Cyclometalated and Alkoxyphenyl-Substituted Palladium Imidazolin-2-ylidene Complexes. Synthetic, Structural, and Catalytic Studies

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Some new *N*,*N*′-bis(aryl)imidazolinium salts (**3a**−**h**), in which the N-aryl groups have one unsubstituted ortho position and alkyl (Me, Pr^i) or alkoxy (OMe, OPr^i) substitution at the other ortho and/or para positions, have been prepared. They were used for the synthesis of N-heterocyclic carbene complexes of palladium in which the N-heterocyclic carbene is attached to cyclometalated or electron-rich aromatic rings (**4**, **5**, **11d**,**e**). The reaction of Pd(tmed)$(CH_3)_2$ with the N-heterocyclic carbene generated from **3b** and base gave the dimethyl complex **6**, which quantitatively eliminated ethane to form the Pd(0) complex **7**. The latter was converted to a new type of "pincer" complex (**8**) by facile cyclometalation of both aromatic groups of the N-heterocyclic carbene ligand. The activities of the new complexes **4** and **9d**,**e** in the Heck reaction of aryl halides were compared. At higher temperatures the complexes **9d**,**e** show low activity in the coupling of aryl chlorides.

Introduction

The use of N-heterocyclic carbenes (NHCs) as ligands in homogeneous catalysis is still an area of intensive research.[1] The originally proposed electronic "analogy" between NHCs and trialkylphosphines[2] has been the guiding idea for the design of new catalysts with enhanced activity and stability, by replacing phosphine ligands with NHCs. However, the detailed picture that is emerging from this work reveals many subtle differences associated with the electronically similar ligand types. For example, in late-transition-metal complexes with organometallic coligands (σ-alkyls, alkylidenes, hydrides, etc.) the coordinated NHC can participate in unusual rearrangement reactions leading to imidazolium or alkylimidazolium salt formation (formally reductive eliminations),[3] conversion to β-heteroatom alkyls by migration of anionic ligands to the carbene carbon,[4] cleavage of the heterocyclic ring,[5] or C−N bond cleavage between the heterocyclic ring and the alkyl or aryl substituents.[6] Furthermore, the aliphatic or aromatic substituents of NHCs coordinated to low-oxidation-state rhodium, iridium, and ruthenium metal centers can sometimes undergo metalation under thermal or photochemical conditions.[7] The majority of the coordination chemistry of the NHC ligands has been based on "unsaturated" imidazol-2-ylidenes. This is due to the convenient synthetic methods leading to their precursor imidazolium salts and the easier handling of the free NHCs (dimerization to Wanzlick alkenes is completely suppressed). Recently, ligand design aspects of "saturated" NHCs have been investigated,[8,4c] especially in relation to the development of highly active and chiral Ru metathesis catalysts. These studies included the variation of the nature and size of NHC substitution and the attachment of other heteroatom donors to the NHC functionality. In comparison to the unsaturated analogues, the

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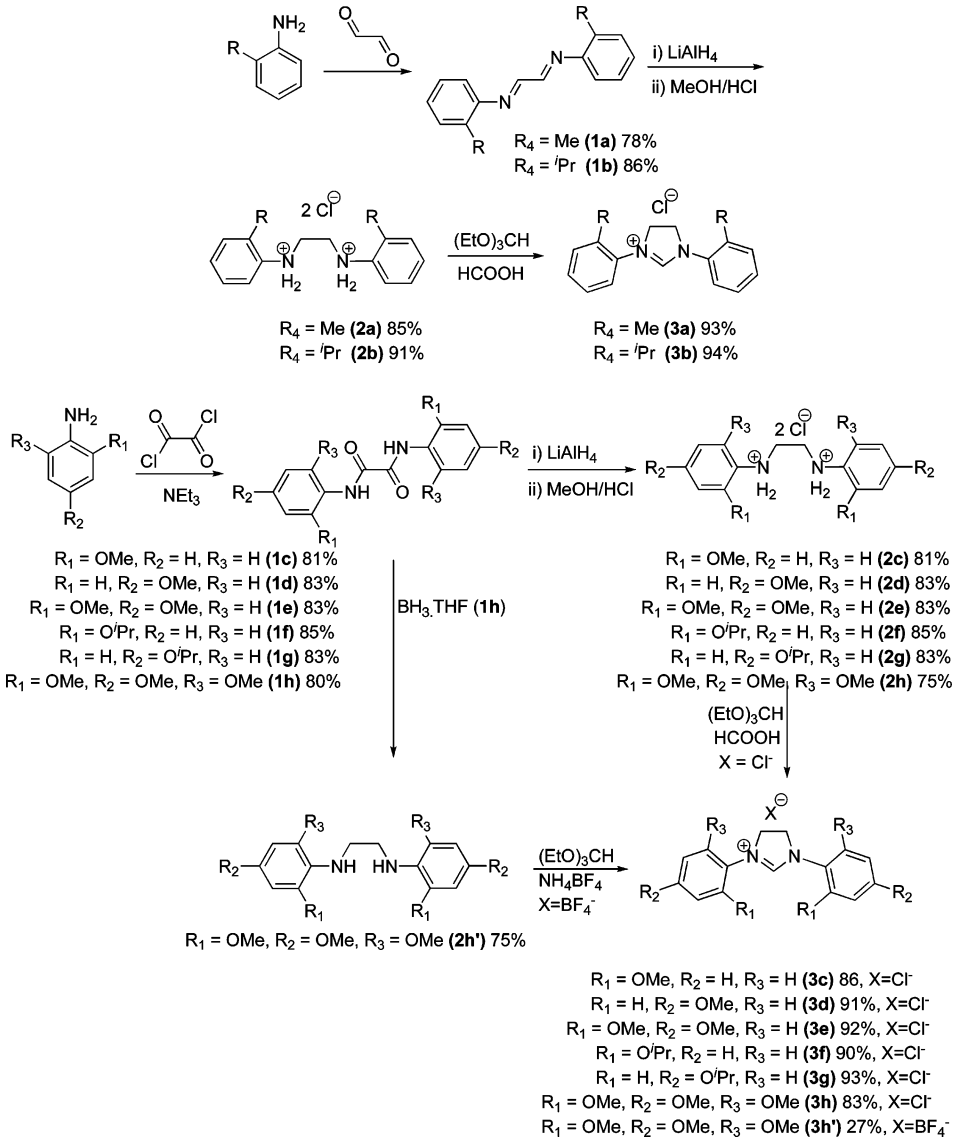
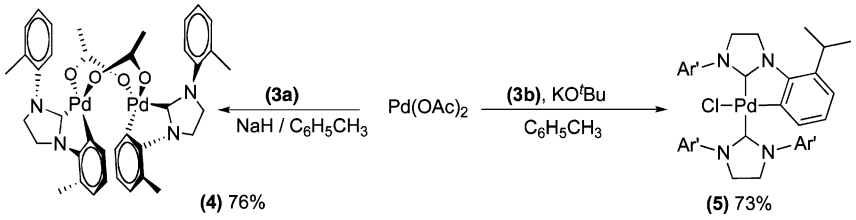
Scheme 1. Synthesis of Imidazolinium Salts Described in This Paper



Scheme 2. Synthesis of Cyclometalated Palladium Acetates and Halides



saturated NHCs are stronger σ-donors, giving rise to reactive low-oxidation-state metal centers.[1b,9]

As a continuation of our work aiming at the development of well-defined NHC complexes suitable for cross-coupling reactions, we initiated a study of Pd complexes with "saturated" NHCs substituted with electron-rich or cyclometalated aromatic rings. Palladium complexes with cyclometalated phosphines and phosphites have shown activity in Suzuki and C−heteroatom bond formation reactions.[10] Surprisingly, there has been a very limited number of spectroscopically characterized cyclometalated Pd(NHC) complexes reported by Hiraki et al.[11]

In this paper we report (i) the synthesis of *N*,*N*′-bis(aryl)-imidazolinium salts in which the aryl groups have one vacant ortho position and alkyl (Me, Pr^i) or alkoxy (OMe, OPr^i) substitution at the other ortho and/or para positions (see Scheme 1), (ii) the synthesis and full characterization of new Pd complexes with "saturated" cyclometalated NHC ligands (Schemes 2 and 3), and (iii) studies of the catalytic activity of selected new complexes in the Heck reaction.

