

Synthesis and characterization of novel Pd(II) and Pt(II) complexes with 5-ring chelating iminoylcarbene ligands

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Abstract

A novel *N*-iminoylimidazolium salt serves as a precursor to an iminoyl-substituted *N*-heterocyclic carbene ligand system with the potential to form 5-ring chelates. Reaction of 3-Me-1-[C(C₆H₅)=N(2,6-*i*-Pr₂C₆H₃)]C₃H₃N₂⁺Cl⁻ (**3**; (C–N)H⁺Cl⁻) with Ag₂O leads to the silver carbene complex (C–N)AgCl **4**. A crystallographic analysis of **4** reveals a monomeric (carbene)AgCl moiety with a κ¹-(C) bonded iminoylcarbene ligand, in accord with NMR and IR spectroscopic data. Carbene transfer from Ag to Pd occurs upon reaction of **4** with (COD)PdCl₂, resulting in the κ²-(C,N) iminoylcarbene complex (C–N)PdCl₂ (**5**). Carbene transfer from **4** to Pt takes place with Pt₂Me₄(μ-SMe₂)₂ yielding (C–N)PtMe₂ (**6**), which was characterized by X-ray crystallography. The monomeric Pt complex contains a 5-ring chelate with a κ²-(C,N)-bonded iminoylcarbene ligand. The Pt–Me bond distances in **6** are nearly identical (2.071(5) Å *trans* to carbene-C; 2.051(4) Å *cis*) but the ²*J*(¹⁹⁵Pt–H) coupling constants are significantly different (63.1 Hz *trans*; 92.0 Hz *cis*), as are the ¹*J*(¹⁹⁵Pt–C) coupling constants (618 Hz *trans*; 799 Hz *cis*).

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1. Introduction

Arduengo's report of stable heterocyclic carbenes of the imidazolin-2-ylidene type [1,2] led to the immediate use of such species as ligands for organometallic complexes. *N*-heterocyclic carbene complexes are often thermally robust and easy to handle, and act as very efficient catalysts or catalyst precursors for a range of chemical transformations [3–6].

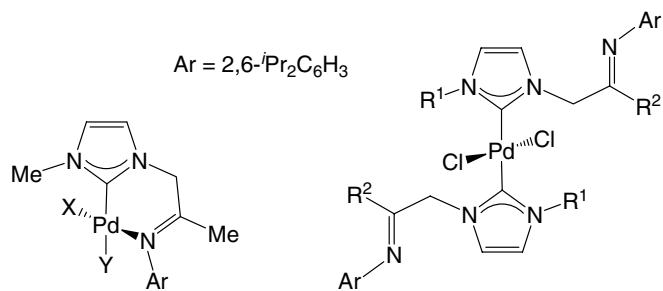
We recently reported the synthesis and characterization of neutral, cationic, and dicationic Pd(II) complexes bearing the chelating iminocarbene ligand system shown at the left in Scheme 1 [7]. The presence of a 6-membered chelate ring was verified by a crystallographic investigation for X,Y = Cl. The chelate complexes exhibited complex dynamic behavior in solution, involving conformational “ring flip” of the boat conformation of the 6-membered chelate

ring and solvent-dependent interconversion of chelating κ²-(C,N) and non-chelating κ¹-(C) solvento species. Subsequently, it was demonstrated that sterically more demanding substituents (Scheme 1, right; R¹/R² = Me/Ph, Ph/Me, 2,4,6-Me₃C₆H₂/Me, 2,6-*i*-Pr₂C₆H₃/Me) changed the structural preferences from chelating mono(κ²-(C,N)) to non-chelating bis(κ¹-(C)) iminocarbene Pd complexes that also exhibited dynamic conformational changes in solution [8].

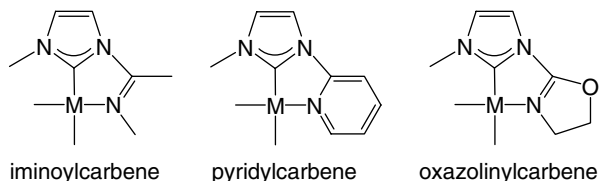
The synthetic strategy in our previous contributions [7,8] involved the preparation of imidazolium salt precursors of the carbene moiety. Deprotonation of these with concomitant carbene formation could not be effected with conventional bases (KH, KO^tBu) due to competing deprotonation at the activated methylene linker between the imine and the imidazole ring. We avoided this problem by deprotonation of the imidazolium salts with Ag₂O as a milder base with concomitant silver carbene formation, a previously well-established procedure [9]. Bildstein and coworkers [10] recently reported that deprotonation with KH could successfully yield carbenes if both acidic methylene hydrogens

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Scheme 1.



Scheme 2.

were replaced by methyl groups, but this approach obviously allows less flexibility in ligand design.

In this contribution, we describe the first synthesis and characterization of related 5-membered ring Pd and Pt complexes in which the imine C atom is directly attached at the imidazole N atom. Previously, 5-ring iminocarbene analogues have been described in which the imine functionality arises from a 2-pyridyl [11–18] or 2-oxazolinylic [19–21] moiety that is directly attached at the imidazolium N, but not from a “free” imine or iminoyl group (Scheme 2). It will be seen that due to the reduced conformational flexibility of the 5-membered ring when compared with the 6-membered ring in Scheme 1, the dynamic processes that were seen in the 6-membered chelate structures are eliminated.

