Synthesis and characterization of palladium(II) complexes with a novel chelating iminocarbene ligand †

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The reaction between 1-chloro-2-(2,6-diisopropylphenylimino)propane and *N*-methylimidazole yields 3-methyl-1-{2-(2,6-diisopropylphenylimino)propyl}imidazolium] chloride, (C–N)·HCl (**2**). A silver(I) iminocarbene complex formulated as $(C–N)_2Ag^+AgCl_2^-$ is formed in the reaction between **2** and Ag_2O. Carbene transfer to Pd occurs when **2** is treated with (COD)Pd(Cl)(X) to yield (C–N)Pd(Cl)(X) (**4a**, X = Cl; **4b**, X = CH_3). Chloride abstraction from **4a** and **4b** with $AgPF_6$ in MeCN yields $(C–N)Pd(NCMe)(X)^+PF_6^-$ (**5a** and **5b**). A second chloride abstraction can be done with **5a** to yield $(C–N)Pd(NCMe)_2^{2+}(PF_6^-)_2$ (**6**). An X-ray structure determination of **4a** verifies the chelating nature of the iminocarbene ligand system and shows that the molecule adopts a boat conformation with Pd and the CH_2 link between the carbene and the imine occupying the two apical positions. The species **4–6** have been subjected to extensive analysis by variable-temperature, EXSY, and NOESY NMR spectroscopy in various solvents. In the weakly coordinating solvent nitromethane, **4a** and **4b** exist as square planar species in which the iminocarbene acts as a C,N-chelating ligand. NMR experiments reveal a dynamic behavior of **4a** that involves a boat "flip". This process is fast even at −40 °C for **4b** but considerably slower for **4a**. In more coordinating solvents, evidence is seen for solvent-dependent equilibra that involve rapid interconversion between the chelating $\kappa^2(C,N)$ structures $(\kappa^2-(C–N))Pd(Cl)(X)$ and non-chelating $\kappa^1(C)$ iminocarbene structures $(\kappa^1-(C–N))Pd(Cl)(X)(Solvent)$. Complex **5a** exists as two interconverting species, possibly *cis/trans* isomers by interchange of the MeCN and Cl ligands, whereas no evidence for dynamic processes is seen for **5b** and **6**.

Introduction

Arduengo's discovery of stable heterocyclic carbenes of the imidazolin-2-ylidene type in 1991[1] led to a rapid adaption of such species as ligands in organometallic complexes. The interest in metal–heterocyclic carbene complexes has been fueled by the fact that such species, often thermally robust and easy to handle, act as very efficient catalysts or catalyst precursors for a range of processes.[2] Important applications include various Pd catalyzed reactions such as Heck and Suzuki couplings,[3] CO/ethene copolymerization,[4] hydrosilylation,[5] and alkene metathesis reactions.[6] The heterocyclic carbene moiety offers great possibilities for fine-tuning the ligand structure, and thereby catalytic properties, through the introduction of appropriate substituents at the nitrogen atoms or at the 5-membered ring carbon atoms.

Efficient catalytic performance requires that catalyst deactivation, if it occurs, must take place at a rate that is significantly slower than the rate of the catalytic cycle. Recently, Cavell and co-workers have reported that cationic metal–heterocyclic carbene complexes containing metal-bonded alkyl groups may undergo deactivation by reductive elimination to form alkyl-imidazolium cations.[7] It was suggested that catalyst deactivation by this route might be suppressed by increasing the steric bulk of the carbene ligand and by incorporation of the carbene ligand into a chelating ring structure. Such chelates have attracted considerable interest, in particular those that have an N-atom or another carbene C atom at the other terminus. The N-atom in N-terminated carbene chelates has been incorporated in the form of a pyridine nitrogen,[3c,d,8] one carbene-N being bonded directly[3c,8b,c,g–i] or *via* a CH_2 linkage[3d,8a,c–g,i–k] to the pyridine α carbon, or as an oxazoline nitrogen,[9] with the imine-C of the oxazoline ring being directly bonded to one carbene-N. Chelating bis(carbene) ligands, usually connected *via* a CH_2 link between two heterocycle N atoms, have also been extensively investigated.[10]

In this contribution, we present the synthesis and characterization of Pd(II) complexes that bear a novel chelating carbene ligand in which a sterically demanding imine group constitutes the second metal-bonded part of the chelate structure. The six-membered iminocarbene chelates have been spectroscopically characterized through variable-temperature 1D and 2D (EXSY and NOESY) NMR studies and, in one case, by a single-crystal X-ray diffraction structure determination.

Results and discussion

Ligand synthesis

Iminoimidazolium salts were targeted as precursors to the iminocarbene ligands. These species could conceivably be prepared by condensation of appropriate secondary amines and *N*-(2-oxoalkyl)imidazolium cations, or by reactions between α-chloroimines and monosubstituted imidazoles.[11] The latter procedure was chosen, because undesired decomposition reactions were observed during initial attempts with the condensation method. A procedure similar to the chosen one has been utilized by Cavell and coworkers in a recent report on the synthesis of a 3-methyl-1-(picolylimidazolium) chelating carbene precursor, by the reaction of picolyl chloride with methylimidazole.[3d] The method allows for the introduction of a variety of substituents on the imidazole ring and on the imine carbon and nitrogen atoms. In this contribution, all structures bear the 2,6-diisopropylphenyl group at the imine nitrogen.

The synthesis of the imidazolium precursor to the iminocarbene is shown in Scheme 1. The α-chloroimine **1** was readily prepared from (2,6-diisopropyl)phenylamine and chloroacetone in the presence of $TiCl_4$.[12]

With the 2,6-diisopropyl)phenyl group bonded to the imine nitrogen, these ligand systems should be sterically quite demanding. This will be evidenced in the discussion of the ^{1}H NMR spectra of the investigated systems. It is particularly

Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
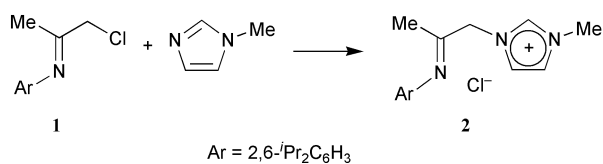
Scheme 1

noteworthy that the ^{1}H NMR spectrum of the imidazolium salt **2** exhibited two doublets at δ 1.00 and 1.10 that are attributed to the ^{i}Pr methyl groups at N–Ar, but only a single methine signal. Similarly, the ^{13}C{^{1}H} NMR spectrum displayed two ^{i}Pr methyl singlets but only one methine singlet. These observations suggest that rotation around the imine N–C(Ar) single bond is severely restricted. For steric reasons, the aryl ring is presumably oriented such that one ^{i}Pr group is preferentially located above the plane defined by the imine functional group and the other below this plane (Fig. 1). The two methyl groups within each ^{i}Pr substituent, denoted ^{a}Me and ^{b}Me in the figure, are then rendered diastereotopic by the hindered rotation. A similar behavior is observed for the ^{i}Pr substituents in the Ag and Pd complexes that will be described. Such splitting of the ^{1}H NMR signals from the ^{i}Pr groups is not observed for the α-chloroimine **1**. However, a small splitting of the corresponding ^{13}C NMR signal is observed.
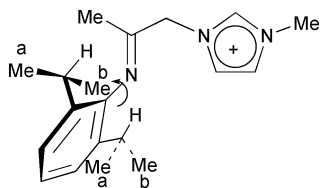

Fig. 1 Hindered rotation around the N–C(aryl) bond renders the ^{a}Me and ^{b}Me groups in the isopropyl substituents diastereotopic.

