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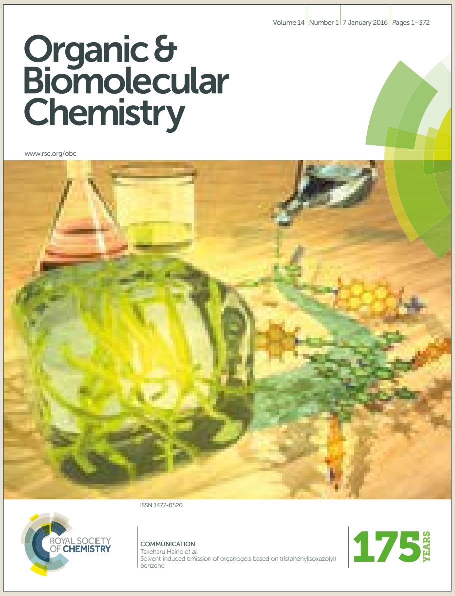

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ARTICLE

Gold Catalyzed Heck-Coupling of Arenediazonium *o*-Benzenedisulfonimides

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Diazonium salts, and precisely arenediazonium *o*-benzenedisulfonimides, have been used for the first time as efficient electrophilic partners in gold catalyzed Heck-coupling reactions. The synthetic protocol was general, easy and gave the target products in satisfactory yields. Mechanistic insights revealed the fundamental roles of the anion of *o*-benzenedisulfonimide as an electron transfer agent which promotes a radical pathway that does not require the presence of photocatalysts or external oxidants

Introduction

Gold catalysis is considered a fundamental topic in organic synthesis with several applications in total syntheses of complex systems, asymmetric syntheses, C-H activation reactions and C-C bond formation.[1a-d] The high importance of gold catalysis is attributable to some peculiar qualities of gold which include good commercial availability, remarkable stability, functional group and oxygen tolerance, tunability, minimal use of additive and excellent chemoselectivity.[1e,f] Many of the investigations into the catalytic reactivity of gold make use of the propensity of cationic Au (I) complexes to activate alkynes towards nucleophilic addition due to their large π-acidic character (alkynophilicity).[1g] Extensive studies in this area have been performed and have found that a wide set of nucleophiles (N, S, O and C nucleophiles) can be added to alkynes in an intramolecular or intermolecular fashion, resulting in the formation of new C-C or C-heteroatom bonds.[1h,i]

In recent years several other gold-catalyzed C-C bond-forming reactions have been reported.[2] While focusing our attention on "classical" cross-coupling reactions, it must be stressed that as Au (I) has the same d^{10} configuration as Pd (0) and Cu (I), meaning that it is able to catalyze reactions typically promoted by Pd (0).[3] A number of Au (I) (or Au (III) in Suzuki coupling[4a]) complexes have successfully been employed for the Suzuki,[4] Sonogashira[5], Stille[6] and Hiyama[7] couplings in high yields and with high selectivity. It is worth noting that strong oxidants were normally required in order to facilitate the Au (I)/Au (IIII) transition in the catalytic cycle.

Arenediazonium salts have been widely used as electrophilic partners in palladium-catalysed cross coupling reactions, including Mizoroki–Heck reactions, Suzuki–Miyaura reactions, and Stille couplings, and so they have become an effective alternative to aryl halides.[8] The use of diazonium salts has some general advantages: they are more reactive, due to the fact that the diazonium group is a better nucleofuge than halide or triflate; they are easily available from anilines, no base or additional ligands are generally needed; they require mild reaction conditions and short reaction times, and the coupling products are generally obtained in high yields.

Interestingly, arenediazonium salts have been recently used as electrophilic reactants in several Au (I) catalyzed arylation reactions[9] and cross-coupling reactions (i.e. Suzuki,[10] Sonogashira[11] coupling), usually under fotoredox conditions.[12] In fact, their capacity to undergo to a single-electron reduction under visible light and in the presence of photosensitizers means that they provide aryl radicals which give sequential oxidative additions onto Au (I) species. The subsequent reductive elimination from the resulting Au (III) complexes, produces the desired coupling adducts and regenerates the Au (I) catalyst.

