


 Cite this: *RSC Adv.*, 2021, **11**, 25504

 Received 9th July 2021
 Accepted 19th July 2021

DOI: 10.1039/d1ra05303e

rsc.li/rsc-advances

Ligand-free Pd/Ag-mediated dehydrogenative alkynylation of imidazole derivatives†

 Fabio Bellina,^a Matteo Biagetti,^b Sara Guariento,^b Marco Lessi,^a Mattia Fausti,^a Paolo Ronchi^b and Elisabetta Rosadoni^a

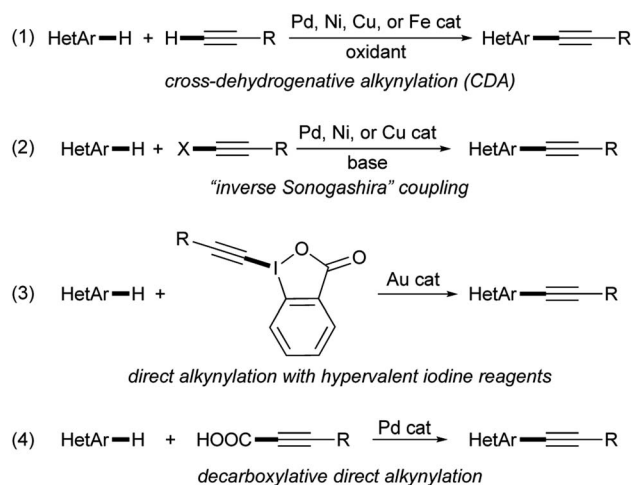
A variety of 2-alkynyl(benzo)imidazoles have been synthesized by dehydrogenative alkynylation of (benzo)imidazoles with terminal alkyne in NMP under air in the presence of Ag₂CO₃ as the oxidant and Pd(OAc)₂ as the catalyst precursor. The data obtained in this study support a reaction mechanism involving a non-concerted metalation deprotonation (n-CMD) pathway.

The development of synthetic protocols that enable the direct and selective functionalization of C_{sp²}-H bonds are of primary importance in the decoration of the imidazole scaffold.^{1–10} The presence of two nitrogen atoms in the pentatomic structure of this important azole in fact introduces a differentiation in the chemical behaviour of the three C-H bonds, allowing their selective involvement in carbon-carbon bond-forming reactions as long as appropriate experimental conditions are identified.

During our studies dedicated to the synthesis and investigation of azole-based fluorophores featuring a π-conjugated backbone end-capped with electron-donating (EDG) and electron-acceptor (EWG) groups (the so-called “push-pull” systems),^{11–15} taking into account the structural characteristics and synthetic versatility of a triple carbon-carbon bond^{16–23} that make it an excellent π-spacer, we recently decided to evaluate the possibility of obtaining alkynyl-substituted imidazoles by transition metal-catalyzed C_{sp²}-C_{sp} bond-forming reactions. Among the synthetic procedures that allow the selective alkynylation of imidazoles and other five-membered heteroarenes,^{5,24} there is no doubt that the possibility of forming the new σ carbon-carbon bond through the double activation of two distinct carbon-hydrogen bonds through a cross-dehydrogenative alkynylation (CDA) represents the best synthetic approach in terms of atom economy and functional group tolerance (eqn (1), Scheme 1).^{25–34} In fact, when compared with the transition metal-catalyzed direct C_{sp²}-H alkynylation protocols involving 1-haloalkynes (the so-called “inverse Sonogashira coupling”) (eqn (2), Scheme 1),^{35–45} hypervalent iodine reagents (eqn (3), Scheme 1),^{46–48} or α,β-ynoic acids

(decarboxylative direct arylation) (eqn (4), Scheme 1),^{26,49,50} the CDA methodology makes it possible to use terminal alkynes without the need for preliminary activation.^{5,24}

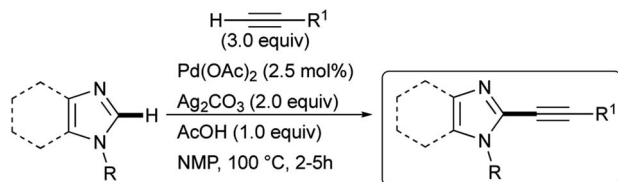
Despite several papers having been dedicated to the dehydrogenative alkynylation of pyrroles,²⁷ indoles,^{27,31} oxazoles,^{27,30,32–34} benzoxazoles,^{26,29,30,32,34} thiazoles,^{27,30} benzothiazoles,^{26,29,31,32,34} pyrazoles,^{25,27} 1,3,4-oxadiazoles,³³ imidazopyridines,^{27,34} and *N*-substituted sydnonones,²⁸ to the best of our knowledge a study specifically devoted to the dehydrogenative alkynylation of imidazoles has never been reported. However, careful reading the literature where alkynylation reactions involving azoles other than imidazole were described, it emerged that two papers reported the C-2 alkynylation of *N*-benzylimidazole and *N*-benzylbenzimidazole with phenylacetylene. In a study mainly devoted to the dehydrogenative alkynylation of imidazo[1,5-*a*]pyridine, Shihabara, Dohke and Murai employed the commercially unavailable Pd(II) complex bi(4-nitropyridinyl)Pd(OAc)₂, Ag₂CO₃ as the oxidant and AcOH


^aDipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124 Pisa, Italy. E-mail: fabio.bellina@unipi.it

^bChemistry Research and Drug Design, Chiesi Farmaceutici S.p.A., Centro Ricerche, Largo Belloli 11/A, 43122 Parma, Italy

 † Electronic supplementary information (ESI) available: Experimental procedures as well as ¹H and ¹³C NMR spectra of the substrates and the products. See DOI: 10.1039/d1ra05303e

 Scheme 1 Synthetic protocols for the transition metal-catalyzed C_{sp²}-H alkynylation of heteroarenes.

Scheme 2 Pd/Ag-Promoted dehydrogenative alkylation of imidazole derivatives.

as additive, in a 95 : 5 mixture of DMF and DMSO for 2 h at 120 °C under argon.³⁴ Due to the propensity of alkynes to give Glaser-type homocoupling side-products in the presence of silver(i) salts,⁵¹ phenylacetylene was slowly added over 90 min to the reaction mixture. In 2015, Likhar, Kantam and co-workers used a synthetic Pd(II) carbene complex. In this case Ag₂O was used as the oxidant, Cs₂CO₃ base, performing the coupling in DMF at 85 °C under air.²⁶

Encouraged by these results but with the intention of developing a simplified procedure that would allow the use of a commercial Pd(II) pre-catalyst in the absence of any palladium ligands, we decided to review the conditions of reaction and, in this work, we are pleased to summarize the results obtained in the synthesis of 2-alkynylimidazole derivatives by

dehydrogenative alkylation with terminal alkynes (Scheme 2). In particular, a careful screening allowed us to show how the reactivity of C_{sp³}-H bond of imidazole derivatives and other azoles can be enhanced simply by performing the alkylation using NMP as the reaction solvent, under air in non-anhydrous conditions, and without the need for palladium ligands.

We decided to start our synthetic investigations by trying a cross-dehydrogenative coupling between *N*-methylbenzimidazole (**1**) and phenylacetylene (**2a**), chosen as typical coupling partners, under conditions very similar to those proposed by Murai and co-workers for the regioselective C-3 dehydrogenative alkylation of 1-alkynyl-3-arylimidazo[1,5-*a*]-pyridines.³⁴

Hence, to a mixture of 1.0 mmol **1**, 5 mol% Pd(OAc)₂, 1.5 equiv. Ag₂CO₃, and 1.0 equiv. AcOH in a 95 : 5 (v/v) mixture of DMF and DMSO under argon 3.0 equiv. of **2a** were added dropwise over 90 min. However, after 2 h at 120 °C a 56% GLC conversion of **1** was recorded, and the required 2-phenylethynyl-*N*-methylbenzimidazole (**3a**) was obtained in only 34% GLC yield (entry 1, Table 1).

Taking note of this unexpected negative result, we decided to re-examine the reaction conditions, starting from the consideration that even if Ag₂CO₃ can theoretically serve as the oxidant, run the reaction in air (open flask) may be critical.²⁸ Gratifyingly, when the coupling was performed under air there

Table 1 Screening of the reaction conditions for the Pd/Ag-promoted dehydrogenative alkylation of **1** with **2a**^a

