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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Synthesis of NHC Complexes by Oxidative Addition of 2-Chloro-*N*-methylbenzimidazole

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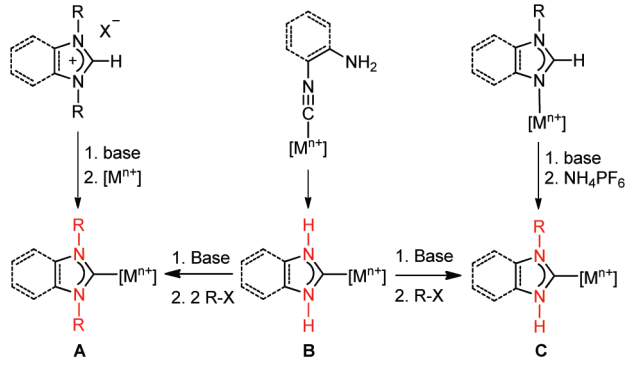
Supporting Information

ABSTRACT: The oxidative addition of 2-chloro-*N*-methylbenzimdazole to complexes of type $[M(PPh_3)_4]$ yields after N-protonation compounds with NH,NMe-substituted NHC ligands. For M = Pd complex compound *trans*-[**3**]BF_4 was obtained, while the oxidative addition for M = Pt yielded a mixture of *cis*-[**4**]BF_4 (major) and *trans*-[**4**]BF_4 (minor).

The chemistry of N-heterocyclic carbenes (NHC) has been studied intensely beginning with the isolation of the first stable derivative by Arduengo et al. in 1991.[1] Today, a large number of different NHCs are known,[2] and these have found numerous applications in different fields such as organocatalysis[3] and as ligands for the preparation of metallosupramolecular[4] and catalytically active metal complexes.[5] NHC complexes are generally prepared from the free NHC ligands or their olefinic dimers,[2,6] via the Ag_2O method developed by Lin et al.[7] and, most commonly, by in situ deprotonation of azolium cations followed by coordination of the NHC ligand to a metal center.[1] The oxidative addition of the C2−X (X = H, R, halogen) bond of various azolium cations to selected transition metals has also been reported.[8] The methods listed above lead to complexes of type **A** bearing "classical" NR,NR-functionalized NHC ligands (Scheme 1).

In our search for NHC complexes which allow modifications at the coordinated NHC ligand, we developed the template-controlled cyclization of β-functionalized isocyanides, leading to complexes of type **B** (Scheme 1) bearing NH,NH-functionalized "protic" NHC ligands.[9] While the free NH,NH-substituted NHCs are not stable, the coordinated ligands can be alkylated stepwise leading to the "classical" NHC complexes of type **A**, and this metal template-controlled reaction has been used, for example, to incorporate NHC donor functions into macrocyclic ligands.[10]

Scheme 1. Synthesis of NHC Complexes A−C



Monoalkylation of the NHC ligand in complexes of type **B** leads to complexes **C**[9,11] where the remaining NH function of the NHC ligand has been shown to act as a recognition unit via formation of intermolecular hydrogen bonds.[11] Recently, complexes of type **C** have also been obtained, initially serendipitiously, by tautomerization of N-coordinated azoles[12] or by the oxidative addition of the C2−H bond of donor-functionalized azoles to selected metal centers,[13] a reaction occasionally followed by a reductive elimination and shift of the M−H hydride to the azole N atom.[14] In addition, the planned synthesis of "classical" NHC complexes of type **A** followed by removal of one N-substituent has also been reported to lead to complexes of type **C**.[15]

We have now found that not only azolium cations but also neutral 2-chloro-substituted benzimidazoles oxidatively add to transition metal complexes. Subsequent protonation yields complexes of type **C** (Scheme 1). Here we describe the oxidative addition of 2-chloro-*N*-methylbenzimidazole **1** to $[M(PPh_3)_4]$ (M = Pd, Pt) followed by protonation with NH_4BF_4 to yield the palladium complex *trans*-[**3**]BF_4 and the platinum complexes *cis*-[**4**]BF_4 and *trans*-[**4**]BF_4 (Scheme 2).

