Bifunctional Catalysts

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Modular "Click" Preparation of Bifunctional Polymeric Heterometallic Catalysts

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***Abstract:** Heterobimetallic molecular complexes or strictly alternating metallated polymers are obtained by a click reaction between mononuclear metal complexes (secondary building units, SBUs) bearing NHCs functionalized with either p-azidophenyl or p-ethynylphenyl wingtips. With a copper-NHC complex as SBU the formation of molecular or polymeric compounds did not require any additives as the copper complex catalyzes the click reaction. Transmetallation from heterobimetallic Cu/Ag derivatives to Cu/Pd derivatives was achieved. The linker between the SBUs (flexible or rigid) influences the catalytic activity of the heterobimetallic compounds. The polymer with alternating copper-NHC and silver-NHC units and a flexible methylene-triazole bridge between them shows the highest activity in the catalytic alkynylation of trifluoromethyl ketones to give fluorinated propargylic alcohols.*

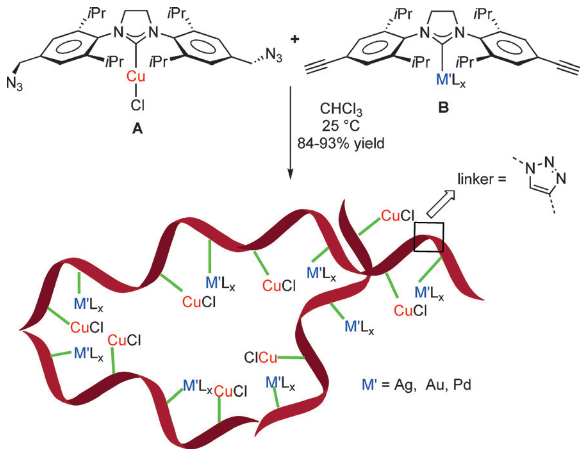
In nature, rather complicated organic compounds are often constructed elegantly via catalysis in environments containing multiple catalytically active sites.[1] Cooperative catalysis, wherein two (or more) catalytic sites work in concert to activate selected substrates and to create new chemical bonds efficiently, has recently emerged as a powerful mechanistic approach for catalytic reaction engineering.[2] The design and preparation of multifunctional catalysts featuring synergistically[3] or cooperatively[4] acting catalytically active sites has become a challenge in the field of catalysis and synthesis.

To mimic the cooperative catalytic efficiency found for selected natural transformations, recent interest has turned towards homo and heterometallic coordination polymers and metal catalysts immobilized on polymers.[5] However, the incorporation of multiple metal sites into a single polymer support is quite rare.[5d,6] Even less common are polymers functionalized with metals complexes at preselected positions in an exactly predetermined sequence. This is largely due to the generally employed "post-synthesis" strategy where the metal centers are introduced after polymer formation.

N-heterocyclic carbene (NHC) complexes have attracted considerable attention over the last two decades owning to their high stability and outstanding applications in homogeneous catalysis.[7] We developed an interest in the immobilization and modification of NHC-metal catalysts with the dual purpose of creating a reactive environment for effective catalysis and of facilitating the recovery of the catalyst.[8]

As an extension of this chemistry we envisioned the preparation of polymers featuring two different NHC-M tethers arranged in an alternating and constantly spaced fashion at the polymer backbone. Such derivatives are potentially very useful as they might function as bifunctional heterometallic catalysts while at the same time offering the possibility of facile catalyst recovery. The strictly alternating metallation of a polymer with two different metal complexes is rather difficult and has not been demonstrated yet. For the preparation of such polymers we have developed a new synthetic methodology based on a "bottom-up" strategy.[9] This strategy involves the synthesis of azide and ethynyl functionalized NHC-metal complex monomers **A** and **B** as secondary building units (SBUs) which are subsequently joined together to form the polymer by classical click chemistry.[10] This approach guarantees the desired strictly equidistant and alternating sequence of the metal complexes tethered to the polymer (Scheme 1). While the click polymerization of various organic alkynes and azides has been demonstrated,[10] this synthetic approach has not yet been used for the preparation of metal-complex-tethered polymers.

Four monometallic NHC-metal building blocks **1**–**4** (SBUs, Scheme 2) were used for the preparation of the



Scheme 1. Click preparation of polymeric catalysts alternatingly functionalized with two different NHC-metal complexes.

