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Cobalt-Catalyzed Hydroalkynylation of Vinylaziridines

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Abstract: Transition metal-catalyzed hydroalkynylation reactions are efficient transformations allowing the straightforward formation of functionalized alkynes. Therein, we disclose the cobalt-catalyzed hydroalkynylation of vinylaziridines giving rise to both linear and branched enynes. The optimization of the reaction conditions allowed to determine the key parameters of the cobalt-based catalytic system. The scope investigation showed that the cobalt-catalyzed hydroalkynylation is mainly limited to phenylacetylene derivatives. In most cases branched and linear enynes were isolated in equimolar proportions (20 examples). Additional experiments allowed us to propose a plausible mechanism. Finally, the hydroalkynylation products were further subjected to an iodocyclization affording a 2,3-dihydropyrrole derivative and a platinum-catalyzed cycloisomerization.

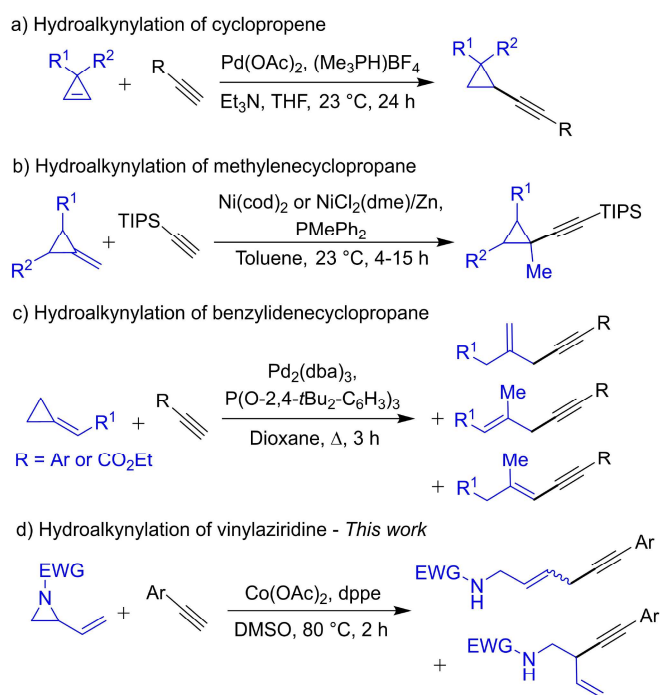
Keywords: 1,4-Enynes; Alkynes; Cobalt; Small ring; Vinylaziridine

Introduction

Alkynes are fundamental and versatile building blocks in organic synthesis as they can be straightforwardly derivatized into various functional groups through a wide array of transformations such as reduction, hydration, halogenation, oxidation, cycloaddition or cycloisomerization among many others.^[1] Alkynylation represents an efficient methodology to introduce nucleophilic alkynyl groups to unsaturated substrates. However, the low reactivity of alkynylides limits their application to addition reactions onto aldehydes, ketones and imines. Metal alkynylide nucleophiles circumvented this drawback and allowed the development of enantioselective alkynylations of carbonyl and imine compounds.^[2] Further improvements were obtained with transition metal (TM)-based complexes allowing catalytic hydroalkynylation^[3] through nucleophilic addition onto less reactive substrates. Dimerization of alkynes could thus be promoted by many TM complexes.^[4] TM-catalyzed hydroalkynylations of carbon-carbon double bonds were further extended to allenes,^[5] activated^[6] or unactivated alkenes,^[7] styrene derivatives,^[8] 1,3-dienes^[8a,9] and norbornene derivatives.^[8a,c,10] Other ring-strained olefins such as cyclopropenes were also investigated. For example, Chisholm disclosed a palladium-catalyzed hydroalky-

