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Reaction Chemistry of Alkynyl-Functionalized Titanocenes. X-ray Structure Analyses of (η^5-$C_5H_4SiMe_3$)$_2$Ti(Cl)(CH_2SiMe_3) and [(η^5-$C_5H_4SiMe_3$)$_2$Ti(Cl)(C≡$CSiMe_3$)]CuBr

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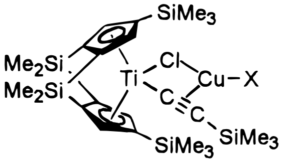
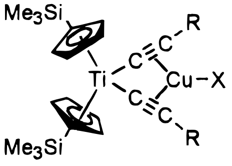
The synthesis and reaction chemistry of the mono (σ-alkynyl) titanocene chlorides [Ti](Cl)(C≡CR) {[Ti] = (η^5-$C_5H_4SiMe_3$)$_2$Ti; **2a**, R = Ph; **2b**, R = $SiMe_3$} is described. Treatment of compounds **2a** and **2b** with $ClMgCH_2SiMe_3$ or LiC≡CR′ yields [Ti](CH_2SiMe_3)(C≡$CSiMe_3$) (**3**) or [Ti](C≡CR)(C≡CR′) (**5a**, R = Ph, R′ = $SiMe_3$; **5b**, R = R′ = Ph; **5c**, R = R′ = $SiMe_3$), respectively. The reaction of compounds **2a**, **2b**, or **5a** with polymeric $[CuX]_n$ (X = Cl, Br, I) produces the heterobimetallic titanium−copper complexes {[Ti](Cl)(C≡CR)}CuX (**6a**, R = Ph, X = Cl; **6b**, R = Ph, X = Br; **6c**, R = Ph, X = I; **7a**, R = $SiMe_3$, X = Cl; **7b**, R = $SiMe_3$, X = Br) or {[Ti](C≡CPh)(C≡$CSiMe_3$)}CuX (**8a**, X = Cl; **8b**, X = Br). While compounds **2a** and **2b** do not react with $[AgX]_n$ (X = Cl, Br), it is found that the bis(σ-alkynyl)titanocene **5a** is able to break down the polymeric structure of $[AgX]_n$ to produce the heterobimetallic compounds {[Ti](C≡CPh)(C≡$CSiMe_3$)}AgX (**10a**, X = Cl; **10b**, X = Br). Moreover, compound **8a** can be synthesized by treatment of **2a** or **2b** with $[CuC≡CR′]_n$ (R′ = $SiMe_3$, Ph). However, when compound **3** is reacted with $[CuCl]_n$ under appropriate reaction conditions, the formation of {[Ti](C≡$CSiMe_3$)$_2$}CuCl (**9b**), $[CuCH_2SiMe_3]_4$, [Ti](Cl)(CH_2SiMe_3) (**4**), and [Ti]Cl_2 (**1**) is observed; a reaction mechanism for the formation of the latter compounds is discussed. The solid state structures of [Ti](Cl)(CH_2SiMe_3) (**4**) and {[Ti](Cl)(C≡$CSiMe_3$)}CuBr (**7b**) were determined. Crystals of **4** and **7b** are monoclinic, space group $P2_1/n$. **4**: $C_{20}H_{37}ClSi_3Ti$, cell constants $a = 6.812(2)$ Å, $b = 11.298(6)$ Å, $c = 33.16(1)$ Å, $\beta = 92.25(3)°$, and $Z = 4$. **7b**: $C_{21}H_{35}BrClCuSi_3Ti$, cell constants $a = 13.257(7)$ Å, $b = 10.470(5)$ Å, $c = 20.39(1)$ Å, $\beta = 100.91(3)°$, and $Z = 4$.

Introduction

Recently, we have shown that the mono(σ-alkynyl)titanocene [(η^5-$C_5H_2SiMe_3$)$SiMe_2$]$_2$Ti(Cl)(C≡$CSiMe_3$),[1] the bis(σ-alkynyl)titanocenes [Ti]$(C≡CR)_2$ {[Ti] = (η^5-$C_5H_4SiMe_3$)$_2$Ti; R = Ph, $SiMe_3$},[2,3] and the (σ)-1,3-butadiyn-1-yltitanocenes [Ti](Cl)(C≡C−C≡CR) and [Ti]$(C≡C−C≡CR)_2$ (R = C_2H_5, $SiMe_3$)[5] can be used as organometallic chelating ligands (organometallic π-tweezers) for the stabilization of monomeric copper(I) fragments CuX (X = singly bonded organic or inorganic ligand) (type **A** and **B** molecules).



A



B

The CuX moiety in type **A** molecules is complexed by the chloro group and the alkynyl ligand of the titanocene fragment [Ti](Cl)(C≡CR), whereas in compounds of type **B** the CuX entity is η^2-coordinated by both C≡CR groups of the organometallic chelating ligand [Ti]$(C≡CR)_2$.[1−4] Similar bonding situations are found for 1,3-butadiyn-1-yltitanocenes.[5] Moreover, the organic groups X in type **B** molecules can easily be transferred to suitable substrates.[4] For enantioselective transfer reactions the starting material must provide chiral information. The chiral information can either arise from the bis(alkynyl) titanocene building block (η^5-C_5H_5)(η^5-C_5H_4R)Ti(C≡CR′)(C≡CR″) (R = R′ = R″ = singly bonded organic ligand; R′ ≠ R″) or from a single enantiomeric pure alkynyl ligand, giving rise to optically active organometallic π-tweezer molecules [Ti](C≡CR)(C≡CR*). For the synthesis of titanocenes, which contain different alkynyl ligands the selective preparation of [Ti](Cl)(C≡CR) compounds {[Ti] = (η^5-$C_5H_4SiMe_3$)$_2$Ti; R = Ph, $SiMe_3$} is necessary at first.

Here, we describe the synthesis of mono(σ-alkynyl)titanocene chlorides, as well as their reaction behavior toward metallated alkynes and copper(I) compounds.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified by distillation from sodium/benzophenone ketyl; *n*-pentane was purified by distillation from calcium hydride. Infrared spectra were obtained with a Perkin-Elmer 983G spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.132 MHz in the Fourier transform mode; ^{13}C NMR spectra were recorded at 50.323 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal. FD, EI, and FAB

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mass spectra were recorded on a Finnigan 8400 mass spectrometer operating in the positive-ion mode. Melting points were determined with use of analytically pure samples, which were sealed in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Organisch-Chemisches Institut der Universität Heidelberg.

Synthesis of (η^5-$C_5H_4SiMe_3$)$_2$Ti(Cl)(C≡CR) (2a, R = Ph; 2b, R = $SiMe_3$). A solution of LiC≡CR (10.50 mmol; R = Ph, 1.14 g; R = $SiMe_3$, 1.09 g)[6,7] in diethyl ether (100 mL) was added at 20 °C to a suspension of (η^5-$C_5H_4SiMe_3$)$_2$$TiCl_2$[8] (**1**) (3.93 g, 10.00 mmol) in diethyl ether (100 mL) within 2 h. After another 15 min of stirring, all volatiles were removed *in vacuo*. Filtration of the residue through Celite (*n*-pentane, 3 × 3 cm) and evaporation of the volatiles *in vacuo* yielded an orange-red powder (**2a**) or oil (**2b**). Compound **2a** could be crystallized from *n*-pentane at −30 °C.

2a. Yield: 4.13 g (9.00 mmol, 90%). Mp: 101 °C. IR (KBr, cm^{-1}): 2077 [$\nu_{C≡C}$]. MS (FD): *m/e* 458 [M^+]. ^1H NMR (200 MHz, $CDCl_3$): δ 0.32 (s, 18H, $C_5H_4SiMe_3$); 6.3 (m, 2H, C_5H_4); 6.5 (m, 2H, C_5H_4); 6.7 (m, 2H, C_5H_4); 6.8 (m, 2H, C_5H_4); 7.2−7.3 (m, 5H, *Ph*). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 0.1 ($SiMe_3$); 114.8 (C_5H_4); 117.0 (C_5H_4); 125.0 (C_5H_4); 125.6 (C_5H_4); 126.3 (C_5H_4, C_{ipso}); 122.4 (C≡*C*Ph); 126.6 (*Ph*); 128.0 (*Ph*); 130.1 (*Ph*); 131.3 (*Ph*, C_{ipso}); 148.3 (Ti*C*≡C). Anal. Calcd for $C_{24}H_{31}ClSi_2Ti$ (459.03): C, 62.80; H, 6.81. Found: C, 62.78; H, 6.82.