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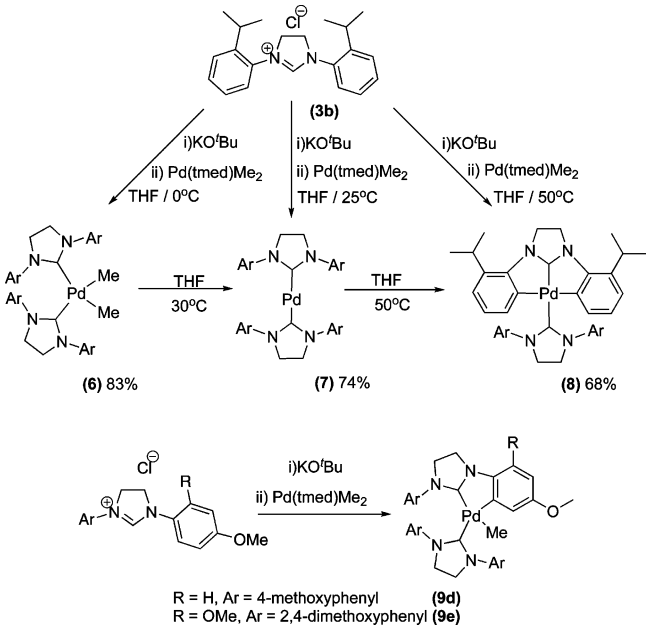
Scheme 3. Synthesis and Reactivity of Cyclometalated Palladium Alkyl Complexes



Results and Discussion

Proligand Synthesis. The imidazolinium salts **3c**−**h** were prepared by the cyclization of the corresponding bidentate anilinium salts with triethyl orthoformate. The anilines **2a**,**b** were prepared by modification of literature methods and **1c**−**h** by reduction of the oxalamides with $LiAlH_4$ or BH_3.[12] All new salts were characterized by analytical and spectroscopic methods. The isolated chlorides **3c**−**h** were sparingly soluble in nonaqueous polar solvents, exhibiting rather broad ^{1}H NMR spectra. However, characteristic peaks in the range δ 9.0−10.5 assignable to the C2 attached proton of the heterocyclic ring were easily seen in all spectra. The identities of **3f**,**h′** were unequivocally established crystallographically (see the Supporting Information). All salts were hygroscopic solids that were dried azeotropically and stored under nitrogen prior to deprotonation. Attempts to isolate the free N-heterocyclic carbenes by the reaction of the imidazolinium salts with various bases were not successful; therefore, for the preparation of the metal complexes described below the NHC was generated in situ in the presence of a Pd precursor.

Synthesis of Palladium Complexes. (i) Alkylaryl-Substituted NHCs. The reaction of the NHC generated from **3a** and NaH with $Pd(OAc)_2$ in toluene at 50 °C led to facile metalation of the aromatic *o*-C−H bond of the *o*-tolyl substituent and formation of the acetato-bridged dimer **4**. The complex was characterized by analytical and spectroscopic methods. The low symmetry of the metal coordination sphere, which was evident from the ^{1}H and ^{13}C{^{1}H} NMR spectra and the appearance of the C_{NHC}−Pd (δ 198.25) and C_{tolyl}−Pd resonances (δ 136.12) in the ^{13}C{^{1}H} NMR spectrum, supported the presence of one metalated aromatic ring attached to the NHC heterocycle. Further confirmation of this was obtained by a single-crystal X-ray diffraction study of **4**. An ORTEP diagram of the molecule is shown in Figure 1.

The molecule is dimeric, with two acetato ligands bridging two distorted-square-planar Pd centers having very similar metrical data. The coordination environment of each Pd comprises one C_{NHC}, one C_{aryl}, and two Pd−O(acetato) bonds. The Pd···Pd separation is ca. 2.87 Å. The Pd−C_{NHC} (1.946(5) and 1.972(5) Å) and Pd−C_{tolyl} (1.972(5) and 1.963(5) Å) bond lengths fall in the short end of the range reported for similar complexes. The Pd−O(acetato) bond lengths trans to the C_{NHC} and C_{tolyl} donor atoms are virtually equal, indicating similar trans influences of the two organometallic ligands. Complex **4** is the first structurally characterized palladium complex with cyclometalated NHC ligands. Cyclometalated Pd−NHC complexes have been previously obtained by the reaction in boiling *m*-xylene of the electron-rich (Wanzlick) olefin 1,3-diphenyl-2-imidazolidinylidene with Pd complexes bearing a donor-stabilized σ-alkyl.[11] Palladium complexes with bridging acetato and phosphine or carbene coligands have been previously prepared by the reaction of $Pd(OAc)_2$ with phosphines or NHCs in specific ratios; reversible cyclometalation of the phosphines has been observed in $[Pd(PPr^i_3)_2(OAc)]^+$.[12]

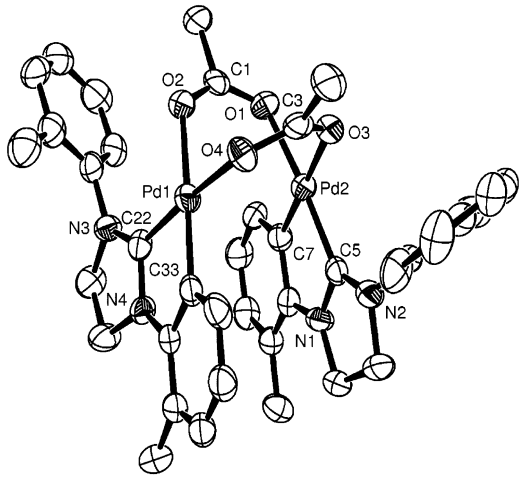


Figure 1. ORTEP representation of the structure of **4** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: O1−Pd2 = 2.090(3), O2−Pd1 = 2.123(4), O3−Pd2 = 2.127(4), O4−Pd1 = 2.094(3), Pd1−Pd2 = 2.8688(6), C5−Pd2 = 1.946(5), C7−Pd2 = 1.963(5), C22−Pd1 = 1.934(5), C33−Pd1 = 1.972(5); C22−Pd1−C33 = 79.5(2), C22−Pd1−O4 = 173.32(19), C33−Pd1−O4 = 93.91(18), C22−Pd1−O2 = 98.78(19), C33−Pd1−O2 = 178.29(18), O4−Pd1−O2 = 87.77(13), C22−Pd1−Pd2 = 101.06(15), C33−Pd1−Pd2 = 103.02(14), O4−Pd1−Pd2 = 81.59(10), O2−Pd1−Pd2 = 77.56(10), C5−Pd2−C7 = 79.6(2), C5−Pd2−O1 = 173.48(19), C7−Pd2−O1 = 93.89(18), C5−Pd2−O3 = 99.72(19), C7−Pd2−O3 = 178.46(19), O1−Pd2−O3 = 86.72(13), C5−Pd2−Pd1 = 95.26(14), C7−Pd2−Pd1 = 97.93(15), O1−Pd2−Pd1 = 84.78(10), O3−Pd2−Pd1 = 80.72(10).