2. Results and discussion

2.1. Ligand synthesis

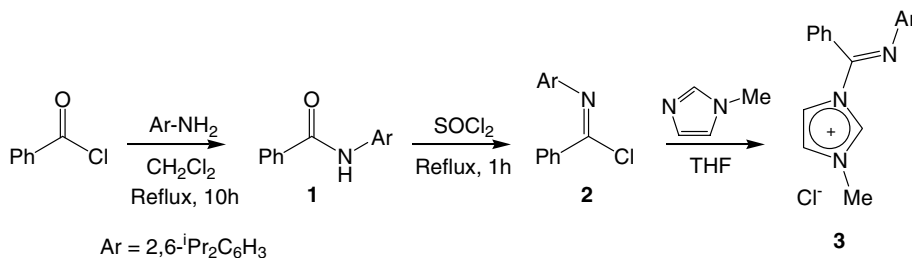
The iminocarbene ligand systems in Scheme 1 are conveniently prepared by the reaction between an α -chloroimine and a monosubstituted imidazole, which provides the iminoimidazolium salt precursor of the carbene [7,8]. We reasoned that an analogous reaction between an iminoyl

chloride and a monosubstituted imidazole should provide the imidazolium salt precursor for the desired 5-membered chelates. The iminoyl chlorides are in turn available by reacting secondary amides with SOCl_2 as described by Boeré et al. [22]. The synthesis of the imidazolium salt **3** is depicted in Scheme 3; details of the synthesis and product characterization are given in the experimental section. Bildstein and coworkers [23] recently reported the synthesis of **3** as its triflate salt by reacting **2** with 2 equivalents of imidazole, followed by N-methylation at the remaining imidazole-N with methyl triflate. In the ^1H NMR spectrum, the signals due to the aryl- ^iPr groups in **3** appear as two doublets and one septet, as was also seen for the precursor to the 6-membered chelate [7]. The splitting of the ^iPr methyl doublets indicates the presence of diastereotopic methyl groups. This is presumably caused by severely hindered rotation around the imine N–C(aryl) single bond, causing the two methyl groups within an ^iPr substituent to become diastereotopic.

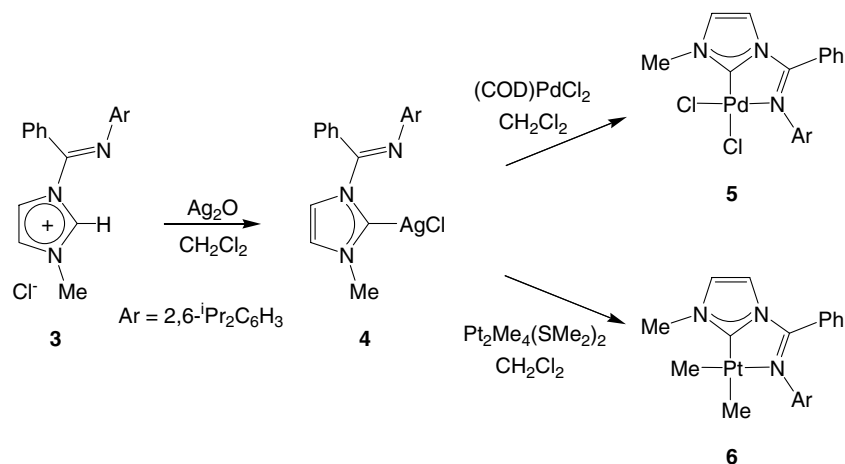
2.2. Silver iminoylcarbene complex **4**

One standard method for generating heterocyclic carbenes from imidazolium salt precursors is the deprotonation at C-2 using strong bases. This works well on simple imidazolium salts without other acidic or otherwise sensitive functional groups. The reaction to form free carbenes has been noted by us and others to be difficult or impossible to achieve when other acidic functional groups are present in the imidazolium salt [7,20,24]. Bildstein [23] found that attempted deprotonation of **3** with KH generated a product that was presumably formed by the desired deprotonation followed by a formal 1,2-shift of the iminoyl group from N to carbene-C. This species was not suited for preparation of metal carbene complexes but did serve as a ligand in closely related N,N-bonded chelate complexes.

The reaction of imidazolium salts with Ag_2O has become an established method for preparation of Ag carbene complexes even from imidazolium precursors that have other acidic protons or sensitive functional groups [9]. The silver complexes in turn are noted for their capacity to transfer the carbene ligand to other metals [25]. Accordingly, when imidazolium salt **3** is treated with Ag_2O in CH_2Cl_2 (Scheme 4), the corresponding Ag(I) carbene complex (**4**) is formed in good yields. The NMR spectra showed the expected signals; the methyls of the diisopropylphenyl



Scheme 3.



Scheme 4.

(DiPP) groups gave rise to two doublets with a separation of 0.16 ppm, which is within the range found for the previously reported imidazolium salts and their non-chelated Ag(carbene) complexes. In the IR spectrum the $\nu_{\text{C=N}}$ absorption was found at 1662 cm^{-1} , slightly shifted to lower frequencies compared to **3** (1673 cm^{-1}), and in the region commonly displayed by imines with a phenyl group attached to the imine carbon. An X-ray crystallographic structure analysis revealed the monomeric nature of the Ag complex (vide infra).

