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Cobalt-Catalyzed (*E*)-*β*-Selective Hydrogermylation of Terminal Alkynes

Maxim R. Radzhabov and Neal P. Mankad*

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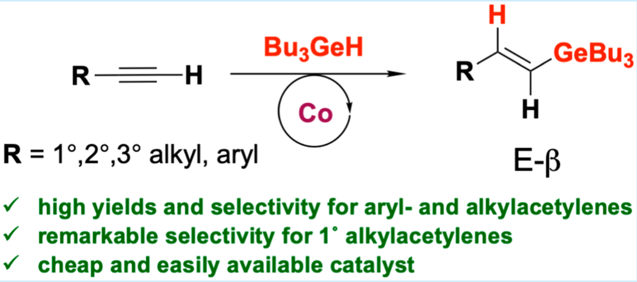
ABSTRACT: A cobalt-catalyzed method for the hydrogermylation of alkynes is reported, providing a selective and accessible route to (*E*)-*β*-vinyl(trialkyl)germanes from terminal alkynes and $HGeBu_3$. As shown in multiple examples, the developed method demonstrates a broad functional group tolerance an practical utility for late-stage hydrogermylation of natural products. The method is compatible with alkynes bearing both aryl and alkyl substituents, providing unrivaled selectivity for previously challenging 1° alkyl-substituted alkynes. Moreover, the catalyst used in this method, $Co_2(CO)_8$, is a cheap and commercially available reagent. Conducted mechanistic studies supported the *syn*-addition of Bu_3GeH to an alkyne *π*-complex.



Given the prominence of Pd-catalyzed cross-coupling for C−C bond formation, there is a continued demand for new coupling partners that enable advanced synthetic methods. Recently, organogermanes[1−3] have emerged as prospective coupling partners to circumvent the limitations of traditional organozinc and organomagnesium reagents[4,5] (low functional group tolerance), organosilanes[6] (low reactivity), organostannanes[7] (acute toxicity), and organoboronic acids[8] (acid and base sensitivity). In this regard, vinylgermanes are of particular interest as versatile synthetic building blocks due to their low toxicity,[9] resistance to protonolysis,[10] and benchtop stability.[11] Vinylgermanes have proven to be useful reagents that can be converted to vinylhalides with retention of the double-bond geometry[12] and used as partners in Pd-catalyzed coupling.[13,14] Thus, catalytic methods for producing vinylgermanes with high regio- and stereoselectivities are desirable, and the most atom-economical approach would be the hydrogermylation of alkynes.

Although a variety of catalysts has been studied to selectively perform the hydrogermylation of alkynes since the middle of the 20th century,[15] control over regio- and stereoselectivity still remains a challenging problem that limits the development of vinylgermane chemistry. In many cases, the selectivity is controlled by specific reaction conditions or functional groups[14,16−19] but is moderate in the absence thereof. Studied hydrogermylation catalysts include Lewis acids; precious metals such as Pd, Ru, Rh, and Pt;[10] and earth-abundant metals such as Mn and Fe (Figure 1). Lewis acids (Figure 1a), represented by boron compounds, tend to yield only (*Z*)-*β*-isomers (*α* for propiolates) if trialkylgermanes are used[12] but can generate germyl radicals from Ph_3GeH and yield both (*Z*)-*β*- and (*E*)-*β*-products.[20] Among precious metals, Pd catalysts have been studied especially well. Oshima and Utimoto[21] demonstrated that the $Pd(PPh_3)_4$ catalyst yields (*E*)-*β*-isomers selectively with Ph_3GeH, but with trialkylgermanes the selectivity was reported to be only 4:1 (*β*/*α*) for primary alkylacetylenes (Figure 1b). In 2009, Maleczka[13] reported that this Pd catalyst affords only the (*E*)-*β*-isomer for tertiary alkylacetylenes, but for unhindered alkynes the selectivity remained no more than 4:1. The (*E*)-*β*- and *α*-selective hydrogermylation of phenylacetylene with tri-*n*-butylgermane, Bu_3GeH, by Rh catalysts was reported by Wada in 1991, though this reaction requires 10 equiv of PhCCH.[22] (*E*)-*β*-Vinylgermanes were also formed by the Ru-catalyzed dehydrogenative germylation of styrene with Bu_3GeH but again required 10 equiv of styrene for a high selectivity.[23]

