# Germylformylation of Terminal Alkynes Catalysed by a Zwitterionic Rhodium(I) Complex

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The germylformylation of terminal alkynes is catalysed by the zwitterionic rhodium complex, [(cod)Rh$^+$($\eta^6$-$C_6H_6BPh_3$)$^-$] (cod = cycloocta-1,5-diene); this highly regio- and stereo-selective reaction affords (*Z*)-3-germylalk-2-enals in 31–82% yield.

The formylation reaction of alkynes using carbon monoxide, and employing hydrosilanes instead of $H_2$ and rhodium or rhodium–cobalt mixed-metal complexes as catalysts, has been developed during the last few years.[1] This transformation generally affords (*Z*)-3-silylalk-2-enals with a high degree of regio- and stereo-control. Although vinylsilanes and vinylstannanes are recognized to be versatile intermediates for the stereoselective synthesis of di- and tri-substituted alkenes,[2] much less attention has been paid to the synthesis of vinylgermanes.

The homogeneous rhodium[3] or platinum catalysed[3,4] hydrogermylation of terminal acetylenes was found to afford (*E*)-1-germylalk-1-enes as major products. A study of the stereochemistry of the hydrogermylation of phenylacetylene showed that the relative percentage of the three isomers obtained depended on the catalyst, the organogermane, the ratio of [alkyne]:[$GeR_3H$] and the catalyst concentration.[3] Rhodium complexes were claimed to be more selective than platinum ones, favouring the formation of (*E*)-β-germylstyrene.

To our knowledge, there are no examples of the addition of both carbon monoxide and hydrogermane to an unsaturated substrate. We now wish to report that the rhodium-catalysed germylformylation of alkynes is a novel and selective route to the corresponding (*Z*)-3-germylalk-2-enals **3** (Scheme 1).

When hex-1-yne (**1**, R = n-$C_4H_9$) was allowed to react with 1 equiv. of $GeBu^n_3H$ using a catalytic amount (1 mol%) of [(cod)Rh$^+$($\eta^6$-$C_6H_6BPh_3$)$^-$] **2**[5] in dichloromethane (5 ml) under CO (20 atm) at 90 °C for 24 h, (*Z*)-2-butyl-3-(tri-n-butylgermyl)propenal (**3**, R = n-$C_4H_9$) was isolated in 69% yield after purification of the reaction mixture by column chromatography (Table 1, entry 1). (*E*)-1-(Tri-n-butylgermyl)-hex-1-ene is the major component amongst the hydrogermyl ation by-products which were isolated in 16% yield. When the reaction was performed at 40 °C, no carbonylation occurred (entry 2).

The scope and limitations of the catalytic germylformylation reaction were examined at 90 °C with a variety of alkynes and the results are summarised in Table 1. The presence of an alkyl or an aryl substituent in the acetylene does not significantly affect the chemoselectivity of the reaction, with the germylpropenals isolated in 66–82% yield. The germylformylation products **3**† were shown by $^1$H NOE experiments to exist in the *trans* configuration. An exception occurred when prop-2-ynyl alcohol was used as the reactant with formation of a mixture of both (*Z*) and (*E*) isomers [(*Z*)(*E*) = 44:56, determined by $^1$H NMR]. The reason for the low and reverse selectivity in the latter case is as yet unknown. Internal alkynes such as hept-2-yne and 1-phenylbut-1-yne were recovered unchanged while *cis*-3-methylpent-2-en-4-yn-1-ol, an enynol, was unreactive towards germylformylation.

The hydrogermylation reaction appeared as a competing reaction in all cases. It is worthwhile noting the regio- and stereo-selectivity of germylformylation and hydrogermylation reactions. Hydrogermylation products were mainly (*E*)-1-(tri-n-butylgermyl)alk-1-enes, and the germylformylation reaction afforded (*Z*)-products.

In summary, the zwitterionic rhodium(I) complex is an excellent catalyst for the reaction of terminal alkynes with tri-n-butylgermane and CO. These first examples of germylformylation occur with high levels of regio- and stereoselectivity. It is anticipated that (*Z*)-3-germylalk-2-enals will be useful building blocks in organic synthesis.

