

A Stable Bimetallic Copper(I) Titanium Acetylide

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Summary: The reaction of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{CuCl}$ (**4**) with 1 equiv of $\text{LiC}\equiv\text{CR}$ ($\text{R} = \text{SiMe}_3$ (**5a**), $t\text{-Bu}$ (**5b**), Ph (**5c**)) affords the monomeric complexes $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{CuC}\equiv\text{CR}$ ($\text{R} = \text{SiMe}_3$ (**3a**), $t\text{-Bu}$ (**3b**), Ph (**3c**)). Complexes **3** were independently prepared by starting from $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2$ (**1**) and $1/n [\text{CuC}\equiv\text{CR}]_n$ ($\text{R} = \text{SiMe}_3$ (**2a**), $t\text{-Bu}$ (**2b**), Ph (**2c**)) and are the first examples of stable monomeric bis(η^2 -alkyne)(η^1 -alkynyl)copper compounds. Reaction of **1** with $1/4 [\text{CuO}-t\text{-Bu}]_4$ (**6**) results in the formation of the remarkably stable bimetallic acetylide complex $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{CCu})_2]$ (**7**) ($m.p. 157^\circ\text{C dec}$) by nucleophilic substitution of one of the alkynyl-SiMe₃ groups in **1**, whereby $t\text{-BuOSiMe}_3$ is eliminated. Other nucleophiles (e.g. F^- and EtO^-) show a similar reactivity, although in this case the substitution is much slower and less selective.

Alkynylcopper(I) compounds are generally encountered as polynuclear species which exist either as discrete aggregates or as oligomers.¹ In these species the alkynyl ligands are σ - and π -bonded to copper(I) centers. Recently we showed that bis(alkynyl)titanocenes are very useful chelating ligands for the stabilization of mononuclear bis(η^2 -alkyne)(η^1 -aryl)copper and -silver compounds, where aryl is for example $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$.² In order to study intramolecular *vs* intermolecular alkyne to copper coordination, we are interested in the isolation of mononuclear bis(η^2 -alkyne)(η^1 -alkynyl)-copper(I) compounds, using the chelate effect of the alkynyl units in the bis(alkynyl)titanocene $(\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2$ (**1**).³

Addition of $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2$ (**1**)^{3f} to solutions or suspensions of alkynylcopper(I) compounds, $[\text{CuC}\equiv\text{CR}]_n$ ($\text{R} = \text{SiMe}_3$ (**2a**), $t\text{-Bu}$ (**2b**), Ph (**2c**)),¹ in a 1:1 molar ratio leads to the quantitative formation of the monomeric complexes $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{CuC}\equiv\text{CR}$ ($\text{R} = \text{SiMe}_3$ (**3a**), $t\text{-Bu}$ (**3b**), Ph (**3c**)). An alternative preparative route is the transmetalation of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{CuCl}$ (**4**) with the corresponding alkynyllithium compounds $\text{LiC}\equiv\text{CR}$ ($\text{R} = \text{SiMe}_3$ (**5a**), $t\text{-Bu}$ (**5b**), Ph (**5c**)) (see Scheme 1). Complexes **3** are stable in solution and in the solid state and can be isolated as orange crystalline solids by cooling their diethyl ether solutions to -30°C . They are soluble in most organic solvents, and solutions of **3** can be handled safely in air for short periods of time. Crystals of **3** are stable to air for a few weeks.

The presence of two different C=C stretching frequencies in the IR spectra of **3** indicates that besides an η^1 -bonded alkynylcopper unit, $\text{CuC}\equiv\text{CR}$, η^2 -bonded disubstituted alkyne ligands are present. Through the η^2 -coordination of these alkyne moieties to the copper atom in **3**, the $\nu(\text{C}\equiv\text{C})$ vibration is shifted from 2012 cm^{-1} in the parent compound **1**^{3f} to 1896 in **3a**, 1902 in **3b**, and 1941 cm^{-1} in **3c**. The η^1 -bonded alkynyl group, $\text{C}\equiv\text{CR}$, is found at $\nu(\text{C}\equiv\text{C})$ 2035 in **3a**, 2095 in **3b**, and 2094 cm^{-1} in **3c**.