Reaction of $Pd(OAc)_2$ with the NHC generated in situ from the salt **3b** and KOBu^t gave complex **5**. It is not known whether the reaction proceeds via the generation of the free imidazolin-2-ylidene which was trapped by the Pd source or by elimination of Bu^{t}OH from the *tert*-butoxide adduct formed by the reaction of the imidazolinium salt with the nucleophilic Bu^{t}O$^-$.[7c,13] The presence of two types of NHC ligands and the occurrence of cyclometalation was evidenced from the two C_{NHC} signals (δ 202.23 and 198.40) and one C_{aryl} signal (δ 162), respectively, in the ^{13}C{^{1}H} NMR spectrum of **5**. The structure of **5** was determined crystallographically, and a diagram of the molecule is shown in Figure 2.

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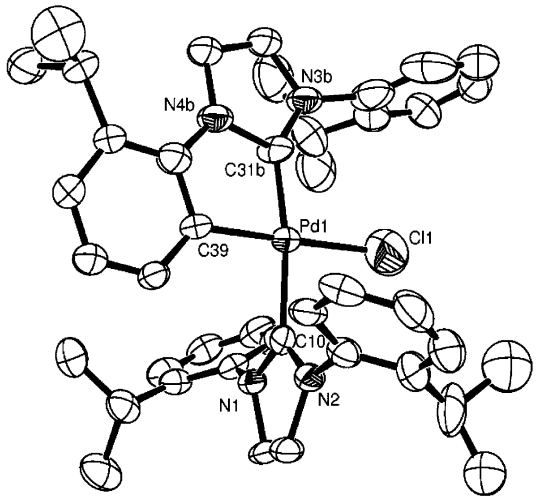


Figure 2. ORTEP representation of the structure of **5** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: C10−Pd1 = 2.029(8), C31−Pd1 = 1.93-(6), C39−Pd1 = 2.024(8), Cl1−Pd1 = 2.366(4); C31−Pd1−C39 = 83.1(16), C31−Pd1−C10 = 168.7(16), C39−Pd1−C10 = 91.9-(3), C31−Pd1−Cl1 = 96.0(16), C39−Pd1−Cl1 = 179.1(2), C10−Pd1−Cl1 = 89.0(2).

Complex **5** is monomeric, with a square-planar Pd. The coordination sphere includes one chloride and one cyclometalated and one monodentate NHC ligand. The angle between the N(1)−C(10)−N(2) plane of the monodentate NHC and the coordinate plane is ca. 80°. The N(3)−C(31)−N(4) plane of the cyclometalated NHC coincides with the coordination plane. All Pd−C bond lengths to the NHC and aryl C fall in the expected range.[4a,14]

The mechanism that could account for the different natures of **4** and **5** is not obvious. The formation of an intermediate of the type bis(carbene)PdX_2, X = acetate, halide (vide infra), which could further rearrange to the cyclometalated product **5**, may be controlled kinetically when $KOBu^t$ is used. In contrast, use of NaH may result in the preferential formation of (carbene)-PdX_2, X = acetate, which after cyclometalation could give **4** by dimerization. It is interesting to notice that attempts to introduce the carbene **3a** by the reaction of $KOBu^t$ with the imidazolinium salt in the presence of a Pd source gave intractable mixtures. Further metalation of **5** by prolonged heating or by carrying out the reaction under different stoichiometries gave only reduced yields of **5**.

Reaction of the NHC generated in situ from the salt **3b** and $KOBu^t$ with Pd(tmed)$(CH_3)_2$ was critically dependent on the reaction temperature. If the reaction mixture was kept below 0 °C, the isolated product was **6**, in which the Pd is coordinated by two monodentate NHC ligands and two methyls. This complex was characterized spectroscopically, analytically, and crystallographically. The ^{1}H NMR data of **6** support a C_2-symmetric structure in solution (one singlet for Pd−CH_3 and two doublets for the diastereotopic CH$(CH_3)_2$ in addition to signals due to the ligand backbone and aromatic protons). The solution structure is maintained in the solid state, as is shown in the ORTEP diagram of the molecule obtained from a single-crystal X-ray diffraction study (Figure 3).

The N(1)−C(1)−N(2) plane of the NHC ligand forms a dihedral angle of ca. 52° with the coordination plane of the square-planar Pd. All Pd−C bond lengths are very similar, as expected for the σ-donating NHCs and methyls, and are within the range reported in the literature.[14]

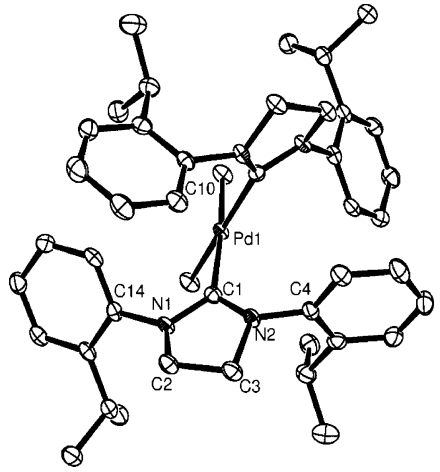


Figure 3. ORTEP representation of the structure of **6** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Pd1−C1 = 2.045(3), Pd1−C10 = 2.088-(3); C1′−Pd1−C1 = 97.09(14), C1′−Pd1−C10 = 88.79(10), C1−Pd1−C10 = 173.81(10), C10−Pd1−C10′ = 85.42(15).

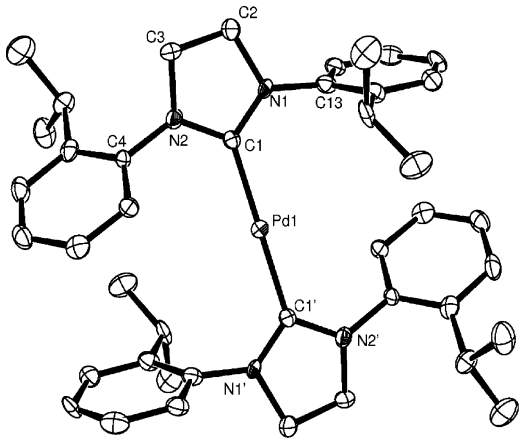


Figure 4. ORTEP representation of the structure of **7** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: C1−Pd1 = 2.022(6); C1−Pd1−C1′ = 180.000(1).

Reaction of the NHC generated in situ from **3b** and $KOBu^t$ with Pd(tmed)$(CH_3)_2$ at room temperature gave good yields of the linear air-sensitive Pd(0) species **7**. The structure of the molecule is shown in Figure 4.

In the solid state **7** shows a C_{2h} molecular symmetry and a linear Pd(0) center. The N1−C1−N2 and N1′−C1′−N2′ planes of the NHC heterocycles adopt an eclipsed conformation with the bulky isopropyl substituents stacked on the same side of the molecule. The Pd−C bond lengths are ca. 2.022 Å.

Complex **7** is the first structurally characterized Pd(0) NHC complex with a saturated NHC backbone. Linear Pd(0) complexes analogous to **7** with bulky imidazol-2-ylidene ligands (unsaturated NHCs) have previously been reported.[15] All adopt a staggered conformation of the two NHC planes in order to minimize steric interactions. The preferred eclipsed conformation of **7** in the solid state may be due to crystal-packing factors and highlights the reduced steric congestion in this linear electronically unsaturated molecule.

(14) Tulloch, A. A. D.; Winston, S.; Danopoulos, A. A.; Eastham, G.; Hursthouse, M. B. *Dalton Trans.* **2003**, 699.