Entry	Pd cat. (mol%)	Ag(I) salt (equiv.)	RCOOH	Solvent	Temp./react. time ^b (°C/h)	1 GLC conversion ^c (%)	3a GLC yield ^d (%)	3a:4 AP ^e
1 ^e	Pd(OAc) ₂ (5)	Ag ₂ CO ₃ (1.5)	AcOH	DMF/DMSO (95 : 5)	120/2	56	34	57 : 43
2	Pd(OAc) ₂ (5)	Ag ₂ CO ₃ (1.5)	AcOH	DMF/DMSO (95 : 5)	100/5.5	67	66	32 : 68
3	Pd(OAc) ₂ (5)	Ag ₂ CO ₃ (2.0)	AcOH	DMF/DMSO (95 : 5)	100/2	73	70	34 : 66
4	Pd(OAc) ₂ (5)	—	AcOH	DMF/DMSO (95 : 5)	100/3.5	NR	—	—
5	Pd ₂ (dba) ₃ (2.5)	Ag ₂ CO ₃ (2.0)	AcOH	DMF/DMSO (95 : 5)	100/3.5	73	69	30 : 70
6	Pd(acac) ₂ (5)	Ag ₂ CO ₃ (2.0)	AcOH	DMF/DMSO (95 : 5)	100/3.5	67	63	27 : 73
7	PdCl ₂ (5)	Ag ₂ CO ₃ (2.0)	AcOH	DMF/DMSO (95 : 5)	100/3.5	72	68	35 : 65
8	Pd(OAc) ₂ (5)	Ag ₂ CO ₃ (2.0)	—	DMF/DMSO (95 : 5)	100/3.5	53	23	72 : 28
9	Pd(OAc) ₂ (5)	Ag ₂ CO ₃ (2.0)	—	AcOH	100/3.5	0	—	0 : 100
10	Pd(OAc) ₂ (2.5)	Ag ₂ CO ₃ (2.0)	AcOH	DMF/DMSO (95 : 5)	100/3.5	76	69	30 : 70
11	Pd(OAc) ₂ (2.5)	AgOAc (2.0)	AcOH	DMF/DMSO (95 : 5)	100/3.5	55	48	25 : 75
12	Pd(OAc) ₂ (2.5)	Ag ₂ O (2.0)	AcOH	DMF/DMSO (95 : 5)	100/3.5	66	62	28 : 72
13	Pd(OAc) ₂ (2.5)	Ag ₂ CO ₃ (2.0)	EtCOOH	DMF/DMSO (95 : 5)	100/3.5	80	71	35 : 65
14	Pd(OAc) ₂ (2.5)	Ag ₂ CO ₃ (2.0)	PivOH	DMF/DMSO (95 : 5)	100/3.5	45	45	22 : 78
15	Pd(OAc) ₂ (2.5)	Ag ₂ CO ₃ (2.0)	AcOH	DMF/DMSO (95 : 5)	80/3.5	43	40	17 : 83
16	Pd(OAc) ₂ (2.5)	Ag ₂ CO ₃ (2.0)	AcOH	DMF	100/3.5	75	70	34 : 66
17	Pd(OAc) ₂ (2.5)	Ag ₂ CO ₃ (2.0)	AcOH	DMA	100/3.5	81	75(68)	33 : 67
18	Pd(OAc)₂ (2.5)	Ag₂CO₃ (2.0)	AcOH	NMP	100/3.5	85	81(69)	36 : 64
19 ^f	Pd(OAc) ₂ (2.5)	Ag ₂ CO ₃ (2.0)	AcOH	NMP	100/3.5	82	66(51)	40 : 60
20 ^g	Pd(OAc) ₂ (2.5)	Ag ₂ CO ₃ (2.0)	AcOH	NMP	100/3.5	83	80	36 : 64

^a Reaction conditions: **2a** (3.0 mmol) in the selected solvent (2.0 mL) was added dropwise over 45 min to a mixture of **1** (1.0 mmol), Pd cat., Ag(I) salt, RCOOH (1.0 mmol) in the selected solvent (2.0 mL) under air, unless otherwise reported. ^b After the reported reaction time the GLC conversion of **2a** was quantitative. ^c GLC conversion of **1** vs. biphenyl. ^d GLC yield vs. biphenyl. In parentheses isolated yield. ^e This reaction was carried out under an argon atmosphere. ^f This reaction was carried out on a 10 mmol scale. ^g This reaction was carried out in the presence of TEMPO (1.0 equiv.) as radical scavenger.



was a marked increase in GLC yield, which went from 34% to 66% (entry 2, Table 1). The use of a slightly more excess of Ag_2CO_3 resulted in a 70% GLC yield (entry 3, Table 1), while air alone resulted ineffective in promoting the alkylation (entry 4, Table 1). The use of palladium pre-catalysts different from $\text{Pd}(\text{OAc})_2$ did not give any significant improvement in terms of conversion and yield (entries 5–7, Table 1). The presence of 1.0 equiv. AcOH revealed to be essential for the coupling (entry 8, Table 1), but when the coupling was carried out using AcOH as the reaction solvent **2a** was entirely converted into the side-product **4** and no conversion of **1** into **3a** was observed (entry 9, Table 1).

Continuing with the screening, we observed that halving the palladium load did not lead to a loss of reaction efficiency (entry 10, Table 1), and that the use of silver(I) salts different from Ag_2CO_3 gave slightly worse results (entries 11 and 12, Table 1).

Propionic acid as additive gave results similar to AcOH (entry 13, Table 1), while pivalic acid resulted less effective, giving rise to **3a** in only 45% GLC yield (entry 14, Table 1). As already observed,³¹ the use of the right buffer system may be crucial for the deprotonation of the terminal alkyne, and also for the reoxidation of $\text{Pd}(0)$ to $\text{Pd}(\text{II})$.

With our delight the chemical yield went up to 69% when the DMF/DMSO mixture was replaced by NMP (entry 18, Table 1), and the efficacy of this solvent was confirmed carrying out the coupling on a ten times higher scale (entry 19, Table 1). A quite similar isolated yield was obtained performing the coupling in DMA as the solvent (entry 17, Table 1), while DMF alone gave a poorer result (entry 16, Table 1).