2b. Yield: 3.55 g (7.80 mmol, 78%). IR (KBr, cm^{-1}): 2022 [$\nu_{C≡C}$]. ^1H NMR (200 MHz, $CDCl_3$): δ 0.10 (s, 9H, C≡$SiMe_3$); 0.27 (s, 18H, $C_5H_4SiMe_3$); 6.2 (m, 2H, C_5H_4); 6.4 (m, 2H, C_5H_4); 6.6 (m, 2H, C_5H_4); 6.7 (m, 2H, C_5H_4). Anal. Calcd for $C_{21}H_{35}ClSi_3Ti$ (455.17): C, 55.42; H, 7.75. Found: C, 55.20; H, 7.86.

Synthesis of (η^5-$C_5H_4SiMe_3$)$_2$Ti(Cl)(CH_2SiMe_3) (4). A solution of $ClMgCH_2SiMe_3$[8a] (1.47 g, 10.00 mmol) in diethyl ether (50 mL) was added dropwise at 25 °C to a solution of (η^5-$C_5H_4SiMe_3$)$_2$$TiCl_2$[8] (**1**) (3.58 g, 9.00 mmol) in CH_2Cl_2 (150 mL) and stirred for 2 h. Afterward the volatiles were removed *in vacuo*. The residue was dispersed in diethyl ether (200 mL) and filtered through a pad of Celite (diethyl ether, 3 × 3 cm). Concentration of the filtrate yielded **4** as orange needles. Yield: 3.2 g (7.20 mmol, 80%).

Mp: 97 °C. MS (EI): *m/e* (%) 429 [M^+ − Me] (3); 401 [M^+ − 3Me] (26); 357 [M^+ − CH_2SiMe_3] (100). ^1H NMR (200 MHz, $CDCl_3$): δ 0.04 (s, 9H, CH_2SiMe_3); 0.29 (s, 18H, $C_5H_4SiMe_3$); 2.14 (s, 2H, CH_2SiMe_3); 5.8 (m, 2H, C_5H_4); 6.1 (m, 2H, C_5H_4); 6.4 (m, 2H, C_5H_4); 7.1 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 0.1 ($C_5H_4SiMe_3$); 2.9 (CH_2SiMe_3); 75.6 (CH_2SiMe_3); 110.9 (C_5H_4); 117.0 (C_5H_4); 121.4 (C_5H_4); 128.0 (C_5H_4); 129.3 (C_5H_4, C_{ipso}). Anal. Calcd for $C_{20}H_{37}ClSi_3Ti$ (445.10): C, 53.97; H, 8.38. Found: C, 53.71; H, 8.27.

Synthesis of (η^5-$C_5H_4SiMe_3$)$_2$Ti(CH_2SiMe_3)(C≡$CSiMe_3$) (3). (η^5-$C_5H_4SiMe_3$)$_2$Ti(Cl)(CH_2SiMe_3) (**4**) (450 mg, 1.00 mmol) was added at −25 °C in one portion to a solution of LiC≡$CSiMe_3$[6,7] (115 mg, 1.10 mmol) in diethyl ether (100 mL). After 2 h of stirring at 25 °C all volatiles were removed *in vacuo*, the residue was dissolved in *n*-pentane (200 mL) and filtered through Celite (*n*-pentane, 3 × 3 cm). Removal of the solvent yielded compound **3** as an orange-red oil. Yield: 430 mg (0.85 mmol, 85%).

IR (KBr, cm^{-1}): 2018 [$\nu_{C≡C}$]. MS (EI): *m/e* (%) 418 [M^+ − CH_2SiMe_3] (100); 322 [M^+ − CH_2SiMe_3 − C_2SiMe_3] (30). ^1H NMR (200 MHz, C_6D_6): δ 0.07 (s, 9H, C≡$CSiMe_3$); 0.24 (s, 9H, CH_2SiMe_3); 0.37 (s, 18H, $C_5H_4SiMe_3$); 1.70 (s, 2H, CH_2SiMe_3); 5.4 (m, 2H, C_5H_4); 5.9 (m, 2H, C_5H_4); 6.2 (m, 2H, C_5H_4); 7.1 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 0.6 ($C_5H_4SiMe_3$); 0.7 (C≡$CSiMe_3$); 3.3 (CH_2SiMe_3); 79.3 (CH_2SiMe_3); 111.3 (C_5H_4); 115.8 (C_5H_4); 120.2 (C_5H_4); 123.4 (C≡*C*$SiMe_3$); 124.4 (C_5H_4); 124.9 (C_5H_4, C_{ipso}); 166.9 (Ti*C*≡C). Anal. Calcd for $C_{25}H_{46}Si_4Ti$ (505.86): C, 59.24; H, 9.15. Found: C, 59.17; H, 9.09.

Synthesis of (η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CPh)(C≡$CSiMe_3$) (5a). A solution of LiC≡$CSiMe_3$[6,7] (1.09 g, 10.50 mmol) in diethyl ether (50 mL) was added within 15 min to a solution of **2a** (4.60 g, 10.00 mmol) in diethyl ether (50 mL) at 20 °C and stirred for 1 h. Evaporation of the volatiles *in vacuo*, filtration of the residue with *n*-pentane through Celite (3 × 3 cm), and removing the volatiles yielded a red oil. Yield: 375 mg (0.72 mmol, 72%).

IR (KBr, cm^{-1}): 2067 [$\nu_{C≡CPh}$]; 2014 [$\nu_{C≡CSiMe_3}$]. MS (FD): *m/e* 520 [M^+]. ^1H NMR (200 MHz, $CDCl_3$): δ 0.07 (s, 9H, C≡$CSiMe_3$); 0.28 (s, 18H, $C_5H_4SiMe_3$); 6.19 (m, 2H, C_5H_4); 6.27 (m, 2H, C_5H_4); 6.67 (m, 2H, C_5H_4); 6.73 (m, 2H, C_5H_4); 7.1−7.4 (m, 5H, *Ph*). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 0.3 (C≡$CSiMe_3$); 0.4 ($C_5H_4SiMe_3$); 113.0 (C_5H_4); 113.5 (C_5H_4); 122.8 (C_5H_4); 122.9 (C_5H_4); 124.8 (C_5H_4, C_{ipso}); 125.7 (C≡*C*Ph); 126.5 (*Ph*); 128.0 (*Ph*); 130.0 (*Ph*); 131.7 (*Ph*); 135.6 (C≡*C*$SiMe_3$); 152.8 (Ti*C*≡CPh); 171.1 (Ti*C*≡$CSiMe_3$). Anal. Calcd for $C_{29}H_{40}Si_3Ti$ (520.79): C, 66.88; H, 7.74. Found: C, 66.80; H, 7.75.

Synthesis of {(η^5-$C_5H_4SiMe_3$)$_2$Ti(Cl)(C≡CPh)}CuX (6a, X = Cl; 6b, X = Br; 6c, X = I). **2a** (200 mg, 0.44 mmol) was added to a suspension of $[CuX]_n$ (0.45 mmol; X = Cl, 50 mg; X = Br, 70 mg; X = I, 80 mg) in tetrahydrofuran (50 mL) and stirred in the dark for 2 h. The reaction solution was filtered through a pad of Celite and all volatile materials were removed *in vacuo*. Compounds **6a**−**6c** were obtained as orange colored solids.

6a. Yield: 220 mg (0.40 mmol, 92%). Mp: 180 °C. IR (KBr, cm^{-1}): 1913 [$\nu_{C≡C}$]. MS (FD): *m/e* (%) 560 [M^+] (20); 458 [M^+ − CuCl] (100). ^1H NMR (200 MHz, $CDCl_3$): δ 0.22 (s, 18H, $C_5H_4SiMe_3$); 6.1 (m, 2H, C_5H_4); 6.3 (m, 2H, C_5H_4); 6.5 (m, 2H, C_5H_4); 6.6 (m, 2H, C_5H_4); 7.2−7.4 (m, 3H, *Ph*); 7.7−7.8 (m, 2H, *Ph*). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ −0.1 ($C_5H_4SiMe_3$); 117.2 (C_5H_4); 117.6 (C_5H_4); 121.1 (C_5H_4); 121.9 (C_5H_4); 124.0 (C_5H_4, C_{ipso}); 127.9 (*Ph*); 128.3 (C≡*C*Ph); 128.4 (*Ph*); 130.6 (*Ph*); 135.2 (*Ph*, C_{ipso}); 145.8 (Ti*C*≡C). Anal. Calcd for $C_{24}H_{31}Cl_2CuSi_2Ti$ (558.03): C, 51.66; H, 5.60. Found: C, 51.86; H, 5.80.

