Monomeric Bis(η^2-alkyne)copper(I) and -silver(I) Halides, Pseudohalides, and Arenethiolates

**Maurits D. Janssen,† Mathias Herres,‡ Laszló Zsolnai,‡ Anthony L. Spek,§,∥ David M. Grove,†
Heinrich Lang,*,‡ and Gerard van Koten*,†,⊥**

Department of Metal Mediated Synthesis, Debye Institute, Utrecht University, Padualaan 8, 3584 CH
Utrecht, The Netherlands, Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im
Neuenheimer Feld 270, D-69120 Heidelberg, Germany, and Department of Crystal and Structural
Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH
Utrecht, The Netherlands

Received June 7, 1995⊗

The synthesis and characterization of the complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]MX$ (M = Cu, X = OTf
(**2**), SC_6H_5 (**4**), $SC_6H_4NMe_2\text{-}2$ (**5**), $SC_6H_4CH_2NMe_2\text{-}2$ (**6**), $S\text{-}1\text{-}C_{10}H_6NMe_2\text{-}8$ (**7**), Cl (**8**), $(N\equiv CMe)PF_6$ (**9**); M =
Ag, X = OTf (**3**)) are described. These complexes contain monomeric MX entities, which are η^2-bonded by
both alkyne functionalities of the organometallic *bis*(alkyne) ligand $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]$ (**1**). The
reactions of **2** with the Lewis bases N≡CPh and N≡CC(H)=C(H)C≡N afford the cationic complexes {[(η^5-
$C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]Cu(N\equiv CPh)$}OTf (**10**) and {[($\eta^5$-$C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]Cu$}$_2(N\equiv CC(H)=C$-
$(H)C\equiv N)(OTf)_2$ (**11**), respectively. The X-ray structures of **2**, **3**, and **6** have been determined. Crystals of **2** are
monoclinic, space group $P2_1/c$, with $a = 12.8547(7)$ Å, $b = 21.340(2)$ Å, $c = 18.279(1)$ Å, $\beta = 133.623(5)°$, V
$= 3629.7(5)$ Å^3, $Z = 4$, and final $R = 0.047$ for 5531 reflections with $I \geq 2.5\sigma(I)$ and 400 variables. The silver
triflate complex **3** is isostructural, but not isomorphous, with the corresponding copper complex **2**, and crystals
of **3** are monoclinic, space group $P2_1/c$, with $a = 13.384(3)$ Å, $b = 24.55(1)$ Å, $c = 13.506(3)$ Å, $\beta = 119.21(2)°$,
$V = 3873(2)$ Å^3, $Z = 4$, and final $R = 0.038$ for 3578 reflections with $F \geq 4\sigma(F)$ and 403 variables. Crystals
of the copper arenethiolate complex **6** are triclinic, space group $P\bar{1}$, with $a = 11.277(3)$ Å, $b = 12.991(6)$ Å, c
$= 15.390(6)$ Å, $\alpha = 65.17(4)°$, $\beta = 78.91(3)°$, $\gamma = 84.78(3)°$, $V = 2008(2)$ Å^3, $Z = 2$, and final $R = 0.079$ for
6022 reflections and 388 variables. Complexes **2**−**11** all contain a monomeric *bis*(η^2-alkyne)M(η^1-X) unit (M =
Cu, Ag) in which the group 11 metal atom is trigonally coordinated by the chelating *bis*(η^2-alkyne) entity Ti-
$(C\equiv CSiMe_3)_2$ and an η^1-bonded monoanionic ligand X. The copper arenethiolate complexes **4**−**7** are fluxional
in solution.

Introduction

Inorganic copper(I) and silver(I) salts CuX and AgX (with
X = halide,[1] alkoxide,[2] phenoxide,[3] thiolate,[4] amide,[5] and
phosphide[6]) are generally encountered as polynuclear species
with either discrete aggregate or oligomeric structures in the

solid state and in solution. Reaction of these salts with suitable
Lewis bases (*e.g.* phosphines, amines, alkynes) generally yields
species with a lower nuclearity[7] and can sometimes even afford
isolable mononuclear copper(I) and silver(I) complexes.[8]

Recently, we reported that the well-designed organometallic
bis(alkyne) ligand $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]$ (**1**) can be
successfully applied to stabilize mononuclear organometallic
entities MR (M = Cu, Ag; R = alkynyl, aryl).[9] In the species
$[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]MR$ (Figure 1) assembled in

* To whom correspondence should be addressed.
† Debye Institute, Utrecht University.
‡ Ruprecht-Karls-Universität Heidelberg.
§ Bijvoet Center for Biomolecular Research, Utrecht University.
∥ To whom correspondence pertaining to crystallographic studies should
be addressed. E-mail: spea@xray.chem.ruu.nl.
⊥ E-mail: vankoten@xray.chem.ruu.nl.
⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1996.
 (1) Little structural information is available on these species: for all copper
halides phase transitions between the low-temperature cubic zinc
blende (γ) structure into the hexagonal wurzite (β) structure have been
reported. Cubic (α) structures have also been reported at higher
temperatures. (a) Lorenz, M. R.; Prener, J. S. *Acta Crystallogr.* **1956**,
9, 538−539. (b) Bhalla, A. S.; White, E. W. *Acta Crystallogr.* **1971**,
B27, 852−853. CuI is associated in the solid state: (c) Kauffman, G.
B.; Pinnell, R. P. *Inorg. Synth.* **1960**, *6*, 3−5.
 (2) [CuO-*t*-Bu]$_4$: (a) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142−
3146. [CuO-*t*-Bu(PPh$_3$)]$_2$: (b) Lemmen, T. H.; Goeden, G. V.;
Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*,
3680−3685. [CuOSiPh$_3$]$_4$ cited in: (c) Coan, P. S.; Huffman, J. C.;
Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 4207−4209. [(L)Cu(OCH$_2$-
CH$_2$OMe)]$_4$: (d) Bidell, W.; Shklover, V.; Berke, H. *Inorg. Chem.*
1992, *31*, 5561−5571.
 (3) (a) Knotter, D. M.; Wehman, E.; Spek, A. L.; Stam, C. H.; van Koten,
G. Unpublished results. (b) Wehman, E.; van Koten, G.; Knotter, D.
M.; Erkamp, C. J. M.; Mali, A. N. S.; Stam, C. H. *Recl. Trav. Chim.
Pays-Bas* **1987**, *106*, 370. (c) Paul, P.; Karlin, K. D. *J. Am. Chem.
Soc.* **1991**, *113*, 6331−6332.

 (4) [Cu(SC$_6$H$_2$-*i*-Pr$_3$-2,4,6)]$_4$ and [Cu(SC$_6$H$_2$-*i*-Pr$_3$-2,4,6)]$_8$: (a) Schroter-
Schmid, I.; Strähle, J. *Z. Naturforsch., B* **1990**, *45*, 1537. (b) Yang,
Q.; Tang, K.; Liao, H.; Han, Y.; Chen, Z.; Tang, Y. *J. Chem. Soc.,
Chem. Commun.* **1987**, 1076−1077. [Cu(SC$_6$H$_3$(SiMe$_3$)$_2$-2,6)]$_4$: (c)
Block, E.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chim. Acta*
1990, *167*, 147−148. [Cu(SSi(O-*t*-Bu)$_3$)]$_4$: (d) Becker, B.; Wojnowski,
W.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Polyhedron* **1990**,
9, 1659−1666. [Cu(SC$_6$H$_4$SiMe$_3$-2)]$_{12}$: (e) Block, E.; Gernon, M.;
Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 1263−
1271. [Cu{SC$_6$H$_4$(CH(Me)NMe$_2$)-2}]$_3$: (f) Knotter, D. M.; van
Maanen, H. L.; Grove, D. M.; Spek, A. L.; van Koten, G. *Inorg. Chem.*
1991, *30*, 3309−3317. [Cu{S(CH(Me)FcPPh$_2$)-2}]$_3$: (g) Togni, A.;
Rihs, G.; Blumer, R. E. *Organometallics* **1992**, *11*, 613−621. [Cu-
{SC$_6$H$_4$(CH$_2$N(Me)CH$_2$CH$_2$OMe)-2}]$_4$: (h) Knotter, D. M.; Janssen,
M. D.; Grove, D. M.; Smeets, W. J. J.; Horn, E.; Spek, A. L.; van
Koten, G. *Inorg. Chem.* **1991**, *30*, 4361−4366. [CuSPy-2]$_6$: (i)
Kitagawa, S.; Munakata, M.; Shimono, H.; Matsuyama, S.; Masuda,
H. *J. Chem. Soc., Dalton Trans.* **1990**, 2105−2109.
 (5) [Cu{NEt$_2$}]$_4$: (a) Hope, H.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 936−
937. [CuNRR′]$_4$: (b) Gambarotta, S.; Bracci, M.; Floriani, C.; Chiesi-
Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans*. **1987**, 1883−
1888. [Cu{N(SiMePh)$_2$}]$_3$ and [Cu{N(SiMe$_2$Ph)$_2$}]$_4$: (c) Chen, H.;
Olmstead, M. M.; Shoner, S. C.; Power, P. P. *J. Chem. Soc., Dalton
Trans.* **1992**, 451−457.
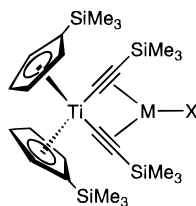
Figure 1. Schematic representation of the complexes [(η^5-C$_5$H$_4$SiMe$_3$)$_2$-Ti(C≡CSiMe$_3$)$_2$]MX.