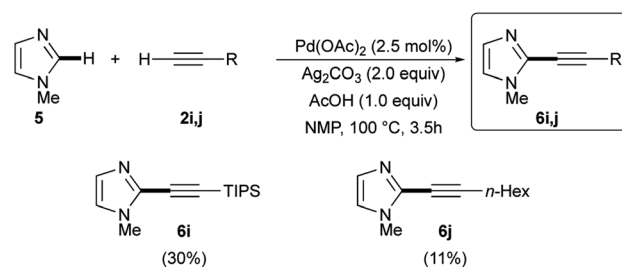
In contrast to what observed by Murai and co-workers,³⁴ it should be highlighted that the slow addition of phenylacetylene never avoided in our hands the formation of Glaser side-product **4**.

Finally, when the reaction was performed in the presence of 1.0 equiv. of TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl as radical scavenger, it still proceeded smoothly to afford 2-alkynylazole **3a** in 80% GLC yield (entry 20, Table 1). This experiment suggests that free radicals should be not involved in the plausible catalytic cycle (see later).

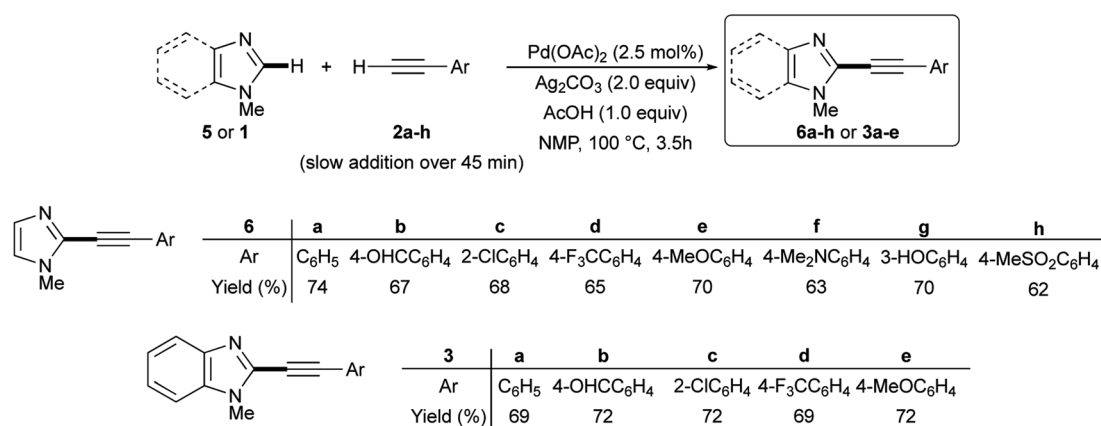
The satisfactory result obtained in the preparation of **3a** from **1** and **2a** under the experimental conditions summarized in entry 18 of Table 1 prompted us to extend this simple methodology to the selective synthesis of 2-arylethynyl-1-methyl-1*H*-imidazoles **6a–h** and 2-arylethynyl-1-methyl-1*H*-benzimidazoles **3a–e** starting from **5** or **1** and terminal alkynes **2a–h**. In details, the slow addition over 45 min of **2** to a mixture of **5** or **1** in the presence of 2.5 mol% $\text{Pd}(\text{OAc})_2$, 2.0 equiv. Ag_2CO_3 , 1.0 equiv. AcOH in NMP as the solvent allowed us to recover the required 2-alkynyl substituted derivatives **6a–h** or **3a–e** in 62–74% isolated yield after 3.5 h at 100 °C under air (Scheme 3).

Noteworthy, the reaction outcome was not influenced by the electronic nature of the aromatic moiety on the terminal alkyne. More importantly, several functional groups on the phenyl ring resulted well tolerated, including formyl and hydroxy groups that are potentially sensitive to the oxidative conditions required by dehydrogenative couplings.

While good results were obtained when arylacetylenes were used as coupling partners, worse results were observed when TIPS-acetylene **2i** or 1-octyne (**2j**) were reacted with **5**. In fact, the expected 2-alkynyl substituted imidazoles **6i** and **6j** were isolated in 30% and 11% yields, respectively (Scheme 4).^{25,31} The low reactivity of these two terminal alkynes in respect to their aryl analogues could be attributed, as already noted,³¹ to the decreased electrophilic nature of the corresponding alkyne-palladium(II) intermediates being generated during the

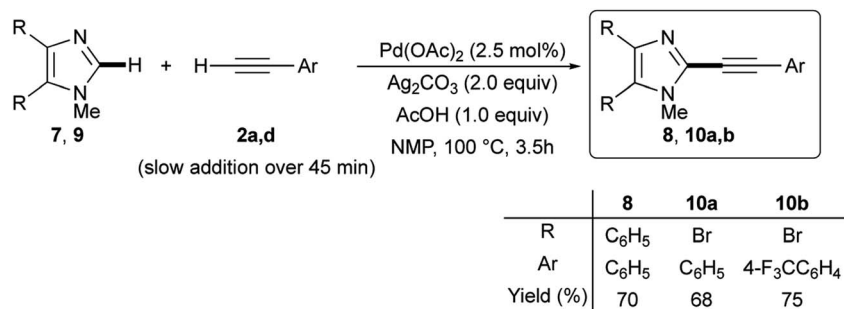


Scheme 4 Ligandless Pd/Ag-promoted dehydrogenative alkylation of 1-methylimidazole **5** with terminal alkynes **2i** and **2j**.



