Protic N-Heterocyclic Carbenes | Hot Paper

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Oxidative Addition of 2-Halogenoazoles—Direct Synthesis of Palladium(II) Complexes Bearing Protic NH,NH-Functionalized NHC Ligands**

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Abstract: *The chemistry of N-heterocyclic carbenes (NHCs) is dominated by N,N′-dialkylated or -diarylated derivatives. Such NHC ligands are normally obtained by C2-deprotonation of azolium cations or by reductive elimination from azol-2-thiones. A simple one-step procedure is described that leads to complexes with NH,NH-functionalized NHC ligands by the oxidative addition of 2-halogenoazoles to complexes of zero-valent transition metals.*

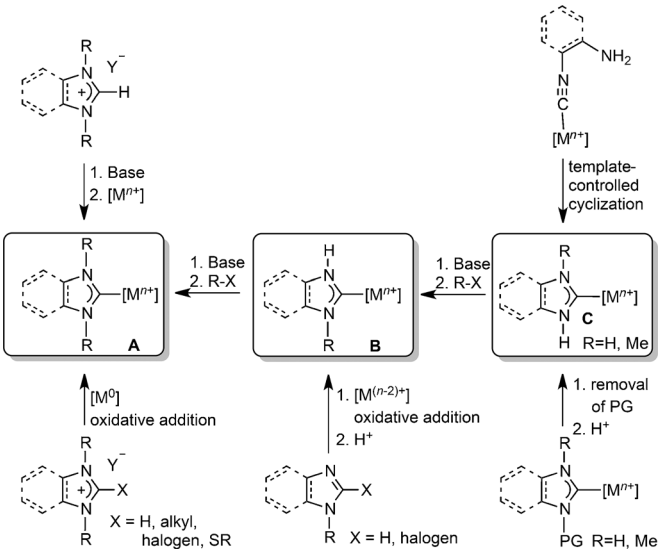
Metal complexes of NR,NR-functionalized NHCs (**A**; NHC = N-heterocyclic carbene; Scheme 1) have been obtained by the direct reaction of the free NHCs with suitable transition metal complexes,[1,2] by the cleavage of enetetramines with transition metal precursors,[3] by the oxidative addition of the C2–X bond (X = H, alkyl, halogen, SR) of azolium cations to low-valent transition metals[4a–g] and by double C–H bond activation in imidazolidines.[4h,i] Metal complexes bearing protic NHCs that is, NHCs featuring an NH,NR- (**B**) or NH,NH-substitution pattern (**C**) have received less attention. Complexes of type **C** bearing protic carbenes, which are not stable when removed from the metal center, are useful intermediates as they can be stepwise N,N′-alkylated in template-controlled reactions[5] which, for example, gives access to macrocyclic ligands featuring NHC donor groups.[6]

Complexes of type **C** have been obtained by the metal-template-controlled cyclization of β-amino-functionalized phenyl or alkyl isocyanides.[5] Alternatively, the removal of the N,N′-protection groups from coordinated alkylated NHCs leads in selected cases to complexes of types **B** or **C**.[7] N-Monoalkylation of complexes of type **C** yields complexes of type **B** with NH,NR-NHCs.[5] Such complexes have recently also been obtained by the direct oxidative addition of neutral 2-halogeno-*N*-alkylbenzimidazoles to suitable transition metal complexes.[8] A related reaction using 2-chlorothiazoles was reported almost 40 years ago.[8d,e] Some additional methods for the preparation of complexes of type **B** like the oxidative addition of the C2–H bond of N-donor-functionalized azoles[9] and the tautomerization of N-metalated azoles have also been described.[10]

Generally, synthesis of protic NHC complexes of type **C** is time consuming and cumbersome. The preparation of β-functionalized isocyanides and their metal-template-controlled cyclization to protic NHC ligands is not straightforward and often significantly influenced by the metal template.[11] In addition, only one example for the synthesis of a complex of type **C** by removal of N,N′-protection groups has been reported.[7b]

As an extension of our studies regarding the oxidative addition of 2-chloro-*N*-alkylbenzimidazoles to transition metals[8] we now studied the oxidative addition of neutral 2-halogenoazoles. Here we demonstrate that even unsubstituted azoles in an unprecedented reaction can oxidatively add to Pd^0 to give complexes with protic NHC ligands of type **C** in a facile one-pot reaction.

