# Highly Efficient Regioselective Silylcarbonylation of Alkynes Catalyzed by Dirhodium(II) Perfluorobutyrate

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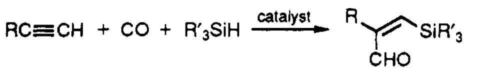
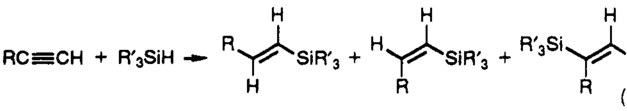
*Received October 21, 1992*

*Summary: Rhodium(II) perfluorobutyrate is an effective catalyst for silylcarbonylation of terminal acetylenes in reactions performed at atmospheric pressure and at or below room temperature. β-Silylacrylaldehydes are formed with exceptional stereocontrol for the Z isomer, which can be isomerized to the E isomer under mild conditions.*

Recently Matsuda[1] and Ojima[2] have independently reported the silylcarbonylation of alkynes catalyzed by $Rh_4(CO)_{12}$ or Rh–Co mixed-metal carbonyl clusters. Addition to the alkyne by both carbon monoxide and trialkylsilane in the manner depicted in eq 1 constitutes this organosilane counterpart to hydroformylation. The original discovery of "silylcarbonylation" by Murai[3] using $Co_2(CO)_8$ found olefin conversion to silyl enol ethers of the homologous aldehydes as the sole carbonylation products, and the same outcome has been reported for enamines catalyzed by $[RhCl(CO)_2]_2$[4] and for terminal alkenes catalyzed by $Ru_3(CO)_{12}$ and $(Ph_3P)_3RhCl$.[5] In contrast, silylcarbonylation reactions catalyzed by $Rh_4(CO)_{12}$ or Rh–Co mixed carbonyl clusters yield the carbon-centered silane exclusively, and with terminal alkynes these transformations generally occur under mild conditions with a high degree of regiocontrol. Intramolecular versions have also been reported,[6-8] and in these and intermolecular silylcarbonylation reactions the only effective catalysts appear to be $Rh_4(CO)_{12}$ or mixed-metal analogs. Their major competing reaction is hydrosilylation (eq 2), but the use of more reactive organosilanes ($Me_2PhSiH$ versus $Et_3SiH$) or higher CO pressures (150 psi versus ambient) generally enhances silylcarbonylation.[2] We have previously described the use of dirhodium(II) catalysts for hydrosilylation reactions of alkynes[9] and alkenes.[10] Their efficiency and proclivity for trans addition prompted this investigation, which enables us now to report their highly efficient application to the silylcarbonylation of alkynes under exceptionally mild conditions.

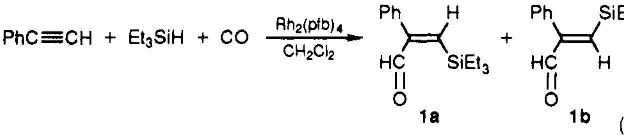


(1)



(2)

Addition of phenylacetylene to an equivalent amount of triethylsilane and only 0.3 mol % of dirhodium(II) perfluorobutyrate,[11] $Rh_2(pfb)_4$, in dichloromethane at 0 °C under carbon monoxide at atmospheric pressure resulted in the regiospecific formation of silylcarbonylation products **1a** and **1b** (eq 3) in a 10:1 ratio (82% isolated yield after distillation). Under these conditions hydrosilylation products (eq 2, R = Ph) were only trace components (<1%) of the reaction mixture, but with 0.1 mol % of $Rh_2(pfb)_4$ these compounds constituted 45% of the reaction products. Addition of phenylacetylene to the organosilane is critical to the success of this transformation, since the reverse addition results in low yields of silylcarbonylation products (<25%) and a significantly higher relative yield of hydrosilylation products. Reactions performed with $Rh_2(OAc)_4$ in place of $Rh_2(pfb)_4$ were not as effective in producing **1** (30% hydrosilylation products), although product yields (84%) and the **1a**:**1b** isomer ratio (12:1) were comparable.



