



Cross-coupling reactions of gold(I) alkynyl and polyynediyl complexes

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ABSTRACT

Gold(I) alkynyl complexes are shown to efficiently couple with aryl iodides under mild conditions in the presence of both Pd(II) and Cu(I) co-catalysts. The reaction is not gold catalysed, but rather the Au(I) centre serves to transfer the alkynyl moiety to Cu(I), which then enters the conventional Sonogashira cycles. Using this method, a small range of 1,4-disubstituted diynes, including examples of differentially substituted compounds $\text{ArC}\equiv\text{CC}\equiv\text{CAr}'$, have been prepared directly from $[(\text{Ph}_3\text{P})\text{AuC}\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3)]$ and aryl iodides ArI.

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1. Introduction

Gold salts and complexes have found an important, rapidly increasing and varied role in stoichiometric and catalytic transformations of organic substrates, which often takes advantage of the strong π -acidity of Au(I) and Au(III) species [1–7]. Whilst the use of gold redox couples within catalytic transformations is not as prevalent nor as well established as for other metals [8–12], recent work has established the viability of cross-coupling reactions of gold(III/I) couples in cross-coupling reactions, with an oxidative agent not involved in the cross-coupling process used to return the gold centre to the +III oxidation state [11–18]. When coupled with the propensity of Au complexes to activate different C–H bonds some quite remarkable cross-coupling reactions of otherwise ‘unactivated’ substrates can be achieved (Scheme 1) [19,20].

However, as noted by Hashmi and colleagues [21], the potential for organogold complexes to enter into transmetalation reactions with other metals [22–27] coupled with the rather high redox potential of Au(III) and stability (in the thermodynamic sense) of many Au(I) species opens an alternative use for Au(I) species in synthetic chemistry in which the orthogonal reactivity of the two metals can be utilised to complete otherwise challenging synthetic processes. The well-established isolobal relationship between $[\text{Au}(\text{PPh}_3)]^+$ and H^+ allows further C–H activation chemistry to be

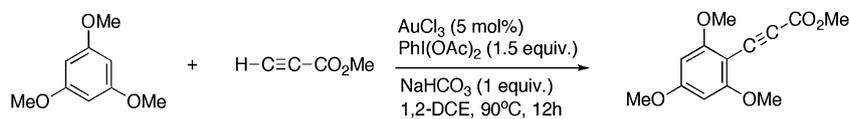
envisioned. Of particular relevance to the present study it must be noted that in addition to the readily formed acetylide derivatives $[\text{Au}(\text{C}\equiv\text{CR})(\text{PPh}_3)]$ [28], the bulky $\{\text{Au}(\text{PPh}_3)\}$ fragment is also able to stabilise terminal alkynes and more highly reactive carbon-containing compounds, including polyynes $\text{H}(\text{C}\equiv\text{C})_n\text{R}$ [29–31] and $\text{H}(\text{C}\equiv\text{C})_n\text{H}$ [32,33] making these linear carbon fragments available for use as cross-coupling partners through their gold synthons.

The use of gold polyynes as reagents in Pd/Cu catalysed Cadiot–Chodkiewicz style cross-coupling reactions with haloalkynes has been shown to be of considerable synthetic utility in the preparation of linear polycarbon chains, including some of substantial length, supported on a variety of organometallic supports (Scheme 2) [34–43]. These reactions generally proceed in moderate to excellent yield in ether-based solvents at ambient temperatures. In this report we describe the use of gold(I) complexes of alkynes and diynes as reagents in the Sonogashira cross-coupling reaction that afford 1,2-di(aryl) acetylenes (tolans) and 1,4-di(aryl)-buta-1,3-diyne. Under the conditions described herein, both Pd(0) and Cu(I) species are necessary to promote the cross-coupling reaction, which is initiated by a transmetalation reaction that transfers the acetylide ligand from Au(I) to Cu(I) and then Pd(II).