nylation of cyclopropenes; albeit limited to alkyl-substituted alkynes (Scheme 1a).^[11] Later, Tenaglia demonstrated that the Herrmann-Beller phosphapalladacycle catalyst enabled the hydroalkynylation of cyclopropenes with alkyl-, aryl- and silyl-substituted alkynes.^[12] Recently, efficient enantioselective versions were disclosed using gadolinium- and palladium-based catalysts.^[13] In 2009, two independent studies on the hydroalkynylation of methylenecyclopropane derivatives were published. Sugimone found that a nickel(0)-based catalytic system could perform addition of (*triisopropylsilyl*)acetylene without ring-opening of the cyclopropane moiety (Scheme 1b).^[14] With benzylidenecyclopropane substrates and a palladium(0)/phosphite catalytic system, López and Mascareñas showed that the hydroalkynylation occurred with a ring-opening of the cyclopropane. The ratio of the resulting three isomers depended on the nature of the R¹ substituent (Scheme 1c).^[15] During the investigation of a platinum-catalyzed [3 + 2] cycloaddition between alkylidenecyclopropanes and alkynes,^[16] we observed, as a side reaction, an hydroalkynylation process leading to the distal bond cleavage of the alkylidene moiety.

As a part of our interest for metal-catalyzed activation of small rings,^[17,18] we disclose herein an unprecedented hydroalkynylation of vinylaziridines^[19]



Scheme 1. TM-catalyzed hydroalkynylation of 3-membered cycle derivatives (TIPS = *triisopropylsilyl*).

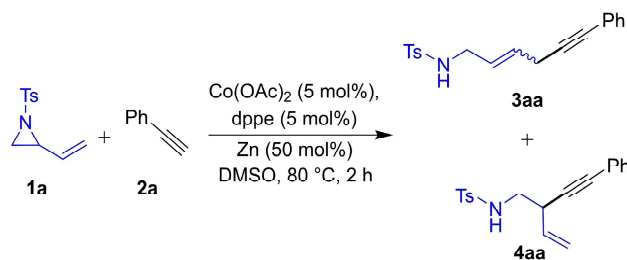
catalyzed by a cobalt salt associated to a phosphorus-based ligand. This strategy led to the ring-opening of vinylaziridines and gave rise to branched and linear enynes (Scheme 1d).

Results and Discussion

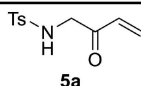
We first investigated the hydroalkynylation of vinylaziridine **1a** with phenylacetylene **2a** as benchmark substrates using the cobalt-based catalytic system developed by Nishimura and Hayashi.^[5h,10d,20] Using 5 mol% of cobalt(II) acetate in combination with 1,2-bis(diphenylphosphino)ethane (dppe) and zinc metal as reducing agent in DMSO at 80 °C, both linear enyne **3aa** and branched enyne **4aa** were isolated in similar quantities (1:1 ratio) and a good overall yield (Table 1, entry 1). Evaluation of the temperature influence determined that the temperature could be decreased to 25 °C, albeit an increase of the reaction time to 4 h was required to achieve full consumption of **1a** (entries 2–4). The reaction temperature did not have a noticeable influence on the branched/linear ratio or on the *E/Z* selectivity of **3aa**. Unexpectedly, the cobalt-based catalytic system also proceeded without zinc as reducing agent, albeit a heating at 60 °C was required in this case (entries 5–7). Therefore, zinc was removed for the continuation of the study. Freshly distilled phenylacetylene **2a** was also used to improve significantly the overall yield while maintaining the same linear/branched ratio (entry 8). Control experiments

showed that no reaction occurred without Co(OAc)₂ (entry 9).^[21] Vinylaziridine **1a** was almost completely recovered and only traces of enone **5a**, resulting from the oxidation of **1a**, were detected.^[22] Among the various metal acetate salts that were tested, only Ni(OAc)₂ displayed a similar reactivity (entry 10) and only DMSO was found suitable to carry out the hydroalkynylation.^[23] dppe was mandatory and the most competent ligand for this reaction (entry 11). Indeed, the catalytic activity decreased when the bite angle of the diphosphine ligand increased (entries 12 and 13). For large bite angle diphosphines, such as 1,1'-bis(diphenylphosphino)ferrocene (dppf), no reaction occurred (entry 14).^[23] Unfortunately, the ligand screening did not enable to improve the selectivity toward the formation of either the branched enyne or the linear one, respectively **4aa** and **3aa**. Chiral ligands were also scrutinized, but only low chiral inductions were observed (up to 32% ee).^[23]