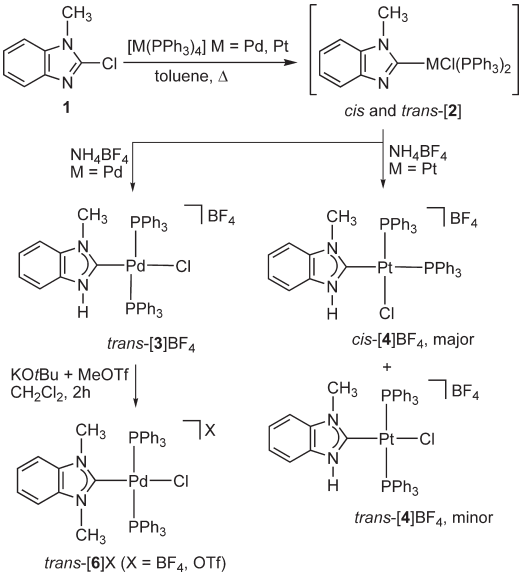
Ligand precursor **1** (Scheme 2) was prepared by the reaction of commercially available 2-chlorobenzimidazole with iodomethane. Formation of **1** was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and microanalytical data (see Supporting Information, [SI]). The ^1H NMR spectrum exhibits a resonance at δ = 3.77 ppm for the protons of the *N*-methyl group, and the $^{13}C\{^1H\}$ NMR spectrum shows the characteristic resonances for the methyl group at δ = 30.5 ppm and for the C2 carbon atom at δ = 140.9 ppm.

Reaction of 1 equiv of **1** with 1 equiv of $[Pd(PPh_3)_4]$ in the presence of an excess of NH_4BF_4 in toluene yielded palladium complex *trans*-[**3**]BF_4 bearing an NH,NMe-substituted NHC ligand (Scheme 2). The reaction proceeds via oxidative addition of the C2−Cl bond of the benzimidazole **1** to the palladium(0) center, giving the intermediate [**2**] followed by protonation of the unsubstituted nitrogen atom.[16] In principle, the oxidative addition leading to both the *cis* and the *trans* intermediate [**2**] is possible. In previous studies with NHC/PPh_3 complexes of palladium(II) and platinum(II) it has been noticed that the NHC ligand normally avoids the *trans* position to the PPh_3

Received: December 2, 2010
Published: January 27, 2011

dx.doi.org/10.1021/ja110634h | *J. Am. Chem. Soc.* 2011, 133, 2112–2115

Scheme 2. Synthesis of NHC Complexes by Oxidative Addition



ligand and that the *cis*-[M(NHC)(PPh$_3$)L$_2$] complexes are the thermodynamically most stable reaction products.[17] In accord with these results, the oxidative addition of **1** to Pd^0 leads ultimately to complex *trans*-[**3**]BF$_4$ which was isolated in 73% yield as colorless solid. Complex *trans*-[**3**]BF$_4$ is unstable in solution but is quite stable toward air and moisture in the solid state.

The important intermediate [**2**] could not be isolated. The conceivable oxidative addition of the benzimidazolium derivative of **1**, obtained by N-protonation of **1** with the excess of NH$_4$BF$_4$ present, appears unlikely as NH$_4$BF$_4$ is not acidic enough to protonate free *N*-alkylbenzimidazoles. A derivative of **1**, 2-chloro-*N*-picolylbenzimidazole, also reacts with [Pt(PPh$_3$)$_4$] in the absence of NH$_4$BF$_4$ under oxidative addition. The resulting complex [**5**] is a dinuclear species obtained via coordination of the free ring imine nitrogen atom to a second platinum(II) center (see SI). This reaction confirms the ability of 2-chloro-*N*-alkylbenzimidazoles to react under oxidative addition in the absence of proton acids and corroborates the reaction mechanism proposed in Scheme 2.

Formation of complex *trans*-[**3**]BF$_4$ was confirmed by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The ^{1}H spectrum showed a dependence of the chemical shift for the N−H proton from the solvent used. In a mixture of CDCl$_3$/DMSO-d_6 the N−H resonance was detected at δ=12.84 ppm, whereas it was observed upfield-shifted at δ=10.90 ppm in CD$_3$CN. The downfield shift of the N−H resonance in DMSO-d_6 is due to the capability of this solvent to engage in O···H−N hydrogen bonds, and related hydrogen bonds involving the N−H proton of NH,NR-functionalized NHC ligands have been described.[11,12g,h,13] The ^{13}C{^{1}H} spectrum shows the resonance for the C2 carbene carbon atom at δ=169.7 ppm as a triplet exhibiting coupling to the two phosphorus atoms coordinated in *cis* positions. The ^{31}P{^{1}H} NMR spectrum shows a singlet for the two chemically equivalent phosphorus atoms at δ = 21.4 ppm confirming the *trans* arrangement of these two donors.

Crystals of *trans*-[**3**]BF$_4$·CH$_2$Cl$_2$ have been obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of *trans*-[**3**]BF$_4$ at ambient temperature. An X-ray diffraction analysis confirmed the composition and coordination geometry of *trans*-[**3**]BF$_4$ (Figure 1, see also SI). The bond lengths for the Pd−C$_{carbene}$ bond (1.979(3) Å) and the Pd−P bonds (Pd−P1 2.3173(8) Å, Pd−P2 2.3264(8) Å) fall into the range previously reported for similar palladium NHC complexes.[8e] The plane of the carbene ligand is oriented perpendicular to the nearly square-planar palladium coordination sphere (Figure 1).