The molecular structure of **3a** was determined by a single-crystal X-ray diffraction analysis.⁴

The molecular structure of **3a** (see Figure 1) shows that $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{CuC}\equiv\text{CSiMe}_3$ is monomeric. Both alkyne groups from the bis(alkynyl)-titanocene are η^2 -coordinated to the copper atom Cu1,

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(1) (a) For a review on metal alkynyls: Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89–124. (b) $[\text{Cu}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_4]$: Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *21*, 957–965. (c) $[\text{Ag}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_3]$: Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *20*, 502–508. (d) $[\text{Cu}_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})_2(\text{dppm})_3]\text{BF}_4$ and $[\text{Cu}_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})(\text{dppm})_3](\text{BF}_4)_2$: Díez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Aguirre, A.; García-Granda, S. *Organometallics* **1993**, *12*, 2213–2220. (e) $[\text{Cu}_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}-t\text{-Bu})(\mu_3\text{-Cl})(\text{dppm})_3]\text{PF}_6$: Yam, V. W.-W.; Lee, W.-K.; Lai, T.-F. *Organometallics* **1993**, *12*, 2383–2387. (f) $[\text{Cu}_3(\text{SAr})_2\text{C}\equiv\text{C}-t\text{-Bu}]_n$: Knotter, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1989**, 1738–1739. Knotter, D. M.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1992**, *11*, 4083–4090. (g) $[\text{CuC}\equiv\text{CPh}]_n$: Corfield, P. W. R.; Shearer, H. M. M. In *Organometallic Compounds*; Coates, G. E., Green, M. L. H.; Wade, K., Eds.; Chapman and Hall: London, 1977; Vol. 2. (h) $[\text{CuC}\equiv\text{C}-t\text{-Bu}]_n$: Coates, G. E.; Parkin, C. J. *Inorg. Nucl. Chem.* **1961**, *22*, 59. (i) $[\text{M}(\text{C}\equiv\text{CCF}_3)_n]$ ($\text{M} = \text{Cu}, \text{Ag}$): Haszeldine, R. N. *J. Chem. Soc.* **1951**, 588–591.

(2) Janssen, M. D.; Herres, M.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. To be submitted for publication.

(3) (a) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7–C11. (b) Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1993**, *12*, 5008–5011. (c) Lang, H.; Imhof, W. *Chem. Ber.* **1992**, *125*, 1307–1311. (d) Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1991**, *406*, C5–C8. (e) Lang, H.; Herres, M.; Zsolnai, L. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 429–431. (f) Lang, H.; Seyferth, D. Z. *Naturforsch.* **1990**, *45B*, 212–220.

(4) Single crystals of **3a** were grown by cooling a saturated Et_2O solution to -20°C . Crystal data for **3a**: $\text{C}_{31}\text{H}_{53}\text{CuSi}_3\text{Ti}$, red crystal ($0.38 \times 0.38 \times 0.63$ mm), monoclinic, space group $P2_1/c$, with $a = 20.9981(9)$ Å, $b = 12.0851(9)$ Å, $c = 15.2434(10)$ Å, $\beta = 100.146(4)^\circ$, $V = 3807.7(4)$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.182$ g cm^{-3} , $F(000) = 1440$, $\mu(\text{Mo K}\alpha) = 9.4$ cm^{-1} . A total of 9267 (8447 unique) reflections ($0.99 < \theta < 27.50^\circ$; $\omega/2\theta$ scan; $T = 150$ K) were measured on an Enraf-Nonius CAD-4T rotating anode diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz polarization effects and absorption (DIFABS minimum and maximum correction: 0.826/1.103). The structure was solved by direct methods (SHELXS86) and difference Fourier techniques and refined on F^2 by full-matrix least squares (SHELXL93) to an R_1 value of 0.055 for 5854 reflections with $F_o > 4\sigma(F_o)$ and 343 parameters, $wR_2 = 0.151$, $S = 1.024$, and $w^{-1} = (\sigma^2(F_o^2) + (0.0826P)^2)$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$. Hydrogen atoms were introduced on calculated positions and refined riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters. A final Fourier map showed no residual density outside -0.43 and 0.58 e/Å³ (near Cu1).