Given the limitations of precious metal-catalyzed hydrogermylations, there exists an opportunity for earth-abundant metal catalysis; however, this has been studied to a lesser extent and is only represented by Mn and Fe (Figure 1c). In 2011, Nakazawa demonstrated that Fe catalysts yield (*Z*)-*β*-isomers for both Bu_3GeH and Ph_3GeH as well as aryl- and alkylacetylenes with excellent yields and selectivities.[24] Very recently, Zhang and Zhang reported the visible light-initiated,

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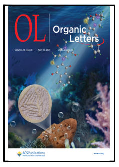

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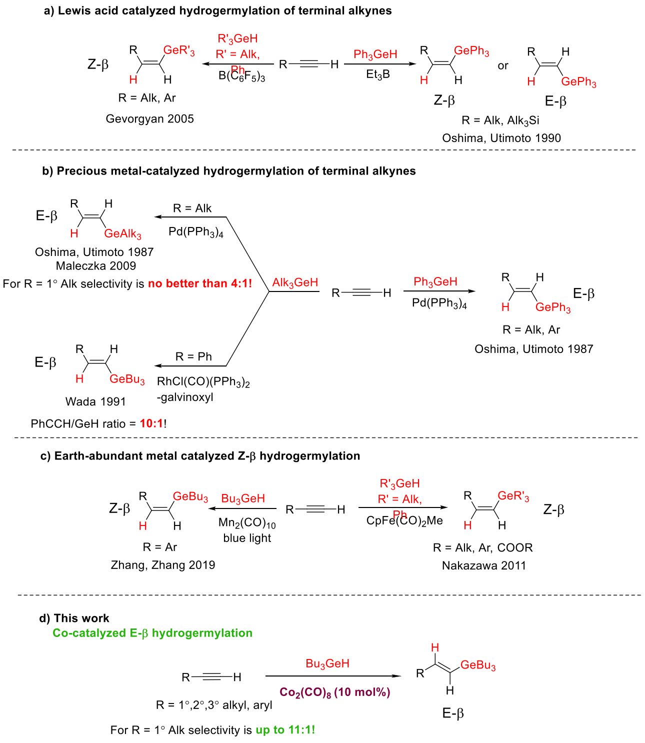


Figure 1. Hydrogermylation of terminal alkynes.

Mn-catalyzed, (Z)-β-selective hydrogermylation of arylalkynes with Bu_3GeH in 2019.[25]

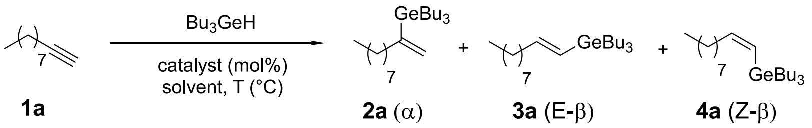
Herein, we report a Co-catalyzed, (E)-β-selective hydrogermylation of alkyl- and arylacetylenes with Bu_3GeH (Figure 1d), a new method that allowed us to obtain (E)-β-isomers from primary alkylacetylenes with selectivities by far surpassing all existing methods, including those that employ precious-metal catalysts.

Initially, we believed that an approach similar to that previously reported by our group for hydrostannylation[26] could be developed for trialkylgermanium hydrides and thus began our investigation using (NHC)CuCl and metal carbonyl anion cocatalysts to catalyze the reaction between 1-decyne and Bu_3GeH (NHC = N-heterocyclic carbene). However, control experiments indicated that the presence of (NHC)-CuCl was not required to observe hydrogermylation activity in some cases. In particular, catalytic Na[$Co(CO)_4$] provided the isomers α (**2a**) and (E)-β (**3a**) with reasonable conversions. Alas, the isomers were in a ~1:1 ratio with no formation of the (Z)-β-product **4a** (Table 1, entry 1). To date, this is the first example of a reported Co-catalyzed hydrogermylation reaction. Other metal carbonyl anions, such as $NaCrCp(CO)_3$, $NaWCp(CO)_3$, and $NaMoCp(CO)_3$, yielded no products at all. An extensive investigation of Na[$Co(CO)_3L$] (L = CO or PPh_3) catalysts did not provide a selectivity greater than 4:1 for **3a**/**2a** (Table 1, entry 2).