If gold catalyzed Suzuki and Sonogashira reactions have now generally become well-established protocols, on the contrary, gold catalyzed Heck reactions are a topic that has so far scarcely been studied.[13] In particular, to the best of our knowledge, arenediazonium salts have never been used as electrophilic partners in this reaction.

Some of our research has resulted in a large family of dry diazonium salts, the arenediazonium *o*-benzenedisulfonimides **1** (Fig. 1).[14a]

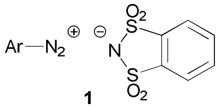

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Fig 1 Arenediazonium *o*-benzenedisulfonimides **1**

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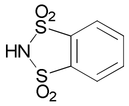
The properties of these compounds mean that they have great potential in numerous synthetic applications. They are easy to prepare and isolate, they are extremely stable, and they can be stored for an unlimited time. Moreover, they react easily both in water and in organic solvents, and *o*-benzenedisulfonimide (**2**; Fig 2) can easily be recovered and reused at the end of the reactions.

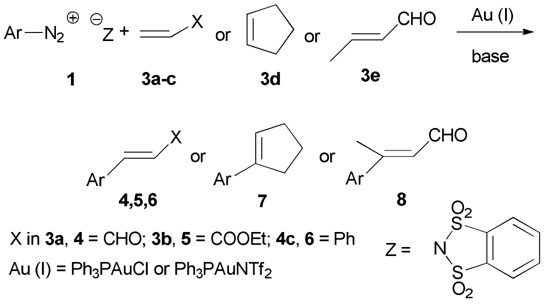


2

Fig 2 *o*-Benzenedisulfonimide (**2**)

Exploration into the synthetic potential of these salts, has led to them giving excellent results, in palladium catalysed coupling reactions, namely Heck reactions,[14b] Stille, [14c,d] Suzuki,[14d] Negishi [14e] and Sonogashira[14f] couplings and in couplings with organoindium derivatives.[14g,h]

The ever growing use of gold as a catalyst in organic synthesis, has driven us to enter this fascinanting field. We herein described the reactivity of said salts **1** as partners in Au(I) catalyzed Heck reactions (Scheme 1).



Scheme 1 Au (I) catalyzed Heck reaction between arenediazonium *o*-benzenedisulfonimides **1** and olefines **3a-e**

Results and discussion

Initially, the model reaction between acrylaldehyde (**3a**) and 4-nitrobenzenediazonium *o*-benzenedisulfonimide (**1a**) was carried out in the presence of [bis(trifluoromethanesulfonyl)imidate] (triphenylphosphine) gold as the catalyst in order to optimize the reaction conditions, as reported in Table 1 (entries 1–19). Various conditions were tested, solvents and/or temperatures were changed and bases and/or photocatalyst were added. The desired coupling product, 4-nitrocinnamaldehyde (**4a**), was formed under heating at 50°C in MeCN or EtOH. It is worthing note that only $CaCO_3$ could be used as a base in EtOH (Table 1, entry 10), while various bases were compatible in MeCN (Table 1, entries 13, 15–19). However the yields were poor and unsatisfactory. It must be stressed that, interestingly, no photocatalyst was necessary (Table 1, entry 18) and the reaction also occurred in the dark (Table 1, entry 19).

So, we decided to change the gold catalyst and we carried out the reaction in the presence of chloro(triphenylphosphine)gold (Table 1, entries 20–30). We tested various solvents and bases at different temperatures and, to our delight, optimal conditions were found: heating at 35°C with MeCN as a solvent and $CaCO_3$ as the base (Table 1, entry 23). A photocatalyst was also unnecessary in this case (Table 1, entry 25) and the reaction also occurred in the dark (Table 1, entry 27). The target **4a** was easily separated, by means of a chromatographic column from three by-products, shown in Figure 3, namely *N*-(4-nitrophenyl)-*o*-benzenedisulfonimide (**9**), nitrobenzene (**10**) and 4,4'-dinitrobiphenyl (**11**).