6b. Yield: 220 mg (0.37 mmol, 85%). Mp: 169 °C. IR (KBr, cm^{-1}): 1933 [$\nu_{C≡C}$]. MS (FD): *m/e* 602 [M^+]. ^1H NMR (200 MHz, $CDCl_3$): δ 0.22 (s, 18H, $C_5H_4SiMe_3$); 6.2 (m, 2H, C_5H_4); 6.3 (m, 2H, C_5H_4); 6.5 (m, 2H, C_5H_4); 6.6 (m, 2H, C_5H_4); 7.2−7.4 (m, 3H, *Ph*), 7.7−7.8 (m, 2H, *Ph*). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ −0.1 ($C_5H_4SiMe_3$); 117.3 (C_5H_4); 117.6 (C_5H_4); 121.2 (C_5H_4); 122.0 (C_5H_4); 124.0 (C_5H_4, C_{ipso}); 128.1 (*Ph*); 128.3 (C≡*C*Ph); 128.4 (*Ph*); 130.9 (*Ph*); 135.4 (*Ph*, C_{ipso}); 146.2 (Ti*C*≡*C*). Anal. Calcd for $C_{24}H_{31}BrClCuSi_2Ti$ (602.46): C, 47.85; H, 5.19. Found: C, 47.68; H, 5.28.

6c. Yield: 270 mg (0.42 mmol, 95%). Mp: 163 °C. IR (KBr, cm^{-1}): 1926 [$\nu_{C≡C}$]. MS (FAB): *m/e* (%) 521 [M^+ − I] (90); 322 [M^+ − CuI − C_2Ph − Cl] (100). ^1H NMR (200 MHz, $CDCl_3$): δ 0.24 (s, 18H, $C_5H_4SiMe_3$); 6.2 (m, 2H, C_5H_4); 6.3 (m, 2H, C_5H_4); 6.5 (m, 2H, C_5H_4); 6.6 (m, 2H, C_5H_4); 7.2−7.4 (m, 3H, *Ph*); 7.7−7.8 (m, 2H, *Ph*). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 0.0 ($C_5H_4SiMe_3$); 117.4 (C_5H_4); 118.0 (C_5H_4); 121.3 (C_5H_4); 122.3 (C_5H_4); 124.2 (C_5H_4, C_{ipso}); 128.0 (*Ph*); 128.3 (*Ph*); 128.5 (C≡*C*Ph); 131.3 (*Ph*); 135.3 (*Ph*, C_{ipso}); 147.9 (Ti*C*≡C). Anal. Calcd for $C_{24}H_{31}ClCuISi_2Ti$ (649.48): C, 44.38; H, 4.81. Found: C, 43.92; H, 4.86.

Synthesis of {(η^5-$C_5H_4SiMe_3$)$_2$Ti(Cl)(C≡$CSiMe_3$)}CuX (7a, X = Cl; 7b, X = Br). **2b** (200 mg, 0.44 mmol) was reacted with $[CuX]_n$ (0.45 mmol; X = Cl, 50 mg; X = Br, 70 mg) under appropriate reaction conditions (see synthesis of compounds **6a**−**6c**), yielding compounds **7a** and **7b** as orange solids.

7a. Yield: 230 mg (0.42 mmol, 95%). Mp: 167°C. IR (KBr, cm^{-1}): 1901 [$\nu_{C≡C}$]. MS (FD): *m/e* 552 [M^+]. ^1H NMR (200 MHz, $CDCl_3$): δ 0.23 (s, 18H, $C_5H_4SiMe_3$); 0.32 (s, 9H, C≡$CSiMe_3$); 6.1 (m, 2H, C_5H_4); 6.2 (m, 2H, C_5H_4); 6.4 (m, 2H, C_5H_4); 6.5 (m, 2H, C_5H_4). Anal. Calcd for $C_{21}H_{35}Cl_2CuSi_3Ti$ (554.12): C, 45.52; H, 6.37. Found: C, 45.14; H, 6.51.

7b. Yield: 250 mg (0.42 mmol, 94%). Mp: 150 °C. IR (KBr, cm^{-1}): 1899 [$\nu_{C≡C}$]. MS (FAB): *m/e* (%) 598 [M^+] (6); 517 [M^+ − Br] (75); 418 [M^+ − CuBr − Cl] (10); 357 [M^+ − CuBr − C_2SiMe_3] (50); 322 [M^+ − CuBr − Cl − C_2SiMe_3] (100). ^1H NMR (200 MHz, $CDCl_3$): δ 0.25 (s, 18H, $C_5H_4SiMe_3$); 0.34 (s, 9H, C≡$CSiMe_3$); 6.1 (m, 2H, C_5H_4); 6.2 (m, 2H, C_5H_4); 6.4 (m, 2H, C_5H_4); 6.5 (m, 2H, C_5H_4). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 0.0 ($C_5H_4SiMe_3$); 0.2 (C≡$CSiMe_3$); 116.9 (C_5H_4); 118.3 (C_5H_4); 120.8 (C_5H_4); 121.8 (C_5H_4);

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127.5 (*C*$_5$H$_4$, C$_{ipso}$); 133.5 (C$\equiv$*C*SiMe$_3$), 176.6 (Ti*C*$\equiv$C). Anal. Calcd for C$_{21}$H$_{35}$BrClCuSi$_3$Ti (598.55): C, 42.14; H, 5.89. Found: C, 42.14; H, 5.91.

Synthesis of {(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C$\equiv$CPh)(C$\equiv$CSiMe$_3$)}CuX (8a, X = Cl; 8b, X = Br). **5a** (150 mg, 0.29 mmol) was reacted with [CuX]$_n$ (0.30 mmol; X = Cl, 30 mg; X = Br, 40 mg) in the above described manner (see synthesis of compounds **6a**−**6c**), yielding compounds **8a** and **8b** as orange colored solids.

8a. Yield: 165 mg (0.27 mmol, 92%). Mp: 186 °C. IR (KBr, cm^{-1}): 1984, 1956 [$\nu_{C\equiv CPh}$]; 1917 [$\nu_{C\equiv CSiMe_3}$]. MS (FD): *m/e* 583 [M$^+$ − Cl]. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.22 (s, 18H, C$_5$H$_4$Si*Me*$_3$); 0.33 (s, 9H, C$\equiv$CSi*Me*$_3$); 6.01 (m, 2H, C$_5$*H*$_4$); 6.04 (m, 2H, C$_5$*H*$_4$); 6.14 (m, 2H, C$_5$*H*$_4$); 6.20 (m, 2H, C$_5$*H*$_4$); 7.2−7.4 (m, 3H, *Ph*); 7.5−7.7 (m, 2H, *Ph*). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 0.0 (C$_5$H$_4$Si*Me*$_3$); 0.4 (C$\equiv$CSi*Me*$_3$); 113.6 (*C*$_5$H$_4$); 113.9 (*C*$_5$H$_4$); 116.7 (*C*$_5$H$_4$); 116.9 (*C*$_5$H$_4$); 122.7 (*C*$_5$H$_4$, C$_{ipso}$); 123.5 (C$\equiv$*C*Ph); 128.0 (*Ph*); 128.5 (*Ph*); 131.9 (*Ph*); 135.5 (*Ph*, C$_{ipso}$); 138.0 (C$\equiv$*C*SiMe$_3$); 144.5 (Ti*C*$\equiv$CPh); 169.1 (Ti*C*$\equiv$CSiMe$_3$). Anal. Calcd for C$_{29}$H$_{40}$ClCuSi$_3$Ti (619.79): C, 56.20; H, 6.50. Found: C, 55.89; H, 6.27.

