Donor-Functionalized Heterocyclic Carbene Complexes of Palladium(II): Efficient Catalysts for C−C Coupling Reactions

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Pd^{II} complexes of donor-functionalized heterocyclic carbene ligands have been synthesized through a route involving carbene transfer from Ag^{I} carbene precursors. The Ag complexes undergo facile reaction with $PdCl_2(MeCN)_2$ to yield $Pd(C\wedge OPh)_2Cl_2$ (**3a**), $Pd(C\wedge OOMe)_2Cl_2$ (**3b**), and $Pd(C\wedge N)_2Cl_2$ (**3c**) (C∧OPh = 3-methyl-1-phenacylimidazolin-2-ylidene, C∧OOMe = 3-methyl-1-(methylacetyl)imidazolin-2-ylidene, C∧N = 3-methyl-1-picolylimidazolin-2-ylidene), from which $[Pd(C\wedge OOMe)_2(MeCN)_2][BF_4]_2$ (**4b**) and $[Pd(C\wedge N)_2][BF_4]_2$ (**4c**) can be prepared by halide abstraction. When PdMeCl(cod) (cod = cyclooctadiene) is treated with the Ag complexes **2b** and **2c**, the Me−Pd carbene complexes $[PdMe(C\wedge OOMe)Cl]_2$ (**5b**), PdMe(C∧N)Cl (**5c**), $PdMe(C\wedge OOMe)_2Cl$ (**6b**), and $PdMe(C\wedge N)_2Cl$ (**6c**) are obtained. The C∧OPh and C∧OOMe ligands are monodentate with a dangling functional moiety in all complexes, while the C∧N ligand exhibits both monodentate and chelating behavior. Several complexes give rise to highly active and very stable catalysts for Heck, Suzuki, and Sonogashira coupling reactions, with turnover numbers of up to 1 700 000 (Heck) and 127 500 (Suzuki) being obtained.

Introduction

With the discovery of stable imidazolin-2-ylidenes, first isolated by Arduengo et al. in 1991,[1] much interest has been generated in the chemistry of both free heteroatom carbenes and metal complexes of these ligands.[2−11] Interest has been stimulated by the realization that these carbenes act as efficient ligands in several transition-metal-catalyzed processes. Reactions include Ru-catalyzed furan synthesis[12] and olefin metathesis,[13,14] Rh-catalyzed hydrosilylation,[15] and Pd-catalyzed copolymerization.[16] However, the most successful application at present appears to be the use of Pd and Ni complexes of heterocyclic carbenes in carbon−carbon coupling reactions such as the Heck type or Suzuki coupling.[17−22] Our recent mechanistic studies,[20,23] along with those of Albert and co-workers,[24] suggest that the role of the carbene is one of stabilizing and activating the *zerovalent* metal center toward oxidative addition of the organic halide. Thus, the carbene ligand plays a role similar to that of traditional phosphine ligands, which have found widespread application in these types of catalysis.

Bidentate or polydentate ligands containing both strong and weak donor groups (hemilabile ligands) have found widespread use in homogeneous catalysis. Notable examples include the use of a 2-pyridylphosphine Pd complex in the carbonylation of alkenes[25] and the P∧O chelating ligand used in conjunction with Ni in the

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(1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.
(2) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674.
(3) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725.
(4) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027.
(5) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121.
(6) Enders, D.; Breuer, K.; Runsink, J.; Teles, J. H. *Liebigs Ann. Chem.* **1996**, 2019.
(7) Alder, R. W.; Butts, C. P.; Orpen, A. G. *J. Am. Chem. Soc.* **1998**, *120*, 11526.
(8) Arduengo, A. J., III; Krafczyk, R. *Chem. Uns. Z.* **1998**, *32*, 6.
(9) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 772.
(10) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.
(11) Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *554*, 175.
(12) Kücükbay, H.; Cetinkaya, B.; Salaheddine, G.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2434.
(13) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490.
(14) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674.
(15) Herrmann, W. A.; Goossen, L. J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2805.
(16) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239.
(17) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.
(18) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1996**, *129*, 1483.
(19) Herrmann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93.
(20) McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165.
(21) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804.
(22) Huang, J. H.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307.
(23) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1569.
(24) Albert, K.; Gisdakis, P.; Rösch, N. *Organometallics* **1998**, *17*, 1608.
(25) Drent, E.; Arnoldy, P.; Budzelaar, P. H. M. *J. Organomet. Chem.* **1994**, *475*, 57.

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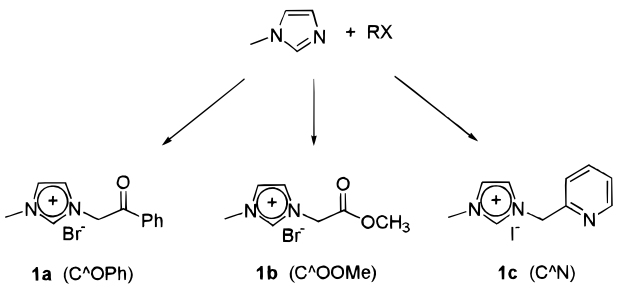
Shell higher olefins process (SHOP).[26] The hemilabile arm in such ligands is capable of reversible dissociation from the metal center. Such dynamic behavior will produce vacant coordination sites that allow complexation of substrates during the catalytic cycle, at the same time the strong donor moiety remains connected to the metal center. The possibility of functionalizing the nitrogens in heterocyclic carbenes makes them suitable for the generation of hemilabile ligands.

There have been few reports of metal complexes containing donor-functionalized carbene ligands, with the majority coming in recent years. The functional groups associated with the carbene include P, O, N, and S atoms, and complexes of Pd, Ni, Pt, Rh, Ru, W, Fe, and Mo have been synthesized.[27−38] Both examples of chelating or bridging behavior and complexes in which the donor group is uncoordinated ("dangling") have been reported. There exists only one report of donor-functionalized carbene complexes having been used in catalysis. Çetinkaya et al.[33] have synthesized Rh and Ru carbene complexes with a pendant or dangling methoxy group which were used as catalysts in cyclopropanation reactions. Furthermore, theoretical work conducted on a chelating carbene−phosphine Pd complex suggested that this type of complex may be suitable for the Heck reaction,[24] but as yet this has not been studied experimentally. Therefore, it was of interest to us to develop a route to donor-functionalized carbene complexes of Pd, with both chelating and dangling donor groups, and to evaluate these complexes as catalysts for Heck-type coupling reactions. The use of a silver carbene complex as an effective carbene transfer agent for the synthesis of a palladium carbene complex has recently been reported.[39] Such an approach, if widely applicable, provides a very convenient method for the formation of carbene complexes and overcomes many of the difficulties arising from the use of strong bases to generate free functionalized-carbene ligands which contain acidic protons associated with the functional group.

Consequently, we report here the synthesis of a variety of Pd complexes, including alkyl Pd complexes, of functionalized carbenes generated via Ag carbene species by carbene transfer routes. Carbene ligands containing pyridine and carbonyl donors have been ligated to Pd to produce both neutral and cationic complexes, with chelating and dangling donors. The new Pd complexes have been tested as catalysts in a variety of carbon−carbon coupling reactions and are shown to be highly active and very stable catalysts for a number of these reactions.

