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Non-Innocence of *N*-Heterocyclic Carbene Ligands: Intermolecular C–H Activation in Allyl Palladium NHC Complexes

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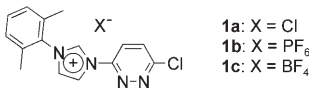
N-Heterocyclic carbenes (NHCs) have gained great popularity as ligands in organometallic chemistry and homogeneous catalysis.[1,2] Due to their excellent performance they have found widespread use, in particular in Ru-based olefin metathesis[3] and Pd-catalyzed cross-coupling reactions and related transformations.[4,5] Chemical and substitutional inertness is often mentioned among their particular advantages, and this is expected to be further amplified by *N*-functionalized NHCs that bear chelating substituents.[6] It has been demonstrated, however, that NHC ligands may occasionally become non-innocent and undergo unanticipated side reactions, including C–C or C–H bond activation,[7,8] and may shift towards abnormal binding modes.[9] While several deactivation mechanisms involving NHC ligands have recently been disclosed for Ru complexes,[7] little is known about related degradation pathways of NHC–Pd systems. Most typical for the latter is reductive elimination yielding Pd^0 and 2-alkyl- or 2-arylimidazolium salts,[10] and palladium colloids and/or anionic Pd^0 and Pd^{II} species resulting from this process are nowadays believed to be the active compounds in Pd-catalyzed Heck–Mizoroki and cross-coupling reactions.[11] Reports on other decomposition reactions of NHC–Pd complexes are scarce and comprise ligand exchange,[12] formation of NHC–olefin coupling products,[13] methyl group migratory insertion[14] and nucleophilic attack of alkoxides on (allyl)Pd(NHC)X compounds.[15] Herein we report an unprecedented reactivity of (allyl)Pd(NHC)X complexes, where the NHC shows a truly non-innocent behaviour and suffers C–H activation at the ligand backbone. Such type of reaction may also prove relevant for various NHC–Pd catalysts. Since degradation reactions are detrimental to catalyst function, understanding them has important implications for catalyst design.

As part of a program directed towards the development of functionalized NHC derivatives with potentially bridging units, we have recently reported a versatile synthesis of pyrazolate-bridged bis(imidazolium) ligand precursors and their dinuclear (allyl)Pd complexes.[16] Related ligands based on pyridazines with two imidazolium groups tethered to the 3- and 6-positions of the diazine heterocycle have also been obtained in a straightforward procedure[17] and are expected to serve as useful scaffolds for the synthesis of bimetallic *N*,*N*′-bridged NHC complexes.[18,19] The corresponding ligand precursors **1** (Figure 1) bearing only one imidazolium moiety and their (allyl)Pd complexes were studied as mononuclear benchmark systems in order to probe the stability of such NHC/pyridazine hybrids and to assess potential cooperative effects in the bimetallic analogues.



1a: X = Cl
1b: X = PF_6
1c: X = BF_4

Figure 1. Ligand precursors **1a**–**c**.

Reaction of $[\{(allyl)PdCl\}_2]$ with the in situ generated NHC ligand derived from **1a** yielded the expected mononuclear palladium complex **2a**, as was confirmed by X-ray crystallographic analysis (Figure 2)[20] as well as by the characteristic ^{13}C NMR signal for the carbene C2 atom (at 185.4 ppm) and other spectroscopic and analytical data (see Supporting Information). In **2a** the [(allyl)PdCl] fragment is solely bound to the NHC subunit, leaving the pyridazine dangling. An *anti*-orientation is observed in the solid state, with the pyridazine-N turned away from the [(allyl)PdCl] fragment.[21]

Complex **2a** is a catalyst precursor in Heck-type C–C coupling under standard conditions (see Supporting Information), although with moderate activity. To probe for aging and stability of **2a** an NMR tube of the pure com-

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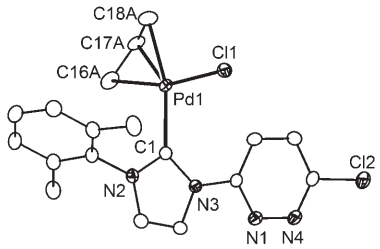