It was recently reported that $Mn_2(CO)_{10}$ can catalyze visible-light-induced radical hydrogermylation of arylalkynes, though results with alkylalkynes were not included.[25] Therefore, we decided to try the reported conditions with alkylalkynes using $Mn_2(CO)_{10}$ and a related Co catalyst, $Co_2(CO)_8$ (Table 1, entries 3 and 4). We found that the Mn-catalyzed reaction mostly yields the (Z)-β-product **4a** with a high selectivity (Z/E = 10:1) but a low conversion (~22%). Under the same conditions, $Co_2(CO)_8$ demonstrated a somewhat better conversion (~55%) but essentially no selectivity, giving all three isomers **2a**, **3a**, and **4a**. The same set of reagents, being activated thermally (Table 1, entry 5), performed much better and mostly yielded the desired (E)-β-isomer (**3a**) with a better selectivity (β/α = 5.5:1) and overall conversion (~70%). Changing the Bu_3GeH:1-decyne stoichiometric ratio from 1.2:1.0 to 1.0:1.1 significantly boosted the reaction selectivity and conversion (Table 1, entry 6). Lowering temperature and the reaction time did not dramatically diminish the results (1, entries 7 and 8, respectively). A lower catalyst loading slightly decreases the selectivity of the reaction, but greater loading does not have any noticeable effect (Table 1, entries 9 and 10). Thus, we decided to proceed with the optimized conditions of entry 8.

Under the optimal conditions, we tested the hydrogermylation for a range of substituted alkynes with various functional groups (Figure 2). The vast majority of tested alkynes smoothly underwent anti-Markovnikov hydrogermylation to afford (E)-β-vinylgermanes with good regioselectivities and excellent yields. Apparently, ester (**3c**), amide (phthalimide **3e**), silyl (**3j**), and silyl ether (**3m**) are very well tolerated

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	T (°C)	**1a** (equiv)	Bu_3GeH (equiv)	time (h)	solvent	**2a** (%)	**3a** (%)	**4a** (%)
1	$NaCo(CO)_4$ (10%)	100	1.0	1.2	15	toluene	56	44	0
2	$NaCo(CO)_4$ (10%)	85	1.1	1.0	15	DCE	20	80	0
3	$Mn_2(CO)_{10}$ (10%)	RT, $h\nu$[b]	1.0	1.2	15	DCM	traces	2	20
4	$Co_2(CO)_8$ (10%)	RT, $h\nu$[b]	1.0	1.2	15	DCM	16	24	16
5	$Co_2(CO)_8$ (10%)	85	1.0	1.2	15	DCE	10	55	6
6	$Co_2(CO)_8$ (10%)	85	1.1	1.0	15	DCE	8	90	0
7	$Co_2(CO)_8$ (10%)	60	1.1	1.0	15	DCE	9	91	0
8	$Co_2(CO)_8$ (10%)	60	1.1	1.0	4	DCE	9	86	0
9	$Co_2(CO)_8$ (5%)	60	1.1	1.0	15	DCE	12	85	0
10	$Co_2(CO)_8$ (15%)	60	1.1	1.0	15	DCE	9	87	0

[a] The reactions were performed on a 0.2 mmol scale. Yields were determined by the ^1H NMR integration of isolated mixtures against an internal standard. [b] The light source was blue LED strip lights (DC 12 V 2A power supply).