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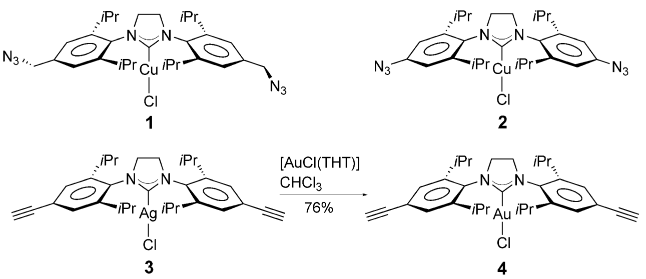


Scheme 2. Complexes **1** and **2** bearing phenylazide wingtips and NHC-silver(I) (**3**) and NHC-gold(I) (**4**) complexes with phenylethynyl wingtips.

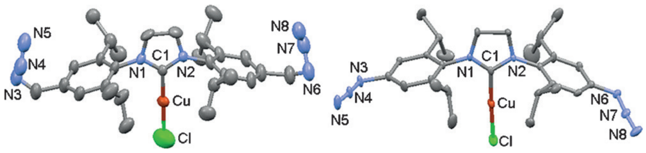


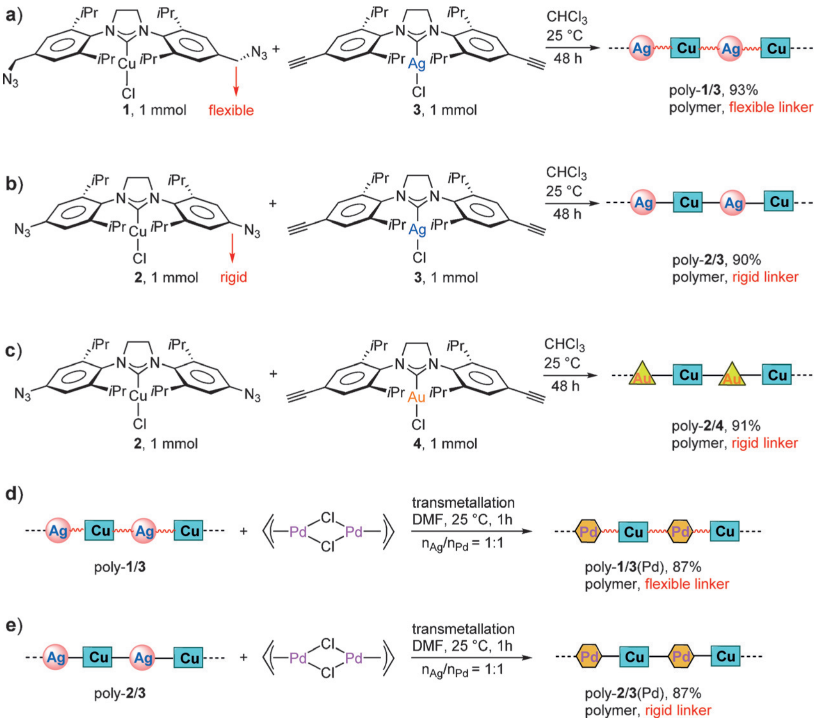
Figure 1. Molecular structure of complexes **1** (left) and **2** (right, thermal ellipsoids set at 30% probability, hydrogen atoms have been omitted for clarity).

polymeric catalysts. Two of these are NHC-copper(I) complexes functionalized with *p*-azidophenyl groups as NHC wingtips (**1** and **2**) while the other two are NHC-silver(I) (**3**) and NHC-gold(I) (**4**) complexes featuring *p*-ethynylphenyl NHC wingtips. Complexes **1** and **2** were obtained by the reaction of CuCl with the suitable imidazolidinium salts in the presence of 1.0 equivalent of $NaOCH_3$ in methanol (see the Supporting Information, Scheme S1).[11a,d,e] In these complexes, the azide groups are attached either directly (**2**) or via a flexible methylene linker (**1**) to the aromatic ring. NHC-gold(I) complex **4** was obtained by transmetalation of the NHC ligand from silver(I) complex **3**[11b] to [AuCl(THT)] (THT = tetrahydrothiophene, see the Supporting Information, Scheme S2).[11c] Note that NHC-Pd^{II} complexes as SBUs cannot be obtained by transmetallation from **3** to the allylpalladium(II) chloride dimer as this method leads to the formation of palladium black as a result of Pd^{II} reduction by the terminal alkyne groups.