(3)

Application of this procedure to other alkynes (Table I) suggests the generality of $Rh_2(pfb)_4$-catalyzed silylcarbonylation. Even in relatively small-scale reactions, product yields (not optimized) are high over the range of alkynes employed. Complete conversion of the alkyne is generally observed, suggesting the efficiency of the catalyst for silylcarbonylation. Terminal alkynes that undergo competitive hydrosilylation with $Et_3SiH$ can be directed to exclusive silylcarbonylation with the use of $Me_2PhSiH$. However, use of $Me_2PhSiH$ with disubstituted alkynes such as 1-phenyl-1-propyne causes a decrease in the relative yield for silylcarbonylation, and in these cases $Rh_4(CO)_{12}$ is a more effective catalyst.[1]

The stereochemistry of the major isomer formed by silylcarbonylation of these alkynes is that of cis addition. This same selectivity is characteristic of $Rh_4(CO)_{12}$-catalyzed reactions, although their *Z*:*E* isomer ratios[1] are generally significantly lower than those reported in Table

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**Table I. Silylcarbonylation of Alkynes Catalyzed by $Rh_2(pfb)_4$ at Atmospheric Pressure[a]**

| alkyne | organosilane | silylcarbonylation product | yield, %[b] | *Z*:*E* isomer ratio | silylcarbonylation: hydrosilylation |
|---|---|---|---|---|---|
| $PhC\equiv CH$ | $Et_3SiH$ | $Et_3SiCH{=}C(Ph)CHO$ | 82 | 10:1 | >99:1 |
| *p*-$TolC\equiv CH$[c] | $Et_3SiH$ | $Et_3SiCH{=}C(p\text{-}Tol)CHO$ | 24 | 13:1 | 38:62 |
| | $Me_2PhSiH$ | $Me_2PhSiCH{=}C(p\text{-}Tol)CHO$ | 84 | 38:1 | >99:1 |
| $p\text{-}i\text{-}BuC_6H_4C\equiv CH$ | $Et_3SiH$ | $Et_3SiCH{=}C(p\text{-}i\text{-}BuC_6H_4)CHO$ | 28 | 10:1 | 91:9 |
| | $Me_2PhSiH$ | $Me_2PhSiCH{=}C(p\text{-}i\text{-}BuC_6H_4)CHO$ | 74 | 11:1 | >99:1 |
| 6-MeONap-2-$C\equiv CH$[d] | $Me_2PhSiH$ | $Me_2PhSiCH{=}C(2\text{-}Nap\text{-}6\text{-}MeO)CHO$ | 95 | 11:1 | >99:1 |
| $PhC\equiv CPh$ | $Et_3SiH$ | $Et_3SiC(Ph){=}C(Ph)CHO$ | 95 | 32:1 | 71:29 |
| $PhC\equiv CCH_3$ | $Et_3SiH$ | $Et_3SiC(CH_3){=}C(Ph)CHO$ | 72 | 40:1 | 56:42 |
| | $Me_2PhSiH$ | $Me_2PhSiC(CH_3){=}C(Ph)CHO$ | 83 | 5:1 | 14:86 |
| *n*-$HexC\equiv CH$ | $Et_3SiH$ | $Et_3SiCH{=}C(n\text{-}Hex)CHO$ | 45 | 36:1 | 40:60 |
| | $Me_2PhSiH$ | $Me_2PhSiCH{=}C(n\text{-}Hex)CHO$ | 81 | 14:1 | >99:1 |
| $AcOCH_2C\equiv CH$ | $Et_3SiH$ | $Et_3SiCH{=}C(CH_2OAc)CHO$ | 71 | 29:1 | 96:4 |
| $MeOCH_2C\equiv CH$ | $Et_3SiH$ | $Et_3SiCH{=}C(CH_2OMe)CHO$ | 87 | 14:1 | >99:1 |
| $Me_2C(OH)C\equiv CH$ | $Et_3SiH$ | $Et_3SiCH{=}C(C(OH)Me_2)CHO$ | 41[e] | 24:1 | 91:9 |

[a] Reactions performed on a 2.5-mmol scale by controlled addition (4–5 h) of the alkyne in 5 mL of dichloromethane to the same amount of silane and 0.3 mol % of $Rh_2(pfb)_4$ in 25 mL of dichloromethane at 0 °C under an atmosphere of CO (ambient). [b] Yield obtained after chromatographic separation of catalyst and distillation of product under reduced pressure. [c] *p*-Tol = $p\text{-}CH_3C_6H_4$. [d] Nap = naphthalene. [e] Reaction only went to ~60% completion.