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**Table 1** Germylformylation of alkynes **1** catalysed by [Rh$^+$($\eta^6$-$C_6H_6BPh_3$)$^-$(cod)] **2**[a]

| Entry | **1**, R = | **3**, Yield (%)[c] | **4** + **5** + **6**: Yield (%)[d] |
|---|---|---|---|
| 1 | n-$C_4H_9$ | **3a**, 69 | 16 |
| 2[b] | n-$C_4H_9$ | — | 21 |
| 3 | n-$C_6H_{13}$ | **3b**, 82 | 13 |
| 4 | $C_2H_5CHMe$ | **3c**, 72 | 14 |
| 5 | $Me_2CHCH_2$ | **3d**, 66 | 23 |
| 6 | $Ph(CH_2)_3$ | **3e**, 81 | n.d.[f] |
| 7 | Ph | **3f**, 67 | 27 |
| 8 | $HOCH_2$ | **3g**, 31[e] | 12 |

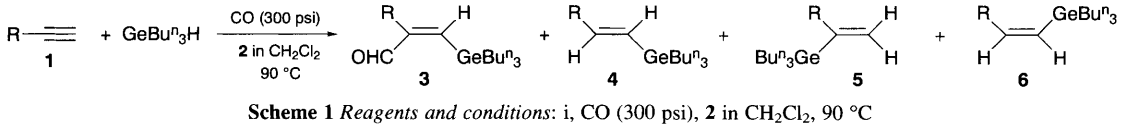
[a] Reactions were conducted in $CH_2Cl_2$ (5 ml) containing 1 mol% of **2**, 1 mmol of **1** and 1 mmol of $GeBu^n_3H$ under a CO pressure of 20 atm for 24 h at 90 °C unless otherwise specified. [b] Reaction at 40 °C. [c] Isolated yield after column chromatography. [d] Combined yield of hydrogermylation products after column chromatography. [e] The (*E*)-isomer of **3g** was also isolated in 40% yield. [f] n.d. = not determined.

## Footnote

† All new compounds **3** were fully characterized by ($^1$H, $^{13}$C) NMR, including NOE experiments, IR (neat), EI-MS and, with exception of **3d**, satisfactory C, H analyses.

*Selected data* for **3a**: IR (neat) $\nu_{CO}$/cm$^{-1}$ 1686; $^1$H NMR (200 MHz, $CDCl_3$) δ 0.8–1.5 (m, 34 H, $GeBu^n_3$ and $C_3H_7$), 2.28 (td, 2 H, *J* = 6.7, 1 Hz, =C$CH_2$), 7.00 (t, 1 H, *J* = 1 Hz, =C*H*), 9.64 (s, 1 H, C*H*O); $^{13}$C NMR (50 MHz, $CDCl_3$) 13.69 ($CH_3$ of butyl germyl), 13.89 ($CH_3$), 15.23 ($GeCH_2$), 22.38 (=$CCH_2$), 26.33 and 27.37 ($CH_2CH_2$ of butyl germyl), 30.74 and 31.39 ($CH_2CH_2$), 153.62 (=*C*H), 155.52 (*C*=CH), 194.13 (*C*HO); EI-MS *m*/*z* 299 (M$^+$ − Bu for $^{74}$Ge).

For **3b**: for IR (neat) $\nu_{CO}$/cm$^{-1}$ 1686; $^1$H NMR (200 MHz, $CDCl_3$) δ 0.8–1.5 (m, 38 H, $GeBu^n_3$ and $C_5H_{11}$), 2.28 (t, 2 H, *J* = 6.8 Hz, =C$CH_2$), 7.00 (s, 1 H, =C*H*), 9.64 (s, 1 H, C*H*O); $^{13}$C NMR (50 MHz, $CDCl_3$) 13.69 ($CH_3$ of butyl germyl), 14.05 ($CH_3$), 15.22 ($GeCH_2$), 22.59 (=$CCH_2$), 26.33 and 27.37 ($CH_2CH_2$ of butyl germyl), 28.48, 28.90 and 31.64 ($CH_2CH_2CH_2CH_2$), 153.66 (=*C*H), 155.51 (*C*=CH), 194.14 (*C*HO); EI-MS *m*/*z* 327 (M$^+$ − Bu for $^{74}$Ge).




**Scheme 1** *Reagents and conditions*: i, CO (300 psi), **2** in $CH_2Cl_2$, 90 °C

For **3c**: IR (neat) $\nu_{CO}/cm^{-1}$ 1686; $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.7–1.5 [m, 35 H, $GeBu^n_3$ and $C_2H_5C(CH_3)$], 2.73 (sext., 1 H, $J$ = 6.8 Hz, =CC$H_2$), 6.97 (s, 1 H, =C*H*), 9.65 (s, 1 H, C*H*O); $^{13}C$ NMR (50 MHz, $CDCl_3$) 11.69 ($CH_3$), 13.70 ($CH_3$ of butyl germyl), 15.28 (Ge$CH_2$), 19.73 ($CH_3$), 26.31 and 27.38 ($CH_2CH_2$ of butyl germyl), 28.88 ($CH_2$), 134.86 (*C*H), 151.68 (=*C*H), 160.28 (*C*=CH), 194.12 (*C*HO); EI-MS *m/z* 299 ($M^+$ − Bu for $^{74}Ge$).