Scheme 3 Ligandless Pd/Ag-promoted dehydrogenative alkylation of 1-methylimidazole **5** or 1-methylbenzimidazole **1** with terminal alkynes **2a–h**.





Scheme 5 Ligandless Pd/Ag-promoted dehydrogenative alkylation of 4,5-disubstituted 1-methylimidazole **7** or **9** with terminal alkynes **2a** or **2d**.

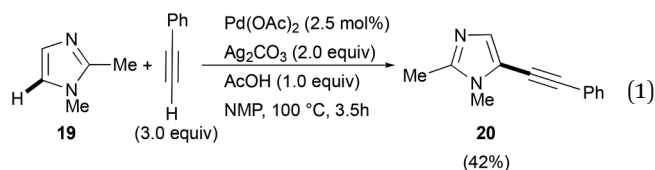
reaction. As a further proof of their lower reactivity, the slow addition of **2i** and **2j** was found to be unnecessary.

Gratifyingly, the optimized Pd(OAc)₂/Ag₂CO₃-promoted coupling conditions proved to be useful also for the C-2 dehydrogenative alkylation of 4,5-diphenyl-1-methylimidazole **7**. In fact, this disubstituted azole gave the expected C-2 alkylation product **8** in 70% isolated yield when reacted with phenylacetylene (**2a**) (Scheme 5).

One of the main advantages of dehydrogenative cross-coupling reactions is the tolerance, among others, of carbon-halogen bonds that, hence, are available for subsequent transformations. We were pleased to confirm this tolerance; in fact, 4,5-dibromo-1-methyl-1*H*-imidazole **9** was efficiently reacted with alkynes **2a** and **2d**, giving rise to the required 2-alkynyl-4,5-dibromoimidazoles **10a,b** in 68 and 75% isolated yields, respectively (Scheme 5). Notably, no conventional Sonogashira-type coupling side-products were observed.

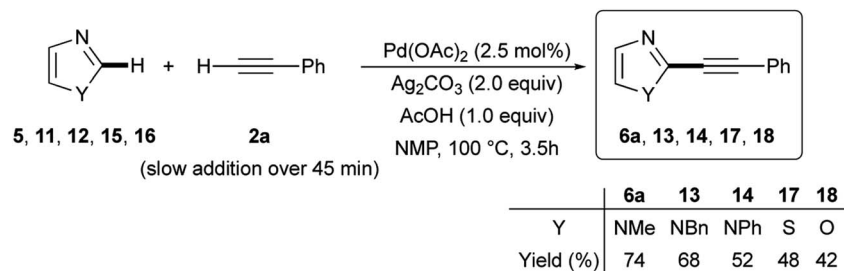
Similar satisfactory yields were obtained when 1-benzyl- and 1-phenyl-1*H*-imidazoles **11** and **12** when reacted with **2a**. The corresponding 2-phenylethynylimidazoles **13** and **14** were recovered in 68% and 52% isolated yields, respectively (Scheme 6). In contrast, the C-2 alkylation of thiazole (**15**) and oxazole (**16**) with **2a** gave the required products **17** and **18** in somewhat lower yields (48 and 42%, respectively). It is noteworthy, however, that the observed reactivity of 1-substituted imidazole **6**, **11** and **12**, *i.e.* 1-methyl > 1-benzyl > 1-phenyl, and that found for the three 1,3-azoles **6**, **13** and **14**, *i.e.* 1-methylimidazole > thiazole > oxazole, parallels that reported in the literature for classical SEAr.^{52,53} As regards the regioselectivity, when the reaction involved 1-substituted imidazoles **5**, **11**, and **12**, thiazole **15** and oxazole **16** a clean C-2 alkylation was observed,

while the corresponding C-5 or even the less probable C-4 alkynyl-substituted regioisomers were never detected in the crude reaction mixtures.⁵⁴ However, it is worth mentioning that when the alkylation was tempted on 1,2-dimethyl-1*H*-imidazole **19**, the C-5 alkynylated product **20** was obtained in 42% isolated yield (eqn (1)).