Scheme 1

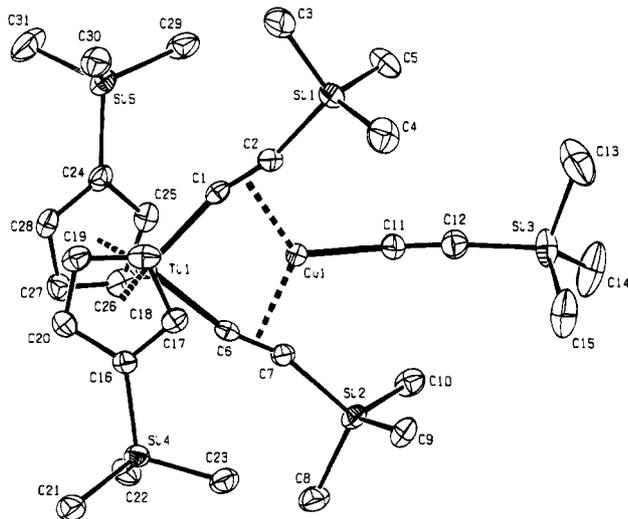
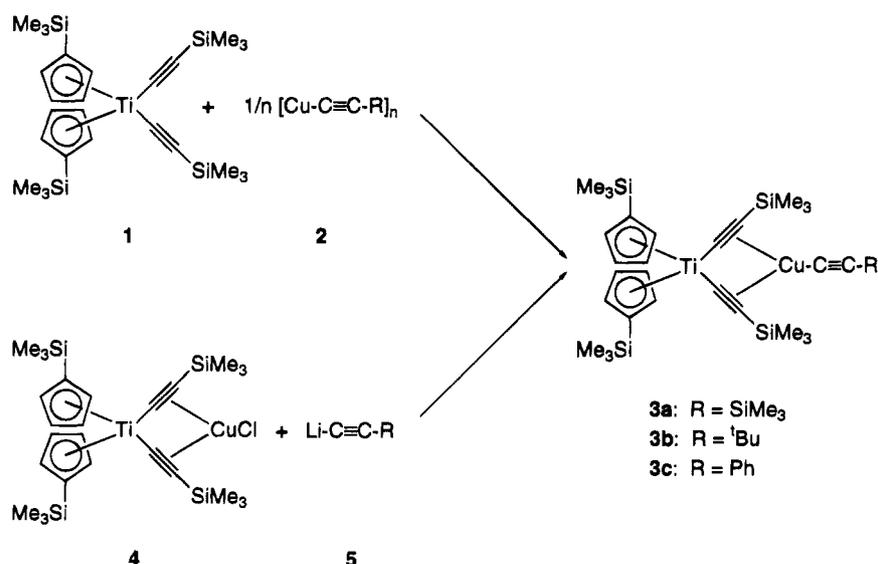


Figure 1. Molecular structure of **3a** (ORTEP, thermal ellipsoids at 50% probability). Selected bond distances (Å) and bond angles (deg): Ti1–Cu1, 2.9665(8); Cu1–C11, 1.898(3); Cu1–C1, 2.074(4); Cu1–C2, 2.112(4); Cu1–C6, 2.069(4); Cu1–C7, 2.111(4); C1–C2, 1.236(5); C6–C7, 1.240(5); C11–C12, 1.215(6); Ti1–C1, 2.081(4); Ti1–C6, 2.095(4); Ti1–C1–C2, 165.0(3); C1–C2–Si1, 162.8(3); Ti1–C6–C7, 165.4(4); C6–C7–Si2, 162.9(4); Cu1–C11–C12, 175.6(3); C11–C12–Si3, 171.4(4).