8b. Yield: 190 mg (0.28 mmol, 96%). Mp: 190 °C. IR (KBr, cm^{-1}): 1984, 1958 [$\nu_{C\equiv CPh}$]; 1913 [$\nu_{C\equiv CSiMe_3}$]. MS (FAB): *m/e* (%) 583 [M$^+$ − Br] (60); 322 [M$^+$ − CuBr − C$_2$Ph − C$_2$SiMe$_3$] (100). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.22 (s, 18H, C$_5$H$_4$Si*Me*$_3$); 0.35 (s, 9H, C$\equiv$CSi*Me*$_3$); 6.0 (m, 2H, C$_5$*H*$_4$); 6.1 (m, 2H, C$_5$*H*$_4$); 6.15 (m, 2H, C$_5$*H*$_4$); 6.2 (m, 2H, C$_5$*H*$_4$); 7.2−7.4 (m, 3H, *Ph*); 7.5−7.6 (m, 2H, *Ph*). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 0.0 (C$_5$H$_4$Si*Me*$_3$); 0.4 (C$\equiv$CSi*Me*$_3$); 113.8 (*C*$_5$H$_4$); 114.1 (*C*$_5$H$_4$); 116.9 (*C*$_5$H$_4$); 117.1 (*C*$_5$H$_4$); 122.9 (*C*$_5$H$_4$, C$_{ipso}$); 123.8 (C$\equiv$*C*Ph); 128.0 (*Ph*); 128.8 (*Ph*); 132.4 (*Ph*); 135.5 (*Ph*); 138.4 (C$\equiv$*C*SiMe$_3$); 145.0 (Ti*C*$\equiv$CPh); 169.8 (Ti*C*$\equiv$CSiMe$_3$). Anal. Calcd for C$_{29}$H$_{40}$BrCuSi$_3$Ti (664.24): C, 52.44; H, 6.07. Found: C, 51.96; H, 5.80.

Synthesis of {(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C$\equiv$CPh)(C$\equiv$CSiMe$_3$)}AgX (10a, X = Cl; 10b, X = Br). **5a** (100 mg, 0.19 mmol) was reacted with [AgX]$_n$ (0.20 mmol; X = Cl, 30 mg; X = Br, 40 mg) under appropriate reaction conditions (see synthesis of compounds **6a**−**6c**), yielding compounds **10a** and **10b** as orange solids.

10a. Yield: 90 mg (0.17 mmol, 81%). Mp: 143 °C. IR (KBr, cm^{-1}): 2015 [$\nu_{C\equiv CPh}$]; 1939 [$\nu_{C\equiv CSiMe_3}$]. MS (FAB): *m/e* (%) 629 [M$^+$ − Cl] (45); 322 [M$^+$ − AgCl − C$_2$Ph − C$_2$SiMe$_3$] (100). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.25 (s, 18H, C$_5$H$_4$Si*Me*$_3$); 0.34 (s, 9H, C$\equiv$CSi*Me*$_3$); 6.32 (pt, J_{HH} = 2.4 Hz, 4H, C$_5$*H*$_4$); 6.37 (pt, J_{HH} = 2.4 Hz, 4H, C$_5$*H*$_4$); 7.3−7.4 (m, 3H, *Ph*); 7.6−7.8 (m, 2H, *Ph*). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 0.0 (C$_5$H$_4$Si*Me*$_3$); 0.4 (C$\equiv$CSi*Me*$_3$); 115.7 (*C*$_5$H$_4$); 116.2 (*C*$_5$H$_4$); 119.0 (*C*$_5$H$_4$); 119.1 (*C*$_5$H$_4$); 122.1 (TiC$\equiv$*C*Ph); 125.0 (*C*$_5$H$_4$, C$_{ipso}$); 128.3 (*Ph*); 128.5 (*Ph*); 131.2 (*Ph*); 132.0 (Ti*C*$\equiv$CPh, J_{CAg} = 16.4 Hz); 139.9 (*Ph*, C$_{ipso}$); 143.7 (TiC$\equiv$*C*SiMe$_3$); 154.8 (Ti*C*$\equiv$CSiMe$_3$, J_{CAg} = 16.4 Hz). Anal. Calcd for C$_{29}$H$_{40}$AgClSi$_3$Ti (664.10): C, 52.45; H, 6.07. Found: C, 52.31; H, 5.97.

10b. Yield: 120 mg (0.17 mmol, 88%). Mp: 151 °C. IR (KBr, cm^{-1}): 2015 [$\nu_{C\equiv CPh}$]; 1939 [$\nu_{C\equiv CSiMe_3}$]. MS (FAB): *m/e* (%) 708 [M$^+$] (2); 629 [M$^+$ − Br] (45); 322 [M$^+$ − AgBr − C$_2$Ph − C$_2$SiMe$_3$] (100). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.26 (s, 18H, C$_5$H$_4$Si*Me*$_3$); 0.35 (s, 9H, C$\equiv$CSi*Me*$_3$); 6.32 (pt, J_{HH} = 2.2 Hz, 2H, C$_5$*H*$_4$); 6.38 (pt, J_{HH} = 2.2 Hz, 6H, C$_5$*H*$_4$); 7.2−7.4 (m, 3H, *Ph*); 7.6−7.8 (m, 2H, *Ph*). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 0.0 (C$_5$H$_4$Si*Me*$_3$); 0.5 (C$\equiv$CSi*Me*$_3$); 115.7 (*C*$_5$H$_4$); 116.3 (*C*$_5$H$_4$); 119.1 (*C*$_5$H$_4$); 119.3 (*C*$_5$H$_4$); 122.0 (TiC$\equiv$*C*Ph); 125.0 (*C*$_5$H$_4$, C$_{ipso}$); 128.3 (*Ph*); 128.7 (*Ph*); 131.5 (*Ph*); 133.1 (*Ph*, C$_{ipso}$); 140.2 (TiC$\equiv$*C*SiMe$_3$); 144.2 (Ti*C*$\equiv$CPh, J_{CAg} = 16.4 Hz); 155.6 (Ti*C*$\equiv$CSiMe$_3$, J_{CAg} = 16.4 Hz). Anal. Calcd for C$_{29}$H$_{40}$AgBrSi$_3$Ti (708.55): C, 49.16; H, 5.69. Found: C, 49.44; H, 5.69.

Structure Determination and Refinement of Compounds 4 and 7b. X-ray data were collected on a Siemens (Nicolet) R3m/V diffractometer for orange crystals sealed in a glass capillary. Accurate unit cell parameters and an orientation matrix were derived from the setting angles of 37 well-centered reflections in the range 13° ≤ 2θ ≤ 26°. The unit cell parameters were checked for the presence of the higher lattice symmetry.[9] Data were corrected for Lorentz polarization effects. An empirical absorption correction was applied based on five reflections in the range 3° ≤ 2θ ≤ 52.5°, ω-scan 8.4° ≤ $\dot{\omega}$ ≤ 22.8°, and $\Delta\omega$ = 1.2°. The structures were solved by direct methods and subsequent difference Fourier techniques (SHELXS 86[10]). Refinement on *F* was carried out by full-matrix least-squares techniques (SHELX 76[11]) using reflections with $I \geq 2.5\sigma(I)$ during refinement. Hydrogen atoms were included in calculated positions, riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Weights were optimized in final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections for structure refinements of compounds **4** and **7b** were taken from ref 12. Crystal data and numerical details of structure determinations and refinements are collected in Table 1. Selected geometrical details of structures of **4** and **7b** are listed in Tables 2 and 3.

Table 1. Crystallographic Parameters for Compounds **4** and **7b**

	4	**7b**
empirical formula	C$_{20}$H$_{37}$ClSi$_3$Ti	C$_{21}$H$_{35}$BrClCuSi$_3$Ti
fw	445.10	598.55
space group	$P2_1/n$	$P2_1/n$
a, Å	6.812(2)	13.257(7)
b, Å	11.298(6)	10.470(5)
c, Å	33.16(1)	20.39(1)
β, deg	92.25(3)	100.91(3)
volume, Å^3	2550.1(8)	2779.0(9)
ρ_{calc}, g cm^{-3}	1.16	1.43
Z	4	4
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, K	295	295
no. of unique reflns	5000	5942
no. of data with $I \geq 2.5\sigma(I)$	2217	3521
R_1[a]	0.064	0.058
R_w[b]	0.051	0.048

[a] $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$ only for observed reflections. [b] $R_w = [\sum[F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections.

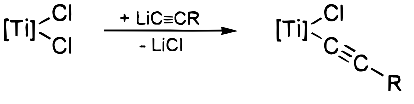
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **4**

bond lengths		bond angles	
Ti(1)−Cl(1)	2.316(2)	Cl(1)−Ti(1)−C(19)	93.5(2)
Ti(1)−C(19)	2.209(6)	Ti(1)−C(19)−Si(3)	133.9(3)
C(19)−Si(3)	1.865(6)	D1−Ti(1)−D2[a]	131.8
Ti(1)−D1[a]	2.115		
Ti(1)−D2[a]	2.071		

[a] D1, D2 = Centers of the cyclopentadienyl ligands.