Formation of complexes **1**–**4** was confirmed by NMR spectroscopy showing the resonances for the C_{NHC} carbon atoms in the expected ranges of $\delta = 203.5$ ppm (Cu–C_{NHC} for **2**),[11a] $\delta = 206.7$ ppm (Ag–C_{NHC})[11b], and $\delta = 196.3$ ppm (Au–C_{NHC})[11c] and by X-ray diffraction studies with **1** and **2** (Figure 1, see also the Supporting Information).[12] Comparable metric parameters found in **1** and **2** fall in the range previously observed for related NHC-copper(I) complexes.[11a]

With the azide-tagged NHC-Cu^{I} (**1**, **2**) and ethynyl-tagged NHC-Ag^{I} (**3**) and NHC-Au^{I} (**4**) SBUs in hand, the preparation of polymers tethered with alternating metal sites was attempted. Reaction of equimolar amounts of the SBUs **1** with **3**, **2** with **3**, or **2** with **4** yielded the polymers poly-**1**/**3**, poly-**2**/**3**, and poly-**2**/**4** by click chemistry in yields of 90–93% (Scheme 3). The polymerizations proceeded at ambient temperature and no additional polymerization catalyst was needed owing to the catalytic activity of the copper(I) containing SBUs **1** and **2**.[10] While a Pd^{II} containing SBU similar to **3** could not be prepared by transmetallation owing to reduction of the Pd^{II} by the terminal alkyne, the Cu/Pd tethered polymers poly-**1**/**3**(Pd) and poly-**2**/**3**(Pd) were obtained in good yield of 87% by transmetallation of the Cu/Ag polymers (poly-**1**/**3** or poly-**2**/**3**, no alkyne present anymore) with allylpalladium(II) chloride dimer[13] (Scheme 3, see also the Supporting Information).

Owing to their linear structure, the heterometallic polymers are highly soluble in DMF. They have been characterized by NMR spectroscopy showing the typical resonance signals for the polymeric backbone ($\delta \approx 9.1$–9.7 ppm, C–H triazole) and, in selected cases, the C_{NHC} resonances ($\delta(C_{\text{NHC}}) = 201.8$ for poly-**1**/**3**, only one resonance detected; $\delta(C_{\text{NHC}}) = 197.9$ and 194.7 for poly-**2**/**4**). The problems in detecting selected C_{NHC} resonances are possibly due to the polymeric nature of the compounds and in accord with previous reports on coinage metal NHC complexes.[11] In addition, elemental analyses and AAS spectrometry (for metal content) confirmed the formation of the polymers (see the Supporting Information, Table S2). Gel permeation chromatography (GPC) was employed to determine the molecular weight of the polymers (see the Supporting



Scheme 3. Preparation of metallated polymers with alternating metal centers by click polymerization from SBUs (a–c) and transmetallation (d, e).

Information, Figure S1 and Table S1). The click polymerization resulted in heterometallic polymers with high molecular weights (MW) in the range of 20–30 kDa and a relatively narrow MW distribution. The high MW and relatively low polydispersity index (PDI) are particularly gratifying since the polymers are presumably formed in a step-growth polymerization process. Note that polymers poly-**1**/**3** and **1**/**3**(Pd) feature a flexible methylene linker in between the NHC ligands while the other polymers are linked by a more rigid linker.

While metal-NHC containing polymers have been described, they are either formed by coordination of rigid benzobiscarbenes to selected metals or by the metalation of polymeric polyazolium salts.[14] These methods offer no control regarding the type of metals or their sequence in the polymer and are in these regards inferior to our click polymerization of metal complex SBUs.

In an attempt to illustrate the efficiency and versatility of the SBU coupling procedure, NHC complexes **5** and **6** bearing only one wingtip substituent each (azide or ethynyl) for click coupling were prepared from the monofunctionalized imidazolidinum salts (Scheme 4). They were fully characterized by NMR spectroscopy and X-ray diffraction studies (Figure 2, see also the Supporting Information).[12] The monofunctionalized building blocks **5** and **6** were used for the preparation of the dinuclear heterobimetallic complex **7** via a click reaction (Scheme 4a). Transmetallation of **7** with $[PdCl(allyl)]_2$ gave the heterobimetallic Cu/Pd complex **8**.

