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Synthesis and characterization of novel Pd(II) complexes with chelating and non-chelating heterocyclic iminocarbene ligands†

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Received 21st January 2005, Accepted 14th March 2005
First published as an Advance Article on the web 4th April 2005

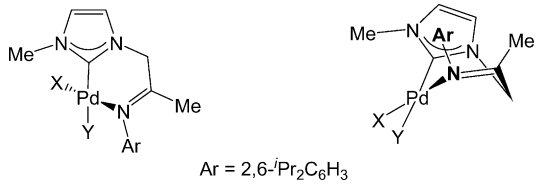
The imidazolium salts [3-R^1-1-{2-Ar-imino)-2-R^2-ethyl}imidazolium] chloride (C–N; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; R^1/R^2 = Me/Me (**a**), Me/Ph (**b**), Ph/Me (**c**), 2,4,6-Me$_3$C$_6$H$_2$ (**d**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**e**)) react with Ag$_2$O to give Ag(I) iminocarbene complexes (C–N)AgCl (**4a–e**) in which the iminocarbene ligand is bonded to Ag *via* the imidazoline-2-ylidene carbon atom. The solid-state structures of **4b** and **4d** were determined by X-ray crystallography and revealed the presence of monomeric (carbene)AgCl units with *Z* and *E* configurations at the imine C=N bonds, respectively. Carbene transfer to Pd occurs when compounds **4b–e** are treated with (COD)PdCl$_2$ to yield bis(carbene) complexes (C–N)$_2$PdCl$_2$ (**6b–e**) containing two κ^1-*C* bonded iminocarbene moieties. NMR spectroscopic data indicated a *trans* coordination geometry at Pd. This conclusion was supported by an X-ray structure determination of **6b** which clearly demonstrated the non-chelating nature of the iminocarbene ligand system. EXSY ^{1}H NMR spectroscopy suggests that the non-chelating structures undergo *E*/*Z* isomerization at the imine C=N double bonds in solution. The preparative results contrast our earlier report that the reaction between **4a** and (COD)PdCl$_2$ results in a chelating κ^2-*C*,*N* bonded iminocarbene complex (C–N)PdCl$_2$. The coordination mode and dynamic behavior of the iminocarbene ligand systems have been found to be dramatically affected by changes in the substitution pattern of the ligand system. Sterically unencumbered systems (**a**) favor the formation of κ^2-*C*,*N* chelate structures containing one iminocarbene moiety per metal upon coordination at Pd(II); these complexes were demonstrated to engage in reversible, solvent-mediated chelate ring-opening reactions. Sterically encumbered systems (**b–e**) form non-chelating κ^1-*C* iminocarbene Pd(II) complexes containing two iminocarbene ligands per metal. Transannular repulsions across the chelate ring are believed to be the origin of these structural differences.

Introduction

Arduengo's reported synthesis of stable heterocyclic carbenes of the imidazolin-2-ylidene type in the early 1990's[1,2] sparked the immediate interest in employing such species as ligands for organometallic complexes. The vigorous pursuit of novel carbene derivatives has been effectively stimulated by the fact that many complexes, often thermally robust and easy to handle, act as very efficient catalysts or catalyst precursors for a range of chemical transformations.[3–5] The heterocyclic carbene moiety offers great possibilities for fine-tuning the ligand structure electronically and sterically.

Recently, heterocyclic carbenes have been incorporated into chelating ring structures, in the form of chelating bis(carbenes)[6–13] or mono-carbenes with pendant heteroatom functional groups that are also attached to the metal.[14–34] Carbenes linked to pyridine-type functional group have attracted particular attention.[22–34]

We have reported the synthesis and characterization of neutral, cationic, and dicationic Pd(II) complexes bearing the chelating iminocarbene ligand system shown in Scheme 1.[35] The presence of a six-membered iminocarbene chelate ring was verified by a crystallographic investigation for X, Y = Cl. The chelate complexes exhibited complex dynamic behavior in solution, as demonstrated by 2D NMR experiments. Two processes that were demonstrated were (1) conformational "ring flip" involving the six-membered chelate ring, and (2) solvent-dependent interconversion of chelating κ^2-*C*,*N* and non-chelating κ^1-*C* species.



Scheme 1

In this contribution, we explore the consequences of changing the substituents at the iminocarbene ligand system on the structures and dynamic behavior of the metal complexes. It will be seen that the steric requirements of the ligand system strongly influences the conformational changes as well as the κ^2/κ^1 equilibria of the six-membered chelates. Additionally, sterically demanding ligands may even enforce the formation of κ^1-*C*,κ^1-*C* bis(iminocarbene) structures rather than the κ^2-*C*,*N* mono(iminocarbene) structure previously reported.

Results and discussion

Ligand synthesis

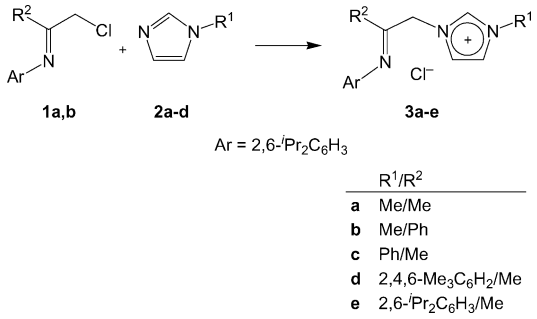
We recently reported[35] that the iminocarbene ligand system is readily prepared by the reaction between an α-chloroimine and a monosubstituted imidazole,[36–38] which provided the desired carbene precursor, the iminoimidazolium salt, in good yields. The method is rather general and allows the introduction of a variety of substituents at the imidazole ring and at the imine carbon and nitrogen atoms. The general synthetic method is outlined in Scheme 2; entry **a** was previously reported.[35] The α-chloroimines **1a,b** were prepared from (2,6-diisopropylphenyl)amine and chloroacetone or phenacyl chloride in the presence of TiCl$_4$.[39]

† Electronic supplementary information (ESI) available: NMR data for major and minor isomers of **3b** and **4b**. See http://www.rsc.org/suppdata/dt/b5/b501081k/

DOI: 10.1039/b501081k

Table 1 Selected spectroscopic data for imidazolium salts and iminocarbene complexes of Ag and Pd

	Compound	R^1	R^2	$\nu_{C=N}$/cm^{-1}	^{1}H NMR separation of ^{i}Pr doublets/ppm	^{1}H NMR: δ NC*H*CN	^{13}C NMR: δ N*C*HN or N*C*N
(N–C)·HCl	**3a**[1]	Me	Me	1682	0.10	10.46	
	3b	Me	Ph	1659, 1634	0.14	10.32, 10.46	137.8
	3c	Ph	Me	1682	0.16	11.13	137.6
	3d	2,4,6-$Me_3C_6H_2$	Me	1682	0.15	10.25	138.9
	3e	2,6-$^i Pr_2C_6H_3$	Me	1680	0.12	10.16	139.8
(N–C)AgCl	**4a**[1]	Me	Me	1682, 1663	0.09		183.8
	4b	Me	Ph	1657, 1634	0.27		
	4c	Ph	Me	1684, 1666	0.11		182.5
	4d	2,4,6-$Me_3C_6H_2$	Me	1684, 1666	0.07		
	4e	2,6-$^i Pr_2C_6H_3$	Me	1684, 1666	0.07		
(N–C)$PdCl_2$	**5a**[1]	Me	Me	1638	0.54		
(N–C)$_2PdCl_2$	**6b**	Me	Ph	1634	0.2, 0.3		
	6c	Ph	Me	1683, 1662	0.03		171.9
	6d	2,4,6-$Me_3C_6H_2$	Me	1683, 1662	0.03		171.6
	6e	2,6-$^i Pr_2C_6H_3$	Me	—	0.03		



Scheme 2

The new imidazolium salts **3b–e** were spectroscopically characterized (see Experimental section for details). Table 1 summarizes some key spectroscopic features of the imidazolium salts **3a–e** and the corresponding Ag and Pd complexes (*vide infra*). The hindered rotation around the N(imine)–C(Ar) bond that was reported[35] for **3a** persists in the new compounds **3b–e**. The hindered rotation renders the two methyl groups in each aryl ^{i}Pr group diastereotopic and this results in the observation of two separate ^{i}Pr methyl doublets in the ^{1}H NMR spectra. We found that non-chelating iminocarbene complexes and the imidazolium salt precursor exhibited a rather small (typically 0.1–0.2 ppm) separation of the ^{1}H NMR doublets arising from the diastereotopic ^{i}Pr methyl groups. On the other hand, the separation of the signals was greater, typically 0.4–0.5 ppm, for chelating structures.[35] Similar characteristic signal separations are exhibited by all metal complexes bearing the novel ligand systems that will be discussed herein.

The ^{1}H NMR spectra of **3c–e** were as anticipated based on the previously described spectrum for **3a**. However, for the imidazolium salt **3b**, which differs from **3a** and **3c–e** in having a phenyl, rather than a methyl, group attached to C(imine), a notable change is seen in the ^{1}H NMR spectrum. Whereas **3a** and **3c–e** each exhibit one well-defined set of signals, the expected signals for **3b** are accompanied by an additional, minor set of signals. The two sets appear in an approximate 6 : 1 ratio (Fig. 1(a)). The relative intensities of the two sets were invariant to the purification process used (repeated washing with and/or repeated crystallizations from different solvents) essentially ruling out that the minor set arises from byproducts. The relative abundance of the two species also was invariant to the sample concentration (0.02–0.15 M), establishing that both species are of the same molecularity. At elevated temperatures (Fig. 1(a), in $C_2D_2Cl_4$) the two signal sets broaden and undergo coalescence at *ca.* 55 °C. At 75 °C, only one set of averaged signals is seen (compound **3b** is stable at least up to 90 °C in $C_2D_2Cl_4$ solution). Changing the NMR solvent to DMSO-d_6