2.3. Palladium iminoylcarbene complex **5**

Attempts to prepare a Pd iminoylcarbene complex by treatment of the imidazolium salt **3** with $\text{Pd}(\text{OAc})_2$ [26] were unsuccessful. However, the silver iminoylcarbene complex **4** underwent smooth carbene transfer when reacted with $(\text{COD})\text{PdCl}_2$ in CH_2Cl_2 at $-70\text{ }^\circ\text{C}$, and provided the $(\kappa^2\text{-iminoylcarbene})\text{PdCl}_2$ complex **5** in high yields (Scheme 4). Spectroscopic and analytical data are in accord with the proposed structure. The mass spectrum showed a signal at $m/z = 486$, corresponding to $\text{M}^+ - \text{Cl}$. In the IR spectrum, the $\nu_{\text{C=N}}$ absorption was found at 1609 cm^{-1} , significantly lowered compared to the precursor **4** (1662 cm^{-1}) and quite indicative of coordination of the imine nitrogen to the Pd center with resulting back bonding into the C=N bond. The NMR spectra were reminiscent to those of the 6-membered ring system, but devoid of any indications of fluxional behavior. The ^1H NMR spectrum exhibited two ^iPr methyl doublets, again caused by the diastereotopic relationship between the two methyls within an ^iPr aryl substituent as a result of hindered C(aryl)–N(imine) rotation. The separation between the two doublets was 0.43 ppm. This separation agrees with a previously observed empirical trend, in which the separation of the two ^iPr doublets is consistently larger in 6-membered chelate $\kappa^2\text{-(C,N)}$ iminocarbene structures than in non-chelating $\kappa^1\text{-(C)}$ structures [7,8]. The same trend appears to be seen in the 5-membered chelate iminoylcarbene complexes reported in this work.

2.4. Platinum iminoylcarbene complex **6**

The new Pt complex (iminoylcarbene) PtMe_2 (**6**) was obtained in good yields by carbene transfer to Pt in the reaction between $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ and **4**. The new compound was characterized by NMR, IR, MS, and elemental analysis. The spectroscopic and analysis data, as well as an X-ray crystallographic structure determination (vide infra) confirms the 5-ring chelate structure in Scheme 4. The low-frequency IR $\nu_{\text{C=N}}$ absorption at 1614 cm^{-1} suggests coordination of the N(imine) to Pt. The ^1H NMR spectrum showed two doublets for the diastereotopic methyl groups within the aryl ^iPr substituents, separated by 0.37 ppm which is in agreement with a chelate structure (see discussion of **5**). The N-Me group at the imidazole ring appeared at δ 3.86, and had no discernible $^{195}\text{Pt-H}$ coupling. On the other hand, the two Pt–Me signals exhibited the diagnostic couplings to ^{195}Pt . The resonance from the methyl group *trans* to the carbene appeared at a much higher field (δ 0.21, $^2J(^{195}\text{Pt-H}) = 63.1\text{ Hz}$) than the methyl group *cis* to the carbene (δ 1.50, $^2J(^{195}\text{Pt-H}) = 92.0\text{ Hz}$). A ^1H NMR NOESY spectrum unambiguously established which resonance arose from the position *cis* to the carbene: A clear cross peak appeared due to the close spatial relationship between the *cis* Pt–Me signal and the imidazole N-Me signal; no cross peak was seen that correlated the *trans* Pt–Me signal with N-Me. The *cis* Pt–H coupling constant is the greater of the two, as expected from the differences in *trans* effects between the imine and the carbene ends of the chelating ligand. The coupling constant difference $\Delta^2J(^{195}\text{Pt-H}) = 29\text{ Hz}$ between *cis* and *trans* couplings is considerable, and may be compared to the smaller differences of $\Delta^2J(^{195}\text{Pt-H}) = 4\text{--}7\text{ Hz}$ in 5-membered ring imine-amine chelating complexes [27,28]. On the other hand, P,N-coordinated aminophosphine 5-ring chelates exhibit coupling constant differences $\Delta^2J(^{195}\text{Pt-H})$ ranging from 14 to 26 Hz [29]. The magnitude of the coupling constants in **6** can be compared to the values found in typical (diimine) PtMe_2 complexes, 85–87 Hz [30–32]. The significantly lowered J value for the Pt–Me *trans* to the carbene

attests to the great *trans* effect of the carbene ligand relative to the imine. In the ^{13}C NMR spectra, the two Pt–Me resonances also exhibited considerable differences in chemical shifts and $^1J(\text{Pt}–\text{C})$ coupling constants (Pt–Me *trans* to carbene, δ 5.6 with $^1J(\text{Pt}–\text{C}) = 618$ Hz; *cis* to carbene, δ –22.7 with $^1J(\text{Pt}–\text{C}) = 799$ Hz).