Reaction of the doubly azide-functionalized copper complex **1** with the mono-ethylnyl functionalized complex **5** gave the trinuclear Ag/Cu/Ag-NHC complex **9** which reacts with $[PdCl(allyl)]_2$ in a transmetallation reaction to give the trinuclear Pd/Cu/Pd complex **10** (Scheme 4b). The molecular heterobimetallic complexes **7**–**10** have been characterized by NMR spectroscopy und ESI HRMS spectrometry (see the Supporting Information). The molecular heterobimetallic complexes are fragments of the polymers poly-**1**/**3** and poly-**1**/**3**(Pd) featuring a flexible linker (Scheme 3). Their synthesis demonstrates once more the versatility of the SBU/click procedure. In addition, the molecular complexes constitute a useful addition to the toolbox for subsequent catalytic investigations.

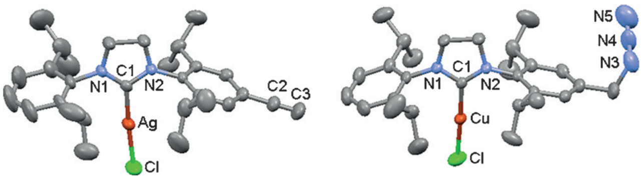
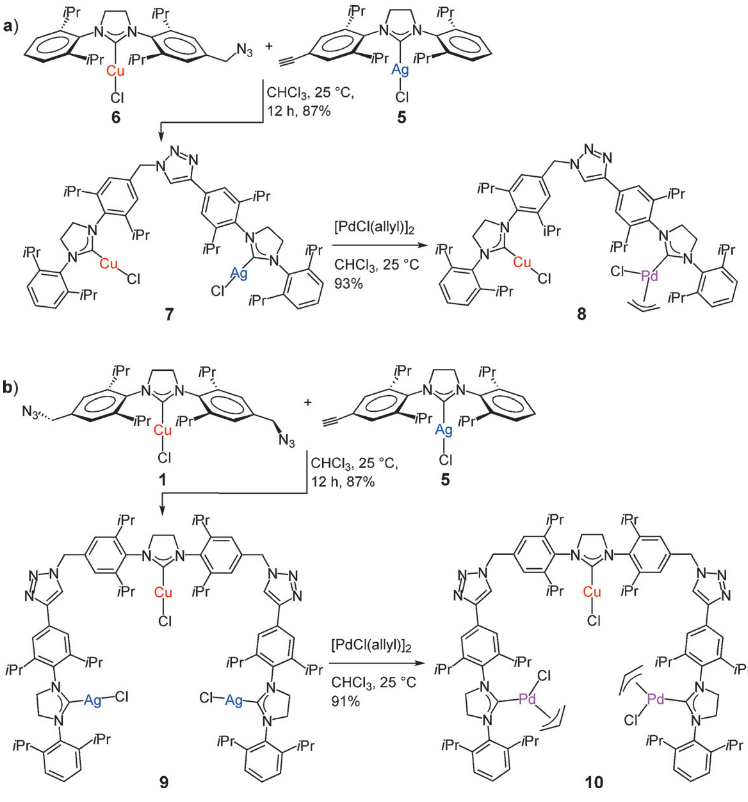


Figure 2. Molecular structure of complexes **5** (left) and **6** (right, thermal ellipsoids set at 30% probability, hydrogen atoms have been omitted for clarity).



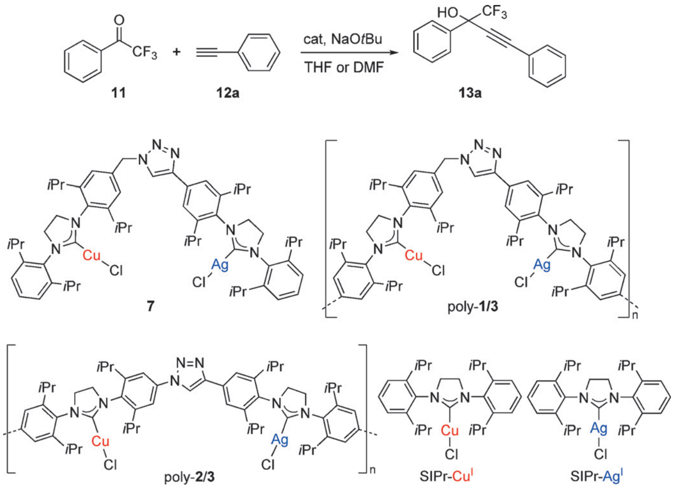
Scheme 4. Synthetic routes to heterodinulear and heterotrinclear complexes.