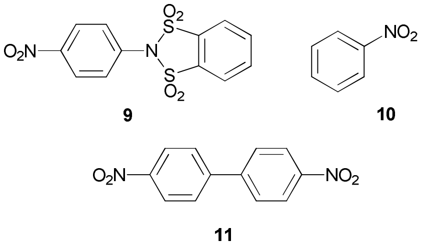


Fig 3 By-products

The high yield and simplicity of the procedure encouraged us to explore the generality and scope of this reaction further, using different salts **1** and olefines **3a–e** (Scheme 1). The results are shown in Table 2. The Heck couplings of various salts **1a–k** in MeCN, in the presence of chloro(triphenylphosphine)gold as the catalyst and $CaCO_3$ as the base, gave the corresponding adducts **4-8** in excellent yields, under simple and mild reaction conditions. The reaction was chemoselective; no traces of disubstituted adducts were detected in the reactions of diazonium salts containing a bromine or iodine atom, which could potentially react in the same way as the diazonium group (Table 2, entries 11–15, 34). The reaction was not affected by electronic effects; adducts **4-7** were obtained in satisfactory yields from salts **1** bearing either electron-donating or electron-withdrawing groups. On the other hand, the influence of steric hindrance was evident both in salts **1** and in crotonaldehyde (**3e**). Reactions of salts **1** bearing *ortho* substituents failed (Table 2, entries 26, 28, 29, 30, 32, 33, 34, 36, 37) with the only exception being those carried out with **3b** (Table 2, entries 27, 31, 35)**.** Regarding **3e**, the presence of an α-methyl group reduced drastically the yields of the reactions carried out with less reactive salts **1b**, **1c** and **1d** bearing electron donating-group (Table 2, entries 10, 20).

Moreover, the reactions of heteroarene diazonium *o*-benzenedisulfonimides **1i-k** (Table 2, entries 43, 44), with the only exception of **1h** (Table 2, entries 38–42) also failed. Finally, it is interesting to highlight that the reactions between **1** and **3d** were highly regioselective: only traces of possible 3-arylcyclopentenes were detected (Table 2, entries 4, 9, 14, 19, 24, 41). Finally,

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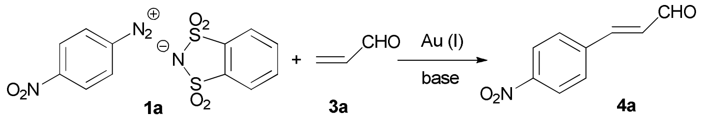
It was possible to recover *o*-benzenedisulfonimide (**2**) in about 80% yields from all the reactions described above. **2** was recycled for the preparation of further salts **1**, which is beneficial from economic and ecological point of view.

Table 1 Trial reactions between acrilaldehyde (**3a**) and 4-nitrobenzenediazonium *o*-benzenedisulfonimide (**1a**)