Scheme 1



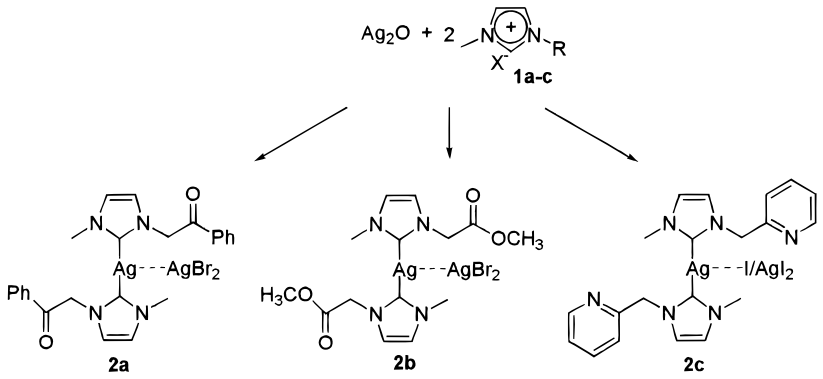
Results and Discussion

Preparation and Characterization of Functionalized Carbene Complexes. The functionalized imidazolium salts **1a**−**c** were synthesized by reacting the corresponding halides with 1-methylimidazole according to Scheme 1. Attempts to prepare the free carbenes by deprotonation of the imidazolium salts failed due to the high acidity of the methylene protons in **1a**−**c**. Likewise, the reaction of **3a** with $Pd(OAc)_2$ resulted in decomposition of the ligand and no carbene complex could be isolated. Recently, Wang and Lin[39] reported that simple imidazolium salts react with Ag_2O to yield Ag^I bis(carbene) complexes, which were then used as transfer agents to synthesize Pd^{II} carbene complexes. It was thought that this may provide a suitable route to functionalized carbene complexes. Indeed, the salts **1a**−**c** reacted with Ag_2O in DCM (dichloromethane) to afford the Ag^I bis(carbene) complexes **2a**−**c** according to Scheme 2. Both **2a** and **2b** have the same stoichiometry as reported by Wang and Lin, $[Ag(carbene)_2][AgBr_2]$. However, the picolyl-functionalized complex **2c**, which contains the iodide anion, is consistently analyzed as $Ag(C\wedge N)_2I\cdot 0.4AgI$. This may be due to a degree of substitution of I^- by the AgI_2^- anion, or alternatively, coordination of the pyridine donor to AgI could incorporate some of this (normally insoluble) species into the complex. In this case I^- would be the counterion. Attempts to grow crystals of **2c** suitable for an X-ray analysis were invariably unsuccessful. Therefore, the exact structure of this complex is uncertain, although this has no effect of the further reactions of the complex (vide infra).

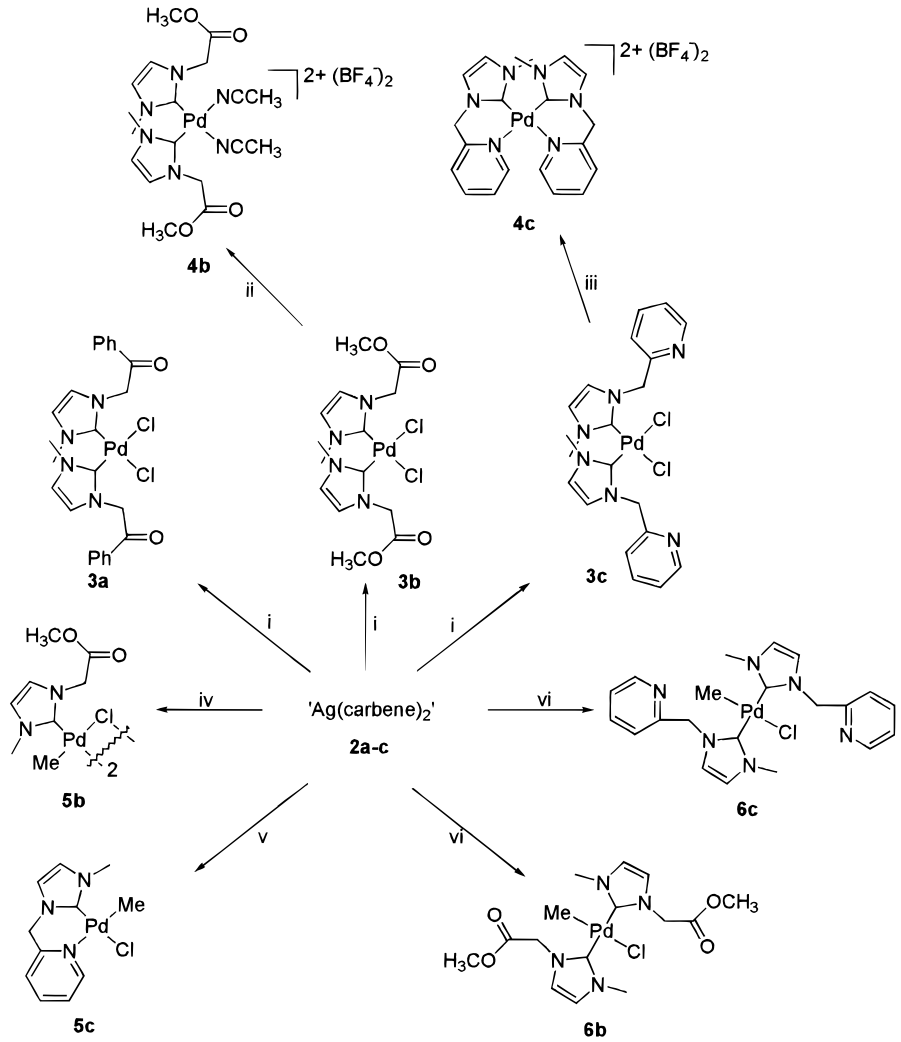
Importantly, the Ag complexes reacted smoothly with the Pd^{II} precursors $PdCl_2(MeCN)_2$ and PdMeCl(cod) to yield a range of both mono- and bis(carbene) complexes containing the donor-functionalized carbene ligands **a**−**c** (Scheme 3). In a typical reaction the Ag complex was stirred with the Pd precursor in DCM solution for 1 h before being filtered to remove the precipitated AgX. Subsequent workup of the solution afforded the complexes in 60−100% yield. The complexes were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, MS, and IR spectroscopy. Several of the complexes contain fractional amounts of DCM which is

(26) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235.
(27) Nesmeyanov, A. N.; Sal'nikova, T. N.; Struchkov, Y. T.; Andrianov, V. G.; Pogrebnyak, A. A.; Rybin, L. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1976**, *117*, C16.
(28) Dean, W. K.; Charles, R. S.; VanDerveer, D. G. *Inorg. Chem.* **1977**, *16*, 3328.
(29) Johnson, L. K.; Angelici, R. J. *Inorg. Chem.* **1987**, *26*, 973.
(30) Chamizo, J. A.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F. *J. Organomet. Chem.* **1993**, *451*, 89.
(31) Sellmann, D.; Prechtel, W.; Knoch, F.; Moll, M. *Inorg. Chem.* **1993**, *32*, 538.
(32) Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, R. J. *Chem. Eur. J.* **1996**, *2*, 1627.
(33) Çetinkaya, B.; Özdemir, I.; Dixneuf, P. H. *J. Organomet. Chem.* **1997**, *534*, 153.
(34) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *J. Organomet. Chem.* **1997**, *547*, 357.
(35) Liu, C.-Y.; Chen, D.-Y.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1996**, *15*, 1055.
(36) Sellmann, D.; Allmann, C.; Heinemann, F.; Knoch, F.; Sutter, J. *J. Organomet. Chem.* **1997**, *541*, 291.
(37) Lang, H.; Vitall, J. J.; Leung, P.-H. *J. Chem. Soc., Dalton Trans.* **1998**, 2109.
(38) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162.
(39) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

Scheme 2



Scheme 3. Synthesis of Pd^{II} Complexes[a]



[a] Reagents: (i) $PdCl_2(MeCN)_2$, DCM, 1 h; (ii) $AgBF_4$, MeCN/DCM, 30 min; (iii) $AgBF_4$, DCM, 30 min; (iv) 2 PdMeCl(cod), DCM, 0 °C, 40 min; (v) 2 PdMeCl(cod), DCM, 40 min; (vi) PdMeCl(cod), DCM, 1 h.

not removed by drying under vacuum. This is observed in the NMR spectra and the elemental analyses of these complexes (see Experimental Section).