The catalytic alkynylation of trifluoromethyl ketones to give fluorinated propargylic alcohols is an important reaction in organic synthesis, pharmaceutical science, and organofluorine chemistry.[15] Copper complexes have been shown to catalyze this reaction via the formation of Cu–alkyne intermediates.[15a,16] We assumed that Lewis acids, such as silver-NHC complexes, could support the catalytic alkynylation via an activation of the carbonyl group of the trifluoromethyl ketone. For a cooperative Cu/Ag catalysis the copper and silver metal centers would have to be located in close proximity to allow the concurrent activation and reaction/activation of the alkyne and the trifluoromethyl ketone. Such a situation exists in the dinuclear, flexibly linked molecular complex **7** and the polymers poly-**1**/**3** and poly-**2**/**3** described above. We therefore studied the catalytic activity of these derivatives in the catalytic alkynylation of 2,2,2-trifluoro-1-phenylethanone with phenylacetylene.

The dinuclear complex **7** represents a fragment of the polymer poly-**1**/**3** (Scheme 3) featuring a flexible methylene-triazole linker between the NHC donors. It is freely soluble in THF and DMF and was first used as a catalyst in the homogeneous catalytic alkynylation of 2,2,2-trifluoro-1-phenylethanone (**11**) with phenylacetylene (**12a**). As shown in Table 1, the use of 1.0 mol% or 0.5 mol% of **7** in THF resulted in almost quantitative yields of the fluorinated propargylic alcohol **13a** within 16 h (TON of 97 and 192, respectively). Reduction of the amount of catalyst to 0.3 mol% led to 62% yield in THF and a slightly lower yield in DMF (Table 1, entries 1–4).

Since compounds poly-**1**/**3** and poly-**2**/**3** are highly soluble in DMF they were used as catalysts in this solvent for the alkynylation of 2,2,2-

Table 1: Catalytic alkynylation of 2,2,2-trifluoro-1-phenylethanone **11** with phenylacetylene **12a** using different catalysts.[a]



Entry	Catalyst	Loading (mol %)	Yield [%][c]	TON
1	**7**	1	97	97
2	**7**	0.5	96	192
3	**7**	0.3	62	207
4	**7**[b]	0.3	55	183
5	poly-**1**/**3**[b]	0.5	95	190
6	poly-**1**/**3**[b]	0.3	61	203
7	poly-**2**/**3**[b]	0.5	67	134
8	SIPr-Cu^{I}	0.5	18	36
9	SIPr-Cu^{I}[b]	0.5	10	20
10	SIPr-Ag^{I}	0.5	21	42
11	SIPr-Ag^{I}[b]	0.5	17	34
12	SIPr-Cu^{I} + SIPr-Ag^{I}	0.5 + 0.5	65	65
13	SIPr-Cu^{I} + SIPr-Ag^{I}[b]	0.5 + 0.5	39	39

[a] Reaction conditions: 2,2,2-trifluoro-1-phenylethanone (1.0 mmol), phenylacetylene (2.0 mmol), NaO*t*Bu (2 mol %), 1 mL THF, $T = 50$ °C, $t = 16$ h. [b] 1 mL DMF instead of 1 mL THF. [c] Determined by GC analysis with tridecane as an internal standard.

trifluoro-1-phenylethanone. Metal polymer poly-**1**/**3** proved to be a very active catalyst. When used in a concentration of 0.5 mol % (this number was calculated from the weight% of copper in the polymer, which is 5.41 %) compound **13a** was obtained in 95 % yield (TON = 190). Reduction of the catalyst loading to 0.3 mol % yielded **13a** in 61 % yield with a TON of 203 (Table 1, entries 5–6). The catalytic reaction in THF produced only trace amounts of **13a** owing to the poor solubility of poly-**1**/**3** in this solvent thus verifying the homogenous nature of the catalytic reaction.

