Notes

The π-(Hydroxyalkenyl)germane Complexes Rh(acac){η^2-(*E*)-$Et_3GeCH{=}CHC(OH)R_2$}(PCy_3) (R = Me, Ph) as Intermediates in the Hydrogermylation of Alkynols Catalyzed by Rh(acac)(cyclooctene)(PCy_3)

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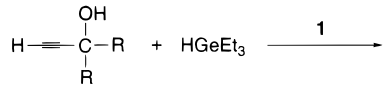
Summary: The (hydroxyalkenyl)germanes (E)-R_3Ge-CH=CHC(OH)R'_2 (R = Et, Ph; R′ = Me, Ph) are prepared in quantitative yield, and in a catalytic manner, by addition of germanes to the alkynols HC≡CC-(OH)R'_2 (R′ = Me, Ph) in the presence of the complex Rh(acac)(cyclooctene)(PCy_3). During the reactions four cycles are evident. They have as a common point the intermediates Rh(acac){η^2-(E)-CH(GeR_3)=CHC(OH)-R'_2}(PCy_3), which have been isolated for R = Et and R′ = Me, Ph.

Alkenylstannanes are very versatile organometallic reagents in palladium-catalyzed coupling reactions.[1] Some, however, are toxic. Alkenylgermanes show a very low toxicity,[2] and therefore, they could serve as alternatives to the organotin reagents.

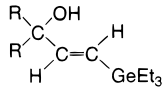
The hydrogermylation of alkynes is a simple route to alkenylgermanes. These reactions take place readily in the presence of catalytic amounts of a free radical initiator such as azobis(isobutyronitrile), but such reactions generally are not highly regio- and stereoselective.[3] The stereoselective formation of alkenylgermanes by addition of a germanium hydride to alkynes requires the presence of transition-metal catalysts.[4] From a mechanistic point of view, the transition-metal-catalyzed hydrogermylation of alkynes is a field which has not been previously investigated.

Previously, we have reported that the cyclooctene complex Rh(acac)(cyclooctene)(PCy_3) (**1**) reacts with $HGeEt_3$ to give the hydrido−germyl compound Rh(acac)H($GeEt_3$)(PCy_3) (**2**).[5] As a part of our work on the reactivity of transition-metal complexes toward alkynols,[6] we have investigated the use of **1** and **2** as catalysts for the preparation of (hydroxyalkenyl)germanes.

The compounds (*E*)-$Et_3GeCH{=}CHC(OH)R_2$ (R = Me (**5**), Ph (**6**)) can be synthesized via the stoichiometric reactions shown in eq 1. The cyclooctene ligand of **1** is



R = Me (**3**), Ph (**4**)



(1)

R = Me (**5**), Ph (**6**)

displaced by the alkynols HC≡CC(OH)R_2 (R = Me (**3**), Ph (**4**)) to afford the π-hydroxyalkyne compounds Rh-

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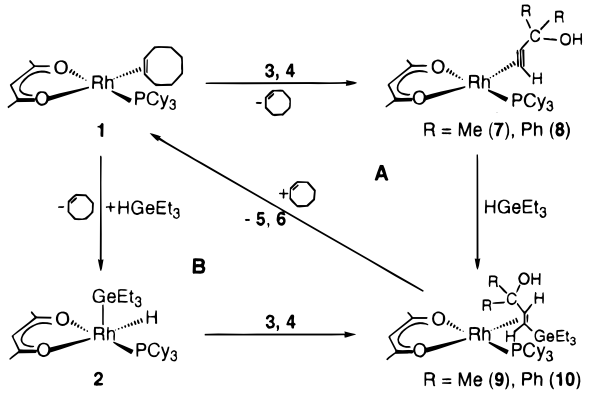
Scheme 1