Next, the scope of the cobalt-catalyzed hydroalkynylation was examined with respect to the alkyne partner (Table 2). Phenylacetylene derivatives substituted in *para* position with electron donating groups such as OMe, NMe₂, or NMeOAc were tolerated providing moderate to good overall yields (entries 2, 4 and 5). Branched and linear enynes were isolated in equimolar ratios with good *E* selectivities for linear ones. Of note, it was not possible to separate enynes **3ae** and **4ae** by silica gel chromatography and thus to determine the *E/Z* ratio of **3ae** (entry 5). A good overall yield was obtained with phenylacetylene derivative **2f**, substituted by a chlorine atom in *para* position, i.e. a weak electron withdrawing group (64%, entry 6). However, alkynes bearing strong electron withdrawing groups such as NO₂ and CF₃ were found completely inefficient in this transformation (entries 7 and 8). With tolylacetylenes, similar results were observed with either *para*- or *ortho* substituents providing equimolar mixtures of enynes in 24–25% overall yields (entries 9 and 10). Unexpectedly, with a methyl group in *meta*-position, the catalytic system displayed a higher reactivity (60% overall yield, entry 11). This observation led us to reconsider the influence of the substituents position on the reactivity. Whereas a CF₃ group in *para* position of the phenylacetylene derivative did not allow the formation of hydroalkynylation products, enynes **3al** and **4al**, with a CF₃ in *meta* position were isolated, albeit in low yields, 13% and 10% respectively (entries 8 and 12). The cobalt-catalyzed hydroalkynylation was also found tolerant toward ester group in *meta* position (entry 13), 1-naphthylacetylene (entry 14), and alkynes containing a heterocycle such as 2-thienyl or 1-tosylindolyl (entries 15–16). In all the above mentioned examples, no noticeable selectivity between linear and branched enynes was observed, and the *E/Z* selectivity in linear enynes **3a** was found moderate to good (4:1 to 10:1).

Table 1. Optimization of the reaction conditions.^[a]

Entry	Change from the "standard conditions"	3 aa Yield (%) (<i>E/Z</i> ratio) ^[b]	4 aa Yield (%)	Overall yield (%)
1	None	34 (4:1)	36	70
2	at 60 °C, 4 h	42 (5:1)	40	82
3	at 40 °C, 4 h	44 (4:1)	38	82
4	at 25 °C, 4 h	42 (6:1)	31	73
5	No Zn	33 (6:1)	34	67
6	No Zn, at 60 °C, 4 h	36 (7:1)	28	64
7	No Zn, at 40 °C, 20 h	–	–	NR
8 ^[c]	No Zn	44 (6:1)	48	92
9 ^[c]	No $\text{Co}(\text{OAc})_2$, No dppe, no Zn	–	–	NR
10 ^[c]	$\text{Ni}(\text{OAc})_2$ instead of $\text{Co}(\text{OAc})_2$, no Zn	41 (6:1)	43	84
11 ^[c]	No dppe, no Zn	–	–	NR
12 ^[c]	dppp instead of dppe, no Zn	38 (7:1)	31	69
13 ^[c]	dppb instead of dppe, no Zn	11 (8:1)	15	26
14 ^[c]	dppf instead of dppe, no Zn	–	–	NR



^[a] Reaction conditions: vinylaziridine **1a** (56 mg, 0.25 mmol, 1 equiv.), phenylacetylene **2a** (102 mg, 1 mmol, 4 equiv.), $\text{Co}(\text{OAc})_2$ (2 mg, 5 mol%), dppe (5 mg, 5 mol%), Zn (8 mg, 50 mol%), DMSO (0.5 mL).