**Table II. Triethylsilylcarbonylation of Alkynes Catalyzed by $Rh_2(pfb)_4$ at 10 atm of CO pressure[a]**

| alkyne | silylcarbonylation product | yield, %[b] | *Z*:*E* isomer ratio | silylcarbonylation: hydrosilylation |
|---|---|---|---|---|
| $PhC\equiv CH$ | $Et_3SiCH{=}C(Ph)CHO$ | 75 | 24:1 | 92:8 |
| *p*-$TolC\equiv CH$ | $Et_3SiCH{=}C(p\text{-}Tol)CHO$ | 63 | 17:1 | 96:4 |
| $p\text{-}i\text{-}BuC_6H_4C\equiv CH$ | $Et_3SiCH{=}C(p\text{-}i\text{-}BuC_6H_4)CHO$ | 72 | 10:1 | 96:4 |
| *n*-$HexC\equiv CH$ | $Et_3SiCH{=}C(n\text{-}Hex)CHO$ | 81 | 35:1 | >99:1 |
| $AcOCH_2C\equiv CH$ | $Et_3SiCH{=}C(CH_2OAc)CHO$ | 51 | 22:1 | >99:1 |
| $MeOCH_2C\equiv CH$ | $Et_3SiCH{=}C(CH_2OMe)CHO$ | 77 | 30:1 | >99:1 |
| $Me_2C(OH)C\equiv CH$ | $Et_3SiCH{=}C(C(OH)Me_2)CHO$ | 36[c] | 36:1 | 92:8 |

[a] Reactions performed at room temperature with 0.3 mol % of $Rh_2(pfb)_4$ in a stainless steel autoclave with a Pyrex reaction vessel (50 mL) at a 2–10-mmol scale with an equivalent amount of alkyne and $Et_3SiH$. [b] Yield obtained after chromatographic separation of catalyst and distillation of product under reduced pressure. [c] Reaction only went to ~50% completion.

I. With the silylcarbonylation products formed from phenylacetylene, isomerization of **1a** to **1b** occurs with relative ease under mild conditions using either aqueous iodine in refluxing benzene (85% yield, **1a**:**1b** = 1:6) or hydroiodic acid in benzene at room temperature (95% yield, **1a**:**1b** = 1:13).[12] Similar treatment of the silylcarbonylation product formed from propargyl acetate with hydroiodic acid also resulted in isomerization (*Z*:*E* = 1:3). Thus, both isomers of these β-silylacrylaldehydes are conveniently accessible in high yield with substantial stereocontrol.

At 10 atm of CO pressure silylcarbonylation with triethylsilane is significantly enhanced (Table II) relative to reactions performed at atmospheric pressure (Table I). Furthermore, the need for controlled addition of the alkyne to the silane–catalyst solution is remediated under these conditions, although a residue of hydrosilylation products is sometimes in evidence. Product yields are generally higher at 10 atm of CO than from reactions performed at atmospheric pressure (63% versus 24% with *p*-$TolC\equiv CH$, 72% versus 28% with $p\text{-}i\text{-}BuC_6H_4C\equiv CH$, 81% versus 45% with 1-octyne). However, disubstituted acetylenes gave predominantly hydrosilylation under these conditions (90% with $PhC\equiv CPh$).

The advantages of $Rh_2(pfb)_4$ as a silylcarbonylation catalyst for alkynes lie in the mild conditions employed, high catalyst turnovers, and exceptional *E*:*Z* isomer ratios. However, internal alkynes appear to be better served by the $Rh_4(CO)_{12}$ catalyst. Modification of $Rh_2(pfb)_4$ occurs upon combination with $R_3SiH$ and CO, but the nature of the modification is unknown at this time. These investigations are continuing.

**Acknowledgment.** We are grateful to Hoechst Celanese for their support of this research. The participation of Danica C. Mueller, supported by an NSF-REU grant, in these investigations is gratefully acknowledged.

OM920665C

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