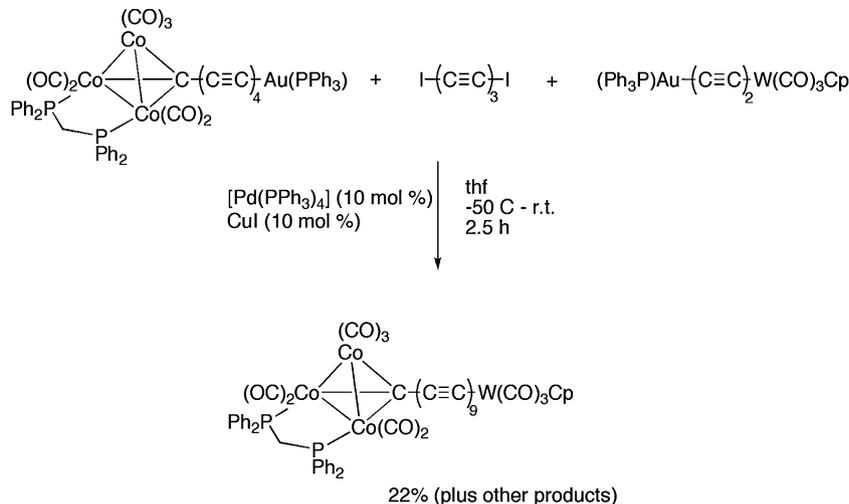
2. Results and discussion

The notion of ‘palladium-free’, gold-catalysed Sonogashira cross-coupling reactions has attracted some attention [44], but very

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Scheme 1. A gold catalyzed cross-coupling of unactivated substrates [19].



Scheme 2. The preparation of a C₁₉ chain from a gold-modified Cadiot–Chodkiewicz coupling reaction [43].

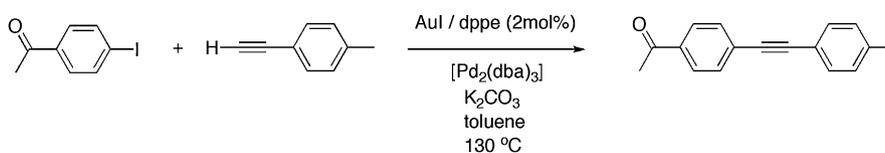
recent re-examination of the conditions suggests that the role of adventitious palladium contamination of the gold salts used in these processes must be considered carefully. Indeed, as little as 0.1 mol % Pd in the form of [Pd₂(dba)₃] and 2 mol% AuI/dppe in the presence of K₂CO₃ can catalyse the cross-coupling reaction of 4-iodoacetophenone with 1-ethynyl-4-methylbenzene (tolylacetylene) in refluxing toluene (Table 1) [45].

Similar results have been obtained from mixed Pd/Au catalyzed cross-coupling reactions of aryl halides [46,47] and arene diazonium salts [48] with terminal alkynes in amine or amine containing solvent mixtures, at temperatures ranging from ambient to the reflux point of the solvent. In each case, no effective coupling was observed in the absence of palladium, and the reactions can be considered as analogues of the conventional Pd/Cu co-catalyzed Sonogashira reaction, with the gold reagent taking the place of the Cu(I) salts more commonly employed. Very recently, pre-formed gold-alkynyl complexes [Au(C≡CAr)(L)] (L = phosphine, Ar = aryl

group) have also been cross-coupled with aryl iodides Ar'-I under 'copper-free' palladium-catalyzed conditions to give the corresponding tolan, Ar-C≡C-Ar', in quantitative yield, albeit under rather forcing conditions (Scheme 3) [45].

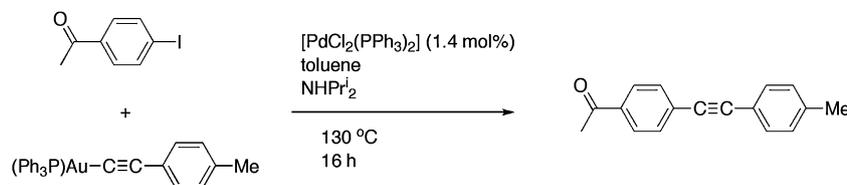
Given the considerably milder conditions under which organometallic halides and gold-alkynyl derivatives enter into cross-coupling reactions in the presence of both Pd(II) and Cu(I) complexes and salts (ether-based solvents, room temperature), a range of simple cross-coupling reactions of [Au(C≡CPh)(PPh₃)] (**1**) were explored. Treatment of **1** with iodo benzene in thf in the presence of [PdCl₂(PPh₃)₂] (1 mol %) and CuI (1 mol %) resulted in complete conversion to diphenylacetylene (tolan) within 2 h at 60 °C. There was no significant conversion in the absence of either of the co-catalysts. The reaction mechanism under these mild conditions therefore likely involves transmetalation of the alkynyl moiety from Au(I) to Cu(I), which then enters the normal Sonogashira cycle. The more activated aryl iodides 4-iodo nitrobenzene

Table 1
The Au^(I)/Pd⁽⁰⁾ catalyzed cross-coupling of 4-iodoacetophenone and tolylacetylene [45].