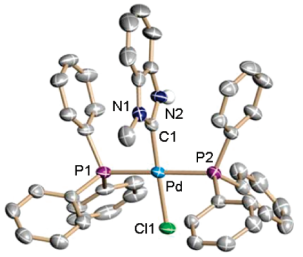


Figure 1. Molecular structure of *trans*-[**3**]$^+$ in *trans*-[**3**]BF$_4$·CH$_2$Cl$_2$ (hydrogen atoms except the one bound to N2, the anion and the solvent molecule have been omitted for clarity). Selected bond distances (Å) and angles (deg): Pd−Cl1 2.3374(7), Pd−P1 2.3173(8), Pd−P2 2.3264(8), Pd−C1 1.979(3), N1−C1 1.346(4), N2−C1 1.342(4); Cl1−Pd−P1 87.79(3), Cl1−Pd−P2 90.39(3), Cl1−Pd−C1 178.88(8), P1−Pd−P2 176.79(3), P1−Pd−C1 91.22(8), P2−Pd−C1 90.59(8).

The platinum complexes *trans*-[**4**]BF$_4$ and *cis*-[**4**]BF$_4$ were prepared as described for the palladium complex *trans*-[**3**]BF$_4$ from [Pt(PPh$_3$)$_4$] as starting material (Scheme 1). Surprisingly and in contrast to the palladium complex, both the *cis* (95%) and *trans* (5%) platinum complexes were detected in the product mixture. This coexistence of both complexes was confirmed by ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy. The ^{13}C NMR spectrum of the product mixture shows two signals for the carbene carbon atom. The resonance at δ = 170.7 ppm appears as a doublet of doublets (dd, $^2J_{CP(cis)}$=10.3 Hz, $^2J_{CP(trans)}$=142.4 Hz) and can therefore be assigned to *cis*-[**4**]BF$_4$, while the carbene carbon resonance for complex *trans*-[**4**]BF$_4$ was observed as a broad singlet at δ = 166.9 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at δ=18.2 ppm (Pt satellites, $^1J_{PtP}$=2524 Hz) for the two chemically equivalent phosphorus atoms of complex *trans*-[**4**]BF$_4$ and two doublets at δ=15.7 ppm (d, $^2J_{PP}$= 19.2 Hz, Pt satellites $^1J_{PtP}$ =2223 Hz, PPh$_3$ *trans* to NHC) and δ = 11.1 ppm (d, $^2J_{PP}$ = 19.2 Hz, Pt satellites $^1J_{PtP}$ =3702 Hz, PPh$_3$ *cis* to NHC). Similarly to *trans*-[**3**]BF$_4$, a downfield resonance at δ = 12.98 ppm was observed for the N−H proton in the ^{1}H NMR spectrum (in CDCl$_3$/DMSO-d_6).

While separation of complexes *cis*-[**4**]BF$_4$ and *trans*-[**4**]BF$_4$ by column chromatography was not possible, the two isomeric complexes led to differently shaped crystals upon diffusion of diethyl ether into a dichloromethane solution of the mixture. Crystals of *cis*-[**4**]BF$_4$ and *trans*-[**4**]BF$_4$·0.5CH$_2$Cl$_2$ were obtained as prisms or needles, respectively. X-ray diffraction structure analyses confirmed the composition and coordination geometry of the two isomeric complex cations (Figure 2).

The arrangement of the four ligands around the metal center is nearly square-planar in both *cis*-[**4**]$^+$ and *trans*-[**4**]$^+$, and the carbene plane in both cations is oriented almost perpendicular to the metal coordination sphere (Figure 2). There are noticeable differences in the bond lengths of the two isomeric cations. The Pt−C$_{NHC}$ bond length is significantly shorter in *trans*-[**4**]$^+$ (Pt−C1 1.972(4) Å) than in *cis*-[**4**]$^+$ (Pt−C1 2.017(2) Å) with the