Results

Synthesis of Compounds [Ti](Cl)(C≡CR) (2). The mono-(σ-alkynyl)-substituted compounds [Ti][Cl](C≡CR) {[Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti; **2a**, R = Ph; **2b**, R = SiMe$_3$} are obtained in 90% (**2a**) or 78% (**2b**) yield when titanocene dichloride [Ti]Cl$_2$ (**1**) is reacted with equimolar amounts of LiC≡CR (R = Ph, SiMe$_3$) in diethyl ether or tetrahydrofuran solutions at 25 °C. The bis(σ-alkynyl)titanocenes [Ti](C≡CR)$_2$ (**5b**, R = Ph; **5c**, R = SiMe$_3$) were formed as byproducts in 5−10% yield, depending on the reaction conditions used.



(1)

1

2a: R = Ph
2b: R = SiMe$_3$

After appropriate purification product **2a** gave orange-red crystals, which are stable for months in the solid state. In contrast, compound **2b** is obtained as an orange oil. In solution

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(9) Spek, A. L.; *J. Appl. Crystallogr.* **1988**, *21*, 578.

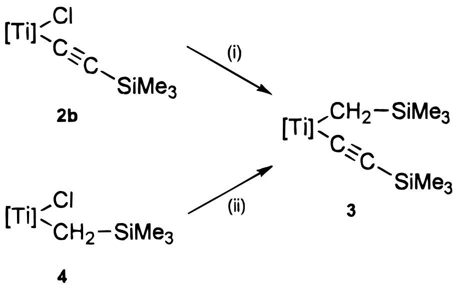
(10) Sheldrick, G. M. SHELX 86. Program for crystal structure determination. University of Göttingen, Göttingen, Germany 1986.

(11) Sheldrick, G. M. SHELX 76. Program for crystal structure analysis. University of Cambridge, U.K. 1976.

(12) Wilson, A. J. C., Ed. *International Tables of Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; Vol. C.

both compounds slowly redistribute their ligands, thus forming $[Ti](C{\equiv}CR)_2$ (**5**)[13] and $[Ti]Cl_2$ (**1**).[8] Complexes **2** readily dissolve in most common organic solvents.

Reaction of [Ti](Cl)(C≡CR) (2) with Organic Nucleophiles. Reaction of $[Ti](Cl)(C{\equiv}CSiMe_3)$ (**2b**) with equimolar amounts of $ClMgCH_2SiMe_3$ in diethyl ether, after appropriate workup, gave air-stable deep orange $[Ti](CH_2SiMe_3)(C{\equiv}CSiMe_3)$ (**3**) in 80% yield. Likewise, the preparation of compound **3** can be effected by treatment of $[Ti](Cl)(CH_2SiMe_3)$ (**4**)[8] with 1 molar equiv of $LiC{\equiv}CSiMe_3$ in diethyl ether solutions at −25 °C.



(2)

(i) + $ClMgCH_2SiMe_3$, - $MgCl_2$; (ii) + $LiC{\equiv}CSiMe_3$, - LiCl

When compound **2a** or **2b** is reacted with $LiC{\equiv}CR'$ (R′ = Ph, $SiMe_3$) in diethyl ether solution at 25 °C, the bis(σ-alkynyl)titanocenes $[Ti](C{\equiv}CR)(C{\equiv}CR')$ (**5a**−**5c**) are cleanly formed in 90−95% yield. **5a** is the first example of an organometallic π-tweezer molecule, which contains two different σ-bonded alkynyl ligands (route a, Scheme 1).

Compounds **3** and **5** are soluble in *e.g.* *n*-pentane and toluene and can be precipitated as orange (**3**, **5c**) or orange-red (**5a**, **5b**) solids by cooling their *n*-pentane solutions to −50 °C. Compounds **3** and **5a** tend to melt when their crystals are warmed to 25 °C.

Reaction of [Ti](Cl)(C≡CR) (2) and [Ti](C≡CPh)(C≡CSiMe₃) (5a) with Copper(I) Compounds. Equimolar addition of $[Ti](Cl)(C{\equiv}CR)$ (**2a**, R = Ph; **2b**, R = $SiMe_3$) to a suspension of polymeric $[CuX]_n$ (X = Cl, Br, I) in tetrahydrofuran at 25 °C resulted in the formation of the heterobimetallic titanium−copper complexes $\{[Ti](Cl)(C{\equiv}CR)\}CuX$ (**6**, R = Ph; **7**, R = $SiMe_3$) in quantitative yield (route b, Scheme 1). These compounds feature a monomeric CuX moiety, which is stabilized by the alkynyl ligand C≡CR and the chloro group of the $[Ti](Cl)(C{\equiv}CR)$ fragment.

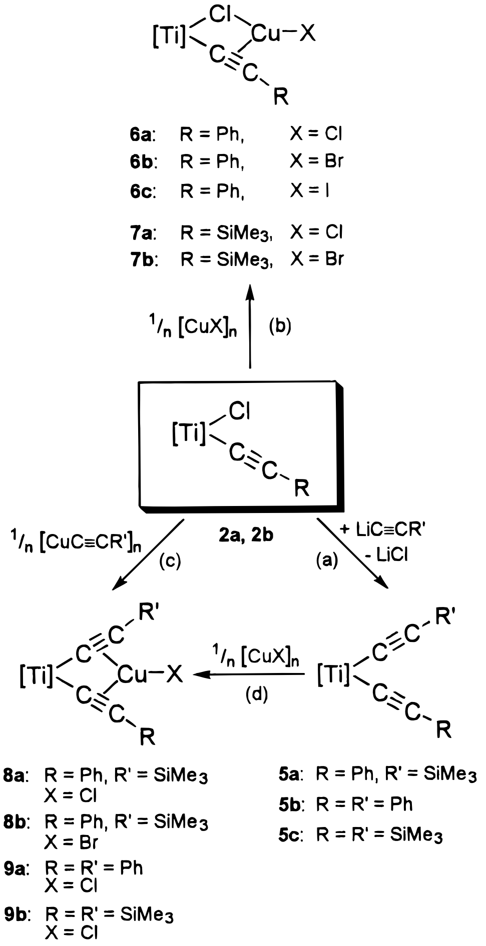
When $[CuC{\equiv}CR']_n$ (R′ = $SiMe_3$, Ph)[14] is used instead of $[CuX]_n$ (X = Cl, Br, I), the heterobimetallic tweezer molecules $\{[Ti](C{\equiv}CR)(C{\equiv}CR')\}CuCl$ (**8a**, R = Ph, R′ = $SiMe_3$; **9a**, R = R′ = Ph; **9b**, R = R′ = $SiMe_3$) are formed (route c, Scheme 1).

The latter molecules feature a monomeric copper(I) chloride entity with the copper atom in a trigonal-planar environment.

The formation of compounds **8** and **9** by reaction of **2** with $(1/n)[CuC{\equiv}CR']_n$ plausibly can be explained by taking an intermediate such as $\{[Ti](Cl)(C{\equiv}CR)\}CuC{\equiv}CR'$ into account. Intramolecular rearrangement of this complex affords the tweezer-like molecules **8** and **9**.

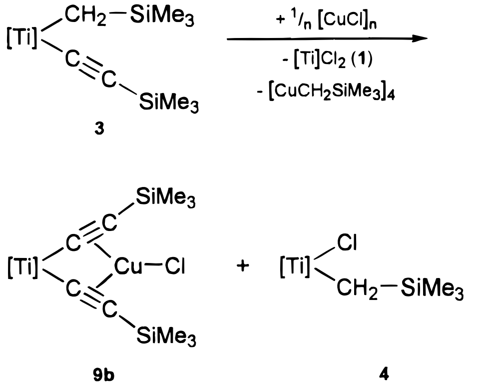
Moreover, the latter compounds can be synthesized by the reaction of *e.g.* $[Ti](C{\equiv}CPh)(C{\equiv}CSiMe_3)$ (**5a**) with $[CuX]_n$ (X = Cl, Br) in tetrahydrofuran at 25 °C (route d, Scheme 1).

Scheme 1. Synthesis of Compounds **5**−**9**



Compounds **6**−**9** are soluble in toluene, tetrahydrofuran and acetone and can be precipitated as orange to red solids by cooling their tetrahydrofuran/*n*-pentane solutions to −30 °C. In the solid state **6** and **7** can be handled in air for a short period of time while **8** and **9** are stable to air for months.