The reaction of equimolar amounts of 2-chlorobenzimidazole (**1**) and $[Pd(PPh_3)_4]$ in the presence of an excess of NH_4BF_4 in refluxing toluene afforded complex *trans*-[**2**]BF_4 in an excellent yield of 77% as a colorless solid (Scheme 2). The reaction proceeds by the oxidative addition of the C2–Cl



Scheme 1. Synthetic routes leading to NHC complexes **A**–**C**. PG = protecting group.

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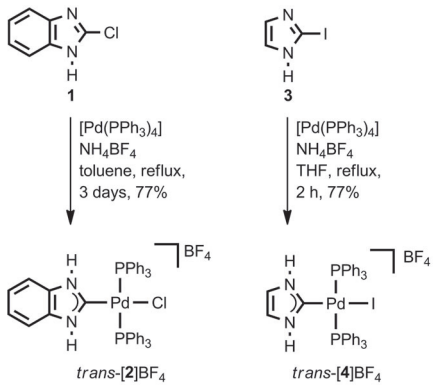

Scheme 2. Oxidative addition of 2-halogenoazoles **1** and **3** to Pd^0.

bond to the Pd^0 center followed by protonation of the ring nitrogen atom.[8a–c] The conceivable protonation of **1** to give the 2-chlorobenzimidazolium cation by an initial N-protonation by NH_4BF_4 is unlikely as NH_4BF_4 is not acidic enough to protonate the neutral benzimidazole.[8a]

In previous studies we found that 2-chloro-*N*-methylbenzimidazole oxidatively adds to zero-valent Group 10 metals giving a C2-metalated intermediate which upon subsequent protonation with the weak acid NH_4BF_4 yields the complex with an NH,NR-substituted NHC ligand.[8a–c] The oxidative addition of 2-chlorobenzimidazole is assumed to proceed in the same fashion but we were so far unable to isolate the initially formed neutral complex bearing anionic NHC and chloro ligands. Initial experiments indicate that the reaction sequence described above to give protic NH,NH-NHC complexes also works with Ni^0, Pt^0, and Ir^I.

The oxidative addition reaction can lead to a mixture of *cis* and *trans* isomers when carried out with $[Pt(PPh_3)_4]$[8a] but yields only the thermodynamically most stable *trans* isomer with Pd^0 and Ni^0.[8a,b] Related studies on square-planar NHC/PPh_3 complexes of palladium(II) have shown that the NHC ligand normally prefers a *cis* position relative to the PPh_3 ligand.[12] In accord with this observation, the benzimidazole **1** reacts with $[Pd(PPh_3)_4]$ in the presence of NH_4BF_4 leading exclusively to complex *trans*-[**2**]BF_4.

Complex *trans*-[**2**]BF_4 is sensitive towards air and moisture in solution but rather stable in the solid state. Formation of *trans*-[**2**]BF_4 was confirmed by NMR spectroscopy and ESI mass spectrometry. The ^1H NMR spectrum of *trans*-[**2**]BF_4 (see also the Supporting Information) features the resonance for the strongly deshielded N-H protons at $\delta = 12.72$ ppm. This value is in good agreement with previously recorded resonances for the N-H protons of protic benzimidzolin-2-ylidene ligands.[5a,b,d,6a] The $^{13}C\{^1H\}$ NMR spectrum shows a triplet for the C_{NHC} atom at $\delta = 165.9$ ppm (t, $^2J_{C,P} = 9.1$ Hz in CD_2Cl_2/[D_6]DMSO) indicating coupling to the two chemically equivalent phosphorus atoms which also implies a *trans* arrangement of the phosphine donors. Consequently, only one singlet at $\delta = 21.2$ ppm was detected in the $^{31}P\{^1H\}$ NMR spectrum. The high-resolution electrospray ionization (HR-ESI) mass spectrum (positive ions) showed the highest intensity peak at $m/z = 783.1084$ corresponding to the molecular ion $[\mathbf{2}]^+$ (calcd $m/z = 783.1090$).