Figure 2. Molecular structure of **2a** (thermal ellipsoids drawn at the 30% probability level). Hydrogen atoms and the disorder of the allyl ligand are omitted for clarity. Only one of the two crystallographically independent molecules is shown. Selected bond lengths [Å] and angles [°]: Pd1−Cl1 2.4006(6), Pd1−C1 2.055(2), Pd1−C16A 2.184(19), Pd1−C17A 2.146(5), Pd1−C18A 2.111(19); Cl1-Pd1-C1 96.72(6), C16A-Pd1-C1 97.8(3), C17A-Pd1-C1 131.59(16), C18A-Pd1-C1 164.5(4), C16A-Pd1-Cl1 165.1(3), C17A-Pd1-Cl1 129.95(15), C18A-Pd1-Cl1 97.2(3), N2-C1-N3 103.35(18).

pound in CD_3CN was left standing at room temperature. Unexpectedly, small pale orange crystals of a new compound **3** gradually formed over approximately four months. The identity of **3** was elucidated by X-ray analysis

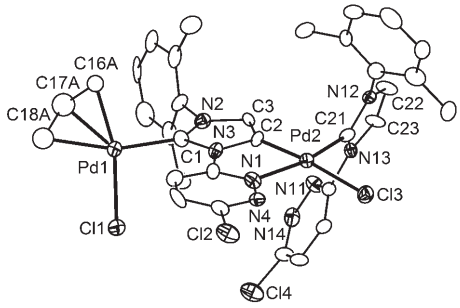
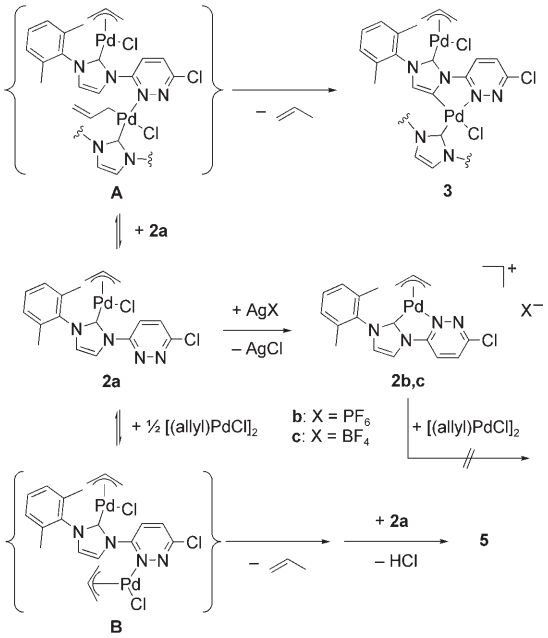


Figure 3. Molecular structure of **3** (thermal ellipsoids drawn at the 30% probability level). Hydrogen atoms and the disorder of the allyl ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]:Pd1−Cl1 2.381(5), Pd1−C1 2.041(14), Pd1−C16A 2.09(3), Pd1−C17A 2.13(3), Pd1−C18A 2.20(3), Pd2−Cl3 2.373(4), Pd2−N1 2.104(13), Pd2−C2 1.991(15), Pd2−C21 1.965(15); Cl1-Pd1-C1 97.4(4), C16A-Pd1-C1 97.2(8), C17A-Pd1-C1 128.4(10), C18A-Pd1-C1 161.6(10), C16A-Pd1-Cl1 164.8(8), C17A-Pd1-Cl1 129.9(8), C18A-Pd1-Cl1 100.4(9), N1-Pd2-C21 167.3(5), C2-Pd2-Cl3 172.9(5), N1-Pd2-C2 80.0(6), C2-Pd2-C21 87.4(6), C21-Pd2-Cl3 92.4(4), Cl3-Pd2-N1 100.3(4), N2-C1-N3 102.1(12), N12-C21-N13 104.8(13).

