Dalton Transactions

PAPER



Cite this: DOI: 10.1039/c6dt04513h

Received 29th November 2016,

Accepted 19th December 2016

DOI: 10.1039/c6dt04513h

www.rsc.org/dalton

Hydrophenoxylation of internal alkynes catalysed with a heterobimetallic Cu-NHC/Au-NHC system[†]

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A straightforward method for the hydrophenoxylation of internal alkynes, using N-heterocyclic carbenebased copper(i) and gold(i) complexes, is described. The heterobimetallic catalytic system proceeds *via* dual activation of the substrates to afford the desired vinylether derivatives. This methodology is shown to be highly efficient and tolerates a wide range of substituted phenols and alkynes.

Introduction

The functionalisation of alkynes is a critical transformation in synthetic chemistry leading to key building blocks.¹⁻⁹ The use of late transition-metal complexes has been widely investigated in such transformations, allowing the formation of C-N, C-O, C-S and C-B bonds.¹⁻⁹ Recently, attention has focused on C-O bond formation, through hydroalkoxylation and hydrophenoxvlation reactions.¹⁰⁻⁴⁰ The hydroalkoxylation reaction has been widely studied and several metal complexes consisting mainly of Cu,¹¹ Ru,¹²⁻¹⁶ Pd,^{17,18} Au,¹⁹⁻²⁵ Zn,²⁶ Pt,²⁷⁻²⁹ Ir³⁰ and Rh³¹ have been reported as catalysts. As for the hydrophenoxylation of alkynes, reports remain scarce, especially in the case of nonactivated internal alkynes.³²⁻³⁸ Yamamoto reported the first example in 2002, using a Pd(0) complex.³² Sahoo and coworkers achieved a significant breakthrough when they reported on a gold(III)/phosphine system.33 More recently, based on the discovery of a digold hydroxide species,³⁶ Nolan and co-workers have developed a novel methodology permitting access to vinylether derivatives.37 This methodology was later applied to access benzo[c]chromenes and benzo[b]furans through a one-pot [Au]/[Pd]-catalysed process.³⁸ More recently, the mechanism of this reaction was elucidated (Scheme 1).^{39,40} These mechanistic studies clearly showed that gold performs a dual role in this transformation, highlighting the need for two gold centres acting in synergy.41 It was proposed that the digold hydroxide Ia was in equilibrium with the gold hydroxide II and cationic gold species III. Species II activated the phenol

Scheme 1 Intermediates in the digold-catalysed hydrophenoxylation.^{37–40} IPr = N,N'-bis-[2,6-(di-iso-propyl)phenyl]imidazol-2-ylidene.

to generate species **IV**, whilst **III** activated the alkyne to afford **V**. The coupling of both intermediates (**IV** and **V**) was followed by protonation to afford the desired hydrophenoxylation product.

Based on these observations, we reasoned that a more costeffective method for the hydrophenoxylation of alkynes could be developed using a different bimetallic catalytic system. To this end, gold species **II** could be substituted by [Cu(OH) (IPr)]⁴² (1) and gold species **III** could be generated from a cationic gold precursor. In this context, we now report the hydrophenoxylation of alkynes *via* a dual activation process, using a heterobimetallic system consisting of Cu(i)- and Au(i)-NHC (NHC = N-heterocyclic carbene) complexes, under mild and solvent-free conditions. The use of a simple copper complex as a gold surrogate for activation of one substrate in the addition reaction further supports the dual activation mechanism previously described for the gold-only mediated hydrophenoxylation of alkynes.

Results and discussion

Initial testing consisted of using [Cu(OH)(IPr)], **1**, and two gold complexes; $[Au(OTf)(IPr)]^{43}$ (**2**, OTf = trifluoromethanesulfonate) and $[Au(NTf_2)(IPr)]^{44}$ (**3**, NTf₂ = bis(trifluoromethan-



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[†]Electronic supplementary information (ESI) available: Detailed synthetic and mechanistic procedures, full characterisation details for new complexes and catalytic reactions. See DOI: 10.1039/c6dt04513h



Fig. 1 Catalysts used in this study.

esulfonyl)amide) (Fig. 1). The strategy makes use of the copper hydroxide synthon **1** to activate the phenolic substrate while the cationic gold species concomitantly activates the alkyne.