Pd/mol%	conversion/%	yield/%
–	<2	<2
1.2 × 10 ⁻⁴	6	6
1.2 × 10 ⁻³	16	16
1.2 × 10 ⁻²	24	24
0.12	100	82
1.2	100	78
1.2	<2	<2 ^a

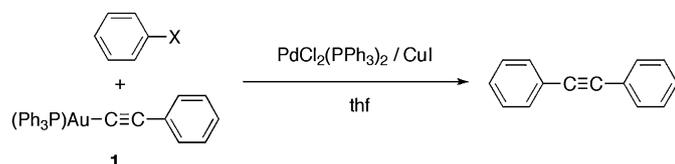
^a Room temperature.



Scheme 3. The palladium-catalysed cross-coupling of 4-iodoacetophenone with a gold(I) alkynyl complex [45].

Table 2

Effect of catalyst and halide on the Sonogashira cross-coupling of **1** with aryl halides.



Ar-X	[Pd] ^a /mol%	CuI/mol%	T/°C	t/h	%conversion
C ₆ H ₅ I	–	5	60	17	–
C ₆ H ₅ I	5	–	60	17	–
C ₆ H ₅ I	1	1	60	2	100
C ₆ H ₅ Br	5	5	60	22	Trace
C ₆ H ₅ Cl	5	5	60	22	–
IC ₆ H ₄ NO ₂	1	1	25	1.5	100
IC ₆ H ₄ CO ₂ Me	1	1	25	1.5	100
IC ₆ H ₄ NH ₂	1	1	25	16	–
IC ₆ H ₄ NH ₂	1	1	60	2	100
IC ₆ H ₄ OMe	1	1	60	2	100
BrC ₆ H ₄ NO ₂	1	1	25	20	–

^a [Pd] = [PdCl₂(PPh₃)₂]

and 4-iodo methylbenzoate smoothly cross-coupled with **1** at 25 °C, and on a preparative scale 1-phenyl-2-(4'-nitrophenyl) acetylene was isolated in 87% yield from **1** and 4-iodo nitrobenzene. Bromobenzene coupled significantly more slowly, at 60 °C, whilst chlorobenzene was essentially an inactive coupling partner: such results fall completely in line with expectation based on the ease of oxidative addition to the palladium catalyst (Table 2). When compared with the conditions summarised in Scheme 3, it can be seen that the introduction of CuI permits the cross-coupling of a gold acetylide with, preferably, and aryl iodide under very mild conditions, in ether-based solvent and without an additional base. Although not generally superior to the 'normal' Sonogashira cross-

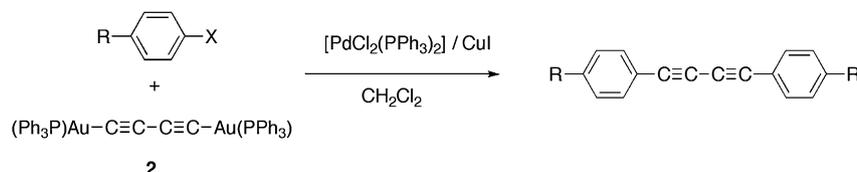
coupling protocol, the conditions described in Table 2 may be useful when attempting to cross-couple aryl halides bearing particularly base-sensitive substituents. Despite the cost differential of gold- and silyl-substituted alkynes, there are also some identifiable advantages in the conditions employed in Table 2 over Nishihara's sila-Sonogashira protocol in terms of the quantity of copper salt necessary to effect the cross-coupling and the use of the lower-boiling thf solvent [49].

With these results in hand, attention was turned to the cross-coupling reactions of the bis(gold) compound [(Ph₃P)AuC≡CC≡CAu(PPh₃)] (**2**). Preparative routes to symmetric 1,4- substituted diynes are commonly based on oxidative homo-coupling reactions of terminal alkynes [50–53], and as such end-group transformations of a pre-formed 1,3-diyne such as **2** offer an interesting alternative reaction sequence.

