# Reactions of Tetraalkynylsilanes $(RC{\equiv}C)_4Si$ (R = Ph, $^t$Bu, $SiMe_3$) with Titanocene and Zirconocene Complexes

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*Summary: Reactions of the branched tetraalkynylsilanes $(RC{\equiv}C)_4Si$ (**1a**: R = Ph, **1b**: $^t$Bu, **1c**: $SiMe_3$) with the metallocene source $Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (**2**) led to complexes **4**−**6**, and those of **1a** with $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (**3**) to complex **7**. These, via 2-fold migration and C−C coupling of the alkynyl groups, gave a novel type of dinuclear carbon-rich spiro complexes. The conversions proved to be independent of the metals, the substituents R, and the stoichiometries employed. All new complexes have been characterized spectroscopically. Additionally, an X-ray crystal structure analysis was performed for **7**.*



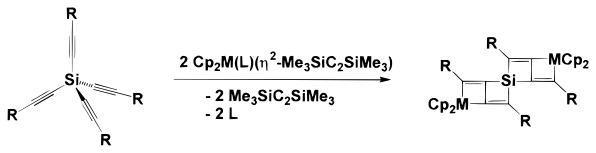
Carbon-rich organometallics[1] have attracted increasing interest in recent years because of manifold applications. Such metal complexes containing branched carbon−carbon triple bonds[2] are potentially useful for building up carbon-rich networks[3] and nanoarchitectures for material science.[4]

Following earlier investigations into disubstituted 1,3-butadiynes $R(C{\equiv}C)_2R$,[5] α,ω-diynes $R(C{\equiv}C)-X-(C{\equiv}C)R$,[6] and linear octatetraynes $R(C{\equiv}C)_4R$,[7a] we recently turned our attention to branched polyynes such as tris(*tert*-butylbutadiynyl)benzene, 1,3,5-($^t$Bu-C≡C−C≡C)$_3C_6H_3$.[7b]

Herein we report on the results of the reactions of the branched polyynes $(RC{\equiv}C)_4Si$ (**1a**: R = Ph, **1b**: $^t$Bu, **1c**: $SiMe_3$) with the metallocene sources $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**)[8] and those of **1a** with $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**3**).[9] In contrast to previously established expectations, these conversions are not dependent on the metal, the substituent R attached to the polyyne, and the stoichiometry employed and lead to novel dinuclear organometallic carbon-rich complexes. Similar products were recently found by Takahashi et al. in the reaction of dialkynylsilanes $(RC{\equiv}C)_2SiR_2$ with zirconocene complexes, in which an intramolecular coupling of two alkynyl groups mediated by zirconocene occurred.[10]

The tetraalkynylsilanes **1a, 1b**, and **1c** were synthesized according to literature procedures starting from tetrachlorosilane and the corresponding lithium acetylides.[11]

In the reaction of **1a**−**c** with 2 equiv of complex **2** or of **1a** with **3**, which easily release bis(trimethylsilyl)-acetylene and thus are superb preparative sources for the unstable metallocenes "$Cp_2Ti$" and "$Cp_2Zr$",[5a] respectively, the red complexes **4**−**7** are formed (eq 1).




(1)

1a: R = Ph
1b: R = $^t$Bu
1c: R = $SiMe_3$

M = Ti, L = -
M = Zr, L = THF

4: M = Ti, R = Ph
5: M = Ti, R = $^t$Bu
6: M = Ti, R = $SiMe_3$
7: M = Zr, R = Ph

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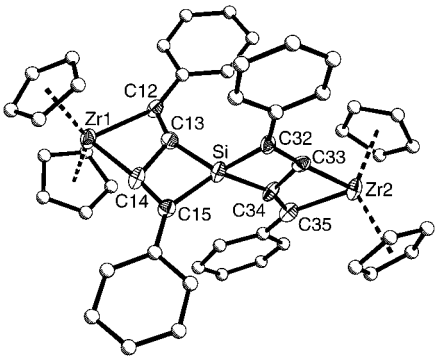


