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Pd(0)-Catalyzed Reaction of Alkynes with Trifurylgermane and CO Providing Acylgermanes: The Example of Hydrometalcarbonylation of Alkynes

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Rhodium complexes catalyze the carbonylation reaction of alkynes with triorganosilanes and carbon monoxide. This reaction has been extensively investigated and is now regarded as a "silylformylation" reaction.[1,2] The process represents metalformylation reactions to provide β-metalated α,β-unsaturated aldehydes (Scheme 1, Path A).[3] On the other hand, hydrometalcarbonylation is very rare (Scheme 1, Path B). Murai et al. have reported an iridium complex-catalyzed reaction of *alkenes* to furnish acylsilanes indirectly.[4] To our best knowledge, there are no precedent reports on direct synthesis of acylmetals from *alkynes* with group 14 metal hydrides. Herein we wish to report that the Pd(0)-catalyzed reaction of alkynes with germanium hydride under CO provided α,β-unsaturated acylgermanes in good yields.[5]

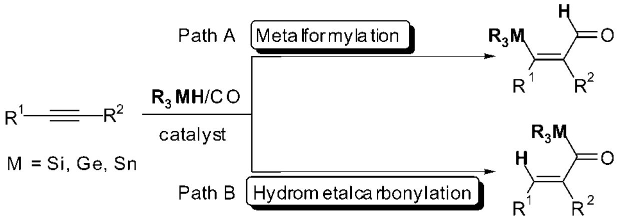
To a solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and phosphite **4** in toluene was added tri(2-furyl)germane[6] under 1.0 atm of CO. After 5 min, 1-octyne was introduced dropwise at room temperature. The reaction mixture was stirred for 5.5 h, and the solution turned yellow during this period. Concentration and purification of the reaction mixture provided 2-nonenoylgermane **1a** in 58% yield with a small amount of the regioisomer **2a** (1%) (Scheme 2). Dienylgermane **3a** via double insertion of 1-octyne was also obtained in 5% yield.[6d]

After extensive optimization of reaction conditions, we found that quinoline can suppress the formation of dineylgermane **3a** and improve the yield of acylgermane **1a** up to 78%. The use of phosphine ligands such as Ph_3P or trifurylphosphine resulted in predominant formation of **3a**. Toluene proved to be the best among reaction solvents we examined.[7] Interestingly, the reaction in water as the solvent instead of toluene provides **1a** in moderate yield (54%).

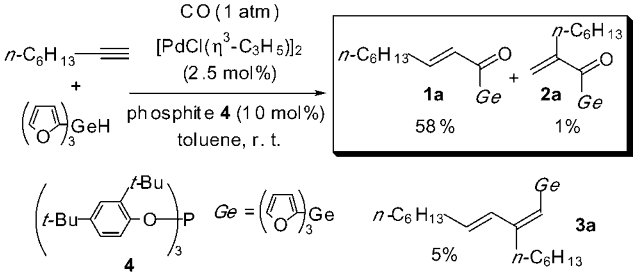
Having optimized reaction conditions, we examined various alkynes to prepare α,β-unsaturated acylgermanes. The results are summarized in Table 1. Several characteristics of this process are noteworthy. A variety of alkynes afforded the desired products in good yields. A free hydroxy group, an amino group, and an olefinic moiety are compatible (entries 5−8). A conjugated enyne, isopropenylacetylene, provided dienoylgermane **1d** in moderate yield (entry 4). None of cyclized products were obtained in the reaction with 1,6-enyne (entry 8). Unfortunately, the use of internal alkynes such as 6-dodecyne yielded none of the cylgermanes under the same conditions.

We propose the plausible reaction mechanism as depicted in Scheme 3.[8] (1) Oxidative addition of tri(2-furyl)germane to Pd(0) providing hydridopalladium **5**, (2) regioselective hydropalladation across an alkyne, and (3) CO insertion into vinylpalladium species **6** followed by reductive elimination produce acylgermane **1**, and regenerate the Pd(0) catalyst. Insertion of a second alkyne into **6** is a minor pathway furnishing dienylgermane **3** as a byproduct. Quinoline coordinated to palladium likely retards the second alkyne insertion but not the CO insertion. In general, analogous alkenylstannylpalladiums do not allow insertion of CO, because of their rapid reductive elimination to furnish alkenylstannanes. In fact, the use of triphenylstannane instead of tri(2-furyl)germane provided none of the carbonylation products.[9] We speculate that a relatively long lifetime of alkenylgermylpalladium **6** enables insertion of CO.