The bis(gold) reagent **2**, which is readily available from [AuCl(PPh₃)] and Me₃SiC≡CC≡CSiMe₃, was only sparingly soluble in thf, and consequently all reactions with this reagent were carried out in CH₂Cl₂ to ensure homogenous reaction conditions. At room temperature, **2** reacted smoothly and essentially completely with 2 M equivalents of 4-iodonitrobenzene, 4-iodo methyl benzoate and 4-iodo methyl benzene in the presence of 0.5 mol% (per gold equivalent) [PdCl₂(PPh₃)₂] and CuI (Table 3). An entirely analogous reaction with the bis(halide) 4-iodo bromobenzene also proceeded smoothly and with excellent chemoselectivity to afford 1,4-bis(4'-bromophenyl)-buta-1,3-diyne as the only detectable product. Aryl iodides bearing more electron donating groups were also quantitatively converted in [PdCl₂(PPh₃)₂]/CuI catalysed reactions with **2** to give the 1,4-disubstituted buta-1,3-diynes in reactions that proceeded slowly at room temperature, but much more efficiently at slightly elevated temperatures (Table 3). These results are complementary to preparative routes involving Glaser, Hay or other oxidative dimerisation reactions of 1-alkynes [54]. Clearly the conditions set out in Table 3 will not be competitive with known strategies in every case, and certainly not for the preparation of

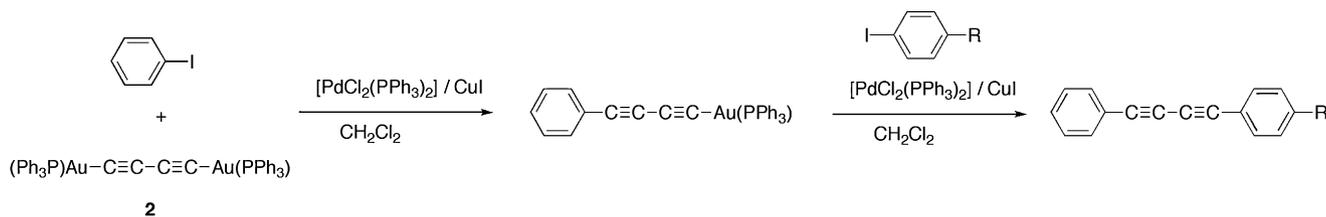
Table 3

Cross-coupling reactions of **2** with aryl halides.



Ar-X	[Pd] ^a /mol%	CuI/mol%	T/°C	t/h	%conversion
IC ₆ H ₄ NO ₂	0.5	0.5	25	6	100
IC ₆ H ₄ CO ₂ Me	0.5	0.5	25	24	97
IC ₆ H ₄ Br	0.5	0.5	25	24	90
IC ₆ H ₄ CH ₃	0.5	0.5	25	24	100
IC ₆ H ₄ NH ₂	0.5	0.5	60	2	100
IC ₆ H ₄ OMe	0.5	0.5	60	2	100

^a [Pd] = [PdCl₂(PPh₃)₂]

Table 4The preparation of differentially substituted diynes from **2**.

Ar-X	[Pd] ^a /mol%	CuI/mol%	T/°C	t/h	%conversion
IC ₆ H ₄ NO ₂	0.5	0.5	35	24	100
IC ₆ H ₄ CO ₂ Me	0.5	0.5	35	24	100
IC ₆ H ₄ NH ₂	0.5	0.5	35	24	100
IC ₆ H ₄ OMe	0.5	0.5	35	24	100
IC ₆ H ₄ Br	0.5	0.5	35	24	100

^a [Pd] = PdCl₂(PPh₃)₂.

bulk quantities of material. However, there is a potential advantage for the preparation of compound libraries in that only a single, readily available diyne precursor is used in conjunction with an aryl halide, as opposed to requiring the initial pre-synthesis of the terminal alkyne, which normally entails a coupling and deprotection approach.

To further test the applicability of the reaction conditions, the sequential reactions of **2** with two different aryl iodides was also examined. Initial reactions of **2** with one equivalent of either 4-iodo methylbenzoate or 4-iodo nitrobenzene, followed by the addition of a second aryl iodide were complicated by the facile reaction of the activated iodide with both gold groups in the initial stage of the reaction. Cleaner reactions were obtained from initial reaction of iodobenzene and **2** for 3 h, presumably to generate [Au(C≡CC≡CPh)(PPh₃)] in situ, followed by treatment with other aryl iodides (Table 4). Careful control of the stoichiometry of the first reaction step is required if double coupling to give 1,4-diphenyl-buta-1,3-diyne is to be avoided. Nevertheless, this sequence of cross-coupling reactions neatly illustrates the preparation of differentially substituted 1,4-diynes from a symmetrically substituted precursor, and complements existing preparative methods such as the Cadiot–Chodkiewicz coupling protocol.