Substituted imidazolium salts are frequently used as precursors for *N*-heterocyclic carbene metal complexes. The most obvious route may be to deprotonate the imidazolium salt with a base to provide the free heterocyclic carbene which can be further reacted with appropriate metal complexes. Suitable bases that have been employed include NaH,[1a] KO^{t}Bu, NaH/KO^{t}Bu,[13] and NaH/NH$_3$(l).[14] It has been noted that the preparation of free carbenes is difficult or impossible to achieve by deprotonation when other acidic functional groups, such as enolizable protons, are present in the imidazolium salts.[3d,9c] Accordingly, intractable reaction mixtures resulted when **2** was treated with bases. This is presumably a consequence of the acidity of the imine α-protons. Direct reactions of imidazolium salts with suitable basic transition metal salts are also frequently used.[15] Thus, Pd(OAc)$_2$ has reportedly worked well with some imidazolium salts,[3a] but led to no success in our case.

Synthesis of a silver iminocarbene complex

In 1998, Wang and Lin[16] described a useful method whereby heterocyclic carbene ligands could be transferred from silver complexes to other transition metals. The silver(I) carbene complexes were conveniently prepared by treatment of imidazolium salts with Ag$_2$O.[17] The reaction was remarkably tolerant towards the presence of acidic functional groups. The reaction has subsequently been successfully adapted by Cavell[3d] in systems related to ours, and by others[8c,d,f,g,j,9c,19] for a wide range of systems.

Silver(I) heterocyclic carbene complexes exhibit a fascinating structural diversity,[17,19] including monomeric, dimeric, and polymeric solid-state structures. Some structural types that have been encountered are depicted in Fig. 2. Two structural classes stand out when the coordination mode of Ag is considered: (1) Cationic complexes with two carbenes attached to one
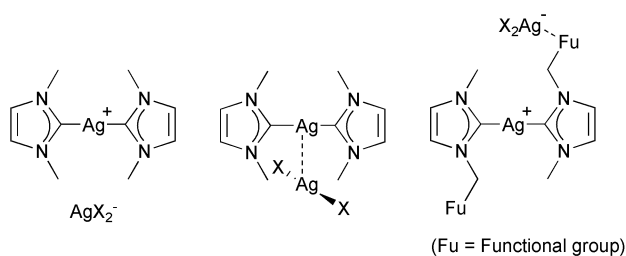
Fig. 2 Schematic presentation of reported solid-state structures of silver(I) carbene complexes. Adapted from ref. 19.

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. Evidently, it is often far from trivial to establish what structures exist in solution for these species.

Treatment of the imidazolium salt **2** with a slurry of Ag$_2$O in dichloromethane furnished the Ag(I) iminocarbene complex **3**, formulated as a "carbene$_2$Ag$^+$AgCl$_2^-$" structure in Scheme 2. The elemental analysis data for **3** are in agreement with a [Ag(carbene)Cl]$_n$ composition. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** show the presence of diastereotopic methyl groups within the ^{i}Pr substituents of the imine N-aryl group. The IR (CH$_2$Cl$_2$) spectrum of **3** shows two $\nu_{C=N}$ absorptions at 1685 and 1665 cm^{-1}. The higher-energy absorption is essentially unchanged compared to that seen for the corresponding imidazolium chloride **2**. This suggests that the iminocarbene is bonded in a monodentate fashion to Ag through the carbene carbon, rendering the imine group free. Similarly, Ag(3-methyl-1-phenacylimidazolin-2-ylidene)$_2^+$ and Ag(3-methyl-1-methyl-acetylimidazolin-2-ylidene)$_2^+$, both of which contain ligands with non-complexed carbonyl groups, displayed $\nu_{C=O}$ absorptions almost coinciding with those of the imidazolium precursors.[3d]


Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

Scheme 2
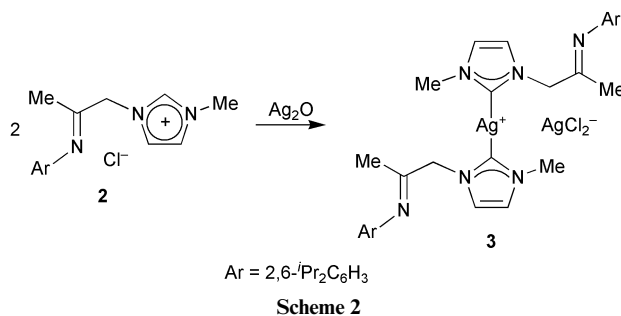
NMR, IR and elemental analysis data cannot unambiguously establish the structure of **3** in solution. Electrospray mass spectrometry analysis gave clear indications of a Ag-(carbene)$_2^+$ species with AgCl$_2^-$ as the counter-anion. The related complexes that were prepared by Cavell and co-workers were presumed to have analogous structures.[3d] Attempts at obtaining crystals of sufficient quality for an X-ray crystal structure determination have not been successful.

Preparation of neutral Pd iminocarbene complexes

The silver complex **3** smoothly transferred the carbene ligand to Pd when it was reacted with (COD)PdClX (X = Cl, Me; COD = 1,5-cyclooctadiene) in cold dichloromethane to give the corresponding (N,C-chelating iminocarbene)PdClX complexes (**4a**,

X = Cl; **4b**, X = Me) (Scheme 3). The dichloro complex **4a** was soluble only in polar organic solvents (nitromethane, DMSO, acetonitrile) and was thermally stable in solution at elevated temperatures. The chloromethyl complex **4b** was soluble also in less polar solvents (THF, dichloromethane), but was thermally unstable and underwent partial decomposition during 1 h at ambient temperature in solution.
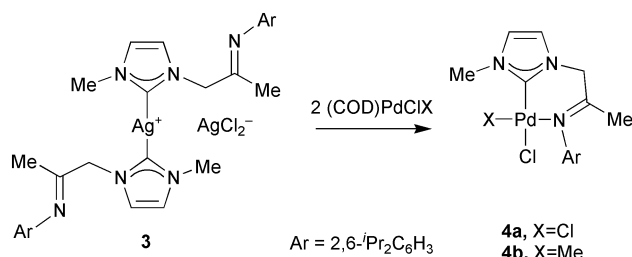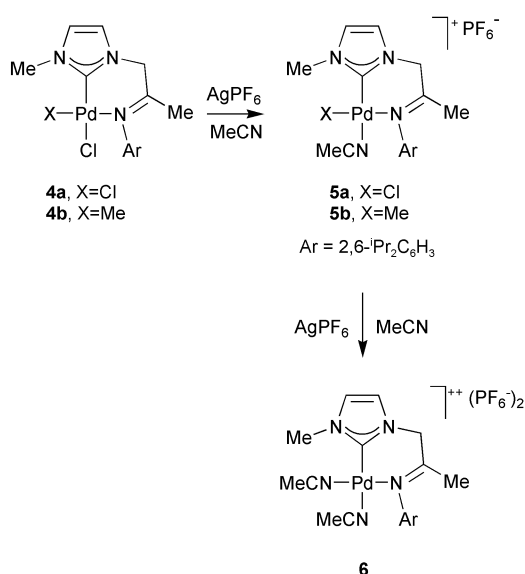
Scheme 3