Entry	Temp (°C)	Time (h)	Solvent	Catalyst	Base	Photocatalyst	Yield (%) of **4a** [a,b]
1	r.t	24	THF	$Ph_3PAuNTf_2$	NaOH	$Ru(bpy)_3(PF6)_2$	-
2	50	24	THF	$Ph_3PAuNTf_2$	NaOH	$Ru(bpy)_3(PF6)_2$	-
3	50	24	THF	$Ph_3PAuNTf_2$	Na_2CO_3	$Ru(bpy)_3(PF6)_2$	-
4	50	24	THF	$Ph_3PAuNTf_2$	Cs_2CO_3	$Ru(bpy)_3(PF6)_2$	-
5	50	24	THF	$Ph_3PAuNTf_2$	$CaCO_3$	$Ru(bpy)_3(PF6)_2$	-
6	50	24	DMSO	$Ph_3PAuNTf_2$	NaOH	$Ru(bpy)_3(PF6)_2$	-
7	50	24	DMSO	$Ph_3PAuNTf_2$	$CaCO_3$	$Ru(bpy)_3(PF6)_2$	-
8	r.t	24	EtOH	$Ph_3PAuNTf_2$	NaOH	$Ru(bpy)_3(PF6)_2$	-
9	50	24	EtOH	$Ph_3PAuNTf_2$	Na_2CO_3	$Ru(bpy)_3(PF6)_2$	-
10	50	24	EtOH	$Ph_3PAuNTf_2$	$CaCO_3$	$Ru(bpy)_3(PF6)_2$	15[c]
11	r.t.	24	MeCN	$Ph_3PAuNTf_2$	NaOH	$Ru(bpy)_3(PF6)_2$	-
12	50	24	MeCN	$Ph_3PAuNTf_2$	NaOH	$Ru(bpy)_3(PF6)_2$	traces
13	50	8	MeCN	$Ph_3PAuNTf_2$	Na_2CO_3	$Ru(bpy)_3(PF6)_2$	22
14	50	24	MeCN	$Ph_3PAuNTf_2$	Cs_2CO_3	$Ru(bpy)_3(PF6)_2$	-
15	50	12	MeCN	$Ph_3PAuNTf_2$	K_2CO_3	$Ru(bpy)_3(PF6)_2$	18
16	50	16	MeCN	$Ph_3PAuNTf_2$	K_3PO_4	$Ru(bpy)_3(PF6)_2$	12
17	50	6	MeCN	$Ph_3PAuNTf_2$	$CaCO_3$	$Ru(bpy)_3(PF6)_2$	39[c]
18	50	6	MeCN	$Ph_3PAuNTf_2$	$CaCO_3$	-	41
19	50	6	MeCN	$Ph_3PAuNTf_2$	$CaCO_3$	dark	40
20	35	8	MeCN	Ph_3PAuCl	Na_2CO_3	$Ru(bpy)_3(PF6)_2$	45
21	50	6	MeCN	Ph_3PAuCl	Na_2CO_3	$Ru(bpy)_3(PF6)_2$	58
22	35	5	MeCN	Ph_3PAuCl	K_3PO_4	$Ru(bpy)_3(PF6)_2$	40
23	35	6	MeCN	Ph_3PAuCl	$CaCO_3$	$Ru(bpy)_3(PF6)_2$	85
24	50	6	MeCN	Ph_3PAuCl	$CaCO_3$	$Ru(bpy)_3(PF6)_2$	85
25	35	6	MeCN	Ph_3PAuCl	$CaCO_3$	-	84[c,d,e]
26	35	24	MeCN	-	$CaCO_3$	-	-
27	35	6	MeCN	Ph_3PAuCl	$CaCO_3$	dark	81
28	35	10	EtOH	Ph_3PAuCl	$CaCO_3$	-	64
29	35	24	DMSO	Ph_3PAuCl	$CaCO_3$	-	traces
30	35	12	THF	Ph_3PAuCl	$CaCO_3$	-	44
31	35	8	Toluene	Ph_3PAuCl	$CaCO_3$	-	58

[a] All the reactions were carried out heating at 35°C, under nitrogen flow, with 1 mmol of **1a**, 1.5 mmol of **3a**, 5 mol% of Au catalysts, 1 mmol of various bases and 5 mol% of photocactalyst [b]Yields refer to pure and isolated **4a**, purified on a silica gel chromatography column. The eluent was petroleum ether/diethyl ether (9 : 1). [c] Higher amount of base or Au catalysts oh higher temperatures does not lead to a yield increase.[d] At room temperature the yield of **4a** was remarkably lower (45%). [e] When the reaction was carried out in the presence of 1,3-dinitrobenzene (1 mmol, 170 mg) no **4a** was formed

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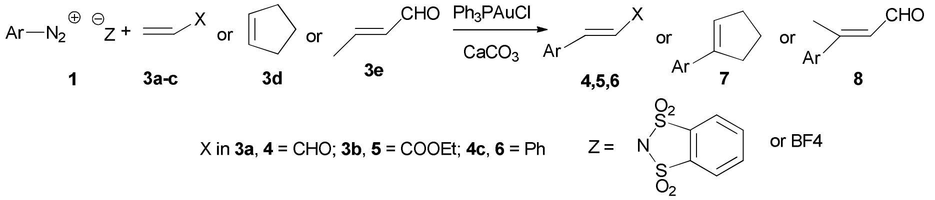
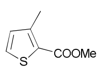
Table 2 Gold catalyzed reactions between **1a-j** and **3a-d**