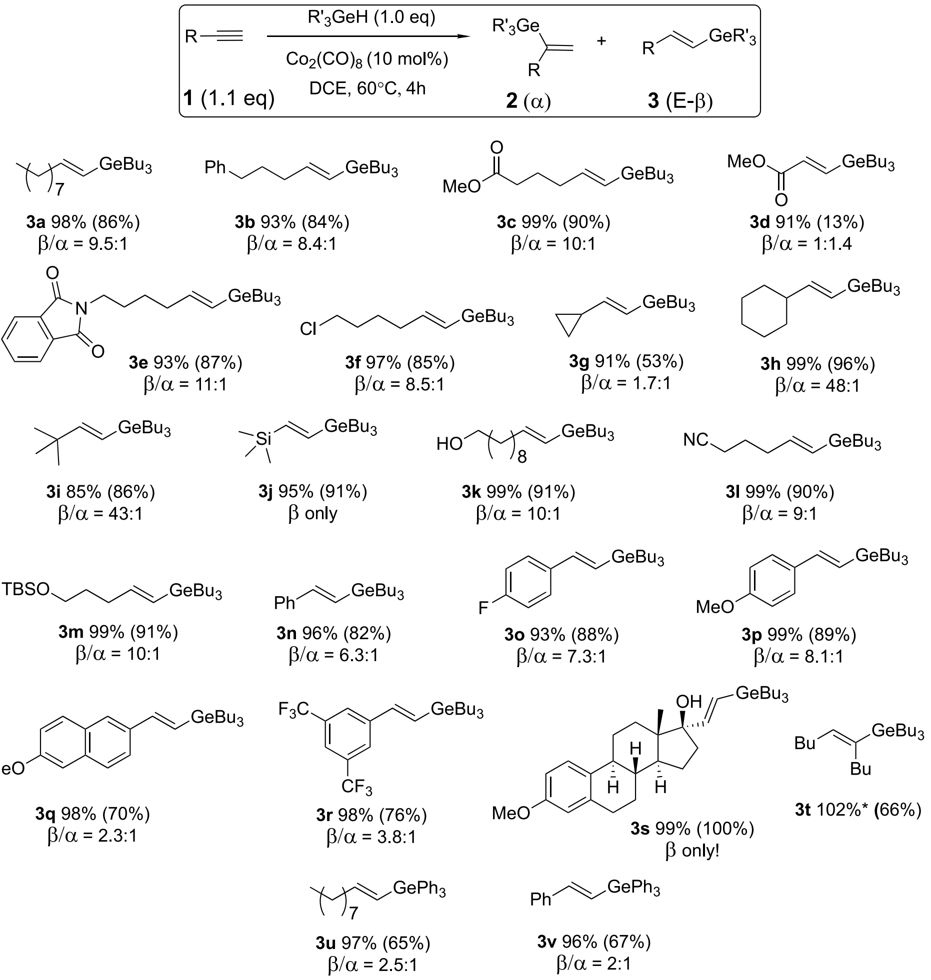


Figure 2. Hydrogermylation of various alkynes using the $Co_2(CO)_8$ catalyst (0.2 mmol scale). Reported values correspond to isolated mixtures (α + (E)-β). Values in parentheses are NMR yields for the (E)-β isomer only. (*) For **3t**, the isolated yield is >100% because some 5-decyne remained in the mixture.