Based on earlier reports and our observations, a possible reaction mechanism for this Pd/Ag-promoted dehydrogenative alkylation of imidazoles is summarized in Fig. 1, using 1-methylimidazole **5** as an example. Initial transmetalation involving a Pd(II) complex and a (presumed) silver(I) acetylide generates the alkynyl Pd(II) species **A**, which then affords the imidazole-Pd-alkyne complex **E** through a sequence of base-assisted carbanion generation from an azole-Pd complex (**B** → **C**), followed by a C-palladation step *via* carbene **D**. This particular C-H palladation mechanism, known as non-concerted metalation-deprotonation (n-CMD) pathway, was initially proposed by Hoarau and co-workers to justify the observed C-2 regioselectivity in the copper-free Pd-catalyzed direct arylation of oxa(thia)zoles-4-carboxylate with aryl bromides.⁵⁵⁻⁵⁷

Although the comparison of the reactivity of 1-methylimidazole **5** with both the other two 1-substituted imidazoles **11** and **12**, and with thiazole (**15**) and oxazole (**16**) suggested a SEAr



Scheme 6 Ligandless Pd/Ag-promoted dehydrogenative alkylation of 1-substituted imidazoles **5**, **11**, **12**, thiazole (**15**), and oxazole (**16**) with phenylacetylene (**2a**).



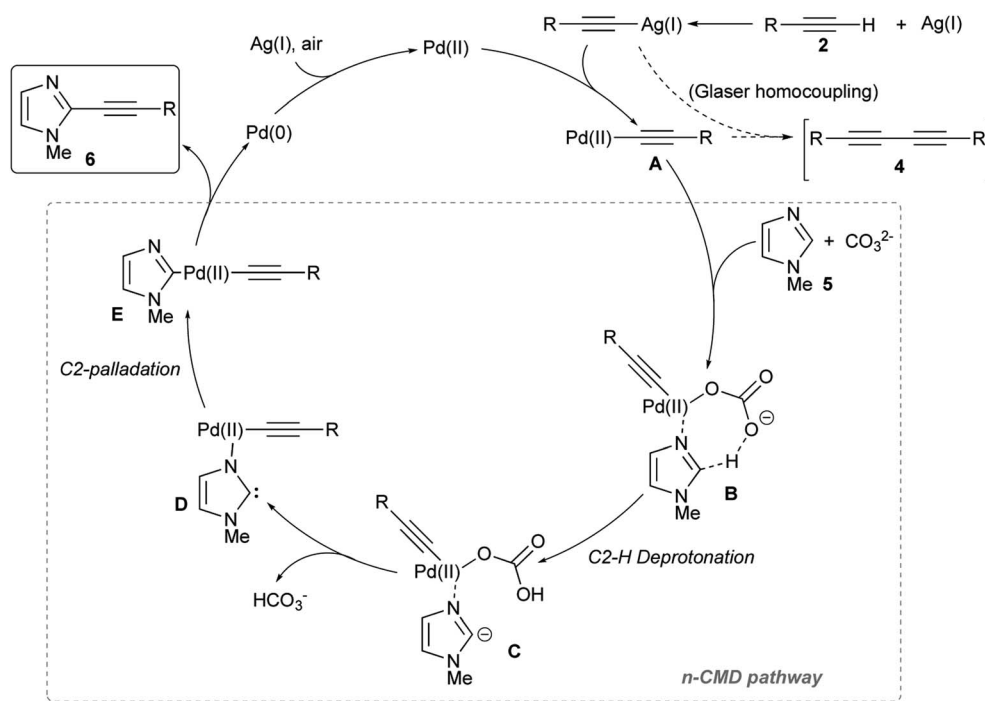


Fig. 1 Proposed n-CMD mechanistic pathway for the Pd(OAc)₂/Ag₂CO₃-promoted dehydrogenative alkylation of 1-methylimidazole 5.

mechanism (hence *via* a classic Wheland intermediate),^{58–60} it should be noted that the most reactive position should have been C-5, and not the position C-2 that instead has the most acidic C–H bond. Similarly, a pure concerted metalation–deprotonation (CMD) pathway can reasonably be excluded considering that DFT calculations have shown that in the case of 1,3-azoles position C-5 is, again, the most reactive.⁶¹ The n-CMD mechanism hypothesizes that the deprotonation occurs through the formation of an azole–Pd(II) complex and, therefore, justifies the observed reactivity by the most acidic C–H bond, *i.e.* the one in position 2 on the azole nucleus. On the other hand, one key step of this mechanism is the formation of N3–Pd complex C, which is the more effective the more the terminal alkyne is electron-poor (hence having the C_{sp}–H bond more acid). That the steps of the mechanism from A to E are certainly critical for the success of the reaction is also proved by the beneficial effect resulting from the slow addition of the terminal alkyne 2 to the reaction mixture. Finally, reductive elimination involving complex E gave the coupling product 6, and reoxidation of Pd(0) to Pd(II) by Ag(I) or air closed the catalytic cycle.