(acac){η^2-HC≡CC(OH)R_2}(PCy_3) (R = Me (**7**), Ph (**8**)[7]) (Scheme 1). The reactions were carried out at −78 °C, in pentane as solvent, and the reaction products were isolated as yellow solids in 84% (**7**) and 71% (**8**) yields. Treatment of toluene solutions of **7** and **8** with 1 equiv of $HGeEt_3$ at room temperature leads to the π-(hydroxyalkenyl)germane derivatives Rh(acac){η^2-(*E*)-Et_3GeCH═CHC(OH)R_2}(PCy_3) (R = Me (**9**), Ph (**10**)), which were isolated as orange solids in 65% (**9**) and 60% (**10**) yields. Complexes **9** and **10** can also be obtained by addition of 1 equiv of the alkynols **3** and **4** to toluene solutions of **2**. By this route, **9** and **10** were obtained in 55% and 50% yields, respectively.

The presence in **9** and **10** of π-(hydroxyalkenyl)-germane ligands with *E* stereochemistry at the carbon−carbon double bond is strongly supported by the ^{1}H NMR spectra of these compounds, which show olefinic resonances at 4.49 and 2.33 (**9**) and 4.96 and 2.72 (**10**) ppm, with H−H coupling constants of 13.8 (**9**) and 13.5 (**10**) Hz. In the ^{13}C{^{1}H} NMR spectra, the resonances due to the sp^2 carbons appear at 91.0 and 36.9 (**9**) and 86.6 and 40.0 (**10**) ppm.

The (hydroxyalkenyl)germane ligands of **9** and **10** can be displaced by cyclooctene to give **5** and **6** and to regenerate **1**. These reactions along with those previously mentioned constitute two stoichiometric cycles (A and B in Scheme 1) for the formation of the (hydroxyalkenyl)germanes **5** and **6** by addition of $HGeEt_3$ to the alkynols **3** and **4**, using the cyclooctene complex **1** as a template. These cycles, which differ in the entry order of the reagents into **1**, have the complexes **9** and **10** as common intermediates.

The hydrido−germyl complex **2** and the π-hydroxyalkyne compounds **7** and **8** can also be used as templates for the stoichiometric synthesis of **5** and **6** (cycles C and D in Scheme 2). Thus, we have also observed that, in the absence of cyclooctene and in toluene at room temperature, complexes **9** and **10** react with 1 equiv of $HGeEt_3$ to give the (hydroxyalkenyl)germanes **5** and **6** in 70% and 78% yields, respectively, and that the addition at −78 °C of the alkynols **3** and **4** to pentane solutions of **9** and **10** affords **5** and **6** and the π-hydroxyalkyne compounds **7** and **8**.

As expected from the chemistry described above, complex **1** efficiently catalyzes the addition of $HGeEt_3$ to the alkynols **3** and **4**. In fact, treatment of 0.67 mmol of **3** and **4** with 0.67 mmol of $HGeEt_3$ in 0.5 mL of benzene-d_6 and in the presence of 6.7 μmol of **1**, at room temperature, leads after 48 h to 0.67 mmol of the (hydroxyalkenyl)germanes **5** and **6**, according to eq 1.

Scheme 2

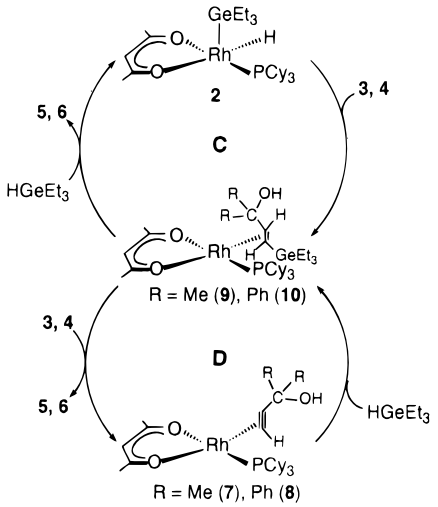


Table 1. Product Yields after 48 h of Reaction for the Hydrogermylations of Alkynes Catalyzed by Rh(acac)(cyclooctene)(PCy_3) (1)