while the alkynyl ligand from the starting alkynyl-copper(I) compound is exclusively η^1 -coordinated. The C≡C bond lengths of the $Ti(C\equiv CSiMe_3)_2$ unit are lengthened from an average of 1.208 Å in **1^{3b}** to 1.236–(5) Å (C1–C2) and 1.240(5) Å (C6–C7) in **3a**. The copper atom possesses a trigonal-planar geometry and is surrounded by the two η^2 -bonded alkynyl ligands from **1** and by one η^1 -bonded alkynyl ligand and represents the first example in organocopper chemistry for which the monomeric structure is brought about by η^2 -bonded alkyne ligands. The Ti–C≡C–Si units are significantly bent (Ti1–C1–C2 = 165.0(3)°, Ti1–C6–C7 = 165.4(4)°, C1–C2–Si1 = 162.8(3)°, C6–C7–Si2 = 162.9(4)°; see Figure 1) due to the η^2 -coordination of the Ti–C≡C–SiMe₃ ligands to the copper atom. The same behavior is observed in similar bis(η^2 -alkyne)CuX complexes (X = singly bonded organic or inorganic ligand).^{2,3}

The η^1 -bonded (trimethylsilyl)ethynyl unit, $CuC\equiv CSiMe_3$, has a geometry typical for a noncoordinating alkynyl ligand (C11–C12 = 1.215(6) Å, Cu1–C11–C12 = 175.6(3)°, C11–C12–Si3 = 171.4(4)°; see Figure 1).

Surprisingly, complex **1** reacts selectively with 1/4 $[CuO-t-Bu]_4$ (**6**)⁵ in Et₂O at ambient temperature to yield quantitatively the dimeric complex $[(\eta^5-C_5H_4SiMe_3)_2Ti-(C\equiv CSiMe_3)(C\equiv CCu)]_2$ (**7**). The intermediate formation of the bis(η^2 -alkyne) coordination complex $[(\eta^5-C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]CuO-t-Bu$ (**8**) is not observed; elimination of *t*-BuOSiMe₃ (as detected with GC–MS) and the formation of **7** is instantaneous and quantitative. Other nucleophiles (e.g. F[−] and EtO[−]) show a similar reactivity toward complexes **3**, although the reaction is much slower and less selective due to competitive cleavage of the Ti–C≡C bond (see Scheme 2).

Complex **7** is a dark red solid which melts with decomposition at 157 °C; it is air-stable and is soluble in most organic solvents. The thermal and kinetic stability of **7** is remarkable, since bimetallic acetylide species of copper(I) ($CuC\equiv CM$) are usually very reactive and can be explosive.¹⁵

A cryoscopic molecular weight determination of **7** in benzene indicates that it is dimeric in solution. Variable-temperature ¹H NMR experiments indicate that **7** maintains this aggregation state in solution; in the temperature range 207–353 K the ¹H spectra remain essentially identical.

The molecular structure of **7** (see Figure 2)⁶ comprises

(5) Lemmen, T. H.; Goeden, G. V.; Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3680–3685.

(6) Single crystals of **7** were grown from a saturated diethyl ether solution at −30 °C. **7** contains one molecule of Et₂O in the unit cell: C₄₆H₇₀Cu₂Si₆Ti₂Et₂O, dark orange crystal (0.30 × 0.20 × 0.40 mm), secured in a glass capillary and sealed under nitrogen, triclinic, space group *P*1̄, with *a* = 11.714(3) Å, *b* = 12.190(4) Å, *c* = 12.581(3) Å, α = 101.12(2)°, β = 117.39(2)°, γ = 90.54(2)°, *V* = 1555.2(8) Å³, *Z* = 1, *d*_{calc} = 1.241 g cm^{−3}, *F*(000) = 616, μ (Mo K α) = 10.7 cm^{−1}. Diffraction data were collected on a Siemens (Nicolet Syntex) R3m/V diffractometer by using the θ – 2θ technique (2θ limits 2 ≤ 2θ ≤ 47°, scan range 0.75°, scan speed 3 ≤ ω ≤ 29.3° min^{−1} and Mo K α radiation (λ = 0.710 79 Å). The structure was solved by direct methods (SHELXTL-PLUS) on 4240 unique reflections with *F* > 4 σ (*F*). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions (number of variables 284). An empirical absorption correction was applied. Final discrepancy indices: *R* = 0.030 and ωR = 0.031.