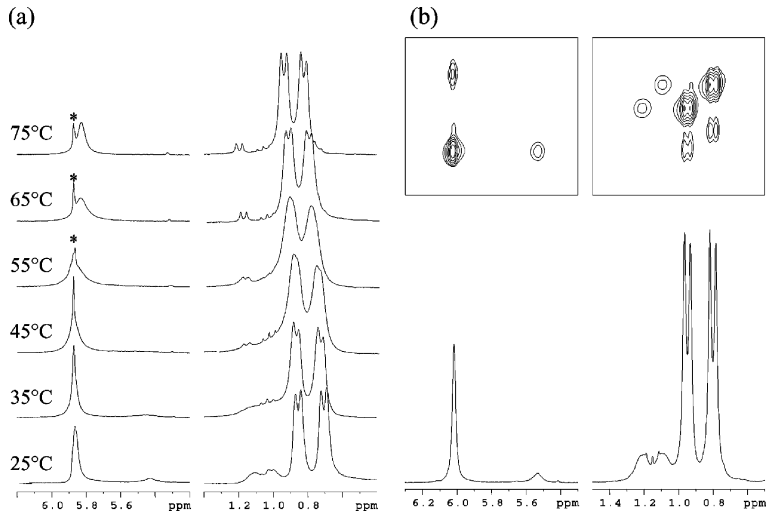
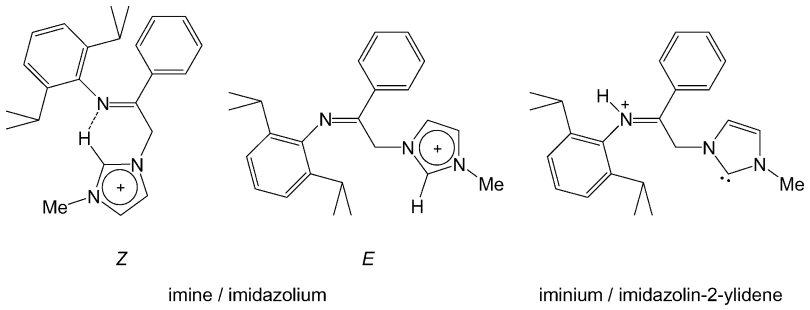


Fig. 1 (a) Variable-temperature ^{1}H NMR spectrum of **3b** in $C_2D_2Cl_4$ (* = residual H in solvent). (b) 2D-EXSY spectra of **3b** (mixing time 350 ms) and the corresponding regular ^{1}H NMR spectrum at 25 °C in $CDCl_3$.



Scheme 3

causes the minor signals to disappear. The exchange process is also observable by EXSY ^{1}H NMR spectroscopy in $CDCl_3$.[40,41] The resulting 2D EXSY spectrum shows cross correlations between exchanging protons in the two equilibrating structures (Fig. 1(b)), for example between the methylene resonances in the minor (δ 5.53) and major (δ 6.07) species. Analogous correlations are seen for all the other resonances in the ^{1}H NMR spectrum.

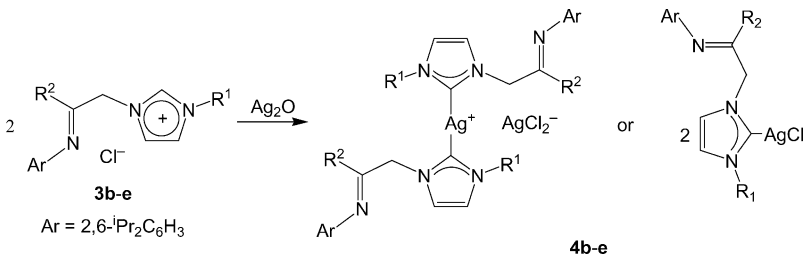
One possible explanation for the double set of signals could be the presence of *E* and *Z* conformers (Scheme 3). Compounds **3a** and **3c–e** are presumed to prefer the *E* conformation for steric reasons. Replacement of the methyl group at C(imine) with a phenyl group (as in **3b**) affects the steric interactions at the imine C=N bond. The Ph and imidazole rings have more or less the same steric requirements and it is not obvious which conformer will be the predominant one. In addition, the somewhat acidic proton[42–44] of the imidazolium ring might engage in hydrogen bonding to N(imine) in what would constitute a six-membered cyclic structure. This interaction would stabilize the conformer with a *syn* relationship between the H and imidazole groups at the imine C=N bond, *i.e.* the *E* conformation for **3a,c–e** and the *Z* conformation for **3b**. Related cyclic structures are quite common for imines with properly oriented acidic groups such as –OH.[45–47] Another possible cause of the signal duplication might be that the compound exists as interconverting imine/imidazolium and iminium/imidazolin-2-ylidene isomers. The observed ^{1}H NMR shifts for the acidic proton are δ 10.5 (major, relatively sharp) and 10.7 (minor, broadened) in $CDCl_3$. Imidazolium C–H chemical shifts typically fall in the range δ 9.5–11.5 ($CDCl_3$)[21,48] (see also Experimental section) and iminium N–H shifts are seen in the δ 11–15 range,[47,49] so it appears that chemical shifts can not be used to distinguish between the possibilities. Aqueous pK_a data for iminium cations are not straightforwardly determined, but it has been estimated that iminium cations are more acidic than corresponding primary ammonium ions by about 3 pK_a units;[50–52] primary alkyliminium cations therefore have estimated pK_a values around 7 or less.[50] Recent estimates for the C–H acidities of protonated imidazolin-2-ylidene carbenes are as high as 21–24.[42] The great pK_a difference between iminium ions and imidazolium ions effectively rules out the equilibrium between imine/imidazolium and iminium/imidazolin-2-ylidene as an explanation for the two signal sets, rendering a simple *E*/*Z* isomerism most likely. Changing the solvent from $CDCl_3$ to the strong hydrogen bond acceptor DMSO might disrupt the putative stabilizing intramolecular hydrogen bond, and indeed, only one conformer is seen in DMSO-d_6. Interestingly, Coleman *et al.* recently reported the synthesis of an imine-functionalized imidazolium salt according to Scheme 2. This system also exhibited two sets of signals in the ^{1}H NMR spectrum,[20] and this was attributed to the presence of *E* and *Z* isomers.

Silver iminocarbene complexes

Imidazolium salts are frequently used as precursors for metal N-heterocyclic carbene complexes. The deprotonation of the imidazolium salt is accomplished by the use of a suitable base. If enolizable functional groups are present (such as the doubly activated CH_2 group that links the imine and the imidazolium ring) the use of Ag_2O as the base has been found advantageous.[53] The resulting Ag(I) carbene complexes can transfer the carbene ligands to a variety of other metals.[54] Ag(I) heterocyclic carbene complexes exhibit a fascinating structural diversity, including monomeric, dimeric, and polymeric solid-state structures.[48,55–57] Two structural classes stand out when the coordination mode of Ag is considered: (1) cationic complexes with two carbenes attached to one silver atom. The counter-anion, usually $AgCl_2^-$, is more or less separated from the Ag(carbene)$_2^+$ moiety. (2) Neutral complexes with only one carbene attached to the silver atom. Obviously, it may often be far from trivial to establish what structures exist in solution for these species.

Treatment of the imidazolium salts **3b–e** with a slurry of Ag_2O in dichloromethane led to the corresponding Ag(I) iminocarbene complexes **4b–e** that yield elemental analysis data in agreement with a [Ag(carbene)Cl]$_n$ formulation (Scheme 4). Some key spectroscopic features are listed in Table 1. As expected, the ^{1}H and ^{13}C{^{1}H} NMR spectra indicated the presence of diastereotopic methyl groups within the ^{i}Pr substituents of the N(imine)-aryl groups. The IR spectra show two $\nu_{C=N}$ absorptions at *ca.* 1685 and 1665 cm^{-1} (**4c–e**). In the case of **4b**, the phenyl at the imine carbon causes a lowering of the absorptions to 1657 and 1634 cm^{-1}. The higher-energy absorptions are essentially unchanged compared to those seen for the corresponding imidazolium chloride precursors **3b–e**. This suggests that the iminocarbene is bonded in a monodentate fashion to Ag through the carbene carbon, rendering the imine group free.

NMR, IR, and elemental analysis can not unambiguously establish whether the structures of **4b–e** are monomeric or oligomeric, or whether they are of the [Ag(carbene)$_2^+$][$AgCl_2^-$]



Scheme 4

or AgCl(carbene) type, neither in solution nor in the solid state. Electrospray mass spectrometry analysis indicated the presence of a [(carbene)$_2$Ag$^+$] moiety for all the complexes **4b–e**. This is in accordance with observations by others[28,34] on related complexes. We also assumed a similar structure for the smaller Ag(I) iminocarbene complex **4a**[35] on the basis of the mass spectrometry analysis. Crystals that were suitable for X-ray crystal structure determination were obtained of **4b** and **4d**. The solid-state structures (*vide infra*) contrasted the ES-MS findings in establishing that the solid-state structure is of the type (κ^1-*C*-carbene)AgCl with monomeric (carbene)AgCl units. Other monomeric (carbene)AgX complexes have been previously characterized.[48,57]

In analogy with the corresponding imidazolium salt **3b**, the Ag carbene complex **4b** (but not **4c–e**) displays two sets of ^{1}H NMR signals in *ca.* 2 : 1 ratio. Again the low-intensity set appears to vanish when the solvent is changed from $CDCl_3$ to DMSO-d_6. The two sets of signals undergo partial coalescence when the temperature is increased (the complex decomposes at *ca.* 50 °C, before complete coalescence), and the two sets of resonances exhibit EXSY correlations also in this case. The *E*–*Z* isomerism observed in **3b** apparently is retained in the Ag complex. However, the stabilizing effect of the hydrogen bonding on the *Z* structure is now lost and probably steric effects control the distribution between the *E* and *Z* isomers. The *E* isomer is believed to be the major species, based on the solid-state structure (*vide infra*).