When two of the carbene ligands are coordinated to the Pd center, the donor groups remain dangling, as observed in the complexes **3a**−**c** and **6b**,**c**. The picolyl- and phenacyl-functionalized complexes **3a**,**c** have limited solubility in common solvents, and their ^{1}H NMR spectra consist of very broad, merged signals. The ^{13}C NMR spectra of these complexes could not be obtained. At higher temperature (ca. 80 °C) the ^{1}H NMR signals sharpen and two sets of peaks are observed, corresponding to the *cis* and *trans* isomers. This indicates that the dynamic behavior leading to broad signals at lower temperature does not result from rapid *cis*/*trans* isomerization but is most likely due to restricted rotation around the $Pd-C_{carbene}$ bond resulting from the bulky functional groups attached to the carbene ligand. Complex **3b**, which contains the less bulky methylacetyl donor group, does not display room-temperature broad-

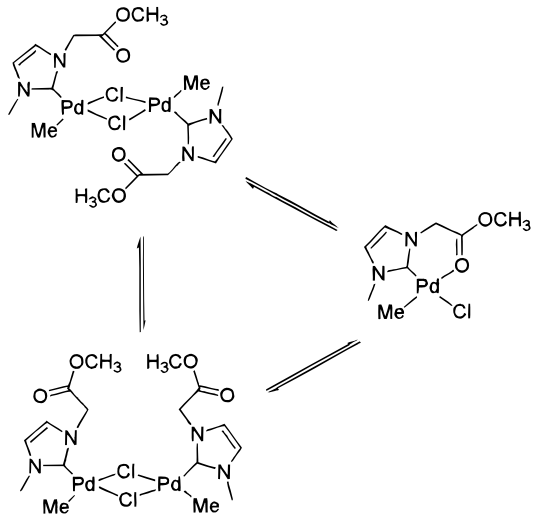
ening of the signals, and both the *cis* and *trans* isomers are observed in the ^{1}H and ^{13}C NMR spectra.

When the chloride ligands were abstracted from **3a**,**b** in the absence of a coordinating solvent, complex mixtures of products were obtained that could not be identified. However, when **3b** was treated with $AgBF_4$ in the presence of acetonitrile, the bis(acetonitrile) complex **4b** was obtained in 74% yield. The two coordinated acetonitrile ligands are clearly seen at 2.37 ppm in the ^{1}H NMR spectrum, compared to 2.00 ppm for free acetonitrile (CD_3NO_2), confirming that the carbonyl donor groups remain pendant. Only in the case of **3c**, which contains the more strongly coordinating pyridine moiety, was a discrete complex obtained upon halide abstraction in the absence of a coordinating solvent. In this case the chelated complex **4c** was obtained in 82% yield. **4b**,**c** are both insoluble in ether and THF, slightly soluble in DCM, and soluble in CH_3NO_2. The good yields obtained rely on the use of CH_3NO_2 to dissolve the complexes before filtration to remove AgCl.

Complex **4b** exists as the *cis* isomer, as determined by NMR spectroscopy. The $C_{carbene}$ signal appears at 157.0 ppm in the ^{13}C NMR spectrum, upfield of the characteristic shift of 175−186 ppm for a carbene *trans* to another carbene.[20,23] This large upfield shift of the signal also results from the strong π-acceptor properties of acetonitrile together with the dicationic charge on Pd. These influences would increase donation from the carbene carbon, which in turn is reflected in the chemical shift. The ^{1}H and ^{13}C NMR spectra of the C∧N complex **4c** indicate that both the *cis* and the *trans* isomers are present in a ca. 2:1 ratio. The carbenoid carbon signals occur at 166.1 ppm (major) and 180.5 ppm (minor) in the ^{13}C NMR spectrum. As discussed above, the position of the low-field signal is characteristic of a *trans* arrangement of the carbene ligands, while the higher field peak is indicative of a *cis* arrangement, indicating that the *cis* geometry is the major isomer in solution. The methylene protons occur as two doublets for each isomer with geminal coupling constants of 15 Hz, resulting from the bent, conformationally rigid six-membered ring that is formed by chelation.

When the methylpalladium precursor PdMeCl(cod) is treated with $^1/_2$ equiv of **2b**, the dimeric complex **5b** results in 71% yield. In the mass spectrum of this complex, two strong clusters at *m*/*z* 607 and 587 corresponding to $[M - CH_3]^+$ and $[M - Cl]^+$ for the dimeric complex are observed. At ambient temperature the ^{1}H NMR signals are broad, which is indicative of *cis*−*trans* isomerization, as has been observed for the unfunctionalized carbene analogues.[11,20] At 0 °C the signals start to split. However, at lower temperatures (−10 to −20 °C) a further species besides the *cis*/*trans* isomers is indicated by a third Pd−CH_3 peak in ca. 10% abundance. A third OCH_3 signal is also observed, while the methylene protons appear as complex multiplets. To explain this observation, the equilibrium shown in Scheme 4 is proposed, in which the two dimeric isomers are in equilibrium with a monomeric chelated species, resulting from bridge splitting and coordination of the carbonyl group. Complex **5b** is unstable both in the solid state and in solution. Palladium deposits form in DCM solutions of the complex, and the product can be seen to darken at ambient temperature in the solid state.

Scheme 4



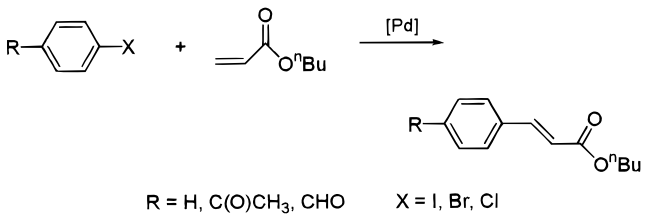
This resulted in an unsatisfactory elemental analysis of the complex.

In contrast to the C∧OOMe ligand, when one C∧N ligand is bound to the methylpalladium complex, a monomeric species (**5c**) results. Evidently the pyridine donor is strong enough to break the Cl bridge in any dimeric complex that may form, and a chelated complex is formed instead. At ambient temperature a singlet peak is observed for the methylene protons in the ^{1}H NMR spectrum, resulting from dynamic conformational flipping of the six-membered chelate ring. As the solution is cooled, the signal splits, until at −30 °C two sharp doublets at 5.59 and 5.00 ppm are observed with geminal coupling constants of 14 Hz. No additional splitting or broadening of other signals in the spectrum is observed at these lower temperatures.

When two of the appropriate functionalized carbene ligands are transferred to PdMeCl(cod), the complexes **6b** and **6c** are formed in 94% and 79% yield, respectively. In the ^{1}H NMR spectrum of **6b** two signals of equal intensity are observed for the OCH_3 protons, indicating that they are inequivalent due to restricted rotation around the Pd−$C_{carbene}$ and N−CH_2COOMe bonds. Furthermore, all four methylene protons are inequivalent and give rise to four doublets with coupling constants of 18 Hz. This is also evident in the ^{13}C NMR, which contains two peaks for the methylene carbons and a further two for the NCH_3 carbons. Such a restrained geometry of the pendant arms in the ligand is not expected on the basis of the modest steric bulk of the methyacetyl group. In view of the geminal coupling between the methylene protons it seems possible that weak apical bonding of the carbonyl oxygens may be present.