Diphenylacetylene and phenol were selected as model substrates for the initial investigation (Table 1). Using 1 mol% of 1 and 1 mol% of 2, full conversion to the desired product was achieved after 16 hours (Table 1, entry 1). When the loading of each catalyst was decreased to 0.2 mol%, significant loss of efficiency was observed (Table 1, entries 2 and 3). Solvents such as acetonitrile, CPME (CPME = cyclopentyl methyl ether) or DMSO (DMSO = dimethyl sulfoxide) led to no or low catalytic activity, whereas the use of benzene afforded a 53% conversion (Table 1, entries 4–7). The most interesting result was obtained when no solvent was used (Table 1, entry 8). Indeed, under solvent-free conditions, the hydrophenoxylation product

 Table 1
 Influence of temperature and solvent on the catalytic activity^a

4a 5a 6aa

Catalyst	Loading (mol%)	Solvent	Temp. (°C)	$\begin{array}{c} \text{Conv.}^{b} \\ (\%) \end{array}$
1 + 2	1	Toluene	80	>99
1 + 2	0.5	Toluene	80	83
1 + 2	0.2	Toluene	80	30
1 + 2	0.2	Acetonitrile	80	0
1 + 2	0.2	DMSO	80	0
1 + 2	0.2	CPME	80	6
1 + 2	0.2	Benzene	80	53
1 + 2	0.2	_	80	97
1 + 2	0.1	_	80	69
1 + 3	0.1	_	80	9
1	0.2	_	80	0
2	0.2	_	80	2
3	0.2	—	80	3
1 + 2	0.2	—	60	>99 (99) ^c
1 + 2	0.2	—	40	74
1 + 2	0.1	—	60	64
1 + 2	0.5	—	60	$>99^{d}$
Ia	0.5	—	80	>99 ^e
Ib	0.5	Toluene	80	60
2	0.2	—	60	<3
	Catalyst 1 + 2 1 + 3 1 2 3 1 + 2 1 = 2 1 + 2 1 = 2 2 1 = 2 1 = 2 2 1 = 2 1 = 2 2 2 1 = 2 2 2 2 2 2 2 2	$\begin{array}{c cccc} & \text{Loading} \\ \hline \text{Catalyst} & (mol\%) \\ \hline 1 + 2 & 1 \\ 1 + 2 & 0.5 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.1 \\ 1 + 3 & 0.1 \\ 1 & 0.2 \\ 2 & 0.2 \\ 3 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.2 \\ 1 + 2 & 0.1 \\ 1 + 2 & 0.5 \\ 1 + 2 & 0.5 \\ 1 a & 0.5 \\ 1 b & 0.5 \\ 2 & 0.2 \\ \end{array}$	Loading (mol%)Catalyst(mol%)Solvent $1 + 2$ 1Toluene $1 + 2$ 0.5Toluene $1 + 2$ 0.2Toluene $1 + 2$ 0.2DMSO $1 + 2$ 0.2DMSO $1 + 2$ 0.2CPME $1 + 2$ 0.2Benzene $1 + 2$ 0.2 $1 + 2$ 0.1 $1 + 2$ 0.1 $1 + 3$ 0.1 $1 + 2$ 0.2 3 0.2 $1 + 2$ 0.2 $1 + 2$ 0.2 $1 + 2$ 0.5 $1 + 2$ 0.5 $1 = 0.5$ <td>Loading CatalystTolueng (mol%)Toluene SolventRemp. (°C)$1+2$1Toluene80$1+2$0.5Toluene80$1+2$0.2Toluene80$1+2$0.2DMSO80$1+2$0.2DMSO80$1+2$0.2CPME80$1+2$0.2Benzene80$1+2$0.2-80$1+2$0.2-80$1+2$0.1-80$1+3$0.1-80$1$0.2-80$1+2$0.2-60$1+2$0.2-60$1+2$0.2-60$1+2$0.5-60$1+2$0.5-80$1+2$0.5-80$2$0.5-60</td>	Loading CatalystTolueng (mol%)Toluene SolventRemp. (°C) $1+2$ 1Toluene80 $1+2$ 0.5Toluene80 $1+2$ 0.2Toluene80 $1+2$ 0.2DMSO80 $1+2$ 0.2DMSO80 $1+2$ 0.2CPME80 $1+2$ 0.2Benzene80 $1+2$ 0.2-80 $1+2$ 0.2-80 $1+2$ 0.1-80 $1+3$ 0.1-80 1 0.2-80 $1+2$ 0.2-60 $1+2$ 0.2-60 $1+2$ 0.2-60 $1+2$ 0.5-60 $1+2$ 0.5-80 $1+2$ 0.5-80 2 0.5-60