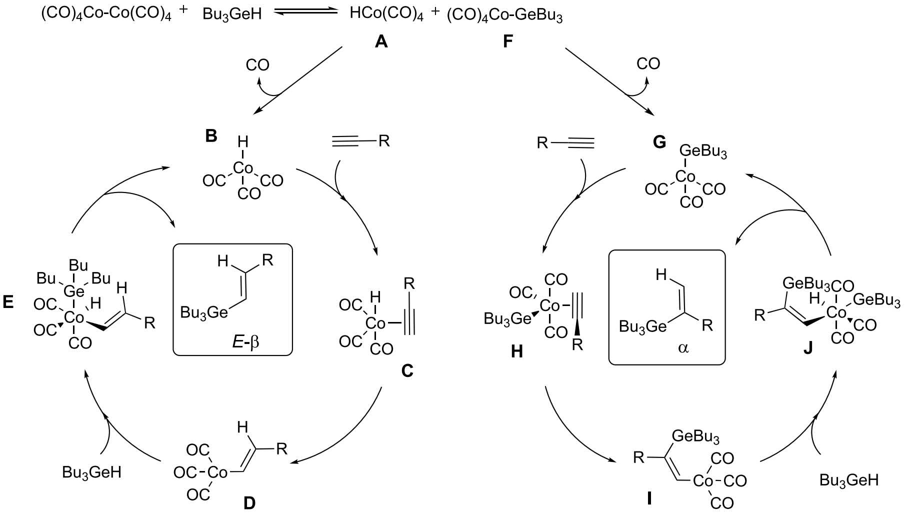


Figure 3. Plausible mechanism for the Co-catalyzed hydrogermylation.

among alkyl-substituted vital functional groups. Halide groups (**3f**), strongly coordinating alkyl nitrile (**3l**), and even an unprotected alcohol group (**3k**) are totally compatible with the reaction conditions. Bulky tertiary and secondary alkyl substituents (such as **3h** and **3i**) greatly increase the selectivity of the reaction (with the unfortunate exception of cyclopropylacetylene **3g**, which gave a low selectivity). It is also interesting to note that a low selectivity and yield were observed for methyl propiolate (**3d**), but propiolates generally tend to yield α-products.[12] Internal alkynes do react under the

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given conditions, though with somewhat lower yields (**3t**), probably due to substantial steric hindrance. Remarkably, the reaction proved to be regiospecific for silyl acetylene (**3j**) and especially Mestranol (**3s**), as no traces of the undesired α-isomer were observed in the corresponding NMR spectra. Therefore, our method demonstrated its practical utility for the late-stage hydrogermylation of natural compounds and pharmaceuticals.

Aryl-substituted alkynes were also tested under the same conditions (Figure 2), giving (E)-β-vinylgermanes as the major products with good yields. Activated arylalkynes with electron-donating or electron-withdrawing groups have higher selectivities for (E)-β isomers (**3o** and **3p**), compared to nonactivated phenyl acetylene (**3n**). However, overly strong electron-withdrawing groups can decrease the selectivity (**3r**). Poor selectivity was also observed for ethynyl naphthalene (**3q**).

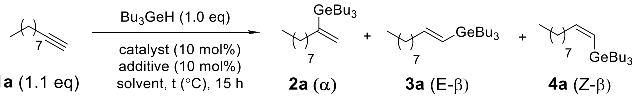
We also investigated the reactivity of triphenylgermanium hydride, Ph_3GeH, under the studied conditions (Figure 2), but unfortunately only moderate yields and a poor selectivity were obtained with 1-decyne and phenyl acetylene (**3u** and **3v**, respectively). The reaction mechanism for Ph_3GeH is probably different from Bu_3GeH, as the former is prone to form radicals.[20]

We would like to propose the following mechanism (Figure 3) for our (E)-β-selective hydrogermylation, which is based on analogies found in the literature.[27,28] The reaction between $Co_2(CO)_8$ and Bu_3GeH most likely generates cobalt tetracarbonyl hydride, $HCo(CO)_4$, and $Bu_3Ge{-}Co(CO)_4$ (analogous to that studied by Jeannin),[29] and then both cores can probably catalyze the hydrogermylation reaction (albeit with different selectivities and efficiencies).

Just like the well-known hydroformylation, the cycles begin with the thermally induced dissociation of the carbonyl CO from original $HCo(CO)_4$ **A** and $Bu_3Ge{-}Co(CO)_4$ **F** complexes to generate active 16-electron species **B** and **G**, respectively (Figure 3). Then, the addition of an alkyne generates the corresponding π-complexes **C** and **H**. For the $HCo(CO)_4$ pathway, a hydride complex **C** easily undergoes 1,2-migratory insertion to form a new 16-electron alkenyl tricarbonyl complex **D**. Then, complex **D** undergoes oxidative addition with Bu_3GeH to give a new 18-electron germylvinyl-(tricarbonyl)cobalt **E**, which releases the desired alkene by reductive elimination. It is quite probable that $Bu_3Ge{-}Co(CO)_4$ **F** actively takes part in the studied reaction, since higher amounts of Bu_3GeH significantly change the reaction yields and selectivity (please see the Supporting Information). In this pathway, a tributylgermyl group in **H** can undergo migratory insertion to form a new 16-electron **I**. That new species can undergo oxidative addition with another molecule of Bu_3GeH to give **J**, which then releases the product via reductive elimination. An analogous hydrosilylation of ethylene by $Et_3Si{-}Co(CO)_4$ was studied by Wrighton under photochemical conditions.[30]