2.5. X-ray crystal structure determination of Ag complex 4

Light yellow prismatic crystals suitable for X-ray crystallography were obtained from a chloroform/pentane solution at room temperature. Experimental and crystallographic data are collected in Table 1, and selected bond distances and angles for 4 are given in Table 2. Fig. 1 shows an ORTEP plot of the molecular structure. The solid-state structure consists of monomeric (carbene)AgCl units with an included chloroform molecule. As can clearly be seen from the ORTEP drawing, the coordination geometry at the silver atom is slightly distorted from linearity, with a Cl–Ag–C(carbene) angle of 177.8° , and the carbene is bonded in a $\kappa^1\text{-C}$ mode at Ag. The Ag–Cl and Ag–C(carbene) bond distances of 2.3355(3) and 2.0770(12) Å, respectively, are close to the predicted values of 2.32 and 2.10 Å based on the covalent radii of the atoms [33,34]. Bond distances and angles in the coordination sphere of Ag are in accordance with other reported monomeric two-coordinated (N-heterocyclic carbene)AgCl structures [8,35–38]. The carbene C(4)–N(2) and C(4)–N(3) distances are 1.3377(17) and 1.3699(16) Å, respectively, and the bond an-

Table 1
X-ray crystallographic data for 4 and 6

Compound	4	6
Chemical Formula	$\text{C}_{23}\text{H}_{27}\text{N}_3\text{AgCl} \cdot \text{CHCl}_3$	$\text{C}_{25}\text{H}_{33}\text{N}_3\text{Pt}$
F_w	488.81	570.64
Crystal system	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$Pca2_1$
Z	4	8
a (Å)	8.884(1)	15.074(1)
b (Å)	16.622(1)	18.684(1)
c (Å)	17.732(1)	16.956(1)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å ³)	2618.36(10)	4775.5(2)
ρ_{calc} (g cm ⁻³)	1.543	1.587
Crystal dimensions (mm)	$0.5 \times 0.2 \times 0.07$	$0.45 \times 0.3 \times 0.17$
Temperature (K)	105(2)	105(2)
Diffractometer	Bruker SMART CCD	Bruker SMART CCD
Radiation, Mo K α (Å)	0.71073	0.71073
θ Range (°)	1.68–36.4	1.09–33.15
No. of data collected	49596	87900
No. of unique data	12667	17877
No. of observed data ($I > 2\sigma(I)$)	12081	16399
Agreement between equivalent data (R_{int})	0.0248	0.0385
No. of parameters	401	523
μ (mm ⁻¹)	1.195	5.891
Absorption correction	SADABS	SADABS
$R^1(F_o)$, $wR^2(F_o^2)$ ($I > 2\sigma$)	0.0239, 0.0624	0.0311, 0.0785

Table 2
Selected bond lengths (Å) and bond angles (°) in 4 and one of the two molecules in the asymmetric unit of 6

4 (Ag)		6 (Pt)	
Ag(1)–C(4)	2.0770(12)	Pt(1)–C(4)	2.008(4)
–	–	Pt(1)–N(1)	2.126(3)
Ag(1)–Cl(1)	2.3355(3)	Pt(1)–C(1)	2.071(5)
–	–	Pt(1)–C(2)	2.051(4)
N(2)–C(7)	1.4592(18)	N(2)–C(7)	1.458(5)
N(2)–C(4)	1.3377(17)	N(2)–C(4)	1.349(5)
N(3)–C(4)	1.3699(16)	N(3)–C(4)	1.400(5)
C(5)–C(6)	1.3506(18)	C(5)–C(6)	1.340(6)
C(3)–N(1)	1.2712(17)	C(3)–N(1)	1.294(5)
C(3)–C(20)	1.4875(17)	C(3)–C(20)	1.486(5)
C(3)–N(3)	1.4315(16)	C(3)–N(3)	1.387(5)
N(1)–C(8)	1.4201(17)	N(1)–C(8)	1.443(5)
C(4)–Ag(1)–Cl(1)	177.81(4)	C(4)–Pt(1)–C(1)	173.50(18)
–	–	C(4)–Pt(1)–C(2)	99.97(18)
–	–	C(4)–Pt(1)–N(1)	77.37(14)
–	–	N(1)–Pt(1)–C(1)	96.67(16)
–	–	C(1)–Pt(1)–C(2)	86.0(2)
N(2)–C(4)–N(3)	104.43(10)	N(2)–C(4)–N(3)	103.0(3)
N(2)–C(4)–Ag(1)	131.74(9)	N(2)–C(4)–Pt(1)	143.2(3)
N(3)–C(4)–Ag(1)	123.81(9)	N(3)–C(4)–Pt(1)	113.8(3)
N(3)–C(3)–N(1)	116.18(11)	N(3)–C(3)–N(1)	114.5(3)
N(3)–C(3)–C(20)	115.21(11)	N(3)–C(3)–C(20)	117.9(3)
C(3)–N(3)–C(4)	123.42(10)	C(3)–N(3)–C(4)	118.2(3)
C(3)–N(1)–C(8)	121.85(11)	C(3)–N(1)–C(8)	121.4(3)

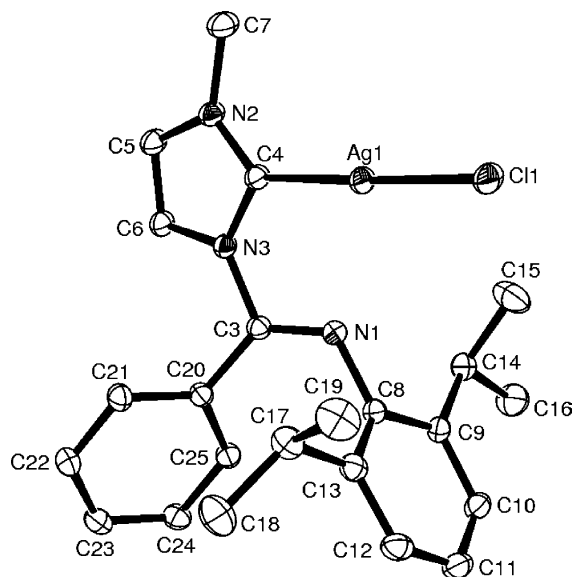


Fig. 1. ORTEP plot of 4. Hydrogen atoms and a CHCl_3 solvent molecule are omitted for clarity. Selected bond distances and angles are listed in Table 2.