It can not be ruled out, however, that the complexity of the NMR spectra could also be due to the coexistence of interchanging (carbene)AgCl and (carbene)$_2$Ag$^+$AgCl$_2^-$ or {(carbene)AgCl}$_2$ species (the latter is likely ruled out through the lack of concentration dependence on the spectra), or to a weak interaction between the N(imine) and Ag in a six-membered chelate ring system. The existence of trigonal Ag atoms in similar environments has been recently demonstrated.[48,55]

X-Ray crystal structure determination of 4b

Crystals of **4b** suitable for X-ray diffraction structure determination were obtained by crystallization from chloroform–pentane. The structure showed some disorder in the aromatic rings. The phenyl group is found in two different positions with the ring planes twisted *ca.* 35° relative to each other in a 64 : 36 relative ratio. Furthermore, the 2,6-diisopropylphenyl group is found to be equally probable with two different orientations. Selected bond distances and angles for the most abundant structure are shown in Table 2. The most probable conformer of **4b** is depicted in the ORTEP plot in Fig. 2. Interestingly, **4b** is made up from monomeric (carbene)AgCl units in the solid state and not from bis(carbene) units [(carbene)$_2$Ag]$^+$ and [AgCl$_2^-$] that were suggested by the ES-MS analysis. The structural data reveal

Table 2 Selected distances (Å) and angles (°) in **4b**

Ag–C1	2.087(3)	N2–C5	1.450(3)
Ag–Cl	2.3424(8)	N3–C6	1.269(3)
N1–C1	1.347(3)	N3–C13	1.423(6)
N1–C3	1.380(4)	C3–C4	1.341(4)
N1–C2	1.462(4)	C5–C6	1.522(3)
C1–N2	1.348(3)	C6–C7	1.494(5)
N2–C4	1.381(3)		
C1–Ag–Cl	172.63(7)	C4–N2–C5	125.0(2)
C1–N1–C3	111.0(2)	C6–N3–C13	130.9(9)
C1–N1–C2	124.8(2)	C4–C3–N1	106.8(2)
C3–N1–C2	124.2(2)	C3–C4–N2	106.6(3)
N1–C1–N2	104.6(2)	N2–C5–C6	112.2(2)
N1–C1–Ag	129.8(2)	N3–C6–C7	127.6(4)
N2–C1–Ag	125.56(18)	N3–C6–C5	116.4(2)
C1–N2–C4	111.0(2)	C7–C6–C5	115.9(3)
C1–N2–C5	123.7(2)		

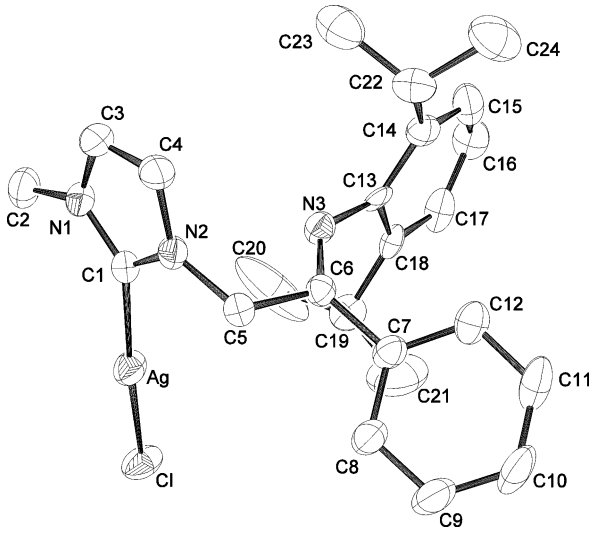


Fig. 2 ORTEP drawing of the most abundant (64%) conformer of **4b**. Hydrogen atoms are omitted for clarity.

a relatively short distance (3.3 Å) between the Ag atom in one molecule and the Cl in the neighbor. A small distortion that might be caused by this can be seen in the C(carbene)–Ag–Cl angle (173°). Other Ag(carbene) crystal structures that have two interacting units have been previously reported.[48,55] In these, the C(carbene)–Ag–Cl angle depends on the Ag···Cl distance between the two (carbene)AgCl units, ranging from 145° and 2.72 Å[55] to 163° and 2.99 Å.[48] Monomeric Ag(Carbene)X species without close interactions between neighboring units tend to have C(carbene)–Ag–X angles greater than 176°.[48] It is also noteworthy that the N(imine) atom points away from the silver atom, confirming the presumed lack of interaction between N(imine) and Ag. The Ag–C(carbene) and Ag–Cl distances of 2.087 and 2.342 Å, respectively, are in accordance with most reported complexes of this kind, Ag–C(carbene) *ca.* 2.07 Å and Ag–Cl *ca.* 2.35 Å.[48,55] The imine C=N bond assumes the *Z* geometry.

X-Ray crystal structure determination of 4d

Crystals of **4d** suitable for X-ray diffraction structure determination were obtained by crystallization from chloroform–pentane. Selected bond distances and angles are shown in Table 3 and an ORTEP plot of the structure of **4d** is shown in Fig. 3. Compound **4d** crystallizes with one $CHCl_3$ solvent molecule. The solid-state structure is made up from monomeric (carbene)AgCl units and in this case there are no close spatial relationships between the Ag atom in one molecule and the chloride in an adjacent one,

Table 3 Selected distances (Å) and angles (°) in **4d**

Ag1–C1	2.086(3)	N1–C4	1.455(4)
Ag1–Cl1	2.3451(8)	N3–C5	1.265(4)
N2–C1	1.347(4)	N3–C7	1.426(4)
N2–C3	1.395(4)	C5–C6	1.507(5)
N2–C19	1.445(4)	C5–C4	1.524(4)
N1–C1	1.352(4)	C2–C3	1.340(5)
N1–C2	1.394(4)		
C1–Ag1–Cl1	176.31(9)	C3–C2–N1	107.0(3)
C1–N2–C3	111.0(3)	C20–C19–N2	119.1(3)
C1–N2–C19	125.0(3)	C24–C19–N2	118.6(3)
C3–N2–C19	123.9(3)	N1–C4–C5	113.5(3)
C1–N1–C2	110.6(3)	C8–C7–N3	119.3(3)
C1–N1–C4	125.9(3)	C12–C7–N3	119.9(3)
C2–N1–C4	123.4(3)	C2–C3–N2	106.4(3)
C5–N3–C7	120.7(3)	N2–C1–N1	105.0(3)
N3–C5–C6	127.4(3)	N2–C1–Ag1	123.4(2)
N3–C5–C4	119.6(3)	N1–C1–Ag1	131.1(2)
C6–C5–C4	112.9(3)		

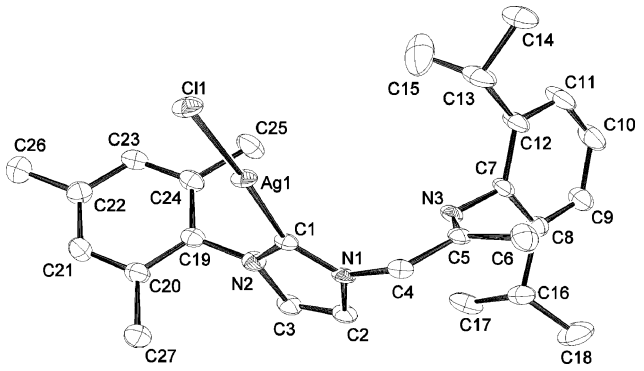
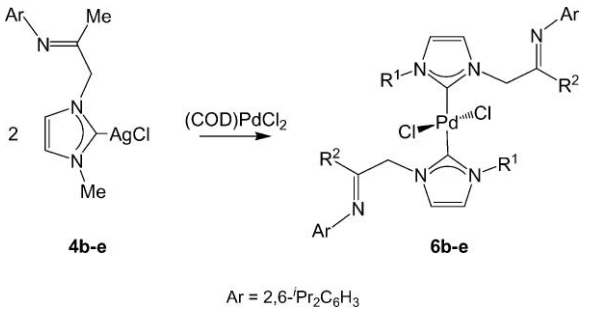


Fig. 3 ORTEP drawing of **4d**. Hydrogen atoms and a $CHCl_3$ solvent molecule are omitted for clarity.

as was observed for **4b**. In **4d**, the C(carbene)–Ag–Cl angle is 176.3°, which is somewhat greater than in **4b**, and within the range found in previously reported Ag(carbene)X complexes.[48] The Ag–C(carbene) and Ag–Cl distances of 2.086 and 2.345 Å, respectively, are almost identical to those in **4b**. The imine C=N bond assumes the expected (for steric reasons) *E* geometry.

Palladium iminocarbene complexes

The Ag iminocarbene complex **4a** reacts cleanly with $(COD)PdCl_2$ to give the (*N*,*C*-chelating carbene)$PdCl_2$ complex (**5a**).[35] Similar reactions were attempted starting from the Ag iminocarbenes **4b–e**. The reactions were initially performed in the same manner, with a carbene : Pd ratio of 1 : 1. To our surprise, the reactions proceeded differently and only half of the $(COD)PdCl_2$ was consumed. The stoichiometry of the reaction was changed according to a 2 : 1 carbene : Pd ratio and all material was consumed. The four new Pd complexes that resulted, **6b–e**, were characterized by ^1H and $^{13}C\{^1H\}$ NMR, IR, MS, and elemental analysis. Key spectroscopic data are listed in Table 1. The elemental analyses established that there were two iminocarbene ligands per Pd, in accordance with the observed reaction stoichiometry. Mass spectrometry indicated ions with *m*/*z* values corresponding to the $(carbene)_2PdCl^+$ ion. Significant changes in the IR $\nu_{C=N}$ data compared to those of the Ag carbene complexes **4b–e** were not observed, suggesting a lack of bonding of the imine. In our previous paper[35] we suggested that the separation of the two doublets from the diastereotopic ^{i}Pr methyl groups was a good indicator on whether N(imine) was coordinated to Pd or not. The separations of the doublets in the new complexes **6b–e** are in the range 0.03–0.3 ppm, which is somewhat less than in the corresponding Ag carbene complexes. The ^1H NMR data therefore indicate that N(imine) is not coordinated to Pd in **6b–e**. The combined spectroscopic and analysis data are consistent with the reaction outlined in Scheme 5.



Scheme 5

A Pd bis(carbene) complex may exist with the carbene ligands either *cis* or *trans* disposed relative to the Pd center. The X-ray structures of numerous Pd bis(carbene) complexes have been reported in the literature, and both *cis* and *trans* complexes have been described.[23,34,53,58–63] One might expect the *trans* isomers to be favored for steric reasons, and *cis* for electronic reasons due to the strong *trans* influence of the carbene ligands. The first structurally characterized Pd bis(carbene) was reported by Herrmann and co-workers in 1995,[61] and was prepared from $Pd(OAc)_2$ and an appropriate imidazolium salt. The two heterocyclic carbene ligands, bearing two *N*-methyl substituents, were coordinated in a *cis* fashion at Pd. Later, the same group isolated another *cis* complex utilizing related triazolium carbenes.[58] The latter *cis* bis(carbene) complex underwent subsequent isomerization to the thermodynamically preferred *trans* complex. Bulkier substituents at the heterocyclic carbene appear to change the geometrical preference. Enders and co-workers[62] found both *cis* (minor) and *trans* (major product) isomers when a bis(1-phenylethyl) *N*-substituted heterocyclic carbene was coordinated at Pd, again in a reaction between $Pd(OAc)_2$ and the imidazolium salt precursor. Also in this case, the *cis* complex was found to undergo gradual isomerization to the *trans* isomer when heated. Cavell and co-workers[34] reported the coexistence of *cis* and *trans* bis(carbene) complexes in a study of Pd-bonded functionalized carbenes bearing pyridine and carbonyl functional groups. The distribution of *cis* and *trans* $(carbene)_2PdCl_2$ species, obtained by carbene transfer from Ag(carbene) precursors to $PdCl_2(NCMe)_2$, depended on the reaction temperature, and importantly it was reported that the *cis* and *trans* isomers did not interconvert at temperatures up to 80 °C. Observed ^1H NMR line broadening phenomena in these species was attributed to restricted rotation around Pd–C(carbene) bonds, imposed by bulky functional groups attached to the carbene ligands. Available ^{13}C NMR data at that time suggested that the C(carbene) chemical shift was diagnostic of the *cis vs. trans* arrangement. The shift values for *trans* Pd bis(carbene) complexes were in the range δ 175–186, whereas *cis* species gave values at higher field, *ca.* δ 157–167.[34,64] In the ^{13}C NMR spectra of the Pd bis(carbene) complexes that are reported herein, the C(carbene) resonances (when detectable) are located at *ca.* δ 171. In the Ag carbene complexes, C(carbene) appears at δ 182, and in the neutral Pd(κ^2-iminocarbene) complex **5a**, at δ 175.[35] Hence, it appears that a firm conclusion regarding the preferred coordination geometry of **6b–e** can not be drawn solely on the basis of their ^{13}C NMR chemical shifts.