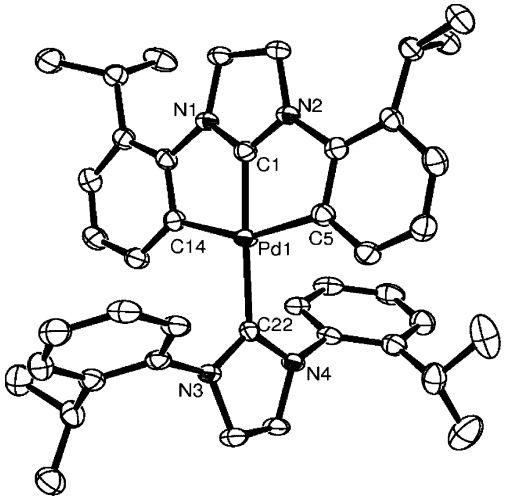


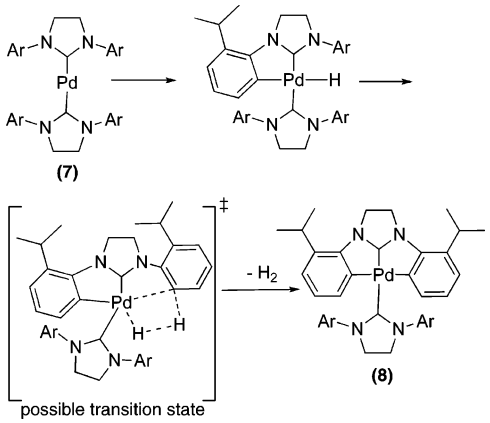
Figure 5. ORTEP representation of the structure of **8** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: C1−Pd1 = 1.901(3), C5−Pd1 = 2.101(3), C14−Pd1 = 2.092(3), C22−Pd1 = 2.038(3); C1−Pd1−C22 = 176.06(11), C1−Pd1−C14 = 77.59(11), C22−Pd1−C14 = 101.68(10), C1−Pd1−C5 = 77.72(11), C22−Pd1−C5 = 102.85(10), C14−Pd1−C5 = 155.27(10).

Previous methods leading to linear $Pd^0(carbene)_2$ included metal vapor synthesis,[15a] substitution of P(*o*-tol)$_3$ from Pd(P(*o*-tol)$_3$)$_2$[15c,e] by free NHC, and reaction of [Pd(allyl)Cl]$_2$ with sodium malonate in the presence of NHC.[15b] All require the use of thermally stable NHC ligands, which is generally feasible with imidazol-2-ylidenes and bulky imidazolin-2-ylidenes. The synthesis of **7** constitutes a mild and clean method for the reduction of Pd(II), compatible with sterically less hindered saturated NHCs; however, its scope is still under investigation and may be limited due to other competing reactions, as exemplified below.

Reaction of the NHC generated in situ from **3b** and KOBu^t with Pd(tmed)(CH$_3$)$_2$ at 50 °C afforded good yields of the complex **8** as yellow air-stable crystals. The identity of **8** was established crystallographically. An ORTEP diagram of the molecule is given in Figure 5.

Complex **8** is a square-planar Pd(II) complex in which cyclometalation has taken place on the two aromatic substituents of the same NHC ligand, leading to a unique, formally dianionic tridentate "pincer". The fourth coordination site of the Pd is occupied by an ordinary monodentate NHC ligand. The tridentate "pincer" is almost planar, while the N3−C22−N4 plane of the monodenate carbene forms an angle of ca. 81° with the coordination plane. The Pd−C_{NHC} bond length within the "pincer" (1.901(3) Å) is shorter than that of the monodentate NHC (2.038(3) Å). Furthermore, the N1−C1−N2 angle of the tridentate NHC (113.1(2)°) is much larger than the corresponding angle for the monodentate species (106.5(2)°), possibly due to steric constraints. Distortions are also seen in the coordination angles C1−Pd1−C5 (77.72(11)°) and C1−Pd1−C14 (77.59-(11)°) involving the tridentate species. Metalations leading to bis-NHC "pincer" complexes have been reported for Rh and Zr.[16]

Scheme 4. Plausible Mechanism Leading to the Formation of 8



Better insight into the mechanism of the formation of **6**−**8** was obtained by monitoring the thermolysis of **6** in d_8-THF by ^{1}H NMR spectroscopy. At room temperature **6** was cleanly transformed to **7** and ethane. Thermolysis of **7** at 55−60 °C gave the "pincer" complex **8**. No other products (i.e., methylimidazolinium salts) were observed. However, conditions for the clean monometalation of **7** have not been found.

It has been established on many occasions that a dominant decomposition pathway of Pd(NHC) alkyls involves reductive coupling of the alkyl and NHC ligands to form imidazolium salts.[3] This reaction has been studied by experimental and computational methods for "unsaturated" NHCs.[17] It is surprising that the reductive elimination of ethane responsible for the conversion of **6** to **7** occurs in preference to imidazolinium salt reductive elimination.

On the other hand, the preferred double metalation of aromatic rings associated with the formation of **8** is also remarkable; 2,6-diphenylpyridines have been bis-cyclometalated at the aromatic rings by Au(III) following a transmetalation methodology.[18] Bis-cyclometalated phosphines and phosphites complexed to Pd are not known, even though a limited number of examples with iridium and platinum have been reported.[19] Metalation of the alkyl substituents of two different alkyl-NHC ligands coordinated to the same Ir center has been reported by Nolan.[19e] However, double metalation on the same NHC has not been observed before. A plausible mechanism accounting for the formation of products **6**−**8** may proceed via a sequence of Pd(0)−Pd(II)//Pd(II)−Pd(IV) or, more likely, by Pd(0)−Pd(II) and σ-bond metathesis steps (see Scheme 4). The former sequence has been postulated in the presence of co-oxidants.[20]

(ii) Alkoxyaryl-Substituted NHCs. Imidazolin-2-ylidene complexes bearing alkoxy-substituted aromatic rings have only

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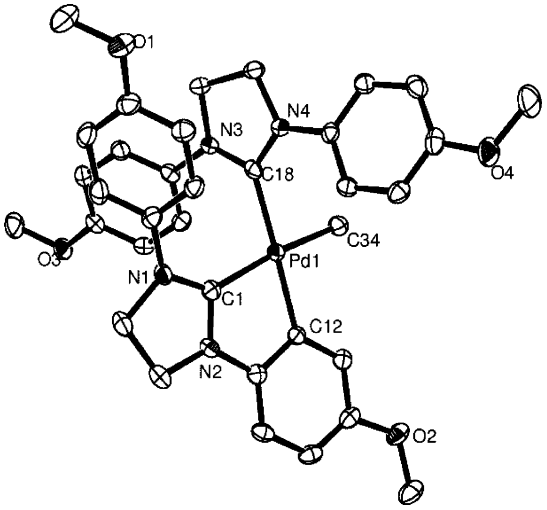

Figure 6. ORTEP representation of the structure of **9d** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Pd1−C18 = 2.036(3), Pd1−C12 = 2.048(3), Pd1−C1 = 2.053(3), Pd1−C34 = 2.086(3); C18−Pd1−C12 = 178.53(10), C18−Pd1−C1 = 98.64(10), C12−Pd1−C1 = 80.26(11) C18−Pd1−C34 = 88.40(10), C12−Pd1−C34 = 92.61-(11), C1−Pd1−C34 = 171.33(11).