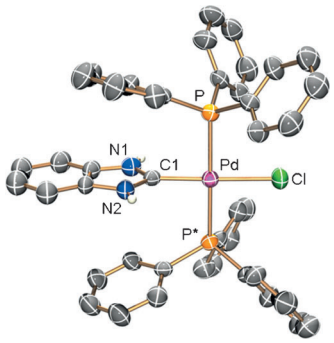

Figure 1. Molecular structure of *trans*-[**2**]$^+$ in *trans*-[**2**]BF_4·C_4H_8O. Solvent molecule and hydrogen atoms, except for the N-H hydrogen atoms, have been omitted for clarity. Cation *trans*-[**2**]$^+$ resides on a crystallographic mirror plane. Selected bond lengths [Å] and angles [°]: Pd–Cl 2.338(5), Pd–P 2.334(2), Pd–C1 1.963(16), N1–C1 1.360(18), N2–C1 1.306(18); Cl-Pd-P 90.19(10), Cl-Pd-C1 176.1(5), P-Pd-P* 178.95(19), P-Pd-C1 89.77(10), N1-C1-N2 106.7(13).

The composition and coordination geometry of *trans*-[**2**]BF_4 was established by an X-ray diffraction study. Suitable crystals of the composition *trans*-[**2**]BF_4·C_4H_8O were obtained by cooling a saturated THF solution of compound *trans*-[**2**]BF_4 to −20 °C. The structure analysis (Figure 1)[16] confirms the *trans* arrangement of the two triphenylphosphine donors. The coordination geometry around the palladium atom is slightly distorted square-planar with bond angles of P-Pd-P* 178.95(19)° and Cl-Pd-C1 176.1(5)°. The plane of the carbene ligand is oriented perpendicular to the palladium coordination plane. The Pd–Cl (2.338(5) Å), Pd–P (2.334(2) Å), and Pd–C1 (1.963(16) Å) bond lengths fall in the range previously observed for the related palladium(II) complexes bearing protic NH,NR-NHC[8a] or NR,NR-NHC ligands.[4d] The N1-C1-N2 angle in the complex *trans*-[**2**]BF_4 measures 106.7(13)° and is slightly smaller than the equivalent angle in palladium complexes bearing NH,NR-NHCs (107.3(2)°)[8a] or NR,NR-NHCs (≈108°).[12] The N-C-N angle in the free benzimidazolin-2-ylidenes measures 103.5(1)° to 104.3(1)°.[2c]

In order to explore the scope of the oxidative addition of unsubstituted 2-halogenoazoles for the synthesis of complexes with protic NHC ligands, we studied the reaction of 2-iodoimidazole with Pd^0. Reaction of 2-iodoimidazole (**3**) with an equimolar amount of $[Pd(PPh_3)_4]$ in the presence of an excess of NH_4BF_4 led to formation of complex *trans*-[**4**]BF_4 as a yellow solid in 77% yield (Scheme 2). The reaction is completed after only 2 h in refluxing THF. In accord with previous observations, the time required for completion of the oxidative addition to Pd^0 is shorter for **3** than for **1** since the C2–I bond in the former is weaker than the C–Cl bond in the latter.[4a,b]