Provided that the imidazole rings are perpendicular to the Pd coordination plane in **6b–e**, which is reasonable on steric grounds, the two protons of the methylene linkage between the imine and the heterocyclic ring will be diastereotopic in a *cis* coordination geometry. This will cause a splitting of the ^1H NMR signal into two mutually coupled doublets. In a *trans* geometry, on the other hand, the methylene protons will be equivalent and one simple singlet should be observed. In the case of *cis* geometry, low barriers for rotation around the Pd–C(carbene) bond might however cause the diastereotopic methylene protons to equilibrate on the NMR time scale, resulting in a deceptively simple spectrum. We find that the bis(carbene) complexes **6b–e** exhibit only a singlet for the methylene groups, even at temperatures as low as −90 °C (CD_2Cl_2). The steric demand of the iminocarbenes reported herein appear to be at least as severe as that of the systems recently investigated by Cavell and co-workers[34] (see above paragraph) and therefore, low barriers for rotation around the Pd–C(carbene) bonds are precluded. We conclude that the bis(carbene) complexes **6b–e** exist with a preferred *trans* coordination geometry. These observations and conclusions are entirely in line with other reports of bis(carbene) complexes of Pd and Pt.[53,63] The structural assignment for **6b–e** is further supported by the solid-state structure of **6b**.

X-Ray crystal structure determination of 6b

Crystals of **6b** that were suitable for X-ray diffraction structure determination were obtained by crystallization from a chloroform–dichloromethane–pentane mixture. Selected bond

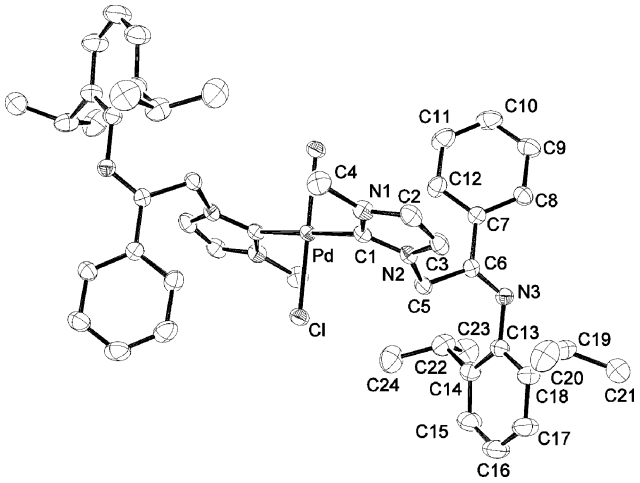


Fig. 4 ORTEP drawing of **6b**. Hydrogen atoms are omitted for clarity.

distances and angles are shown in Table 4 and an ORTEP plot of the structure of **6b** is shown in Fig. 4. A cluster of residual electron density, likely corresponding to solvent molecules (chloroform and/or methylene chloride) was found, but heavy disorder made it too difficult to determine its contents. The SQUEEZE procedure as implemented in program PLATON[65,66] was therefore applied to the data, *cf.* the Experimental section for further details. The molecular structure of compound **6b** is centrosymmetric. The Pd center bears two iminocarbene ligands that are mutually *trans* disposed. The iminocarbene ligands are coordinated through the carbene carbon atoms only. The imidazole-2-ylidene ring systems are located in the same plane with the imine functional group pointing in opposite direction. Analogous conformations are found for other *trans* bis(carbene) complexes.[24,28,63,67–69] The plane spanned by the two carbene ligands is tilted with respect to the coordination plane by 66.4° (as measured by the N2–C1–Pd–Cl torsional angle). The two remaining coordination sites of the square-planar Pt(II) center (the sum of the four *cis* L–Pd–L′ angles is 360°) are occupied by the chloride ligands (Table 4).

The Pd–C(carbene) and Pd–Cl distances (2.037 and 2.307 Å, respectively) are both within the distances measured on similar *trans* bis(carbene) complexes.[28,59,63,68,70] Even though the structure shows only small deviations when compared to the precursor **4b**, is noteworthy that the configuration of the imine bond has changed. In **4b**, the imine C=N bond assumed the *E* geometry, but in the Pd complex it has changed to the *Z* geometry.

Table 4 Selected distances (Å) and angles (°) in **6b**

Pd–C1	2.037(1)	N2–C5	1.461(2)
Pd–Cl	2.3070(3)	C2–C3	1.345(2)
C1–N1	1.356(1)	N3–C6	1.279(2)
C1–N2	1.353(2)	N3–C13	1.426(2)
N1–C2	1.376(2)	C5–C6	1.524(2)
N1–C4	1.459(2)	C6–C7	1.486(2)
N2–C3	1.386(2)		
C1–Pd–C1	180.0	C1–N2–C5	124.8(1)
C1–Pd–Cl	90.44(3)	C3–N2–C5	124.2(1)
C1–Pd–Cl	89.56(3)	C3–C2–N1	106.9(1)
Cl–Pd–Cl	180.0	C6–N3–C13	121.7(1)
N1–C1–N2	104.4(1)	C2–C3–N2	106.5(1)
N1–C1–Pd	127.5(1)	N2–C5–C6	112.5(1)
N2–C1–Pd	128.0(1)	N3–C6–C7	118.7(1)
C1–N1–C2	111.1(1)	N3–C6–C5	123.1(1)
C1–N1–C4	124.4(1)	C8–C7–C6	119.9(1)
C2–N1–C4	124.5(1)	C18–C13–N3	119.2(1)
C1–N2–C3	111.0(1)	C14–C13–N3	119.8(1)

Solution dynamic behavior of the Pd bis(carbene) complexes 6c–e

Double sets of signals were found in the ^{1}H NMR spectra for the Pd bis(carbene) complexes **6c–e**. This suggests the presence of two different isomers or conformers in solution. It is unlikely that this phenomenon is caused by imine *E–Z* isomerism, since similar spectroscopic behavior was not observed for the precursors **3c–e** or **4c–e**. The identity of the solvent (CD_2Cl_2 *vs.* DMSO-d_6) had no significant effect on the relative amounts of the two species. The lack of solvent effect suggests that the two species are not examples of κ^2-*C*,*N* *vs.* κ^1-*C* isomers.[35]

The relative intensities of the two signal sets depend strongly on the size of the N(imidazole) substituent R^1 (see Scheme 2). Starting with the smallest ligand system, the N(imidazole) phenyl complex **6c**, one set of resonances dominated (*ca.* 94%) the ^{1}H NMR spectrum. Even though the minor set (6%) of resonances is weak, clear correlation signals appear in the 2D-EXSY ^{1}H NMR spectrum of **6c**. Thus, the two species undergo interchange on the observation time scale. The ^{1}H NMR spectra were more complicated, but still had well-resolved signals, when the N(imidazole) phenyl group in **6c** was replaced by a 2,4,6-trimethylphenyl group in **6d**. In this case, the two sets of signals appeared in a 72 : 28 ratio. This ratio was independent of the sample concentration, demonstrating that both species must be of the same molecularity. The signals of the two sets are again related by an exchange process observed as cross-peaks in the 2D-EXSY ^{1}H NMR spectrum (Fig. 5), and the signals in the regular ^{1}H NMR spectrum undergo coalescence at *ca.* 70 °C. If the steric bulk of the N(imidazole) substituent is further increased to 2,6-^{i}Pr$_2$C$_6$H$_3$ as in **6e**, two sets of signals are still seen, this time in an 80 : 20 ratio. The major signals are sharp and well-resolved, but the minor ones are somewhat broadened. An exchange process relating the two isomers, as for **6c** and **6d**, is again observed by 2D-EXSY ^{1}H NMR.

In a *trans* coordination geometry, the two carbene ligands can have their two N(imidazole) substituents oriented in the same or in the opposite directions with respect to the coordination plane, denoted *syn* and *anti* for **6d** in Fig. 5. Depending on the relative abundance of the two orientations and on the barrier for rotation around the Pd–C(carbene) bond, the signals from one, both, or a weighted average of the two rotamers may be observed by ^{1}H NMR. The rotation barriers and relative stabilities of the two conformers might change appreciably within the three complexes **6c–e** because of the increased steric bulk of the N(imidazole) substituents in the series. It has been indicated that there is essentially no electronic barrier towards M–C(carbene) rotation in the *N*-heterocyclic carbenes,[71] and that documented instances of hindered rotation[21,62,71–75] are steric in origin.

