Copper $N$-heterocyclic carbene (NHC) complexes as carbene transfer reagents†‡

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A method is described that makes use of easily prepared, inexpensive copper synthons as $N$-heterocyclic carbene (NHC) transfer agents to generate catalytically relevant gold and palladium complexes.

Transition metal catalysed reactions represent powerful synthetic tools. Cross-coupling reactions permitting the creation of carbon–carbon bond using palladium as catalyst are amongst the most important and have found numerous applications in the pharmaceutical industry,1 in the synthesis of natural products and liquid crystals.2 A more recent area of interest is the use of gold in catalysis.3 In this context, the use of numerous gold–phosphine and –NHC has proven very useful in the assembly of simple and complex architectures.4,5 The development of catalysts and their ultimate usefulness is often associated with the cost of their synthesis. The assembly of NHC–transition metal complexes can be problematic6 and is most often accomplished by generating the free NHC followed by binding to a metal centre either in a ligand substitution or in dimer scission reactions. The direct transfer from one metal centre to another, in one reaction, appears most practical and straightforward. As an example of this transmetallation approach, the silver-mediated reaction is the most practiced solution to NHC transfer.7 In this manner, transmetallation can be achieved successfully with numerous metals.8 However, the NHC transfer from silver does not always proceed cleanly.9 An alternative route recently reported makes use of a gold (I)–NHC complex as a transfer agent to palladium (II).10 Nevertheless, both NHC transfer reagents (Au and Ag) have important drawbacks: the transfer from silver(i) must be conducted in the dark whilst the transfer from gold requires PPh3 and an oxygen-free atmosphere. Moreover, both approaches have obvious economic disadvantages. Therefore, a more effective, practical and cost effective method is highly desirable. In this context, we considered that the least expensive congener of Group 11, copper, might represent a viable alternative to gold and silver complexes. Recently, Albrecht and co-workers showed that transfer from copper to ruthenium was possible.11 However, the main drawback to the copper approach is the presently used synthetic routes to Cu–NHC complexes that are based on the addition of free NHC (in situ or preformed) to copper halide. In addition, such preparations involve the use of strong and expensive bases under inert atmosphere and generate inorganic salts. This problem was recently overcome by using a novel methodology that uses Cu2O and the imidazolium salt.12 Our group concurrently reported a similar synthetic protocol.13 Thus, a facile and versatile synthetic route leading to NHC–copper(i) complexes now exists (Scheme 1). The potential use of such complexes in transmetalation reactions can hence be considered.

Herein, we report a study dealing with reactions involving the transfer of $N$-heterocyclic carbenes from copper(i) to gold(i) and palladium(II) to support our original hypothesis that Cu–NHC complexes could be used in this fashion. Four copper(i) complexes were selected for this study (Fig. 1). This choice was motivated by the fact that they would lead to Au and Pd complexes frequently used in catalytic applications.14

The transmetallation from copper(i) to gold(i) and palladium(II) was performed in dichloromethane. This solvent appeared judicious because of the solubility of starting materials and organometallic product and because of the insolubility of CuCl. We therefore foresaw the reaction to proceed with efficient kinetics as all starting materials are soluble and one of the products is insoluble, which should drive the reaction towards completion. Furthermore, the purification of the final product should be facilitated as a

![Scheme 1](image1)

**Scheme 1** Facile synthesis of NHC copper(i) complexes.

![Fig. 1](image2)

**Fig. 1** NHC copper(i) complexes used in carbene transfer reactions.
simple filtration should allow the separation of the desired product from CuCl. Also for solubility reasons, the gold and palladium precursors chosen are [AuCl(SMe2)] or [PdCl2(NCPh)].

Reactions of [CuCl(IMes)]\textbf{1a} and [CuCl(SIMes)]\textbf{1b} with [AuCl(SMe2)] lead, within one hour at 40 °C, to the complete transfer of the mesityl-derived N-heterocyclic carbene from copper to gold. In this manner, [AuCl(IMes)]\textbf{2a} and [AuCl(SIMes)]\textbf{2b} were obtained in high yields (Scheme 2). When [CuCl(IPr)]\textbf{1c} was used, a slightly longer reaction time was required (2 h) for complete transfer of the NHC leading to the formation of [AuCl(IPr)]\textbf{2c} which was isolated in a 84% yield (Scheme 2).

Following the same synthetic strategy, copper complexes \textbf{1a}–\textbf{c} were reacted with [PdCl2(NCPh)]\textbf{2}, leading to the formation of the chloro-bridged dimeric species [Pd(μ-Cl)(NHC)]\textbf{2} via carbene-transfer reaction (Scheme 3).

Interestingly, the reaction times necessary to reach complete transfer of the NHC to the palladium centre match those needed for the gold reactions. Indeed, whilst IMes and SIMes are transferred within an hour, IPr requires nearly two hours. This might be due to the slightly higher steric hindrance of the latter compared to the mesityl-derivatives.\textsuperscript{15} Finally, when using the even more hindered SIPr ligand, decomposition of the gold and palladium salts was observed, even when the reaction was carried out at lower temperature. This degradation of the starting salts to metallic Au and Pd impeded the isolation of the final product in high yields.

In conclusion, the NHC transfer from copper to gold(i) and to palladium(ii) has proven efficient and rapid for three of the most frequently encountered NHCs. This represents, to the best of our knowledge, the first example of the transfer of a NHC ligand from [CuCl(NHC)] to another metal centre. Furthermore the use of Cu-NHC complexes as carbene transfer reagents has been shown viable for the synthesis of Au(i) and Pd(ii) complexes, systems that are frequently used in transition metal-mediated catalysis.\textsuperscript{16} This new method possesses obvious economic and practical advantages over the common silver-based and over the less frequently encountered gold-based approaches.

We are currently studying the scope and limitations of this reaction both in terms of the nature of the metal and of the characteristic of the NHC ligand involved.

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Notes and references

16. \textbf{[AuCl(IPr)]\textsuperscript{2c}} and [Pd(μ-Cl)(IPr)]\textsuperscript{2c} are commercially available on small and large quantities from Aldrich, Strem and Umicore.
17. See ESI for full analysis of all complexes.