Practical One-Pot, Three-Component Synthesis of N-Heterocyclic Carbene (NHC) Ligated Palladacycles Derived from *N*,*N*-Dimethylbenzylamine

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Further explorations of the catalytic potential of N-heterocyclic carbene (NHC) ligated palladacycles as catalysts for Pd-mediated transformations have been hampered by the lack of general and practical methods for their synthesis. In this work, we describe a novel, practical approach to NHC-ligated palladacycles by a three-component, one-pot reaction of imidazolium salts, $PdCl_2$, and *N*,*N*-dimethylbenzylamine in the presence of excess K_2CO_3 under reflux in reagent-grade acetonitrile in air. 1,3-Diarylimidazolium salts afford the corresponding NHC−Pd(dmba)Cl (dmba = *N*,*N*-dimethylbenzylamine-κ^2N,*C*) complexes in >80% yield. The conversion of 1,3-diaryl-4,5-dihydroimidazolium and 1,3-dialkylimidazolium or benzimidazolium salts requires the use of stronger base (Cs_2CO_3) and/or higher temperature (100 °C). The Pd-bound chloride anion can be exchanged with silver salts or sodium salts. The NHC−palladacycle adducts have been characterized by single-crystal X-ray crystallography.

Introduction

N-heterocyclic carbenes (NHCs)[1−3] have recently emerged as high-performance ligands or organocatalysts in a variety of organic reactions,[4] including Pd-mediated cross-couplings.[5] In particular, monoligated Pd complexes of bulky *N*,*N*-diaryl-substituted carbenes[6] (**1**−**4**, Figure 1) have shown high levels of activity and wide applicability. Usually, NHCs **1**−**4** are prepared by deprotonation of imidazolium or 4,5-dihydroimidazolium salts with strong bases[1,3] and then captured by suitable Pd precursors. As many Pd-catalyzed cross-coupling reactions involve either basic organometallic reagent or external base, active catalysts can be prepared directly in the reaction mixture starting from common Pd precursors and imidazolium salts, usually in a 1:1 or 1:2 molar ratio.[7,8] However, since these conditions are not optimized for the complexation of NHC to Pd, often the yield of the active catalyst is low and its chemical composition is hard to control.[8,9] Therefore, the preparation of well-defined NHC−Pd precatalysts that can be easily activated when introduced into the reaction in high yields under optimized conditions represents a significant improvement over the in situ catalyst generation. Such precatalysts usually require additional, sacrificial ligands for the stabilization of the active species, a monoligated NHC−Pd complex. In the past few years, IPr−Pd(0) or IPr−Pd(II) derivatives with *p*-quinone,[10] π-allyl,[11] carboxylate,[12] 3-chloropyridine,[9,13] and acetylacetonate (acac)[14] stabilizing ligands have been shown to exhibit high activity in a number

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of Pd-mediated processes. Some of these complexes are now commercially available. Palladacycles[15] are also suitable for the stabilizing ligand role. Under the reaction conditions, palladacycles behave as well-defined precatalysts[16] that release catalytically active, ligandless Pd species in a controlled manner, depending on the temperature, solvent, coreactants, and nature of the cyclopalladated ligand.[17] Ligation of dimeric palladacycles with a single spectator ligand (e.g., a bulky phosphane) enhances the usefulness of the corresponding precatalysts because a more active monoligated phosphane−Pd complex[18] is formed when the precatalyst is activated. For instance, the palladacycle derived from *N*,*N*-dimethylbenzylamine (**5**; dmba)[19−22]—a commercially available, inexpensive palladacycle precursor—and its phosphane adducts[19,23] have been shown to be highly active precatalysts for Suzuki−Miyaura, Buchwald−Hartwig, and Heck−Mizoroki reactions, even with such challenging substrates as nonactivated aryl chlorides. NHC-ligated palladacycles have been somewhat less explored. Nolan et al. showed that N,C-palladacycles derived from *N*,*N*-dimethyl-2-aminobiphenyl ligated with IPr or IMes efficiently mediated Suzuki−Miyaura, Buchwald−Hartwig, enolate arylation, and haloarene dehalogenation reactions even at room temperature.[24] The precatalysts were prepared by simple substitution of a bridging chloride in the palladacyclic dimer with the isolated carbenes **1** and **2**. In a similar fashion, a catalyst was prepared very recently by the reaction of the free

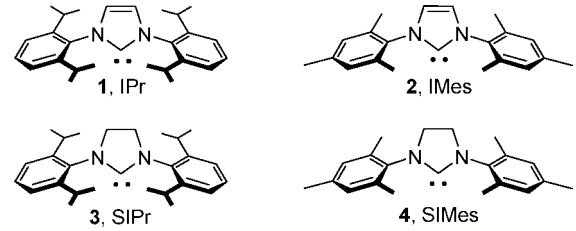

Figure 1. Highly active, versatile NHC ligand for catalytic applications.

IPr carbene and cyclopalladated ferrocenylimine[25] donor ligands. The resulting NHC−palladacycles were excellent catalysts for Buchwald−Hartwig amination and Suzuki−Miyaura coupling. Iyer et al. explored N,C-palladacycles derived from *N*,*N*-dimethylbenzylamine, acetophenone, and benzophenone oximes with simple 1,3-diphenyl-4,5-dihydroimidazolyl-2-ylidene as catalysts for Heck−Mizoroki and Suzuki−Miyaura couplings of activated substrates at low catalyst loadings.[26] Remarkably, these complexes were first prepared by Hiraki et al. as early as 1978 via thermal decomposition of the corresponding saturated carbene dimer in situ.[27] As that was almost two decades before the potential of NHCs as spectator ligands in Pd-catalyzed organic transformations was recognized in the seminal paper by Herrmann et al.,[28] no catalytic studies were reported at that time. Herrmann et al. have prepared a number of NHC-ligated N,C- and P,C-palladacycles in a similar manner.[29] Among them, excellent precatalysts for Heck−Mizoroki reaction were found. Very recently, the same group disclosed a more practical procedure for NHC−palladacycle preparation relying on the in situ generation of the carbene in the presence of purified, preformed palladacycles.[30] Whereas NaOAc was a suitable base for the unsaturated NHCs, cyclic diaminocarbene precursors still demanded the use of *t*BuOK. Bedford et al. prepared phosphite-derived P,C-palladacycles ligated with SIPr (**3**) and SIMes (**4**) via μ-chloride displacement with the saturated carbene prepared in situ from the corresponding chloroform adduct.[31] These precatalysts showed moderate activity in the Suzuki couplings of aryl bromides. However, aryl chlorides and alkyl bromides[32] failed to couple. With the above in mind, we reasoned that hitherto unknown complexes of $[Pd(dmba)Cl]_2$ (**6**) with carbenes **1**−**4** have the potential to be highly active and versatile cross-coupling catalysts. However, all the methods discussed above suffer from practical drawbacks, such as handling of isolated moisture- and air-sensitive carbenes and the strong bases required for NHC preparation (for instance, in a glovebox), narrow scope, and/or medium-to-low yields. Thus, the first step

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Scheme 1. One-Pot, Three-Component Synthesis of NHC−Pd(dmba)Cl from Imidazolium Salts

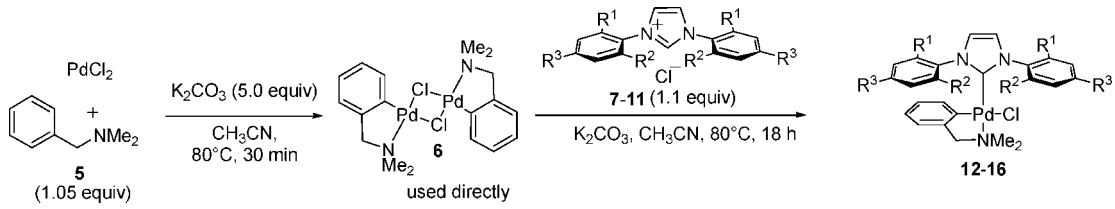


Table 1. Yields of NHC-Ligated Palladacycles from Scheme 1

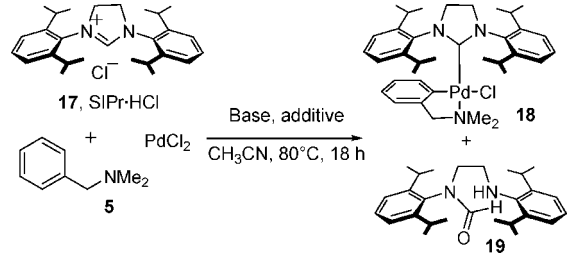
entry	NHC·HCl	R^1	R^2	R^3	yield, %
1	none				98 (**6**)
2	IPr·HCl (**7**)	*i*Pr	*i*Pr	H	82 (**12**)
3	IEt·HCl (**8**)	Et	Et	H	81 (**13**)
4	IMes·HCl (**9**)	Me	Me	Me	96 (**14**)
5	ITbp·HCl (**10**)	*t*Bu	H	H	81 (**15**)
6	IPrp·HCl (**11**)	*i*Pr	H	H	86 (**16**)

toward successful catalysts[33] would be to develop a practical and general synthetic method for preparing a range of NHC−palladacycle adducts.