^[b] Determined by ^1H NMR.

^[c] freshly distilled phenylacetylene. NR = no reaction.

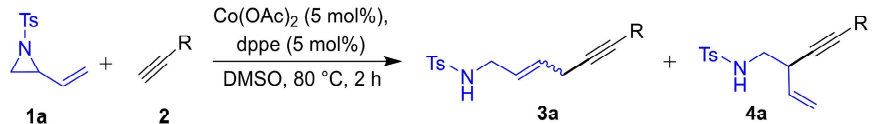
Despite a longer reaction time (20 h), no reaction occurred with 1-cyclohexenylacetylene, 1-butyne or propargyl acetate (entries 17–19). With silyl-substituted acetylene, no hydroalkynylation product was formed under the optimized reaction conditions. However, upon addition of Zn as reducing agent (50 mol%), enynes **3at** and **4at** were isolated even though in moderate overall yield (entry 20). The scope investigation highlighted the strong influence of the alkyne nature on the reactivity as previously reported in hydroalkynylation reactions.^[5h,8,10d,f,11,13b,24]

The scope of the cobalt-catalyzed hydroalkynylation was then evaluated with various vinylaziridines as depicted in Table 3. Sulfonyl-substituted vinylaziridines reacted in moderate to good overall yields (entries 1–4), even with sterically hindered sulfonyl groups (entries 3 and 4). Vinylaziridine **2f** bearing an electron withdrawing phthalimidyl group reacted slowly, and even after 20 h of reaction at 80 °C, tiny amounts of linear and branched enynes were formed (entry 5). Despite a low yield, the hydroalkynylation of

vinylaziridine bearing a $\text{Ph}_2\text{P}(\text{O})$ was interesting since only the branched enyne **4ga** was obtained (entry 6). The influence of the nature of the electron withdrawing group on the regioselectivity of the hydroalkynylation was further confirmed with vinylaziridine **2h** (entry 7). The benzyl carbamate group favored the formation of the branched enyne **4ha** over the linear product **3ha** (55% vs. 26%) for an overall yield of 81%. Interestingly, the minor product **3ha** was also formed with an excellent stereoselectivity (*E/Z* ratio up to 20:1).

With the methyl-substituted vinylaziridine **6a**, no product of hydroalkynylation was detected under the optimized reaction conditions. Only enone **7a** was isolated in 33% yield after 3 h at 80 °C (Scheme 2).

The same reactivity was observed with the cyclic vinylaziridine **6b**; enone **7b** was the only product formed in 26% yield (Scheme 3a). Formation of the enone was suspected to arise from the action of DMSO as oxidant. Hence, a control experiment was performed in the absence of the cobalt catalyst. As depicted in Scheme 3b, treatment of **6b** with 10 equivalents of

Table 2. Investigation of the scope of the cobalt-catalyzed hydroalkynylation with various alkynes.^[a]


Entry	R	3 a Yield (E/Z ratio) ^[b]	4 a Yield	Overall yield
1	Ph	44% (6:1)- 3 aa	48%- 4 aa	92%
2		X=OMe 30% (7:1)- 3 ab	36%- 4 ab	66%
3		X=OAc 40% (10:1)- 3 ac	41%- 4 ac	81%
4		X=NMe ₂ 14% (7:1)- 3 ad	16%- 4 ad	30%
5 ^[c]		X=NMeAc 27% (ND)- 3 ae	27%- 4 ae	54%
6		X=Cl 33% (10:1)- 3 af	31%- 4 af	64%
7		X=NO ₂ —	—	—
8		X=CF ₃ —	—	—
9		X=Me 13% (6:1)- 3 ai	12%- 4 ai	25%
10		12% (5:1)- 3 aj	12%- 4 aj	24%
11		X=Me 29% (6:1)- 3 ak	31%- 4 ak	60%
12		X=CF ₃ 13% (4:1)- 3 al	10%- 4 al	23%
13		X=CO ₂ Et 25% (6:1)- 3 am	27%- 4 am	52%
14		34% (7:1)- 3 an	34%- 4 an	68%
15		32% (7:1)- 3 ao	29%- 4 ao	61%
16		25% (5:1)- 3 ap	28%- 4 ap	53%
17 ^[d]		—	—	—
18 ^[d]	<i>n</i> Bu	—	—	—
19 ^[d]		—	—	—
20 ^[d,e]	Si(<i>i</i> Pr) ₃ (TIPS)	16% (4:1)- 3 at	17%- 4 at	33%