**Figure 1.** Structural representation of **7** (only atoms regarded significant are drawn as 30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) an angles (deg): Si−C13 1.87(2), Si−C14 2.33(2), Si−C15 1.83(2); Si−C32 1.85(1), Si−C33 2.36(1), Si−C34 1.88(2), Zr1−C12 2.18(2), Zr1−C13 2.43(1), Zr1−C14 2.15(2); Zr2−C33 2.18(2), Zr2−C34 2.43(1), Zr2−C35 2.18(1), C15−Si−C34 127.9(7), C15−Si−C32 131.1(6), C13−Si−C32 126.5(7), C13−Si−C34 123.1(5), C15−Si−C13 78.4(6), C32−Si−C34 77.3(6).

These compounds are readily soluble in THF, slightly less soluble in benzene, and only sparingly soluble in *n*-hexane. The IR spectra show no band in the range expected for a complexed C−C triple bond between 1900 and 1600 $cm^{-1}$. The structural assignment follows NMR spectroscopic investigations. The signals for the different substituents R in the NMR spectra confirm a differing environment of the alkynyl moieties. This view is additionally supported by the nonequivalence of the Cp ligands (two signals) and the alkynyl carbon atoms (four signals) in each complex.

The crystal structure analysis of **7**[12] (Figure 1) shows a silicon center whose coordination geometry can be described as a distorted tetrahedron. It interlinks two intact 1,4-disubstituted tetradehydro-$\mu$-(1-3-$\eta$):(2-4-$\eta$)-*trans*,*trans*-butadiene units[5a] that are further coordinated to one zirconocene core each.

These "zigzag butadienes" are, together with the respective metals, nearly planar by themselves (largest deviation from those planes: 0.0185 and 0.0239 Å) and are connected to each other through the silicon atom. The angle between these two planes is about 92° (Figure 2).

The reaction depicted in eq 1 and the products obtained are interesting, because they provide another example that supports a formal analogy of the elements titanium and zirconium with silicon.[13a] These considerations approximate the isolobal principle.[13b] They concern at least carbene-like adducts of alkynes under

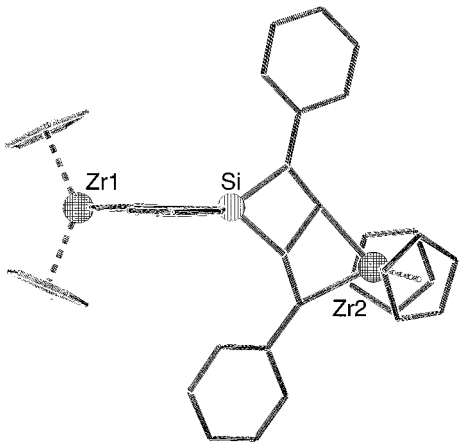


**Figure 2.** Perspective view of complex **7** parallel to the plane Zr1−C12−C13−C14−C15−Si.

the formation of silacyclopropenes (silirenes)[13c] and titana- or zirconacyclopropenes.[5a] It is well-known that these two groups of compounds behave similarly as found, for example, for the insertion of carbonyl groups and C−C double and triple bonds to yield corresponding cyclic products.[5a,13c,14] Additionally, the alkyne adducts (sila-, titana-, and zirconacyclopropenes) show the same type of reaction with 1,3-butadiynes: a substitution of the diyne for the alkyne linkage leading to $\eta^2$-complexes.[5a,15a]

Reacting 1,3-butadiynes with "silacarbenes" and permethyltitanocene "$Cp^*_2Ti$" in one-to-one ratios, analogous compounds $R_2Si[\eta^2\text{-}(R-C_2-C\equiv CR)]$[15] and $Cp^*_2Ti[\eta^2\text{-}(R-C_2-C\equiv CR)]$[16] were obtained.