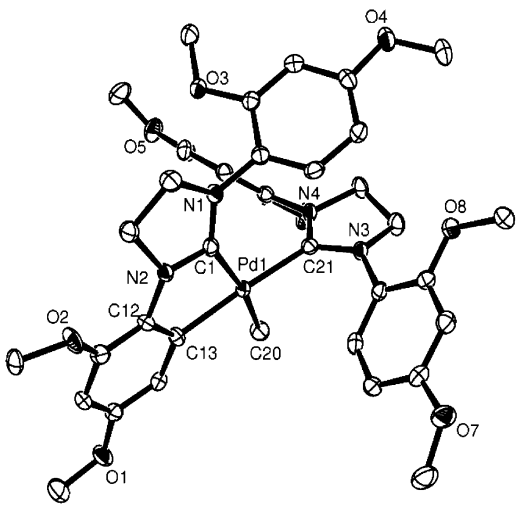

Figure 7. ORTEP representation of the structure of **9e** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Pd1−C21 = 2.038(3), Pd1−C13 = 2.044(3), Pd1−C1 = 2.054(4), Pd1−C20 = 2.095(4); C21−Pd1−C13 = 176.17(14), C21−Pd1−C1 = 103.88(14), C13−Pd1−C1 = 79.86(14), C21−Pd1−C20 = 84.57(14), C13−Pd1−C20 = 91.80(14), C1−Pd1−C20 = 169.63(14).

recently been reported in relation to the development of ruthenium metathesis catalysts.[8a] The electron-releasing properties, the easily tunable bulk, and the possible hemilability of the alkoxo substituents provide a wide scope of the alkoxo-substituted NHCs ligands for catalyst tuning. Our initial results in this area are reported here, focusing on the synthesis of selected Pd complexes and their application as catalysts in the Heck reactions. One feature that became apparent from our study is the propensity of the ligands without ortho substituents on the aromatic ring to undergo facile cyclometalation.

Reaction of Pd(tmed)$(CH_3)_2$ with the NHC generated in situ from **3d**,**e** and KOBu^t (vide supra) gave good yields of complexes **9d**,**e**, respectively. The ^{1}H NMR spectra of the new complexes suggest a low molecular symmetry and the presence of one methyl group on Pd. In addition, signals associated with two Pd−C_{NHC} and one Pd−C_{aryl} point to cyclometalation of the NHC ligand. The structures of **9d**,**e** were determined by single-crystal X-ray diffraction. ORTEP diagrams of the complexes are shown in Figures 6 and 7, respectively.

Both complexes are square planar, the coordination sphere comprising one singly metalated NHC, one monodentate NHC, and one methyl group. The planes of the NHC and the cyclometalated rings coincide with the coordination plane, while the plane of the monodentate NHC forms an angle of ca. 67° with the coordination plane. The Pd−C_{NHC} and Pd−C_{aryl} bond lengths are virtually equal and are slightly shorter than the Pd−C_{methyl} bond length. There is no effect of the additional methoxy group in **9e** on the metrical data. In contrast to the case for **8**, complexes **9d**,**e** do not undergo further metalation, even if they are heated to 100 °C.

It is interesting to notice that in this reaction a Pd(0) product analogous to **7** has not been observed. The reason for this may be the increased electron-releasing nature of the alkoxy-substituted aromatic rings, which is expected to destabilize lower (i.e., Pd(0)) and stabilize higher oxidation states (i.e., Pd(II), Pd(IV)). Therefore, the metalations leading to **9d**,**e** and **8** are probably different mechanistically.

Catalytic Studies. The use of Pd−NHC complexes as catalysts in the Heck reaction has been intensively studied. The initial work by Herrmann and co-workers[21] was focused on reactive aryl iodides. More recent efforts have been extended to the less reactive bromides and chlorides.[22] There is no generally applicable, high-TON and -TOF homogeneous catalyst for the non- or deactivated aryl chlorides. The best phosphine-containing system is based on PBu$^t_3$.[23] Furthermore, there is still ongoing debate about the nature of the active species formed from soluble Pd complexes in high-temperature Heck reactions under catalytic conditions (nanoparticles, molecular underligated species, or both).[24]

In view of the success of cyclometalated Pd phosphine and phosphite complexes in various C−C coupling reactions,[10] we compared the activity of **4** and **9d**,**e** in the Heck reaction of aryl bromides and chlorides with *n*-butyl acrylate under different conditions. Selected data are compiled in Table 1.

The data show that **4** and **9d**,**e** are good catalysts for the coupling of nonactivated and deactivated aryl bromides with acrylates at low catalyst loading (1.5 mol %). With the activated aryl chlorides the best conversions are observed at higher temperatures (160 °C) and in Bu_4NBr. Complexes **9d**,**e** catalyze the coupling of chlorobenzene in Bu_4NBr, albeit in low yields. In comparison to other NHC[22a] and phosphine[23] catalysts, the new complexes show inferior activity for the coupling of aryl chlorides and operate under more forcing conditions.

Conclusions

Palladium complexes with saturated NHCs bearing cyclometalated aromatic substituents can be prepared under mild conditions. The ease of cyclometalation was dependent on the

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Table 1. Comparable Activity Data in the Coupling of Various Aryl Halides with *n*-Butyl Acrylate Catalyzed by the Complexes Described in the Paper[a]

	aryl halide	catalyst	solvent	temp	time (h)	base	yield (%)
1	C_6H_5Br	**4**	dioxane	110	18	NEt_3	90
2	C_6H_5Br	**9e**	dioxane	110	18	NEt_3	99
3	C_6H_5Br	**4**	NMP	140	18	NEt_3	96
4	C_6H_5Br	**9e**	NMP	140	18	NEt_3	99
5	4-$CH_3C_6H_4Br$	**4**	NMP	140	18	NEt_3	90
6	4-$CH_3C_6H_4Br$	**9d**	NMP	140	18	NEt_3	99
7	4-$CH_3C_6H_4Br$	**9e**	NMP	140	18	NEt_3	99
8	4-$CH_3COC_6H_4Cl$	**4**	DMF	140	18	NEt_3	50
9	4-$CH_3COC_6H_4Cl$	**4**	Bu_4NBr	140	18	NaOAc	70
10	4-$CH_3COC_6H_4Cl$	**9d**	DMF	140	18	NEt_3	38
11	4-$CH_3COC_6H_4Cl$	**9d**	Bu_4NBr	160	18	NaOAc	84
12	4-$CH_3COC_6H_4Cl$	**9e**	Bu_4NBr	160	18	NaOAc	79
13	C_6H_5Cl	**4**	NMP	140	18	NEt_3	0
14	C_6H_5Cl	**9d**	DMF	140	18	NEt_3	15
15	C_6H_5Cl	**9d**	DMF	160	18	NBu_3	25
16	C_6H_5Cl	**9d**	Bu_4NBr	160	18	NaOAc	35
17	C_6H_5Cl	**9e**	Bu_4NBr	160	18	NaOAc	25

[a] See the Experimental Section for details.

nature of the substitution of the aromatic ring. The ring substitution and the coligands are important factors that determine the nature of the products and the mechanism of the cyclometalation. In fact, in one case cyclometalation was preceded by the formation of an isolable $Pd(NHC)_2$, suggesting that the metalation step involved C−H oxidative addition. In contrast, the isolation of cylometalated $Pd^{II}(NHC)(CH_3)$ complexes when Pd(tmed)$(CH_3)_2$ was reacted with alkoxy-substituted NHCs suggests that the metalation in this case may involve Pd(II)/Pd(IV) or σ-bond metathesis steps. Finally, the reaction with $Pd(OAc)_2$ may proceed via electrophilic attack or agostic intermediates.[25] The new cyclometalated complexes show good activity in the Heck coupling of aryl bromides with acrylates and low to moderate activity in the coupling of aryl chlorides with acrylates.

Experimental Section

General Methods. Elemental analyses were carried out by the London Metropolitan University microanalytical laboratory. All manipulations were performed under nitrogen in a Braun glovebox or using standard Schlenk techniques, unless stated otherwise. Solvents were dried using standard methods and distilled under nitrogen prior use. The light petroleum used throughout had a boiling point of 40−60 °C.

The starting materials 2-methoxyaniline, 4-methoxyaniline, 2,4-dimethoxyaniline, 2,4,6-trimethoxyaniline, 2-isopropoxyaniline, and 4-isopropoxyaniline were prepared by the reduction of the corresponding nitro compounds by modification of literature procedures (see the Supporting Information for full details).[26−29] NMR data were recorded on Bruker AV-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^{1}H), respectively. The spectra were referenced internally using the signal from the residual protio solvent (^{1}H) or the signals of the solvent (^{13}C).

