Synthesis and Application of Functionalized NHC-Gold Complexes

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Introduction

First investigated by Wanzlick and Öfele in the early 1960s,[1] N-heterocyclic carbenes (NHC’s) are a topic of high current interest, in particular in transition metal catalysis. They are an attractive alternative to phosphine ligands, thanks to their strong σ-donating capability and low level of π-acidity. Moreover, extensive variation of the steric and electronic features of NHC’s is possible.[2]

Still, the number of NHC’s bearing reactive functionalities, which might allow their linkage to solid supports or surfaces, is limited. Based on precedent by Grubbs and Nolan,[3] we developed a new route to functionalized, unsymmetrical N-heterocyclic carbenes which were converted into the corresponding gold complexes. Both complexes catalyze the cycloisomerization of functionalized allenes.

Results

As known in literature, NHC-metal complexes show a broad range of catalytic activities.[4] Here, we report the application to the cycloisomerization of functionalized allenes.[5]

SYNTHESIS OF THE NHC-PRECURSORS

Starting from 4-(Chloromethylbenzoyl)chloride, two new imidazolium salts were built up in a two step synthesis. By changing the amine in the first step, it is possible to obtain new functionalized imidazolium salts with different chemical properties.

SYNTHESIS OF THE NHC-GOLD COMPLEXES

The formation of the corresponding gold complexes was carried out under conditions developed by Nolan. He described the synthesis of gold complexes via transmetalation from silver to gold. The application of this procedure was successful with moderate yields.

Cycloisomerization of Allenes

We observed that catalyst 2 shows the best results without any additives. In contrast to this, the cycloisomerization with catalyst 1 takes place only in the presence of AgBF₄.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1[a]</td>
<td>93%</td>
<td>CH₂Cl₂, 3 d</td>
</tr>
<tr>
<td>2</td>
<td>2[a]</td>
<td>98%</td>
<td>CH₂Cl₂, 45 min</td>
</tr>
<tr>
<td>3</td>
<td>2[a]</td>
<td>42%</td>
<td>CH₂Cl₂, 75 min</td>
</tr>
</tbody>
</table>

[a] Addition of 5 mol% AgBF₄.

Changing the allene to a more bulky substrate gave different results. The yields are lower and the presence of AgBF₄ as additive is required for both catalysts in order to achieve a satisfactory reactivity.

Conclusion

In the recent years transition metal catalysis has become a topic of high interest. In comparison to phosphines, NHC’s are an attractive alternative as ligands for transition metal catalysts. Here, we report the development of two new catalytically active NHC-gold complexes. Due to their reactive functionalities, it might be possible to link them to solid supports or surfaces.

References