Nucleophilic and electrophilic platinum compounds for C-H bond activation

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Summary

During the last decades, the quest for the most economic ways for the formation of C-C bonds has become a matter of increasing importance for both industrial and academic research. From a point of view of atom economy, reduction of waste and reduction of the number of reaction steps it would be desirable to circumvent the formation of salt, hence prevent the use of carbon-halogen containing compounds, esters, and the like. Substrates which contain a reactive C-H bond rather than a C-X bond (X = halide) are very interesting alternatives for synthetic purposes.

The aim of this work has been the design of novel late transition metal compounds that are able to activate C-H bonds of hydrocarbons in an intermolecular way. As it is known that platinum hydrides are generally quite stable and Pt$^0$L$_2$ species possess suitable filled and empty d-orbitals of appropriate energy and symmetry, to allow C-H activation processes, we decided to use this transition metal to investigate C-H activation processes. Platinum is known to activate C-H bonds of hydrocarbons via two pathways: The first method consists of the in situ generation of an unsaturated electron-rich platinum(0) center which is reactive towards C-H bonds of hydrocarbons in a nucleophilic way. The second method consists of the synthesis of cationic platinum(II) complexes, which are reactive towards C-H bonds of hydrocarbons in an electrophilic way. In this thesis, platinum-systems are described which possess one of these two properties for C-H bond activation of hydrocarbons.

In chapter 2 (part A) the synthesis of novel, thermally stable Pt$^0$(R-DAB)(η$^2$-alkene) complexes is described. These complexes are synthesized in good yield from Pt(cod)$_2$ or Pt(nbe)$_3$ as the Pt$^0$ precursor, via stepwise substitution of the labile dienes by an electron poor alkene, followed by the appropriate R-DAB ligand. In contrast, when using Pt(dba)$_2$ or Pt(dipdba)$_2$, the exchange of dba and dipdba for the alkenes and R-DAB-ligand is slow, much metallic platinum is formed and separation of the Pt(0)-complex from dba or dipdba is difficult, resulting in very low yields of the desired complexes.
The compounds obtained are members of a very useful category of starting materials for various endeavors in synthetic organoplatinum chemistry and catalysis. Not only may these be employed in the oxidative addition of organic halides, to give models for related C-C bond forming Pd-catalysts, but also, by addition of appropriate acids, they provide access to systems suitable for activation of C-H bonds.

Indeed, addition of HX can give alkene-insertion into the platinum hydride (described in part B of chapter 2), but this reactivity is only found when the weak-coordinating X = BF₄⁻ is employed. Addition of HCl only gave disproportionation-products. Some insight in the mechanism has been gained by NMR spectrometry at low temperature, which makes clear that initially a 5-coordinate complex is formed upon HX addition. Probably a 4-coordinate [Pt⁴⁺(R-DAB)(η²-alkene)(H)]⁺X⁻ intermediate is involved for X = BF₄⁻, unlike the situation for X = Cl. Due to coordination of the carbonyl towards the cationic platinum center in the insertion product, insertion of the alkene in the platinum hydride is facilitated.

In chapter 3 the synthesis of the first examples of zerovalent platinum mono-carbene bis(alkene) complexes, where the carbene is an N-heterocyclic carbene, (see Figure 1) is described. These complexes are air-, moisture- and temperature-stable for months in solution and in the solid state. Two different routes for the synthesis of these complexes have been employed. The in situ
preparation of the carbene is the most facile method for obtaining the (carbene) platinum bis(alkene) complexes in good yield.

\[
\begin{align*}
\text{Mes} & \quad \text{Mes} \\
\begin{array}{c}
\text{N} \\
\text{Pt} \\
\text{N}
\end{array} & \quad \begin{array}{c}
\text{R'} \\
\text{R'} \\
\text{R'}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{Mes} & \quad \text{Mes} \\
\begin{array}{c}
\text{N} \\
\text{Pt} \\
\text{N}
\end{array} & \quad \begin{array}{c}
\text{R'} \\
\text{R'} \\
\text{R'}
\end{array}
\end{align*}
\]

\[R = \text{Ph, Mes} \quad R' = \text{COOMe}\]

**Figure 1**

These Pt(0) complexes are valuable compounds for several Pt(0)-catalyzed reactions, such as hydrogenation and hydrosilation, and can be of interest for comparison with (carbene)Pd(0)- and Ni(0)-catalyzed reactions, to give information about intermediates in these reactions.

\[
\begin{align*}
\begin{array}{c}
\text{N} \\
\text{Pt} \\
\text{N}
\end{array} & \quad \begin{array}{c}
\text{R'} \\
\text{R'} \\
\text{R'}
\end{array}
\end{align*}
\]

\[R = \text{COOMe}\]

**Scheme 3**

Surprisingly, these Pt(0) complexes react under relatively mild conditions with dihydrogen to form neutral hydridoplatinum(II)(alkyl)carbene complexes with a hemilabile coordinating carbonyl moiety (see Scheme 3). Despite the quite strong coordination of the carbonyl function, these neutral hydridoplatinum(II)(alkyl)carbene complexes are reactive towards certain C-H bonds of hydrocarbons.