Scheme 2

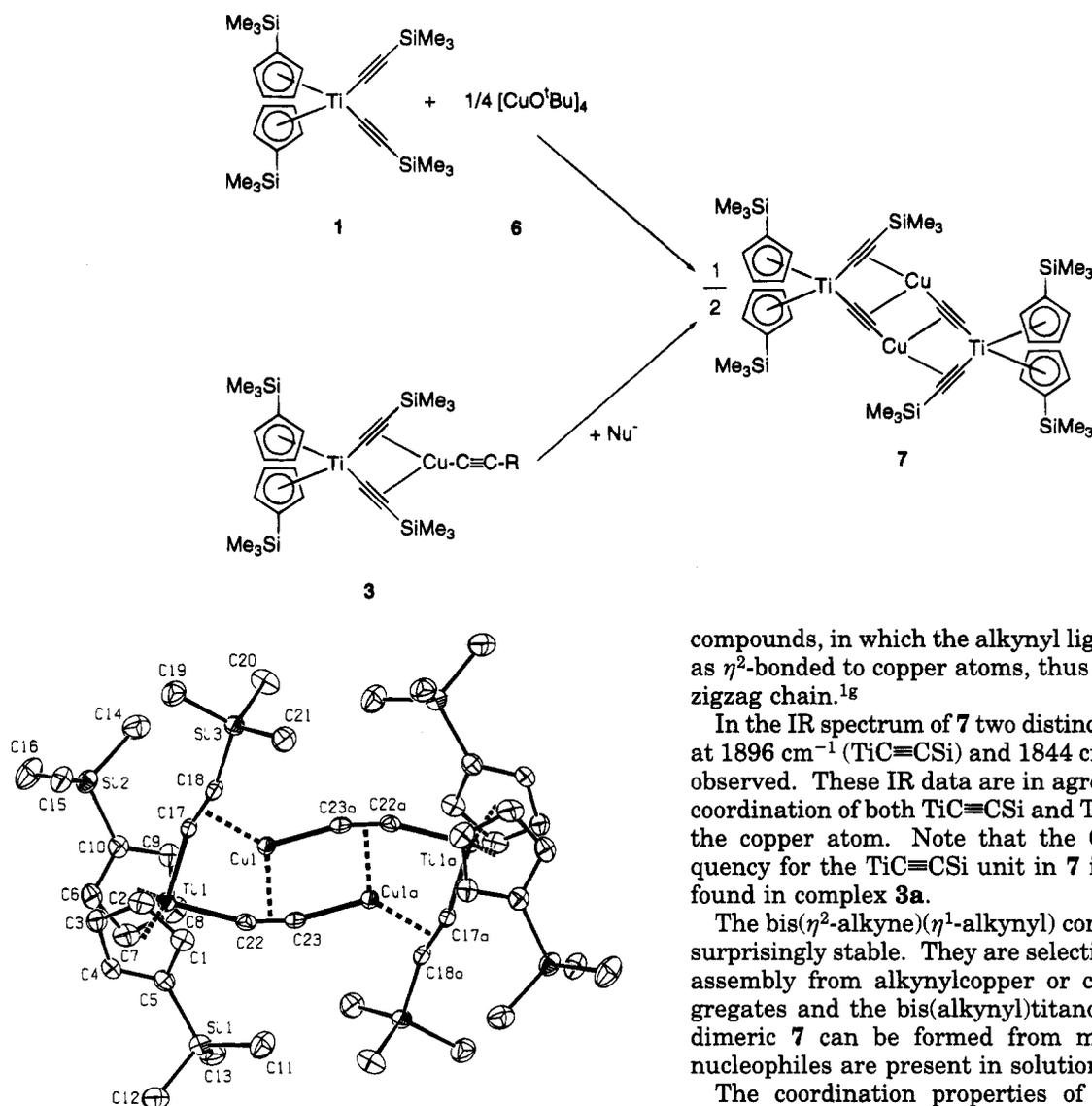


Figure 2. Molecular structure of **7** (ORTEP, thermal ellipsoids at 50% probability). Selected bond distances (Å) and bond angles (deg): Ti1–Cu1, 2.911(1); Cu1–Cu1a, 2.998(1); Cu1–C22, 2.107(2); Cu1–C23, 2.161(3); Cu1–C23a, 1.920(3); Cu1–C17, 2.030(3); Cu1–C18, 2.086(3); C17–C18, 1.234(3); C22–C23, 1.243(4); Ti1–C17, 2.097(3); Ti1–C22, 2.079(3); Ti1–C17–C18, 164.6(2); C17–C18–Si3, 165.0(2); Ti1–C22–C23, 163.4(2); C22–C23–Cu1a, 165.0(2); C17–Ti1–C22, 90.5(1); Cu1–C23–Cu1a, 94.4(1).

a dimer of the bimetallic acetylide $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{CCu})$ in which the alkynyl ligand within the Ti–C≡C–Cu entity is also η^2 -bonded to a second copper atom, thus forming an alkyne-bridged dimer. The C≡C bond lengths of the alkyne ligands within this building block are lengthened from 1.208 Å in **1** to 1.234(3) Å (TiC≡CSi) and 1.243(4) Å (TiC≡CCu) in **7**. Each copper atom exhibits a somewhat distorted trigonal planar geometry with two η^2 - and one η^1 -bonded alkynyl ligands. The Ti–C≡C–Cu moiety deviates from linearity upon its η^2 -coordination to a second copper atom (Cu1) (Ti1–C22–C23 = 163.4(2)°, Cu1a–C23–C22 = 165.0(2)°). The central $\text{Cu}_2(\eta^2\text{-C}\equiv\text{C})_2$ core of **7** has a structural arrangement which corresponds to that observed in most polynuclear alkynylcopper(I)

compounds, in which the alkynyl ligands are η^1 - as well as η^2 -bonded to copper atoms, thus forming an infinite zigzag chain.^{1g}