alkyne	germane	product	yield (%)
HC≡CC(OH)Ph_2	$HGeEt_3$	(*E*)-Et_3GeCH═CHC(OH)Ph_2	100
HC≡CC(OH)Ph_2	$HGePh_3$	(*E*)-Ph_3GeCH═CHC(OH)Ph_2	71
		CH_2═C($GePh_3$)C(OH)Ph_2	12
HC≡CC(OH)Me_2	$HGeEt_3$	(*E*)-Et_3GeCH═CHC(OH)Me_2	100
HC≡CPh	$HGeEt_3$	(*E*)-Et_3GeCH═CHPh	87
		CH_2═C($GeEt_3$)Ph	10
HC≡CCy	$HGeEt_3$	(*E*)-Et_3GeCH═CHCy	81
		CH_2═C($GeEt_3$)Cy	17
HC≡C$SiMe_3$	$HGeEt_3$	(*E*)-Et_3GeCH═CH$SiMe_3$	97

Complex **1** catalyzes not only the addition of $HGeEt_3$ to 2-methyl-3-butyn-2-ol and 1,1-diphenyl-2-propyn-1-ol but also the addition of $HGeEt_3$ to phenylacetylene, cyclohexylacetylene, and (trimethylsilyl)acetylene and the addition of $HGePh_3$ to 1,1-diphenyl-2-propyn-1-ol (Table 1). These reactions are less selective than those shown in eq 1. Thus, in addition to the *E* isomer the *gem* isomers are also obtained.

In conclusion, (hydroxyalkenyl)germanes, (*E*)-R_3GeCH═CHC(OH)R'_2, can be prepared in a catalytic process, by addition of R_3GeH to the alkynols in the presence of the complex Rh(acac)(cyclooctene)(PCy_3). Four cycles (A and B in Scheme 1 and C and D in Scheme 2) seem to be involved in the catalytic reaction. Interestingly, they have as a common point the intermediates Rh(acac){η^2-(*E*)-R_3GeCH═CHC(OH)R'_2}(PCy_3), which have been isolated for R = Et and R′ = Me and Ph. These compounds are the first isolated transition-metal complexes containing (hydroxyalkenyl)germane ligands.

Experimental Section

All reactions were carried out under an atmosphere of argon using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon

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prior to use. The starting material Rh(acac)(cyclooctene)-(PCy_3) (**1**) was prepared by a published method.[8]

Preparation of Rh(acac)$\{\eta^2$-HC≡CC(OH)$Me_2\}$-(PCy_3) (7). A solution of Rh(acac)(cyclooctene)(PCy_3) (**1**; 148.2 mg, 0.25 mmol) in 15 mL of pentane was cooled to −78 °C, and then a stoichiometric amount of 2-methyl-3-butyn-2-ol (**3**; 25 μL, 0.25 mmol) was added. After the mixture was stirred for 1 h, a yellow solid was formed, which was separated by decantation, washed with pentane, and dried in vacuo. Yield: 119 mg (84%). Anal. Calcd for $C_{28}H_{48}O_3PRh$: C, 59.36; H, 8.54. Found: C, 59.12; H, 8.08. IR (KBr, cm^{-1}): ν(OH) 3416, ν(C≡C) 1837, $\nu(CO)_{acac}$ 1580 and 1520. ^1H NMR (300 MHz, toluene-d_8, 293 K): δ 5.14 (s, 1H, C*H* of acac), 4.29 (s, 1H, OH), 3.89 (s, 1H, *H*C≡C), 1.9−1.1 (m, 33H, C_6H_{11}), 1.92 (s, 6H, Me), 1.88 and 1.70 (both s, 6H, CH_3 of acac). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, 233 K): δ 50.5 (d, J_{RhP} = 179.7 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, toluene-d_8, 233 K): δ 186.7 and 184.2 (both s, *C*O of acac), 99.9 (s, *C*H of acac), 92.4 (d, J_{RhC} = 15.7 Hz, HC≡*C*), 66.3 (s, *C*OH), 66.0 (dd, J_{RhC} = 18.0 Hz, J_{PC} = 6.5 Hz, H*C*≡C), 32.9 and 32.0 (both s, Me), 31.8 (d, J_{PC} = 22.5 Hz, P*C*H), 30.3, 28.8, 28.4, 28.3, 28.2, 28.1, and 26.9 (all s, PCy_3), 27.9 and 27.2 (both s, *C*H_3 of acac).