this way, both alkyne units of the chelating bis(alkyne) entity Ti(C≡CSiMe$_3$)$_2$ coordinate to the group 11 metal center in an η^2 fashion. The organic monoanionic ligand R in these systems is η^1-bonded to the copper or silver atom, resulting in a unique and stable trigonally planar environment of these copper and silver centers.[9] The fundamental characteristics of such mononuclear group 11 metal complexes can be of significant interest in areas of applied material science related to copper-containing ceramics, semiconductors, and superconductors.

This paper describes the use of the organometallic bis(alkyne) ligand [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$] (**1**) to develop a series of complexes containing stabilized mononuclear inorganic CuX and AgX entities, where X is a halide, pseudohalide, and arenethiolate anionic grouping. Some aspects of this work have already been communicated.[9d] The solution and solid-state structures and characterization of these new complexes as well their reaction behavior toward Lewis bases are reported.

(6) [Cu{P(*t*-Bu$_2$)}]$_4$: (a) Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 208–209. [Cu$_5${PPh$_2$}$_5$(PMe$_3$)$_3$]: (b) Eichhöfer, A.; Fenske, D.; Holstein, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 242–245. [Cu$_2$-(PPh$_2$)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]: (c) van Koten, G.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* **1978**, *159*, 441–463.
(7) [Cu$_2$(R$_2$DAB)$_2$Cl$_2$] (R = (Me$_2$CH)$_2$CH): (a) Dieck, H. T.; Stamp, L. *Acta Crystallogr.* **1983**, *C39*, 841–843. [CuX(tmtch)]$_2$ (X = Cl, Br, I; tmtch = 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne): (b) Olbrich, F.; Schmidt, G.; Behrens, U.; Weiss, E. *J. Organomet. Chem.* **1991**, *418*, 421–429. [(Me$_3$SiC≡CSiMe$_3$)CuCl]$_2$: (c) Aleksandrov, G. G.; Gol'ding, I. R.; Sterling, S. R.; Sladkov, A. M.; Struchkov, Yu. T.; Garbuzova, I. A.; Aleksanyan, V. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, *29*, 2679. (d) Lang, H.; Köhler, K.; Rheinwald, G.; Zsolnai, L. *J. Organomet. Chem.*, submitted for publication. (e) Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 5325–5329. [CuBr-(SMe)]$_\infty$: (f) Lenders, B.; Grove, D. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L.; van Koten, G. *Organometallics* **1991**, *10*, 786–791. [Cu(L)OTf]$_\infty$ and [Ag(L)OTf]$_\infty$ (L = 1,6- or 1,7-cyclodecadiyne, 1,8-cyclotetradecadiyne): (g) Gleiter, R.; Karcher, M.; Kratz, D.; Ziegler, M. L.; Nuber, B. *Chem. Ber.* **1990**, *123*, 1461–1468. [Cu-(L)$_2$OTf]$_\infty$ (L = cyclooctene): (h) Budzelaar, P. H. M.; Timmermans, P. J. J. A.; Mackor, A.; Spek, A. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1987**, *C43*, 2298–2300. [(L)(OTf)Cu]$_2${H$_2$C═C(Me)C-(H)═CH$_2$} (L = bis(amine) ligand): (i) Song, L.; Trogler, W. C. *J. Organomet. Chem.* **1993**, *452*, 271–275.
(8) Monomeric Lewis base species: [CuX(PPh$_3$)$_2$] (X = Cl, I, Br): (a) Bowmaker, G. A.; Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1089–1097. [AgX(PR$_3$)] (X = Cl, Br): (b) Baker, L.-J.; Bowmaker, G. A.; Camp, D.; Effendy; Healy, P. C.; Schmidbaur, H.; Stiegelmann, O.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3656–3662. [(L)CuX] (L = polypyrazole ligand; X = Cl, OTf, (N≡CMe)BF$_4$): (c) Tokar, C. J.; Kettler, P. B.; Tolman, W. B. *Organometallics* **1992**, *11*, 2737–2739. [(Me$_2$phen)Cu(N≡CMe)]X (X = ClO$_4$, PF$_6$): (d) Munakata, M.; Maekawa, M.; Kitagawa, S.; Matsuyama, S.; Masuda, H. *Inorg. Chem.* **1989**, *28*, 4300–4302. [(phen)Cu(HC≡CR)]ClO$_4$ (R = H, Ph): (e) Munakata, M.; Kitagawa, S.; Kawada, I.; Maekawa, M.; Shimono, H. *J. Chem. Soc., Dalton Trans.* **1992**, 2225–2230. [Cu(16S6)]ClO$_4$: (f) de Groot, B.; Loeb, S. J. *Inorg. Chem.* **1989**, *28*, 3573–3578. [Cu-(L)$_2$OTf] (L = C$_{18}$H$_{22}$N$_2$S$_2$): (g) Spek, A. L.; Duisenberg, A. J. M.; van Stein, G. C. *Acta Crystallogr.* **1985**, *C41*, 374–377. [Cu(L)OTf] (L = C$_{18}$H$_{18}$N$_2$S$_2$ and C$_{20}$H$_{22}$N$_2$S$_2$): (h) Martin, J. W. L.; Organ, G. J.; Wainwright, K. P.; Weerasuria, K. D. V.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1987**, *26*, 2963–2968. [Cu(L)PF$_6$] (L = Cp$_2$Ti(SCH$_2$CH$_2$)$_n$S): (k) Huang, Y.; Drake, R. J.; Stephan, D. W. *Inorg. Chem.* **1993**, *32*, 3022–3028.