(Figure 3).[20] Obviously, two molecules of **2a** reacted to yield a dinuclear complex, in which C–H activation at the backbone of one of the NHC moieties has occurred, while the second molecule of **2a** has lost its allyl coligand. The resulting propene was indeed found when the reaction was carried out in a sealed NMR tube. At 60°C, formation of propene could already be detected after few hours. Complex **3**, which is very poorly soluble, is of interest as it can be described as the first example of an NHC moiety bound simultaneously to two transition-metal ions in both the normal (C2) and the abnormal (C4 or C5) positions.[9,22–24]

Additional experiments were carried out to gain some insight into the mechanism leading to the formation of **3**. Presumably, **2a** is in equilibrium with an intermediate such as **A** (Scheme 1, top; note that **A** may alternatively be formulated with an η^3-allyl group and an ionic chloride), which positions the allyl fragment and the imidazole backbone C−H in close proximity suitable for a slow process of C−H insertion or—more likely—formation of a four-membered metallacycle transition state that leads to elimination of propene.



Scheme 1. Proposed mechanism for the formation of **3** and **5** from **2a**.

Similar chelate functionalization of imidazolium salts has recently been reported to provide a rational access to nonclassical palladium NHC complexes via an oxidative addition protocol.[25] Further support for the proposed initial step leading to **A** comes from the investigation of **2b**,**c**, in which the pyridazine-N is no longer available for binding (Scheme 1, middle). Treatment of **2a** with one equivalent of $AgPF_6$ or $AgBF_4$ induces chloride abstraction and concomitant coordination of the adjacent pyridazine-N to give **2b** ($X=PF_6^-$) or **2c** ($X=BF_4^-$), which is accompanied by significant changes of the NMR signals for the allyl group and the pyridazine backbone. Complexes **2b**,**c** can also be prepared from **1b**,**c** or by transmetallation of the corresponding mercury complexes **4b**,**c** (not shown)—an uncommon strategy that has some advantages compared to the well-known transmetallation of Ag compounds,[26] including lower costs and light-insensitivity. Synthetic procedures and analytical data as well as molecular structures of **1b**, **1c**, **2b** and **4c** are given as supporting information.

In contrast to **2a**, complex **2b** proved to be stable in solution. Even after several weeks at 60°C no signs of any decomposition reaction were found. This suggests that a noncoordinated pyridazine ring is required for the first step of

the sequence that in the end results in formation of **3**. When an excess of [{(allyl)PdCl}$_2$] was added to **2a** or **2b**, no interaction was observed in the latter case, whereas reaction with **2a** slowly gave a new trinuclear palladium complex **5** (Scheme 1, bottom).

Unfortunately, the very poor solubility of **5** in any organic solvent hampered its NMR-spectroscopic characterization. However, the molecular structure of **5** was determined by X-ray crystallography and is depicted in Figure 4.[20] It reveals two fragments of the complex **2a** that have been metallated and that are linked by an additional central Pd^{II} ion bound to the pyridazine-N1 and backbone C4 atoms of the NHC moieties.

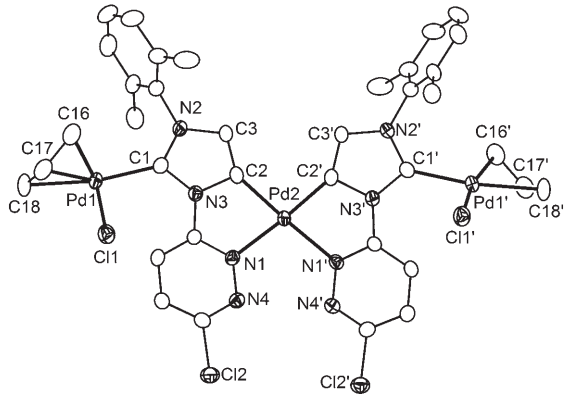


Figure 4. Molecular structure of **5** (thermal ellipsoids drawn at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Cl1 2.3873(13), Pd1–C1 2.030(4), Pd1–C16 2.110(5), Pd1–C17 2.150(6), Pd1–C18 2.191(4), Pd2–C2 1.965(4), Pd2–N1 2.089(3); Cl1-Pd1-C1 90.89(13), C16-Pd1-C1 100.99(19), C17-Pd1-C1 134.1(2), C18-Pd1-C1 169.1(2), C16-Pd1-Cl1 167.23(14), C17-Pd1-Cl1 132.62(17), C18-Pd1-Cl1 99.34(16), C2-Pd2-N1 79.92(15), C2′-Pd2-N1 174.49(16), N1′-Pd2-N1 103.96(18), C2-Pd2-C2' 96.5(2). Symmetry transformation used to generate equivalent atoms ('): $1-x$, y, $1.5-z$.