Entry	Ar in **1**	**3**	Time (h)	Products **4**-**8** and yields (%)[a,b]
1	**1a**; 4-$NO_2C_6H_4$	**3a**; X=CHO	6	**4a**; 84[c]
2	**1a**	**3b**; X= COOEt	4	**5a**; 87
3	**1a**	**3c**; X= C_6H_5	3.5	**6a**; 91
4	**1a**	**3d**	7	**7a**; 67
5	**1a**	**3e**	16	**8a**;78[d]
6	**1b**; 4-MeC_6H_4	**3a**	8	**4b**; 72[c]
7	**1b**	**3b**	7.5	**5b**; 68
8	**1b**	**3c**	9	**6b**; 75
9	**1b**	**3d**	12	**7b**; 63
10	**1b**	**3e**	24	**8b**; 37[d]
11	**1c**; 4-BrC_6H_4	**3a**	6.5	**4c**; 81
12	**1c**	**3b**	3.5	**5c**; 90
13	**1c**	**3c**	5	**6c**; 82
14	**1c**	**3d**	7.5	**7c**; 79
15	**1c**	**3e**	24	**8c**; 40[d]
16	**1d**; 4-$MeOC_6H_4$	**3a**	5	**4d**; 77
17	**1d**	**3b**	5	**5d**; 91
18	**1d**	**3c**	3	**6d**; 89
19	**1d**	**3d**	8	**7d**; 81
20	**1d**	**3e**	24	**8d**;-[d,e]
21	**1e**; 3-$NO_2C_6H_4$	**3a**	4.5	**4e**; 82
22	**1e**	**3b**	6	**5e**; 87
23	**1e**	**3c**	5	**6e**; 90
24	**1e**	**3d**	8	**7e**; 69
25	**1e**	**3e**	12	**8e**; 76[d]
26	**1f**; 2-$NO_2C_6H_4$	**3a**	24	-[d]
27	**1f**	**3b**	8	**5f**; 32[d]
28	**1f**	**3c**	24	**6f**; traces
29	**1f**	**3d**	24	-[d]
30	**1g**; 2-MeC_6H_4	**3a**	24	-[d]
31	**1g**	**3b**	10	**5g**; 35[d]
32	**1g**	**3c**	24	**6g**; traces[d]
33	**1g**	**3d**	24	-[d]
34	**1h**; 2-IC_6H_4	**3a**	24	-[d]
35	**1h**	**3b**	10	**5h**; 28[d]
36	**1h**	**3c**	24	-[d]
37	**1h**	**3d**	24	-[d]
38	**1i**; 	**3a**	4.5	**4i**; 86
39	**1i**	**3b**	3.5	**5i**; 91
40	**1i**	**3c**	5	**6i**; 84
41	**1i**	**3d**	8	**7i**; 64

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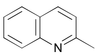
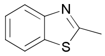
42	**1i**	**3e**	16	**8i**; 78[d]
43	**1j**; 	**3b**	24	-[d]
44	**1k**; 	**3b**	24	-[d]

[a] Unless otherwise stated, all the reactions were performed using arenediazonium *o*-benzenedisulfonimides **1** in MeCN at 35°C under nitrogen flow and in the presence of $CaCO_3$ (1 mmol) and Ph_3PAuCl (5 mol%). The **1** (1 mmol) : **3** ratio was 1:1.5. [b] Yields refer to pure and isolated **4-8**, purified from the by-products on a silica gel chromatography column. [c] The reactions were carried out using 4-nitrobenzenediazonium tetrafluoroborate or 4-toluenediazonium tetrafluoroborate (1 mmol) instead of **1a** or **1b** in two different solvents, namely EtOH and MeCN at 35°C under nitrogen flow and in the presence of $CaCO_3$ (1 mmol) and Ph_3PAuCl (5 mol%). The tetrafluoroborate (1 mmol) : **3** ratio was 1:1.5. The yield of **4a** was 76% carrying out the reaction in EtOH and 12% in MeCN. The yield of **4b** was 25% in EtOH; no **4b** was formed in MeCN. [d]The reaction was performed heating at 50°C in the presence of $CaCO_3$ (1.5 mmol). The **1** (1 mmol) : **3** ratio was 1:2.[e] After 24h the reaction was not complete; GC-MS analyses of the crude residue showed the presence of **8d (**MS (EI): *m/z* = 176 $[M]^+$). However, **8d** could not be obtained with an adequate purity.