Experimental Section

All experiments were carried out by using standard Schlenk techniques under an inert, oxygen-free nitrogen atmosphere. THF, Et$_2$O, and C$_6$H$_6$ were distilled from sodium benzophenone–ketyl prior to use. CH$_2$Cl$_2$ was distilled from CaH$_2$. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC200 or Bruker AC300 spectrometer, and chemical shifts are quoted relative to TMS (^{1}H and ^{13}C) or 85% H$_3$-PO$_4$ (^{31}P). FT-IR spectra were recorded on a Mattson Galaxy 5000 series spectrometer. Melting (decomposition) points were determined with a Büchi melting point apparatus or a Mettler TA-4000 differential scanning calorimeter. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany, and at the Organisch-Chemisches Institut der Universität Heidelberg, Heiberg, Germany. Commercial PhSH, [AgOSO$_2$CF$_3$], and [Cu(MeCN)$_4$]PF$_6$ were used. [CuOSO$_2$CF$_3$]·0.5C$_6$H$_6$,[10] [CuSC$_6$H$_4$-NMe$_2$-2]$_3$,[11] [CuSC$_6$H$_4$CH$_2$NMe$_2$-2]$_3$,[4f] [CuS-1-C$_{10}$H$_6$NMe$_2$-8]$_9$,[11] [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$] (**1**),[12] and [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]-CuCl (**8**)[9d] were prepared according to literature procedures. [CuO-*t*-Bu]$_4$ was prepared according to a literature procedure and purified by sublimation (170 °C, 0.6 mmHg) before use.[2b]

Preparation of Copper(I) Thiophenolate. Thiophenol (0.25 g, 2.27 mmol) was added to a solution of [CuO-*t*-Bu]$_4$ (0.27 g, 1.98 mmol based on Cu) in C$_6$H$_6$ (20 mL) at room temperature, and a yellow powder precipitated immediately. The reaction mixture was stirred for 1 h, after which all volatiles were removed *in vacuo*. Washing of the yellow solid with pentane (3 × 15 mL) and with C$_6$H$_6$ (15 mL) yielded 0.33 g (96%, 1.91 mmol) of yellow CuSPh. Since CuSPh is insoluble in all common solvents, its purity was determined by elemental microanalysis. Anal. Calcd for [C$_6$H$_5$CuS]$_\infty$: C, 41.73; H, 2.92. Found: C, 41.56; H, 2.81.

Synthesis of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]CuOTf (2). To a solution of [CuOSO$_2$CF$_3$]·0.5C$_6$H$_6$ (0.16 g, 0.64 mmol) in THF (20 mL) was slowly added a solution of **1** (0.33 g, 0.64 mmol) in THF (10 mL). On addition of **1**, the yellow solution immediately turned dark red. After the mixture was stirred for 1 h, the solvent was removed *in vacuo* and the product was quantitatively isolated as an orange-red powder. Crystals suitable for X-ray analysis were obtained by crystallization from a concentrated solution in Et$_2$O at −20 °C. Mp: 141.0 °C (DSC). IR (C≡C): 1924 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ 728 (calcd 728). ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 0.13 (s, 18 H, SiMe$_3$), 0.48 (s, 18 H, SiMe$_3$), 5.84 (t, 4 H, C$_5$H$_4$, *J* = 2 Hz), 5.90 (t, 4 H, C$_5$H$_4$, *J* = 2 Hz). ^{13}C NMR (75.47 MHz, C$_6$D$_6$): δ 0.0 (SiMe$_3$), 0.4 (SiMe$_3$), 115.2 (C$_5$H$_4$), 118.6 (C$_5$H$_4$), 121.2 (q, CF$_3$, J_{CF} = 319 Hz), 125.0 (*ipso*-C$_5$H$_4$), 140.2 (C≡*C*–Si), 162.2 (Ti–*C*≡C). Anal. Calcd for C$_{27}$H$_{44}$CuF$_3$O$_3$SSi$_4$Ti: C, 44.45; H, 6.08; Cu, 8.71. Found: C, 44.34; H, 6.10; Cu, 8.81.

Synthesis of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]AgOTf (3). To a solution of [AgOSO$_2$CF$_3$] (0.23 g, 0.90 mmol) in THF (100 mL) was added **1** (0.47 g, 0.91 mmol), and this reaction mixture was stirred for 4 h at room temperature. Filtration through Kieselgur (5 × 2.5 cm) and evaporation of the volatiles *in vacuo* yielded a red powder. Crystalline material was obtained by recrystallization from *n*-pentane/THF (2:1 v:v) at −20 °C. Yield: 0.52 g (75%, 0.73 mmol). Mp: 137 °C (DSC). IR (C≡C): 1956 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ 774 (calcd 774). ^{1}H NMR (200.13 MHz, CD$_2$Cl$_2$): δ 0.27 (s, 18 H, SiMe$_3$), 0.30 (s, 18 H, SiMe$_3$), 6.38 (t, 4 H, C$_5$H$_4$, *J* = 2 Hz), 6.49 (t, 4 H, C$_5$H$_4$, *J*

(9) (a) Janssen, M. D.; Herres, M.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1995**, 925–926. (b) Janssen, M. D.; Köhler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.*, in press. (c) Janssen, M. D.; Herres, M.; Zsolnai, L.; Grove, D. M.; Spek, A. L.; Lang, H.; van Koten, G. *Organometallics* **1995**, *14*, 1098–1100. (d) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7–C11. (e) Lang, H.; Köhler, K.; Herres, M.; Rheinwald, G.; Zsolnai, L. Unpublished results. (f) Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1994**, *12*, 5008–5011.
(10) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1897.
(11) Janssen, M. D.; Donkervoort, J. G.; van Berlekom, S. B.; Spek, A. L.; Grove, D. M.; van Koten, G. *Inorg. Chem.*, in press.
(12) (a) Lang, H.; Seyferth, D. *Z. Naturforsch, B* **1990**, *45*, 212–220. For the synthesis of related (η^5-C$_5$H$_5$)$_2$Ti(C≡CSiMe$_3$)$_2$: (b) Wood, G. L.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382–384.

= 2 Hz). ^{13}C NMR (50 MHz, CD$_2$Cl$_2$): δ 0.1 (SiMe$_3$), 117.7 (C$_5$H$_4$), 120.7 (C$_5$H$_4$), 125.3 (q, CF$_3$, J_{CF} = 309 Hz), 127.3 (*ipso*-C$_5$H$_4$), 143.3 (C≡C−Si), 150.3 (Ti−C≡C). Anal. Calcd for C$_{27}$H$_{44}$AgF$_3$O$_3$SSi$_4$-Ti: C, 41.91; H, 5.73. Found: C, 41.71; H, 5.77.

Synthesis of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]CuSC$_6$H$_5$ (4). The synthetic procedure is similar to that of **2** but starts from CuSPh (0.14 g, 0.81 mmol) in Et$_2$O (30 mL) with solid **1** (0.42 g, 0.81 mmol) added in one portion. Yield: 0.56 g (100%, 0.81 mmol). Crystalline material was obtained by crystallization from a concentrated solution in Et$_2$O at −20 °C. Mp: 158 °C dec. IR (C≡C) 1908 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ 688 (calcd 688). ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 0.19 (s, 18 H, SiMe$_3$), 0.45 (s, 18 H, SiMe$_3$), 5.53 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 5.83 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 6.91 (t, 1 H, Ar H-4, ^3J = 8 Hz), 7.09 (t, 2 H, Ar H-3,5, ^3J = 8 Hz), 7.66 (d, 2 H, Ar H-2,6, ^3J = 8 Hz). ^{13}C NMR (75.47 MHz, C$_6$D$_6$): δ 0.2 (SiMe$_3$), 0.9 (SiMe$_3$), 113.1 (C$_5$H$_4$), 115.5 (C$_5$H$_4$), 121.0, 121.2 (Ar C-4 and *ipso*-C$_5$H$_4$), 127.9 (Ar C-2,6), 133.2 (C≡C−Si), 133.3 (Ar C-3,5), 150.0 (Ar C-1), 179.5 (Ti−C≡C). The assignments of the signals for Ar C-2,6 and Ar C-3,5 are tentative. Anal. Calcd for C$_{32}$H$_{49}$CuSSi$_4$Ti: C, 55.73; H, 7.16; S, 4.65. Found: C, 55.89; H, 7.12; S, 4.58.