Elemental analysis of **6c** consistently gave values that indicated an inert compound/component was present in the complex, and when 0.7 equiv of AgI is included in the calculations, the analysis is correct. Subsequent analysis by ICP-MS showed approximately this amount of Ag to be present in the complex. Thus, it seems that normally insoluble AgI which is produced during the transfer reaction is in some way incorporated in the complex, as was also observed for the Ag complex **2c**. It seems probable in this case that the inclusion of AgI results from the ability of the pendant pyridine donors

Scheme 5. Heck Coupling



to coordinate to the AgI. The complex does not crystallize well, precluding an X-ray analysis to determine the exact structure of the complex. Like its dichloro analogue, **6c** gives rise to broad overlapping signals for the C∧N ligands in the ^{1}H NMR spectrum at ambient temperature, while the Pd−CH$_3$ peak remains relatively sharp. At 40 °C the peaks sharpen somewhat and the expected singlets due to the C∧N ligands are observed. The ^{13}C NMR spectrum likewise contains broad signals for the carbene ligands. This probably results again from restricted rotation around the Pd−C$_{carbene}$ bond which is accelerated at higher temperature.

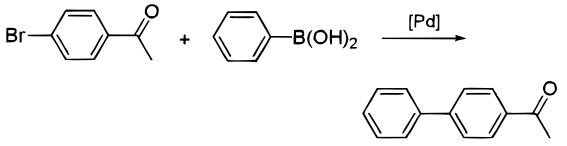
Catalysis: Heck-Type Reactions. In initial catalytic experiments the Heck coupling of phenyl iodide and *n*-butyl acrylate (Scheme 5) was attempted using the cationic complexes **4b,c** as the precatalysts (Table 1, runs 1 and 2). Both complexes led to good conversions at low catalyst concentrations (2.0×10^{-2} mol %), although the C∧N complex **4c** did so in a much shorter time. In both cases no side products formed and only *n*-butyl (*E*)-cinnamate was observed by GC and ^{1}H NMR analysis. Following this, the dichloro complexes **3a**−**c** were tested as precatalysts for the coupling of *n*-butyl acrylate with 4-bromoacetophenone to yield *n*-butyl (*E*)-4-acetylcinnamate. In combination with 20−50 μL of hydrazine hydrate as a reducing agent all three complexes gave rise to active catalysts, producing near-quantitative conversion at low catalyst concentration (runs 3−5). In no case was a Pd deposit observed during the run, but a deposit did start to form some time after all the substrate had been consumed if the solution was maintained at elevated temperature.

To test the long-term stability of the catalysts, the Pd−Me complexes were tested at very low concentrations. The excellent stabilities and high activities achieved with these complexes are shown in Table 1, runs 6−11. We have shown previously the activating influence a methyl group has on catalyst formation. It is thought that the methyl group provides a facile route to (catalytically active) Pd^0, possibly through insertion of the olefin and subsequent β-hydride elimination.[20] This "methyl effect" was again exploited in preparing highly active catalysts (showing no induction period) with the functionalized carbenes of the present study. Comparison of runs 8 and 10, which were conducted with complexes **5c** and **6c**, respectively, illustrates the positive effect a second carbene ligand has on the overall activity of the catalyst. The bis(carbene) complex **6c** leads to a greater turnover number (TON) (947 000) in less time and with less catalyst than the mono(carbene) complex **5c**. Nevertheless, precatalyst **5c** still gave a TON of 610 000 with 61% conversion. In general, the catalysts showed exceptional long-term stability; little evidence of catalyst decomposition was observed, except where all substrate was consumed and the catalyst was left at the higher temperatures. The turnover numbers quoted were those obtained when the reactions were terminated after set times and do not necessarily represent maximum turnovers or any indication that the catalyst had ceased to operate. Not surprisingly, the least active of the Pd−Me complexes is the dimer **5b** (run 6). This is attributed to the low thermal stability of this complex. The bis(carbene) analogue **6b** gives rise to a catalyst with considerably greater long-term stability (run 9).

In several runs (9 and 11) tetrapropylammonium bromide was added (10 mmol). Ammonium salts such as this have previously been found to have a positive effect in the Heck reaction,[40] possibly due to the formation of electron-rich, anionic, zerovalent Pd intermediates through coordination of the anion. Especially in the case of complex **6c**, this was also found to be the case with the present systems. Thus, in run 11 a TON of 1 700 000 was achieved with good conversion (85%), corresponding to an average TOF of 14 200 turnovers h^{-1} over 120 h. To our knowledge, this is one of the highest TONs yet achieved in a Heck reaction.[41] Analysis of the product from bromoacetophenone coupling showed predominately *n*-butyl (*E*)-4-acetylcinnamate, with the only other product being the *Z* isomer (<10%). This is an important result, as byproducts resulting from aryl dehalogenation and aryl−aryl coupling are often found during Heck couplings, but this was not the case with the present catalysts. Additionally, aryl scrambling has been observed when triarylphosphines are employed as the ancillary ligand. This is not possible for the carbene ligands.

The Heck coupling of 4-chlorobenzaldehyde with *n*-butyl acrylate to afford *n*-butyl (*E*)-4-formylcinnamate was also investigated with selected complexes (runs 12 and 13). In the presence of tetrapropylammonium bromide as cocatalyst, satisfactory conversions can be obtained with low amounts of **5c** and **6c**. In the absence of ammonium salts, only low conversions (ca. 5%) are obtained. In this coupling reaction there was no appreciable difference in activity between the mono- and bis(carbene) complexes, and both **5c** and **6c** had similar activities. Turnover numbers for this reaction up to 1000 were obtained with reduced amounts of catalyst, but this was at the expense of satisfactory conversion. The only products to result from the reaction were the *E* isomer in ca. 80% abundance along with some of the *Z* isomer.

The Suzuki coupling of 4-bromoactophenone with phenylboronic acid (reaction 1) was tested with selected complexes (Table 2, runs 1−3). Excellent TONs of over



(1)

100 000 were achieved with quantitative conversion (run 2). With lower catalyst concentration, higher total

(40) Jeffery, T. *J. Chem. Soc. Chem. Commun.* **1984**, 1287.

(41) In a recent paper Albisson and co-workers noted that TONs as high as 5.75×10^6 have been achieved with phosphite palladacycles, but no details were given: Albisson, D. A.; Bedford, R. B.; Lawrence, S. E.; Scully, P. N. *Chem. Commun.*, in press.

Table 1. Heck Coupling Reactions[a]

run	catalyst	amt (mol %)	aryl halide	coupling partner	time (h)	conversn[b] (%)	TON
1	**4b**[c]	2.0×10^{-2}	phenyl iodide	butyl acrylate	20	90	4 500
2	**4c**	2.0×10^{-2}	phenyl iodide	butyl acrylate	5	92	4 600
3	**3a**[c]	7.8×10^{-2}	4-bromoacetophenone	butyl acrylate	0.75	99	1 280
4	**3b**[c]	3.0×10^{-2}	4-bromoacetophenone	butyl acrylate	5	98	3 270
5	**3c**[c]	3.0×10^{-2}	4-bromoacetophenone	butyl acrylate	4.5	98	3 270
6	**5b**	1.0×10^{-3}	4-bromoacetophenone	butyl acrylate	24	70	70 000
7	**5c**	1.6×10^{-4}	4-bromoacetophenone	butyl acrylate	48	63	393 800
8	**5c**	1.0×10^{-4}	4-bromoacetophenone	butyl acrylate	120	61	610 000
9	**6b**[d]	1.0×10^{-4}	4-bromoacetophenone	butyl acrylate	140	70	700 000
10	**6c**	7.5×10^{-5}	4-bromoacetophenone	butyl acrylate	72	71	947 000
11	**6c**[d]	5.0×10^{-5}	4-bromoacetophenone	butyl acrylate	120	85	1 700 000
12	**5c**[d]	2.1×10^{-1}	4-chlorobenzaldehyde	butyl acrylate	24	75	360
13	**6c**[d]	2.0×10^{-1}	4-chlorobenzaldehyde	butyl acrylate	24	66	330

[a] Conditions for catalysis given in Experimental Section. [b] Conversions determined by GC. [c] 20−50 μL of hydrazine hydrate added to facilitate reduction of the Pd^{II} precatalyst. [d] 10 mmol of $(^nPr)_4NBr$ added to run.