Preparation of Rh(acac)$\{\eta^2$-(*E*)-Et_3GeCH=CHC(OH)$R_2\}$(PCy_3) (R = Me (9), Ph (10)). To a solution of **7** (141.6 mg, 0.25 mmol) or **8** (172.7 mg, 0.25 mmol) in 15 mL of toluene was added a stoichiometric amount of $HGeEt_3$ (161 μL, 0.25 mmol). A change in color from yellow to orange occurred almost instantaneously. The solution was concentrated to ca. 0.1 mL in vacuo; addition of methanol caused the precipitation of orange-yellow solids. The solids were separated by decantation, washed with methanol, and dried in vacuo.

Data for **9** are as follows. Yield: 118 mg (65%). Anal. Calcd for $C_{34}H_{64}GeO_3PRh$: C, 56.14; H, 8.87. Found: C, 56.58; H, 9.19. IR (KBr, cm^{-1}): ν(OH) 3600, $\nu(CO)_{acac}$ 1580 and 1516. NMR (C_6D_6): ^1H, δ 5.16 (s, 1H, C*H* of acac), 4.44 (d, 1H, J_{HH} = 13.8 Hz, =C*H*), 2.33 (dd, 1H, J_{HH} = 13.8, J_{PH} = 6.0 Hz, =C*H*GeEt$_3$), 2.1−1.2 (m, 33H, C_6H_{11}), 1.94 (s, 3H, Me), 1.80 and 1.75 (both s, 6H, CH_3 of acac), 1.43 (s, 3H, Me), 1.01 (s, 1H, OH); $^{31}P\{^1H\}$, δ 41.0 (d, J_{RhP} = 182.7 Hz); $^{13}C\{^1H\}$, δ 185.8 and 183.0 (both s, *C*O of acac), 99.3 (s, *C*H of acac), 91.0 (d, J_{PC} = 16.7 Hz, =*C*H), 72.2 (s, *C*OH), 39.6 (dd, J_{PC} = 15.3 Hz, J_{RhC} = 3.3 Hz, =*C*HGeEt$_3$), 34.5 (d, J_{PC} = 19.5 Hz, P*C*H), 32.6 and 31.5 (both s, Me), 31.8, 30.6, 28.6, 28.5 28.4, 28.3, and 26.9 (all s, PCy_3), 27.8 (d, J_{PC} = 5.7 Hz, *C*H_3 of acac), 26.4 (s, *C*H_3 of acac), 9.9 (s, GeCH_2*C*H_3), 7.0 (s, Ge*C*H_2CH$_3$).