Solution dynamic behaviour of 6b

As might be expected from the discussion above, compound **6b** also exhibits two sets of ^{1}H NMR signals. At ambient temperature, the two sets appear in a 66 : 34 ratio in the broadened ^{1}H NMR spectrum. The appearance is quite similar to that of the corresponding Ag carbene **4b**, and the two species undergo an exchange process as observed by 2D-EXSY ^{1}H NMR spectroscopy. The correlating signals coalesce at elevated temperatures (50 °C) and sharpen at lower temperatures (10 °C). The methylene group gives rise to diagnostic singlets, suggesting that the Pd coordination geometry is *trans* also in this case. Further lowering of the temperature leads to additional signal splitting. The added complexity probably is the result of the occurrence of at least two dynamic processes, hindered rotation around the Pd–C(carbene) bonds (*cf.* **6c–e**) as well as imine *E–Z* isomerization (*cf.* **3b** and **4b**). NOESY NMR spectroscopy indicates a spatial proximity between the methylene protons and an isopropyl group, but only for the major species seen at ambient temperature. Thus, the appearance of a double signal appears to arise from the *E/Z* isomerization process. The hindered rotation around the Pd–C(carbene) bonds must then cause the

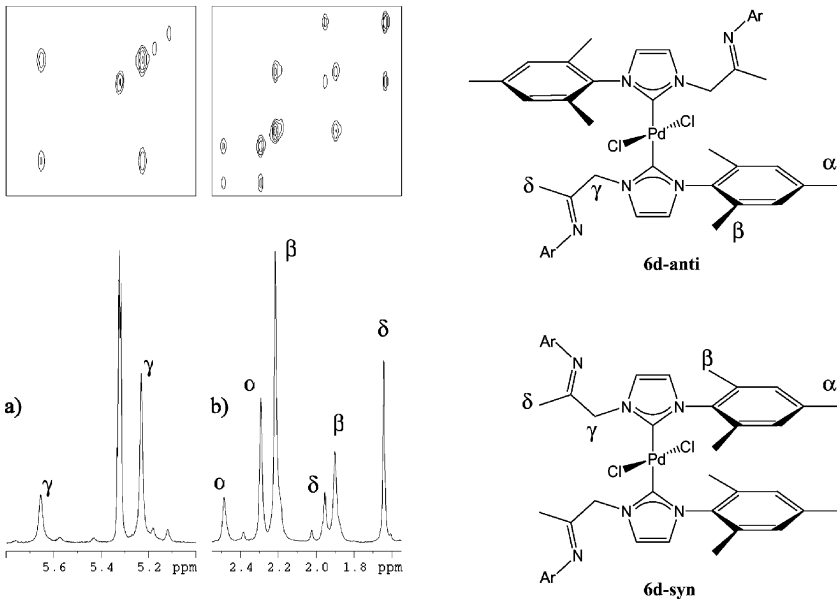
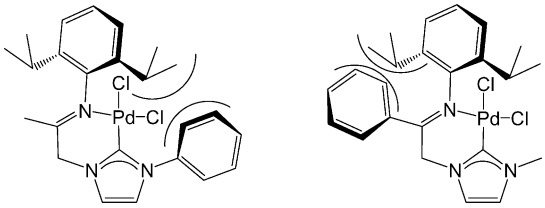


Fig. 5 300 MHz ^{1}H NMR spectrum and the corresponding 2D-EXSY NMR (mixing time 350 ms) of selected regions of **6d** in CD_2Cl_2: (a) methylene resonances (solvent signal at δ 5.32), (b) C(imine)-Me (δ) and N(imidazole) aryl-Me resonances (β = *o*-Me and α = *p*-Me).

additional low-temperature signal splitting. Consequently, the Pd–C(carbene) rotational barrier must be lower in **6b** than in **6c–e**. This is probably caused by the reduced (methyl *vs.* phenyl and substituted phenyls) steric bulk of the R^1 substituent (Scheme 2) at the non-chelating side of the imidazole ring.

Formation of κ^1-*C* *vs.* κ^2-*C*,*N* complexes

Cavell[34] demonstrated that mono(carbene) and bis(carbene) Pd complexes bearing the same, potentially chelating, carbene ligands could be selectively generated simply by adjusting the molar ratio of carbene and Pd precursor. In the reactions described herein, the bis(carbene) products **6b–e** were formed regardless of the Pd : carbene ratio. Two different effects may contribute to the favored bis(carbene) complex formation. (1) **6c–e** bear large N(imidazole) aromatic groups R^1. The aromatic rings adopt an orientation more or less perpendicular to the imidazole ring plane. In the structure that would result from chelate formation, steric repulsions will arise between these aromatic groups and the $^iPr_2C_6H_3$ moiety at N(imine). (Simple structural modeling using Chem3D[76] starting with the X-ray structure of **5a**[35] reveals a close proximity between the N(imine) aryl isopropyl group and the N(imidazole) group R^1 even when the latter is an unsubstituted phenyl as in **6c**. Increasing the size of the N(imidazole) substituents obviously will enhance the steric repulsions.) (2) In **6b**, similar transannular steric interactions will be less severe, but there is now a possibility that the C(imine) phenyl group contributes to sterically disfavor chelate formation.



6c **6b**

Concluding remarks

In this contribution, it has been demonstrated that the coordination mode and dynamic behavior of the previously reported iminocarbene ligand systems can be dramatically affected by changes in the substitution pattern of the ligand. Sterically unencumbered systems favor the formation of κ^2-*C*,*N* chelate structures containing one iminocarbene moiety per metal upon coordination at Pd(II); these complexes were demonstrated to engage in reversible, solvent-mediated chelate ring-opening reactions. Sterically encumbered systems form non-chelating κ^1-*C* iminocarbene Pd(II) complexes containing two iminocarbene ligands per metal. Transannular repulsions across the chelate ring is believed to be the origin of these structural differences. We hope to explore the potential of these novel complexes in Pd-catalyzed reactions in future contributions.

Experimental

General procedures

All reactions involving organometallic compounds were carried out with use of drybox, vacuum line, syringe, and Schlenk techniques unless otherwise noted. Solvents for reactions and NMR were dried according to standard procedures. NMR spectra were recorded on Bruker Avance DPX 200 and 300 instruments with QNP probes. The NMR spectra were recorded at 25 °C unless otherwise noted. ^{1}H and ^{13}C assignments were aided by NOESY ^{1}H NMR. For brevity, the following abbreviations are used for the assignments: Ph = phenyl, Mes = 2,4,6-trimethylphenyl; Ar = 2,6-diisopropylphenyl. Mass spectrometry measurements were done on a Micromass QTOF II spectrometer. IR spectra were recorded on a Nicolet Magna-IR 550 FT-IR spectrophotometer. Elemental analyses were preformed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

Commercial grade glyoxal (40% in H_2O), 2,6-diisopropylaniline, 2,4,6-trimethylaniline, and aniline were used. The anilines were distilled prior to use. Chloroacetone, phenacyl chloride, 1-methylimidazole, 1-phenylimidazole, and Ag_2O were purchased from Acros, Fluka, or Aldrich, and used as received. Anhydrous $PdCl_2$ was purchased from Fluka, and $(COD)PdCl_2$[77] and 1-chloro-2-(2,6-diisopropylphenylimino)propane (**1a**) were prepared as described previously.[35]

1-Chloro-2-(2,6-diisopropylphenylimino)-2-phenylethane (1b). Phenacyl chloride (3.72 g, 0.024 mol) and 2,6-diisopropylaniline (6.26 g, 0.035 mol) were dissolved in diethyl ether (100 mL). The contents were cooled to 0 °C in an ice bath. A 1.0 M pentane solution of $TiCl_4$ (20 mL, 0.02 mol) was added dropwise to the contents under vigorous stirring. The mixture was stirred for

15 min at 0 °C and then for 2 h at ambient temperature. Aqueous 1.0 M NaOH (100 mL) was added to the mixture and stirring was continued for 10 min. The aqueous phase was removed and extracted with ether (3 × 50 mL). The combined extracts were dried with potassium carbonate. The solvent was removed under vacuum, and the product was purified by removing unreacted 2,6-diisopropylaniline by careful vacuum distillation (80 °C, *ca.* 0.8 mm Hg). The product was pure as judged by ^{1}H NMR. Yield: 2.72 g (32%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.06 (dd, 2 H, Ph) 7.50 (m, 3 H, Ph), 7.12 (m, 3 H, Ar), 4.20 (s, 2 H, CH_2), 2.71 (septet, $J = 6.8$ Hz, 2 H, CHMe$_2$), 1.17 and 1.12 (d, $J = 6.8$ Hz, 6 H each, CHMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 161.1 (*C*=N), 145.0, 135.8, 135.5, 131.0, 128.6, 127.9, 124.0, 123.1 (Ph and Ar), 35.77 (CH_2Cl), 28.30 (CHMe$_2$), 23.34 and 22.46 (CHMe_2). IR (CH_2Cl_2) $\nu_{C=N}$ 1652 and 1631 cm^{-1}. MS (EI): *m*/*z* 313.2 (M$^{+\bullet}$, 24%), 264.2 (M$^+$ − CH_2Cl, 100%). HRMS (EI): *m*/*z* 313.15878 (M$^{+\bullet}$) (calc. 313.15973). Anal. Calc. for $C_{20}H_{24}$ClN: C, 76.53; H, 7.71; Cl, 11.30; N, 4.46. Found: C, 76.40; H, 7.60; Cl, 11.39; N, 4.39%.

1-(2,4,6-Trimethylphenyl)imidazole (2b)[78]. A mixture of 2,4,6-trimethylphenylammonium dihydrogenphosphate (18.0 g, 0.077 mol), prepared *in situ* by adding phosphoric acid to aqueous 2,4,6-trimethylaniline until a pH of 2 was reached, paraformaldehyde (3.19 g, 0.106 mol), and glyoxal (12 mL, 40% in H_2O, 0.106 mol) in a mixture of 150 mL H_2O and 150 mL 1,4-dioxane was heated to 100 °C before a saturated ammonium chloride solution (20 mL) was carefully added at this temperature. During the addition, the solution turned yellow and then black. The solution was cooled on an ice-bath after 1 h, and solid NaOH was gradually added until a pH of 12 was reached. Water (100 mL) was added to the mixture which was then extracted with hexane (3 × 50 mL). The extract was dried over $MgSO_4$ and concentrated under vacuum, giving a light brown powder. The desired product was recrystallized from ethyl acetate (3.31 g, 23% yield). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.40 (t, $J = 1.1$ Hz, 1 H, NC*H*N), 7.19 (t, $J = 1.1$ Hz, 1 H, *H*C=CH), 6.93 (s, 2 H, *m*-Mes), 6.86 (t, $J = 1.2$ Hz, 1 H, HC=C*H*), 2.30 (s, 3 H, *p*-Me), 1.95 (s, 6 H, *o*-Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 138.8 (ipso-Mes), 137.4 (N*C*N), 135.3 (*o*-Mes), 133.3 (*p*-Mes), 129.4 (N*C*=CN), 128.9 (*m*-Mes), 120.0 (NC=*C*N), 20.92 (*p*-Me), 17.21 (*o*-Me). IR (CH_2Cl_2) $\nu_{C=N}$ 1496 cm^{-1}. MS (EI): *m*/*z* 186 (M$^{+\bullet}$, 96%), 159 (M$^{+\bullet}$ − HCN, 100%). HRMS (EI): *m*/*z* 186.11497 (M$^{+\bullet}$) (calc. 186.11570). Anal. Calc. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 76.84; H, 7.53; N, 15.63%.