Both of the most active catalysts, **7** and poly-**1**/**3**, feature a flexible linker between metal-NHC groups potentially enabling a close approach of two neighboring Cu and Ag centers and thus some cooperative interaction. Contrary to this situation, metal-polymer poly-**2**/**3** contains a rigid triazole linker. The catalytic performance of this polymer was lower in the test reaction compared to poly-**1**/**3** under otherwise identical conditions (entry 7). Apparently, the flexible linker is beneficial for an optimal catalytic performance. This would indicate the presence of some synergism between the metal centers in the catalytic action of poly-**1**/**3** which due to geometric constraints is absent in poly-**2**/**3**.

In addition, we studied the catalytic activity of the mononuclear complexes SIPr-Cu^{I}, SIPr-Ag^{I} and a 1:1 mixture of these complexes (Table 1, entries 8–13). In all cases and both in THF or DMF a much lower catalytic activity of these complexes or mixtures of them was observed compared to **7** or poly-**1**/**3**.

A plot of the GC yield versus reaction time for the six catalysts tested in shown in Figure 3. This plot nicely illustrates the significant differences in the catalytic activities. The lowest yields were observed for the individual mononuclear catalysts SIPr-Cu^{I} and SIPr-Ag^{I}. If complexes SIPr-Cu^{I} and SIPr-Ag^{I} were used as a 1:1 mixture, the resulting yield corresponds well to the one obtained with the rigidly bridged metalpolymer poly-**2**/**3** as a catalyst. The highest catalytic activity was observed for the flexibly bridged complex **7** and the metalpolymer poly-**1**/**3**. These data indicate to us that indeed cooperative effects exist for the flexibly linked catalysts which enable the NHC-Cu and NHC-Ag metal centers to approach each other. To our knowledge, the Cu/Ag bimetallic molecular complex **7** and the polymeric compound poly-**1**/**3** are the most active catalysts reported to date for the alkynylation of trifluoromethyl ketones.

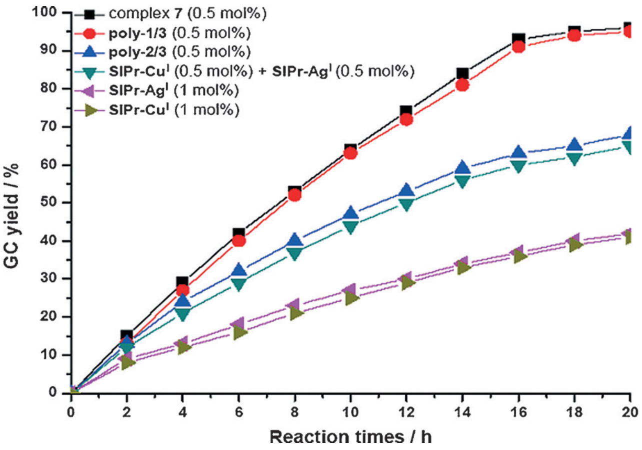
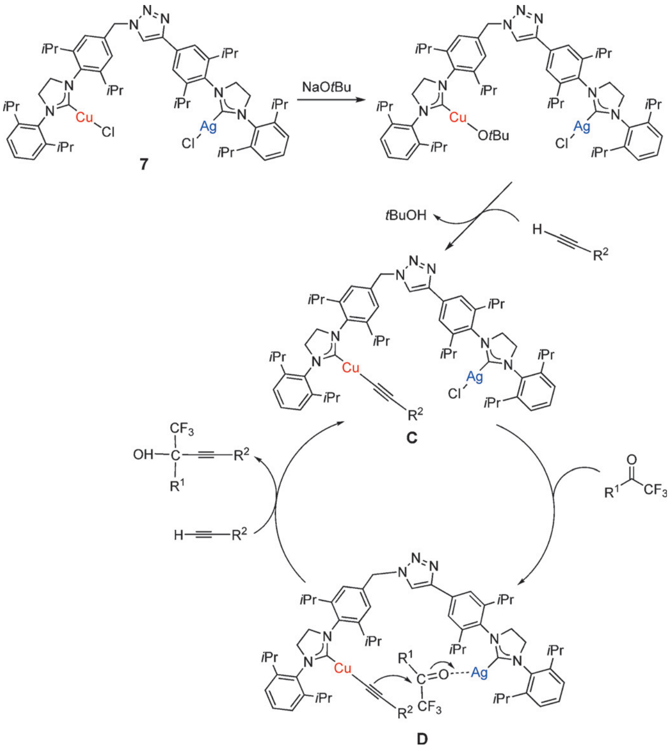


Figure 3. Reaction profile for the catalytic alkynylation of 2,2,2-trifluoro-1-phenyletanone with phenylacetylene using different catalyst.