One-to-two combinations of 1,3-butadiynes and "silacarbenes" "$R_2Si$" or metallocenes "$Cp_2M$" generate the same type of product as shown by the structures found in complexes **4**−**7**. With M = Ti and various butadiynes, dinuclear complexes with intact $C_4$ units between the two metal centers are formed.[17] The starting diynes are transformed to "zigzag-butadiyne ligands" or $\mu$-$\mu$(1-3),$\eta$-(2-4)-*trans*,*trans*-tetradehydrobutadiene moieties between two titanocene cores (Chart 1).

So far this bond type is not known for M = Zr, although theoretical calculations predict its existence in the case of certain substituents.[17c] Very similar

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(12) Crystal data for **7**: monoclinic, $P2_1/c$, $a$ = 12.478(2) Å, $b$ = 15.671(3) Å, $c$ = 34.143(7) Å, $\beta$ = 96.71(3)°, $V$ = 6631(2) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.024 g $cm^{-1}$, $T$ = 220 K, 8608 reflections were measured, 4605 were independent of symmetry, and 2666 were observed ($I > 2\sigma I$), $R$ = 0.083, $wR2$ (all data) = 0.320, 504 parameters, residual electron density 0.75 e Å$^{-3}$.

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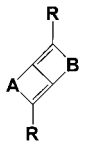
(18) STOE-IPDS diffractometer, graphite-monochromated Mo K$\alpha$ radiation, the structure was solved by direct methods (SHELXS-86; Sheldrick, G. M. *Acta Crytallogr. Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares techniques against $F^2$ (SHELXL-93); structure representation with XP (Siemens). The crystals diffract weakly and contain a high amount of solvent, causing a rapid decay of the material when taken out of solution. This is observed even at low temperatures. The atoms of two phenyl groups and of one cyclopentadienyl ligand are refined isotropically. All other nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions and refined riding with the corresponding atom.

**Chart 1**




| | | Reference |
|---|---|---|
| A = $TiL_2$ | B = $TiL_2$ | 17c |
| A = $Si^tBu_2$ | B = $Si^tBu_2$, R = Me | 15a |
| A = $Si^tBu_2$ | B = $Si^tBu_2$, R = $SiMe_3$ | 15b |
| A = $ZrCp_2$ | B = $SiMe_2$, R = *p*-$MeOC_6H_4$ | 10a |
| A = $ZrCp_2$ | B = $SiPh_2$, R = Ph | 10b |
| A = $Zr(C_5H_4{}^tBu)_2$ | B = $SiPh_2$, R = Ph | 10b |

structures were also elucidated with two "$R_2Si$" instead of "$Cp_2Ti$".[15b,c] Additionally, combinations of substituted zirconocenes and different "$R_2Si$" were found in the reaction of dialkynylsilanes $(RC{\equiv}C)_2SiR_2$ with zirconocene complexes, showing an intramolecular coupling of two alkynyl groups mediated by zirconocene.[10]

It seems reasonable to assume that the reactivities of "silacarbenes" and metallocenes "$Cp_2M$" toward diynes are very similar and that these groups are compatible in some examples as proven for compounds **4**−**7**.

## Experimental Section

All operations were carried out under the exclusion of oxygen and moisture. X-ray crystal structure investigations were conducted according to ref 18.

**Preparation of Complexes Si{*μ*,*η*-(1,3)-($Cp_2M$)-*μ*,*η*-(2,4)-R−$C_2$−$C_2$−R]$_2$ (4−7).** About 0.3 mmol of the tetraalkynylsilane was dissolved in 5 mL of THF and treated with 2 equiv of the complexes **2** or **3**. After stirring for 2 h at room temperature all volatiles are removed in a vacuum. The residue was dissolved in THF and the solution carefully treated with *n*-hexane. In 24 h at room temperature crystals formed, which were separated from the mother liquor, washed with cold *n*-hexane, and dried in a vacuum to give complexes **4**−**7**.