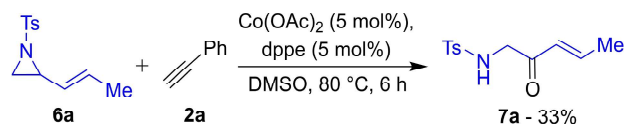
^[a] Reaction conditions: vinylaziridine **1 a** (56 mg, 0.25 mmol, 1 equiv.), alkyne **2** (1 mmol, 4 equiv.), Co(OAc)₂ (2 mg, 5 mol%), dppe (5 mg, 5 mol%), DMSO (0.5 mL), 80 °C, 2 h.

^[b] Determined by ¹H NMR.

^[c] branched and linear alkynes were unseparable by silica gel chromatography.

^[d] reaction time = 20 h.

^[e] with Zn (8 mg, 50 mol%). ND = not determined.

**Scheme 2.** Reactivity of substituted vinylaziridine **6 a**.

DMSO in DCE at 60 °C for 20 h gave 63% of **7 b**. Of note, several reports in the literature detail the oxidation of vinylaziridines into enones with various

oxidants (pyridine *N*-oxide, *N*-bromosuccinimide, ceric ammonium nitrate, 2-iodoxybenzoic acid).^[22] Moreover, the absence of reactivity using a phenylaziridine substrate highlighted the requirement of the vinyl moiety to achieve the hydroalkynylation reaction.^[23]

To shed light on the mechanism of this cobalt-catalyzed hydroalkynylation, additional experiments were carried out. In order to probe the formation of a cobalt(II)-acetylide intermediate, as suggested in several literature reports,^[5h,10d,20b,25] deuterium incorpora-

Table 3. Scope of the cobalt-catalyzed hydroalkynylation with various vinylaziridines.^[a]

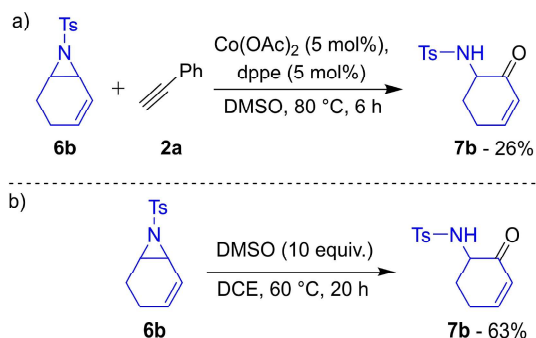
Entry	EWG	3 a Yield (<i>E/Z</i> ratio) ^[b]	4 a Yield	Overall yield
1	SO ₂ Me	29% (15:1)- 3 ba	32%- 4 ba	61%
2	SO ₂ Ph	29% (6:1)- 3 ca	24%- 4 ca	53%
3		28% (7:1)- 3 da	36%- 4 da	64%
4		27% (8:1)- 3 ea	23%- 4 ea	50%
5 ^[c]		3% (ND)- 3 fa	3%- 4 fa	6%
6		—	27%- 4 ga	27%
7		26% (> 20:1)- 3 ha	55%- 4 ha	81%

^[a] Reaction conditions: vinylaziridine **1** (0.25 mmol, 1 equiv.), phenylacetylene **2 a** (102 mg, 1 mmol, 4 equiv.), Co(OAc)₂ (2 mg, 5 mol%), dppe (5 mg, 5 mol%), DMSO (0.5 mL), 80 °C, 2 h.

