 127.82, 127.80, 121.8, 121.7, 120.5, 120.2, 120.0, 119.3, 118.9 (C_B), 117.4 (C_B), 75.3 (C_A), 74.7 (C_A), 57.9 ($CH_{2\ linker}$), 54.1 ($CH_{2\ linker}$), 53.9 ($NC(CH_3)_3$), 53.4 ($NC(CH_3)_3$), 51.3 (C_C), 50.7 (C_C), 31.4 (CH_3), 31.3 (CH_3). Anal. Calcd for $C_{20}H_{24}BF_4N_3Pd$ (499.65): C, 48.08; H, 4.84; N, 8.41. Found: C, 48.01; H, 4.87; N, 8.54.

Complex 12. The synthetic procedure is directly analogous to that for **10a** using **6** (0.34 mmol) and $[Pd(allyl)Cl]_2$ (64 mg, 0.17 mmol). Compound **12** was obtained as a yellow air sensitive solid (124 mg, 84%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.96−8.94 (m, 1H), 8.58 (d, 1H, $J = 7.2$ Hz), 8.26 (d, 1H, $J = 8.2$ Hz), 7.90 (d, 1H, $J = 8.1$ Hz), 7.67−7.63 (m, 1H), 7.54−7.50 (m, 2H), 7.16 (d, 1H, $J = 1.5$ Hz, $CH_{imidazole}$), 4.83 (m, 1H, H_B), 4.38 (t, 2H, $J = 7.4$ Hz, NCH_2), 4.07 (d, 1H, $J = 7.4$ Hz, syn H_A), 2.98 (d, 1H, $J = 13.5$ Hz, anti H_A), 2.67 (br s, 1H, syn H_C), 2.04−1.97 (m, 2H, NCH_2CH_2), 1.51 (br, 1H, anti H_C), 1.04 (t, 3H, $J = 7.4$ Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 180.8 (carbene), 151.0, 142.4, 137.0, 136.6, 129.2, 128.8, 128.6, 126.2, 124.4, 121.8, 120.5, 114.3 (C_B), 71.6 (C_A), 52.8 (NCH_2), 49.0 (C_C), 24.3 (NCH_2CH_2), 11.4 (CH_3). Anal. Calcd for $C_{18}H_{20}ClN_3Pd$ (420.24): C, 51.44; H, 4.80; N, 10.00. Found: C, 51.32; H, 4.91; N, 10.21.

Complex 13. Palladium complex **12** (80 mg, 0.19 mmol) was dissolved in dichloromethane (5 mL), to which was quickly added $AgBF_4$ (37 mg, 0.19 mmol). The mixture was stirred for 3 h in the dark. The precipitates generated were filtered off to give a clear solution. The solvent was removed in vacuo to give a light yellow solid (94 mg, 97%). ^1H NMR (acetone-d_6, 400 MHz): δ 9.59 (dd, 1H, $J = 4.9$ Hz and 1.4 Hz), 8.92 (dd, 1H, $J = 4.9$ Hz and 1.4 Hz), 8.40 (d, 1H, $J = 7.8$ Hz), 8.26 (d, 1H, $J = 8.2$ Hz), 8.13 (d, 1H, $J = 2.0$ Hz, $CH_{imidazole}$), 7.95 (t, 1H, $J = 7.9$ Hz), 7.84−7.90 (m, 2H), 5.82 (m, 1H, H_B), 4.37−4.33 (m, 3H, NCH_2 + allyl syn H_A), 4.04 (d, 1H, $J = 6.8$ Hz, syn H_C), 3.80 (d, 1H, $J = 13.8$ Hz, anti H_A), 3.05 (d, 1H, $J = 12.0$ Hz, anti H_C), 1.06 (t, 3H, $J = 7.3$ Hz, CH_3). The $NCH_2CH_2CH_3$ signals overlap with the solvent residue peaks at δ 2.05. The ^{13}C NMR spectrum of complex **13** could not be obtained because of its poor solubility in acetone-d_6 or $CDCl_3$.

^1H NMR (CD_3CN, 300 MHz) of complex **14**: δ 9.30−9.32 (m, 1H), 8.72−8.70 (m, 1H), 8.16−8.09 (m, 2H), 7.84 (t, 1H, $J = 8.0$ Hz), 7.76 (d, 1H, $J = 1.8$ Hz, $CH_{imidazole}$), 7.72−7.69 (m, 1H), 7.52 (d, 1H, $J = 1.9$ Hz, $CH_{imidazole}$), 5.69 (m, 1H, H_B), 4.20−4.17 (m, 3H, NCH_2 + syn H_A), 3.93 (br, 1H, syn H_C), 3.65 (d, 1H, $J = 13.8$ Hz, anti H_A), 2.94 (br d, 1H, anti H_C), 1.96−1.94 (m, 2H, CH_2CH_3), 1.02 (t, 3H, $J = 7.34$ Hz, CH_3); $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz): δ 175.6 (carbene), 161.1, 141.7, 139.1, 135.3, 132.0, 129.8, 128.7, 125.4, 124.4, 123.1, 122.5, 121.7 (C_B), 77.6 (C_A), 54.1 (NCH_2), 49.2 (C_C), 25.4 (NCH_2CH_2), 11.2 (CH_3), 1.32 (septet, $^1J_{DC} = 20.6$ Hz, CD_3CN-Pd). The resonance signal of CD_3CN−Pd overlaps with that of the solvent peak (δ 118.2). Anal. Calcd for $C_{18}H_{20}BF_4N_3Pd$ (471.60): C, 45.84; H, 4.27; N, 8.91. Found: C, 45.47; H, 4.31; N, 8.78.

X-ray Crystallographic Analyses of Complexes 5b, 9b, 10a, 10c, and 11c. Crystals of each compound suitable for X-ray structure studies were obtained by the slow diffusion of ether to their dichloromethane solutions at room temperature. A single crystal of each complex of suitable size was mounted on a glass fiber using a glue. Intensity data were collected on a Bruker-AXS X8 Kappa diffractometer equipped with an Apex-II CCD detector, using a graphite monochromator $\lambda(Mo\ K_{\alpha 1}) = 0.71073$ Å radiation. The structures were solved by direct methods and refined against all F^2 data by full-matrix least-squares techniques. All the non-hydrogen atoms were refined with an anisotropic displacement parameter. The hydrogen atoms were introduced into the geometrically calculated position and refined riding on the corresponding parent atoms. See the Supporting Information for detailed crystallographic data.

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Supporting Information Available: Detailed VT NMR measurements, the Eyring plots, the ROESY and COSY spectra of complex **11c**, and the X-ray crystallographic files in the forms of CIF and PDF for complexes **5b**, **9b**, **10a**, **10c**, and **11c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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