Results and Discussion

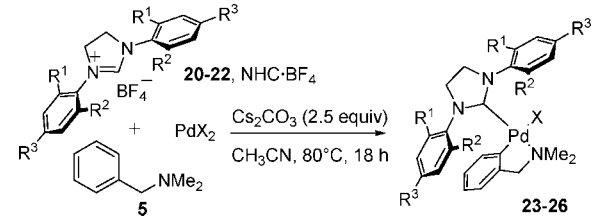
Synthesis of NHC−Palladacycles from 1,3-Diarylimidazolium Salts and Their 4,5-Dihydro Analogues. We reasoned that the addition of an equimolar amount of *N*,*N*-dimethylbenzylamine (**5**) to $PdCl_2$ would lead to formation of a 1:1 adduct, which could be converted to the corresponding dimeric palladacycle **6** upon addition of a weak base. Moreover, if the same base could also be used to generate NHC in situ from imidazolium salts, then the desired NHC-ligated palladacycles would be formed directly, without any intermediate isolation. Our initial attempts to carry out the palladacycle formation using $PdCl_2/K_2CO_3$ or $Pd(OAc)_2$ in a number of solvents (e.g., CH_2Cl_2, toluene, THF, dioxane, and neat **5**) resulted in rapid decomposition of the reactants and formation of Pd black. However, heating of $PdCl_2$ and the amine **5** (1.00 and 1.05 equiv, respectively) in CH_3CN led to the formation of a dark orange, clear solution, which turned canary yellow within 5 min upon the addition of 5 equiv of K_2CO_3 at that temperature (Scheme 1). The known palladacyclic dimer **6**[20] was isolated in 98% yield (Table 1, entry 1). Encouraged by these results, we added the commercially available IPr·HCl (**7**; 1.10 equiv) to the crude palladacyclic solution at 80 °C. After the mixture was stirred for 18 h, complex **12** was isolated in 82% yield (Table 1). The reaction also proceeded well with other imidazolium salts. The known IEt·HCl (**8**)[8,34] and the commercially available IMes·HCl (**9**) led to the corresponding NHC-ligated palladacycles **13** and **14** (81% and 96% isolated yields, respectively). Hitherto unknown, less sterically hindered ligands carrying only one ortho substituent on the N-bound aryl group, *t*Bu (ITbp·HCl, **10**) or *i*Pr (IPrp·HCl, **11**), also gave the corresponding complexes in similarly high yields (81% for **15** and 86% for **16**). We further extended the scope of the reaction to the analogous saturated carbenes. When the commercially available SIPr·HCl (**17**) was used under the standard conditions, the corresponding SIPr−Pd(dmba)Cl complex (**18**) was obtained in moderate yield, which was contaminated with significant amounts of unreacted carbene precursor and *N*,*N*′-bis(2,6-diisopropylphenyl)-*N*-formylethylenediamine (**19**), a product of base-promoted hydrolytic ring opening of the carbene precursor (Table 2). This result can be explained by taking the lower acidity of the 4,5-dihydroimidazolium salts (compared to that of the unsaturated analogues) and their susceptibility to hydrolysis into account. The addition of powdered 4 Å molecular sieves at the beginning of the reaction suppressed the undesirable 4,5-dihydroimidazolium salt hydrolysis without introducing major operational hurdles into the process. The use of a stronger base (Cs_2CO_3) yielded the targeted product **18** in almost quantitative yield (96%). Under these conditions, the commercially available 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (**20**; SIMes·HBF_4) produced the corresponding NHC-ligated palladacycle **23** in similarly high yield (Table 3, entry 1) without

Table 2. Optimization of the Conditions for Synthesis of the SIPr−Pd(dmba)Cl Complex (18)



			yield, %	
entry	base (amt, equiv)	additive	**18**	**19**
1	K_2CO_3 (5.0)	none	34	26
2	K_2CO_3 (5.0)	4 Å MS	74	7
3	Cs_2CO_3 (2.5)	4 Å MS	96	<2

Table 3. Synthesis of NHC−Pd(dmba)X (X = Cl, Br) Complexes from 1,3-Diaryl-4,5-dihydroimidazolium Salts



entry	PdX_2	NHC·HBF_4	R^1	R^2	R^3	yield, %[a]
1	$PdCl_2$	SIMes·HBF_4 (**20**)	Me	Me	Me	98 (**23**)
2	$PdBr_2$	SIMes·HBF_4 (**20**)	Me	Me	Me	67 (**24**)
3	$PdCl_2$	SITbp·HBF_4 (**21**)	*t*Bu	H	H	90 (**25**)
4	$PdCl_2$	SIPrp·HBF_4 (**22**)	*i*Pr	H	H	80 (**26**)

[a] The reactions were conducted in the presence of 4 Å molecular sieves.

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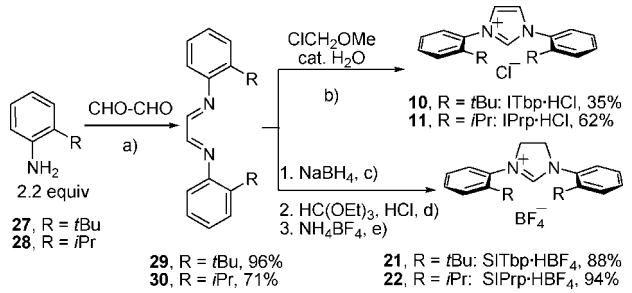
Scheme 2. Synthesis of Novel 1,3-Bis(*o*-alkylaryl)-Substituted NHC Ligand Precursors[a]



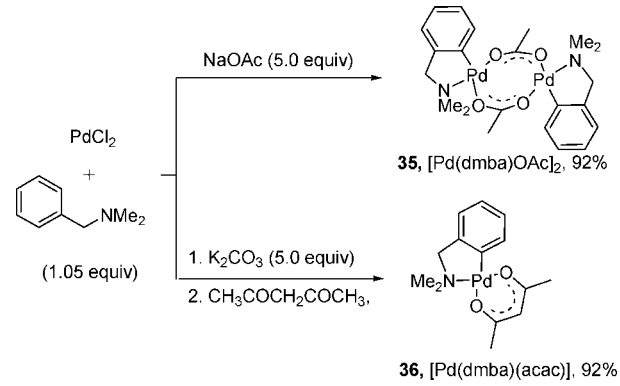
[a] Conditions: (a) MeOH−H_2O (10:1), room temperature, 1.5−18 h; (b) THF, 40 °C, 18 h; (c) MeOH−THF (1:1), reflux, 30 min; (d) concentrated HCl (1.2 equiv), 120 °C, 1 h; (e) H_2O, room temperature, 15 min.

any formation of the corresponding hydrolysis product. The use of $PdBr_2$ instead of $PdCl_2$ resulted in the preparation of an analogous complex containing bromide as the counterion at a somewhat lower yield (**24**, 67%) (Table 3, entry 2). Less sterically hindered analogues (**21**, **22**)[35] also formed palladacyclic complexes in excellent yields (90% for **25** and 80% for **26**) (Table 3, entries 3 and 4) under these conditions. Surprisingly, compound **25** was obtained as a mixture of two unseparable isomers in a molar ratio of 2.6:1 (^{1}H NMR spectroscopy). The X-ray single-crystal structure of complex **25** (Figure 2e) showed the expected trans configuration between the carbene carbon and the dimethylamino ligand. Most likely, the two isomers are atropisomers that only exist in solution and arise from restricted rotation around one or more bonds in the saturated NHC ligand carrying *N*-2-*tert*-butylphenyl substituents.[36]

The novel carbene precursors used in this work were prepared from the corresponding *N*,*N*-diarylazabutadienes (**29** and **30**) (Scheme 2) by either treatment with chloromethyl ethyl ether to yield the unsaturated imidazolium salts ITbp·HCl (**10**, 35%) and IPrp·HCl (**11**, 62%) or reduction with $NaBH_4$ followed by cyclization with triethyl orthoformate/HCl to form the corresponding 4,5-dihydro analogues.[6,8] For easier purification, the saturated carbene precursors were isolated as tetrafluoroborates (SITbp·HBF_4, **21**, 88%; SIPrp·HBF_4, **22**, 94%) after simple precipitation with NH_4BF_4 from aqueous solution.

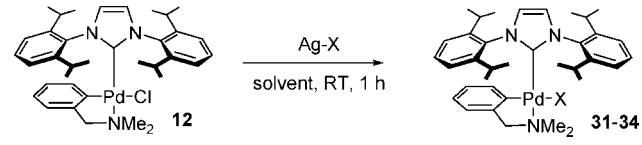
Anion Exchange Reactions of NHC−Palladacycle Chlorides. The nature of the Pd-bound anion could potentially affect the ease of activation of the palladacyclic precatalysts. Therefore, we endeavored to develop methods for preparing NHC−palladacycles carrying anions other than chloride or bromide. Anion exchange between **12** and various Ag salts resulted in the formation of the corresponding carboxylate, sulfonate, or hexafluorophosphate analogues **31**−**34** (Table 4) in high yields. As hexafluorophosphate is a noncoordinating anion, the product was isolated as the acetonitrile adduct (1:1). This anion-exchange reaction is driven by the formation of insoluble AgCl. Hence, we reasoned that the limited solubility of NaCl or KCl in acetonitrile could allow similar reactions to take place with the less expensive Na or K salts, allowing for the palladacycle formation, NHC ligation, and anion exchange to be combined in a single synthetic operation without isolation of any intermediates. Treatment of amine **5** with $PdCl_2$ in refluxing acetonitrile using NaOAc instead of K_2CO_3 resulted in a clean formation (92% isolated yield) (Scheme 3) of the known[22] acetate-bridged dimeric palladacycle **35**. Similarly, the addition of acetylacetone (acac-H) to the crude palladacycle

Scheme 3. Anion-Exchange Reactions of in Situ Prepared Palladacycles[a]



[a] Conditions: CH_3CN, 80°C, 30−45 min.

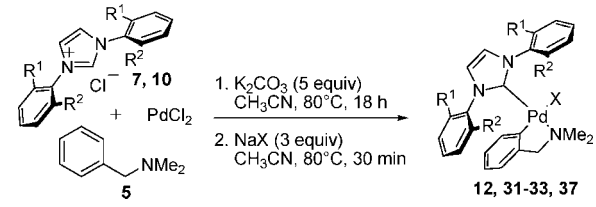
Table 4. Anion Exchange of IPr−Pd(dmba)Cl (12) with Silver Salts



entry	AgX	solvent	yield, %
1	AgOAc	CH_2Cl_2−acetone (4:1)	96 (**31**)
2	AgTFA[a]	CH_2Cl_2−acetone (4:1)	99 (**32**)
3	AgOTf[b]	CH_2Cl_2−acetone (4:1)	96 (**33**)
4	$AgPF_6$	CH_2Cl_2−CH_3CN (5:1)	97 (**34**)[c]

[a] TFA = trifluoroacetate. [b] Tf = trifluoromethylsulfonyl. [c] The compound was obtained as the Pd-bound acetonitrile adduct (Figure 2).