Synthesis of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]CuSC$_6$H$_4$NMe$_2$-2 (5). The synthetic procedure is similar to that of **2** but starts from CuSC$_6$H$_4$NMe$_2$-2 (0.22 g, 1.02 mmol) in THF (20 mL) reacted with **1** (0.50 g, 0.97 mmol) in THF (8 mL). Crystallization from Et$_2$O yielded 0.33 g (46%, 0.45 mmol) of dark green crystals. Mp: 110.8 °C (DSC). T_{dec} = 180 °C. IR (C≡C): 1897 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ 731 (calcd 731). ^{1}H NMR (200.13 MHz, C$_6$D$_6$): δ 0.21 (s, 18 H, SiMe$_3$), 0.44 (s, 18 H, SiMe$_3$), 2.98 (s, 6 H, NMe$_2$), 5.58 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 5.83 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 6.8−7.1 (m, 3 H, Ar H), 7.6 (d, 1 H, Ar H-6, ^3J = 7 Hz). ^{13}C NMR (75.47 MHz, C$_6$D$_6$): δ 0.3 (SiMe$_3$), 0.9 (SiMe$_3$), 44.4 (NMe$_2$), 112.9 (C$_5$H$_4$), 113.4 (Ar), 115.5 (C$_5$H$_4$), 118.7 (Ar), 120.4 (*ipso*-C$_5$H$_4$), 121.9 (Ar), 123.4 (Ar), 132.8 (C≡C−Si), 136.2 (Ar), 154.7 (Ar), 180.4 (Ti−C≡C). Anal. Calcd for C$_{34}$H$_{54}$CuNSSi$_4$-Ti: C, 55.74; H, 7.43; N, 1.91; Cu, 8.67. Found: C, 55.65; H, 7.48; N, 2.02; Cu, 8.54.

Synthesis of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]CuSC$_6$H$_4$CH$_2$NMe$_2$-2 (6). The synthetic procedure is the same as that of **4** but starts from CuSC$_6$H$_4$CH$_2$NMe$_2$-2 (0.21 g, 0.91 mmol) in Et$_2$O (30 mL) reacted with **1** (0.47 g, 0.91 mmol). Yield: 0.66 g (97%, 0.88 mmol). Dark green crystals were obtained by crystallization from a concentrated solution in Et$_2$O at −20 °C. Mp: 143 °C dec. IR (C≡C): 1902 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ 745 (calcd 745). ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 0.20 (s, 18 H, SiMe$_3$), 0.42 (s, 18 H, SiMe$_3$), 2.41 (s, 6 H, NMe$_2$), 4.20 (s, 2 H, CH$_2$), 5.54 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 5.83 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 7.03 (m, 2 H, Ar H-4,5), 7.42 (d, 1 H, Ar H-3, ^3J = 6 Hz), 7.82 (d, 1 H, Ar H-6, ^3J = 6 Hz). ^{13}C NMR (75.47 MHz, C$_6$D$_6$): δ 0.2 (SiMe$_3$), 0.9 (SiMe$_3$), 46.3 (NMe$_2$), 63.1 (CH$_2$), 113.0 (C$_5$H$_4$), 115.5 (C$_5$H$_4$), 121.1, 121.3 (Ar and *ipso*-C$_5$H$_4$), 123.4 (Ar), 125.3 (Ar), 133.0 (Ar), 134.8 (C≡C−Si), 140.5 (Ar), 148.6 (Ar), 179.6 (Ti−C≡C). Anal. Calcd for C$_{35}$H$_{56}$CuNSSi$_4$Ti: C, 56.30; H, 7.56; S, 4.30. Found: C, 56.46; H, 7.14; S, 3.87.

Synthesis of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]CuS-1-C$_{10}$H$_6$NMe$_2$-8 (7). The synthetic procedure is the same as that for **4** but starts from CuS-1-C$_{10}$H$_6$NMe$_2$-8 (0.30 g, 1.13 mmol), which is poorly soluble in Et$_2$O, dissolved in an Et$_2$O/C$_6$H$_6$ mixture (40 mL, 10:1 v:v) and reacted with **1** (0.58 g, 1.12 mmol). Yield: 0.88 g (100%, 1.12 mmol). Green crystalline material was obtained by crystallization from a concentrated solution in Et$_2$O at −20 °C. Mp: 173 °C dec. IR (C≡C): 1893 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ 781 (calcd 781). ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 0.22 (s, 18 H, SiMe$_3$), 0.34 (s, 18 H, SiMe$_3$), 2.98 (s, 6 H, NMe$_2$), 5.48 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 5.83 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 7.08 (dd, 1 H, Ar H, ^3J = 8 Hz, ^4J = 1 Hz), 7.10 (t, 1 H, Ar H, ^3J = 8 Hz), 7.30 (t, 1 H, Ar H, ^3J = 8 Hz), 7.39 (d, 1 H, Ar H, ^3J = 8 Hz), 7.45 (d, 1 H, Ar H, ^3J = 7 Hz), 7.48 (d, 1 H, Ar H, ^3J = 8 Hz). ^{13}C NMR (75.47 MHz, C$_6$D$_6$): δ 0.3 (SiMe$_3$), 0.8 (SiMe$_3$), 45.9 (NMe$_2$), 112.5 (C$_5$H$_4$), 114.7 (Ar), 114.9 (C$_5$H$_4$), 120.3 (Ar and *ipso*-C$_5$H$_4$), 122.1 (Ar), 123.9 (Ar), 124.2 (Ar), 125.3 (Ar), 131.9 (Ar), 133.1 (C≡C−Si), 138.0 (Ar), 148.9 (Ar), 152.9 (Ar), 182.8 (Ti−C≡C). Anal. Calcd for C$_{38}$H$_{56}$-CuNSSi$_4$Ti: C, 58.31; H, 7.21; S, 4.10. Found: C, 58.04; H, 6.95; S, 4.06.

Synthesis of [{(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF$_6$ (9). To a suspension of [Cu(MeCN)$_4$]PF$_6$ (0.15 g, 0.40 mmol) in THF

(20 mL) was added **1** (0.21 g, 0.41 mmol). The solution slowly turned dark orange, and all [Cu(MeCN)$_4$]PF$_6$ dissolved. After the mixture was stirred for 17 h, the volatiles of the clear orange solution were removed *in vacuo* to yield the product as an orange powder. Crystalline material could be obtained by crystallization from a concentrated solution in THF/Et$_2$O (2:1 v:v) at −20 °C. Yield: 0.28 g (91%, 0.37 mmol). IR (C≡N): 2230 cm^{-1}. IR (C≡C): 1934 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ 766 (calcd 765). ^{1}H NMR (300.13 MHz, acetone-d_6): δ 0.27 (s, 18 H, SiMe$_3$), 0.32 (s, 18 H, SiMe$_3$), 2.61 (s, 3 H, MeCN), 6.55 (m, 8 H, C$_5$H$_4$). ^{13}C NMR (75.47 MHz, acetone-d_6): δ 0.1 (SiMe$_3$), 0.3 (SiMe$_3$), 2.5 (*Me*CN), 117.3 (C$_5$H$_4$), 119.6 (C$_5$H$_4$), 124.4 (*C*≡N), 127.4 (*ipso*-C$_5$H$_4$), 136.2 (C≡C−Si), 163.2 (Ti−C≡C). ^{31}P NMR (81.01 MHz, acetone-d_6): δ −142.9 (septet, PF$_6$, $^1J_{PF}$ = 707.5 Hz). Anal. Calcd for C$_{28}$H$_{47}$CuF$_6$NPSi$_4$Ti: C, 43.88; H, 6.18; N, 1.83; Cu, 8.29. Found: C, 44.04; H, 6.24; N, 1.91; Cu, 8.16.

Synthesis of [{(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$}Cu(N≡CPh)]OTf (10). To a solution of **2** (0.30 g, 0.41 mmol) in Et$_2$O (40 mL) was added in one portion benzonitrile (0.08 g, 0.78 mmol) at room temperature. After the mixture was stirred for 5 min, an orange-yellow solid precipitated. After the mixture was stirred for another 2 h, the solid was collected by filtration and dried *in vacuo*. Crystallization from pentane/THF (3:1 v:v) at −20 °C yielded 0.33 g (96%, 0.40 mmol) of **10** as a yellow solid. Mp: 144 °C dec. IR (C≡N): 2230 cm^{-1}. IR (C≡C): 1918 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ − N≡CPh 729 (calcd 728). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 0.25 (s, 18 H, SiMe$_3$), 0.33 (s, 18 H, SiMe$_3$), 6.31 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 6.33 (t, 4 H, C$_5$H$_4$, J = 2 Hz), 7.6−7.9 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (75.47 MHz, CDCl$_3$): δ 0.0 (SiMe$_3$), 0.4 (SiMe$_3$), 109.0 (Ar C-1), 116.2 (C$_5$H$_4$), 119.1 (C$_5$H$_4$), 122.8 (*C*≡N), 126.3 (*ipso*-C$_5$H$_4$), 130.1 (Ar C-2,6), 132.7 (2C, Ar C-3,5), 135.3 (Ar C-4), 137.0 (C≡C−Si), 161.2 (Ti−C≡C). The assignments of the signals from Ar C-2,6 and Ar C-3,5 are tentative. The CF$_3$ signal was not observed. Anal. Calcd for C$_{34}$H$_{49}$CuF$_3$NO$_3$SSi$_4$Ti: C, 49.05; H, 5.93. Found: C, 49.13; H, 5.93.