Conclusions

In this study we developed a simple and efficient ligandless Pd(II) catalyzed dehydrogenative alkylation of imidazoles with terminal alkynes under air in non-anhydrous conditions, starting from a preliminary screening of the role of silver(I) oxidant, catalyst precursors, solvents, and reaction temperature on the efficiency and selectivity of the alkylation of 1-methylbenzimidazole (1). The optimized reaction conditions allowed us to easily prepare several 2-alkynyl-substituted 1,3-azoles in good isolated yields, working in an open vessel without any added

ligand. The experimental results point towards a non-concerted metalation–deprotonation mechanistic pathway, that allows us to justify both the C-2 regioselectivity and the “SEAr-like” reactivity of the azoles, as well as the higher reactivity of arylacetylenes when compared with that of alkyl- or silyl-substituted analogues. From the proposed mechanistic machinery it also emerged that Ag₂CO₃ plays not only as Pd(0) oxidant, but also has an active role in generating Ag(I) acetylide, and acts as an inner-sphere base in the C2–H deprotonation step. The application of this procedure to the preparation of new push–pull hetero-aromatic fluorophores as functional materials is undergoing and will be published in the next future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by Chiesi Farmaceutici (Parma, Italy) and Università di Pisa (PRA_2020_219).

References

- 1 J. Roger, A. L. Gottumukkala and H. Doucet, *ChemCatChem*, 2010, 2, 20–40.
- 2 F. Bellina, R. Rossi, M. Lessi, C. Manzini and L. Perego, *Synthesis*, 2014, 46, 2833–2883.
- 3 F. Bellina, in *C–H Bond Activation and Catalytic Functionalization I*, ed. P. H. Dixneuf and H. Doucet, Springer, Cham, 2016, vol. 55, pp. 77–102.