The new complexes **4a** and **4b** were characterized by ^{1}H and ^{13}C{^{1}H} spectroscopy. Both species exhibits highly solvent- and temperature dependent spectra (*vide infra*). The X-ray crystal structure of **4a** verifies the chelating nature of the ligand (see next paragraph). The imine IR $v_{C\equiv N}$ absorptions for **4a** and **4b** were seen at 1637 and 1644 cm^{-1} (nujol), respectively. These values are shifted considerably towards lower wavenumbers than in **3**, suggesting a chelating ligand in **4** but not in **3**. Formation of Pd iminophosphine,[20] bis(oxazolinyl)pyrrolide,[21] and oxazolinyl–heterocyclic carbene chelate complexes[9c] has also resulted in a shift of $v_{C\equiv N}$ in the same direction. Electrospray mass spectrometry of **4a** gave an ion corresponding to M$^+$–Cl, and elemental analyses for **4a** and **4b** are in agreement with the proposed composition.

Preparation of cationic and dicationic Pd iminocarbene complexes

Abstraction of a chloride ligand in **4a** and **4b** with AgPF$_6$ in acetonitrile provides PF$_6^-$ salts of the cationic complexes **5a** and **5b**, respectively (Scheme 4). Both complexes have been characterized by elemental analysis, mass spectrometry, IR and NMR spectroscopy. Analogous halide abstraction reactions have been performed with chelating[3d,8a] and non-chelating[4,22] Pd carbene complexes.

Scheme 4

The cationic complexes **5a** and **5b** are considerably more stable, thermally and towards air, than their precursors **4a** and **4b**. In solution, the ^{1}H NMR spectra indicate (*vide infra*) that

Table 1 Selected distances and angles of **4a**

	Dist./Å		Angle/°
Pd(1)–(C19)	1.956(6)	C(19)–Pd(1)–N(1)	85.4(2)
Pd(1)–N(1)	2.077(4)	N(1)–Pd(1)–Cl(1)	93.45(13)
Pd(1)–Cl(2)	2.295(15)	Cl(2)–Pd(1)–Cl(1)	90.63(6)
Pd(1)–Cl(1)	2.366(15)	C(19)–Pd(1)–Cl(2)	90.67(14)
C(13)–C(14)	1.498(8)	N(1)–C(14)–C(13)	126.0(5)
C(14)–C(15)	1.520(8)	N(1)–C(14)–C(15)	117.6(5)
C(16)–C(17)	1.343(10)	C(13)–C(14)–C(15)	116.2(5)
N(1)–C(14)	1.279(7)	N(2)–C(15)–C(14)	108.7(5)
N(1)–C(1)	1.461(7)	C(17)–C(16)–N(2)	105.3(6)
N(2)–C(19)	1.352(7)	C(16)–C(17)–N(3)	108.7(6)
N(2)–C(16)	1.386(8)	N(2)–C(19)–Pd(1)	120.8(4)
N(2)–C(15)	1.452(7)	N(3)–C(19)–Pd(1)	133.5(4)
N(3)–C(19)	1.358(8)	C(14)–N(1)–C(1)	119.4(5)
N(3)–C(17)	1.387(9)	C(14)–N(1)–Pd(1)	122.3(4)
N(3)–C(18)	1.458(8)	C(1)–N(1)–Pd(1)	117.6(3)
		C(19)–Pd(1)–Cl(1)	176.72(17)
		N(1)–Pd(1)–Cl(2)	174.97(14)
		N(2)–C(19)–N(3)	105.2(5)

only κ^2 chelating species are present. This contrasts the behavior of **4a** and **4b**. The cationic charge that is introduced at Pd inhibits ligand dissociation in general and dissociation of the Pt–N(imine) bond in particular.

The remaining chloride ligand in **5a** can also be removed with AgPF$_6$ in acetonitrile (Scheme 4). The new dicationic complex **6** was characterized by elemental analysis, IR and NMR spectroscopy. The $v_{C\equiv N}$ band was found at 1639 cm^{-1}, indicating the presence of a chelating κ^2 iminocarbene structure in solution. This was supported by the ^{1}H NMR data (*vide infra*).

X-Ray crystal structure determination of 4a

Crystals that were suitable for an X-ray diffraction structure determination were found after workup of **4a** by crystallization from a concentrated dichloromethane solution. Selected bond distances and angles are shown in Table 1, and an ORTEP plot of the structure of **4a** is shown in Fig. 3. The crystal structure verifies that the compound is monomeric and contains a C,N-chelating iminocarbene ligand that spans two *cis* coordination sites of Pd. The 6-membered chelate ring assumes a boat conformation in which the Pd and CH$_2$ groups occupy the apical positions. The remaining two coordination sites of the square planar Pd(II) center (the sum of L–Pd–L′ angles is 360.2°) are occupied by the chloride ligands. Deviations from the ideal 90° for the *cis* L–Pd–L′ angles are rather small. The iminocarbene bite angle C(19)–Pd(1)–N(1) is somewhat compressed at 85.41° and the adjacent Cl(1)–Pd(1)–N(1) angle is opened to 93.45°, while C(19)–Pd–Cl(2) and Cl(1)–Pd(1)–Cl(2) deviate from 90°
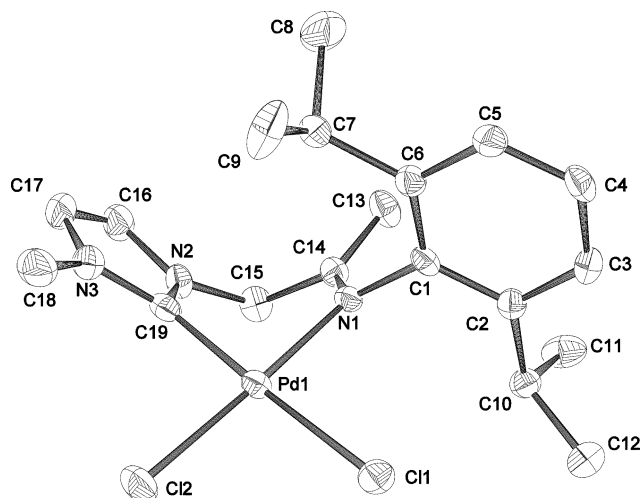
Fig. 3 ORTEP drawing of **4a**. Hydrogen atoms and the dichloromethane molecule of crystallization are omitted for clarity.

by less than 1°. The imidazolin-2-ylidene ring system is twisted relative to the coordination plane of Pd by 41.4° (as measured by the N(1)–Pd(1)–C(19)–N(2) torsional angle). It has been previously noted that the imidazolin-2-ylidene ring system often attains a nearly perpendicular orientation relative to the coordination plane in sterically encumbered non-chelating carbene complexes,[8a,d,g,9a,18,23] and that sterically demanding substituents may restrict the rotation around the metal–C(carbene) bond.[18] For chelating carbene species including CH$_2$-linked bis(carbene),[3b,10b,c,e,g,23d] oxazolyl–carbene[9a] and picolyl–carbene[3c,8c,e,f,g,k] complexes, boat conformations resembling that of **4a** are observed. The two isopropyl substituents of the N-aryl group are located one above and one below the 6-membered chelate "boat", *i.e.* the aryl ring is oriented more or less perpendicularly with respect to the chelate ring, as anticipated.