Table 5. One-Pot, Four-Component, Sequential NHC−Palladacycle Synthesis and Anion Exchange



entry	X	R^1	R^2	yield, %
1	I	*t*Bu	H	96 (**37**, X = I)
2	OAc	*i*Pr	*i*Pr	61 (**12**, X = Cl) + 13 (**31**, *X* = OAc)
3	TFA	*i*Pr	*i*Pr	46 (**12**, X = Cl) + 43 (**32**, *X* = TFA)
4	OTf	*i*Pr	*i*Pr	94 (**33**, X = OTf)

chloride **6** (using 5 equiv of K_2CO_3 as the base) led to the formation of the known[37] complex [Pd(dmba)(acac)] (**36**) in 92% isolated yield. Next, we integrated the in situ NHC−palladacycle preparation protocol and anion exchange by simply adding the corresponding Na salt (3 equiv) and heating for an additional 30 min before workup (Table 5). Whereas the use of NaI gave complete conversion to the corresponding NHC-ligated Pd−I palladacycle **37**, the use of sodium carboxylates resulted in incomplete anion exchange. Sodium acetate yielded 61% of the chloride-ligated complex **12** and its acetate analogue **31** (13%) and sodium trifluoroacetate yielded 46% of **12** and 43% of the trifluoroacetate analogue **32**. In contrast, complete ion exchange was observed with sodium trifluoromethanesulfonate, and complex **33** was obtained in 94% yield.

(37) Reichert, B. E.; West, B. O. *J. Organomet. Chem.* **1974**, *71*, 291–297.

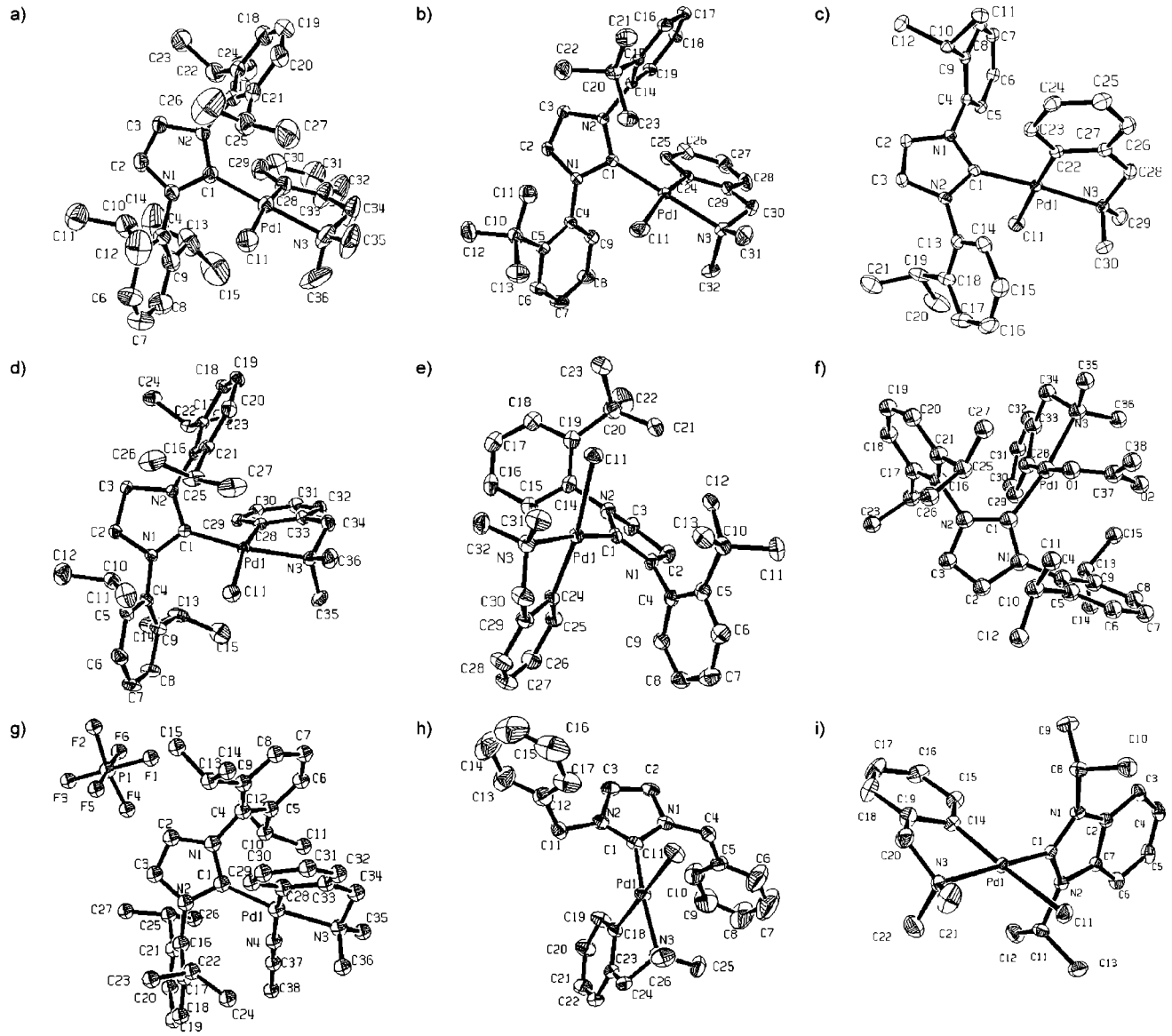


Figure 2. ORTEP representations of the X-ray single-crystal structures of NHC−palladacycles: (a) **12**; (b) **15**; (c) **16**; (d) **18**; (e) **25**; (f) **31** (the unit cell contains two molecules of **31** and one molecule of CH_2Cl_2; only one molecule of **31** is shown for clarity); (g) **33**; (h) **42**; (i) **45**. The thermal ellipsoids were drawn at the 30% probability level, and the hydrogen atoms were omitted for clarity.

Synthesis of NHC−Palladacycles from 1,3-Dialkylimidazolium and 1,3-Dialkylbenzimidazolium Salts. Our initial experiments with 1,3-dibenzylimidazolium hexafluorophosphate[38] (**38**) under the conditions of Scheme 1 resulted in only 4% of the expected product **42** (Table 6). The use of Cs_2CO_3 at 80 and 100 °C resulted in 22% and 31% of **42**, respectively. The reaction mixture at the end point appeared dark, with a significant amount of Pd black present. Shortening the reaction time to 30 min led to an improvement in product yield to 78%. In an analogous fashion, commercially available 1,3-dimethylimidazolium chloride (**39**) yielded 67% and 45% of the corresponding complex **43** at 30 min and 18 h, respectively. However, the commercially available isopropyl analogue **40** yielded about the same amount of product **44** irrespective of the time (65% after 18 h; 62% after 30 min). Presumably, the bulkier carbene results in a more stable palladacycle complex. 1,3-Diisopropylbenzimidazolium hexafluorophosphate[39] (**41**) also reacted in good yield, providing the first example of a benzimidazol-2-ylidene-ligated palladacycle (**45**).

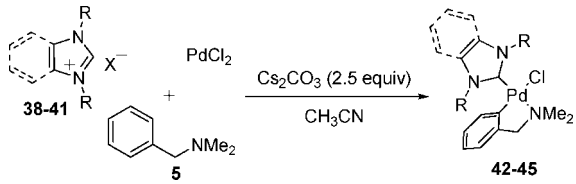
The actual mechanism of the ligation of palladacycles with in situ generated NHCs is not clear at this point. Since N substituents have little effect on the electronic nature and stability of the unsaturated imidazol-2-ylidenes,[1] the relative difficulty with which alkyl-substituted carbenes react with in situ formed $[Pd(dmba)Cl]_2$ most likely rules out the involvement of the free carbene, despite recent reports of NHC generation under similar conditions.[40] The tolerance of the protocol presented herein to air and moisture also corroborates such a conclusion. It is plausible that the palladacycle forms a transient π complex with the imidazolium salts, causing the acidity of the latter to increase and facilitating the complex formation.

(38) Prepared by anion exchange with NH_4PF_6 from the known chloride: Harlow, K. J.; Hill, A. F.; Welton, T. *Synthesis* **1996**, 697–698.

(39) Prepared by anion exchange with NH_4PF_6 from the known bromide: Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267–3274.

(40) Bostai, B.; Novák, Z.; Bényei, A. C.; Kotschy, A. *Org. Lett.* **2007**, *9*, 3437–3439.

Table 6. Synthesis of NHC−Pd(dmba)Cl Complexes from 1,3-Dialkylimidazolium and 1,3-Dialkylbenzimidazolium Salts



entry	conditions[a]	NHC[b]	R	X	yield, %
1	K_2CO_3, 80 °C, 18 h[c]	Im	Bn (**38**)	PF_6	4 (**42**)
2	80 °C, 18 h	Im	Bn (**38**)	PF_6	22 (**42**)
3	100 °C, 18 h	Im	Bn (**38**)	PF_6	31 (**42**)
4	100 °C, 30 min	Im	Bn (**38**)	PF_6	78 (**42**)
5	100 °C, 18 h	Im	Me (**39**)	Cl	45 (**43**)
6	100 °C, 30 min	Im	Me (**39**)	Cl	67 (**43**)
7	100 °C, 18 h	Im	*i*Pr (**40**)	Cl	65 (**44**)
8	100 °C, 30 min	Im	*i*Pr (**40**)	Cl	62 (**44**)
9	80 °C, 18 h	BzIm	*i*Pr (**41**)	PF_6	68 (**45**)[d]
10	100 °C, 30 min	BzIm	*i*Pr (**41**)	PF_6	83 (**45**)[d]

[a] The palladacycle was always prepared at 80 °C. [b] Im = imidazolyl-2-ylidene; BzIm = benzimidazolyl-2-ylidene. [c] 5 equiv of K_2CO_3 was used. [d] The reactions were conducted in the presence of 4 Å molecular sieves.