For **3d**: IR (neat) $\nu_{CO}/cm^{-1}$ 1684; $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.8–1.5 [m, 33 H, $GeBu^n_3$ and $(CH_3)_2C$], 1.74 (m, 1 H, C*H*), 2.17 (d, 2 H, $J$ = 6.4 Hz, =CC$H_2$), 6.97 (s, 1 H, =C*H*), 9.64 (s, 1 H, C*H*O); $^{13}C$ NMR (50 MHz, $CDCl_3$) 13.72 ($CH_3$ of butyl germyl), 15.27 (Ge$CH_2$), 22.29 ($CH_3$), 26.35 and 27.42 ($CH_2CH_2$ of butyl germyl), 41.12 (*C*H), 154.40 (*C*=CH), 155.26 (=*C*H), 194.20 (*C*HO); EI-MS *m/z* 299 ($M^+$ − Bu for $^{74}Ge$).

For **3e** IR (neat) $\nu_{CO}/cm^{-1}$ 1685; $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.8–1.5 (m, 27 H, $GeBu^n_3$), 1.74 (quint. 2 H, $J$ = 7.5 Hz, $CH_2CH_2CH_2$), 2.34 (t, 2 H, $J$ = 7.3 Hz, =C$H_2$), 2.60 (t, 2 H, $J$ = 7.7 Hz, PhC$H_2$), 7.01 (s, 1 H, =C*H*), 7.1–7.3 (m, 5 H, Ph), 9.64 (s, 1 H, C*H*O); $^{13}C$ NMR (50 MHz, $CDCl_3$) 13.70 ($CH_3$ of butyl germyl), 15.23 (Ge$CH_2$), 26.34 and 27.37 ($CH_2CH_2$ of butyl germyl), 30.29, 31.37 and 35.57 ($CH_2CH_2CH_2$), 125.77, 128.31, 128.41 and 142.16 (Ph), 154.07 (*C*=CH), 155.01 (=*C*H), 194.02 (*C*HO); EI-MS *m/z* 361 ($M^+$ − Bu for $^{74}Ge$).

For **3f**: IR (neat) $\nu_{CO}/cm^{-1}$ 1693; $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.8–1.5 (m, 27 H, $GeBu^n_3$), 7.37 (s, 5 H, Ph), 7.43 (s, 1 H, =C*H*), 9.95 (s, 1 H, C*H*O); $^{13}C$ NMR (50 MHz, $CDCl_3$) 13.68 ($CH_3$ of butyl germyl) 15.11 (Ge$CH_2$), 26.32 and 27.39 ($CH_2CH_2$ of butyl germyl), 127.90, 128.08, 128.12 and 137.42 (Ph), 153.59 (*C*=CH), 157.74 (=*C*H), 192.63 (*C*HO); EI-MS *m/z* 319 ($M^+$ − Bu for $^{74}Ge$).

For **3g**: IR (neat) $\nu_{CO}/cm^{-1}$ 1680; $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.8–1.5 (m, 27 H, $GeBu^n_3$), 2.19 (t, 1 H, $J$ = 5.0 Hz, O*H*), 4.34 (d, 2 H, $J$ = 4.9 Hz, C$H_2$), 7.27 (t, 1 H, $J$ = 1.0 Hz, =C*H*), 9.69 (s, 1 H, C*H*O); $^{13}C$ NMR (50 MHz, $CDCl_3$) 13.65 ($CH_3$ of butyl germyl), 15.03 (Ge$CH_2$), 26.31 and 27.28 ($CH_2CH_2$ of butyl germyl), 63.01 ($CH_2$), 153.08 (*C*=CH), 154.38 (=*C*H), 194.15 (*C*HO); EI-MS *m/z* 319 ($M^+$ − Bu for $^{74}Ge$).

For the (*E*)-isomer of **3g**: IR (neat) $\nu_{CO}/cm^{-1}$ 1684; $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.8–1.5 (m, 27 H, $GeBu^n_3$), 2.57 (t, 1 H, $J$ = 5.0 Hz, O*H*), 4.33 (d, 2 H, $J$ = 4.9 Hz, C$H_2$), 7.13 (s, 1 H, =C*H*), 9.45 (s, 1 H, C*H*O); $^{13}C$ NMR (50 MHz, $CDCl_3$) 13.68 ($CH_3$ of butyl germyl), 13.93 (Ge$CH_2$), 26.35 and 27.34 ($CH_2CH_2$ of butyl germyl), 60.43 ($CH_2$), 153.97 (*C*=CH), 159.01 (=*C*H), 195.60 (*C*HO); EI-MS *m/z* 319 ($M^+$ − Bu for $^{74}Ge$).

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