Metal–ligand bond distances in **4a** are rather unexceptional. The Pd–C, Pd–Cl, and Pd–N bond distances are within the range observed in crystallographically characterized Pd–heterocyclic carbene complexes.[8d,g,9c,21,23,10e,24] The Pd–C-(carbene) distance Pd(1)–C(12) is 1.956 Å, with a *trans* Pd–Cl distance Pd(1)–Cl(1) of 2.366 Å. The Pd–N(imine) bond distance Pd(1)–N(1) is 2.077 Å, and the corresponding *trans* Pd–Cl bond length Pd(1)–Cl(2) is 2.295 Å. Gade and co-workers[9c] characterized a (carbene–oxazoline)PdCl$_2$ 5-ring chelate complex and reported a Pd–C(carbene) distance of 2.01 Å with a *trans* Pd–Cl distance of 2.325 Å, and a Pd–N(imine) bond length of 2.064 Å with a *trans* Pd–Cl distance of 2.274 Å, which is very close to the parameters observed in **4a**. Comparable Pd–N(imine) and *trans* Pd–Cl distances were reported as 2.014 and 2.279 Å, respectively, in a Pd diisopropylphenyl imine complex studied by Howie and coworkers.[25] The distance from Pd to the Cl *trans* to the carbene is substantially longer than the distance from Pd to the Cl *trans* to the imine in **4a**, underscoring the considerably stronger *trans* influence from the carbene ligand than from the imine.[9c] Herrmann and coworkers similarly concluded, on the basis of crystal structure data, that the carbene ligand is a stronger donor than the imine in a 6-ring carbene–oxazoline chelated Rh complex.[9a]

NMR Characterization of 4a

The ¹H NMR spectrum of **4a** was relatively uncomplicated when recorded in nitromethane-d_3 at ambient temperature. The spectrum exhibits sharp and well-defined signals in the expected chemical shift regions. The signals of the isopropyl groups at N-aryl appear as two doublets at δ 0.96 at 1.50 and a septet at δ 2.83. The separation of the two methyl doublets is rather large (0.54 ppm) compared to that for the two precursors **2** and **3** (*ca.* 0.1 ppm) in which N(imine) is not bonded to a metal. The greater separation of the two isopropyl methyl doublets appears to be a reliable indicator for a metal-bonded N(imine) in these systems, a distinction that is further supported by the always accompanying lowering of the IR $\nu_{C=N}$ absorption frequency upon complexation. The imidazole–methyl and imine–methyl appear as singlets at δ 4.07 and 2.17, respectively; the CH$_2$ bridge between the imidazole ring and the imine appears as a singlet at δ 5.32. As already discussed, the X-ray structure of **4a** shows that the 6-membered chelate ring assumes a boat-like conformation. This renders the two methylene protons inequivalent. The observed ¹H NMR singlet then suggests that the boat conformation can undergo a "ring flip" that interconverts the two protons, a process that must be quite facile on the NMR time scale at ambient temperature. Analogous ring flip processes have been invoked for other 6-membered chelates involving Pd and chelating carbenes.[3d,4,8c–e,k,10b–d,g]

A gradual lowering of the temperature caused each of the two isopropyl methyl doublets to broaden (0 and −20 °C) and eventually to decoalesce (−40 °C)[26] into four signals. A further lowering of the temperature (which presumably would reveal

each signal to be a doublet) was not possible with the nitro-methane-d_3 solvent. The lowering of the temperature also caused the methylene signal to undergo a gradual broadening, and at −40 °C it emerged as two broadened doublets at δ 5.17 and 5.47 with a mutual geminal coupling constants of 14 Hz (Fig. 4). Heating to ambient temperature restored the original spectrum. The spectroscopic behavior is consistent with a slowing of the "ring flip" of the 6-membered chelate boat conformation at lower temperatures. The low-temperature frozen structure, presumably with the same conformation as the solid-state structure (Fig. 3) will have two diastereotopic methylene hydrogens as well as four diastereotopic ^{i}Pr methyl groups.
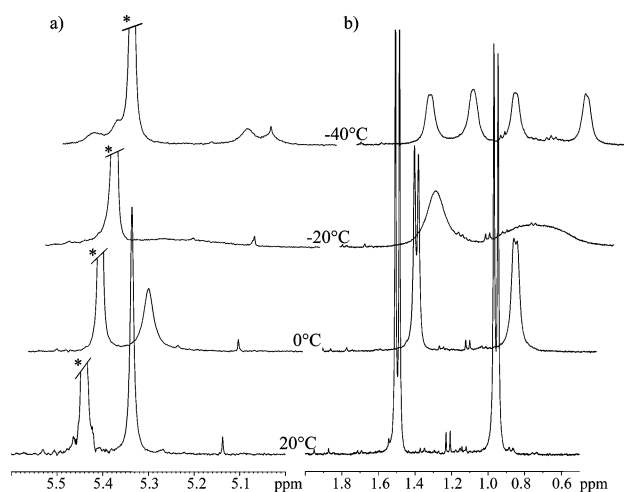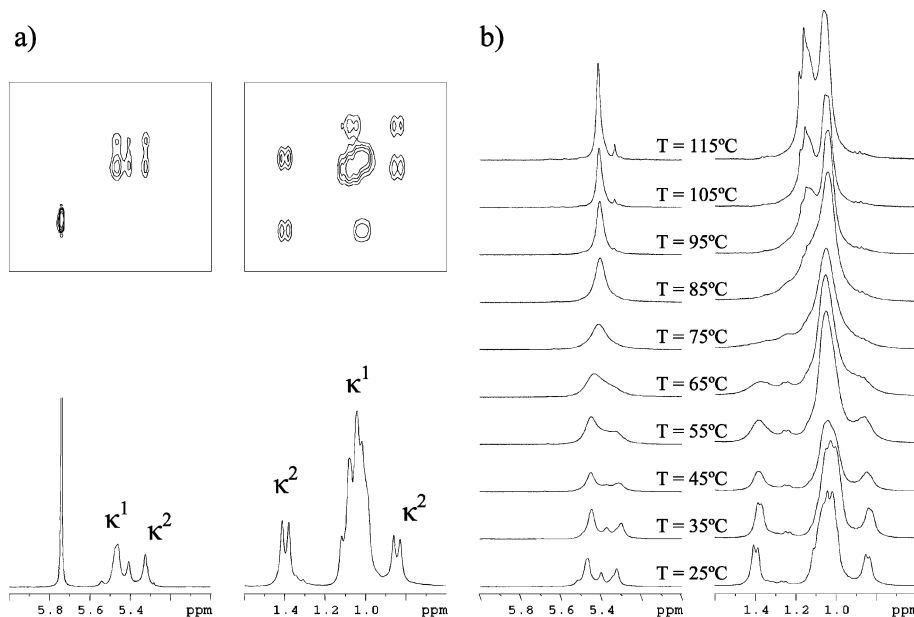

Fig. 4 Variable-temperature ¹H NMR spectra of **4a** in CD$_3$NO$_2$.[26] (a) Methylene signal, split into two mutually coupled doublets at −40 °C. (b) Isopropyl methyl resonances, split into four signals at −40 °C. *=residual solvent protons.