1-(2,6-Diisopropylphenyl)imidazole (2c). A mixture of 2,6-diisopropylaniline (26.3 g, 0.148 mol) and paraformaldehyde (4.6 g, 0.15 mol) in propanol (100 mL) was heated at 50 °C for 1 h. After cooling to room temperature, aqueous NH_3 (12 mL of a 13 M solution) and glyoxal (7.2 mL, 40% in H_2O, 0.15 mol) were added carefully and the mixture was heated at reflux for 12 h. After cooling to room temperature, water (100 mL) was added, and the product mixture was extracted with pentane. Pentane was removed under vacuum and excess aniline distilled under vacuum (80 °C, *ca.* 0.8 mm Hg). The product was separated from the mixture by distillation/sublimation (85 °C, *ca.* 0.8 mm Hg). Yield: 800 mg (2.3%) (most of the aniline was recycled). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.47 (t, $J = 1.1$ Hz, 1 H, NC*H*N), 7.41 (m, 1 H, *p*-Ar), 7.26 (m, 2 H, *m*-Ar), 7.23 (t, $J = 1.1$ Hz, 1 H, *H*C=CH), 6.94 (t, $J = 1.1$ Hz, 1 H, HC=C*H*), 2.40 (septet, $J = 6.8$ Hz, 2 H, C*H*Me$_2$), 1.13 (d, $J = 6.8$ Hz, 12 H, CHMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 146.5 (Ar), 138.5 (N*C*N), 132.8, 129.8 (Ar), 129.4 (N*C*CN), 123.7 (Ar), 121.6 (NC*C*N), 28.09 (*C*HMe$_2$), 24.43 and 24.35 (CHMe_2). IR (CH_2Cl_2) $\nu_{C=N}$ 1505 cm^{-1}. MS (EI): *m*/*z* 228 (M$^{+\bullet}$, 75%), 213 (M$^{+\bullet}$ − CH_3, 17%), 201 (M$^{+\bullet}$ − HCN, 30%) 186 (M$^{+\bullet}$ − ^{i}Pr, 100%). HRMS (EI): *m*/*z* 228.16226 (calc. 228.16265). Anal. Calc. for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 79.19; H, 8.99; N, 11.64%.

[3-Methyl-1-{2-(2,6-diisopropylphenylimino)-2-phenylethyl}-imidazolium] chloride (3b). A round-bottom flask was charged with α-chloroimine **1b** (1.29 g, 4.11 mmol), and excess 1-methylimidazole (10 mL, 0.13 mol) was added. The mixture was stirred for 12 h at 80 °C before cooling and precipitation of the product by addition of ether. The product was filtered and washed with ether before recrystallization from dichloromethane–ether. Yield: 1.312 g (80.6%). ^{1}H NMR (DMSO-d_6, 200 MHz) δ 9.38 (s, 1 H, NC*H*N), 7.88 (s, 1 H, NC*H*CHN, near imine), 7.79 (s, 1 H, NCHC*H*N, near N–Me), 7.33 (m, 5 H, Ph), 6.93 (m, 3 H, Ar), 5.93 (s, 2 H, CH_2), 3.93 (s, 3 H, N*Me*), 2.65 (septet, $J = 6.8$ Hz, 2 H, C*H*Me$_2$, 0.89 and 0.82 (d, $J = 6.8$ Hz, 6 H each, CHMe_2. ^{13}C{^{1}H} NMR (DMSO-d_6, 50 MHz) δ 161.3 (*C*=N), 144.0 (*ipso*-Ar), 137.8 (N*C*HN), 134.8 (*o*-Ar), 133.6 (*ipso*-Ph), 130.3 (*p*-Ph), 128.4 (*o*-Ph), 127.2 (*m*-Ph), 124.0 (N*C*CN, near imine), 123.7 (*p*-Ar), 123.1 (NC*C*N, near N–Me), 122.7 (*m*-Ar), 53.97 (NCH_2), 35.77 (NCH_3), 27.38 (*C*HMe$_2$), 23.46 and 21.65 (CHMe_2). IR (CH_2Cl_2) $\nu_{C=N}$ 1659, 1634 cm^{-1}. HRMS (ES): *m*/*z* 360.2306 (M$^+$ − Cl, 100%) (calc. 360.24397). Anal. Calc. for $C_{24}H_{30}ClN_3$: C, 72.80; H, 7.64; Cl, 8.95; N, 10.61. Found: C, 70.01; H, 7.96; Cl, 9.01; N, 10.65%. NMR data of the two coexisting species seen in $CDCl_3$ and high-temperature NMR data are included in the ESI.†

[3-Phenyl-1-{2-(2,6-diisopropylphenylimino)propyl}imidazolium] chloride (3c). 1-Phenylimidazole (485.4 mg, 3.37 mmol) and 1-chloro-2-(2,6-diisopropylphenylimino)propane (**1a**) (848 mg, 3.36 mmol) were stirred in THF (3 mL) at ambient temperature for three days. Ether was added to precipitate the product before filtration and washing with small portions of ether. The product was recrystallized from dichloromethane–ether. Yield: 835 mg (62%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 11.13 (s, 1 H, NC*H*N), 7.64 (m, 4 H, NC*H*C*H*N and *m*-Ph), 7.51 (m, 3 H, *o*,*p*-Ph), 7.02 (m, 3 H, Ar), 5.88 (s, 2 H, CH_2), 2.51 (septet, $J = 6.7$ Hz, 2 H, C*H*Me$_2$), 1.86 (s, 3 H, imine-*Me*), 1.11 and 0.95 (d, $J = 6.8$ Hz, 6 H, CHMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 163.6 (*C*=N), 144.1 (*ipso*-Ar), 137.6 (N*C*HN), 135.7 (*o*-Ar), 134.4 (*ipso*-Ph), 130.6 (*o*-Ph), 130.3 (*p*-Ph), 124.6 and 119.4 (N*C*H*C*HN), 124.1 (*p*-Ar), 123.0 (*m*-Ar), 121.8 (*m*-Ph), 55.45 (CH_2), 28.13 (*C*HMe$_2$), 23.02 and 22.49 (CHMe_2), 18.98 (imine-*Me*). IR (CH_2Cl_2) $\nu_{C=N}$ 1682 cm^{-1}. HRMS (ES): *m*/*z* 360.2346 (M$^+$ − Cl, 100%) (calc. 360.24397). Anal. Calc. for $C_{24}H_{30}ClN_3$: C, 72.80; H, 7.64; Cl, 8.95; N, 10.61. Found: C, 71.48; H, 7.30; Cl, 9.58; N, 11.32%.

[3-(2,4,6-Trimethylphenyl)-1-{2-(2,6-diisopropylphenylimino)-propyl}imidazolium] chloride (3d). -(2,4,6-Trimethylphenyl)-imidazole (288 mg, 1.55 mmol) and 1-chloro-2-(2,6-diisopropylphenylimino)propane (391 mg, 1.55 mmol) were stirred in MeCN (3 mL) at 40 °C for four days. The MeCN solvent was removed under vacuum and the residue was washed with pentane. The product was recrystallized from dichloromethane–ether. Yield: 500 mg (74%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.25 (s, 1 H, NC*H*N), 7.75 (s, 1 H, *H*CCH near imine), 7.09 (s, 1 H, HCC*H* near N–Me), 7.02 (m, 3 H, Ar), 6.95 (s, 2 H, *m*-Mes), 6.02 (s, 2 H, CH_2), 2.51 (septet, $J = 6.8$ Hz, 2 H, C*H*Me$_2$), 2.29 (s, 3 H, *p*-Me), 2.01 (s, 6 H, *o*-Me), 1.85 (s, 3 H, imine-*Me*), 1.11 and 0.96 (d, $J = 6.8$ Hz, 6 H each, CHMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 163.4 (*C*=N), 143.7 (*ipso*-Ar), 140.7 (*p*-Mes), 138.9 (N*C*HN, 135.4 (*o*-Ar), 133.8 (*o*-Mes), 130.1 (*ipso*-Mes), 129.2 (*m*-Mes), 123.9 (NC*C*N), 123.5 (*p*-Ar), 122.4 (*m*-Ar), 121.3 (N*C*CN), 54.88 (CH_2), 27.54 (*C*HMe$_2$), 22.68 and 22.03 (CHMe_2), 20.50 (*p*-Me), 18.36 (imine-*Me*), 16.84 (*o*-Me). IR (CH_2Cl_2) $\nu_{C=N}$ 1682 cm^{-1}. HRMS (ES): *m*/*z* 402.2828 (M$^+$ − Cl) (calc. 402.29092). Anal. Calc. for $C_{27}H_{36}ClN_3$: C, 74.03; H, 8.28; Cl, 8.09; N, 9.59. Found: C, 69.92; H, 8.39; Cl, 7.52; N, 9.06%.

[3-(2,6-Diisopropylphenyl)-1-{2-(2,6-diisopropylphenylimino)-propyl}imidazolium] chloride (3e). 1-(2,6-diisopropylphenyl)-imidazole (146 mg, 0.64 mmol) and 1-chloro-2-(2,6-diisopropylphenylimino)propane (164 mg, 0.65 mmol) were stirred

in MeCN (3 mL) at 40 °C for four days. The solvent was removed under vacuum and the residue was washed with pentane. The product was recrystallized from dichloromethane–pentane. Yield: 200 mg (65%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.16 (s, 1 H, NC*H*N), 7.92 (s, 1 H, *H*CCH near imine), 7.50 (m, 1 H, *p*-Ar at imidazole), 7.28 (m, 2 H, *m*-Ar at imidazole), 7.11 (s, 1 H, *H*CCH), 7.06 (m, 3 H, *m*,*p*-Ar at imine), 6.11 (s, 2 H, C*H*$_2$), 2.53 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$ at imine-Ar), 2.35 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$ at imidazole-Ar), 1.89 (s, 3 H, imine-*Me*), 1.13 and 1.07 (d, J = 6.8 Hz, 6 H each, CH*Me*$_2$ at imidazole-Ar), 1.11 and 0.99 (d, J = 6.8 Hz, 6 H each, CH*Me*$_2$ at imine-Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 163.9 (*C*=N), 145.5 (*p*-Ar at imidazole), 144.2 (*ipso*-Ar at imine), 139.8 (N*C*HN), 135.9 (*o*-Ar at imine), 131.9 (*o*-Ar at imidazole), 130.2 (*ipso*-Ar at imidazole), 124.6 (*m*-Ar at imidazole) 124.3 (N*C*CN near imidazole-Ar), 124.1 (N*C*CN near imine), 123.0 (*m*,*p*-Ar at imine), 55.49 (*C*H$_2$), 28.58 (*C*HMe$_2$ at imidazole-Ar), 28.13 (*C*HMe$_2$ at imine-Ar), 24.34 and 24.09 (CH*Me*$_2$ at imidazole-Ar), 23.15 and 22.71 (CH*Me*$_2$ at imine-Ar), 19.08 (imine-*Me*). IR (CH_2Cl_2) $\nu_{C=N}$ 1680 cm^{-1}. HRMS (ES): m/z 444.3254 (M$^+$ − Cl, 100%) (calc. 444.33787). Anal. Calc. for $C_{30}H_{42}ClN_3$: C, 75.05; H, 8.82; Cl, 7.38; N, 8.75. Found: C, 71.54; H, 8.42; Cl, 7.59; N, 8.49%.