3. Conclusion

Gold(I) alkynyl and diyndiyl complexes can be cross-coupled with aryl iodides under mild conditions in the presence of both Pd(II) and Cu(I) co-catalysts, without the need for any additional base. The reaction likely proceeds via the ready transmetalation of the alkynyl fragment to Cu(I), followed by a conventional Sonogashira cross-coupling mechanism. The simple conversion of the masked butadiyne reagent Me₃SiC≡CC≡CSiMe₃, via [(Ph₃P)AuC≡CC≡CAu(PPh₃)] to 1,4-diaryl buta-1,3-diynes has been achieved, and stepwise functionalisation of each Au moiety has been demonstrated to afford differentially 1,4-disubstituted 1,3-diynes.

4. Experimental

4.1. General details

The compounds [Au(C≡CPh)(PPh₃)] [28], [(Ph₃P)AuC≡CC≡CAu(PPh₃)] [32] and [PdCl₂(PPh₃)₂] [55] were prepared according to literature methods, or the minor variations described below. Other

reagents were purchased and used as received. All reactions were performed under nitrogen atmosphere in air-tight sealed test-tubes or GC-vials which were prepared and filled in an Innovative Technologies glove box. GC–MS analyses were performed on an Agilent Technologies 6890 N gas chromatograph equipped with a 5973 Inert Mass Selective Detector and a 10 m fused silica capillary column (5% cross-linked phenylmethylsilicone). UHP helium was used as the carrier gas. The percentage conversion of the starting material was monitored with reference to an internal dodecane calibrant, which was present in all solutions at 100 μl/100 ml of solvent, and estimated to be accurate to within ±10%.

4.2. General conditions

The gold reagent **1** (25 μmol), arylhalide (25 μmol), [PdCl₂(PPh₃)₂] (1.0 ml of a 1.24 × 10⁻³ M stock solution in thf, 1.24 × 10⁻⁶ mol), CuI (0.5 ml of a 2.47 × 10⁻³ M stock solution in NCMe, 1.24 × 10⁻⁶ mol) were added successively to a vial, topped up to 5 ml with THF and sealed with a rubber septum or crimp-cap. The reaction was stirred, and heated if indicated, and monitored by GC–MS. For reactions described in Table 3, 50 μmol of aryl iodide was employed. For the reactions described in Table 4, 25 μmol of iodobenzene was added initially. After 3 h of reaction at 35 °C, 25 μmol of the second aryl iodide was added, and the reaction allowed to proceed overnight before analysis.

4.3. Preparation of 1,4-bis-triphenylphosphinegold-buta-1,3-diyne (**2**)

1,4-Bis-trimethylsilyl-buta-1,3-diyne [0.16 g, 0.8 mmol] and sodium hydroxide [0.64 g, 16 mmol] were dissolved in methanol [120 ml]. After stirring for 30 min, [AuCl(PPh₃)] [0.75 g, 1.52 mmol] was added, and the resulting white suspension stirred for 3 h. The resulting solid was collected by filtration and recrystallised (CH₂Cl₂/Et₂O) to afford the title compound (0.5 g, 65%). ³¹P NMR (CD₂Cl₂): δ = 43.39 ppm.

4.4. Preparation of 1-phenyl-2-(4'-nitrophenyl) acetylene

A Schlenk flask was charged with compound **1** (0.150 g, 0.27 mmol) and 4-iodo nitrobenzene (0.067 g, 0.27 mmol) in thoroughly degassed thf (10 ml) and treated with [PdCl₂(PPh₃)₂] [9 mg, 0.01 mmol] and CuI [2 mg, 0.01 mmol]. The reaction was allowed to stir at room temperature for 4 h, after which time the

solvent was removed. The residue was dissolved in the minimum volume of benzene, and hexane added, causing the precipitation of $[\text{Au}(\text{PPh}_3)]$ as a white solid (0.105 g, 67%). The solution was purified by preparative TLC using hexane as eluant. The first band contained $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$ (1.7 mg, 6%), the major slightly yellow band contained the title compound (0.052 g, 87%). The last band contained additional $[\text{Au}(\text{PPh}_3)]$, together with some unidentified material.

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