^{*a*} Reaction conditions: diphenylacetylene (0.5 mmol), phenol (0.6 mmol), [Cu(OH)(IPr)]/[Au(OTf)(IPr)] (1 + 2) or $[Cu(OH)(IPr)]/[Au(NTf_2)(IPr)]$ (1 + 3) (0.1–1 mol%), solvent (1 mL) or solvent-free, 16 h, under argon. ^{*b*} Determined by GC, relative to diphenylacetylene, average of two reactions. ^{*c*} Isolated yield in parentheses. ^{*d*} Full conversion reached after 35 minutes. ^{*e*} Full conversion reached after 1 hour.

6aa was obtained with 97% conversion. Thus, further optimisation was carried out under solvent-free conditions. Decreasing the catalytic loading of both catalysts to 0.1 mol% significantly lowered the conversion (Table 1, entry 9). Interestingly, the use of complex 3 instead of 2 afforded only 9% conversion, indicating that the counterion plays an important role in this reaction (Table 1, entry 10).³⁹ When [Cu(OH) (IPr)], 1, was used, in the absence of gold(1) complex, no catalytic activity was observed and only starting materials were recovered after 16 hours (Table 1, entry 11). Similarly, when only gold(1) complexes (2 or 3) were used, only traces of the desired product were observed (Table 1, entries 12 and 13). These results clearly highlight the need for a bimetallic system in order to effectively perform the targeted dual catalysis. Next, the reaction temperature was varied; the best result was obtained at 60 °C and afforded full conversion after 16 hours, using 0.2 mol% of 1 and 0.2 mol% of 2 (Table 1, entry 14). Of note, lowering either the temperature or the catalyst loading resulted only in a decrease of catalytic activity (Table 1, entries 15 and 16).

It should be mentioned that when the digold analogue, $[{Au(IPr)}_2(\mu-OH)][OTf]$ (Ib), was tested under the same conditions as entry 2 using a catalyst loading of 0.5 mol% (1 mol% of gold), only 60% conversion was observed (Table 1, entry 19). This result strongly highlights the higher efficiency of the heterobimetallic [Cu]/[Au] catalytic system compared to the homobimetallic gold system. Furthermore, in order to compare the present system with literature precedents, the hydrophenoxylation reaction was performed under our optimised conditions and those reported by Nolan and coworkers,³⁷ using the same total amount of catalysts. Interestingly, our conditions afforded full conversion to the desired product 6aa after 35 minutes, using 0.5 mol% of each catalyst (1 and 2) at 60 °C; whereas digold hydroxide Ia only afforded full conversion after 1 hour at 80 °C (Table 1, entries 17 and 18). This result emphasises a synergistic effect of the heterobimetallic system. Although we cannot fully eliminate the possibility of a homobimetallic activation route, the latter data strongly indicate that this pathway is highly unlikely. Finally, when the reaction was performed using gold catalyst 2, only traces of the desired product were observed (<3%), further demonstrating the need for a bimetallic system (Table 1, entry 20).

Kinetic profiling of this transformation under the optimal conditions (Table 1, entry 14) showed that, whilst the reaction progresses slightly faster under argon, completion is also reached within 7 hours under aerobic conditions (see the ESI†). This result showcases the stability of the catalytic system in air.