The NMR characterization of **4a** was less straightforward when the analysis was done in solvents that are better donors than nitromethane. In DMSO-d_6, *two* sets of signals are seen for all groups, in an approximate 1 : 2 ratio. The signals in the minor set match the spectrum obtained in nitromethane-d_3 quite well, and exhibit the same relatively large separation (0.65 ppm) of the two signals of the diastereotopic isopropyl methyl groups. We assume that these signals arise from the same 6-membered ring chelate as seen in nitromethane-d_3. The major species is significantly different by ¹H NMR (see Experimental for full details), in particular because the separation between the two partially overlapping diastereotopic isopropyl methyl doublets is diminished to *ca.* 0.01 ppm. This suggests that the major species has a non-chelating (κ¹) iminocarbene ligand. The relative amounts of the two species was independent of the concentration of **4a** (this rules out the involvement of species in which a Cl⁻ ligand has dissociated, or of dimeric species). Therefore, the data suggest that the equilibrium in Scheme 5 is established in solution. In support of this, it was seen that gradual addition of increasing quantities of DMSO-d_6 to a nitromethane-d_3 solution of **4a** led to increasing amounts of the putative non-chelated species.
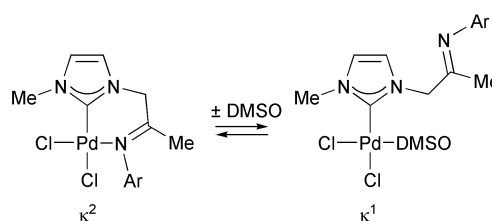
Scheme 5

Fig. 5 (a) 2D EXSY spectra of **4a** and the corresponding normal 1D spectrum in DMSO-d_6 at 25 °C. (b) Variable temperature ^{1}H NMR spectra of **4a** in DMSO-d_6. The spectra show the bridge methylene region (left) and isopropyl methyl (right).

Further evidence for the equilibrium between the κ^2 and κ^1 species was obtained from ^{1}H NMR spectra obtained in DMSO-d_6 at higher temperatures. The two sets of signals undergo coalescence at *ca.* 75–85 °C, and at 115 °C (Fig. 5), only one set of signals is seen. Complex **4a** is stable in DMSO-d_6 solution at least up to 120 °C, since the original spectrum is recovered when the temperature is lowered again.

The exchange process was directly observed in a 2D EXSY ^{1}H NMR experiment. The EXSY inserts at the top of Fig. 5a clearly show cross correlations between the methylene signals of the κ^2 and κ^1 species, and between the isopropyl methyl signals of the κ^2 and κ^1 species.

Crabtree, Eisenstein and coworkers recently reported an investigation of conformer interconversions in neutral CCC and cationic CNC pincer bis(carbene) complexes.[8k] The interconversions may be described as "double boat-flip" processes occurring at two adjacent 6-membered chelate rings. Dynamic NMR studies supported by DFT calculations suggested that two mechanisms may operate: An inner-sphere (unassisted) process that essentially involves the stepwise rearrangement of one ring at a time, and an outer-sphere mechanism that involves nucleophilic assistance by counteranions in the cationic CNC complexes. The latter process was proposed to occur by an unusual anion-induced decoordination of the N atom of the central pyridine ring. Significantly, the interconversion rates were independent of the solvent (CDCl$_3$ *vs.* DMSO-d_6). Apparently, and contrasting the behavior of **4a**, pyridine-N ligand displacement by DMSO does not take place in the pincer systems.

Complex **4a** qualitatively exhibited a similar behavior in acetonitrile-d_3 as that seen in DMSO-d_6. The κ^2 and κ^1 species were in this case observed in a *ca.* 2 : 1 ratio as opposed to *ca.* 1 : 2 for DMSO-d_6, presumably reflecting the better coordination capability of DMSO when compared to acetonitrile. The complex was insufficiently soluble to be investigated in THF or dichloromethane.

NMR Characterization of 4b

The structure of **4b** is assumed to be similar to **4a**, although X-ray quality crystals have not been obtained. The Pd–methyl group is assumed to be located *trans* to N(imine) in the chelate (Scheme 3) on the basis of an observed correlation signal between the Pd–methyl and imidazole–methyl moieties in a 2D NOESY ^{1}H NMR spectrum. This coordination geometry is analogous to observations by Tulloch *et al.*[8a,g] who reported a bidentate pyridylcarbene complex in which the Pd–methyl is *trans* to N(pyridine). Green and co-workers have reported a similar bidentate iminophosphine complex with the methyl *trans* to the imine.[20c] Compound **4b** was also subjected to a ^{1}H NMR spectroscopic investigation in various solvents. The spectroscopic observations were considerably more complex than for **4a**, suggesting the involvement of other dynamic processes in addition to the ring flip seen for **4a**. In short, evidence for the coexistence of the κ^2 and κ^1 solvento species were seen also in this case. In nitromethane-d_3, only the κ^2 species is seen; in acetonitrile-d_3, a 1 : 2 ratio of κ^1 and κ^2 species; and in THF-d_8 and DMSO-d_6, only the κ^1 species. The observations made for nitromethane-d_3, THF-d_8, and mixtures of the two will be described in detail in the following.

The ^{1}H NMR spectrum of **4b** is least complicated in nitromethane-d_3, and only one set of signals is observed. The spectrum is similar to that of **4a** but with the additional Pd–methyl signal at δ 0.56. The separation of the two isopropyl methyl doublets is rather large, 0.40 ppm, suggesting a chelating structure. The presence of only one methylene signal for the carbene–imine link, and only one ^{i}Pr methyl signal, again is indicative of a rapid "flip" of the chelate boat conformation. No splitting of the isopropyl methyl or bridge methylene signals is observed at temperatures down to the freezing point of the nitromethane solution.[26] Thus, the "boat flip" appears to be considerably faster for **4b** than it is for **4a**.