Perhaps this complexation is more pronounced for 1,3-diarylimidazolium salts: hence, the relative ease of complexation when such carbene precursors are employed. Alternative mechanistic explanations also cannot be discounted at this point.

Molecular Structure of NHC−Palladacycles. The NHC−Pd(dmba)Cl complexes were characterized by X-ray crystallography (Figure 2). Selected bond lengths and angles and dihedral angles are given in Table 7, and the single-crystal data and X-ray collection parameters are given in Table 8. In the crystalline state, the complexes all show the characteristic slightly distorted square-planar Pd(II) center with the NHC and dimethylamino ligands mutually trans. The carbene ligand's five-membered-ring topology varies slightly for different carbenes. The NHC ligand retains the bond angles characteristic for a singlet carbene (∼104° for the imidazol-2-ylidenes and ∼107° for benzimidazol-2-ylidene and 4,5-dihydroimidazol-2-ylidene). The C1−N1 bond is 1.346−1.362 Å, regardless of the carbene type, whereas the N1−C4 bond is 1.384−1.394 Å for imidazol-2-ylidene and benzimidazol-2-ylidene and 1.485−1.490 Å for the backbone saturated analogues. Likewise, the C4−C5 bond length lies in the range of 1.327−1.336 Å for imidazol-2-ylidene, 1.394 Å for benzimidazol-2-ylidene, and 1.502−1.524 Å for the saturated carbenes, in accordance with changing bond types from double to single. This is accompanied by puckering of the carbene ring—the N1−C4−C5−N2 dihedral angle is close to 0 (−1.09 to +1.20°) for the unsaturated carbenes (sp^2) and +16.71 to +19.05° for the saturated analogues (sp^3). The two N-aryl rings are in all cases rotated out of conjugation, and the dihedral angles C1−N1/2−C2/6−C3/7 show large variation from carbene to carbene (58.83−128.66°). There is no apparent correlation between compound structure and dihedral angle value and sign for these low-barrier torsions. In all complexes, the Pd−C1 (1.966−1.996 Å) and Pd−C8 bonds (1.985−2.004 Å) are within the expected range for a single Pd−C bond. The Pd−N3 and Pd−Cl bond lengths are within the ranges of 2.128−2.142 and 2.379−2.424 Å, respectively. The substitution of the chloride for acetate or acetonitrile leads to shorter C−O and C−N bonds (2.112 and 2.118 Å, respectively), without significantly affecting the rest of the structure. The Pd center exhibits a slight distortion from the perfect square-planar configuration as a result from its being a part of the five-membered palladacycle ring. The ranges for the C1−Pd−X angle (X = Cl, O, N), C1−Pd−C8 angle, and N3−Pd−X angle (X = Cl, O, N) are 89.37−95.56, 90.86−94.61, and 90.13−95.37°, respectively. The imidazole and palladacycle rings are closer to perpendicular than to coplanar: the absolute values for the N1−C1−Pd−C8 dihedral angle vary between 60.46 and 117.65°. The five-membered palladacycle moiety is puckered (with the C8−C9−C10−N3 dihedral angle in the range of 25.67−36.20°) due to the presence of sp^3 carbon and nitrogen atoms (the N3−C10−C9 angle ranges from 107.89 to 109.53°, typical for tetrahedral carbons).

Conclusions

We have developed a novel, practical synthesis of NHC-ligated palladacycles by one-pot, three-component, sequential reaction of *N*,*N*-dimethylbenzylamine, $PdCl_2$ or $PdBr_2$, and a wide range of imidazolium salts and their 4,5-dihydro- or benzo-fused counterparts in refluxing acetonitrile in the presence of mild bases (K_2CO_3 and Cs_2CO_3, respectively) in air. Whereas the complexation of the in situ prepared 1,3-diarylimidazol-2-ylidenes is facile, the saturated analogues require a stronger base and the addition of 4 Å molecular sieves to suppress the competing carbene precursor hydrolysis. 1,3-Dialkylimidazolium and 1,3-dialkylbenzimidazolium salts generally require more forcing conditions and strict control of the reaction time for satisfactory complexation. All complexes show a characteristic distorted-square-planar Pd(II) center with the carbene and dimethylamino ligands mutually trans and the planes of the imidazole ring and the heterocycle close to perpendicular. The extension of this methodology to other classes of cyclometalated ligands and the use of the resulting complexes in catalysis are underway.

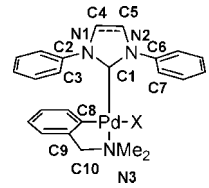
Experimental Section

General Considerations. All reagents and solvents were purchased from commercial sources and were used without further purification, unless otherwise indicated. Deuterated solvents were purchased from Sigma-Aldrich. TLC plates were purchased from VWR. ^1H and ^{13}C NMR data were acquired at 25 °C with a Bruker AV 400 spectrometer. Flash chromatography was performed in a CombiFlash Sq16 on normal phase silica gel cartridges with hexane−ethyl acetate gradients.

General Procedure for the Synthesis of NHC−Pd(dmba)Cl Complexes from 1,3-Diarylimidazolium Salts (Table 1). A pressure tube was charged with $PdCl_2$ (177 mg, 1.00 mmol) and a stir bar, and then acetonitrile (5 mL, HPLC grade) and *N*,*N*-dimethylbenzylamine (160 μL, 178 mg, 1.05 mmol) were added. The mixture was stirred at 80 °C until $PdCl_2$ dissolved completely, forming a dark orange, clear solution (in ∼20−25 min). Finely powdered K_2CO_3 (691 mg, 5.00 mmol) was added, and the mixture was heated at 80 °C until the palladacycle formation was complete, as indicated by the change in the color of the mixture to canary yellow (in ∼5 min). Immediately, NHC·HCl (1.10 mmol) was added, and the mixture was heated at 80 °C with vigorous stirring over 18 h. The mixture was filtered on a pad of Celite (CH_2Cl_2), the volatiles were removed, and the residue was purified by flash chromatography (ethyl acetate gradient in CH_2Cl_2: 0% over 5 min, 0−30% over 15 min).

IPr−Pd(dmba)Cl (12). From IPr·HCl (**7**; 467 mg), **12** (543 mg, 82%) was obtained as an off-white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.21 (s, 2H), 6.82−6.70 (m, 3H), 6.53 (d, *J* = 7.6 Hz, 1H), 3.46 (s, 2H), 3.37 (m, 2H), 3.15 (m, 2H), 2.39 (s, 6H), 1.49 (d, *J* = 6.8 Hz, 6H), 1.18 (d, *J* = 6.8 Hz, 6H), 1.02 (d, *J* = 6.8 Hz, 6H), 0.81 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.5, 150.5,

Table 7. Selected Bond Lengths, Bond Angles, and Dihedral Angles for NHC−Pd(dmba)X Complexes: X = Cl for 12, 15, 16, 18, 25, 42, and 45; X = O for 31, and X = N for 33



param	12	15	16	18	25	31	33	42	45
				Bond Lengths, Å					
C1−N1	1.360	1.362	1.362	1.353	1.345	1.361	1.349	1.346	1.350
N1−C4	1.395	1.394	1.402	1.485	1.490	1.387	1.384	1.384	1.394
C4−C5	1.330	1.335	1.336	1.502	1.524	1.327	1.327	1.332	1.392
C1−Pd	1.996	1.988	1.966	1.976	1.972	1.974	1.992	1.978	1.973
C8−Pd	2.004	1.989	1.997	1.999	1.994	1.985	1.985	2.006	1.991
Pd−X	2.379	2.408	2.415	2.402	2.424	2.112	2.118	2.406	2.393
Pd−N3	2.133	2.133	2.128	2.142	2.140	2.139	2.131	2.138	2.137
				Bond Angles, deg					
N1−C1−N2	104.94	103.99	104.34	107.76	107.71	103.88	104.57	104.59	107.16
C1−Pd−X	91.56	95.88	90.48	97.46	95.53	93.01	95.96	89.37	89.75
C1−Pd−C8	94.61	91.13	92.15	91.64	90.86	91.47	90.93	94.16	92.74
N3−Pd−X	91.40	95.36	95.36	90.13	91.83	93.77	92.05	94.73	95.57
N3−C10−C9	108.61	109.53	109.53	108.24	109.39	108.31	107.89	109.04	108.79
				Dihedral Angles, deg					
N1−C4−C5−N2	1.05	0.09	0.32	19.05	16.71	−0.81	−1.09	−0.58	1.20
C1−N1−C2−C3	120.67	90.51	72.74	128.66	104.89	62.30	58.83		106.71
C1−N2−C6−-C7	−78.34	−73.84	−117.70	−88.42	−59.44	86.15	−100.19		−113.93
N1−C1−Pd−C8	−69.37	−74.95	−96.36	117.65	−68.29	64.63	60.46	70.62	78.46
C8−C9−C10−N3	33.65	28.55	25.67	36.20	31.44	−34.59	−36.51	−29.81	−29.60

147.8, 147.8, 144.7, 136.2, 136.1, 129.7, 125.4, 124.6, 124.0, 123.8, 122.6, 121.5, 72.6, 49.8, 29.0, 28.3, 26.4, 26.2, 23.2, 23.2. Anal. Calcd for $C_{36}H_{48}ClN_3Pd$ (664.66): C, 65.05; H, 7.28; N, 6.32. Found: C, 65.14; H, 7.41; N, 6.53.