General Method for the Synthesis of the Imidazolinium Salts 3c−h. The alkoxy-substituted imidazolinium salts **3c−g** were prepared by cyclization of the suitably substituted bis anilinium chloride salts with triethyl orthoformate. Full experimental details for each individual compound have been included as Supporting Information. The imidazolinium salt **3h** was prepared by cyclization of *N*,*N*′-bis(2,4,6-trimethoxyphenyl)ethylenediamine (**2h**) with triethyl orthoformate in the presence of NH_4BF_4.

***N*,*N*′-Bis(aryl)oxalamides 1c−h.** To a diethyl ether solution (200 mL) of substituted aniline (22.00 mmol) and Et_3N (2.90 mL) was added dropwise at 0 °C a solution of oxalyl chloride (0.90 mL, 10.00 mmol) in ether (50 mL). The mixture was then stirred at room temperature overnight. The precipitate that formed was filtered and triturated in methanol to remove triethylammonium chloride. The solid was then filtered, washed with ether, and dried under vacuum.

***N*,*N*′-Bis(aryl)ethylenebis(ammonium) Dichlorides 2c−h.** These compounds were prepared by the reduction of the oxalamides **1c−h** with $LiAlH_4$. The oxalamide (8.10 mmol) was dissolved in THF, and the solution was added dropwise to a precooled (0 °C) $LiAlH_4$ (0.61 g, 16.00 mmol) suspension in THF (10 mL). The mixture was refluxed overnight. After this mixture was cooled to 0 °C, methanol was added dropwise until the effervescence ceased. The mixture was further hydrolyzed with a solution of NaOH (2.0 g) and $MgSO_4$ (2.0 g) in water (10 mL). The resulting slurry was filtered, and the solid was washed with THF. The filtrate was evaporated, and the resulting oil was dissolved in methanol. Concentrated HCl was then added, and the solvents were removed to yield a solid which was collected, washed with acetone, and dried under vacuum.

***N*,*N*′-Bis(2,4,6-trimethoxyphenyl)ethylenediamine (2h′).** *N*,*N*′-Bis(2,4,6-trimethoxyphenyl)oxalamide (3.40 g, 8.00 mmol) was dissolved in THF, and to this was added a BH_3·THF solution (10 mL). The mixture was refluxed overnight. Methanol was then added dropwise, after cooling, until the bubbling ceased. The solvents were removed, and methanol was added again and removed under vacuum. This was repeated three times. The methanol-insoluble solid was then filtered and dried under vacuum. Yield: 2.35 g (6.00 mmol), 75%. ES^+ MS (*m*/*z* (%)): 391.9, 393.0, and 394.0 $[M + H]^+$. ^{1}H NMR (300 MHz, d_6-DMSO; δ): 9.30 (2H, s, −N*H*), 6.30 (4H, s, *m*-*H* aromatics), 6.10 (4H, s, CH_2 ethylene), 3.90 (6H, s, *p*-OCH_3), 3.80 (12H, s, *o*-OCH_3). ^{13}C NMR data could not be collected, as the compound was almost insoluble in all common deuterated solvents.

1,3-Bis(aryl)imidazolinium Chlorides 3c−h. The salts **2c−h** (6.89 mmol) were suspended in triethyl orthoformate (5 mL) along with formic acid (2 drops), and these suspensions were refluxed at 120 °C for 2 h. The mixtures were cooled to room temperature, and ether was added. The precipitated products were filtered, washed with ether, and dried azeotropically before storing in a glovebox.

1,3-Bis(2,4,6-trimethoxyphenyl)imidazolinium Tetrafluoroborate (3h′). *N*-*N*′-Bis(2,4,6-trimethoxyphenyl)ethylenediamine (**2h′**; 0.30 g, 0.74 mmol) and ammonium tetrafluoroborate (0.10 g, 0.90 mmol) were suspended in triethyl orthoformate (5 mL) and refluxed overnight at 120 °C. The mixture was cooled to room temperature, and the precipitated product was filtered, washed with ether, and dried under vacuum. Yield: 0.10 g (0.20 mmol), 27%. ES^+ MS (*m*/*z* (%)): 403.2 and 404.2 $[M]^+$. HRMS (ES^+; *m*/*z*): calcd for $[C_{21}H_{27}N_2O_6]^+$, 403.1869; found, 403.1872. Anal. Calcd for $C_{21}H_{27}BF_4N_2O_6$: C, 51.45; H, 5.55; N, 5.71. Found: C, 51.41; H, 5.57; N, 5.70. ^{1}H NMR (300 MHz, d_6-DMSO; δ): 9.30 (1H, s, imidazolinium *H*), 6.30 (4H, s, aromatic C*H*), 3.85 (4H, s, backbone CH_2), 3.80 (6H, s, *p*-OCH_3), 3.35 (12H, s, *o*-OCH_3). ^{13}C NMR data could not be collected, as the compound was almost insoluble in all common deuterated solvents.

Bis(μ_2-Acetato-κ^2*O*,*O*′)bis{2-[3-(2-methylphenyl)imidazolin-2-ylidene]-3-methylphenyl-κ^2*C*,*C*′}dipalladium(II) (4). The imidazolinium chloride **3a** (0.25 g, 0.89 mmol), $Pd(OAc)_2$ (0.20 g, 0.89 mmol), and NaH (0.24 g, 1.0 mmol) were placed in an ampule.

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Toluene (15 mL) was added, the ampule was sealed under partial vacuum, and the mixture was heated at 50 °C for 3 h. The resulting suspension was filtered through Celite, and the filtrate was reduced to ca. 5 mL and layered with petroleum ether to yield yellow crystals. Yield: 0.28 g (0.68 mmol), 76%. Anal. Calcd for $C_{97}H_{104}N_8O_8Pd_4$: C, 60.19; H, 5.42; N, 5.79. Found: C, 60.33; H, 5.53; N, 5.87. ^{1}H NMR (300 MHz, $C_6D_5CD_3$; δ): 7.52 (2H, d, J = 7.2 Hz, aromatic C*H*), 7.13 (2H, d, J = 6.3 Hz, aromatic C*H*), 7.00−6.40 (10H, m, aromatic C*H*), 6.21 (2H, d, J = 5.9 Hz, aromatic C*H*), 3.40 (4H, t, J = 10.2 Hz, 2 × backbone CH_2), 2.68 (4H, t, J = 10.2 Hz, 2 × backbone CH_2), 2.31 (6H, s, CH_3COO), 1.60 (6H, s, aromatic CH_3), 1.20 (6H, s, aromatic CH_3). ^{13}C{^{1}H} NMR (75 MHz, $C_6D_5CD_3$; δ): 198.25 (carbene *C*−Pd), 136.12 (aromatic *C*−Pd), 130.33 (aromatic *C*−N), 130.16 (aromatic *C*−N), 129.84, 129.06, 124.07, 123.75, 123.43, 120.67, 118.27, 115.82, and 107.73 (aromatic carbons), 52.58 (acetate *C*CH$_3$), 44.04 (backbone *C*H$_2$), 41.72 (backbone *C*H$_2$), 22.32 (acetate *C*H$_3$), 16.28 (*o*-*C*H$_3$), 15.94 (o-*C*H$_3$).