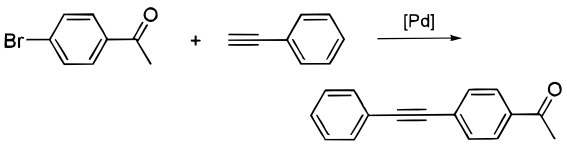
Table 2. Suzuki and Sonogashira Coupling Reactions[a]

run	catalyst	amt (mol %)	aryl halide	coupling partner	time (h)	conversn[b] (%)	TON
1	**5c**	1.8×10^{-2}	4-bromoacetophenone	$C_6H_5B(OH)_2$	1	99	5 500
2	**5c**	9.1×10^{-4}	4-bromoacetophenone	$C_6H_5B(OH)_2$	24	100	109 900
3	**6c**	4.0×10^{-4}	4-bromoacetophenone	$C_6H_5B(OH)_2$	48	51	127 500
4	5c	1.0×10^{-1}	4-bromoacetophenone	phenylacetylene	48	54	540
5	**6c**	2.0×10^{-1}	4-bromoacetophenone	phenylacetylene	48	39	195

[a] Conditions for catalysis given in Experimental Section. [b] Conversions determined by GC.

TONs could be obtained at the expense of conversion. As noted for the Heck reaction, the formation of aryl dehalogenation and aryl−aryl coupling products can be a problem in Suzuki coupling reactions using other catalyst systems. However, no side products were observed during catalysis with these carbene complexes.

The Sonogashira coupling of 4-bromoactophenone and phenylacetylene (reaction 2) was also undertaken using complexes **5c** and **6c** (Table 2, runs 4 and 5). Although



(2)

the results were not as impressive as the Heck and Suzuki coupling reactions, the catalyst performance was comparable to that observed for traditional phosphine complexes. For this reaction the mono(carbene) complex proved to be the superior catalyst, possibly indicating that the availability of a free coordination site is important in this reaction. Surprisingly, the addition of 2 equiv of CuI to the catalyst, which is normally required in Sonogashira coupling reactions, resulted in almost complete deactivation of the catalyst. We are unsure of the reason for this. One possibility is that the carbene ligands are transferred to Cu, resulting in deactivation of the catalyst. Liu and co-workers have recently reported Cu^I-mediated transfer and cleavage of heterocyclic carbene ligands.[42]

Preliminary attempts at Stille coupling (between tributylphenyltin and bromoacetophenone) using complex **6c** resulted in TONs up to 30 000, but conversions were low (ca. 30%). Reactions using more catalyst were unsuccessful due to catalyst solubility problems at higher concentrations. It is therefore clear that careful optimization of reaction conditions is required in order to maximize catalyst performance with these new complexes. Attempts at amination of *o*-tolyl bromide with piperidine were unsatisfactory, resulting in low conversions and a mixture of products, including toluene and dimethylbiphenyl as the major products with a small amount of the desired product. In this case rapid decomposition of the catalyst was observed. It is thought that this results from the presence of the strong base, NaO^tBu, which seems to be required for amination reactions.[43] Strong bases can be expected to attack the acidic methylene protons of the carbene at the functional group link, leading to decomposition. Functionalized carbene complexes without acidic protons may be necessary to achieve satisfactory results in amination chemistry.

Experimental Section

General Comments. Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox (Innovative Technology Inc.). All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature unless otherwise stated, and peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). Elemental analysis, MS, and GC-MS were carried out by the Central Science Laboratory, University of Tasmania.

Heck Coupling. In a typical run, a 100 mL flask was charged with aryl halide (25 mmol) and anhydrous NaOAc (28 mmol) and put under nitrogen. *N*,*N*-Dimethylacetamide (25 mL) and *n*-butyl acrylate (5 mL, 27 mmol) were then injected and the solution heated to 120 °C before the catalyst, dissolved in DCM (200 μL), was added. After the desired time, the solution was cooled and analyzed by gas chromatography.

Suzuki Coupling. A two-necked 100 mL flask equipped with a reflux condenser and septum was charged with 4-bromoacetophenone (1.99 g, 10 mmol), phenylboronic acid (1.34 g,

(42) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Reddy, K. J.; Chen, Y.-C.; Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1999**, *18*, 2145.

(43) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046.

11 mmol), and potassium carbonate (2.76 g, 20 mmol) before being put under an atmosphere of nitrogen. Toluene (20 mL) was injected and the solution brought to reflux in an oil bath with vigorous stirring. A solution of the catalyst (DCM, 200 μL) was then injected and the solution left for the desired period, after which time it was analyzed by GC and ^{1}H NMR.

Sonogashira Coupling. A two-necked 100 mL flask equipped with a reflux condenser and septum was charged with 4-bromoacetophenone (1.99 g, 10 mmol) and the catalyst before being put under nitrogen. Phenylacetylene (1.32 mL, 12 mmol) was injected along with triethylamine (30 mL) and the mixture heated to 90 °C. After the desired time the solution was analyzed by GC and ^{1}H NMR.

Preparation of Compounds: 3-Methyl-1-phenacylimidazolium Bromide (1a). 1-Methylimidazole (3.7 mL, 46 mmol) was syringed into a stirred solution of 2-bromoacetophenone (9.05 g, 45.5 mmol) in 50 mL of THF. The solid white cake that formed was broken up, washed twice with 50 mL of ether, and dried in vacuo. Yield: 11.17 g (87%). Anal. Calcd for $C_{12}H_{13}N_2OBr$: C, 51.26; H, 4.66; N, 9.96. Found: C, 51.33; H, 4.86; N, 9.99. MS (LSIMS): *m*/*z* 201, $[M]^+$ (100%). ^{1}H NMR (200 MHz, DMSO-d_6): δ 9.18 (s, 1H, NC(*H*)N), 8.08 (m, 2H, *H*CC*H*), 7.85−7.62 (m, 5H, phenyl *H*), 6.17 (s, 2H, NCH_2), 3.99 (s, 3H, NCH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 191.7 (*C*O), 138.0 (N*C*N), 134.8, 133.9 (ipso-*C* and *p*-*C*), 129.4, 128.5 (*o*- and *m*-*C*), 124.2, 123.6 (N*CC*N), 55.7 (NCH_2), 36.3 (NCH_3). IR (KBr): 1699 cm^{-1} (ν_{CO}).

3-Methyl-1-(methylacetyl)imidazolium Bromide (1b). This compound was prepared in the same manner described for **1a**. Anal. Calcd for $C_7H_{11}N_2O_2Br$: C, 35.77; H, 4.72; N, 11.92. Found: C, 35.73; H, 4.68; N, 11.96. MS (LSIMS): *m*/*z* 155, $[M]^+$ (100%). ^{1}H NMR (200 MHz, D_2O): δ 8.79 (s, 1H, NC(*H*)N), 7.47 (m, 2H, *H*CC*H*), 5.15 (s, 2H, NCH_2), 3.91 (s, 3H, NCH_3), 3.80 (s, 3H, OCH_3). ^{13}C NMR (50 MHz, D_2O): δ 171.5 (*C*O), 140.3 (N*C*N), 126.4, 126.3 (N*CC*N), 56.4 (NCH_2), 52.6 (OCH_3), 38.8 (NCH_3). IR (KBr): 1754 cm^{-1} (ν_{CO}).