IEt−Pd(dmba)Cl (13). From IEt·HCl (**8**; 406 mg), **13** (492 mg, 81%) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (t, J = 7.6 Hz, 2H), 7.24 (dd, J = 7.6, 1.2 Hz, 2H), 7.16 (s, 2H), 7.04 (dd, J = 7.6, 1.2 Hz, 2H), 6.78 (td, J = 7.6, 1.2 Hz, 1H), 6.71 (d, J = 7.2, 1.0 Hz, 1H), 6.68 (td, J = 7.6, 1.2 Hz, 1H), 6.58 (d, J = 7.2, 1.0 Hz, 1H), 3.44 (s, 2H), 2.94 (m, 2H), 2.87 (m, 2H), 2.70 (m, 2H), 2.61 (m, 2H), 2.40 (s, 6H), 1.19 (t, J = 7.2 Hz, 6H), 1.18 (d, J = 7.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.6, 150.0, 147.2, 143.1, 140.0, 137.3, 137.1, 129.1, 126.3, 126.0, 124.1, 123.4, 122.7, 121.1, 72.3, 50.0, 25.9, 25.2, 15.3, 14.7. Anal. Calcd for $C_{32}H_{40}ClN_3Pd$ (608.55): C, 63.16; H, 6.63; N, 6.90. Found: C, 63.16; H, 6.69; N, 6.65.

IMes−Pd(dmba)Cl (14). From IMes·HCl (**9**; 375 mg), **14** (555 mg, 96%) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10 (s, 2H), 6.99 (s, 2H), 6.83−6.76 (m, 4H), 6.70 (td, J = 7.6, 1.2 Hz, 1H), 6.58 (d, J = 7.2, 1.2 Hz, 1H), 3.53 (s, 2H), 2.45 (s, 6H), 2.44 (s, 6H), 2.29 (s, 6H), 2.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.6, 149.3, 147.6, 138.3, 138.3, 137.4, 136.2, 133.9, 129.4, 128.7, 123.9, 123.2, 123.0, 121.2, 72.2, 50.0, 21.1, 20.2, 19.8. Anal. Calcd for $C_{30}H_{36}ClN_3Pd$ (580.50): C, 62.07; H, 6.25; N, 7.24. Found: C, 62.02; H, 6.37; N, 7.40.

ITbp−Pd(dmba)Cl (15). From ITbp·HCl (**10**; 406 mg), **15** (492 mg, 81%) was obtained as an off-white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (dd, J = 8.4, 1.6 Hz, 2H), 7.42 (dd, J = 8.0, 1.2 Hz, 2H), 7.30−7.22 (m, 2H), 7.29 (s, 2H), 6.93−6.81 (m, 5H), 6.39 (d, J = 7.2 Hz), 3.51 (s, 2H), 2.42 (s, 6H), 1.51 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 151.8, 148.0, 146.7, 137.6, 137.5, 131.8, 129.8, 128.7, 125.1, 125.1, 124.7, 123.0, 121.6, 72.4, 49.6, 36.7, 32.8. Anal. Calcd for $C_{32}H_{40}ClN_3Pd$ (608.55): C, 63.16; H, 6.63; N, 6.90. Found: C, 63.13; H, 6.44; N, 6.56.

IPrp−Pd(dmba)Cl (16). From IPrp·HCl (**11**; 375 mg), **16** (500 mg, 86%) was obtained as an off-white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.62 (broad s, 2H), 7.38 (broad m, 6H), 7.23 (s, 2H), 6.92−6.15 (broad m, 4H), 3.51 (broad s, 2H), 2.97 (broad s, 2H), 2.50 (broad s, 6H), 1.58−1.18 (broad s, 6H), 1.18−0.76 (broad s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 147.9, 146.1−144.4 (broad), 137.5 (broad), 135.7 (broad), 130.7 (broad), 129.2, 126.5 (broad), 125.4 (broad), 125.4, 123.1, 123.0, 121.6, 71.8, 50.1, 27.7, 25.6 (broad), 24.2 (broad). Anal. Calcd for $C_{32}H_{40}ClN_3Pd$ (580.50): C, 62.07; H, 6.25; N, 7.24. Found: C, 61.93; H, 6.45; N, 6.71.

Reaction of SIPr·HCl (17) and Palladacycle 6 under the Conditions of Table 2, Entry 1. SIPr·HCl (460 mg, 1.05 mmol) was used. The crude mixture was purified using flash chromatography (solvent A was 9:1 hexane−CH_2Cl_2, solvent B was ethyl acetate; gradient of 0−15% B over 30 min). The amide **19** eluted first (at 8% solvent B), followed by complex **18** (at 12% solvent B). Compound **19** (113 mg, 26%) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (s, 1H), 7.27−7.22 (m, 2H), 7.09−7.02 (m, 3H), 3.89 (t, J = 7.1 Hz, 2H), 3.31 (broad s, 1H), 3.21 (heptet, J = 6.8 Hz, 2H), 3.14 (t, J = 7.1 Hz, 2H), 3.04 (heptet, J = 6.8 Hz, 2H), 1.26 (d, J = 6.8 Hz, 6H), 1.23−1.13 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.9, 147.6, 142.9, 142.2, 135.4, 129.5, 124.5, 123.8, 123.5, 48.8, 48.7, 28.3, 27.7, 25.4, 24.2, 24.1, 23.5. A small amount (7%) of another carbonyl bond rotamer was also observed. Selected resonances: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56 (s, 1H), 3.77 (t, J = 7.1 Hz, 2H).; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.0, 52.0, 50.0. Anal. Calcd for $C_{27}H_{40}N_2O$ (408.62): C, 79.36; H, 9.87; N, 6.86. Found: C, 79.04; H, 9.76; N, 6.72.

General Procedure for the Synthesis of NHC−Pd(dmba)Cl Complexes from 1,3-Diaryl-4,5-dihydroimidazolium Salts (Table 3). A pressure tube was charged with $PdCl_2$ (177 mg, 1.00 mmol), finely powdered 4 Å molecular sieves (1 g), and a stir bar, and then acetonitrile (5 mL, HPLC grade kept over 4 Å molecular sieves) and *N*,*N*-dimethylbenzylamine (160 μL, 177 mg, 1.05 mmol) were added. The mixture was stirred at 80 °C until $PdCl_2$ dissolved completely, forming a dark orange, clear solution (in ∼20−25 min). Finely powdered Cs_2CO_3 (815 mg, 2.50 mmol) was added, and the mixture was heated at 80 °C until the palladacycle formation was complete, as indicated by the change in the color of the mixture to canary yellow (in ∼5 min). Immediately, the required 4,5-dihydroimidazolium salt (1.05 mmol) was added, and the mixture was heated at 80 °C with vigorous stirring over 18 h. The mixture was filtered over a pad of Celite (CH_2Cl_2), the volatiles were removed, and the residue was purified by flash chromatography

Table 8. Selected Crystallographic Data and X-ray Collection Parameters for NHC−Pd(dmba)Cl Complexes 12, 15, 16, 18, 25, 31, 33, and 45

param	12	15	16	18	25	31·0.5CH_2Cl_2	33	42	45
formula	$C_{36}H_{48}ClN_3Pd$	$C_{32}H_{40}ClN_3Pd$	$C_{30}H_{36}ClN_3Pd$	$C_{36}H_{50}ClN_3Pd$	$C_{32}H_{42}ClN_3Pd$	$C_{38.50}H_{52}ClN_3O_2Pd$	$C_{38}H_{51}F_6N_4PPd$	$C_{26}H_{28}ClN_3Pd$	$C_{22}H_{30}ClN_3Pd$
mol wt	664.62	608.52	580.47	666.64	610.54	730.68	815.20	524.36	478.34
temp, K	243(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	orthorombic	monoclinic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1/c$	$P2_1/c$	$C2/c$	*Pbca*	$P2_1/n$	$P2_1/c$	$P2_1/c$
cryst size, mm^3	0.36 × 0.36 × 0.16	0.56 × 0.46 × 0.26	0.30 × 0.18 × 0.06	0.50 × 0.40 × 0.32	0.40 × 0.06 × 0.06	0.60 × 0.50 × 0.36	0.58 × 0.16 × 0.04	0.60 × 0.20 × 0.08	0.30 × 0.20 × 0.10
a, Å	14.5682(5)	13.5849(6)	13.1003(7)	15.2685(7)	27.2962(11)	22.1198(7)	10.3961(18)	13.6799(10)	13.201(2)
b, Å	18.4516(7)	16.2049(7)	15.2782(8)	13.3002(6)	16.6141(7)	18.1254(6)	20.434(3)	12.6283(10)	9.5609(16)
c, Å	26.1633(10)	14.0474(6)	15.1532(8)	17.3267(8)	16.1329(6)	37.6542(13)	19.073(3)	15.7681(11)	17.634(3)
α, deg	90	90	90	90	90	90	90	90	90
β, deg	90	106.5850(10)	115.0280(10)	102.8110(10)	104.4150(10)	90	103.673(3)	114.944(2)	93.208(4)
γ, deg	90	90	90	90	90	90	90	90	90
V, $Å^3$	7032.9(4)	2963.8(2)	2748.1(3)	3431.0(3)	7086.0(5)	15096.7(9)	3937.0(12)	2469.9(3)	2222.2(6)
Z	8	4	4	4	8	16	4	4	4
D_{calcd}, Mg m^{-3}	1.255	1.364	1.403	1.291	1.145	1.286	1.375	1.410	1.430
μ, mm^{-1}	0.630	0.741	0.795	0.646	0.620	0.597	0.572	0.877	0.966
θ range, deg	1.56−25.00	1.84−27.50	1.72−27.49	1.95−27.50	1.45−27.50	1.42−27.50	1.48−27.50	1.64−27.50	1.55−27.50
no. of rflns collected	39 455	20 537	19 174	24 147	27724	116 608	26 984	17 005	16 920
no. of indep rflns	6181	6796	6273	7892	8130	17 343	9055	5682	5097
R_{int}	0.0713	0.0257	0.0459	0.0296	0.0572	0.0500	0.0804	0.0451	0.0661
max/min transmissn	0.9059/0.8049	0.8307/0.6817	0.9538/0.7963	0.8199/0.7383	0.9638/0.7896	0.8137/0.7157	0.9775/0.7328	0.9332/0.6213	0.9096/0.7603
final *R* indices ($I > 2\sigma(I)$)									
R1	0.0671	0.0307	0.0422	0.0360	0.0680	0.0460	0.0695	0.0563	0.0479
wR2	0.1374	0.0773	0.0910	0.0857	0.1854	0.1048	0.1540	0.1205	0.1101
R indices (all data)									
R1	0.0956	0.0361	0.0588	0.0431	0.0886	0.0614	0.0998	0.0758	0.0696
wR2	0.1495	0.0801	0.0947	0.0893	0.1998	0.1100	0.1672	0.1280	0.1213
goodness of fit on F^2	1.142	1.026	1.023	1.055	1.106	1.047	1.014	1.108	1.022
peak/hole, e $Å^{-3}$	0.864/−0.539	0.768/−0.304	0.828/−0.326	0.846/−0.246	1.692/0.562	1.224/−0.950	1.503/−1.452	1.015/−0.817	1.152/−0.576

(solvent A was 9:1 hexane−CH_2Cl_2, solvent B was ethyl acetate; gradient of 0−40% B over 20 min).