^[b] Determined by ¹H NMR.

^[c] reaction time = 3 h.

^[d] reaction time = 20 h. ND = not determined.

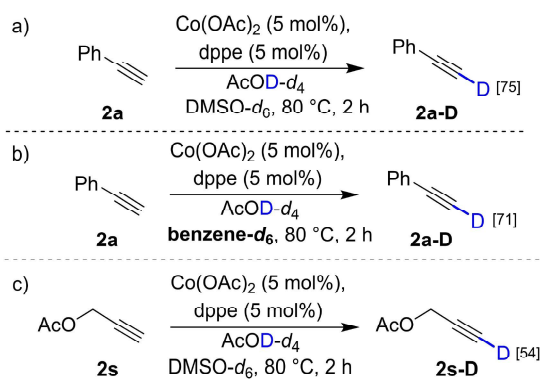
**Scheme 3.** Reactivity of cyclic vinylaziridine **6b**.

tion experiments were performed using 5 equivalents of acetic acid-*d*₄. After 2 hours of heating at 80 °C, phenylacetylene was recovered with 75% of deuterium labelling (Scheme 4,a). Of note, the deuterium incorporation also occurred at 25 °C but slowly (20% after 6 h). Similar partial deuterium incorporation occurred in benzene (Scheme 4,b) highlighting that the nature of the solvent might not play a role during the Co(II)

acetylide formation. The deuterium incorporation also took place with propargylacetate **2 s** (54% after 2 h at 80 °C, c).

Scheme 5 depicts the catalytic cycle proposed for the cobalt-catalyzed hydroalkynylation of vinylaziridines. Through a ligand exchange, the cobalt acetylide **B** would be formed from cobalt acetate **A** and alkyne **2**. **B** would then coordinate vinylaziridine **1** either through the carbon-carbon double bond or the nitrogen atom, leading to intermediates **C1** and **C2**, respectively. Subsequent acetylide addition would give intermediates **D1** and **D2**. The alkylation selectivity would be related to the nature of the electron withdrawing group on the nitrogen atom as observed experimentally. Finally, a protodemetalation step would release products **3** and **4** and regenerate active species **A**.

To illustrate the synthetic usefulness of the hydroalkynylation adducts, the branched enyne **4 aa** was first treated with iodine in acetonitrile in presence of silver acetate and potassium carbonate (Scheme 6). This iodocyclization afforded the iododihydropyrrole **8** in



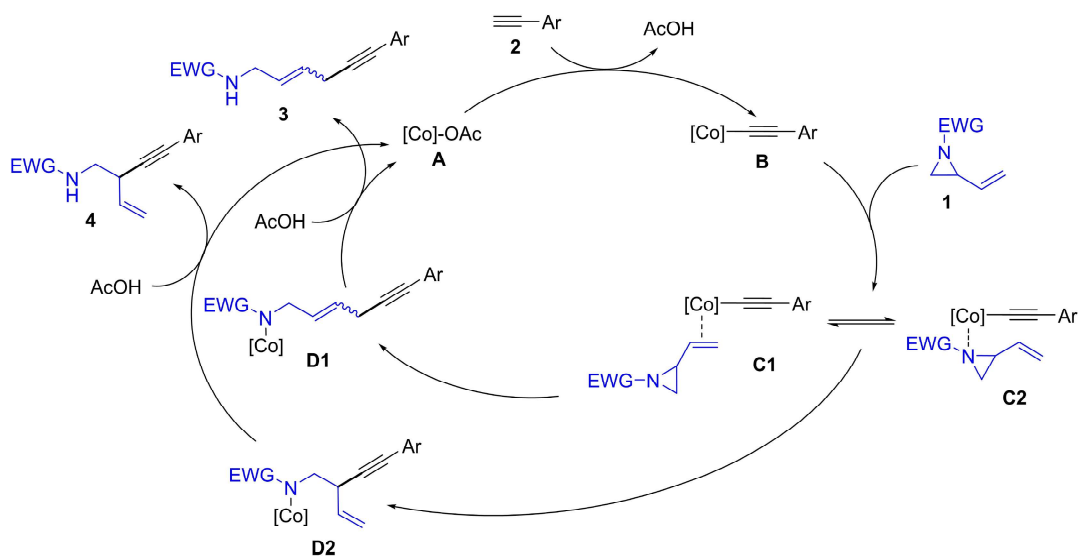
Scheme 4. Hydrogen-deuterium exchange experiments.