3-Methyl-1-picolylimidazolium Iodide (1c). To a solution of picolyl chloride (5.85 mmol, prepared by basifying 0.96 g of picolyl chloride hydrochloride) in 20 mL of acetone were added 1-methylimidazole (0.470 mL, 5.89 mmol) and NaI (0.88 g, 5.9 mmol). After it was stirred for 48 h, the solution was filtered through Celite and the solvent removed in vacuo to afford a thick brown syrup. The syrup was redissolved in 15 mL of DCM and the solution filtered to remove residual NaCl. Addition of 25 mL of ether caused an oil to separate out. The solvent was decanted off, the oil taken up in 8 mL of DCM, and 20 mL of ether added to precipitate the product. The oily solid that formed was triturated for 2 h and the resultant powder washed with 10 mL of ether. Drying in vacuo overnight yielded a light orange solid. Yield: 1.22 g (69%). Anal. Calcd for $C_{10}H_{12}N_3I$: C, 39.89; H, 4.02; N 13.95. Found: C, 39.60; H, 3.91; N, 13.76. MS (LSIMS): *m*/*z* 174, $[M]^+$ (100%). ^{1}H NMR (200 MHz, DMSO-d_6): δ 9.27 (s, 1H, NC(*H*)N), 8.56 (m, 1H, pyridyl H_6), 7.91 (m, 1H, pyridyl H_4), 7.80 (s, 1H, *H*CC*H*), 7.76 (s, 1H, *H*CC*H*), 7.52 (m, 1H, pyridyl H_3), 7.41 (m, 1H, pyridyl H_5), 5.60 (s, 2H, NCH_2), 3.91 (s, 3H, NCH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 153.9 (pyridyl C_2), 149.9 (pyridyl C_6), 137.8, 137.5 (pyridyl C_4, N*C*N), 123.9, 123.4, 122.8 (pyridyl C_3, pyridyl C_5, N*CC*N), 53.2 (NCH_2), 36.2 (NCH_3).

[Ag(3-methyl-1-phenacylimidazolin-2-ylidene)$_2$][AgBr$_2$] (2a). A mixture of **1a** (1.11 g, 3.95 mmol) and silver(I) oxide (0.46 g, 1.98 mmol) was taken up in 100 mL of DCM and the mixture stirred for 2 h. The solution was filtered through Celite and the solvent removed in vacuo to give an orange solid. The product was recrystallized from DCM/ether (7 mL/14 mL), collected by filtration, and washed with 10 mL of ether. After drying in vacuo a yellow powder was obtained. Yield: 0.33 g (22%). Anal. Calcd for $C_{24}H_{24}N_4O_2Br_2Ag_2$: C, 37.15; H, 3.12; N, 7.22. Found: C, 37.15; H, 3.07; N, 7.22. ^{1}H NMR (200 MHz, DMSO-d_6): δ 8.07 (s, 2H, *H*CC*H*), 8.03 (s, 2H, *H*CC*H*), 7.8−7.4 (m, 10H, phenyl *H*), 5.92 (s, 4H, NCH_2), 3.80 (s, 6H, NCH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 193.6 (*C*O), 182.2 (N*C*N), 134.6 134.4 (ipso-*C* and *p*-*C*), 129.2 128.3 (*o*- and *m*-*C*), 123.7 122.8 (N*CC*N), 57.4 (NCH_2), 38.4 (NCH_3). IR (KBr): 1703 cm^{-1} (ν_{CO}).

[Ag{3-methyl-1-(methylacetyl)imidazolin-2-ylidene}$_2$][AgBr$_2$] (2b). This compound was prepared in the same manner as that described for **2a**, from 4.11 g (17.5 mmol) of **1b** and 2.03 g (8.75 mmol) of silver(I) oxide in 300 mL of DCM, to afford a white powder. Yield: 4.88 g (82%). Anal. Calcd for $C_{14}H_{20}N_4O_4Br_2Ag_2$: C, 24.59; H, 2.95; N, 8.19. Found: C, 25.02; H, 2.91; N, 8.38. ^{1}H NMR (200 MHz, DMSO-d_6): δ 7.45 (s, 4H, *H*CC*H*), 5.13 (s, 4H, NCH_2), 3.81 (s, 6H, NCH_3), 3.70 (s, 6H, OCH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 182.0 (N*C*N), 168.9 (*C*O), 123.2, 122.8 (N*CC*N), 52.4, 51.6 (NCH_2, OCH_3), 38.2 (NCH_3). IR (KBr): 1759, 1743 cm^{-1} (ν_{CO}).

[Ag(3-methyl-1-picolylimidazolin-2-ylidene)$_2$I·0.4AgI] (2c). This compound was prepared as described above from 0.99 g (3.3 mmol) of the imidazolium salt and 0.38 g (1.6 mmol) of silver(I) oxide in 50 mL of DCM, yielding a white solid. Yield: 0.43 g (40%). Anal. Calcd for $C_{20}H_{22}N_6AgI$·0.4AgI: C, 35.58; H, 3.28; N, 12.45. Found: C, 35.24; H, 3.42; N, 12.27. ^{1}H NMR (200 MHz, DMSO-d_6): δ 8.51 (m, 2H, pyridyl H_6), 7.80 (m, 2H, pyridyl H_4), 7.57 (s, 2H, *H*CC*H*), 7.47 (s, 2H, *H*CC*H*), 7.4−7.3 (m, 4H, pyridyl H_3, pyridyl H_5), 5.47 (s, 4H, NCH_2), 3.81 (s, 6H, NCH_3). ^{13}C NMR (50 MHz, DMSO-d_6): δ 182.2 (N*C*N), 156.5 (pyridyl C_2), 149.7 (pyridyl C_6), 137.6 (pyridyl C_4), 123.4, 123.2, 122.9, 122.4 (pyridyl C_3, pyridyl C_5, N*CC*N) 55.9 (NCH_2), 38.4 (NCH_3).

[Pd(3-methyl-1-phenacylimidazolin-2-ylidene)$_2$Cl$_2$] (3a). To a suspension of **2a** (0.29 g, 0.37 mmol) in 10 mL of DCM was added a DCM (30 mL) solution of $Pd(MeCN)_2Cl_2$ (96.8 mg, 0.37 mmol). After it was stirred for 1 h, the solution was filtered through Celite to remove precipitated silver bromide. The solvent was removed in vacuo until ca. 5 mL remained, and 10 mL of hexane was added, causing a yellow precipitate to form. Recrystallization from DCM/hexane (5 mL/10 mL) followed by washing twice with 10 mL of hexane afforded a yellow fluffy powder. Yield: 0.134 g (63%). Anal. Calcd for $C_{24}H_{24}N_4O_2Cl_2Pd$·0.6CH_2Cl_2: C, 46.99; H, 4.04; N, 8.91. Found: C, 46.80; H, 4.12; N, 9.13. MS (ESI): *m*/*z* 543, $[M - Cl]^+$ (100%); 505, $[M - 2Cl]^+$ (33%); 201, $[ylideneH]^+$. ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C; two isomers in a ca. 1:4 ratio (a:b)): δ 8.12 (s, 2H, HCCH_a), 8.10 (s, 2H, *H*CCH_a), 8.01 (s, 2H, HCCH_b), 7.99 (s, 2H, *H*CCH_b), 7.7−7.5, 7.21 (m, 10H, phenyl H_{a+b}), 6.10 (s, 2H, NCH_{2a}), 6.04 (s, 2H, NCH_{2b}). IR (KBr): 1704 cm^{-1} (ν_{CO}).