Synthesis of {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]Cu}$_2$(μ(N),μ(N')-N≡CC(H)=C(H)C≡N)(OTf)$_2$ (11). To a solution of **2** (0.15 g, 0.21 mmol) in Et$_2$O (50 mL) was added in one portion fumaronitrile (0.02 g, 0.26 mmol) at room temperature. After the mixture was stirred for 5 min, an orange-yellow solid precipitated. After the mixture was stirred for another 2 h, the solid was collected by filtration, washed with cold Et$_2$O (10 mL), and dried *in vacuo*. Crystallization from *n*-pentane/THF (2:1 v:v) at −20 °C yielded 0.14 g (87%, 0.09 mmol) of **11** as an orange solid. Mp: 76 °C dec. IR (C≡N): 2230 cm^{-1}. IR (C≡C): 1930 cm^{-1}. FD-MS (*m/e*): M$^{•+}$ 1507 (calcd 1537). ^{1}H NMR (200.13 MHz, C$_6$D$_6$): δ 0.12 (s, 36 H, SiMe$_3$), 0.48 (s, 36 H, SiMe$_3$), 4.53 (s, 2 H, =CH), 5.85 (t, 8 H, C$_5$H$_4$, J = 2 Hz), 5.90 (t, 8 H, C$_5$H$_4$, J = 2 Hz). Anal. Calcd for C$_{58}$H$_{90}$Cu$_2$F$_6$N$_2$O$_6$S$_2$Si$_8$Ti$_2$: C, 45.32; H, 5.90. Found: C, 45.37; H, 6.05.

Structure Determination and Refinement of 2, 3, and 6. X-ray data (total/unique reflections: **2**, 8744/8165; **3**, 4782/4530; **6**, 6272/6022) were collected on an Enraf-Nonius CAD4T rotating anode diffractometer (**2** and **6**; Utrecht) or a Siemens (Nicolet) R3m/V diffractometer (**3**; Heidelberg) for an orange (**2**), yellow-red (**3**) or greenish (**6**) crystal glued on top of a glass fiber (**2** and **6**) or sealed in a glass capillary (**3**). Accurate unit-cell parameters and an orientation matrix were derived from the setting angles of 25 (23 for **3**) well-centered reflections (SET4 for **2** and **6**) in the range 11° < θ < 14°. The unit-cell parameters were checked for the presence of higher lattice symmetry.[13] Data were corrected for Lorentz−polarization effects. An empirical absorption correction was applied (**2**, DIFABS;[14] **3**, based on five reflections in the range 4° ≤ 2θ ≤ 40°, ψ-scan, 0° ≤ ψ ≤ 360°, $\Delta\psi$ = 10°; **6**, DIFABS[14] as implemented in PLATON[15]). The structures were solved by automated Patterson methods (**2**) or direct methods (**3** and **6**) and subsequent difference Fourier techniques (SHELXS86[16]). Refinement on F was carried out for **2** by full-matrix least-squares techniques (SHELX76[17]) using 5531 reflections with I

(13) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578−579.
(14) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.
(15) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
(16) Sheldrick, G. M. SHELXS86: Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1986.
(17) Sheldrick, G. M. SHELX76: Program for Crystal Structure Analysis; University of Cambridge, Cambridge, U.K., 1976.

Table 1. Experimental Data for the X-ray Diffraction Studies of **2**, **3**, and **6**

	2	**3**	**6**
formula	$C_{27}H_{44}CuF_3O_3SSi_4Ti$	$C_{27}H_{44}AgF_3O_3SSi_4Ti \cdot 0.5\ C_6H_6$	$C_{35}H_{56}CuNSSi_4Ti$
fw	729.49	812.87	746.69
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
cryst syst	monoclinic	monoclinic	triclinic
Z	4	4	2
a (Å)	12.8547(7)	13.384(3)	11.277(3)
b (Å)	21.340(2)	24.55(1)	12.991(6)
c (Å)	18.279(1)	13.506(3)	15.390(6)
α (deg)			65.17(4)
β (deg)	133.623(5)	119.21(2)	78.91(3)
γ (deg)			84.78(3)
V (Å^3)	3629.7(5)	3873(2)	2008(2)
d_{calc} (g cm^{-3})	1.335	1.394	1.235
μ(Mo Kα) (cm^{-1})	10.4	9.31	9.2
radiation (Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp (K)	150	210	150
R^a	0.047^b	0.038^c	0.079^c
wR/wR_2	0.045^b	0.091^c	0.27^c

^{a} $R = \sum ||F_o| - |F_c||/\sum |F_o|$. ^{b} Refinement on F: $wR = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. ^{c} Refinement on F^2: $wR_2 = \{\sum [w(F_o{}^2 - F_c{}^2)^2]/\sum [w(F_o{}^2)^2]\}^{1/2}$.

$\geq 2.5\sigma(I)$ during refinement. Refinement on F^2 was carried out for **3** and **6** by full-matrix least-squares techniques (SHELXL93[18]) using no observance criterion. Hydrogen atoms were included on calculated positions, riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. For the structures of **2** and **3**, the hydrogen atoms were refined with common isotropic atomic displacement parameters for the C≡CSiMe₃, SiMe₃, and C₅H₄ groups. For the structure of **6** all hydrogen atoms were refined with a fixed isotropic atomic displacement parameter related to the value of the equivalent isotropic atomic displacement parameter of their carrier atom by a factor of 1.2 for the CH₂ and aromatic hydrogen atoms and a factor of 1.5 for the methyl hydrogen atoms. Weights were optimized in the final refinement cycles. In the structure refinement of **2**, neutral atom scattering factors were taken from Cromer and Mann[19] and anomalous dispersion corrections were taken from Cromer and Liberman.[20] In the structure refinements of **3** and **6**, neutral atom scattering factors and anomalous dispersion corrections were taken from ref 21. Geometrical calculations and illustrations on **2** and **6** were performed with PLATON.[15] All calculations on **2** and **6** were performed on a DECstation 5000 cluster. Crystal data and numerical details of the structure determinations and refinements are collected in Table 1. Selected geometrical details of the structures of **2**, **3**, and **6** are listed in Table 2.
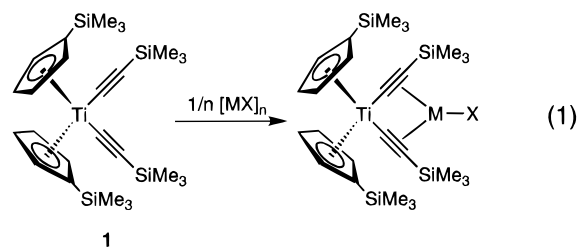
Results

The new complexes [(η^5-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)₂]MX (M = Cu, X = OTf (**2**), SC₆H₅ (**4**), SC₆H₄NMe₂-2 (**5**), SC₆H₄CH₂NMe₂-2 (**6**), S-1-C₁₀H₆NMe₂-8 (**7**), Cl (**8**), (N≡CMe)PF₆ (**9**); M = Ag, X = OTf (**3**)) featuring a monomeric CuX or AgX entity (eq 1) are obtained in high yield when the organometallic bis(alkyne) ligand [(η^5-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)₂] (**1**)[12] is reacted with equimolar amounts (based on Cu or Ag) of inorganic copper(I) or silver(I) salts (CuX or AgX) in THF, Et₂O, benzene, or toluene at ambient temperature.