**Preparation of 4.** $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**) (221 mg, 0.63 mmol) and $Si(C{\equiv}CPh)_4$ (**1a**) (139 mg, 0.32 mmol) gave **4** (203 mg, 83%) as red crystals; mp 256−258 °C (dec under argon). Anal. Calcd for $C_{52}H_{40}SiTi_2$ (788.7): C, 79.19; H, 5.11. Found: C, 79.11; H, 5.42. $^1$H NMR (297 K, THF-$d_8$) $\delta$/ppm: 5.68 (s, 10H, Cp), 5.70 (s, 10H, Cp), 7.04−7.64 (m, 20H, Ph). $^{13}$C NMR (297 K, THF-$d_8$) $\delta$/ppm: 78.6 (alkynyl), 107.1, 107.3 (Cp), 127.7, 127.8, 128.5, 128.9, 129.4, 130.1, 140.9, 141.0 (Ph), 155.2, 216.2, 269.3 (alkynyl). MS (70 eV) *m*/*z*: 610 (M − $Cp_2Ti^+$).

**Preparation of 5.** **2** (280 mg, 0.80 mmol) and **1b** (141 mg, 0.40 mmol) gave **5** (242 mg, 86%) as a red microcrystalline solid; mp 252−253 °C (dec under argon). Anal. Calcd for $C_{44}H_{56}SiTi_2$ (708.8): C, 74.56; H, 7.96. Found: C, 74.25; H, 8.24. $^1$H NMR (297 K, THF-$d_8$) $\delta$/ppm: 1.17 (s, 9H, C*Me*$_3$), 1.29 (s, 9H, C*Me*$_3$), 5.40 (s, 10H, Cp), 5.41 (s, 10H, Cp). $^{13}$C NMR (297 K, THF-$d_8$) $\delta$/ppm: 31.5, 32.9 (C*Me*$_3$), 36.8, 40.7 (*C*Me$_3$), 73.7 (alkynyl), 105.9, 106.0 (Cp), 166.1, 226.1, 266.2 (alkynyl). MS (70 eV) *m*/*z*: 708 ($M^+$), 530 (M − $Cp_2Ti^+$).

**Preparation of 6.** **2** (330 mg, 0.66 mmol) and **1c** (146 mg, 0.33 mmol) gave **6** (199 mg, 78%) as deep red crystals; mp 164−165 °C (dec under argon). Anal. Calcd for $C_{40}H_{56}Si_5Ti_2$ (773.1): C, 62.15; H, 7.30. Found: C, 61.92; H, 7.19. $^1$H NMR (297 K, THF-$d_8$) $\delta$/ppm: 0.18 (s, 9H, Si*Me*$_3$), 0.26 (s, 9H, Si*Me*$_3$), 5.25 (s, 10H, Cp), 5.27 (s, 10H, Cp). $^{13}$C NMR (297 K, THF-$d_8$) $\delta$/ppm: 0.1, 1.1 (Si*Me*$_3$), 104.9 (alkynyl), 105.3, 105.4 (Cp), 157.1, 205.6, 265.8 (alkynyl). MS (70 eV) *m*/*z*: 594 (M − $Cp_2Ti^+$).

**Preparation of 7.** **3** (275 mg, 0.59 mmol) and **1a** (128 mg (0.30 mmol) produced **7** (186 mg, 71%) as red crystals; mp > 250 °C. Anal. Calcd for $C_{52}H_{40}SiZr_2$ (875.4): C, 71.35; H, 4.61. Found: C, 70.88; H, 4.44. $^1$H NMR (297 K, THF-$d_8$) $\delta$/ppm: 5.96 (s, 10H, Cp), 5.97 (s, 10H, Cp), 6.98−7.67 (m, 20H, Ph). $^{13}$C NMR (297 K, THF-$d_8$) $\delta$/ppm: 98.9 (alkynyl), 107.6, 107.7 (Cp), 127.8, 128.0, 128.1, 128.8, 129.3, 130.6, 141.2, 142.5 (Ph), 162.8, 207.7, 256.8 (alkynyl). MS (70 eV) *m*/*z*: 652 (M − $Cp_2Zr^+$).

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**Supporting Information Available:** Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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