A further method for the preparation of the tweezer-like molecules **8** and **9** is given by treatment of the mono(σ-alkynyl)-substituted complex $[Ti](CH_2SiMe_3)(C{\equiv}CSiMe_3)$ (**3**) with equimolar amounts of $[CuCl]_n$ in diethyl ether at 25 °C. Besides dinuclear $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCl$ (**9b**),[3] the titanocene dichloride $[Ti]Cl_2$ (**1**),[8] the neosilyl-substituted titanocene chloride $[Ti](Cl)(CH_2SiMe_3)$ (**4**),[8] and tetrameric $[CuCH_2SiMe_3]_4$[15] could be isolated.



(3)

Possible reaction pathways for the formation of the corresponding products obtained by treatment of $[Ti](CH_2SiMe_3)(C{\equiv}CSiMe_3)$ with $[CuCl]_n$ are given in Scheme 2.

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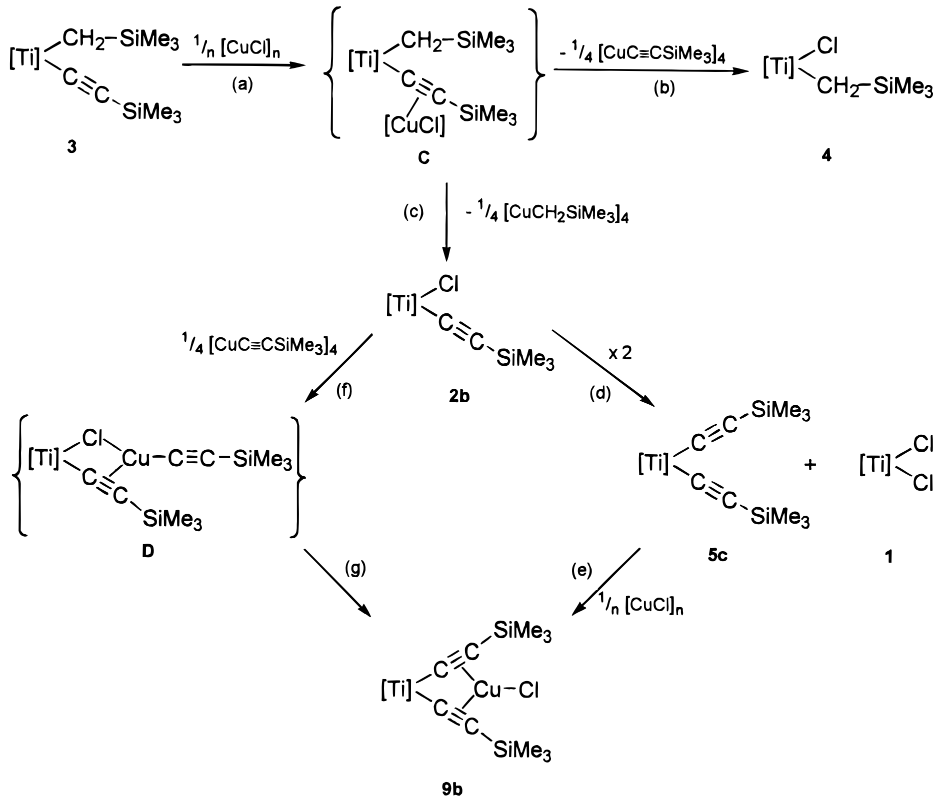
[13] (a) Lang, H.; Seyferth, D. *Z. Naturforsch.* **1990**, *45b*, 212. (b) for related synthesis of $(\eta^5\text{-}C_5H_5)_2Ti(C{\equiv}CSiMe_3)_2$ see: Wood, G. L.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382.

[14] (a) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89. (b) 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. (c) Coates, G. E.; Perkin, C. *J. Inorg. Nucl. Chem.* **1961**, *22*, 59. (d) Haszeldine, R. W. *J. Chem. Soc.* **1951**, 588.

[15] Jarvis, J. A. J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 999.

Scheme 2. Possible Reaction Pathways for the Reaction of [Ti]($C{\equiv}CSiMe_3$)(CH_2SiMe_3) (**3**) with $[CuCl]_n$



The ability of main-group element[16−18] and organometallic substituted alkynes[1−5] to break down the polynuclear structure of copper(I) compounds into discrete $[CuX]_n$ ($n = 1, 2, 3, ...$) aggregates is well-known. Therefore, we assume that the alkynyl ligand $Me_3SiC{\equiv}C$ in compound **3**, as initial step, coordinates in an η^2-fashion to a copper(I) center, thus forming the intermediate **C** (route a, Scheme 2). **C** either eliminates $^1/_4[CuC{\equiv}CSiMe_3]_4$ to produce [Ti](Cl)(CH_2SiMe_3) (**4**) (route b, Scheme 2) or eliminates $^1/_4[CuCH_2SiMe_3]_4$ to afford [Ti](Cl)($C{\equiv}CSiMe_3$) (**2b**) (route c, Scheme 2). This compound exchanges its ligands under the reaction conditions applied to yield $[Ti]Cl_2$ (**1**) and $[Ti](C{\equiv}CSiMe_3)_2$ (**5c**) (route d, Scheme 2). The final step of the proposed mechanism is the formation of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCl$ (**9b**) on treatment of **5c** with $[CuCl]_n$ (route e, Scheme 2), the synthetic approach to the tweezer-like molecules of type $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCl$ most commonly used.[2,3]

Another possibility to prepare molecule **9b** is given by routes f and g (Scheme 2). The reaction of [Ti](Cl)($C{\equiv}CSiMe_3$) (**2b**) with the earlier formed $[CuC{\equiv}CSiMe_3]_4$ (route b, Scheme 2) generates a molecule of composition **D**, which undergoes an intramolecular rearrangement, thus yielding dinuclear **9b**. This reaction sequence could independently be evidenced by treatment of **2b** with equimolar amounts of $^1/_4[CuC{\equiv}CSiMe_3]_4$ in diethyl ether at 25 °C (route c, Scheme 1).

When copper(I) halides are used instead of copper(I) acetylides, type **D** molecules could be isolated (see above). Since the reaction sequence (a) → (c) → (f) → (g) (Scheme 2) gives no rise to the formation of titanocene dichloride (**1**) we consider this sequence to be of minor importance. As a final conclusion the formation of the products obtained by the reaction of [Ti](CH_2SiMe_3)($C{\equiv}CSiMe_3$) (**3**) and $[CuCl]_n$ can best be explained by the synthetic sequence (a) → (c) → (d) → (e) (Scheme 2).

Structure of the Neosilyl-Substituted Titanocene Chloride 4. The molecular structure of compound **4** has been determined by X-ray diffraction (Figure 1). Crystallographical parameters are given in Table 1; selected bond lengths and angles are listed in Table 2.

Compound **4** crystallizes in the monoclinic space group $P2_1/n$. The geometrical environment of the Ti(1) center is fixed by the arrangement of the chloro group Cl(1), the CH_2SiMe_3 unit and the η^5-coordinated cyclopentadienyl ligands. The Ti(1)−C(19) distance at 2.209(6) Å is similar to those titanium-to-carbon bonds involving sp^3-hybridized carbon atoms as found in *e.g.* $(\eta^5\text{-}C_5H_5)_2TiMe_2$ [2.170(2), 2.181(2) Å],[19] $(\eta^5\text{-}C_9H_7)_2TiMe_2$ [2.21(2) Å],[20] and $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Ph)_2$ [2.239(6), 2.210(5) Å].[21] In accordance with this, the Ti(1)−Cl(1) distance at 2.316(2) Å in **4** corresponds to other titanocene chloride compounds described.[1,8,22]

Structure of the Heterobimetallic Titanium−Copper Complex 7b. In order to establish the solid state structure of

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[16] For example: (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1156. (b) Lenders, B.; Grove, D. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L.; van Koten, G. *Organometallics* **1991**, *10*, 786. (c) Knotter, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1990**, *112*, 5895.

[17] For example: (a) Coan, P. S.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Organometallics*, **1989**, *8*, 2724. (b) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1984**, *3*, 1444. (c) He, X.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 9668. d) Uson, R.; Laguna, A.; Uson, A.; Jones, P. G.; Meyer-Base, K. *J. Chem. Soc., Dalton Trans.* **1988**, 341.