The zerovalent platinum mono-carbene bis(alkene) complexes were designed in particular to investigate reactivity towards C-H bonds of certain imidazolium salts in a nucleophilic way (see Scheme 4). C-H bonds of various imidazolium salts have been activated intermolecularly to yield hydridoplatinum(II) biscarbene complexes, in which the two different carbenes occupy mutual trans-positions (Chapter 4, part A). These activations also take place at room temperature. This method of C-H bond activation of imidazolium salts by zerovalent platinum mono-carbene bis(alkene) complexes has been compared to the well known Whitesides system \([\text{Pt}^0(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{Cy}_2)]\) and was found to be more effective.

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The substituents on the nitrogen-atoms of the imidazolium salts are very important; if at least one nitrogen is substituted with a primary alkyl-chain, the C-H bond activation reaction goes to completion. However, introduction of two secondary alkyl-chains results in equilibria in the C-H bond activation reactions, while tertiary alkyl-chains make the imidazolium salts unreactive towards the zerovalent platinum mono-carbene bis(alkene) complexes.

It should be obvious that the described reactivity of imidazolium salt may strongly influence the behavior of d$^{10}$ metal(0) catalysts which are used in imidazolium-based ionic liquids as solvents. Most of the latter bear primary alkyl chains on the nitrogen atoms and might therefore react analogously to the reactions described for [emim][BF$_4$] and [bmim][BF$_4$] with zero-valent platinum mono-carbene bis(alkene) complexes. The C-H bond activation reaction described in this chapter has opened an easy access to hydrido-d$^{10}$-metal complexes which are known to be involved in a variety of catalytic reactions.

In part B of chapter 4 the C-H this property has been shown by the use of an ionic liquid. When [bmim][BF$_4$] was reacted with a platinum mono-carbene bis(alkene) complex, a cationic hydridoplatinum bis(carbene) complex was formed in situ. This complex catalyzes the selective C-H bond activation of CH$_3$ groups in hydrocarbons and non-activated aromatic C-H bonds (see Scheme 5). In this way, selective transfer of deuterium from benzene-$d_6$ to CH$_3$-groups of [bmim][BF$_4$] was achieved. In this reaction [bmim][BF$_4$] acted as ligand, substrate and solvent!
In chapter 5 various types of NNO-ligands, all based on a pyridinecarbaldimine backbone, were prepared and investigated as potential tridentate ligands in combination with neutral and cationic (methyl)Pt$^{II}$-complexes. The idea for the design of these complexes is that these complexes are expected to be more easy to handle than their didentate counterparts, the (NN) platinum complexes, but that these tridentate NNO platinum complexes retain the reactivity towards C-H bonds of hydrocarbons described for these didentate NN platinum complexes. The NNO ligands could potentially coordinate in a tridentate fashion in such a way that reactivity and stability go together, i.e. the ligand provides stabilization in a tridentate mode and enough reactivity in a didentate mode. Pt$^{II}$(Me)$_2(\sigma^2NN'-NNO)$-complexes have been prepared, after which an internal (phenolic hydroxy-function) or external (HBF$_4$) proton addition resulted in the neutral and cationic, respectively, [Pt$^{II}$(Me)(\sigma^3NN'\text{-}O\text{-}NNO)] and [Pt$^{II}$(Me)(\sigma^3NN'\text{-}O\text{-}NNO)]BF$_4$ complexes, in which the NNO-ligand is coordinated in a tridentate fashion (see Figure 2).

![Figure 2](image)

The obtained neutral [Pt$^{II}$(Me)(\sigma^3NN'\text{-}O\text{-}NNO)] and cationic [Pt$^{II}$(Me)(\sigma^3NN'\text{-}O\text{-}NNO)]BF$_4$ complexes are not suitable for performing C-H bond activation reactions. The neutral Pt$^{II}$(Me)(NNO) complexes are too stable to display any reactivity, whereas the cationic [Pt$^{II}$(Me)(NNO)]$^+\text{BF}_4^-$ complexes are too reactive, so that activation reactions are not selective towards specific C-H bonds. Nevertheless, these neutral and cationic platinum complexes are very interesting compounds and can be compared to other tridentate ligand systems in the field of their coordination and organometalllic chemistry.