(Iminoimidazolin-2-yliden)AgCl (4b–e): general procedure

The iminoimidazolium chloride **3b–e** was dissolved in dichloromethane and added to a slurry of Ag_2O in CH_2Cl_2. The mixture was stirred for 30 min at ambient temperature before filtration through Celite to remove excess Ag_2O. The solvent was removed under vacuum, and the product was dried and recrystallized from dichloromethane–pentane. The products were isolated as air-stable yellowish powders.

{3-Methyl-1-[2-(2,6-diisopropylphenylimino)-2-phenylethyl]-imidazolin-2-ylidene}AgCl (4b). From **3b** (131 mg, 0.331 mmol) and Ag_2O (40 mg, 0.173 mmol) in 5 mL CH_2Cl_2. Yield: 152 mg (91%). ^{1}H NMR (DMSO-d_6, 200 MHz) δ 7.47 (s, 1 H, NC*H*CHN), 7.40 (s, 1 H, NC*H*CHN), 7.30 (m, 5 H, Ph), 6.90 (m, 3 H, Ar), 5.64 (s, 2 H, C*H*$_2$), 3.77 (s, 3 H, N*Me*), 2.71 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$, 0.91 and 0.82 (d, J = 6.8 Hz, 6 H each, CH*Me*$_2$). IR (CH_2Cl_2) $\nu_{C=N}$ 1657, 1634 cm^{-1}. Anal. Calc. for $C_{24}H_{29}AgClN_3$: C, 57.33; H, 5.81; Ag, 21.45; Cl, 7.05; N, 8.36. Found: C, 57.92; H, 5.80; Ag, 20.90; Cl, 6.95; N, 8.02%. MS (ES): m/z 825 (M$_2$ − AgCl$_2$, 15%), 466 (M$^+$ − Cl, 13%), 360 (M$^+$ − AgCl, 85%), 194 (100%). NMR data of the two coexisting species seen in $CDCl_3$ are included in the ESI.†

{3-Phenyl-1-[2-(2,6-diisopropylphenylimino)propyl]imidazolin-2-ylidene}AgCl (4c). From **3c** (224 mg, 0.566 mmol) and Ag_2O (70 mg, 0.302 mmol) in 10 mL CH_2Cl_2. Yield: 196 mg (69%). ^{1}H NMR (C_6D_6, 200 MHz) δ 7.30 (m, 2 H, Ph,Ar), 7.03 (m, 6 H, Ph, Ar), 6.75 and 6.52 (d, J = 1.7 Hz, 2 H each, *H*C=C*H*), 4.92 (s, 2 H, C*H*$_2$), 2.81 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$), 1.51 (s, 3 H, imine-*Me*), 1.24 and 1.13 (d, J = 6.8 Hz, 6 H each, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 50 MHz) δ 182.5 (N*C*N), 165.5 (*C*=N), 145.8 (*ipso*-Ar), 140.3 (*ipso*-Ph), 136.0, 129.7, 128.3 (Ph), 124.1 (*p*-Ar), 124.0 (Ph), 123.4 (H*C*=CH near NPh), 123.3 (*m*-Ar), 120.8 (HC=*C*H near imine), 58.24 (*C*H$_2$), 28.58 (*C*HMe$_2$), 23.54 and 22.98 (CH*Me*$_2$), 18.63 (imine-*Me*). IR (CH_2Cl_2) $\nu_{C=N}$ 1684, 1666 cm^{-1}. MS (ES): m/z 825 (M$_2$ − AgCl$_2$, 15%), 466 (M$^+$ − Cl, 15%), 360 (M$^+$ − AgCl, 100%). Anal. Calc. for $C_{24}H_{29}AgClN_3$: C, 57.33; H, 5.81; Ag, 21.45; Cl, 7.05; N, 8.36. Found: C, 57.34; H, 5.57; Ag, 19.03; Cl, 9.43; N, 8.69%.

{3-(2,4,6-Trimethylphenyl)-1-[2-(2,6-diisopropylphenylimino)-propyl]imidazolin-2-ylidene}AgCl (4d). From **3d** (200 mg, 0.457 mmol) and Ag_2O (63 mg, 0.27 mmol) in 10 mL CH_2Cl_2. Yield: 130 mg (25%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.25 (s, 1 H, *H*C=CH), 7.05 (m, 3 H, Ar), 6.93 (s, 1 H, HC=C*H*), 6.91 (s, 2 H, Mes), 5.15 (s, 2 H, C*H*$_2$), 2.56 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$), 2.29 (s, 3 H, *p*-Me), 1.94 (s, 6 H, *o*-Me) 1.74 (s, 3 H, imine-*Me*), 1.11 and 1.04 (d, J = 6.8 Hz, 6 H each, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 164.1 (*C*=N), 144.7 (*ipso*-Ar), 139.5 (*p*-Mes), 135.6 (*o*-Ar), 135.1 (*ipso*-Mes), 134.6 (*o*-Mes), 129.3 (*m*-Mes), 123.8 (*p*-Ar), 122.9 (*m*-Ar), 122.6 and 122.3 (N*C*=*C*N), 58.38 (*C*H$_2$), 28.15 (*C*HMe$_2$), 23.18 and 22.56 (CH*Me*$_2$), 20.95 (*p*-Me), 18.48 (imine-*Me*), 17.49 (*o*-Me). IR (CH_2Cl_2) $\nu_{C=N}$ 1684, 1666 cm^{-1}. IR (nujol) $\nu_{C=N}$ 1679 cm^{-1}. Anal. Calc. for $C_{27}H_{35}AgClN_3$: C, 59.51; H, 6.47; Ag, 19.80; Cl, 6.51; N, 7.71. Found: C, 60.63; H, 7.04; Ag, 18.70; Cl, 6.01; N, 7.08%. MS (ES): m/z 909 (M$_2$ − AgCl$_2$, 5%), 508 (M$^+$ − Cl, 10%), 401 (M$^+$ − AgCl, 100%).

{3-(2,6-Diisopropylphenyl)-1-[2-(2,6-diisopropylphenylimino)-propyl]-imidazolin-2-ylidene}AgCl (4e). From **3e** (108 mg, 0.225 mmol) and Ag_2O (36 mg, 0.155 mmol) in 10 mL CH_2Cl_2. Yield: 78 mg (30%).^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.45 (m, 1 H, *p*-Ar at imidazole), 7.28 (s, 1 H, *H*C=CH near imine), 7.24 (m, 2 H, *m*-Ar at imidazole), 7.10 (m, 3 H, *m*,*p*-Ar at imine), 7.00 (s, 2 H, HC=C*H* near imidazole-Ar), 5.17 (s, 2 H, C*H*$_2$), 2.58 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$), 2.40 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$), 1.76 (s, 3 H, imine-*Me*), 1.17 and 1.06 (d, J = 6.8 Hz, 6 H each, CH*Me*$_2$) 1.13 and 1.06 (d, J = 6.8 Hz, 6 H each, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 164.0 (N=*C*), 145.7 (*o*-Ar at imidazole), 144.8 (*ipso*-Ar at imine), 135.7 (*o*-Ar at imine), 134.5 (*ipso*-Ar at imidazole), 130.6 (*p*-Ar at imidazole), 124.2 (*m*-Ar at imine), 124.1 (H*C*=CH near aryl) 123.9 (*p*-Ar at imine), 122.9 (*m*-Ar at imidazole), 121.76 (HC=*C*H near imine), 58.50 (*C*H$_2$), 28.30 and 28.22 (*C*HMe$_2$), 24.41, 24.34, 23.20 and 22.59 (CH*Me*$_2$), 18.58 (imine-*Me*). IR (CH_2Cl_2) $\nu_{C=N}$ 1684, 1666 cm^{-1}. MS (ES): m/z 993 (M$_2$ − AgCl$_2$, 75%), 550 (M$^+$ − Cl, 25%), 506 (100%).

(Iminoimidazolin-2-yliden)$_2$PdCl$_2$ (6b–e): general procedure

A solution of the Ag iminocarbene complex (**4b–e**) in CH_2Cl_2 was added to a stirred solution of (COD)$PdCl_2$ in CH_2Cl_2. The solution was stirred for 1 h and filtered through Celite. The solvent was removed under vacuum, and the residue was washed with MeCN to remove unreacted (COD)$PdCl_2$.

[3-Methyl-1-{2-(2,6-diisopropylphenylimino)-2-phenylethyl}-imidazolin-2-ylidene]$_2$PdCl$_2$ (6b). From **4b** (290 mg, 0.576 mmol) in 1 mL CH_2Cl_2 and (COD)$PdCl_2$ (165 mg, 0.578 mmol) in 5 mL CH_2Cl_2. Yield: 140 mg (54%). ^{1}H NMR (CH_2Cl_2, 200 MHz) showed dynamically broadened signals of two species in a 66 : 34 ratio. Data for major species: ^{1}H NMR (CH_2Cl_2, 200 MHz) δ 8.26 (2 H, *o*-Ph), 7.41 (br, 3 H, *m*,*p*-Ph), 7.16 (3 H, Ar), 6.49 (1 H, HC=C*H* near N–Me), 6.73 (1 H, HC=C*H* near imine), 5.66 (2 H, C*H*$_2$), 4.05 (3 H, N*Me*), 2.86 (br septet, 2 H, C*H*Me$_2$), 1.17 and 1.07 (br d, 6 H each, CH*Me*$_2$). Data for minor species: δ 7.39 (2 H, *o*-Ph), 7.25 (3 H, *m*,*p*-Ph), 6.98 (3 H, Ar), 7.15 (1 H, *H*C=CH near NMe), 6.92 (1 H, HC=C*H* near imine), 6.00 (2 H, C*H*$_2$), 4.11 (3 H, N*Me*), 2.86 (br septet, 2 H, C*H*Me$_2$), 1.27 and 0.87 (br d, 6 H each, CH*Me*$_2$). IR (CH_2Cl_2) $\nu_{C=N}$ 1634 cm^{-1}; (Nujol) $\nu_{C=N}$ 1634 cm^{-1}. Anal. Calc. for $C_{48}H_{58}Cl_2N_6Pd$: C, 64.32; H, 6.52; Cl, 7.91; N, 9.38; Pd, 11.87. Found: C, 63.85; H, 6.38; Cl, 8.37; N, 8.82; Pd, 12.41%. HRMS (ES): m/z 859.3566 (M$^+$ − Cl) (calc. 859.35541).