We conducted some experiments to obtain additional support for the proposed mechanism (Table 2). The first test was to study the susceptibility of the reaction to acids and bases present in the reaction mixture, since we believe the key intermediate is cobalt tetracarbonyl hydride, $HCo(CO)_4$, which is known to be acidic. While acids have little to no effect on the reaction for both $NaCo(CO)_4$ and $Co_2(CO)_8$ (Table 2, entries 1 and 3, respectively), strong bases like *t*BuONa inhibit the reaction (Table 2, entry 2). It is worth noting that $NaCo(CO)_4$ demonstrated a much higher selectivity for the (E)-β-product in 1,2-dichloroethane (DCE) than in other solvents (see the Supporting Information). Based on precedents from Chatani and Murai,[31,32] it is reasonable to speculate that $NaCo(CO)_4$ generates $HCo(CO)_4$ in situ from DCE by a S_N2/β-hydride elimination sequence.

Table 2. Mechanistic Studies[a]



entry	catalytic system	T (°C)	solvent	**2a** (%)	**3a** (%)	**4a** (%)
1	$NaCo(CO)_4$ + PhCOOH	85	DCE	9	82	0
2	$NaCo(CO)_4$ + *t*BuONa	100	toluene	5	3	2
3	$Co_2(CO)_8$ + PhCOOH	60	DCE	9	91	0
4	$Ph_3Si{-}Co(CO)_4$	100	toluene	15	68	2
5	$Ph_3Si{-}Co(CO)_4$ + MeOH	100	toluene	8	66	1

[a] The reaction was performed on a 0.2 mmol scale. Yields were determined by the ^1H NMR integration of isolated mixtures against an internal standard.

To further probe the cobalt hydride mechanism, we synthesized $Ph_3Si{-}Co(CO)_4$ for the subsequent alcoholysis of the cobalt−silicon bond (to generate $HCo(CO)_4$ in situ according to a known procedure).[33] We found that, in toluene, the selectivity for the (E)-β isomer is significantly lower than under the optimized conditions, but the selectivity is restored upon the addition of MeOH to the mixture (Table 2, entries 4−5).

Radical pathways can be ruled out, since the direct visible-light-induced generation of radicals from $Co_2(CO)_8$ proved to be unselective (Table 1, entry 10). We can also conclude that the studied reaction does not proceed via η^1-vinylidene Co complex; such a pathway would yield a mixture of (E/Z)-β isomers,[34] whereas for most $Co_2(CO)_8$-catalyzed reactions we observed a mixture of α- and (E)-β-isomers with little to no (Z)-β-product.

In summary, Co complexes were demonstrated for the first time as viable catalysts of a hydrogermylation reaction, enabling a selective and accessible protocol for the synthesis of previously limited (E)-β-vinyl(trialkyl)germanes from terminal alkynes and Bu_3GeH. Tertiary, secondary, and most importantly primary alkylacetylenes react well and with high selectivities under the optimized conditions. Arylacetylenes are also applicable under the reaction conditions. Obtained data and mechanistic studies supported the *syn*-addition of Bu_3GeH to a π-alkyne complex and demonstrated the crucial role of $HCo(CO)_4$ in the catalytic cycle.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00928.

Experimental details, additional experimental results, characterization data, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Neal P. Mankad − *Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States;* orcid.org/0000-0001-6923-5164; Email: npm@uic.edu

Author

Maxim R. Radzhabov − *Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.orglett.1c00928

Notes

The authors declare no competing financial interest.

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