moderate yield through a 5-endo-dig cyclization process.^[26]

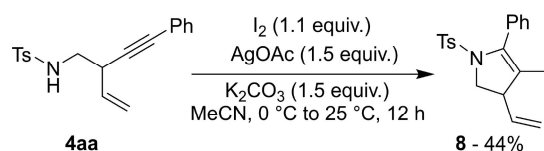
Linear 1,4-enyne **3aa** was further functionalized with alkyne moieties to give 1,6-enynes **9a** and **9b** as potential substrates for metal-catalyzed cycloisomerizations. Several cationic gold complexes were then tested but only degradation was observed. Upon heating in toluene in the presence of 10 mol% of PtCl_2 , enyne **9a** rapidly decomposed whereas enyne **9b** gave the expected cyclic product **10b** in moderate yield (Scheme 7).

Conclusion

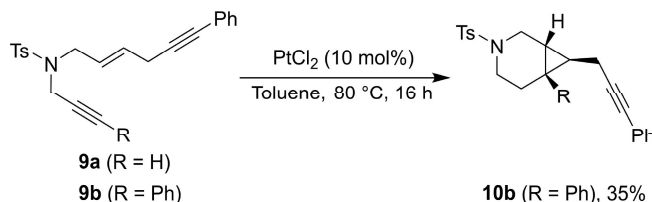
In summary, we have described an unprecedented cobalt-catalyzed hydroalkynylation of vinylaziridines. This transformation represents one of the rare examples of cobalt-catalyzed transformations allowing the ring opening of small rings.^[27] Despite a low selectivity between linear and branched adducts, the latter were



Scheme 5. Proposed catalytic cycle for the cobalt-catalyzed hydroalkynylation of vinylaziridines.



Scheme 6. Iodocyclization of branched enyne **4aa**.



Scheme 7. Platinum-catalyzed cycloisomerization of enynes **9a** and **9b**.

isolated in good overall yields. Scope investigation showed that this reaction was strongly influenced by the electronic effect of the arylalkyne substituents. The utility of both linear and branched enynes was highlighted in the synthesis of cyclic product **8** by iodocyclization or bicyclic compound **10b** through platinum-catalyzed cycloisomerization. Further developments are currently underway in our laboratory and will be reported in due course.

Experimental Section

General procedure for cobalt-catalyzed hydroalkynylation reaction: In a glovebox, an oven-dried Schlenk tube was charged with anhydrous cobalt (II) acetate (2 mg, 0.012 mmol, 5 mol%) and 1,2-bis(diphenylphosphino)ethane (5 mg, 0.012 mmol, 5 mol%). Outside of the glovebox, anhydrous

DMSO (0.3 mL), vinylaziridine **1** (0.25 mmol, 1 equiv.) and alkyne **2** (1 mmol, 4 equiv.) were added in turn followed by an additional amount of anhydrous DMSO (0.2 mL). The reaction mixture was heated to 80 °C and stirred for 1–3 h. The reaction was monitored by TLC and after complete consumption of vinylaziridine **1**, the reaction mixture was cooled to room temperature and diluted with AcOEt. The organic layer was washed with water (2 times), brine and dried over MgSO₄. After concentration under reduced pressure, the residue containing a mixture of linear and branched adducts, **3** and **4** respectively, was purified by silica gel column chromatography with a gradient of eluents (PE/Et₂O = 9:1–7:3).

Acknowledgements

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