A substrate scope study was undertaken next to demonstrate the versatility of the heterobimetallic system (Scheme 2). Phenols bearing various functional groups were first screened in the presence of diphenylacetylene as the alkyne substrate. *para*-Substituted phenols bearing electron-donating groups (EDGs), such as OMe and Me, underwent the desired transformation without any loss in efficiency and both products



Scheme 2 Reaction scope of the hydrophenoxylation reaction catalysed by a [Cu]/[Au] bimetallic system; variation of the phenol. Reaction conditions: alkyne (0.5 mmol), Ar–OH (0.6 mmol), [Cu(OH)(IPr)]/ [Au(OTf)(IPr)] (1:1) (0.2/0.2 mol%), solvent-free, 16 h, 60 °C, under Ar. Conversion determined by GC based on the alkyne; minimum average of 2 reactions. Isolated yield in parentheses. ^a 0.4 mol% of both catalysts.

(6ab and 6ac) were isolated in 99% yield. Interestingly, phenols bearing *para*-substituted B(pin) (pin = pinacolato) and fluoro-groups were also successfully transformed under our conditions, affording the desired products 6ad and 6ae in good isolated yields (78% and 96%, respectively). The case of B(pin)-substituted phenol represents an attractive feature as it could allow further functionalisation in possible tandem reactions.⁴⁵ In contrast, phenols bearing electron-withdrawing groups (EWGs), such as the weakly deactivating Cl group and moderate to strong deactivating groups (C(O)H, C(O)Me, CN and NO₂), afforded low conversion to the desired products. To overcome this problem, the catalyst loading was increased to 0.4 mol%; under these conditions, the desired products 6af, 6ag, 6ah, 6aj and 6ak were obtained in good to excellent yields. Interestingly, 6ai, bearing a moderately deactivating group (C(O)OMe), was obtained in good yield (68%), using only 0.2 mol% catalyst loading. meta- and ortho-Substituted phenols were also screened under these conditions. Following the same trend as before, meta-substituted methyl- and fluorophenols (5l and 5m) as well as ortho-substituted methylphenol (50) performed very well under our optimal conditions, affording the desired products 6al, 6am and 6ao in 95%, 85% and 81% isolated yields, respectively. Similarly, meta- and ortho-substituted chlorophenols (5n and 5r) only afforded high conversions when the catalyst loading was increased to

0.4 mol%; under these conditions, the desired products 6an and 6ar were obtained in good isolated yields (96% and 89%, respectively). ortho-Substituted phenyl- and allylphenols (5p and 5q) also needed 0.4 mol% catalyst loading to afford good isolated yields of the desired products (6ap, 79%; 6aq, 75%), presumably for steric reasons. meta-Disubstituted 3,5-xylenol (5s) also performed well under our conditions, affording the desired product 6as in excellent isolated yield (96%). However, when ortho-disubstituted 2,6-xylenol (5t) was used, a significant decrease in reaction efficiency was observed and the desired product 6at was only obtained in moderate yield (46%), using 0.4 mol% catalyst loading. Considering the high steric hindrance induced by phenol 5t, this last example still constitutes an impressive result for this heterobimetallic catalytic system. Finally, 2-naphthol was subjected to the optimal reaction conditions, affording the desired product 6au in 81% isolated yield.

Next the alkyne substrate was varied (Scheme 3). A number of symmetrical and unsymmetrical alkyne derivatives, bearing alkyl, aryl and heteroaryl groups, successfully underwent conversion under our reaction conditions to afford moderate to very good isolated yields of the products. When 3-hexyne (**4b**) was used, the desired product **6ba** was obtained in very good yield (90%), thus further underlining the versatility of such a methodology. In all cases where unsymmetrical alkynes were used, moderate to good yields were obtained; however, a mixture of Z/Z' (**6ca-ja/6'ca-ja**) was always observed with a ratio varying from 7:3 to 2:8.

A mechanism operating *via* a dual activation process is proposed and illustrated in Scheme 4, based on recent reports by Nolan and co-workers (Scheme 1)^{37–40} and our own mechanistic investigations (Schemes 5–7).



Scheme 3 Reaction scope of the hydrophenoxylation reaction catalysed by a [Cu]/[Au] bimetallic system; variation of the alkyne. Reaction conditions: alkyne (0.5 mmol), phenol (0.6 mmol), [Cu(OH)(IPr)]/ [Au(OTf)(IPr)] (1:1) (0.2/0.2 mol%), solvent-free, 16 h, 60 °C, under Ar. Isolated yields are given; Z/Z' ratio in parentheses is determined by ¹H NMR. ^a Isolated yield of each isomer.