gle N(2)–C(4)–N(3) at C(carbene) is 104.4° . These bond distances and angles are in the range found in related functionalized N-heterocyclic carbene complexes of AgCl, ranging from 1.335 to 1.357 Å and 104.0° to 105.0° , respectively [8,35–38]. There are no close spatial interactions between adjacent molecules that suggest weakly interacting (carbene)AgCl dimeric units as discussed for the previously studied Ag iminocarbenes [8]. The imine $\text{C}=\text{N}$ bond in 4 is nearly coplanar with the plane of the imidazole ring, with

the C(4)–N(3)–C(3)–N(1) torsion angle of 20.6°. This generates a relatively short distance between the N(imine) and the Ag atom, 2.826 Å.

2.6. X-ray crystal structure determination of Pt complex 6

Light red prismatic crystals of **6** suitable for X-ray diffraction analysis were obtained from a dichloromethane/pentane solution at room temperature. The asymmetric unit contains two molecules that differ slightly by rotation of the aromatic groups relative to the coordination plane. Experimental and crystallographic data are given in Table 1. Selected bond lengths and angles for one of the two molecules of **6** are given in Table 2. Fig. 2 shows an ORTEP drawing of the molecular structure of **6**. The structure verifies that the complex is monomeric and contains a κ^2 -(C,N)-chelating iminocarbene ligand. The molecule assumes a slightly distorted square-planar structure that is expected for a four-coordinate d^8 species (the sum of the four *cis* L–Pt–L' angles is 360.0°). Deviations from the ideal 90° L–Pt–L' angles are however significant, ranging from 77.4° for the N(1)–Pt(1)–C(4) chelate bite angle, to 100.0° for the C(4)–Pt(1)–C(2) angle. These observations are consistent with previous structural studies on functionalized diimine (κ^2 -N,N)PtMe₂ complexes [39,40]. The imidazole ring and the 5-membered chelate ring are essentially coplanar. Significant ring strain on the chelate is evidenced by the fact that the two N(imidazole)–C(carbene)–Pt angles differ by 29.4° (N(2)–C(4)–Pt(1): 143.2°; N(3)–C(4)–Pt(1): 113.8°), as seen for a number of functionalized N-heterocyclic carbenes complexes of Pd that form 5-membered chelate rings [11,14,20,41].

The Pt–C(carbene) bond distance is 2.008(4) Å. The Pt–Me distance *trans* to the carbene, Pt(1)–C(1), is 2.071(5) Å, and the Pt–Me distance *cis* to imine-N is 2.051(4) Å. These

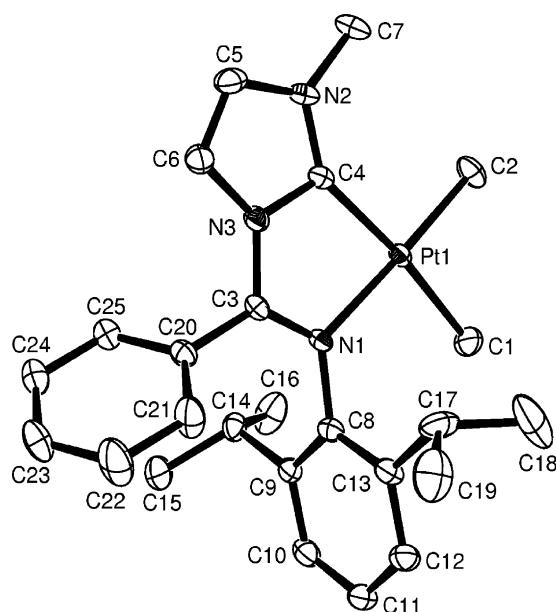


Fig. 2. ORTEP drawing of **6**. Hydrogen atoms and the second molecule of the asymmetric unit (see text) are omitted for clarity. Selected bond distances and angles are listed in Table 2.

values are in the range 2.037–2.079 Å spanned by Pt–Me bonds in three (diimine)PtMe₂ complexes [39,40,42] and a number of recently reported pyridinium-derived cyclometalated Pt methyl complexes [43]. Thus, although considerable differences were seen between the two ²J(Pt–H) coupling constants in **6**, only a slight *trans* effect difference is exerted on the two Pt–Me bond distances. The Pt–N(imine) bond length of 2.126(3) Å is in the range found in (diimine)PtMe₂ complexes [39,40], ranging from 2.094 to 2.138 Å. No 5-ring chelated (κ^2 -carbene)PtMe₂ or (κ^2 -carbene)PtCl₂ crystal structures have been reported for comparison, but differences in the *cis* and *trans* M–X (X = halide, Me) distances are found in other functionalized carbenes [20,44].