[1,3-Bis(2-isopropylphenyl)imidazolin-2-ylidene]chloro{2-[3-(2-isopropylphenyl)imidazolin-2-ylidene]-3-isopropylphenyl-κ^2*C,C′*}palladium(II) (5). The salt **3b** (0.62 g, 1.80 mmol), $Pd(OAc)_2$ (0.20 g, 0.89 mmol), and KO^{t}Bu (0.22 g, 2.0 mmol) were placed in an ampule. Toluene (15 mL) was added, and the ampule was sealed under partial vacuum and heated at 50 °C for 3 h. The resulting suspension was filtered through Celite, and the filtrate was reduced to ca. 3 mL and layered with petroleum ether to yield colorless crystals. Yield: 0.49 g (0.65 mmol), 73%. Anal. Calcd for $C_{42}H_{51}ClN_4Pd$: C, 66.92; H, 6.82; N, 7.43. Found: C, 66.90; H, 6.81; N, 7.42. ^{1}H NMR (300 MHz, C_6D_6; δ): 7.41 (3H, d, J = 8.7 Hz, aromatic C*H*), 6.49 (3H, dd, J = 8.7, 2.7 Hz, aromatic C*H*), 6.42 (3H, d, J = 2.7 Hz, aromatic C*H*), 6.31 (6H, m, aromatic C*H*), 3.63 (4H, s, 2 × backbone CH_2), 3.41 (4H, s, 2 × backbone CH_2), 3.37 and 3.26 (2 × 2H, septet, J = 6.9 Hz, 4 × C*H*(CH$_3$)$_2$), 1.59, 1.56, 1.48, and 1.42 (4 × 6H, d, J = 6.9 Hz, 4 × CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ, 202.23 (carbene *C*−Pd), 198.40 (carbene *C*−Pd), 161.99 (aromatic *C*−Pd), 155.32 (aromatic quaternary *C*−N), 149.25 (aromatic quaternary *C*−N), 142.61 (aromatic quaternary *C*−CH(CH$_3$)$_2$), 129.69, 139.86, 137.45, 132.44, 129.56, 128.27, 126.92, 126.54, 126.02, 123.50, and 121.37 (aromatic), 56.26 and 54.01 (backbone *C*H$_2$), 52.89 and 49.16 (backbone *C*H$_2$), 29.01 and 27.99 (*C*H(CH$_3$)$_2$), 27.31 and 26.40 (*C*H(CH$_3$)$_2$), 25.89 and 24.91 (CH(*C*H$_3$)$_2$), 24.51 and 23.85 (CH(*C*H$_3$)$_2$).

Bis[1,3-bis(2-isopropylphenyl)imidazolin-2-ylidene]dimethylpalladium(II) (6). To a solution of the salt **3b** (0.57 g, 1.66 mmol) dissolved in THF (20 mL) at −78 °C was added a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL). The mixture was warmed to −10 °C and stirred for 2 h. It was then recooled to −78 °C and added to a cold (−78 °C) solution of Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction mixture was warmed to 0 °C and stirred overnight at this temperature. The volatiles were removed under reduced pressure, and the solid residue was extracted in toluene. The extracts were filtered through Celite, concentrated to ca. 5 mL, and layered with petroleum ether to give white crystals. Yield: 0.49 g (0.65 mmol), 83%. Anal. Calcd for $C_{44}H_{58}N_4Pd$: C, 70.33; H, 8.05; N, 7.46. Found: C, 70.51; H, 8.12; N, 7.52. ^{1}H NMR (300 MHz, C_6D_6; δ): 7.53 (2H, d, J = 9.0 Hz, aromatic C*H*), 7.40 (4H, m, aromatic C*H*), 7.18 (2H, m, aromatic C*H*), 4.45 (4H, s, 2 × backbone CH_2), 3.40 (2H, septet, J = 6.9 Hz, 2 × C*H*(CH$_3$)$_2$), 1.58 (12H, d, J = 6.9 Hz, 2 × CH(C*H*$_3$)$_2$), 0.42 (3H, s, Pd−CH_3). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6; δ): 211.33 (carbene *C*−Pd), 143.58 (aromatic quaternary *C*−N), 132.38 (aromatic quaternary *C*−CH(CH$_3$)$_2$), 128.56, 128.01, 127.51, and 126.90 (4 × aromatic *C*H), 52.98 (backbone *C*H$_2$), 27.35 (*C*H(CH$_3$)$_2$), 23.28 (CH(*C*H$_3$)$_2$), 18.55 (Pd−*C*H$_3$).

Bis[1,3-bis(2-isopropylphenyl)imidazolin-2-ylidene]palladium(0) (7). To a solution of **3b** (0.57 g, 1.66 mmol) in THF (20 mL) at −78 °C was added a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL). The mixture was warmed to −10 °C and stirred for 2 h. It was then recooled to −78 °C and added to a cold (−78 °C) solution of Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction mixture was warmed to 25 °C and stirred at this temperature overnight. The resulting deep red solution was evaporated to dryness, the solid residue was extracted into petroleum ether, and the extracts were filtered through Celite concentrated to ca. 3 mL, and cooled to −35 °C to give dark red crystals. Yield: 0.42 g (0.58 mmol), 74%. Anal. Calcd for $C_{42}H_{52}N_4Pd$: C, 69.93; H, 7.55; N, 7.77. Found: C, 69.86; H, 7.58; N, 7.79. ^{1}H NMR (300 MHz, C_6D_6; δ): 7.45 (2H, d, J = 9.0 Hz, aromatic C*H*), 7.31 (4H, m, aromatic C*H*), 7.12 (2H, m, aromatic C*H*), 3.43 (2H, septet, J = 6.9 Hz, 2 × C*H*(CH$_3$)$_2$), 3.30 (4H, s, 2 × backbone CH_2), 1.31 (12H, d, J = 6.9 Hz, 2 × CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6; δ): 142.56 (aromatic *ipso C*−N), 131.29 (aromatic *C*−CH(CH$_3$)$_2$), 129.97, 128.29, 126.98, and 125.95 (4 × aromatic *C*H), 53.54 (backbone *C*H$_2$), 28.29 (*C*H(CH$_3$)$_2$), 24.23 (CH(*C*H$_3$)$_2$).

[1,3-Bis(2-isopropylphenyl)imidazolin-2-ylidene]{1,3-bis(6-isopropylphenyl-2-yl)imidazolin-2-ylidene-κ^3*C,C′,C″*}palladium-(II) (8). To a solution of **3b** (0.57 g, 1.66 mmol) in THF (20 mL) at −78 °C was added a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL). The mixture was warmed to −10 °C and stirred for 2 h. It was then recooled to −78 °C and added to a cold (−78 °C) solution of Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction mixture was warmed to 50 °C and stirred overnight at this temperature. The solvent was removed from the resulting yellow solution, the solid residue was extracted with benzene, and the extracts were filtered through Celite, concentrated, and layered with petroleum ether to give yellow crystals. Yield: 0.39 g (0.54 mmol), 68%. Anal. Calcd for $C_{42}H_{50}N_4Pd$: C, 70.13; H, 7.29; N, 7.79. Found: C, 70.35; H, 7.38; N, 7.91. ^{1}H NMR (300 MHz, CD_2Cl_2; δ): 8.09 (2H, m, aromatic C*H*), 7.61 (6H, m, aromatic C*H*), 7.32 (2H, m, aromatic C*H*), 7.10 (2H, m, aromatic C*H*), 6.95 (2H, m, aromatic C*H*), 4.50 (4H, s, 2 × backbone CH_2), 4.36 (4H, s, 2 × backbone CH_2), 3.82 (2H, septet, J = 6.9 Hz, 2 × C*H*(CH$_3$)$_2$), 3.43 (2H, septet, J = 6.9 Hz, 2 × C*H*(CH$_3$)$_2$), 1.62 (12H, d, J = 6.9 Hz, 2 × CH(C*H*$_3$)$_2$), 1.53 (12H, d, J = 6.9 Hz, 2 × CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2; δ): 214.21 (carbene *C*−Pd), 157.91 (aromatic *C*−Pd), 152.27 (aromatic *C*−N), 145.72 (aromatic *C*−N), 140.60 (aromatic *C*−CH(CH$_3$)$_2$), 130.29 (aromatic *C*−CH(CH$_3$)$_2$), 138.38, 129.56, 128.27, 126.92, 126.54, 126.02, 123.50, and 121.37 (7 × aromatic *C*H), 55.25 (backbone *C*H$_2$), 51.99 (backbone *C*H$_2$), 28.17 (*C*H(CH$_3$)$_2$), 27.23 (*C*H(CH$_3$)$_2$), 24.79 (CH(*C*H$_3$)$_2$), 24.50 (CH(*C*H$_3$)$_2$).