[Pd{3-methyl-1-(methylacetyl)imidazolin-2-ylidene}$_2$Cl$_2$] (3b). This complex was prepared in a manner analogous to that described for **3a**, using 0.91 g (1.3 mmol) of **2b** and 0.34 g (1.3 mmol) of $Pd(MeCN)_2Cl_2$ to yield a white powder. Yield: 0.734 g (97%). Anal. Calcd for $C_{14}H_{20}N_4O_4Cl_2Pd$·CH_2Cl_2: C, 31.58; H, 3.89; N, 9.82. Found: C, 31.20; H, 4.05; N, 9.87. MS (ESI): *m*/*z* 605, $[M - Cl + ylidene]^+$ (100%); 451, $[M - Cl]^+$ (45%); 155, $[ylideneH]^+$ (82%). ^{1}H NMR (400 MHz, $CDCl_3$; two isomers in ca. 0.7:1 ratio (a:b)): δ 6.97 (d, J = 2 Hz, 2H, *H*CCH_a), 6.96 (d, J = 2 Hz, 2H, *H*CCH_b), 6.87 (d, J = 2 Hz, 2H, HCCH_a), 6.86 (d, J = 2 Hz, 2H, HCCH_b), 5.34 (s, br, 4H, NCH_{2b}), 5.28 (s, br, 4H, NCH_{2a}), 4.11 (s, br, 6H, NCH_{3b}), 4.09 (s, br, 3H, NCH_{3a}), 4.08 (s, br, 3H, NCH_{3a}), 3.81 (s, br, 3H, OCH_{3a}), 3.80 (s, br, 6H, OCH_{3b}), 3.79 (s, br, 3H, OCH_{3a}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9 (*C*O$_a$), 170.8 (*C*O$_b$), 168.5 (N*C*N$_b$), 122.5, 122.4, 122.3, 122.2 (N*CC*N$_{a+b}$), 52.9, 52.0, 51.9 (NCH_2 and OCH_{3a}), 52.9, 51.8 (NCH_2 and OCH_{3b}), 38.1 (NCH_{3a}), 37.9 (NCH_{3b}). IR (KBr): 1758 cm^{-1} (ν_{CO}).

[Pd(3-methyl-1-picolylimidazolin-2-ylidene)$_2$Cl$_2$] (3c). This compound was prepared analogously to **3a** using 0.327 g (0.485 mmol) of **2c** and 0.121 g (0.468 mmol) of $Pd(MeCN)_2Cl_2$ to yield a white powder. Yield: 0.143 g (58%). Anal. Calcd for $C_{20}H_{22}N_6Cl_2Pd$·0.5CH_2Cl_2: C, 43.49; H, 4.09; N, 14.84. Found: C, 43.17; H, 4.05; N, 14.72. MS (LSIMS): *m*/*z* 489, $[M - Cl]^+$ (40%); 451, $[M - 2Cl]^+$ (23%); 279, $[M - 2Cl - ylidene]^+$

(23%); 226, $[M - 2Cl]^{2+}$ (10%); 174, $[ylideneH]^+$. ^1H NMR (200 MHz, DMSO-d_6, 90 °C; two isomers in a 1:2 ratio (a:b)): δ 8.77 (m, 2H, pyridyl H_{6b}), 8.32 (m, 2H, pyridyl H_{6a}), 8.0−7.7 (m, 2H, pyridyl H_{4a+b}), 7.6−7.3 (m, 8H, pyridyl H_{3a+b}, pyridyl H_{5a+b}, $HCCH_{a+b}$), 5.67 (s, 4H, NCH_{2a+b}), 3.95 (s, 6H, NCH_{3a}), 3.50 (s, 6H, NCH_{3b}).

[Pd{3-methyl-1-(methylacetyl)imidazolin-2-ylidene}$_2$-(MeCN)$_2$][BF$_4$]$_2$ (4b). A solution of $AgBF_4$ (0.101 g, 0.512 mmol) in MeCN (7 mL) was added to a DCM (10 mL) solution of **3b** (0.117 g, 0.242 mmol) and the mixture stirred for 30 min. The solvent was removed in vacuo, the residue extracted with 20 mL of CH_3NO_2, and the solution filtered through Celite. The solvent was reduced to ca. 2 mL in vacuo and 10 mL of ether added, causing a light yellow oil to separate out, which changed to a white solid upon further stirring. The solvent was decanted off before the product was washed with 30 mL of ether and dried in vacuo. Yield: 0.120 g (74%). Anal. Calcd for $C_{18}H_{26}N_6O_4B_2F_8Pd\cdot0.75CH_2Cl_2$: C, 30.68; H, 3.77; N, 11.45. Found: C, 30.73; H, 3.62; N, 11.65. MS (LSIMS): *m*/*z* 414, $[M - 2MeCN]^+$ (70%); 155, $[ylideneH]^+$. ^1H NMR (400 MHz, CD_3NO_2): δ 7.34 (s, 4H, *H*CC*H*), 5.28 (s, 4H, NCH_2), 4.17 (s, 6H, NCH_3), 3.87 (s, 6H, OCH_3), 2.37 (s, 6H, $NCCH_3$). ^{13}C NMR (100 MHz, CD_3NO_2): δ 167.7 (*C*O), 157.0 (N*C*N), 126.3 ($NCCH_3$), 123.7, 123.5 (H*CC*H), 51.7, 49.9 (NCH_2 and OCH_3), 36.1 (NCH_3), 1.4 ($NCCH_3$). IR (KBr): 1760 cm^{-1} (ν_{CO}).

[Pd(3-methyl-1-picolylimidazolin-2-ylidene)$_2$][BF$_4$]$_2$ (4c). A DCM (10 mL) solution of $AgBF_4$ (88 mg, 0.45 mmol) was added to **3c** (0.11 g, 0.19 mmol) suspended in 15 mL of DCM and the solution stirred for 30 min. The solvent was removed in vacuo and the remaining solid taken up in 25 mL of CH_3NO_2 before filtration through Celite. The solvent was reduced in vacuo until ca. 5 mL remained, and the product was precipitated with 15 mL of ether. After the solvent was decanted, the product was washed twice with 10 mL of ether before being dried in vacuo to yield an off-white powder. Yield: 98 mg (82%). Anal. Calcd for $C_{20}H_{22}N_6B_2F_8Pd\cdot0.3CH_2Cl_2$: C, 37.29; H, 3.45; N, 12.83. Found: C, 36.87; H, 3.51; N, 13.08. MS (LSIMS): *m*/*z* 539, $[M + BF_4]^+$ (46%); 451, $[M - H]^+$ (73%); 280, $[MH - ylidene]^+$ (75%); 226, $[M]^{2+}$ (4%); 174, $[ylideneH]^+$ (100%). ^1H NMR (400 MHz, CD_3NO_2; two isomers in a ca. 1:2 ratio (a:b)): δ 8.70 (m, 2H, pyridyl H_a), 8.54 (m, 2H, pyridyl H_a), 8.30 (m, 2H, pyridyl H_b), 8.20 (m, 2H, pyridyl H_b), 7.97 (m, 2H, pyridyl H_{a+b}), 7.59 (d, J = 2 Hz, 2H, $HCCH_b$), 7.26 (d, J = 2 Hz, 2H, $HCCH_b$), 7.56 (m, 2H, pyridyl H_{a+b}), 7.50 (d, J = 2 Hz, 2H, $HCCH_a$), 7.13 (d, J = 2 Hz, 2H, $HCCH_a$), 6.23 (d, J = 15 Hz, 2H, NCH_{2a}), 6.17 (d, J = 15 Hz, 2H, NCH_{2b}), 5.69 (d, J = 15 Hz, 2H, NCH_{2b}), 5.64 (d, J = 15 Hz, 2H, NCH_{2a}), 3.44 (s, 6H, NCH_{3b}), 3.34 (s, 6H, NCH_{3a}). ^{13}C NMR (100 MHz, CD_3NO_2): δ 180.5 (NCN_a), 166.1 (NCN_b), 155.6 (pyridyl C_{2a}), 154.8 (pyridyl C_{2b}), 152.8 (pyridyl C_{6a}), 151.5 (pyridylC_{6b}), 140.9 (pyridyl C_{4a}), 140.8 (pyridyl C_{4b}), 126.0, 125.5 (pyridyl C_{3+5a}), 125.3, 124.9 (pyridyl C_{3+5b}), 122.9, 122.2 ($NCCN_b$), 122.6, 121.2 ($NCCN_a$), 54.4 (NCH_{2b}), 54.3 (NCH_{2a}), 35.7 (NCH_{3b}), 35.1 (NCH_{3a}).