The copious and homogeneous results collected provide a good basis for some comments on the reaction mechanism. The first and fundamental fact is that this reaction also occurred in the dark and without any photocatalyst. Furthermore, it must be stressed that, gold catalyst is absolutely necessary; in fact the reaction carried out under optimal conditions, but without gold catalyst, failed (Table 1, entry 26).

S. Shin[15] and coworkers have recently reported an interesting study concerning the cross-coupling of vinyl gold derivatives with diazonium salts under photoredox or thermal conditions. In fact, they found that the reaction can run in the dark under thermal conditons, where arenediazionium tetrafluoroborate decomposed under heating at 60°C In MeOH, forming aryl radicals which oxidize the Au(I) catalyst, allowing the coupling reaction to occur.

In the light of this, we believe that the reaction mechanism of this Heck coupling may be similar to that proposed by Schin. First, a reaction was carried out between **1a** and **3°** in the presence of 1,3-dinitrobenzene, an excellent electron acceptor. This reaction failed and so we confirmed its homolytic course by means of this known diagnostic test (Table 1, entry 25 note e).

Under Shin conditions, the formations of aryl radicals from arenediazonium tetrafluoroborate was possible in MeOH at 60°C. In fact , a thorough study on this topic which proves that the formation of aryl radicals from arenediazonium tetrafluoroborates is the result of an electron transfer-homolysis mechanism, promoted by EtOH and followed by dediazoniation, has been reported in the literature.[16] Moreover, it is also known from the literature that this thermal reduction of arenediazonium tetrafluoroborates in alcoholic solvents, producing free-radicals, is favoured in the order of p-MeO > p-NO_2, p-Br > p-CH_3 >H group in the diazonium salts.[17]

In our conditions, reacting **3a** and 4-toluenediazonium tetrafluoroborate in EtOH, we obtained **4b** in very low yields (25%; Table 2, entry 6 note c), while good results were achieved with 4-nitrobenzenediazonium tetrafluoroborate: **4a** was obtaneid in good yield (75%; Table 2, entry 1 note c). On the other hand, the same reactions, carried out in MeCN gave low yields of target **4a** (12%; Table 2, entry 6, note c), whilst no **4b** formed (Table 2, entry 6, note c). This means that, accordingly to the literature, the aryl radicals necessary for completion of the reaction mainly formed in EtOH and in the presence of NO_2 group in the tetrafluoroborates. On the contrary, it is interesting to note that various solvents were suitable for use with salt **1a** (EtOH, MeCN, THF, toluene; Table 1, entries 25, 28–31) and that the yields of **4a** and **4b** in the reactions carried out in MeCN with **1a** and **1b** were both good and almost the same (Table 2, entries 1, 6). In order to explain this different reactivity between **1** and corresponding tetrafluoroborates, we can use an attractive hypothesis presented in two our previous paper (concerning the bromodediazotation[18a] and the Sandmeyer reaction[18b] of salts **1**) and based on the possibility that the anion of salts **1** could act by a primary electron donor reagent toward the arenediazonium cations, most likely giving rise to the outer-sphere (or not bonded) electron transfer complex **12** (Fig 4). Such charge transfer would be actively favored in salts **1** (and not in tetrafluoroborates) by the formation of a complex where the partner of the aryldiazenyl radical is a species that is highly stabilized by resonance (**12a, 12b**)

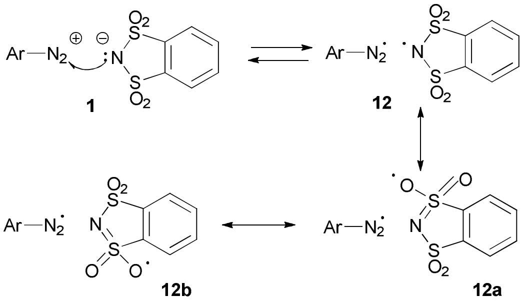


Fig 4 Electron transfer complex **12**

Furthermore, we highlighted that the formation of **12** occurred**,** as in this research, in a variety of solvents, regardless of the type of aromatic ring-bonded substituents and even at room temperature.[18a,b] In the light of this, we believe that the formation of **12,** may explain the homolitic course (partial, however) of this reaction as shown in Scheme 2.