Scheme 4 Proposed mechanism for the hydrophenoxylation of alkynes.



 $\label{eq:scheme 5} \begin{array}{l} \mbox{Scheme 5} & \mbox{Stoichiometric tests to elucidate the reaction mechanism;} \\ \mbox{formation of F and G.} \end{array}$



Scheme 6 Stoichiometric tests to elucidate the reaction mechanism; establishing the equilibrium in Mixture A and Mixture B.

As shown in Scheme 5, phenol 5a only reacts with copper hydroxide 1 to afford copper phenoxide F, whilst diphenylacetylene 4a only reacts with gold species 2 to afford intermediate G.



Scheme 7 Stoichiometric tests to elucidate the reaction mechanism; confirming the involvement of intermediate species F and G in the catalytic cycle.

Similarly to the reports on the digold hydroxide species Ia (Scheme 1),³⁷⁻⁴⁰ we suspected an equilibrium between species (1 + 2) and (A + B) via intermediate C. Indeed, upon mixing complexes 1 and 2, a mixture was obtained (Mixture A. Scheme 6); the same mixture was also obtained upon mixing complexes A and B, highlighting the existence of an equilibrium between these species as proposed in Scheme 4. а similar manner, we observed an equilibrium between species (F + 2) and (B + E), most likely via intermediate D_{3}^{38} upon mixing (F + 2) and (B + E), the same mixture was obtained (Mixture B, Scheme 6). Interestingly, when phenol 5a was added to Mixture A, we observed the formation of Mixture B after 1 hour at 45 °C. The addition of diphenylacetylene 4a to Mixture B delivers a complex reaction blend; however, the formation of the final product 6aa was not observed. Nonetheless, when phenol 5a was added to the latter mixture, product 6aa was finally obtained along with the concurrent formation of Mixture B (Scheme 6).

Furthermore, upon reacting copper complex **F** with intermediate **G**, the same complex reaction mixture as above was obtained; and in a similar fashion, addition of phenol **5a** allowed us to observe the formation of product **6aa** and **Mixture B** (Scheme 7). The same result can be obtained by reacting **F** with **G**, in the presence of phenol under our optimal conditions (solvent-free, at 60 °C for 16 h). Finally, the catalytic involvement of the isolated copper phenoxide **F** was further ascertained by carrying out a catalytic test using 0.2 mol% of **F** and 0.2 mol% of **2** (Scheme 7). Indeed, under the standard conditions, full conversion to **6aa** was obtained.

These observations suggest that the mixture of 1 and 2 (Mixture A) first reacts with phenol 5a to afford Mixture B. The latter enters the catalytic cycle by further reaction with diphenylacetylene 4a to give F and G. Reaction of F and G affords species H, which is in equilibrium with I and (J + B). The addition of phenol (5a) drives the equilibrium towards the formation of the final product 6aa, thus closing the catalytic cycle *via* the concurrent regeneration of Mixture B.

Conclusions

A new dual catalytic process based on a heterobimetallic system, consisting of Cu-NHC and Au-NHC complexes, is reported. The methodology was shown to be highly efficient at low catalyst loading (0.2 mol% of each catalyst), under mild reaction conditions (solvent-free at 60 °C). A wide range of phenol derivatives, bearing electron-donating and electronwithdrawing groups, was successfully converted into vinyl ethers. Various alkynes were also tested and a mixture of Z/Z'isomers was always obtained with unsymmetrical alkynes. Finally, mechanistic studies revealed that both metals play a unique and distinct role in this atom-efficient transformation. Further investigations into the nature of the mixed species involved in the mechanism are ongoing. The use of copper as a gold surrogate in this bimetallic transformation bodes well for the use of this more earth-abundant and less costly metal in related bimetallic transformations.

Acknowledgements

The authors gratefully acknowledge the Royal Society (University Research Fellowship to C. S. J. C) for funding and Umicore for the gift of gold salts.

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