[3-Phenyl-1-{2-(2,6-diisopropylphenylimino)propyl}imidazolin-2-ylidene]$_2$PdCl$_2$ (6c). From **4c** (90 mg, 0.178 mmol) in 1 mL CH_2Cl_2 and (COD)$PdCl_2$ (51 mg, 0.18 mmol) in 5 mL CH_2Cl_2. Yield: 22 mg (27%). ^{1}H NMR (CH_2Cl_2, 300 MHz) δ 8.1 (d, 2 H, J = 7.4 Hz, *o*-Ph), 7.61 (m, 2 H, *m*-Ph), 7.50 (m, 1 H, *p*-Ph), 7.24 (d, 1 H, J = 1.9 Hz, *H*C=CH near N–Ph), 7.18 (d, 1 H, J = 1.9 Hz, HC=C*H* near imine), 7.10 (m, 3 H, Ar), 5.40 (s, 2 H, C*H*$_2$), 2.74 (septet, 2 H, J = 6.8 Hz, C*H*Me$_2$), 1.66 (s, 3H, imine-*Me*), 1.17 and 1.14 (d, 6 H each, J = 6.8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz) δ 171.9 (N*C*N), 166.7 (*C*=N), 145.6 (*ipso*-Ar), 140.8 (*ipso*-Ph), 136.3

Table 5 X-Ray crystallographic data for **4b**, **4d** and **6b**

Compound	**4b**	**4d**	**6b**
Chemical formula	$C_{24}H_{29}N_3AgCl$	$C_{27}H_{35}N_3AgCl + CHCl_3$	$C_{48}H_{58}Cl_2N_6Pd$
M_r	502.83	544.96 + 119.37	869.30
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2/c$	$P\bar{1}$
Z	4	4	1
a/Å	8.2541(3)	14.8538(8)	8.7228(2)
b/Å	35.5587(12)	12.2478(7)	12.2967(3)
c/Å	8.9422(3)	17.8594(11)	13.4859(3)
α/°	90.00	90.00	117.058(1)
β/°	115.0840(10)	104.943(2)	95.306(1)
γ/°	90.00	90.00	96.593(1)
V/Å^3	2377.05(14)	3139.2(3)	1262.44(5)
D_c/g cm^{-3}	1.405	1.406	1.179
Crystal dimensions/mm	0.55 × 0.25 × 0.10	1 × 0.7 × 0.1	0.37 × 0.13 × 0.10
T/K	150(2)	105(2)	150(2)
Diffractometer	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD
Radiation (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
2θ Range/°	4.6–60.2	4.1–61.0	4.8–60.1
No. of data collected	20955	34116	21600
No. of unique data	6796	9401	7375
No. of obs. data ($I > 2\sigma(I)$)	6258	7650	7028
Agreement between equivalent data (R_{int})	0.0191	0.0680	0.0208
No. of parameters varied	319	333	264
μ/mm^{-1}	0.974	1.003	0.509
Absorption correction	Numerical (SHELXTL), Bruker AXS, 2003.[79]	Multi-scan (SADABS), Sheldrick, 1996[80]	Numerical (SHELXTL), Bruker AXS, 2003.[79]
$R1(F_0)$, $wR2(F_0^2)$ ($I > 2\sigma$)	0.0434, 0.0918	0.058, 0.1647	0.0239, 0.0631

(*o*-Ar), 129.4 (*m*-Ph), 128.6 (*p*-Ph), 126.4 (*o*-Ph), 124.1 (*p*-Ar), 123.3 (*m*-Ar), 122.8 (H*C*=CH, near N–Ph), 121.8 (HC=*C*H, near imine), 58.45 (*C*H$_2$), 28.36 (*C*HMe$_2$), 23.44 and 23.05 (CH*Me*$_2$), 19.08 (imine-*Me*). IR (nujol) $\nu_{C=N}$ 1657 cm^{-1}. Anal. Calc. for $C_{48}H_{58}Cl_2N_6Pd{\cdot}CH_2Cl_2$: C, 59.98; H, 6.16; Cl, 14.45; N, 8.56; Pd, 10.84. Found: C, 58.76; H, 6.11; Cl, 15.75; N, 7.78; Pd, 11.48%. HRMS (ES): *m*/*z* 859.3591 (M$^+$ − Cl) (calc. 859.34872).

[3-(2,4,6-Trimethylphenyl)-1-{2-(2,6-diisopropylphenylimino)-propyl}imidazolin-2-ylidene]$_2$PdCl$_2$ (6d). From **4d** (100 mg, 0.178 mmol) in 1 mL CH_2Cl_2 and (COD)PdCl$_2$ (53 mg, 0.18 mmol) in 5 mL CH_2Cl_2. Yield: 47 mg (43.7%). ^{1}H NMR (CH_2Cl_2, 200 MHz) showed two species in a 72 : 28 ratio. NMR data for major species: ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 7.23 (d, 1 H, J = 1.8 Hz, *H*C=CH near imine), 7.08 (m, 3 H, Ar), 6.97 (s, 2 H, *m*-Mes), 6.81 (d, 1 H, J = 1.8 Hz, HC=C*H* near N–Mes), 5.23 (s, 2 H, C*H*$_2$), 2.66 (septet, 2 H, J = 6.8 Hz, C*H*Me$_2$), 2.29 (s, 3 H, *p*-Me), 2.21 (s, 6 H, *m*-Me), 1.64 (s, 3 H, imine-*Me*), 1.12 and 1.09 (d, 6 H each, J = 6.8 Hz, CH*Me*$_2$).^{13}C{^{1}H} NMR (CD_2Cl_2, 50 MHz) δ 171.6 (N*C*N), 167.1 (*C*=N), 145.7 (*ipso*-Ar), 138.9 (*ipso*-Mes), 137.0 (*p*-Mes), 136.5 (*o*-Mes), 136.3 (*o*-Ar), 129.0 (*m*-Mes), 124.0 (*p*-Ar), 123.2 (*m*-Ar), 123.1 (H*C*=CH, near N–Ph), 122.2 (HC=*C*H, near imine), 57.62 (*C*H$_2$), 28.18 (*C*HMe$_2$), 23.58 and 23.14 (CH*Me*$_2$), 21.21 (*p*-Me), 19.32 (*o*-Me), 18.98 (imine-*Me*). NMR data for minor species: ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 7.21 (d, 1 H, J = 1.8 Hz, *H*C=CH near imine), 7.08 (m, 3 H, Ar), 6.91 (s, 2 H, *m*-Mes), 6.78 (d, 1 H, J = 1.8 Hz, HC=C*H* near N–Mes), 5.65 (s, 2 H, C*H*$_2$), 2.66 (septet, 2 H, J = 6.8 Hz, C*H*Me$_2$), 2.48 (s, 3 H, *p*-Me), 1.95 (s, 3 H, imine-*Me*), 1.90 (s, 6 H, *m*-Me), 1.12 and 1.09 (d, 6 H each, J = 6.8 Hz, CH*Me*$_2$). IR (CH_2Cl_2) $\nu_{C=N}$ 1683, 1662 cm^{-1}. HRMS (ES): *m*/*z* 943.4493 (M$^+$ − Cl) (calc. 943.44269). Anal. Calc. for $C_{54}H_{70}Cl_2N_6Pd$: C, 66.15; H, 7.20; Cl, 7.23; N, 8.57; Pd, 10.85. Found: C, 64.74; H, 7.06; Cl, 7.11; N, 8.11; Pd, 12.75%.

[3-(2,6-Diisopropylphenyl)-1-{2-(2,6-diisopropylphenylimino)-propyl}imidazolin-2-ylidene]$_2$PdCl$_2$ (6e). From **4e** (73 mg, 0.124 mmol) in 1 mL CH_2Cl_2 and (COD)PdCl$_2$ (36 mg, 0.12 mmol) in 5 mL CH_2Cl_2. Yield: 13 mg (16.6%). ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 7.40, 7.28 and 7.02 (8 H, overlapping imidazole-Ar, imine-Ar and *H*C=C*H*), 5.85 and 5.27 (s, 2 H, C*H*$_2$), 2.92 (septet, 2 H, J = 6.8 Hz, C*H*Me$_2$), 2.60 (septet, 2 H, J = 6.8 Hz, C*H*Me$_2$), 1.45 (s, 3 H, imine-*Me*), 1.31 and 0.96 (d, 6 H each, J = 6.8 Hz, CH*Me*$_2$), 1.11 and 1.08 (d, 6 H each, J = 6.8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 50 MHz) δ 147.8 (*ipso*-Ar at imidazole), 145.8 (*ipso*-Ar at imine), 136.5, 130.0, 125.0, 123.8, 123.2, 121.2 (Ar), 57.60 (*C*H$_2$), 28.66, 28.21, 26.59, 23.48, 23.00, 22.93, 19.62.

X-Ray crystal structure determination of 4b, 4d and 6b

Crystals of **4b** and **4d** were obtained by crystallization from chloroform–pentane, and **6b** was crystallized from a chloroform–dichloromethane–pentane mixture. Details of the data collection and refinement for all compounds are summarized in Table 5. The refinement of the structural model for **6b** does not include a heavily disordered solvent molecule(s), positioned around an inversion center; 0, $\frac{1}{2}$, $\frac{1}{2}$. The SQUEEZE procedure as implemented in PLATON[65,66] was applied to subtract the structure factor contribution from the solvent volume. This contribution was estimated to be around 52 electrons contained in a volume of about 220 Å^3. These numbers correspond quite well with *e.g.* a 50 : 50 mix disorder of chloroform/dichloromethane. The presence of a chlorine-containing solvent is suggested by the residual peaks in the difference Fourier map (max. 4.5 e$^-$Å^{-3}) of the parent intensity data.

CCDC reference numbers 261436–261438.

See http://www.rsc.org/suppdata/dt/b5/b501081k/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We gratefully acknowledge the support from Borealis AS and the Norwegian Research Council (stipends to M. F. and A. D.) and from the Department of Chemistry, University of Oslo (stipend to K. A. N.)

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