In the IR spectrum of **7** two distinct $\nu(\text{C}\equiv\text{C})$ vibrations at 1896 cm^{-1} (TiC≡CSi) and 1844 cm^{-1} (TiC≡CCu) are observed. These IR data are in agreement with the η^2 -coordination of both TiC≡CSi and TiC≡CCu entities to the copper atom. Note that the C≡C vibration frequency for the TiC≡CSi unit in **7** is the same as that found in complex **3a**.

The bis(η^2 -alkyne)(η^1 -alkynyl) complexes **3** and **7** are surprisingly stable. They are selectively formed by self-assembly from alkynylcopper or copper alkoxide aggregates and the bis(alkynyl)titanocene **1**. Moreover, dimeric **7** can be formed from monomeric **3**, when nucleophiles are present in solution (Scheme 2).

The coordination properties of the chelating bis-(alkyne) ligand **1** are currently being investigated for the synthesis and isolation of stabilized mononuclear aryl-, alkenyl-, or alkylcopper(I) fragments out of heterocopper and cuprate reagents. As an example, the isolation of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{Cu}\{\text{C}_6\text{H}_4\text{-NMe}_2\text{-4}\}$ from *in situ* prepared $\text{Cu}\{\text{C}_6\text{H}_4\text{NMe}_2\text{-4}\}^7$ has recently been achieved.²

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Supplementary Material Available: Text giving synthetic procedures and analytical and spectroscopic data for **3** and **7** and tables of all atom parameters for **3a** and **7** (27 pages). Ordering information is given on any current masthead page.

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(7) van Koten, G.; Leusink, A. J.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *85*, 105–114.