Some additional structural features of the Pt iminocarbene complex **6** and the Ag iminocarbene complex **4** are also noteworthy. A slight elongation of both carbene C–N bond distances (0.030 and 0.011 Å) is seen when changing from the less electron-rich Ag complex **4** to the more electron-rich Pt complex **6**, with a concomitant decrease of the N–C–N angle by 1.4°. While the chelating vs. non-chelating nature of the ligand coordination mode may play a role, this trend is consistent with a small decrease in the extent of N–C(carbene)–N, π bonding in the imidazole ring, which may again reflect enhanced π back bonding from Pt to C(carbene). Furthermore, the imine C=N bond of 1.294(5) Å in **6** is slightly longer than the corresponding imine C=N bond of 1.2712(17) Å in **4**, which may also be caused by better back bonding from the relatively electron-rich Pt center to π^* of the imine bond. If it is indeed a metal–carbene π -bonding interaction that causes these effects, it is in contrast to the common assumption that N-heterocyclic carbene ligands act as essentially pure σ donors with little π -accepting capacity [4]. In this regard, it is interesting that Meyer and coworkers [45] have recently asserted that such assumptions are purely empirical and by itself not sufficient to corroborate the nature of the metal–ligand interaction. Strong evidence for π back bonding interactions in electron-rich N-heterocyclic carbene complexes, backed by crystallographic data and quantum-mechanical calculations, were provided by Meyer [45].

2.7. Concluding remarks

With the synthetic approaches described in this contribution and in our past work, fairly general methods are now available for the preparation of Pd and Pt complexes that are coordinated by iminocarbene ligands in 5- and 6-membered ring chelates. The use of these complexes in stoichiometric and catalytic reactions, in particular C–C coupling reactions, will be addressed in future contributions.

3. Experimental section

3.1. General procedures

All reactions involving organometallic compounds were carried out with use of dry box, 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, DPX 300 and DRX 500 instruments with QNP or TXI probes. The NMR spectra were recorded at 25 °C. Assignments of ^1H and ^{13}C signals were aided by DEPT45, HMQC, HMBC, HETCOR, COLOC, COSY45, and NOESY ^1H NMR (mixing times 0.3 s where relevant). For brevity, the following abbreviations are used for the assignments: Ph = phenyl, DiPP = 2,6-diisopropylphenyl. Mass spectra (electrospray ionization) were obtained from acetonitrile solutions on a Micromass QTOF II spectrometer. All other mass spectra were measured on a Micromass Prospec Q spectrometer using the EI technique. IR spectra were recorded on a Nicolet Magna-IR 550 FT-IR spectrophotometer. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

Commercial grade 2,6-diisopropylaniline was distilled prior to use. Benzoyl chloride, 1-methylimidazole, and Ag_2O were purchased from Acros, Fluka, or Aldrich, and used as received. The amide **1** was prepared following the procedure of Boeré et al. [22]. Anhydrous PdCl_2 was purchased from Fluka, $(\text{COD})\text{PdCl}_2$ and $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ were prepared as described previously [46,47].

3.2. Preparation of $\text{C}_6\text{H}_5\text{C}(\text{Cl})\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2**)

This compound was prepared using the procedure of Bildstein and coworkers [48], who reported its X-ray structure but no spectroscopic data. The data are included here for completeness. A round-bottom flask was charged with **1** (11.06 g, 39.31 mmol), and SOCl_2 (38 mL) was added. The mixture was heated at reflux for 1 h before the remaining SOCl_2 was removed in vacuo. The residue was dissolved in pentane (70 mL) and filtered, and the pentane was removed under vacuum yielding the yellow oily product. Yield: 11.35 g, 96%. ^1H NMR (CDCl_3 , 200 MHz) δ 8.26 (m, 2H, H_o , Ph), 7.58 (m, 3H, H_m and H_p , Ph), 7.24 (m, 3H, H_m and H_p , DiPP), 2.87 (sept., 2H, $J = 6.9$ Hz, CHMe_2), 1.77 (d, 6H, $J = 6.9$ Hz, CHMe_2), 1.21 (d, 6H, $J = 6.9$ Hz, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50 MHz) δ 143.9 (C=N), 143.5 (C_{ipso} , DiPP), 136.7 (C_o , DiPP), 135.0 (C_{ipso} , Ph), 132.1 (C_p , Ph), 129.4 (C_o , Ph), 128.6 (C_m , Ph), 124.9 (C_p , DiPP), 123.1 (C_m , DiPP), 28.7 (CHMe_2), 23.3 and 22.9 (CHMe_2). MS (EI): m/z 299 (M^+ , 22.6%), 264 ($\text{M}^+ - \text{Cl}$, 100%). HRMS (EI): m/z 299.1449 (M^+).