[Pd(Me){3-methyl-1-(methylacetyl)imidazolin-2-ylidene}Cl]$_2$ (5b). A mixture of PdMeCl(cod) (0.31 g, 1.2 mmol) and **2b** (0.40 g, 0.58 mmol) was taken up in 50 mL of DCM and the mixture stirred for 40 min, after which time it was filtered through Celite into a flask at 0 °C. The solvent was removed in vacuo until ca. 5 mL remained and 10 mL of hexane added. The solvent was removed further until 10 mL remained and a white solid had precipitated. The solvent was decanted and the product was recrystallized from DCM/ether (2 mL/10 mL), washed with hexane (10 mL, 0 °C), and dried in vacuo to afford a white powder. Yield: 0.26 g (71%). MS (LSIMS): *m*/*z* 607, $[M - CH_3]^+$ (30%); 587, $[M - Cl]^+$ (52%); 429, $[PdMe(ylidene)_2]^+$ (20%); 260, $[Pd(ylidene)]^+$ (56%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.91 (m, br, 4H, *H*CC*H*), 5.76 (br, 2H, NCH_2), 5.00 (br, 2H, NCH_2), 4.02 (s, br, 6H, NCH_3), 3.79 (s, br, 6H, OCH_3), 0.36 (s, br, $PdCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (*C*O), 122.3, 121.7 (N*CC*N), 52.8, 52.0 (NCH_2, OCH_3), 38.3 (NCH_3). IR (KBr): 1752 cm^{-1} (ν_{CO}).

[Pd(Me)(3-methyl-1-picolylimidazolin-2-ylidene)Cl] (5c). This complex was prepared in the same manner as described for **5b** (ambient temperature) using 0.35 g (0.50 mmol) of **2c** and 0.27 g (1.0 mmol) of PdMeCl(cod). Yield: 0.335 g (100%). Anal. Calcd for $C_{11}H_{14}N_3ClPd$: C, 40.02; H, 4.27; N, 12.73. Found: C, 40.06; H, 4.43; N, 12.52. MS (ESI): *m*/*z* 467, $[PdMe(ylidene)_2]^+$ (49%); 371, $[467 - C_5H_8N_2]^+$ (100%); 294, $[M - Cl]^+$ (5%); 188, $[ylideneMe]^+$ (47%). ^1H NMR (400 MHz, CD_2Cl_2, −30 °C): δ 9.01 (m, 1H, pyridyl *H*), 7.75 (m, 1H, pyridyl *H*), 7.43 (d, 1H, pyridyl *H*), 7.33 (m, 1H, pyridyl *H*), 7.11 (d, J = 2 Hz, 1H, *H*CCH), 6.86 (d, J = 2 Hz, 1H, HCC*H*), 5.59 (d, J = 14 Hz, 1H, NC*H*H), 5.00 (d, J = 14 Hz, 1H, NCH*H*), 3.70 (s, 3H, NCH_3), 0.55 (s, 3H, $PdCH_3$). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 172.0 (N*C*N), 153.0, 152.7, 138.7 (pyridyl *C*), 124.9, 123.9, 122.3, 121.3 (pyridyl *C*, N*CC*N), 56.0 (NCH_2), 38.0 (NCH_3), −11.5 ($PdCH_3$).

[Pd(Me){3-methyl-1-(methylacetyl)imidazolin-2-ylidene}$_2$Cl] (6b). This complex was prepared in the same manner described for **5c** using 0.59 g (0.86 mmol) of **2b** and 0.22 g (0.83 mmol) of PdMeCl(cod). Yield: 0.363 g (94%). Anal. Calcd for $C_{15}H_{23}N_4O_4ClPd$: C, 38.73; H, 4.98; N, 12.04. Found: C, 38.70; H, 4.92; N, 12.08. MS (ESI): *m*/*z* 895, $[2 M - Cl]^+$ (5%); 583, $[PdMe(ylidene)_3]^+$ (37%); 429, $[M - Cl]^+$ (73%); 169, $[ylideneMe]^+$ (100%); 155, $[ylideneH]^+$ (5%). ^1H NMR (200 MHz, $CDCl_3$): δ 6.92 (d, J = 2 Hz, *H*CCH), 6.87 (d, J = 2 Hz, HCC*H*), 5.92 (br, d, J = 18 Hz, 1H, NC*H*H), 5.89 (br, d, J = 18 Hz, 1H, NC*H*H), 4.79 (two coincident d, J = 18 Hz, 2H, NCH*H*) (at 10 °C these two doublets are resolved), 4.01 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 3.78 (s, 6H, NCH_3), −0.15 (s, 3H, $PdCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5 (N*C*N), 169.2 (*C*O), 121.7, 121.4 (H*CC*H), 52.6, 51.8 (NCH_2), 37.8, 37.7 (NCH_3), −15 (br, $PdCH_3$). IR (KBr): 1749, 1636 cm^{-1} (ν_{CO}).

[Pd(Me)(3-methyl-1-picolylimidazolin-2-ylidene)$_2$Cl·0.7AgI] (6c). This complex was prepared in the same manner described for **5c** using 0.92 g (1.32 mmol) of **2c** and 0.35 g (1.32 mmol) of PdMeCl(cod). Yield: 0.693 g (79%). Anal. Calcd for $C_{21}H_{25}N_6ClPd\cdot0.7AgI$: C, 37.78; H, 3.77; N, 12.59. Found: C, 38.20; H, 3.93; N, 12.07. MS (ESI): *m*/*z* 640, $[PdMe(ylidene)_3]^+$ (10%); 467, $[M - Cl]^+$ (87%); 371, $[467 - C_5H_8N_2]^+$ (100%); 279, $[Pd(ylidene)]^+$ (12%); 188, $[ylideneMe]^+$ (38%); 174, $[ylideneH]^+$ (7%). ^1H NMR (400 MHz, DMSO-d_6, 40 °C): δ 8.17 (s, br, 2H, pyridyl *H*), 7.76 (m, br, 2H, pyridyl *H*), 7.49 (s, 4H, *H*CC*H*), 7.37 (s, br, 2H, pyridyl *H*), 7.24 (s, br, 2H, pyridyl *H*), 5.59−5.43 (m, br, 4H, NCH_2), 3.86 (m, br, 6H, NCH_3), 0.15 (s, 3H, $PdCH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, 40 °C): δ 179.7 (br, N*C*N), 154.6, 150.4, 137.3 (br, pyridyl *C*), 122.9, 122.4, 121.9, 121.4 (pyridyl *C*, H*CC*H), 54.3 (br, NCH_2), 36.9 (NCH_3), −16.4 ($PdCH_3$).

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