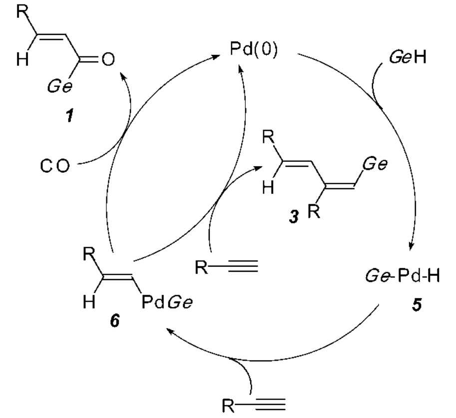
Scheme 1



Scheme 2



Scheme 3



We have also commenced a preliminary study of synthetic application of acylgermanes.[10] We found that acylgermanes reacted with secondary amines to provide the corresponding amides in good yields in the presence of a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (Scheme 4).[11] Tri(2-furyl)germane can be recovered in good yield. Furthermore, carbonylation and amide formation can be conducted in a one-pot operation. This two-step procedure achieves highly regioselective hydrocarbamoylation of alkynes.[12]

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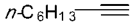
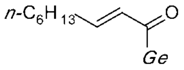
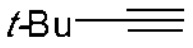
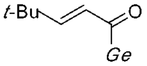
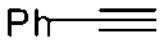
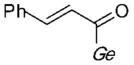
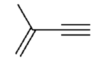
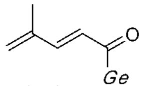
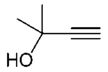
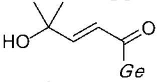
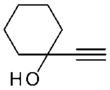
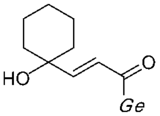
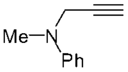
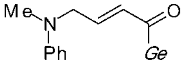
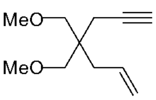
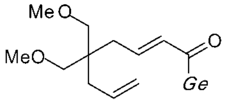
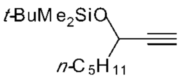
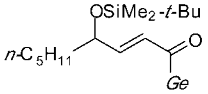
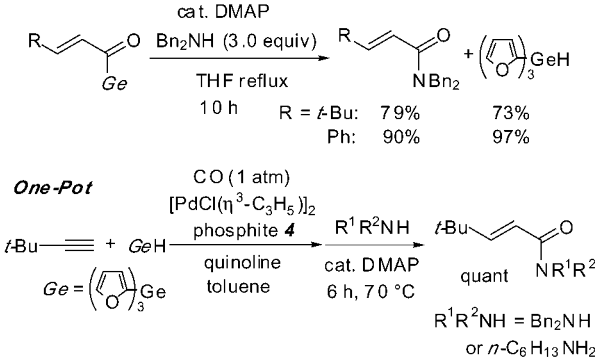
Table 1. Conversion of Alkynes into α,β-Unsaturated Acylgermanes[a]

Entry	Alkyne	Acylgermane		Yield (%)
1			**1a**	78
2			**1b**	83
3			**1c**	75
4			**1d**	69
5			**1e**	72
6			**1f**	62
7			**1g**	72
8			**1h**	60
9			**1i**	75

[a] Reaction conditions: alkyne (1.0 mmol), tri(2-furyl)germane (1.0 mmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.025 mmol), phosphite **4** (0.1 mmol), quinoline (0.1 mmol), toluene (5 mL), CO (1.0 atm), room temperature.

Scheme 4



In conclusion, we have found the first example of hydrometalcarbonylation of alkynes to furnish an acylmetal. The palladium–phosphite complex efficiently catalyzes the reaction of alkynes with tri(2-furyl)germane providing α,β-unsaturated acylgermanes under ambient pressure of CO.[13] We have also accomplished conversion of acylgermanes to the corresponding amides in good yields. Further synthetic application of acylgermanes obtained with this protocol is currently under investigation.

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Supporting Information Available: General procedures and spectral data for compounds. This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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(7) The reaction in THF or CH_2Cl_2 provided **1a** in 59% or 65% yield, respectively.

(8) The alternative mechanism that involves insertion of CO into HPdGe **5** prior to hydropalladation cannot be ruled out. However, preliminary calculations at the B3LYP/LANL2DZ level indicate that hydropalladation ($E_a = 15.2$ kcal/mol) is more feasible than CO insertion ($E_a = 57.2$ kcal/mol). See Supporting Information.

(9) No reactions proceeded with Ph_3GeH, Ph_3SiH, or tri(2-furyl)silane under otherwise the same reaction conditions.

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(11) The reaction of **1b** with diethylamine provided the corresponding amide in 88% yield. No reaction proceeded with methylaniline.

(12) Direct hydrocarbamoylation of alkynes with palladium catalysts provides the regioisomeric α,β-unsaturated amides (2-alkylacrylamides), see: (a) Kiss, G. *Chem. Rev.* **2001**, *101*, 3435. (b) Beller, M.; Cornils, M.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A* **1995**, *104*, 17. (c) Torii, S.; Okumoto, H.; Sadakane, M.; Xu, L. H. *Chem. Lett.* **1991**, 1673.

(13) In contrast, tri(2-furyl)germane was not effective for germylformylation with a rhodium catalyst. None of the aldehydes were obtained in the reaction of 1-octyne with tri(2-furyl)germane in the presence of $Rh_4(CO)_{12}$ under CO atmosphere.

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