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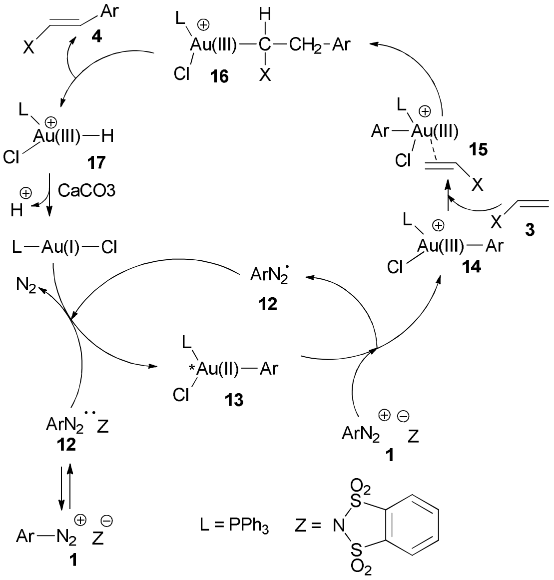
In particular, we postulate that the complex **12** interacts with the Au (I) catalyst, transferring on it an aryl radical; the Au(II) complex **13** forms. A further oxidation of **13**, most likely due to an electron donated by **1**, gives the Au(III) complex **14** and other diazenyl radicals **12** which contribute to oxidizing the Au (I) catalyst. It is interesting to note that this radical chain, triggered by Au (I) catalyst interaction with **12**, allows the oxidation of the Au (I) catalyst to Au (III) to occur, without the participation of photocatalysts or external oxidants. At this point, the Au (III) complex **14** is ready to undergo the typical reactions occurring in the Heck coupling catalytic cycle.[19] First, the insertion reaction with **3** leads, through Au(III)/π-complex **15**,[20a,b] to Au(III) complex **16** and then a β-H elimination reaction produces target **4** and Au (III) complex **17**. The reductive elimination reaction of the latter, in the presence of $CaCO_3$, restores the starting catalyst Ph_3PAuCl.



Scheme 2 Hypothesized mechanism

As shown above (Table 1), catalyst type was crucial to the success of the reaction. In fact, the reaction carried out in the presence of [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine) gold led to unsatisfactory results. It is likely that the strong electron withdrawing group bis(trifluoromethanesulfonyl)imidate destabilizes intermediates **13–16**, making their formation difficult. Finally, we believe that the by-product **10** shown in Figure 3, may be a clue to this radical mechanism. It may derive from the coupling of some of the radicals that form in the reaction pathway.

An aspect of this hypothesized mechanism is that the formation of complex **16** requires alkene **3** insertion into an Au(III)-C bond of **14**, followed by a β-H elimination of **4** from **16**. These processes are not facile at all;[20b] however evidences of an alkene insertion into a Au(III)-C bond[20c-d] and subsequent β-H elimination[20d-f] were recently reported. In particular, Amgoune and Bourissou stated that *"migratory insertion of olefins into the Au(III)–Ph bond is a very facile process*[20d] and *that β-hydride elimination appears as a very easy process for gold(III) alkyl species."*[20e]

Clearly, in order to confirm this supposed mechanism, other evidences are needed. For this purpose, theoretical investigations are currently underway.

Finally, it must be stressed that other mechanisms could have been proposed for this coupling reaction, but this is the only one that allows to explain in a convincing way all the experimental data.

Conclusions

We have herein proposed a mild, easy and efficient gold catalyzed Heck coupling of arenediazonium *o*-benzenedisulfonimides **1**. The target products **4**-**7** were generally obtained in satisfactory yields (32 positive examples, 73% average yield). It is worth noting the interesting role that the *o*-benzenedisulfonimide anion plays as an electron transfer agent in enabling a radical pathway that does not require the presence of photocatalysts or external oxidants. To the best of our knowledge, arenediazonium salts have been used as partners in gold catalyzed Heck reaction for the first time in this paper.