Apart from the model reaction (2,2,2-trifluoro-1-phenylethanone plus phenylacetylene) we have studied the substrate scope of the catalytic reaction. Terminal alkynes with electron-donating or electron-withdrawing groups as well as alkyl alkynes afforded good yields of fluorinated propargyl alcohols in the presence of the dinuclear catalyst **7** or the metal polymer poly-**1**/**3**. For all substrates a mixture of SIPr-Cu^{I} and SiPr-Ag^{I} complexes was also examined but the yields were always significantly lower than those obtained for the heterobimetallic catalysts **7** or poly-**1**/**3**. The results are summarized in the Supporting Information, Figure S3. These results indicate once more that some catalytic cooperativity between the NHC-Cu and NHC-Ag units in **7** and poly-**1**/**3** exists.

Based on our observations and in accord with literature reports[15,16] we propose the reaction mechanism depicted in Scheme 5 for the cooperative catalytic alkynylation of



Scheme 5. Proposed mechanism for the cooperative catalytic alkynylation of trifluoromethyl ketones using the bimetallic Cu/Ag-complex **7**.

trifluoromethyl ketones. Previously, it has been shown that an NHC-Cu^I center in the presence of a base activates terminal alkynes with formation of a copper–acetylide intermediate **C**. The neighboring NHC-Ag^I center can then act as a Lewis acid and interacts with the carbonyl group of the trifluoromethyl ketone to give **D**. This double activation of two substrate molecules in close proximity will facilitate the subsequent nucleophilic addition of the acetylide to the carbonyl group. Following the formation of the new C−C bond, the catalyst is regenerated by a metathesis reaction with an acetylene molecule.

Taking advantage of click chemistry, we have developed a novel, highly efficient synthetic route leading to molecular heterobimetallic complexes **7**–**10** or sequentially metallated heterobimetallic polymers poly-**1**/**3**–poly-**2**(Pd)/**3**. The novel compounds were obtained by the reaction of task-specific mononuclear metal complexes (secondary building units, SBUs) bearing NHCs functionalized with either *p*-azidophenyl or *p*-ethynylphenyl wingtips. As long as one of the SBUs is an NHC-copper complex, the synthesis of molecular or polymeric compounds by click chemistry did not require any additives as the copper complex also catalyzes the click reaction. Anhydrous conditions or an inert atmosphere are also not necessary and the work-up procedure is rather simple. The molecular and polymeric heterobimetallic derivatives have been investigated regarding their catalytic activity in the alkynylation of trifluoromethyl ketones to give fluorinated propargylic alcohols. The heterobimetallic polymer poly-**1**/**3** featuring alternating NHC-copper and NHC-silver units and a flexible methylene-triazole bridge between them show the highest catalytic activity. Control experiments using a very similar polymer with a rigid linker between the NHC-copper and NHC-silver units (poly-**2**/**3**) or with 1:1 mixtures of mononuclear NHC-Cu^I and NHC-Ag^I complexes produced lower yields of propargylic alcohols. Linkage of the two NHC-metal complex fragments with a flexible linker in such a way, that the metal centers can approach each other appears greatly beneficial for the outcome of the catalytic reaction. Similar observations were made with flexibly methylene-triazole bridged molecular NHC-Cu^I/NHC-Ag^I complex **7** and mixtures of mononuclear NHC-Cu^I NHC-Ag^I complexes where the flexible linkage of the two NHC-metal centers again proved beneficial for the catalytic outcome. A reaction mechanism for the alkynylation of trifluoromethyl ketones based on a cooperative substrate activation is proposed based on these observations. Efforts towards the synthesis of new heterobimetallic tagged molecular compounds and polymers by click linkage of suitable SBUs are currently in progress.

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