SIPr−Pd(dmba)Cl (18). From SIPr·HCl (**17**; 460 mg), **18** (640 mg, 96%) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36−7.28 (m, 4H), 7.22 (m, 1H), 7.10 (dd, J = 7.2, 1.6 Hz, 2H), 6.85 (m, 3H), 6.78 (m, 1H), 4.16 (m, 2H), 4.10 (m, 2H), 3.59 (m, 4H), 3.40 (s, 2H), 2.32 (s, 6H), 1.60 (d, J = 6.8 Hz, 6H), 1.26 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.8 Hz, 6H), 0.74 (d, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.4, 150.7, 148.0, 147.9, 146.3, 136.9, 136.0, 128.8, 125.3, 124.4, 124.0, 122.8, 121.7, 72.6, 54.2, 49.5, 29.0, 28.4, 27.0, 26.3, 24.3, 23.6. Anal. Calcd for $C_{36}H_{50}ClN_3Pd$ (666.68): C, 64.86; H, 7.56; N, 6.30. Found: C, 65.19; H, 7.76; N, 6.39.

SIMes−Pd(dmba)Cl (23). From SIMes·HBF_4 (**20**; 414 mg), **23** (570 mg, 98%) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17 (dd, J = 7.2, 1.3 Hz, 1H), 6.96 (broad s, 2H), 6.89−6.83 (m, 2H), 6.79 (td, J = 6.9, 1.9 Hz, 1H), 6.75 (broad s, 2H), 4.12−4.03 (m, 2H), 4.01−3.94 (m, 2H), 3.46 (s, 6H), 2.67 (s, 6H), 2.36 (s, 6H), 2.29 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 204.1, 149.0, 147.6, 138.8, 137.8, 137.5, 136.4, 135.3, 129.6, 128.8, 123.9, 123.0, 121.3, 72.1, 51.8, 49.8, 21.0, 20.4, 20.0. Anal. Calcd for $C_{30}H_{38}ClN_3Pd$ (582.52): C, 61.86; H, 6.58; N, 6.93. Found: C, 61.40; H, 6.68; N, 6.93.

SIMes−Pd(dmba)Br (24). From SIMes·HBF_4 (**20**; 414 mg) and $PdBr_2$ (266 mg, 1.00 mmol), **24** (417 mg, 67%) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (dd, J = 7.2, 1.6 Hz, 1H), 6.96 (broad s, 2H), 6.89−6.85 (m, 2H), 6.79 (m, 1H), 6.74 (broad s, 2H), 4.12−4.05 (m, 2H), 4.01−3.96 (m, 2H), 3.45 (s, 2H), 2.67 (s, 6H), 2.44 (s, 6H), 2.28 (s, 6H), 2.26 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.8, 150.8, 147.5, 138.6, 137.6, 137.5, 136.5, 135.3, 129.7, 129.6, 128.9, 123.9, 123.1, 121.4, 72.1, 51.9, 50.0, 21.0, 20.9, 20.2. Anal. Calcd for $C_{30}H_{38}BrN_3Pd$ (625.13): C, 57.47; H, 6.11; N, 6.70. Found: C, 57.04; H, 5.81; N, 6.44.

SITBp−Pd(dmba)Cl (25). From SITBp·HBF_4 (**21**; 441 mg), **25** (552 mg, 90%) was obtained as a white solid. The compound was obtained as a mixture of two inseparable atropisomers: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.68−6.80 (12H), 4.42−3.80 (4H), 3.57−3.27 (4H), 2.40−2.28 (6H), 1.70−1.63 (12H), 1.40−1.38 (6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.1, 204.3, 151.8−121.7 (36 aromatic carbons), 72.3, 72.0, 57.7, 57.0, 56.3, 50.2, 49.4, 49.1, 36.9, 36.5, 33.0, 32.6, 32.3. Anal. Calcd for $C_{32}H_{42}ClN_3Pd$ (610.57): C, 62.95; H, 6.93; N, 6.88. Found: C, 62.90; H, 7.01; N, 6.79.

SIPrp−Pd(dmba)Cl (26). From SIPrp·HBF_4 (**22**; 414 mg), **26** (469 mg, 80%) was obtained as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.0−7.6 (broad s, 2H), 7.39−7.24 (broad m, 6H), 7.05 (broad m, 1H), 6.87−6.79 (broad m, 3H), 4.22 (broad s, 2H), 4.12 (broad s, 2H), 3.45 (s, 2H), 3.16 (broad s, 2H), 2.39 (broad s, 6H), 1.50−1.24 (broad s, 6H), 1.10−0.82 (broad s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.7, 147.8, 146.0−144.7 (broad), 138.7, 135.7, 131.7−130.3 (broad), 128.4, 126.5 (broad), 126.2 (broad), 125.2, 123.1, 121.6, 71.6, 54.2, 49.8, 28.2, 25.0 (broad), 23.9 (broad). Anal. Calcd for $C_{30}H_{38}ClN_3Pd$ (582.52): C, 61.86; H, 6.58; N, 6.93. Found: C, 61.64; H, 6.28; N, 7.06.

***N,N*-(2-*tert*-Butylphenyl)-1,4-diazabuta-1,4-diene (29).** To a solution of 2-*tert*-butylaniline (**27**; 20.4 mL, 19.6 g, 131 mmol) in a mixture of methanol (50 mL) and water (5 mL) was added glyoxal solution (40% in water; 7.5 mL, 9.43 g, 65 mmol), and the resulting mixture was stirred over 1.5 h. The yellow crystalline mass was filtered off, dried with a stream of air, and vacuum-dried over P_2O_5. Diimine **29** was obtained as a yellow solid (19.91 g, 96%) and used directly for the next step. A small portion was crystallized (methanol) to provide an analytically pure sample. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (s, 2H), 7.44 (m, 2H), 7.27 (m, 4H), 6.94 (m, 2H), 1.47 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.6, 150.2, 143.7, 127.2, 127.1, 126.4, 118.9, 35.8, 30.5. Anal. Calcd for $C_{22}H_{28}N_2$ (320.47): C, 82.45; H, 8.81; N, 8.74. Found: C, 82.88; H, 8.65; N, 8.79.

ITbp·HCl (10). To a solution of the diimine **29** (6.41 g, 10 mmol) in THF (20 mL) were added chloromethyl ethyl ether (1.0 mL, 1.04 g, 11 mmol) and water (0.2 mL) in succession, and the mixture was stirred at 40 °C over 18 h. The solvent was removed to dryness, and the residue was partitioned between ethyl acetate (50 mL) and water (50 mL). The organic layer was further extracted with water (25 mL × 2). The combined aqueous layers were then extracted with CH_2Cl_2 (25 mL × 4). The combined CH_2Cl_2 layers were dried ($MgSO_4$), the solvent was removed under reduced pressure, and the residue was triturated with CH_2Cl_2/ethyl acetate (1:5). ITBp·HCl (**10**; 1.28 g, 35%) was obtained as an off-white solid. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 11.7−9.7 (broad s, 1H), 8.4−6.7 (broad s, 2H), 7.74 (m, 2H), 7.62 (td, J = 8.8, 1.6 Hz, 2H), 7.45 (td, J = 7.6, 1.2 Hz, 2H), 1.36 (s, 18H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 145.9 (broad), 140.9 (broad), 131.7, 129.1 (broad), 127.6, 125.6 (broad), 36.0, 31.8. Anal. Calcd for $C_{23}H_{29}ClN_2$ (368.94): C, 74.88; H, 7.92; N, 7.59. Found: C, 75.05; H, 7.89; N, 7.72.

SITbp·HBF_4 (21). In a two-necked 250 mL round-bottomed flask equipped with a reflux condenser and a stopper, a solution of diimine **29** (3.20 g, 10 mmol) in THF (50 mL) and methanol (50 mL) was brought to reflux. $NaBH_4$ (3.78 g, 100 mmol) was added portionwise over 30 min. After the mixture was cooled, the colorless solution obtained was quenched with water (200 mL), most of the organic solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was dissolved in $HC(OEt)_3$ (25 mL), and concentrated HCl (12.0 M, 1.00 mL, 12 mmol) was added dropwise. The mixture was heated at 120 °C over 1 h and cooled. The volatiles were removed under high vacuum to dryness, the crude chloride salt was dissolved in water (10 mL), and a solution of NH_4BF_4 (5.24 g, 50 mmol) in water (20 mL) was added. The solid was filtered off, rinsed with a minimal amount of water followed by diethyl ether, and redissolved in CH_2Cl_2 (50 mL). The solution was dried ($MgSO_4$) and evaporated. SITBp·HBF_4 (**21**; 3.68 g, 88%) was obtained as an off-white solid after drying under high vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (broad m, 1H), 7.82−7.72 (broad m, 2H), 7.54 (dd, J = 8.0, 0.8 Hz, 2H), 7.54 (m, 2H), 7.35 (broad m, 2H), 4.68 (broad s, 4H), 1.48 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.0, 146.6, 133.6, 131.0, 130.8, 128.7, 128.6, 55.8, 35.9, 32.2. Anal. Calcd for $C_{23}H_{31}BF_4N_2$ (422.31): C, 65.41; H, 7.40; N, 6.63. Found: C, 65.40, H, 7.47, N 6.53.