Addition of THF-d_8 to a nitromethane-d_3 solution of **4b** caused the appearance of a new set of signals in addition to the ones arising from the κ^2 structure that is observed in neat nitromethane-d_3. The relative intensities of the new signals increase with increasing concentrations of THF-d_8 until in neat THF-d_8, only the new signals are discernible. These signals are rather complex (further evidenced from low-temperature spectra, *vide infra*) and somewhat broadened at ambient temperature. However, it is possible to extract some useful information from the spectrum. The two isopropyl methyl signals have a rather small separation (0.2 ppm) which, together with the relatively high-energy $\nu_{C=N}$ absorptions at 1680 and 1662 cm^{-1} (THF) in the IR spectrum, indicates the presence of a κ^1 iminocarbene with a non-coordinating imine. Importantly, the two species that are seen simultaneously in nitromethane-d_3/THF-d_8 mixtures are dynamically related. Cross correlation peaks are seen between the two sets of signals in a 2D EXSY ^{1}H NMR spectrum. The spectra suggest the occurrence of a solvent-

dependent dynamic equilibrium between a κ^2 structure (the only one seen in nitromethane) and a κ^1 structure with a coordinated THF molecule as indicated in the upper left part of Scheme 6.


Scheme 6
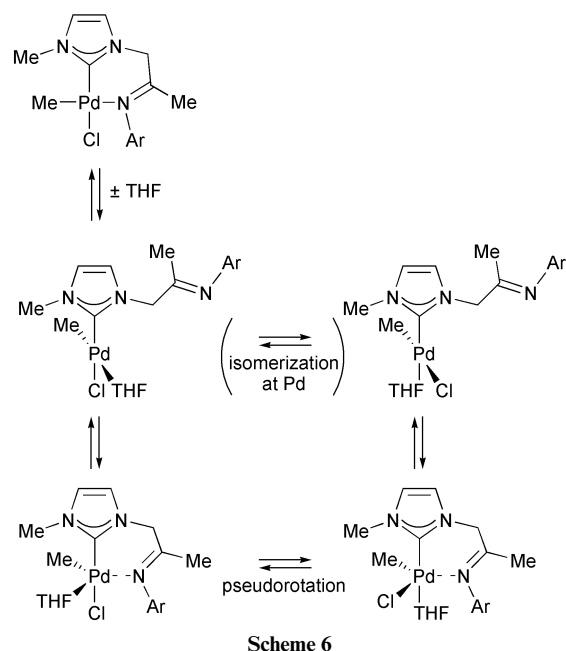
Surprisingly, the low-temperature ($-60\ ^\circ$C) ^{1}H NMR spectrum of **4b** in THF-d_8 reveals the presence of *four* different species in a *ca.* 1 : 1 : 1 : 1 ratio, by the presence of four well-resolved Pd–methyl signals, four N-methyl signals, and four imine–methyl signals. This added complexity of the spectra of **4b** in THF-d_8 remains somewhat puzzling. These species may represent isomers through differences in coordination geometry at Pd, conformers through processes of hindered rotation, or the presence of pentacoordinate species. Significantly, all species have the characteristics of a κ^1 coordination mode of the iminocarbene as inferred from the observed small separation between the diastereotopic ^{i}Pr methyl signals. The CH$_2$ group of the complex gives rise to a complex set of multiplets counting at least 13 peaks. This is consistent with the expectations if each of the four species have diastereotopic methylene protons: each CH$_2$ group will give rise to two mutually coupled doublets, resulting in an expected 16-line pattern overall. A carbene ring structure that is more or less perpendicularly oriented with respect to the square planar Pd(II) center will have diastereotopic CH$_2$ protons if four different ligands are bonded to Pd and at the same time rotation around the Pd–C(carbene) bond is restricted. Under these circumstances, the CH$_2$ protons will remain diastereotopic also in the event that the imine-N is *not* coordinated to the Pd center.

A *cis/trans* isomerism involving the relative positions of the carbene and methyl groups is unlikely, since this should bring about significant changes in the chemical shifts of the Pd–methyl groups. Puddephatt and Prokopchuk reported a chemical shift difference of 0.45 ppm for methyl groups that were *cis* and *trans* with respect to the carbene ligand in a dimethyl platinum carbene complex.[27] In comparison, chemical shift differences for the isomers of **4b** amount to less than 0.03 ppm at $-60\ ^\circ$C. On the other hand, isomerism through interchange of the positions of the chloride and the solvent (THF) ligand might perturb the chemical shifts of the methyl group to a lesser extent. A *cis/trans* isomerization may proceed by an associative mechanism involving an additional solvent molecule or the non-coordinated imine nitrogen. An interaction between imine-N and Pd, yielding possible 5-coordinate intermediates in an imine-assisted isomerization, might even rationalize the presence of multiple isomeric species (Scheme 6).

NMR Characterization of 5a, 5b and 6

The ^{1}H NMR spectrum of the cationic chloro complex **5a** in nitromethane-d_3 exhibits distinct signals that are broadened to a varying extent. In particular, the resonance from the imidazole–methyl group has decoalesced to appear as two broad peaks in an approximate 1 : 1 ratio at ambient temperature. The two species that give rise to the two signals undergo an exchange process, as demonstrated by the 2D EXSY ^{1}H NMR spectrum. Low-temperature NMR spectra also provides evidence for the presence of two interconverting structures, as the whole ^{1}H NMR spectrum decoalesces in to two sets of signals at 0 $^\circ$C. The relative ratio of the two observed species is *ca.* 5 : 2 at $-10\ ^\circ$C. Both species appear to have the chelating κ^2 coordination mode of the iminocarbene, as the separation of the diastereotopic isopropyl methyl signal is quite large for both species (0.51 ppm for major and 0.43 for minor). One possible explanation for this phenomenon is an interchange of the chloride and acetonitrile ligands (Scheme 7), which might have a great influence on the spatially nearby imidazole–methyl resonance.

Scheme 7
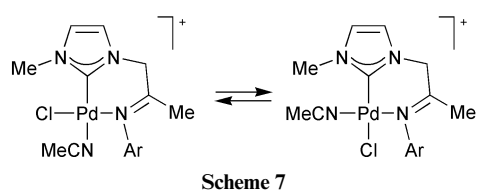
In contrast, the ^{1}H NMR spectrum of the cationic methyl complex **5b** is simple and unambiguously interpreted in nitromethane-d_3. Variable-temperature spectra show no indication of dynamic processes and exhibit well-defined, sharp signals even at temperatures as low as $-40\ ^\circ$C. The separation of the diastereotopic ^{i}Pr methyl resonances is rather large (0.31 ppm), indicative of a κ^2 iminocarbene coordination mode. The Pd–methyl group is assumed to be *trans* to the imine, as was the case for its precursor **4b**. This is supported by a correlation signal in the 2D NOESY ^{1}H NMR spectrum, which indicates a close spatial relationship between Pd–methyl and imidazole–methyl.

Finally, the ^{1}H NMR spectrum of **6** in nitromethane-d_3 displays sharp signals that agree with the κ^2 coordination mode of the iminocarbene ligand. The separation of the signals arising from the diastereotopic ^{i}Pr methyl groups is quite large, at 0.41 ppm. There were no indications of dynamic behavior through line-broadening or decoalescence phenomena even at temperatures down to $-40\ ^\circ$C (nitromethane-d_3).[26]

Conclusion

The first members of a class of complexes bearing the novel iminocarbene ligand system have been prepared and characterized. The Pd complexes have the tendency to exhibit rather complex, solvent-dependent structural changes in solution as a result of changes in conformation, metal coordination geometry, and ligand hapticity. These effects must be taken into account when such ligand systems are employed in catalysis. We hope to address these issues in a future contribution.