The preparation of **2–9** is straightforward, and the new species **2**, **3**, and **5–7** are formed rapidly on mixing the reagents. However, when the starting materials CuX have a low solubility (*i.e.* X = SPh, PF₆, Cl), affording the complexes **4**, **8**, and **9**, respectively, reaction times of several hours are required. In all cases, the polymeric or oligomeric structure of the starting material (CuSPh and CuCl are polymeric, CuSC₆H₄NMe₂-2 and

(18) Sheldrick, G. M. SHELXL93: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.
(19) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321−325.
(20) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891−1898.
(21) Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

Table 2. Selected Geometrical Details of Complexes **2**, **3**, and **6**^{a}

	2: M = Cu, X = OSO₂CF₃	**3**: M = Ag, X = OSO₂CF₃	**6**: M = Cu, X = SC₆H₄CH₂NMe₂-2
	Bond Distances (Å)		
Ti⋯M	2.9880(8)	3.157(2)	2.963(2)
M−X	1.969(2)	2.252(4)	2.237(3)
M−C1	2.065(4)	2.287(5)	2.072(8)
M−C2	2.157(5)	2.414(5)	2.104(8)
M−C6	2.068(4)	2.307(5)	2.072(8)
M−C7	2.144(5)	2.477(5)	2.120(9)
Ti−C1	2.109(4)	2.137(5)	2.082(8)
Ti−C6	2.106(4)	2.141(6)	2.083(8)
C1−C2	1.233(6)	1.223(7)	1.222(11)
C6−C7	1.236(5)	1.235(7)	1.232(12)
	Bond Angles (deg)		
C1−Ti−C6	87.4(2)	93.3(2)	88.7(3)
Ti−C1−C2	166.7(3)	171.2(4)	164.5(7)
Ti−C6−C7	166.9(3)	173.2(4)	165.0(7)
C1−C2−Si1	156.7(4)	163.8(5)	161.2(7)
C6−C7−Si2	158.0(4)	170.5(4)	157.5(7)
Ti−M−X	177.4(1)	173.5(1)	176.89(8)^b
m1−M−m2^c	124.1(1)	115.9(2)	123.6(2)

^{a} The estimated standard deviations of the last significant digits are shown in parentheses. ^{b} Cu−S−C27 = 101.6(3)°. ^{c} m1 and m2 are defined as the midpoints of C1−C2 and C6−C7, respectively.
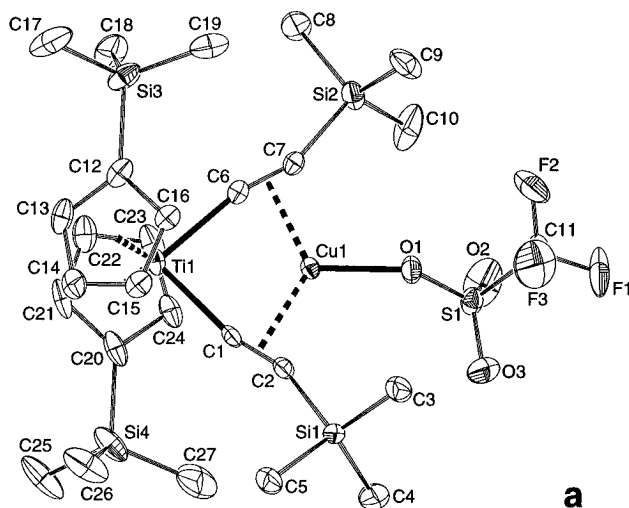

MX = CuOTf (**2**), AgOTf (**3**), CuSC₆H₅ (**4**), CuSC₆H₄NMe₂-2 (**5**), CuSC₆H₄CH₂NMe₂-2 (**6**), CuS-1-C₁₀H₆NMe₂-8 (**7**), CuCl (**8**), Cu(N≡CMe)PF₆ (**9**)
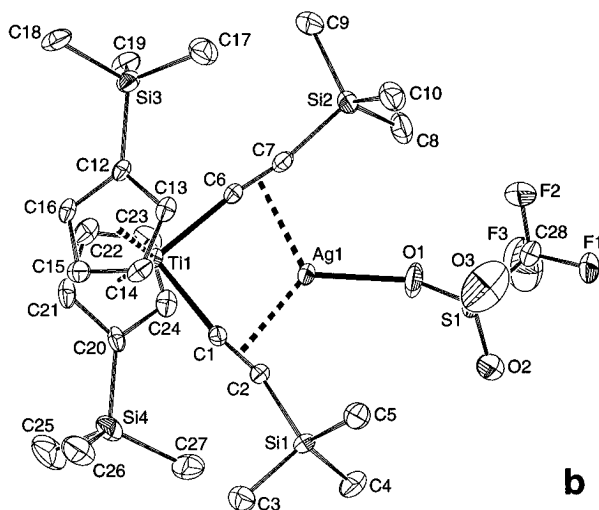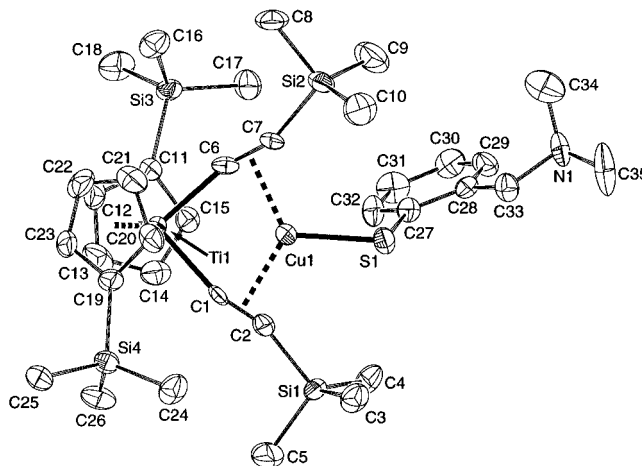
CuSC₆H₄CH₂NMe₂-2 are trimeric, and CuS-1-C₁₀H₆NMe₂-8 is nonameric)[11] is converted into monomeric units which bind to the chelating bis(alkyne) entity Ti(C≡CSiMe₃)₂ in a 1:1 ratio. Complexes **2**, **3**, **8**, and **9** are isolated as orange crystalline materials, whereas the copper arenethiolates **4–7** are greenish, almost black, crystalline materials. The solid complexes are all slightly sensitive to air and are somewhat hygroscopic.

The complexes **2–9** readily dissolve in polar solvents (Et₂O, THF) and, with the exception of **8** and **9**, in apolar organic

Figure 2. ORTEP drawings (drawn at the 30% probability level) of the complexes [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]MOSO$_2$CF$_3$ (with the exclusion of the hydrogen atoms) with the adopted atom-labeling scheme: (a) M = Cu (**2**); (b) M = Ag (**3**).

solvents (benzene, toluene) but are only slightly soluble in pentane and hexane.

Structures of the Monomeric Copper(I) and Silver(I) Triflate Complexes 2 and 3 in the Solid State. The molecular structures of **2** and **3** have been determined by X-ray diffraction; selected geometrical details are listed in Table 2.

The molecular structures show **2** (Figure 2a) and **3** (Figure 2b) to be isostructural monomeric species [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]MOTf (M = Cu (**2**), Ag (**3**)), containing a trigonally coordinated group 11 metal atom. This metal center is η^1(O)-bonded by a monoanionic trifluoromethanesulfonate (OTf) ligand and η^2-bonded by the two alkyne groups of [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$] (**1**). The latter η^2 bonding to the group 11 metal atom is forced by the chelating bis(alkyne) entity Ti(C≡CSiMe$_3$)$_2$ to occur in-plane (Cu (**2**) and Ag (**3**) are only −0.027(1) and 0.016(1) Å out of the least-squares plane through the Ti(C≡CSi)$_2$MO entity).[22]

(22) The alkyne ligands each donate two electrons. For examples of four-electron-donating alkynes in alkyne−copper complexes see: (a) Villacorta, G. M.; Gibson, D.; Williams, I. D.; Whang, E.; Lippard, S. J. *Organometallics* **1987**, *6*, 2426−2431. (b) Villacorta, G. M.; Gibson, D.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6732−6734. (c) Aalten, H. L.; van Koten, G.; Riethorst, E.; Stam, C. H. *Inorg. Chem.* **1989**, *28*, 4140−4146. (d) Reger, D. L.; Huff, M. F. *Organometallics* **1990**, *9*, 2807−2810.