***N,N*-(2-Isopropylphenyl)-1,4-diazabuta-1,4-diene (30).** Freshly distilled 2-isopropylaniline (**28**; 5.7 mL, 5.41 g, 40 mmol) and glyoxal solution (40% in water; 2.3 mL, 2.93 g, 20 mmol) were added to a degassed (Ar stream over 20 min) mixture of methanol (20 mL) and water (2 mL), and this mixture was stirred over 18 h. The dark-colored reaction mixture was diluted with water (50 mL), and methanol was removed under reduced pressure. The crude product was extracted in diethyl ether (50 mL × 3), the combined organic layers were dried ($MgSO_4$), and the volatiles were evaporated under reduced pressure. Diimine **30** was obtained as a yellow oil (4.84 g, 71%) after flash chromatography (80 g Combiflash cartridge, ethyl acetate gradient in hexane: 0% over 10 min, followed by 0−3% over 15 min, and 3% over 10 min). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.35 (s, 2H), 7.38 (dd, J = 7.6, 1.6 Hz, 2H), 7.30 (td, J = 7.6, 1.6 Hz, 2H), 7.24 (td, J = 7.6, 1.2 Hz, 2H), 7.00 (dd, J = 7.6, 1.2 Hz, 2H), 3.59 (heptet, J = 6.8 Hz, 2H), 1.28 (d, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.7, 148.4, 143.2, 127.7, 126.8, 125.8, 117.4, 27.9, 23.3. Anal. Calcd for $C_{20}H_{24}N_2$ (292.42): C, 82.15; H, 8.81; N, 8.74. Found: C, 81.86; H, 9.17; N, 9.00.

IPrp·HCl (11). The procedure for compound **10** was followed, using diimine **30** (2.92 g, 10 mmol), chloromethyl ethyl ether (1.0 mL, 1.04 g, 12 mmol), and water (0.1 mL) in THF (10 mL).

IPrp·HCl (**11**; 2.11 g, 62%) was obtained as an off-white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.7−9.7 (broad s, 1H), 8.4−6.7 (broad s, 2H), 7.74 (m, 2H), 7.62 (td, J = 8.8, 1.6 Hz, 2H), 7.45 (td, J = 7.6, 1.2 Hz, 2H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 138.2, 132.3, 131.8, 127.8, 127.7, 127.0, 124.7, 28.3, 23.9. Anal. Calcd for $C_{21}H_{25}ClN_2$ (340.89): C, 73.99; H, 7.39; N, 8.22. Found: C, 74.07; H, 7.24; N, 8.02.

SIPrp·HBF$_4$ (22). The procedure for compound **21** was followed, starting with **30** (2.92 g, 10 mmol). SIPrp·HBF_4 (**22**; 3.94 g, 94%) was obtained as an off-white solid after drying under high vacuum. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.74−7.70 (m, 3H), 7.48−7.40 (m, 4H), 7.32−7.27 (m, 2H), 4.61 (s, 4H), 3.08 (heptet, J = 6.8 Hz), 1.36 (d, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.9, 144.7, 132.5, 131.0, 128.1, 127.7, 127.0, 54.0, 28.4, 24.2. Anal. Calcd for $C_{21}H_{27}BF_4N_2$ (394.26): C, 63.97; H, 6.90; N, 7.11. Found: C, 63.57, H, 6.46; N, 6.83.

General Procedure for the Ion Exchange of IPr−Pd(dmba)Cl Complexes with Ag Salts (Table 4). To a solution of the silver salt (1 mmol) in acetone (2 mL), a solution of complex **12** (665 mg, 1 mmol) in CH_2Cl_2 (8 mL) was added. The mixture was stirred over 1 h, filtered, and evaporated to dryness.

IPr−Pd(dmba)OAc (31). From AgOAc (167 mg), **31** (663 mg, 96%) was obtained as a white solid after chromatography with CH_2Cl_2−ethyl acetate/methanol (volume ratio 5:1) gradient, 0−100% over 20 min. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (t, J = 7.6 Hz, 2H), 7.22 (broad d, J = 7.6 Hz, 2H), 7.12 (s, 2H), 7.10 (broad d, J = 7.6 Hz, 2H), 6.68 (t, J = 7.2 Hz, 2H), 6.61 (m, 3H), 6.38 (d, J = 7.6 Hz, 1H), 3.24 (s, 2H), 3.20 (m, 2H), 2.81 (m, 2H), 2.18 (s, 6H), 1.40 (s, 3H), 1.33 (d, J = 6.4 Hz, 6H), 1.10 (d, J = 6.4 Hz, 6H), 0.93 (d, J = 6.8 Hz, 6H), 0.79 (d, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.3, 176.0, 148.2, 148.0, 147.0, 145.1, 136.0, 135.8, 129.6, 125.4, 124.2, 124.1, 123.8, 122.4, 121.7, 72.3, 49.2, 28.7, 28.5, 26.3, 25.3, 23.0, 22.8. Anal. Calcd for $C_{38}H_{51}N_3O_2Pd$ (688.25): C, 66.31; H, 7.47; N, 6.11. Found: C, 66.70; H, 7.63; N, 6.31.

IPr−Pd(dmba)TFA (32). From AgTFA (221 mg), **32** (733 mg, 99%) was obtained as a white solid after chromatography with CH_2Cl_2−ethyl acetate gradient, 0−100% over 20 min. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.25 (s, 2H), 7.21 (d, J = 7.6 Hz, 2H), 6.80 (td, J = 6.8, 1.2 Hz, 2H), 6.70 (m, 2H), 6.70 (d, J = 7.6 Hz, 1H), 3.34 (s, 2H), 3.29 (m, 2H), 2.84 (m, 2H), 2.24 (s, 6H), 1.36 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.8 Hz, 6H), 1.03 (d, J = 6.8 Hz, 6H), 0.88 (d, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.3, 160.8 (q, $^2J_{C-F}$ = 35 Hz), 147.6, 146.7, 145.9, 145.0, 136.0, 135.8, 135.4, 129.7, 125.7, 124.5, 124.3, 123.9, 122.7, 121.0, 116.6 (q, $^1J_{C-F}$ = 292 Hz), 72.0, 49.1, 28.6, 28.5, 26.3, 26.3, 23.0, 22.4. Anal. Calcd for $C_{38}H_{49}F_3N_3O_2Pd$ (742.22): C, 61.49; H, 6.52; N, 5.66. Found: C, 62.06; H, 6.67; N, 5.77.

IPr−Pd(dmba)OTf (33). From AgOTf (257 mg), **33** (745 mg, 96%) was obtained as a white solid after chromatography with CH_2Cl_2−ethyl acetate gradient, 0−100% over 20 min. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (t, J = 4.0 Hz, 2H), 7.31 (d, J = 4.0 Hz, 4H), 7.30 (s, 2H), 7.21 (td, J = 7.6, 1.2 Hz, 1H), 6.76−6.71 (m, 2H), 6.36 (dd, J = 4.2, 0.8 Hz, 1H), 3.45 (s, 2H), 3.03 (broad s, 4H), 2.38 (s, 6H), 1.35−0.95 (broad, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5, 160.8, 147.3, 145.7, 141.1, 135.5, 134.6, 130.7, 126.3, 125.1, 124.9, 124.6, 122.6, 121.8, 121.0, 120.3 (q, $^1J_{C-F}$ = 317 Hz), 71.0, 49.5, 29.0, 26.3, 22.8. Anal. Calcd for $C_{37}H_{48}F_3N_3O_3PdS$ (778.28): C, 57.10; H, 6.22; N, 5.40. Found: 57.07; H, 6.08; N, 4.94.

IPr−Pd(dmba)PF$_6$·CH$_3$CN (34). From $AgPF_6$ (257 mg) in CH_2Cl_2 (10 mL) and CH_3CN (2 mL), **34** (745 mg, 96%) was obtained as a white solid after chromatography with CH_2Cl_2−acetonitrile, 0−20% over 20 min. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (t, J = 8.0 Hz, 2H), 7.38 (m, 2H), 7.39−7.17 (broad m, 4H), 6.88 (t, J = 6.8 Hz, 2H), 6.79−6.74 (m, 2H), 6.30 (d, J = 7.2 Hz, 1H), 3.44 (s, 2H), 3.21 (broad s, 2H), 2.60 (broad s, 2H), 2.36 (s, 6H), 2.05 (s, 3H), 1.59−1.26 (broad s, 6H), 1.26−1.00 (broad m, 12H), 0.92−0.52 (broad s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.7, 147.7, 145.9 (broad), 145.2 (broad), 135.3, 134.8, 130.5, 126.3, 125.3, 124.9 (broad), 124.5 (broad), 123.9, 122.7, 120.7, 71.8, 50.0, 28.9 (broad), 28.6 (broad), 26.3, 26.3, 22.9 (broad), 22.7 (broad), 21.1. Anal. Calcd for $C_{38}H_{51}F_3N_4PPd$ (815.22): C, 55.99; H, 6.31; N, 6.87. Found: C, 55.78; H, 6.65; N, 6.89.