[18] (a) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41. (b) Nadasdi, T. T.; Stephan, D. W. *Organometallics* **1992**, *11*, 116. (c) Maelger, H.; Olbrich, F.; Kopf, J.; Abeln, D.; Weiss, E. *Z. Naturforsch.* **1992**, *47B*, 1276. (d) Küppers, H. J.; Wieghart, K.; Tsay, Y. H.; Krüger, C.; Nuber, B.; Weiss, J. *Angew. Chem.* **1987**, *99*, 583. (e) Braterman, P. S.; Wilson, V. A. *J. Organomet. Chem.* **1971**, *31*, 131. (f) Thompson, J. S.; Whitney, J. F.; *Inorg. Chem.* **1984**, *23*, 2813. (g) Manukata, M.; Kitagawa, S.; Kawada, I.; Maekawa, M.; Shimono, H. *J. Chem. Soc., Dalton Trans.* **1992**, 2225. (h) Reger, D. L.; Huff, M. F. *Organometallics* **1992**, *11*, 69. (i) Lenders, B.; Kläui, W. *Chem. Ber.* **1990**, *123*, 2233. (j) Ferrara, J. D.; Tessler-Youngs, C.; Youngs, W. J. *Organometallics* **1987**, *6*, 676.

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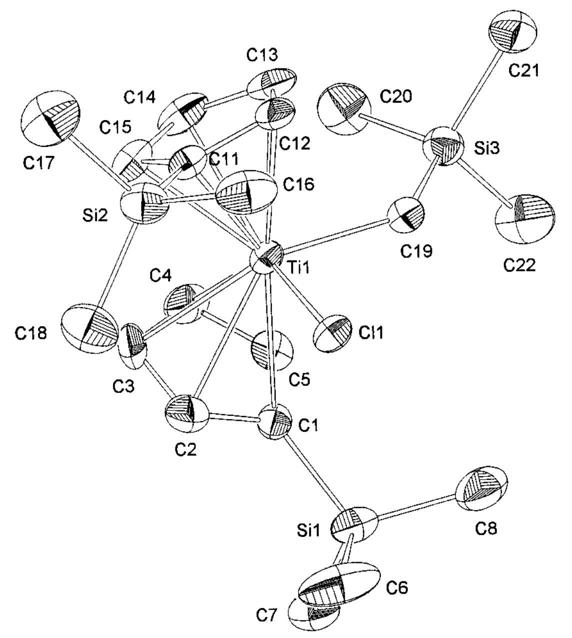

Figure 1. ORTEP drawing (drawn at 50% probability level) of the molecular geometry of compound **4** (with exclusion of the hydrogen atoms) with the atom numbering scheme (Tables 1 and 2).

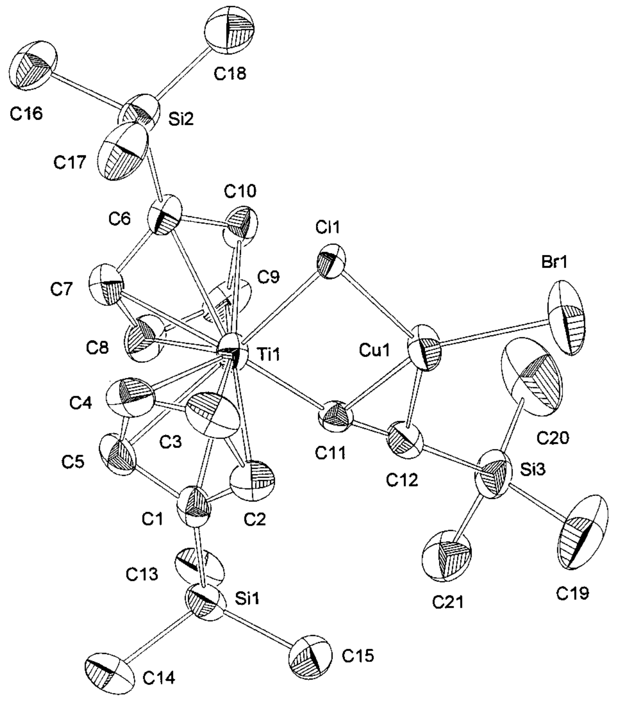

Figure 2. ORTEP drawing (drawn at 50% probability level) of the molecular geometry of compound **7b** (with exclusion of the hydrogen atoms) with the atom numbering scheme (Tables 1 and 3).

compounds **6** and **7** a X-ray diffraction study was exemplarly carried out on single crystals of **7b** (Figure 2, Table 3).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **7b**

bond lengths		bond angles	
Ti(1)−Cu(1)	2.958(3)	Ti(1)−C(11)−Cu(1)	91.8(3)
Ti(1)−Cl(1)	2.445(3)	Ti(1)−C(11)−C(12)	167.5(8)
Ti(1)−C(11)	2.107(9)	Br(1)−Cu(1)−Cl(1)	108.8(1)
Cu(1)−C(11)	2.012(9)	Br(1)−Cu(1)−C(11)	152.1(3)
Cu(1)−C(12)	2.102(8)	Br(1)−Cu(1)−C(12)	117.7(3)
Cu(1)−Br(1)	2.296(2)	Cl(1)−Cu(1)−C(12)	133.5(3)
Cu(1)−Cl(1)	2.314(3)	Cl(1)−Ti(1)−C(11)	92.4(2)
C(11)−C(12)	1.23(1)	C(11)−C(12)−Si(3)	165.0(8)
D1−Ti(1)[a]	2.072	D1−Ti(1)−D2[a]	132.3
D2−Ti(1)[a]	2.030		

[a] D1, D2 = Centers of the cyclopentadienyl ligands.

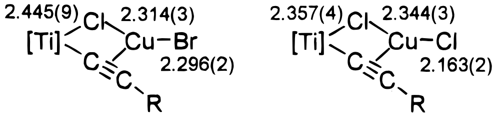

Figure 3. Comparison of interatomic bond lengths [Å] in compounds $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(Cl)(C{\equiv}CSiMe_3)]CuBr$ (**7b**) (left) and $\{[Me_2Si(\eta^5\text{-}C_5H_2SiMe_3)]_2Ti(Cl)(C{\equiv}CSiMe_3)\}CuCl$ (right).

The molecular structure of compound **7b** comprises a trigonally planar coordinated copper atom, which is η^1-bonded by the bromo ligand, datively bonded by the chloro atom Cl(1) and η^2-bonded by the $C{\equiv}C$ triple bond of the $C{\equiv}CSiMe_3$ ligand. The atoms Ti(1), Cu(1), Br(1), Cl(1), C(11), and C(12) form a plane (maximum atomic deviation: 0.059 Å). Compound **7b** represents the first example in copper(I) chemistry for which the monomeric structure of the CuBr moiety is caused by the alkynyl titanocene chloride fragment. As a result of the dative Cl(1)−Cu(1) bonding the Ti(1)−Cl(1) distance is significantly lengthened from approximately 2.30 Å in titanocene chlorides[18,22] to 2.445(3) Å in **7b**. A molecule that can be taken into account for comparison is the doubly Me_2Si-bridged heterobimetallic titanium−copper complex $\{[Me_2Si(\eta^5\text{-}C_5H_2SiMe_3)]_2Ti(Cl)(C{\equiv}CSiMe_3)\}CuCl$.[1] In this compound the interatomic titanium−chloro distance is at 2.357(4) Å considerably shorter than that in compound **7b** (Figure 3). Reversed bonding situations were observed for the copper-to-chloro distances [**7b**, 2.314(3) Å; $\{[Me_2Si(\eta^5\text{-}C_5H_2SiMe_3)]_2Ti(Cl)(C{\equiv}CSiMe_3)\}CuCl$, 2.344(2) Å[1]] (Figure 3). The established facts point to a stronger dative interaction between the chloro and the copper atom in compound **7b**.