Complex *trans*-[**4**]BF_4 is quite stable at ambient temperature in moderately polar solvents like dichloromethane and THF but decomposes in dimethyl sulfoxide solution after a couple of weeks. Its ^1H NMR spectrum reveals the characteristic resonance for the N-H protons at $\delta =$ 11.90 ppm and its $^{13}C\{^1H\}$ NMR spectrum shows the resonance for the C2 carbene carbon atom at $\delta = 156.5$ ppm (t, $^2J_{C,P} = 9.1$ Hz in CD_2Cl_2/[D_6]DMSO) as a triplet featuring

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coupling to the two chemically equivalent *cis*-coordinated phosphorus atoms. The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at $\delta = 18.8$ ppm confirming the *trans* arrangement of the chemically equivalent PPh_3 ligands. The composition of complex *trans*-[**4**]BF_4 was further analyzed by high-resolution electrospray ionization (HR-ESI) mass spectrometry (positive ions) showing the most intense peak at $m/z = 825.0275$ corresponding to the molecular ion $[\mathbf{4}]^+$ (calcd $m/z = 825.0291$).

An X-ray diffraction analysis with crystals of the composition [**4**]$BF_4 \cdot CH_2Cl_2$,[16] obtained by slow diffusion of diethyl ether into a concentrated solution of *trans*-[**4**]BF_4 in dichloromethane at 4 °C, confirmed the conclusions drawn from the NMR and mass spectra. The metric parameters found in *trans*-[**4**]BF_4 (Figure 2) fall in the typical range observed for square-planar Pd^{II} *trans*-diphosphine complexes bearing NHC donors.[13]

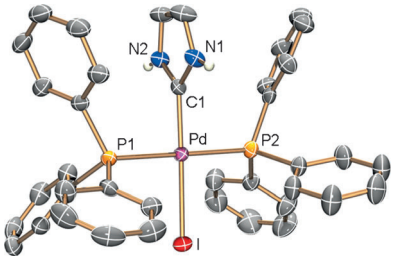
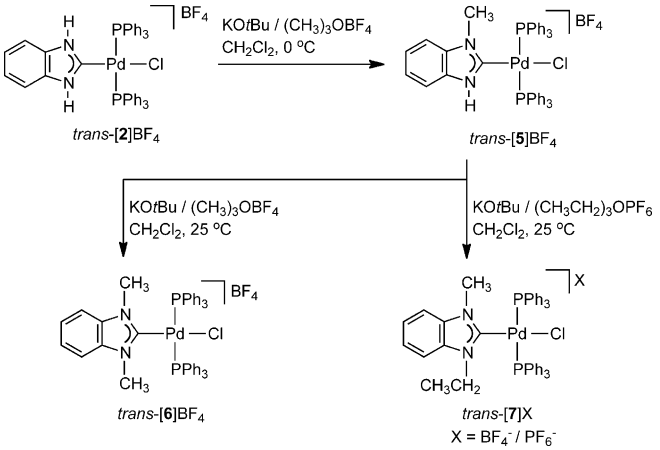


Figure 2. Molecular structure of *trans*-[**4**]$^+$ in *trans*-[**4**]$BF_4 \cdot CH_2Cl_2$. Solvent molecule and hydrogen atoms, except for the N-H hydrogen atoms, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd–I 2.6472(5), Pd–P1 2.332(2), Pd–P2 2.344(2), Pd–C1 1.978(5), N1–C1 1.334(7), N2–C1 1.322(7); I-Pd-P1 90.90(4), I-Pd-P2 89.55(4), I-Pd-C1 178.67(17), P1-Pd-P2 178.18(6), P1-Pd-C1 89.83(16), P2-Pd-C1 89.76(16), N1-C1-N2 103.8(5).