Figure 3. ORTEP drawing (drawn at the 50% probability level) of **6** (with the exclusion of the hydrogen atoms) with the adopted atom-labeling scheme.

The copper to carbon distances within the bis(η^2-alkyne)-copper entity of **2** (Cu−C1 = 2.065(4) Å, Cu−C2 = 2.157(5) Å, Cu−C6 = 2.068(4) Å, and Cu−C7 = 2.144 (5) Å) are approximately 0.26 Å shorter than the corresponding distances in the silver complex **3** (Ag−C1 = 2.287(5) Å, Ag−C2 = 2.414(5) Å, Ag−C6 = 2.307(5) Å, and Ag−C7 = 2.477(5) Å). Similarly, the Cu−O1 distance in the Cu−η^1-OTf entity in **2** is 0.28 Å shorter than the Ag−O1 distance in the Ag−η^1-OTf entity in **3** (1.969(2) and 2.252(4) Å, respectively). These data reflect the smaller ionic radius of copper(I) (0.96 Å) compared to that of silver(I) (1.26 Å).[23]

The C≡C bonds in the (η^2-alkyne)Cu and (η^2-alkyne)Ag moieties of the triflate complexes **2** (1.233(6) and 1.236(5) Å) and **3** (1.223(7) and 1.235(7) Å) are significantly longer than those in the organometallic bis(alkyne) ligand **1** (1.203(9) and 1.214(6) Å). In addition, the Ti−C≡C−Si groups show significant distortions from linearity: the angles Ti−C−C decrease from 175.8(4) and 178.2(5)° in **1** to 171.2(4) and 173.2(4)° in **3** and 166.7(3) and 166.9(3)° in **2**, while the angles C−C−Si go from 174.8(4) and 178.3(5)° in **1** to 163.8(5) and 170.5(4)° in **3** and 156.7(4) and 158.0(4)° in **2**.

Structure of the Monomeric Copper(I) Arenethiolate Complex 6 in the Solid State. The molecular structure of **6** was established by means of X-ray crystallography, and selected geometrical details are listed in Table 2.

The molecular structure of **6** (Figure 3) is similar to those of **2** and **3** and comprises a trigonally coordinated group 11 metal atom that is η^1(S)-bonded by the arenethiolate ligand SC$_6$H$_4$-CH$_2$NMe$_2$-2 and η^2-bonded by both alkyne functions of the organometallic bis(alkyne) ligand [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$] (**1**). The *o*-(dimethylamino)methyl substituent of the arenethiolate ligand does not coordinate to the copper atom. In **6**, as in **2** and **3**, both alkyne ligands are in-plane bonded to the copper(I) center.[22] The angle between the plane of the arenethiolate ligand (containing S1 and C27−C33) and the Ti-(C≡CSi)$_2$CuS plane is 108.2(4)° (as given by the torsion angle C2−Cu1−S1−C27; see Figures 3 and 4).

The copper−carbon distances in the bis(η^2-alkyne)copper fragment of **6** (Cu−C1 = 2.072(8) Å, Cu−C2 = 2.104(8) Å, Cu−C6 = 2.072(8) Å, and Cu−C7 = 2.120(9) Å) are similar to the corresponding distances in **2**, and the Ti···Cu distances in **2** and **6** differ only slightly (2.9880(8) and 2.963(2) Å, respectively). The bite angle (C1−Ti−C6) of the unique

(23) *Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; Chemical Rubber Publishing: Boston, 1992.

chelating bis(alkyne) entity in the triflate complexes [(η^5-C$_5$H$_4$-SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]MOTf varies with the group 11 metal from 87.4(2)° in **2** (M = Cu) to 93.3(2)° in **3** (M = Ag). This bite angle is hardly affected by changes in the ligand X, and in **6** (M = Cu, X = SC$_6$H$_4$CH$_2$NMe$_2$-2) this angle is 88.7(3)°.

The Ti−C≡C−Si entities in **6** show deviations from linearity comparable to those observed for **2** and **3**: the C≡C bond lengths are 1.222(11) and 1.232(12) Å, while bending in the Ti−C≡C−Si moieties affords angles of 164.5(7) and 165.0(7)° for Ti−C−C and 161.2(7) and 157.5(7)° for C−C−Si.

Structure of Complexes [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]-MX in Solution. The ^{1}H and ^{13}C NMR spectra of solutions of **2**, **3**, **4**, **8**, and **9** in toluene-d_8 remain essentially unchanged in the temperature range of 193−353 K. Moreover, cryoscopic molecular weight determinations of **2** and **6** in benzene showed that these complexes exist in solution as monomeric species. These data are consistent with a monomeric structure in solution that is like that established for **2**, **3**, and **6** in the solid state.

The ^{1}H NMR spectra of **5**−**7** in toluene-d_8 at 298 K are well-defined and comprise one set of sharp signals in which there is equivalence of not only the two η^5-C$_5$H$_4$SiMe$_3$ ligands and the two benzylic protons from the arenethiolate entity but also of the two C≡CSiMe$_3$ ligands. However, when the temperature is lowered, the spectra change significantly: in the ^{1}H NMR spectrum of **6** at 213 K some signals from the η^5-C$_5$H$_4$SiMe$_3$ ligands have broadened, and below 203 K there are resonances for two separate C$_5$H$_4$SiMe$_3$ ligands. At this temperature the ^{1}H NMR spectrum also contains one set of signals for the arenethiolate ligand and one set for two equivalent C≡CSiMe$_3$ groups. The low-temperature spectra of **5** and **7** change accordingly, although decoalescence occurs at different temperatures.

This temperature dependence of the ^{1}H NMR spectra of **5**−**7** can be explained by a fluxional process involving the arenethiolate ligand. At high temperatures the complexes appear to contain two apparent planes of molecular symmetry: one coinciding with the Ti(C≡CSiMe$_3$)$_2$Cu plane and another perpendicular to this plane through the Ti−Cu−S atoms. Consequently, at high temperatures there is rapid interconversion between the preferred (low-energy) orientations of the arenethiolate on the NMR time scale and this is achieved by rotation around the Cu−S bond.

In the slow-exchange spectra of **5**−**7** there are two inequivalent η^5-C$_5$H$_4$SiMe$_3$ ligands and the symmetry plane containing the Ti(C≡CSiMe$_3$)$_2$Cu moiety no longer exists. The arenethiolate moiety is thus positioned either below or above this plane, and this is to be expected since an orientation in this plane is sterically unfavored (Figure 4); an alternative explanation of this inequivalence of the η^5-C$_5$H$_4$SiMe$_3$ rings based on freezing of their rotation can be excluded, since the minimum energy structure would probably involve a C_2-symmetry-related staggered orientation, as exemplified in the crystal structure of **6**. In detail, this freezing out of the arenethiolate orientation leads to inequivalent η^5-C$_5$H$_4$SiMe$_3$ ligands (in positions either *syn* or *anti* to the arenethiolate ligand), but both C≡CSiMe$_3$ units remain equivalent. Moreover, when the rotamer structure around the S−C(aryl) bond is considered, two further conformers relating to the position of the CH$_2$NMe$_2$ group are possible. The conformer in Figure 4 represents the least hindered situation; the other conformer, which is obtained by a 180° rotation around S−C(aryl), has the CH$_2$NMe$_2$ group close to the copper atom. However, the NMR data show no evidence for N−Cu coordination. The asymmetry in such complexes in the slow-exchange limit is most clearly illustrated by signals of the C$_5$H$_4$ groups. For complexes **5** and **6**, one observes three signals (ratio 2:1:1)
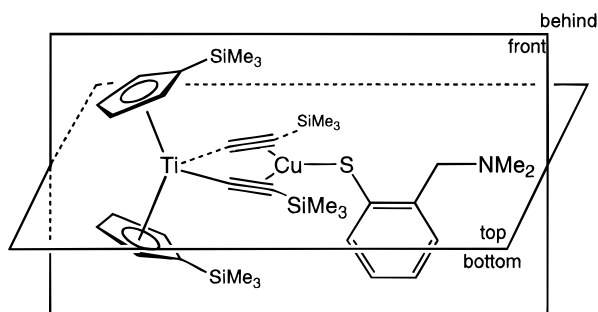

Figure 4. Planes of symmetry in the structure of complex **6**.

for the C$_5$H$_4$ entities and these comprise four individual resonances (H-2,5*anti*, H-3,4*anti*, H-2,5*syn*, and H-3,4*syn*), two of which are overlapping. Complex **7** shows four separate nonresolved multiplets in the C$_5$H$_4$ region in the slow exchange spectrum.