Experimental

General procedures

All reactions involving organometallic compounds were carried out with the use of dry box, vacuum line, syringe and Schlenk techniques if not otherwise noted. Solvents for reactions and NMR were dried according to standard procedures. NMR spectra were recorded on a Bruker Avance DPX 200 and 300 instruments with QNP probes. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standards. MS measure-

ments were preformed on a Micromass QTOF II spectrometer. IR spectra recorded on a Nicolet Magna-IR 550 FT-IR spectrophotometer. Elemental analysis were preformed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany. The iminocarbene ligand will for brevity be denoted as "C–N" in this section.

Glyoxal (Fluka, 8.8 M in H_2O), 2,6-diisopropylaniline (Fluka), chloroacetone (Fluka), 1-methylimidazole (Acros), Ag_2O (Alfa Aesar), $AgPF_6$ (Fluka) and anhydrous $PdCl_2$ (Acros) were used as received from commercial suppliers. (COD)$PdCl_2$ and (COD)PdClMe were prepared according to published procedures.[28]

1-Chloro-2-(2,6-diisopropylphenylimino)propane (1)

The compound was prepared by analogy with the method described by de Kimpe et al.[12] Chloroacetone (9.5 g, 0.103 mol) and 2,6-diisopropylaniline (18.8 g, 0.106 mol) were dissolved in dichloromethane (200 mL). The contents were cooled to 0 °C on an ice bath. A 1.0 M dichloromethane solution of $TiCl_4$ (20 mL, 0.02 mol) was slowly added to the contents with a syringe while the mixture was vigorously stirred. The mixture was stirred for 1 h at 0 °C and then for 3 h at ambient temperature. A 1.0 M NaOH solution (100 mL) was added to the mixture and stirring was continued for 10 min. The aqueous phase was separated and the dichloromethane solution was dried with K_2CO_3. The solvent was evaporated, and the product was purified by careful removal of the unreacted aniline by vacuum distillation (10^{-3} mbar, 45 °C). 7.5 g 2,6-diisopropyl aniline was recovered from the product mixture. The product was collected by sublimation (10^{-3} mbar, 48 °C) and was pure as judged by ^{1}H NMR. Yield: 5.0 g (18%). ^{1}H NMR (CDCl$_3$, 200 MHz, 25 °C) δ 7.09 (m, 3H, aryl-H), 4.27 (s, 2H, CH_2), 2.69 (septet, J = 6.9 Hz, 2H, CHMe$_2$), 1.81 (s, 3H, MeC=N–), 1.12 (d, J = 6.9 Hz, 12H, CHMe_2). ^{13}C{^{1}H} NMR (CDCl$_3$, 50 MHz, 25 °C) δ 166.2 (C=N–C), 144.7 (aryl-C_{ipso}), 136.1 (aryl-C_o), 124.0 (aryl-C_p), 123.0 (aryl-C_m), 49.14 (CH$_2$Cl, 27.85 (CHMe$_2$), 23.26 and 23.00 (C(CH$_3$)$_2$), 17.90 (CH$_3$C=N). IR (CH$_2$Cl$_2$) $\nu_{C=N}$ 1682 and 1660 cm^{-1}. MS(EI): m/z 251.2 (M$^{+\bullet}$, 23%), 202.2 (M$^+$–CH$_2$Cl, 100%). HRMS (EI): m/z 251.14535 (calcd 251.14408). Anal. Calcd. for C$_{15}$H$_{22}$ClN: C, 71.55; H, 8.81; Cl, 14.08; N, 5.56. Found: C, 71.47; H, 8.75; Cl, 14.07; N, 5.47%.

(C–N)·HCl = [3-methyl-1-{2-(2,6-diisopropylphenylimino)-propyl}imidazolium] chloride (2)

1-Methylimidazole (2.0 g, 24.4 mmol) and α-chloroimine 1 (3.0 g, 11.9 mmol) were heated at reflux in THF (100 mL) for 5 h. The mixture was concentrated to 20 mL by rotary evaporation and cooled in a refrigerator overnight. The precipitated white powdery product was filtered, washed with ether, and recrystallized from dichloromethane/ether. Yield: 2.5 g (63%). ^{1}H NMR (CDCl$_3$, 200 MHz, 25 °C) δ 10.46 (s, 1H, NCHN), 7.43 (s, 1H, HCCH), 7.42 (s, 1H, HCCH), 7.02 (m, 3H, aryl-H), 5.58 (s, 2H, CH_2), 4.02 (s, 3H, NCH_3), 2.45 (septet, J = 6.8 Hz, 2H, CHMe$_2$), 1.79 (s, 3H, MeC=N), 1.10 (d, J = 6.8 Hz, 6H, C(CH_3)$_2$), 1.00 (d, J = 6.8 Hz, 6H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 50 MHz, 25 °C) δ 163.3 (C=N), 144.0 (aryl-C_{ipso}), 138.7 (NCHN), 135.6 (aryl-C_o), 124.0 (aryl-C_p), 123.5 (NCCN), 122.9 (aryl-C_m), 122.5 (NCCN), 55.10 (CH$_2$), 36.45 (NCH$_3$), 27.97 (CHMe$_2$), 22.95 (C(CH$_3$)$_2$), 22.47 (C(CH$_3$)$_2$), 18.74 (CH$_3$C=N). IR (ATR, solid and CH$_2$Cl$_2$) $\nu_{C=N}$ 1682 cm^{-1}. HRMS (ES): m/z 298.2094 (M$^+$–Cl) (calcd 298.22832). Anal. Calcd. for C$_{19}$H$_{28}$ClN$_3$: C, 68.35; H, 8.45; Cl, 10.62; N, 12.58. Found: C, 66.33; H, 8.32; Cl, 10.57; N, 12.61%.

[Ag(C–N)$_2$][AgCl$_2$] (3)

The imidazolium chloride 2 (772 mg, 2.3 mmol) was dissolved in dichloromethane (20 mL), and a slurry of Ag_2O (270 mg,

1.16 mmol) in dichloromethane (3 mL) was added. The mixture was stirred for 30 min at ambient temperature before excess Ag_2O was removed by filtration through celite. The solvent was removed in vacuo and the product was washed with pentane, dried under vacuum, and recrystallized from dichloromethane/pentane. Yellowish powder, yield: 746 mg (73%). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 25 °C) δ 7.08 (m, 6H, aryl-H), 6.34 (s, 2H, HC=CH), 5.90 (s, 2H, HC=CH), 4.61 (s, 4H, CH_2), 2.88 (s, 6H, NMe), 2.76 (septet, J = 6.8 Hz, 4H, CHMe$_2$), 1.43 (s, 6H, MeC=N), 1.24 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$) 1.15 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz) δ 183.8 (NCN), 165.4 (C=N), 145.8 (aryl-C_{ipso}), 136.0 (aryl-C_o), 124.1 (aryl-C_p), 123.3 (aryl-C_m), 121.8 (HC=CH), 121.1 (HC=CH), 57.68 (CH$_2$), 37.79 (NCH$_3$), 28.52 (CHMe$_2$), 23.47 (C(CH$_3$)$_2$), 23.0 (C(CH$_3$)$_2$), 18.39 (CH$_3$C=N). IR (CH$_2$Cl$_2$) $\nu_{C=N}$ 1682, 1663 cm^{-1}. MS-ES: m/z 701 (M$^+$–AgCl$_2$). Anal. Calcd. for C$_{38}$H$_{54}$Ag$_2$Cl$_2$N$_6$: C, 51.78; H, 6.17; Cl, 8.04; N, 9.53. Found: C, 51.40; H, 6.22; Cl, 6.95; N, 9.13%.