[1,3-Bis(4-methoxyphenyl)imidazolin-2-ylidene]{2-[3-(4-methoxyphenyl)imidazolin-2-ylidene]-5-methoxyphenyl-κ^2*C,C′*}-methylpalladium(II) (9d). To a solution of **3d** (0.53 g, 1.66 mmol) in THF (20 mL) at −78 °C was added a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL). The mixture was warmed to −10 °C and stirred for 2 h. It was then recooled to −78 °C and added to a cold (−78 °C) solution of Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction mixture was warmed to room temperature and stirred overnight. Evaporation of the volatiles under reduced pressure followed by extraction of the residue in benzene filtration through Celite, concentration, and layering with petroleum ether gave brown crystals. Yield: 0.35 g (0.51 mmol), 64%. Anal. Calcd for $C_{35}H_{38}N_4O_4Pd$: C, 61.36; H, 5.59; N, 8.18. Found: C, 61.29; H, 5.65; N, 8.08. ^{1}H NMR (300 MHz, C_6D_6; δ): 7.52 (4H, d, J = 8.7 Hz, aromatic C*H*), 6.83 (8H, m, aromatic C*H*), 6.51 (3H, m, aromatic C*H*), 4.10 (4H, s, 2 × backbone CH_2), 3.97 (4H, s, 2 × backbone CH_2), 2.34 (6H, s, O−CH_3), 2.01 (3H, s, O−CH_3), 1.85 (3H, s, O−CH_3), 0.41 (3H, s, Pd−CH_3). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6; δ): 154.32 (aromatic *C*−N), 153.02 (aromatic *C*−N), 132.31 (aromatic *C*−OCH$_3$), 131.53 (aromatic *C*−OCH$_3$), 130.08,

Table 2. Crystallographic Data for the Complexes Described in the Paper

	4	**5**	**6**	**7**	**8**	**9d**	**9e**
chem formula	$C_{97}H_{104}N_8O_8Pd_4$	$C_{42}H_{51}ClN_4Pd$	$C_{44}H_{58}N_4Pd$	$C_{42}H_{52}N_4Pd$	$C_{42}H_{50}N_4Pd$	$C_{35}H_{38}N_4O_4Pd$	$C_{39}H_{46}N_4O_8Pd$
formula wt	1935.48	753.72	749.34	718.88	717.26	685.09	805.24
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	*P*2/*c*	$P\bar{1}$	*P*2/*c*	*C*2/*c*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	16.7336(18)	12.309(2)	22.4014(7)	23.344(2)	10.063(2)	10.4722(5)	11.5140(2)
b/Å	11.2402(12)	12.969(2)	8.0114(3)	8.0765(4)	12.528(2)	16.0850(9)	17.8268(4)
c/Å	22.3834(16)	13.570(2)	24.4471(8)	19.6151(18)	14.840(3)	18.4923(9)	18.5840(5)
α/deg	90	115.906(4)	90	90	71.63(3)	90	87.6150(10)
β/deg	100.888(7)	97.093(4)	114.925(2)	100.456(3)	86.25(3)	92.636(2)	86.8100(10)
γ/deg	90	95.803(5)	90	90	89.04(3)	90	85.3690(10)
V/Å^3	4134.3(7)	1904.3(5)	3978.8(2)	3636.8(5)	1771.7(6)	3111.6(3)	3793.52(15)
Z	4	2	4	4	2	4	4
T/K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
μ/mm^{-1}	0.921	0.591	0.282	0.545	0.559	0.642	0.546
no. of data	65 825	15 723	39 959	9163	52 811	17 972	80 693
no. of unique data	9583	5080	9055	2219	8200	7094	17 373
R_{int}	0.1604	0.0524	0.0608	0.0718	0.0755	0.0410	0.0722
final $R(\|F\|)$ for	0.0617	0.0777	0.0421	0.0560	0.0392	0.0393	0.0492
final $R(F^2)$	0.1224	0.2129	0.0927	0.1212	0.0858	0.0780	0.1046

129.56, 128.13, and 109.10 (aromatic *C*H), 112.35 (aromatic *C*−Pd), 58.18 and 56.32 (backbone *C*H$_2$), 43.76 (O−*C*H$_3$), 18.38 (O−*C*H$_3$).

[1,3-Bis(2,4-dimethoxyphenyl)imidazolin-2-ylidene]{2-[3-(2,4-dimethoxyphenyl)imidazolin-2-ylidene]-3,5-dimethoxyphenyl-κ^2*C,C′*}methylpalladium(II) (9e). This was prepared in a way analogous to that for complex **9e** using **3e** (0.63 g, 1.66 mmol), KO^{t}Bu (0.22 g, 1.99 mmol), and Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) to yield colorless crystals. Yield: 0.45 g (0.56 mmol), 71%. Anal. Calcd for $C_{39}H_{46}N_4O_8Pd$: C, 58.17; H, 5.76; N, 6.96. Found: C, 58.10; H, 5.95; N, 6.98. ^{1}H NMR (300 MHz, C_6D_6; δ): 7.38 (4H, d, J = 8.7 Hz, aromatic C*H*), 6.47 (4H, dd, J = 8.7, 2.7 Hz, aromatic C*H*), 6.39 (3H, d, J = 2.7 Hz, aromatic C*H*), 3.64 (6H, s, 2 × O−C*H*$_3$), 3.58 (10H, s, 2 × backbone C*H*$_2$ and 2 × O−C*H*$_3$), 3.41 (10H, s, 2 × backbone C*H*$_2$ and 2 × O−C*H*$_3$), 2.10 (3H, s, O−C*H*$_3$), 1.76 (3H, s, O−C*H*$_3$), 0.60 (3H, s, Pd−C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6; δ): 155.89 (aromatic *C*−N), 153.68 (aromatic *C*−N), 129.93 (aromatic *C*−OCH$_3$), 129.28, 124.16, 103.38, and 99.54 (aromatic *C*H), 117.59 (aromatic quaternary *C*−Pd), 59.12 and 52.51 (backbone *C*H$_2$), 55.06 (O−*C*H$_3$), 47.76 (O−*C*H$_3$).

Catalytic Studies. The aryl halide (1.0 mmol), butyl acrylate (25.6 mg, 2.0 mmol), base (1.2 mmol), diglyme (internal standard 1.0 μmol), and the catalyst (15.0 μmol) were placed in a glass ampule equipped with a Youngs tap. Solvent (2.0 mL) was added, and the ampule was sealed under partial vacuum. It was then placed in a preheated silicon oil bath and heated for 18 h. After the reaction mixture was cooled, it was passed through a short pad of silica and subjected to gas chromatography. The identification was carried out by GC/MS and comparison of the retention data with those for authentic compounds.

When Bu$_4$NBr was used instead of solvent, it was added as a solid to the reaction mixture (2.0 g) After the reaction was stopped, the mixture was cooled, internal standard was added, and this mixture was diluted with water and extracted with ether (3 × 5 mL). Analysis was carried out as above.

X-ray Crystallography. A summary of the crystal data and data collection and refinement parameters for compounds **4**−**8** and **9d,e** are given in Table 2.

All data sets were collected on a Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo Kα radiation) and an Oxford Cryosystems low-temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[30] The crystals were mounted on a glass fiber with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[31] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model.

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Supporting Information Available: Text, tables, and figures giving full details of ligand syntheses and of the X-ray crystal structures, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters; CIF files also give the X-ray structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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