The Cu(1)−Br(1) bond length at 2.296(2) Å in compound **7b** is decisively shorter than the according distances in other copper(I) bromide containing molecules [2.40−2.46 Å].[3,23] As a result of the η^2-coordination of the $C{\equiv}CSiMe_3$ ligand to the copper atom the Ti(1)−C(11)−C(12) [167.5(8)°], as well as the C(11)−C(12)−Si(3) [165.0(8)°] units deviate from linearity. Thereby, the $Ti{-}C{\equiv}C{-}Si$ entity is trans bent, which is typical for heterobimetallic compounds of the type $\{[Ti](C{\equiv}CSiMe_3)_2\}CuR$ in which both alkynyl ligands are η^2-bonded to a CuR moiety.[1−4] Through this deformation different copper-to-carbon bond lengths are observed [Cu(1)−C(11) = 2.012(9) Å and Cu(1)−C(12) = 2.102(8) Å; Table 3]. Similar bonding situations are found in molecules of type $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CR)_2\}MX$ [M = Ag, X = halide, pseudohalide,[2,3b,24] X = organic ligand;[2,4a,c] MX = Ni(CO), $Ni(PR_3)$, $Ni[P(OR)_3]$;[2,25] MX = Co(CO);[2,26] MX = $FeCl_2$, $CoCl_2$, $NiCl_2$[2,3a,4,27]].

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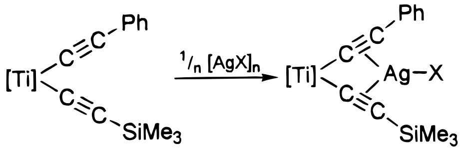
Moreover, it is found that upon η^2-coordination the $C\equiv C$ triple bond is lengthened as compared to non-coordinated alkynyl-substituted titanocene derivatives.[1,2,24b] The bite angle Cl(1)−Ti(1)−C(11) at 92.4(2)° in compound **7b** accords with that found in $\{[Me_2Si(\eta^5\text{-}C_5H_2SiMe_3)_2]Ti(Cl)(C\equiv CSiMe_3)\}CuCl$ [94.9(2)°].[1] As compared to mono(σ-alkynyl)- or bis(σ-alkynyl)-substituted titanocenes these bite angles significantly are reduced in size [$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2$, 102.8°; $[Me_2Si(\eta^5\text{-}C_5H_2SiMe_3)_2]Ti(Cl)(C\equiv CSiMe_3)$, 99.8(4)°], a phenomenon typical for tweezer-like molecules.[2]

Reaction of [Ti](Cl)($C\equiv CR$) (2) and [Ti]($C\equiv CPh$)($C\equiv CSiMe_3$) (5a) with Silver(I) Compounds. While the mono(σ-alkynyl)titanocene chlorides [Ti](Cl)($C\equiv CR$) (**2**) readily react with polymeric copper(I) halides $[CuX]_n$ to produce the heterobimetallic titanium−copper molecules {[Ti](Cl)($C\equiv CR$)}CuX (**6a**, R = Ph, X = Cl, Br, I; **7**, R = $SiMe_3$, X = Cl, Br), no reaction is observed on treatment of compounds **2** with silver(I) halides $[AgX]_n$ (X = Cl, Br). However, the polymeric structure of $[AgX]_n$ can be broken down to monomeric AgX moieties by making use of the chelating effect of the organometallic π-tweezer [Ti]($C\equiv CPh$)($C\equiv CSiMe_3$) (**5a**).

When compound **5a** is reacted with equimolar amounts of $[AgX]_n$ in tetrahydrofuran at 25 °C the complexes {[Ti]($C\equiv CPh$)($C\equiv CSiMe_3$)}AgX (**10a**, X = Cl; **10b**, X = Br) are obtained in 81% or 88% yield, respectively.



(4)

5a

10a: X = Cl
10b: X = Br

Complexes **10a** and **10b** are isostructural with the appropriate copper(I) species {[Ti]($C\equiv CPh$)($C\equiv CSiMe_3$)}CuX. As in these compounds, the silver atom possesses a trigonal-planar environment and the bis(η^2-alkyne)AgX unit represents a 16-valence-electron entity.[2,4a,c,24] Compounds **10a** and **10b** show solubility similar to that of the isostructural copper(I) compounds. As expected, the silver(I) species are somewhat lightsensitive.

Discussion

The organometallic mono(σ-alkynyl)titanocene chlorides [Ti](Cl)($C\equiv CR$) (**2**) as well as the bis(alkynyl)titanocenes [Ti]($C\equiv CR$)($C\equiv CR'$) (**5**) can be used to dissolve monomeric units of polymeric copper(I) halides $[CuX]_n$.

The copper atom in compounds {[Ti](Cl)($C\equiv CR$)}CuX (**6**, **7**) and {[Ti]($C\equiv CR$)($C\equiv CR'$)}CuX (**8**, **9**) is σ-bonded by the inorganic ligands X. Moreover, in compounds **6** and **7** the copper atom is complexed by the chloro group as well as the $C\equiv C$ triple bond of the $C\equiv CR$ substituent, whereas in complexes **8** and **9** the CuX unit is embedded between two η^2-coordinating alkynyl ligands. Therefore, these complexes are predestinated for a detailed study of monomeric copper(I) halides. The same is expected for the isostructural molecules {[Ti]($C\equiv CPh$)($C\equiv CSiMe_3$)} AgX (**10**).

The mono(σ-alkynyl)titanocene chlorides (**2**) as well as the bis(alkynyl)titanocenes (**5**) have a pronounced preference for binding to only one copper halide entity, and it is interesting to compare characteristic features of the new complexes with known examples of alkyne-coordinated copper compounds.[2] The monoanionic bromine in **7b** is η^1-bonded to the copper(I) center, dative bonded by the chloro atom and η^2-coordinated by the $C\equiv C$ triple bond of the [Ti](Cl)($C\equiv CSiMe_3$) entity. This way of stabilizing a monomeric copper(I) bromide is the first example in copper(I) chemistry.

The copper−bromine bond length at 2.296(2) Å is shorter than according distances in for example dimeric $[\eta^2\text{-}Me_3SiC\equiv CSiMe_3)CuBr]_2$ [2.407(1) Å][2,23] or polymeric $[CuBr]_n$ [2.46 Å].[23] In fact for the η^1-chloro and η^2-alkyne interaction in combination with the geometric constraints of the mono(σ-alkynyl)titanocene chloride fragment in compound **7b** a relative short Ti−Cu distance [2.958(3) Å] is observed.[2,28]

Besides the X-ray structure analysis hints on the composition of compounds **6**−**9** are given by NMR and IR spectroscopic measurements. Due to the η^2-coordination of the $C\equiv CR$ units (R = Ph, $SiMe_3$) to the copper atom in compounds **6**−**9**, the $C\equiv C$ stretching vibration is shifted from 2077 cm^{-1} in **2a**, 2022 cm^{-1} in **2b**, or 2067 cm^{-1} ($C\equiv CPh$) and 2014 cm^{-1} ($C\equiv CSiMe_3$) in **5a** to 1926−1935 cm^{-1} in **6**, 1900 cm^{-1} in **7**, or 1956 cm^{-1} ($C\equiv CPh$) and 1915 cm^{-1} ($C\equiv CSiMe_3$) in compounds **8** and **9**, respectively. This shifting indicates a weaker $C\equiv C$ bond in the mono- or bis(σ-alkyne)copper(I) halide complexes **6**−**9**, a phenomenon typical for π-bonding of organic and organometallic alkyne-copper(I) moieties.[2a]

In the $^{13}C\{^1H\}$ NMR spectra it is found that upon η^2-coordination of the $C\equiv C$ triple bonds to the copper atom in complexes **6**−**9** the resonance signals of the C_α atoms in the $TiC\equiv CR$ entity are slightly shifted upfield, whereas resonance signals of the C_β atoms are shifted downfield. This is in agreement with an observation generally made by changing from noncoordinated to η^2-coordinated alkynyl substituted titanocenes.

The asymmetric environment around the titanium atom in compounds **6**−**8** results in the appearance of ABXY resonance patterns for the cyclopentadienyl protons in the region 6.0−6.8 ppm. For the $SiMe_3$ and Ph groupings the ^1H NMR spectra show the expected simplicity with the resonance signals of the $SiMe_3$ groups at around 0.3 and 0.1 ppm, as well as for the phenyl protons in the 7.1−7.8 ppm region.

The ^1H and ^{13}C NMR spectra of solutions of compounds **6**−**9** in toluene-d_8 remain essentially unchanged in the temperature region of 193−353 K. Moreover, cryoscopic molecular weight determinations in benzene showed that these complexes exist as monomeric species in solution. These data are consistent with a monomeric structure established for those molecules in the solid state (see above).

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Supporting Information Available: Tables of crystal data and details of the structure determinations, final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms, hydrogen atom positions and isotropic thermal parameters, anisotropic thermal parameters, bond distances and bond angles for compounds **4** and **7b** (13 pages). Ordering information is given on any current masthead page.

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