[Pd(dmba)OAc]$_2$ (35). A 100 mL round-bottomed flask was charged with $PdCl_2$ (885 mg, 5.00 mmol) and a stir bar. Next, acetonitrile (20 mL, HPLC grade) and *N*,*N*-dimethylbenzylamine (790 μL, 878 mg, 5.25 mmol) were added. The mixture was stirred at 80 °C until $PdCl_2$ dissolved completely, forming a dark orange, clear solution (in ∼20−25 min). Finely powdered NaOAc (2.05 g, 25.0 mmol) was added, and the mixture was heated at 80 °C over 20 min. The mixture was filtered over a pad of Celite (CH_2Cl_2), the volatiles were removed, and the residue was dissolved in CH_2Cl_2 (30 mL), washed with water (50 mL × 3), dried ($MgSO_4$), and evaporated. The dimeric acetate-bridged palladacycle **35** (1.38 g, 92%) was obtained as a yellow solid after trituration with hexanes. The ^{1}H and ^{13}C NMR spectra were in accordance with the literature.

[Pd(dmba)(acac)]$_2$ (36). A 100 mL round-bottomed flask was charged with $PdCl_2$ (885 mg, 5.00 mmol) and a stir bar. Next, acetonitrile (20 mL, HPLC grade) and *N*,*N*-dimethylbenzylamine (790 μL, 878 mg, 5.25 mmol) were added. The mixture was stirred at 80 °C until $PdCl_2$ dissolved completely, forming a dark orange, clear solution (in ∼20−25 min). Finely powdered K_2CO_3 (3.46 g, 25.0 mmol) was added, and the mixture was heated at 80 °C over 10 min. Acetylacetone (540 μL, 527 mg, 5.25 mmol) was added, and the mixture was stirred for another 15 min. The mixture was worked up as specified for compound **35**. Complex **36** (1.56 g, 92%) was obtained as a yellow solid after trituration with hexanes. The ^{1}H and ^{13}C NMR spectra were in accordance with the literature.

ITBp−Pd(dmba)I (37, Table 5). A pressure tube was charged with $PdCl_2$ (177 mg, 1.00 mmol) and a stir bar. Next, acetonitrile (5 mL, HPLC grade) and *N*,*N*-dimethylbenzylamine (160 μL, 178 mg, 1.05 mmol) were added. The mixture was stirred at 80 °C until $PdCl_2$ dissolved completely, forming a dark orange, clear solution (in ∼20−25 min). Finely powdered K_2CO_3 (691 mg, 5.00 mmol) was added, and the mixture was heated at 80 °C until the palladacycle formation was complete, as indicated by the change in the color of the mixture to canary yellow (in ∼5 min). Immediately, ITbp·HCl (**10**; 385 mg, 1.05 mmol) was added, and the mixture was heated at 80 °C with vigorous stirring over 18 h. Next, NaI (450 mg, 3.00 mmol) was added, and the mixture was heated at 80 °C for another 30 min. The mixture was filtered over a pad of Celite (CH_2Cl_2), the volatiles were removed, and the residue was purified by flash chromatography (hexane−ethyl acetate: 0−100% over 20 min). Complex **33** (672 mg, 96%) was isolated as a pale orange solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (dd, J = 8.4, 1.6 Hz, 2H), 7.50 (dd, J = 8.4, 1.6 Hz, 2H), 7.32 (s, 2H), 7.32−7.28 (m, 2H), 6.99 (td, J = 3.2, 1.6 Hz, 1H), 6.92−6.86 (m, 4H), 6.23 (dd, J = 4.00, 1.6 Hz, 2H), 3.56 (s, 2H), 2.60 (s, 6H), 1.50 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.1, 156.2, 148.2, 146.3, 137.6, 136.7, 131.7, 130.0, 128.7, 125.6, 125.1, 125.0, 123.5, 122.0, 72.2, 51.7, 36.8, 33.3. Anal. Calcd for $C_{32}H_{40}IN_3Pd$ (700.00): C, 54.91; H, 5.76; N, 6.00. Found: C, 54.68; H, 6.19; N, 6.02.

General Procedure for the Synthesis of NHC−Pd(dmba)Cl Complexes from 1,3-Dialkylimidazolium and 1,3-Dialkylbenzimidazolium Salts (Table 1). A pressure tube was charged with $PdCl_2$ (177 mg, 1.00 mmol) and a stir bar. Next, acetonitrile (5 mL, HPLC grade) and *N*,*N*-dimethylbenzylamine (160 μL, 178 mg, 1.05 mmol) were added. The mixture was stirred at 80 °C until $PdCl_2$ dissolved completely, forming a dark orange, clear solution (in ∼20−25 min). Finely powdered Cs_2CO_3 (814 mg, 2.50 mmol) was added, and the mixture was heated at 80 °C until the palladacycle formation

was complete, as indicated by the change in the color of the mixture to canary yellow (in ~5 min). Immediately, the required imidazolium or benzimidazolium salt (1.10 mmol) was added, the temperature was increased to 100 °C, and the heating was continued for 30 min at that temperature with vigorous stirring. The mixture was filtered over a pad of Celite (CH_2Cl_2), the volatiles were removed, and the residue was purified by flash chromatography (solvent A, CH_2Cl_2; solvent B, ethyl acetate−methanol (volume ratio 4:1) gradient, 0−30% B in A over 15 min.

Bn_2Im−Pd(dmba)Cl (42). From $Bn_2Im \cdot HPF_6$ (**38**; 356 mg), **42** (411 mg, 78%) was obtained as an off-white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49−7.42 (m, 4H), 7.35−7.29 (m, 6H), 7.02 (dd, J = 7.6, 1.2 Hz, 1H), 6.98 (td, J = 7.6, 1.2 Hz, 1H), 6.79 (td, J = 7.2, 2.4 Hz, 1H), 6.77 (s, 2H), 6.15 (dd, J = 7.6, 1.2 Hz, 1H), 5.69 (d, J = 14.8 Hz, 2H), 5.60 (d, J = 14.8 Hz, 2H), 3.94 (m, 2H), 2.85 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.5, 149.2, 148.5, 136.1, 135.9, 129.0, 128.8, 128.3, 125.6, 123.8, 122.3, 120.9, 72.2, 55.5, 50.3. Anal. Calcd for $C_{26}H_{28}ClN_3Pd$ (524.39): C, 59.55; H, 5.38; N, 8.01. Found: C, 59.52; H, 5.41; N, 7.90.

Me_2Im−Pd(dmba)Cl (43). From $Me_2Im \cdot HCl$ (**39**; 146 mg), **43** (248 mg, 67%) was obtained as an off-white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.02 (dd, J = 1.6, 0.4 Hz, 1H), 6.95 (td, J = 7.6, 1.2 Hz, 1H), 6.95 (s, 2H), 6.75 (ddd, J = 7.6, 1.6, 0.4 Hz, 1H), 5.95 (dd, J = 7.6, 1.2 Hz, 1H), 3.97 (s, 6H), 3.92 (s, 2H), 2.83 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.3, 149.9, 135.3, 124.9, 124.1, 123.4, 123.0, 72.2, 50.1, 38.6. Anal. Calcd for $C_{14}H_{20}ClN_3Pd$ (372.20): C, 45.18; H, 5.42; N, 11.29. Found: C, 45.32; H, 5.47; N, 11.21.

***i*Pr_2Im−Pd(dmba)Cl (44).** From *i*$Pr_2Im \cdot HCl$ (**40**; 259 mg), **44** (256 mg, 62%) was obtained as an off-white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.03 (s, 2H), 7.00 (dd, J = 7.2, 0.8 Hz, 1H), 6.94 (td, J = 7.6, 1.2 Hz, 1H), 6.72 (td, J = 7.6, 1.6 Hz, 1H), 5.97 (dd, J = 7.2, 0.8 Hz, 1H), 5.53−5.43 (m, 2H), 3.91 (s, 2H), 2.83 (s, 6H), 1.54 (d, J = 2.4 Hz, 6H), 1.36 (d, J = 2.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 148.5, 147.8, 136.3, 125.2, 123.6, 122.2, 116.9, 116.5, 72.1, 53.1, 50.2, 23.7, 22.8. Anal. Calcd for $C_{18}H_{28}ClN_3Pd$ (428.31): C, 50.48; H, 6.59; N, 9.81. Found: C, 50.12; H, 6.23; N, 9.80.

***i*Pr_2BzIm−Pd(dmba)Cl (45).** From *i*$Pr_2BzIm \cdot HPF_6$ (**41**; 383 mg), **45** (399 mg, 83%) was obtained as an off-white solid. At the beginning of the reaction, finely powdered 4 Å molecular sieves (1 g) were added. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (m, 2H), 7.28−7.24 (m, 3H); 7.21 (s, 2H), 7.03 (dd, J = 7.6, 1.2 H), 6.94 (td, J = 7.6, 1.2 H), 6.67 (td, J = 7.6, 1.4 Hz, 1H), 6.17−6.06 (m, 2H), 3.96 (s, 2H), 2.88 (s, 6H), 1.76 (d, J = 7.2 Hz, 6H), 1.62 (d, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 183.8, 148.3, 136.7, 125.2, 123.8, 122.4, 122.1, 122.1, 112.6, 112.6, 72.2, 54.6, 50.4, 21.1, 20.8. Anal. Calcd for $C_{22}H_{30}ClN_3Pd$ (478.32): C, 55.24; H, 6.32; N, 7.41. Found: C, 55.26; H, 6.38; N, 7.44.

Single-Crystal X-ray Structural Determination. Single crystals for all complexes were grown by a slow infusion of *n*-pentane into concentrated solutions of the NHC−palladacycles in CH_2Cl_2. Suitable crystals were mounted on quartz fibers, and X-ray data were collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The collecting frames of data, indexing reflection, and determination of lattice parameters and polarization effects were performed with the SMART suite of programs.[41] The integration of intensity of reflections and scaling was performed by SAINT.[41] The empirical absorption correction was performed by SADABS.[42] The space group determination, structure solution, and least-squares refinements on $|F|^2$ were carried out with SHELXTL.[43] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions.

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Supporting Information Available: Crystallographic information files (CIF) for compounds **12**, **15**, **16**, **18**, **25**, **31**, **33**, **42**, and **45**. This material is available free of charge via the Internet at http://pubs.acs.org.

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