The C1-Pd-I (178.67(17)°) and P1-Pd-P2 (178.18(6)°) angles deviate only slightly from linearity indicating the presence of an almost perfectly square-planar complex cation. The bond angle N1-C1-N2 measures 103.8(5)° which is smaller than the N-C-N angle in *trans*-[**2**]BF_4 but a typical value for complexes bearing imidazoline-derived protic NHC ligands.[7b]

The acidity of the N-H protons in complexes bearing protic NH,NH-NHC ligands allows their functionalization and in particular the alkylation of the ring nitrogen atoms of the coordinated NHC.[5,6] Reaction of complex *trans*-[**2**]BF_4 with 1 equiv of KO*t*Bu at 0 °C followed by addition of Me_3OBF_4 yielded the N-monoalkylated complex *trans*-[**5**]BF_4 (Scheme 3, see also the Supporting Information). This reaction sequence can be repeated with *trans*-[**5**]BF_4 at ambient temperature to give the N,N′-dialkylated complex *trans*-[**6**]BF_4 with a classical NMe,NMe-NHC ligand. Complex *trans*-[**5**]BF_4 also reacts with the related alkylating agent Et_3OPF_6 to yield complex *trans*-[**7**]X (X = BF_4^-/PF_6^-) bearing an unsymmetrically N,N′-dialkylated NHC ligand. Complexes like *trans*-[**6**]BF_4 and *trans*-[**7**]X are more conveniently synthesized by deprotonation of the corresponding symmetrically and unsymmetrically substituted benzimidazolium salts, respectively, in the presence of a suitable palladium(II) precursor.[1] However, the reaction sequence selected here illustrates the facile alkylation of the coordinated NH,NH-NHC ligands and their synthetic utility.



Scheme 3. Stepwise alkylation of the protic NHC ligand in *trans*-[**2**]BF_4.

$^{13}C\{^1H\}$ NMR spectra (see also the Supporting Information) of complexes *trans*-[**5**]BF_4 and *trans*-[**6**]BF_4 exhibit a triplet for the carbene carbon resonances at $\delta = 171.9$ ppm (t, $^2J_{C,P} = 9.1$ Hz in CD_2Cl_2) and slightly downfield-shifted at $\delta = 174.2$ ppm (t, $^2J_{C,P} = 9.0$ Hz in CD_2Cl_2), respectively. These values are only slightly downfield from the C_{NHC} resonance recorded for complex *trans*-[**2**]BF_4 at $\delta = 165.9$ ppm (t, $^2J_{C,P} = 9.1$ Hz) illustrating that the electronic situation in palladium(II) complexes bearing NH,NH-, NH,NMe-, and NMe,NMe-NHC ligands is rather similar.

The oxidative addition of 2-halogenoazoles followed by protonation of the ring nitrogen atom constitutes a novel synthetic procedure for the preparation of complexes bearing NH,NH-NHC ligands. The few known examples for such complexes have previously been prepared almost exclusively by the template-controlled cyclization reaction of β-functionalized isocyanides. This cyclization reaction features certain limitations. It proceeds only if the isocyanide is coordinated to an electron-poor metal center which activates the isocyanide carbon atom for the nucleophilic attack by β-substituent.[11,14] Complementary to this situation, the oxidative addition of 2-halogenoazoles described here requires an electron-rich-metal center to proceed.

We have developed a versatile, straightforward synthetic method for the preparation of complexes bearing protic NH,NH-NHC ligands which have been shown to be directly accessible from 2-halogeno-substituted azole precursors by an oxidative addition/N-protonation reaction sequence. This synthetic strategy will be applied in the future to other metal complexes featuring low-valent and thus oxidizable transition metals like Pt^0, Ni^0, Rh^I, and Ir^I. The synthetic utility of the protic NH,NH-NHC ligands has been demonstrated with their stepwise N,N′-alkylation. Apart from the deprotonation/N-alkylation procedure, a deprotonation/N-metalation protocol appears possible which could be utilized for the generation of heterobimetallic C–M/N–M′ complexes,

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where the two metal centers are in close proximity.[15] Experiments towards this aim are in progress.

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[16] CCDC 962104 (*trans*-[**2**]$BF_4 \cdot C_4H_8O$) and 962105 (*trans*-[**4**]$\cdot CH_2Cl_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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