3.3. Preparation of $[3\text{-Me-1-}\{C(\text{C}_6\text{H}_5)\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}\text{-C}_3\text{H}_3\text{N}_2\text{J}^+\text{Cl}^-$ (**3**)

The iminoyl chloride **2** (10.69 g, 35.64 mmol) was flushed with $\text{N}_2(\text{g})$ and dissolved in dry THF (60 mL). A solution of 1-methylimidazole (2.936 g, 35.76 mmol) in dry THF (10 mL) was carefully added over a period of 5 min. The mixture was stirred at ambient temperature for 44 h, with slow precipitation of the product as a light yellow material. After filtration and washing with diethyl

ether, the crude product was recrystallized from a CH_2Cl_2 /hexane mixture to yield the product as white microcrystals (7.097 g, 52%). ^1H NMR (CDCl_3 , 200 MHz) δ 10.14 (s, 1H, NCHN), 8.12 (s, 1H, NHCCHN near N-Me), 7.99 (s, 1H, NHCCHN near imine), 7.46 (m, 5H, Ph), 7.11 (m, 3H, aryl-H of DiPP), 4.42 (s, 3H, NMe), 2.81 (sept., $J = 6.8$ Hz, 2H, CHMe_2), 1.17 (d, $J = 6.8$ Hz, 6H, CHMe_2), 0.96 (d, $J = 6.8$ Hz, 6H, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50 MHz) δ 140.2 (C_{ipso} , Ph), 137.7 (NCN), 136.3 (C_o , DiPP), 132.3 (C_p , Ph), 129.3 and 129.2 (C_o and C_m , Ph), 125.4 (C_p , DiPP), 124.9 (NCCN near N-Me), 123.3 (C_m , DiPP), 119.3 (NCCN near imine), 37.7 (N-Me), 28.4 (CHMe_2), 23.9 and 21.8 (CHMe_2). Resonances from the C-imine and the ipso carbon at DiPP were not observed. IR (CH_2Cl_2) $\nu_{\text{C=N}}$ 1673 cm^{-1} .

3.4. Preparation of $[3\text{-Me-1-}\{C(\text{C}_6\text{H}_5)\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}\text{-C}_3\text{H}_2\text{N}_2\text{JAgCl}$ (**4**)

The imidazolium salt **3** (285 mg, 0.746 mmol) was dissolved in dichloromethane (11 mL). Ag_2O (90 mg, 0.39 mmol) was added and the mixture was stirred for 30 min at ambient temperature before filtration through celite to remove excess Ag_2O . Dichloromethane was removed under vacuum and the product was washed with pentane before drying. Crystallization from CHCl_3 /hexane yielded 200 mg (55%) of yellowish crystals. The reaction is essentially quantitative by ^1H NMR and the crude product, which had a purity of 90–95% by ^1H NMR, can be used for preparation of Pd and Pt complexes without prior purification. ^1H NMR (CD_2Cl_2 , 200 MHz) δ 7.70 (s, 1H, NHCCHN), 7.3–7.4 (m, 3H, Ph), 7.24 (s, 1H, NHCCHN), 7.1–7.2 (m, 2H, Ph), 7.03 (m, 3H, aryl-H of DiPP), 3.84 (s, 3H, N-Me), 2.86 (sept., $J = 6.8$ Hz, 2H, CHMe_2), 1.12 (d, $J = 6.8$ Hz, 6H, CHMe_2), 0.96 (d, $J = 6.8$ Hz, 6H, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 50 MHz) δ 183.9 (NCN), 151.6 (C=N), 142.1 (C_{ipso} , DiPP), 136.7 (C_o , DiPP), 131.6 (Ph), 130.4 (C_{ipso} , Ph), 129.6 (Ph), 128.9 (Ph), 124.9 (aryl-C, DiPP), 123.3 (aryl-C, DiPP), 122.9 and 121.0 (NCCN), 40.2 (NMe), 28.8 (CHMe_2), 24.2 and 21.9 (CHMe_2). IR (CH_2Cl_2) $\nu_{\text{C=N}}$ 1662 cm^{-1} . Anal. Calc. for $\text{C}_{23}\text{H}_{27}\text{AgClN}_3$: C, 56.52; H, 5.57; N, 8.60. Found: C, 56.62; H, 5.66; N, 8.03.

3.5. Preparation of $[3\text{-Me-1-}\{C(\text{C}_6\text{H}_5)\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}\text{-C}_3\text{H}_2\text{N}_2\text{JPdCl}_2$ (**5**)

A cooled solution (-70 °C) of the silver iminoyl carbene **4** (50.9 mg, 0.104 mmol) in CH_2Cl_2 (5 mL) was slowly added to a cooled solution (-70 °C) of $(\text{COD})\text{PdCl}_2$ (29.7 mg, 0.104 mmol) in CH_2Cl_2 (10 mL). The mixture was allowed to slowly warm to ambient temperature before removal of CH_2Cl_2 under vacuum. The crude product was dissolved in acetonitrile and filtered to remove AgCl . The acetonitrile was removed in vacuo and the product was recrystallized from CH_2Cl_2 . Yield: 48.2 mg (89%). ^1H NMR (CD_3CN , 200 MHz) δ 7.48 (m, 5H, Ph), 7.19 (m,

^1H , H_p , DiPP), 7.20 (d, $^3J = 2.2$ Hz, 1H, NCHCHN, near imine), 7.17 (d, $^3J = 2.2$ Hz, 1H, NCHCHN, near N-Me), 7.09 (m, 2H, H_m , DiPP), 4.26 (s, 3 H, N-Me), 3.22 (sept., $J = 6.8$ Hz, 2H, CHMe₂), 1.41 (d, $J = 6.8$ Hz, 6H, CHMe₂), 0.98 (d, $J = 6.8$ Hz, 6H, CHMe₂). $^{13}\text{C}\{\text{H}\}$ NMR (CD₃CN, 50 MHz) δ 164.1 (NCN), 159.7 (C=N), 143.3 (C_o , DiPP), 140.4 (C_{ipso} , DiPP), 134.0 (C_p , Ph), 130.7 (C_o , Ph), 130.1 (C_m , Ph), 129.4 (C_p , DiPP), 126.8 (C_{ipso} , Ph), 126.1 (NCCN near N-Me), 124.7 (C_m , DiPP), 120.4 (NCCN near imine), 39.2 (N-Me), 29.7 (CHMe₂), 24.9 and 23.6 (CHMe₂). MS-ESI: m/z 486 ($\text{M}^+ - \text{Cl}$, 100%), IR $\nu_{\text{C=N}}$ 1609 cm⁻¹. Anal. Calc. for C₂₃H₂₇Cl₂N₃PdCH₂Cl₂: C, 47.43; H, 4.81; N, 6.91. Found: C, 47.18; H, 4.98; N, 6.73.