dx.doi.org/10.1021/ja110634h |*J. Am. Chem. Soc.* 2011, 133, 2112–2115

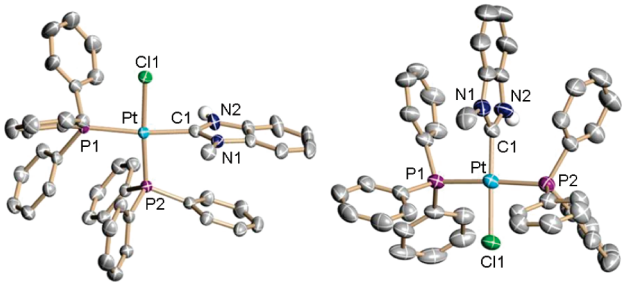


Figure 2. Molecular structures of *cis*-$[\mathbf{4}]^+$ in *cis*-$[\mathbf{4}]BF_4$ (left) and *trans*-$[\mathbf{4}]^+$ in *trans*-$[\mathbf{4}]BF_4 \cdot 0.5CH_2Cl_2$ (right) (hydrogen atoms, excluding the ones bound to N2, the anion, and solvent molecules, have been omitted for clarity). Selected bond distances (Å) and angles (deg) for *cis*-$[\mathbf{4}]^+$ [*trans*-$[\mathbf{4}]^+$]: Pt−Cl1 2.3434(5) [2.3483(11)], Pt−P1 2.3457(5) [2.3171(12)], Pt−P2 2.2452(6) [2.3123(12)], Pt−C1 2.017(2) [1.972(4)], N1−C1 1.347(3) [1.350(6)], N2−C1 1.352(3) [1.349(6)]; Cl1−Pt−P1 87.10(2) [89.59(4)], Cl1−Pt−P2 175.77(2) [87.18(4)], Cl1−Pt−C1 87.02(6) [178.78(14)], P1−Pt−P2 96.97(2) [175.77(4)], P1−Pt−C1 172.77(6) [91.00(13)], P2−Pt−C1 88.99(6) [92.19(13)].

Pt−C_{NHC} separation for *trans*-$[\mathbf{4}]^+$ falling in the range observed previously for related complexes of type *trans*-[PtCl(NH,NR-NHC)$(PR_3)_2$].[15b] These differences can be attributed to the differences in the *trans*-influence of the π-donor chloro ligand in comparison to the σ-donor/π-acceptor phosphine ligand.

Alkylation of the nitrogen atom in complexes bearing protic NH,NR-functionalized NHC ligands has been demonstrated.[9,10] Accordingly, the protic NHC ligand in complex *trans*-$[\mathbf{3}]BF_4$ can be N-alkylated by deprotonation with KO*t*Bu and subsequent reaction with MeOTf (Scheme 2, SI) leading to compound *trans*-$[\mathbf{6}]X$ (X = BF_4, OTf) with a classical NMe,NMe-functionalized NHC ligand. While complexes like *trans*-$[\mathbf{6}]X$ are normally prepared from imidazolium salts (Scheme 1), the alkylation reaction serves to demonstrate the remaining reactivity of the carbene ligand in complex *trans*-$[\mathbf{3}]BF_4$. Complexes bearing NH, NR-functionalized NHC ligands are valuable intermediates for subsequent modifications at the carbene ligand, allowing for example, the generation of unsymmetrical NHCs or the linkage of the NHC to additional donor groups.[10]

The oxidative addition of 2-chloro-*N*-alkylbenzimidazoles followed by protonation of the remaining free ring nitrogen atom constitutes an alternative and complementary synthetic strategy for the generation of complexes bearing "protic" NHC ligands. Such complexes (**C** in Scheme 1) have previously been obtained by template-controlled cyclization of β-functionalized aryl[9a−c,10a] or alkyl[9d,e,10b−d] isocyanides followed by *N*-alkylation. The cyclization reaction proceeds by an intramolecular nucleophilic attack of the β-substituent at the isocyanide carbon atom. This attack is only possible if the coordinated isocyanide is not deactivated by d→π^* backbonding, i.e. if the isocyanide is coordinated to an electron-poor metal center.[9a,18] The oxidative addition of 2-chloro-*N*-alkylbenzimidazoles, on the other hand, requires an electron-rich metal center to proceed and thus constitutes an alternative and complementary synthesis to the template-controlled cyclization of β-functionalized isocyanides.

We have developed a one-pot synthesis for complexes bearing NH,NR-substituted NHC ligands via the oxidative addition of 2-chloro-substituted *N*-methylbenzimidazole to complexes of zero-valent group 10 metals followed by N-protonation. Current studies focus on subsequent modifications at the NH,NR-functionalized NHC ligand and on the use of the N−H function of the NHC ligand for the recognition of selected substrates via intermolecular hydrogen bonds.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details for the synthesis of all compounds; X-ray crystallographic files for compounds *trans*-$[\mathbf{3}]BF_4 \cdot CH_2Cl_2$, *cis*-$[\mathbf{4}]BF_4$, *trans*-$[\mathbf{4}]BF_4 \cdot 0.5CH_2Cl_2$, and $[\mathbf{5}] \cdot H_2O \cdot 0.5Et_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank the Deutsche Forschungsgemeinschaft (SFB 858, IRTG 1444) for financial support.

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