- 4 R. Rossi, M. Lessi, C. Manzini, G. Marianetti and F. Bellina, *Adv. Synth. Catal.*, 2015, **357**, 3777–3814.
- 5 B. Panda, *Asian J. Org. Chem.*, 2020, **9**, 492–507.
- 6 F. Bellina, *Synthesis*, 2021, **53**(15), 2517–2544.
- 7 W. C. Lee, T. H. Wang and T. G. Ong, *Chem. Commun.*, 2014, **50**, 3671–3673.
- 8 Y. Yang, J. Lan and J. You, *Chem. Rev.*, 2017, **117**, 8787–8863.
- 9 H. Kim, Y. J. Hwang, I. Han and J. M. Joo, *Chem. Commun.*, 2018, **54**, 6879–6882.
- 10 J. Le Bras and J. Muzart, *Catalysts*, 2020, **10**, 571–618.
- 11 M. Lessi, C. Manzini, P. Minei, L. A. Perego, J. Bloino, F. Egidi, V. Barone, A. Pucci and F. Bellina, *Chempluschem*, 2014, **79**, 366–370.
- 12 V. Barone, F. Bellina, M. Biczysko, J. Bloino, T. Fornaro, C. Latouche, M. Lessi, G. Marianetti, P. Minei, A. Panattoni and A. Pucci, *Phys. Chem. Chem. Phys.*, 2015, **17**, 26710–26723.
- 13 F. Bellina, C. Manzini, G. Marianetti, C. Pezzetta, E. Fanizza, M. Lessi, P. Minei, V. Barone and A. Pucci, *Dyes Pigm.*, 2016, **134**, 118–128.
- 14 M. Lessi, G. Panzetta, G. Marianetti and F. Bellina, *Synthesis*, 2017, **49**, 4676–4686.
- 15 G. Marianetti, M. Lessi, V. Barone, F. Bellina, A. Pucci and P. Minei, *Dyes Pigm.*, 2018, **157**, 334–341.
- 16 *Modern Acetylene Chemistry*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1995.
- 17 E. Negishi and L. Anastasia, *Chem. Rev.*, 2003, **103**, 1979–2017.
- 18 F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2004, **104**, 3079–3159.
- 19 S. Toyota, *Chem. Rev.*, 2010, **110**, 5398–5424.
- 20 B. Godoi, R. F. Schumacher and G. Zeni, *Chem. Rev.*, 2011, **111**, 2937–2980.
- 21 C. Liu, H. Zhang, W. Shi and A. Lei, *Chem. Rev.*, 2011, **111**, 1780–1824.
- 22 J. P. Brand and J. Waser, *Chem. Soc. Rev.*, 2012, **41**, 4165–4179.
- 23 R. Chinchilla and C. Najera, *Chem. Rev.*, 2014, **114**, 1783–1826.
- 24 F. Bellina, M. La Manna and E. Rosadoni, *Curr. Org. Chem.*, 2021, **25**, 1–26.
- 25 H. Ha, C. Shin, S. Bae and J. M. Joo, *Eur. J. Org. Chem.*, 2018, **2018**, 2645–2650.
- 26 T. Parsharamulu, P. Vishnuvardhan Reddy, P. R. Likhar and M. Lakshmi Kantam, *Tetrahedron*, 2015, **71**, 1975–1981.
- 27 X. Jie, Y. Shang, P. Hu and W. Su, *Angew. Chem., Int. Ed.*, 2013, **52**, 3630–3633.
- 28 C. Wu, P. Li, Y. Fang, J. Zhao, W. Xue, Y. Li, R. C. Larock and F. Shi, *Tetrahedron Lett.*, 2011, **52**, 3797–3801.
- 29 S. S. Patil, R. P. Jadhav, S. V. Patil and V. D. Bobade, *Tetrahedron Lett.*, 2011, **52**, 5617–5619.
- 30 S. H. Kim, J. Yoon and S. Chang, *Org. Lett.*, 2011, **13**, 1474–1477.
- 31 L. Yang, L. Zhao and C. J. Li, *Chem. Commun.*, 2010, **46**, 4184–4186.
- 32 N. Matsuyama, M. Kitahara, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2010, **12**, 2358–2361.
- 33 M. Kitahara, K. Hirano, H. Tsurugi, T. Satoh and M. Miura, *Chem.–Eur. J.*, 2010, **16**, 1772–1775.
- 34 F. Shibahara, Y. Dohke and T. Murai, *J. Org. Chem.*, 2012, **77**, 5381–5388.
- 35 I. V. Seregin, V. Ryabova and V. Gevorgyan, *J. Am. Chem. Soc.*, 2007, **129**, 7742–7743.
- 36 Y. Gu and X.-m. Wang, *Tetrahedron Lett.*, 2009, **50**, 763–766.
- 37 E. Brachet and P. Belmont, *J. Org. Chem.*, 2015, **80**, 7519–7529.
- 38 S. H. Kim and S. Chang, *Org. Lett.*, 2010, **12**, 1868–1871.
- 39 A. Mondal, H. Chen, L. Flamig, P. Wedi and M. van Gemmeren, *J. Am. Chem. Soc.*, 2019, **141**, 18662–18667.
- 40 A. Mondal and M. van Gemmeren, *Angew. Chem., Int. Ed.*, 2021, **60**, 742–746.
- 41 U. N. Patel and B. Punji, *Asian J. Org. Chem.*, 2018, **7**, 1390–1395.
- 42 N. Matsuyama, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2009, **11**, 4156–4159.
- 43 J. Aziz, T. Baladi and S. Piguel, *J. Org. Chem.*, 2016, **81**, 4122–4133.
- 44 T. Kawano, N. Matsuyama, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2010, **75**, 1764–1766.
- 45 F. Besselievre and S. Piguel, *Angew. Chem., Int. Ed.*, 2009, **48**, 9553–9556.
- 46 J. P. Brand, J. Charpentier and J. Waser, *Angew. Chem., Int. Ed.*, 2009, **48**, 9346–9349.
- 47 J. P. Brand and J. Waser, *Angew. Chem., Int. Ed.*, 2010, **49**, 7304–7307.
- 48 Y. Li, J. P. Brand and J. Waser, *Angew. Chem., Int. Ed.*, 2013, **52**, 6743–6747.
- 49 B. Zhao, *Org. Biomol. Chem.*, 2012, **10**, 7108–7119.
- 50 J. Kim, D. Kang, E. J. Yoo and P. H. Lee, *Eur. J. Org. Chem.*, 2013, **2013**, 7902–7906.
- 51 X. Feng, Z. Zhao, F. Yang, T. Jin, Y. Ma and M. Bao, *J. Organomet. Chem.*, 2011, **696**, 1479–1482.
- 52 L. I. Belen'kii and N. D. Chuvylkin, *Chem. Heterocycl. Compd.*, 1997, **32**, 1319–1343.
- 53 J. A. Joule and K. Mills, in *Heterocyclic Chemistry at a Glance*, John Wiley & Sons, 2nd edn, 2013, ch. 12, pp. 107–121, DOI: DOI: 10.1002/9781118380208.ch12.
- 54 M. R. Grimmett, in *Advances in Heterocyclic Chemistry*, 1970, vol. 12, pp. 103–183, DOI: DOI: 10.1016/s0065-2725(08)60973-3.
- 55 L. Theveau, C. Verrier, P. Lassalas, T. Martin, G. Dupas, O. Querolle, L. Van Hijfte, F. Marsais and C. Hoarau, *Chem.–Eur. J.*, 2011, **17**, 14450–14463.
- 56 L. Théveau, O. Querolle, G. Dupas and C. Hoarau, *Tetrahedron*, 2013, **69**, 4375–4380.
- 57 V. Gandon and C. Hoarau, *J. Org. Chem.*, 2021, **86**, 1769–1778.
- 58 S. Pivsa-Art, T. Satoh, Y. Kawamura, M. Miura and M. Nomura, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 467–473.
- 59 F. Bellina, S. Cauteruccio, L. Mannina, R. Rossi and S. Viel, *Eur. J. Org. Chem.*, 2006, **2006**, 693–703.
- 60 C. H. Park, V. Ryabova, I. V. Seregin, A. W. Sromek and V. Gevorgyan, *Org. Lett.*, 2004, **6**, 1159–1162.
- 61 S. I. Gorelsky, *Coord. Chem. Rev.*, 2013, **257**, 153–164.