Data for **10** are as follows. Yield: 128 mg (60%). Anal. Calcd for $C_{44}H_{68}GeO_3PRh$: C, 62.06; H, 8.05. Found: C, 62.31; H, 8.24. IR (KBr, cm^{-1}): ν(OH) 3613, $\nu(CO)_{acac}$ 1582 and 1518. NMR (C_6D_6): ^1H, δ 8.6−7.0 (m, 10H, Ph), 5.23 (s, 1H, C*H* of acac), 4.96 (d, 1H, J_{HH} = 13.5 Hz, =C*H*), 2.72 (dd, 1H, J_{HH} = 13.5 Hz, =C*H*GeEt$_3$), 2.1−1.1 (m, 33H, C_6H_{11}), 1.97 (s, 1H, OH), 1.81 and 1.78 (both s, 6H, CH_3 of acac); $^{31}P\{^1H\}$, δ 42.6 (d, J_{RhP} = 183.5 Hz); $^{13}C\{^1H\}$, δ 186.3 and 183.5 (both s, *C*O of acac), 150.2 and 149.0 (both s, $C_{ipso-Ph}$), 129.6, 128.1, 127.2 and 126.4 (all s, $C_{o,m,p-Ph}$), 99.4 (s, *C*H of acac), 86.6 (d, J_{PC} = 17.3 Hz, =*C*H), 80.5 (s, *C*OH), 40.0 (dd, J_{PC} = 17.3 Hz, J_{RhC} = 4.6 Hz, =*C*HGeEt$_3$), 34.3 (d, J_{PC} = 19.6 Hz, P*C*H), 31.2, 30.2, 28.6, 28.5, 28.3, 28.2, and 27.0 (all s, PCy_3), 27.8 (d, J_{PC} = 5.8 Hz, *C*H_3 of acac), 26.5 (s, *C*H_3 of acac), 9.6 (s, GeCH_2*C*H_3), 6.6 (s, Ge*C*H_2CH$_3$).

The compounds **9** and **10** can also be prepared by reaction of 0.5 mmol of the alkynols **3** and **4** with toluene solutions of 0.5 mmol of compound **2** (yields 200.0 mg (55%) and 212.9 mg (50%), respectively).

Preparation of (*E*)-Et_3GeCH=CHC(OH)R_2 (R = Me (5), Ph (6)). To a solution of **9** (218.1 mg, 0.3 mmol) or **10** (255.4 mg, 0.3 mmol) in 10 mL of toluene was added a stoichiometric amount of cyclooctene (39 μL, 0.3 mmol). After it was stirred for 1 h, the solution was concentrated to dryness. The residual oil was dissolved in ca. 0.5 mL of pentane and chromatographed on Al_2O_3 (neutral, activity grade I, column length 7 cm). With diethyl ether a colorless fraction was eluted, from which the solvent was removed in vacuo. A colorless oil was obtained.

Data for **5** are as follows. NMR (C_6D_6): ^1H, δ 6.12 (part A of an AB system, 1H, J_{HH} = 18.6 Hz, =C*H*), 5.95 (part B of an AB system, 1H, J_{HH} = 18.6 Hz, =C*H*GeEt$_3$), 1.17 (s, 7H, Me and OH), 1.06 (t, 9H, J_{HH} = 7.9 Hz, GeCH$_2$C*H*$_3$), 0.79 (q, 6H, J_{HH} = 7.9 Hz, GeC*H*$_2$-CH$_3$); $^{13}C\{^1H\}$, δ 154.1 (s, =*C*H), 120.9 (s, =*C*HGeEt$_3$), 71.6 (s, *C*OH), 29.7 (s, Me), 9.1 (s, GeCH$_2$*C*H$_3$), 4.6 (s, Ge*C*H$_2$CH$_3$). MS: *m*/*z* 246 (M^+).

Data for **6** are as follows. NMR (C_6D_6): ^1H, δ 7.5−7.0 (m, 10H, Ph), 6.63 (part A of an AB system, 1H, J_{HH} = 18.6 Hz, =C*H*), 6.16 (part B of an AB system, 1H, J_{HH} = 18.6 Hz, =C*H*GeEt$_3$), 1.96 (s, 1H, OH), 1.01 (t, 9H, J_{HH} = 7.7 Hz, GeCH$_2$C*H*$_3$), 0.76 (q, 6H, J_{HH} = 7.7 Hz, GeC*H*$_2$CH$_3$); $^{13}C\{^1H\}$, δ 150.9 (s, =*C*H), 146.8 (s, $C_{ipso-Ph}$), 128.3, 127.5 and 127.3 (all s, $C_{o,m,p-Ph}$), 125.0 (s, =*C*HGeEt$_3$), 80.6 (s, *C*OH), 9.1 (s, GeCH$_2$*C*H$_3$), 4.6 (s, Ge*C*H$_2$CH$_3$). MS: *m*/*z* 370 (M^+).