(C–N)PdCl$_2$ (4a)

A solution of (COD)$PdCl_2$ (238 mg, 0.92 mmol) in dichloromethane (10 mL) was cooled to −35 °C before the addition of a solution 3 (404 mg, 0.46 mmol) in dichloromethane (5 mL), precooled at −35 °C. After 12 h of stirring the mixture was gradually warmed to ambient temperature before the solvent was removed in vacuo. The product was extracted from the mixture with trifluoroethanol (10 mL). After removal of trifluoroethanol in vacuo, the product was dissolved in CH_2Cl_2, from which the product crystallized within 3 min at ambient temperature. The isolated yellow solid was air and moisture stable. Yield: 304 mg (70%). ^{1}H NMR (CD$_3$NO$_2$, 200 MHz, 25 °C) δ 7.36 (d, J = 1.9 Hz, 1H, HC=CH nearest imine), 7.06 (m, 3H, aryl-H), 7.17 (d, J = 1.9 Hz, 1H, HC=CH nearest methyl), 5.44 (s, 2H, CH_2), 4.07 (s, 3H, NCH_3), 2.83 (septet, J = 6.7 Hz, 2H, CHMe$_2$), 2.17 (s, 3H, MeC=N), 1.50 (d, J = 6.7 Hz, 6H, C(CH_3)$_2$), 0.96 (d, J = 6.7 Hz, 6H, C(CH_3)$_2$). ^{13}C{^{1}H} NMR could not be obtained in CD$_3$NO$_2$ due to poor solubility. IR (nujol) $\nu_{C=N}$ 1638 cm^{-1}. HRMS (ES) m/z 438.1006 (M$^+$–Cl) (calcd. 438.10447). Anal. Calcd. for C$_{20}$H$_{29}$Cl$_4$N$_3$Pd (4a·CH$_2$Cl$_2$): C, 42.92; H, 5.22; Cl, 25.34; N, 7.51; Pd, 19.01. Found: C, 44.07; H, 5.31; Cl, 22.8; N, 7.64; Pd, 20.0%. We suspect partial loss of crystallized solvent prior to the elemental analysis. ^{1}H NMR data in DMSO-d_6 are included in the ESI.†

(C–N)PdClMe (4b)

A solution of (COD)PdClMe (99 mg, 0.37 mmol) in dichloromethane (5 mL) was cooled to −20 °C before a solution of 3 (165 mg, 0.19 mmol) in dichloromethane (1 mL) was carefully added. After 1 h of stirring, the mixture was warmed gradually to ambient temperature before removal of the solvent under vacuum. The residue was dissolved in toluene and filtered through celite to remove AgCl. The toluene was removed under vacuum, and the off-white product crystallized from cold ether. Yield: 103 mg (60%). ^{1}H NMR (CD$_3$NO$_2$, 200 MHz, 25 °C) δ 7.27 (br, 1H, HC=CH), 7.14 (br, 1H, HC=CH), 7.14 (br, 3H, aryl-H), 5.16 (br, 2H, CH_2), 3.84 (br s, 3H, NCH_3), 2.71 (septet, J = 6.7 Hz, 2H, CHMe$_2$), 1.96 (br s, 3H, MeC=N), 1.35 (br d, 6H, CH(CH_3)$_2$), 0.94 (br d, 6H, CH(CH_3)$_2$), 0.48 (br s, 3H, PdCH_3). ^{13}C{^{1}H} NMR (CD$_3$NO$_2$, 75 MHz, 25 °C) δ 175.7 (NCN), 174.4 (N=C), 144.9 (aryl-C_{ipso}), 140.5 (aryl-C_o), 127.2 (aryl-C_p), 124.6 (aryl-C_m), 123.6 (HC=CH), 122.6 (HC=CH), 57.27 (CH$_2$), 38.04 (N–CH$_3$), 29.32 (CHMe$_2$), 24.55 (CH$_3$), 25.03 and 24.04 (CH(CH$_3$)$_2$), −11.51 (Pd-CH$_3$). IR (nujol) $\nu_{C=N}$ 1679, 1644 cm^{-1}. Anal. Calcd for C$_{20}$H$_{30}$ClN$_3$Pd: C, 52.87; H, 6.66; Cl, 7.80; N, 9.25; Pd, 23.42. Found: C, 52.85; H, 6.55; Cl, 8.12; N, 9.42; Pd, 23.48%. ^{1}H NMR data in THF-d_8 are included in the ESI.†

(C–N)PdCl(MeCN)⁺PF₆⁻ (5a)

A solution of AgPF$_6$ (35.9 mg, 0.142 mmol) in MeCN (2 mL) was added slowly to a stirred solution **4a** (67.5 mg, 0.142 mmol) in MeCN (5 mL). Stirring was continued for 10 min, after whereupon the mixture was filtered through celite to remove precipitated AgCl. The solvent was removed by rotary evaporation and the yellow crystalline product was washed with pentane before drying under vacuum. Yield: 71.2 mg (80%). Spectroscopic and elemental analysis data are included in the ESI. †

(N–C)PdMe(MeCN)⁺PF₆⁻ (5b)

A solution of AgPF$_6$ (67 mg, 0.265 mmol) in MeCN (2 mL) was gradually added to solution of **4b** (117 mg, 0.258 mmol) in MeCN (5 mL). After 10 min of stirring, the mixture was filtered through celite to remove precipitated AgCl. The solvent was removed *in vacuo* and the white powdered product was washed with pentane before drying under vacuum. Yield: 85 mg (51.5%). Spectroscopic and elemental analysis data are included in the ESI. †

[(N–C)Pd(MeCN)₂]²⁺(PF₆⁻)₂ (6a)

A solution of AgPF$_6$ (56 mg, 0.222 mmol) in MeCN (2 mL) was slowly added to a solution of **4a** (53 mg, 0.111 mmol) in MeCN (5 mL). After 10 min of stirring, the mixture was filtered through celite to remove precipitated AgCl. The solvent was removed *in vacuo* and the off-white crystalline product was washed with pentane before drying under vacuum. Yield: 70 mg (80.8%). Spectroscopic and elemental analysis data are included in the ESI. †

X-Ray crystal structure determination of 4a

Crystals that were suitable for an X-ray diffraction structure determination were found after workup of **4a** by crystallization from a concentrated dichloromethane solution.[29] Selected bond distances and angles are given in Table 1. CCDC reference number 215694. See http://www.rsc.org/suppdata/dt/b3/b308275j/ for crystallographic data in CIF format.

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