In close analogy to the putative intermediate **A** it is likely that the initial step leading to the formation of **5** is binding of excess (allyl)PdCl to the N-atom of the dangling pyridazine. Indeed, significant shifts of ^{1}H NMR signals are observed upon addition of [{(allyl)PdCl}$_2$] to a solution of **2a** in CD_3CN (see Supporting Information), which indicates a fast equilibrium reaction that leads to the weakly coordinated species **B** (Scheme 1, bottom). Given the *anti*-orientation of the pyridazine observed in the structure of **2a** (Figure 1), this brings the incoming (allyl)PdCl moiety very close to the backbone C–H of the NHC core, just like in **A**. Using sealed NMR tubes the evolution of propene could be clearly detected after prolonged standing and/or heating (60 °C), which obviously results from activation of that C–H bond by the pre-coordinated (allyl)PdCl fragment. Subsequent coordination of a second molecule of **2a** via its pyridazine-N followed by elimination of HCl would then finally yield **5** (see Scheme 1). When [{(methallyl)PdCl}$_2$] instead of [{(allyl)PdCl}$_2$] was added to **2a**, formation of both propene and isobutene was observed. This is because rapid scrambling of allyl and methallyl ligands takes place, leading to reaction mixtures that contain [{(methallyl)PdCl}$_2$], [{(allyl)PdCl}$_2$], **2a** and its methallyl analogue **2a^{Me}** (the latter could be prepared and characterized independently, see Supporting Information).

Complex **3** does not react with additional [{(allyl)PdCl}$_2$], clearly showing that **3** is no intermediate in the formation of **5**. This indirectly confirms that the central Pd atom in **5** originates from [{(allyl)PdCl}$_2$] (but not from **2a**). It might be noteworthy that in the present case C–H metallation at the NHC backbone occurs, whereas the activated C–Cl bond of the pyridazine ring remains intact throughout these reactions, underlining the importance of pre-coordination to bring the reactive sites in spatial proximity.

The proposed mechanistic scenario is in agreement with all observations made, but preliminary kinetic investigations suggest that more complex processes might be in operation. Unfortunately, all products formed in the reactions leading to **3** and **5** are either volatile or insoluble, and a variety of fast dynamic equilibrium reactions may occur in ((meth)allyl)Pd systems,[27] which severely hampers the determination of kinetic data by NMR spectroscopy. Nevertheless, a few observations can be derived from the preliminary kinetic studies: The allyl complex **2a** reacts faster than its methallyl analogue **2a^{Me}**. The reaction rate (based on consumption of **2a**) in the presence of additional [{(allyl)PdCl}$_2$] increases at higher concentrations of [{(allyl)PdCl}$_2$] as well as at higher concentrations of starting material (**2a**/**2a^{Me}**), in accordance with the proposed intermolecular reaction. However, neither reaction leading to **3** or **5** appears to follow simple first or second order kinetics, again indicating the importance of preequilibria. Further investigations are necessary to fully elucidate mechanistic details and are currently ongoing in our laboratories.

In conclusion, a novel self-deactivation sequence of (allyl)Pd(NHC) complexes has been discovered, in which the Pd-bound NHC ligand is non-innocent and undergoes C–H metallation at the backbone. Complexes **3** and **5** feature an unprecedented (and unexpected) carbene/alkenyl coordination of an imidazolium-derived NHC ligand to two transition-metal ions, which is assisted by the chelating pyridazine arm. This observation underscores that care has to be taken in reactions employing in situ generated Pd–NHC catalysts, since unforeseen side reactions might lead to species different from the presumed normal Pd–NHC complexes.[28] Additional chelating functions are often introduced to enhance the stability of NHC complexes, but dangling side arms with uncoordinated donor atoms may have an adverse effect, as was shown here. On the other hand, the present findings further broaden the scope of NHC chemistry and suggest to use imidazole-based NHC units as bridging ligands for the construction of oligo- and polynuclear complexes.

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Keywords: C–H activation · carbenes · homogeneous catalysis · oligonuclear complexes · palladium

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