The compounds **5** and **6** can also be obtained by reaction of 0.5 mmol of complexes **9** and **10** with 0.5 mmol of $HGeEt_3$ (yields: 85.4 mg (70%) and 143.9 mg (78%), respectively).

Catalytic Studies. The catalytic reactions were carried out at room temperature in NMR tubes containing 0.0067 mmol of **1**, 0.67 mmol of $HGeR_3$, and 0.67 mmol of alkyne in 0.5 mL of benzene-d_6.

Selected NMR spectroscopic data are as follows. **(*E*)-Ph_3GeCH=CHC(OH)Ph_2**: ^1H, δ 6.97 (part A of an AB system, 1 H, J_{HH} = 18.3, =C*H*), 6.77 (part B of an AB system, 1 H, J_{HH} = 18.3, =C*H*GePh$_3$); $^{13}C\{^1H\}$, δ 154.5 (s, =*C*H), 122.5 (s, =*C*HGePh$_3$), 80.7 (s, *C*OH). **CH_2=C($GePh_3$)C(OH)Ph_2**: ^1H, δ 5.86 (d, 1 H, J_{HH} = 0.9, =CH_2), 5.56 (d, 1 H, J_{HH} = 0.9, =CH_2). **(*E*)-Et_3GeCH=CHPh**: ^1H, δ 6.90 (part A of an AB system, 1 H, J_{HH} = 19.2, =C*H*), 6.61 (part B of an AB system, 1 H, J_{HH} = 19.2, =C*H*GeEt$_3$); $^{13}C\{^1H\}$, δ 144.3 (s, =*C*H), 127.3 (s, =*C*HGeEt$_3$), 9.0 (s, GeCH$_2$*C*H$_3$), 4.5 (s, Ge*C*H$_2$CH$_3$). **CH_2=C($GeEt_3$)Ph**: ^1H, δ 5.90 (d, 1 H, J_{HH} = 2.8, =CH_2), 5.40 (d, 1 H, J_{HH} = 2.8, =CH_2). **(*E*)-Et_3GeCH=CHCy**: ^1H, δ 5.95 (dd, 1 H, J_{HH} = 18.6, $J_{HH'}$ = 5.7, =C*H*), 5.73 (dd, 1 H, J_{HH} = 18.6, $J_{HH'}$ = 1.2, =C*H*GeEt$_3$); $^{13}C\{^1H\}$, δ 152.8 (s, =*C*H), 123.0 (s, =*C*HGeEt$_3$), 9.0 (s, GeCH$_2$*C*H$_3$), 4.4 (s, Ge*C*H$_2$CH$_3$). **CH_2=C($GeEt_3$)Cy**: ^1H, δ 5.65 (dd, 1 H, J_{HH} = 2.2, $J_{HH'}$ = 1.2, =CH_2), 5.19 (dd, 1 H, J_{HH} = 2.2, $J_{HH'}$ = 0.7, =CH_2). **(*E*)-Et_3GeCH=CHSiMe_3**: ^1H, δ 6.85 (part A

of an AB system, 1 H, J_{HH} = 21.9, =C*H*), 6.61 (part B of an AB system, 1 H, J_{HH} = 21.9, =C*H*GeEt$_3$); ^{13}C{^{1}H}, δ 151.2 (s, =*C*H), 148.1 (s, =*C*HGeEt$_3$), 8.9 (s, GeCH$_2$*C*H$_3$), 4.2 (s, Ge*C*H$_2$CH$_3$).

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