3.6. Preparation of [3-Me-1-{C(C₆H₅)N(2,6-*i*-Pr₂C₆H₃)}-C₃H₂N₂]PtMe₂ (6)

A cooled solution (-70 °C) of the silver iminoyl carbene **4** (122 mg, 0.250 mmol) in CH₂Cl₂ (5 mL) was slowly added to a cooled solution (-70 °C) of Pt₂Me₄(μ -SMe₂)₂ (72 mg, 0.125 mmol). The mixture was allowed to warm to room temperature before removal of CH₂Cl₂ under vacuum. The crude product was dissolved in acetonitrile and filtered to remove AgCl. The acetonitrile was removed in vacuo and the product was recrystallized from CH₂Cl₂/CHCl₃/pentane. Yield: 98 mg (69%). The atom numbering for the NMR data that follow for compound **6** refers to the numbering scheme used in Fig. 2. ^1H NMR (CDCl₃, 500 MHz) δ 7.39 (tt, $J = 7.5$, 1.2 Hz, 1H, H_p , Ph), 7.28 (t, $J = 7.9$ Hz, 2H, H_m , Ph), 7.19 (d, $J = 8.3$ Hz, 2H, H_o , Ph), 7.06–7.11 (m, 1H, H_p , DiPP), 7.03–7.11 (m, 2H, H_m , DiPP), 6.95 (d, $^3J = 2.2$ Hz, 1H, NCHCHN near imine), 6.71 (d, $^3J = 2.2$ Hz, 1H, NCHCHN near N-Me), 3.86 (s, 3H, N-Me), 3.05 (sept., $J = 6.8$ Hz, 2H, CHMe₂), 1.50 (s, $^2J(^{195}\text{Pt}-\text{H}) = 92.0$ Hz, 3H, Pt-Me *cis* to carbene), 1.21 (d, $J = 6.7$ Hz, 6H, CHMe₂ H16 and H18), 0.84 (d, $J = 6.9$ Hz, 6H, CHMe₂ H15 and H19), 0.21 (s, $^2J(^{195}\text{Pt}-\text{H}) = 63.1$ Hz, 3H, Pt-Me *trans* to carbene). $^{13}\text{C}\{\text{H}\}$ NMR (CDCl₃, 75 MHz) δ 190.7 ($^1J(^{195}\text{Pt}-\text{C}) = 837$ Hz, C(carbene)), 158.9 (imine-C=N), 140.9 (C_o , DiPP), 139.6 (C_{ipso} , DiPP), 130.9 (C_p , Ph), 128.6 (C_{ipso} , Ph), 128.5 (C_m , Ph), 128.1 (C_o , Ph), 126.6 (C_p , DiPP), 123.2 (NCCN near N-Me), 123.0 (C_m , DiPP), 117.7 ($^3J(^{195}\text{Pt}-\text{C}) = 15.7$ Hz, NCCN near imine), 37.4 (N-Me), 27.6 (CHMe₂), 24.4 (CHMe₂ C16 and C18), 23.0 (CHMe₂ C15 and C19), 5.6 ($^1J(^{195}\text{Pt}-\text{C}) = 618$ Hz, Pt-Me *trans* to carbene), -22.7 ($^1J(^{195}\text{Pt}-\text{C}) = 799$ Hz, Pt-Me *cis* to carbene). IR (CH₂Cl₂) $\nu_{\text{C=N}}$ 1614 cm⁻¹. MS-ESI: m/z 596 ($[\text{M}(^{195}\text{Pt})]^+ + \text{MeCN} - \text{Me}$, 100%), 595 ($[\text{M}(^{194}\text{Pt})]^+ + \text{MeCN} - \text{Me}$, 76%). HRMS-ESI: Calc. for C₂₆H₃₃N₄¹⁹⁴Pt($[\text{M}(^{194}\text{Pt})]^+ + \text{MeCN} - \text{Me}$), 595.2326. Found: 595.2350. Anal. Calc. for C₂₅H₃₃N₃Pt: C, 52.62; H, 5.83; N, 7.36. Found: C, 52.56; H, 6.01; N, 7.19.

3.7. X-ray crystal structure determination of Ag and Pt complexes **4** and **6**

X-ray quality crystals of **4** were obtained by crystallization from chloroform/pentane, and of **6** from a dichloromethane/pentane mixture. Details of the data collection and refinement for both compounds are summarized in Table 1 and in the supplementary material.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited as cif files with the Cambridge Crystallographic Data Centre, CCDC no. 280291 for complex **4** and 280292 for complex **6**. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>).

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