Experimental

General

All the reactions were carried out in oven dried glassware and under a nitrogen flow. Analytical grade reagents and solvents were used and reactions were monitored by GC, GC-MS and TLC. Column chromatography and TLC were performed on Merck silica gel 60 (70-230 mesh ASTM) and GF 254, respectively. Petroleum ether refers to the fraction boiling in the range 40–70 °C. Room temperature is 20 °C. Mass spectra were recorded on an HP 5989B mass selective detector connected to an HP 5890 GC with a methyl silicone capillary column. ^1H NMR and ^{13}C NMR spectra were recorded on a Brucker Avance 200 spectrometer at 200 and 50 MHz respectively. IR spectra were recorded on an IR Perkin-Elmer UATR-two spectrometer. Dry arenediazonium *o*-benzenedisulfonimides **1** were prepared as described previously by us.[14a] The crude salts **1** were virtually pure (by ^1H NMR spectroscopy) and were used in subsequent reactions without further crystallization. 4-Tolyldiazonium and 4-nitrobenzenediazonium tetrafluoroborate were prepared as reported in the literature.[21] All the other reagents were purchased from Sigma-Aldrich or Alfa-Aesar. Structures and purity of all the products obtained in this research were confirmed by their spectral (NMR, MS and IR) and physical data (reported in Supplementary Information), substantially identical to those reported in the literature. Yields of the pure (GC, GC-MS, TLC and NMR) isolated compounds **4-7** are collected in Table 2. Satisfactory microanalyses were obtained for all new compounds.

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4-Nitrocinnamaldehyde (4a): representative procedure for the gold catalyzed Heck reactions

In a oven-dried flask and under nitrogen flow, first anhydrous $CaCO_3$ (100 mg, 1 mmol) and then 4-nitrobenzenediazonium *o*-benzenedisulfonimide (**1a**, 370 mg, 1 mmol) was added to a solution of acrolein (**3a**, 90 mg, 1.5 mmol) and chloro(triphenylphosphine)gold (I) (25 mg, 0.05 mmol, 5mol%) in MeCN (5 ml). The resulting mixture was stirred at 35°C for 6 h; the completion of the reaction was confirmed by the absence of azo coupling with 2-naphthol. Then, the reaction mixture was poured into diethyl ether/water (100 mL, 1:1). The aqueous layer was separated and extracted with diethyl ether (50 mL). The combined organic extracts were washed with water (50 mL), dried with Na_2SO_4 and evaporated under reduced pressure. GC-MS analyses of the crude residue showed 4-nitrocinnamaldehyde (**4a**, MS (EI): *m/z* = 177 $[M]^+$) as the major product, besides traces of 4,4'-dinitrobiphenyl (**11**), MS (EI) *m/z* = 244 $[M]^+$, nitrobenzene (**10**), MS (EI) *m/z* = 123 $[M]^+$, *N*-(4-nitrophenyl)-*o*-benzenedisulfonimide (**9**) MS (EI) *m/z* = 340 $[M]^+$ The crude residue was purified on a short column, eluting with petroleum ether/diethyl ether (9:1). The only isolated product was the title compound (**4a**, 150 mg, 84% yield). The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. The tarry residue was passed through a column of Dowex HCR-W2 ion exchange resin (1.6 g/1 g of product), eluting with water (about 50 mL). After removal of water under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**2**) was recovered (198 mg, 90% yield; mp 192–194 °C. Lit.[14a] 190–193 °C).

Conflicts of interest

There are no conflicts to declare.

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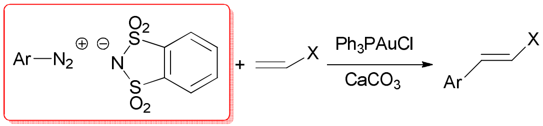

An efficient gold catalyzed Heck coupling of arenediazonium *o*-benzenedisulfonimides is proposed. *o*-Benzenedisulfonimide anion enables a radical pathway that does not require the presence of photocatalysts or external oxidants