The calculated barriers of activation ($\Delta G^{\ddagger}$) of 35.5 ± 0.5 (**5**), 37.5 ± 0.5 (**6**), and 42.7 ± 0.5 kJ/mol (**7**) obtained from the ^{1}H NMR data show that the rotation process is dependent on the size of the arenethiolate ligand. Thus, in this series the energy barrier of the rotation process increases with increasing size of the arenethiolate ligand (C$_6$H$_4$NMe$_2$-2 (**5**) < C$_6$H$_4$CH$_2$NMe$_2$-2 (**6**) < 1-C$_{10}$H$_6$NMe$_2$-8 (**7**)). This can be explained by steric hindrance of the *ortho* substituent with the alkyne SiMe$_3$ groups during rotation of the arenethiolate ligand around the Cu−S bond. Accordingly, the $\Delta G^{\ddagger}$ value for the SC$_6$H$_5$ complex **4** is anticipated to be lower than 35 kJ/mol and decoalescence for this complex could not be reached even at 193 K.

These results show that the rotation of the arenethiolate ligand around the Cu−S axis has a lower energy barrier $\Delta G^{\ddagger}$ than in sulfur-bridged copper arenethiolates, where typical values of 50 kJ/mol have been reported.[4f]

Influence of the Ligand X in [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]MX. Complexes **2**−**9** all have only one C≡C stretching vibration in their solid-state (KBr) IR spectrum. This vibration decreases from 2012 cm^{-1} in the organometallic bis-(alkyne) ligand **1**[12] to 1956 cm^{-1} in the silver triflate complex **3** and in the copper series to 1934 cm^{-1} in **9** (MX = Cu(N≡CMe)PF$_6$), 1924 cm^{-1} in **2** (MX = CuOTf), 1912 cm^{-1} in **8** (MX = CuCl), 1908 cm^{-1} in **4** (MX = CuSC$_6$H$_5$), 1902 cm^{-1} in **6** (MX = CuSC$_6$H$_4$CH$_2$NMe$_2$-2), 1897 cm^{-1} in **5** (MX = CuSC$_6$H$_4$NMe$_2$-2), and 1893 cm^{-1} in **7** (MX = CuS-1-C$_{10}$H$_6$-NMe$_2$-8). These data show that a change of the η^1-bonded ligand X in [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]MX from a weaker (OTf) to a stronger (1-naphthalenethiolate) σ-donor leads to a weaker C≡C triple bond. Moreover, these data show that, in the alkyne−metal interaction, the C≡C triple bond is weakened more in the case of copper (**2**) than in the case of silver (**3**).

The reduction of the Ti−C−C and C−C−Si angles from 175.8(4), 178.2(5)/174.8(4), 178.3(5)° in the parent species **1** to 166.7(3), 166.9(3)/156.7(4), 158.0(4)° in **2**, 164.5(7), 165.0(7)/161.2(7), 157.5(7)° in **6**, and 171.2(4), 173.2(4)/163.8(5), 170.5(4)° in **3** illustrates that bending back of the C1 and C2 substituents increases with increasing σ-donating capacity of the ligand X in these complexes. Furthermore, the Ti−C−C and C−C−Si angles seem to correlate with the C≡C stretching frequency (Table 3).

The effect of incorporating a CuX or AgX fragment in the organometallic bis(alkyne) ligand **1** is clearly shown by the ^{13}C chemical shift of the alkyne carbon atoms: while **1** shows a signal for the Ti−*C*≡C carbon atom at 172.5 ppm, this signal shifts in the series **2**−**9** either upfield (in **2**, **3**, **8**, and **9**) or downfield (in **4**−**7**). The effect of changing the ligand X within

Table 3. Selected Spectroscopic and Crystallographic Data for the Complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]MX^a$

complex	MX	IR $\nu(C\equiv C)$, cm^{-1}	^{13}C NMR $\delta(TiC\equiv)$	$\delta(\equiv CSi)$	X-ray Ti−C−C, deg	C−C−Si, deg
1[b]		2012	172.5	135.4	175.8(4) 178.2(5)	174.6(4) 178.3(5)
2	CuOTf	1924	162.2	140.2	166.7(3) 166.9(3)	156.8(4) 158.0(4)
3	AgOTf	1956	150.3[c]	143.3[c]	170.8(5) 172.7(5)	163.7(6) 170.2(5)
4	CuSC$_6$H$_5$	1908	179.5	133.2		
5	CuSC$_6$H$_4$NMe$_2$-2	1897	180.4	136.2		
6	CuSC$_6$H$_4$CH$_2$NMe$_2$-2	1902	179.6	134.8	164.5(7) 165.0(7)	161.2(7) 157.5(7)
7	CuS-1-C$_{10}$H$_6$NMe$_2$-8	1893	182.8	133.1		
8	CuCl	1912	169.3[d]	134.5[d]	165(2)[e] 169(1)[e]	160(2)[e] 167(2)[e]
9	Cu(N≡CMe)PF$_6$	1934	163.2[f]	136.2[f]		

^{a} IR in KBr; NMR in benzene-d_6. ^{b} See ref 12a. ^{c} In CDCl$_3$. ^{d} In CD$_2$Cl$_2$. ^{e} Data not available. The corresponding angles of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CPh)_2]CuCl$ are listed. ^{f} In acetone-d_6.

the bis(η^2-alkyne)MX unit in **2**−**9** is also reflected in the ^{13}C chemical shift of the Ti−$C\equiv$C carbon atom, which moves to increasingly lower field with increasing electron donation from the ligand X (OTf (**2**) << Cl (**8**) < SC$_6$H$_5$ (**4**) ≈ SC$_6$H$_4$CH$_2$-NMe$_2$-2 (**6**) ≈ SC$_6$H$_4$NMe$_2$-2 (**5**) ≈ S-1-C$_{10}$H$_6$NMe$_2$-8 (**7**)). Moreover, there appears to be a trend between an increasingly lower field Ti−$C\equiv$C ^{13}C chemical shift and decreasing C≡C stretching frequency of complexes **2**−**9** (Table 3). The ^{13}C chemical shifts of the C≡C−Si atom in complexes **2**−**9** are almost identical and do not show a clear trend.

Reaction Behavior of the Copper(I) Triflate Complex 2 toward Lewis Bases. Reactions of **2** with the Lewis bases benzonitrile and fumaronitrile cleanly afford the cationic nitrile adducts **10** and **11**, respectively, in quantitative yields (eq 2).

2

10: L = N≡CPh
11: L = 1/2 N≡CC(H)=C(H)C≡N
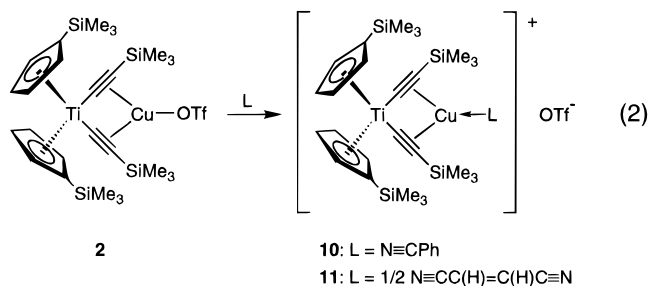
Complex **10** is the 1:1 adduct $[\{1\}Cu(N\equiv CPh)]OTf$ of **2** and benzonitrile, while **11** has the 2:1 composition $[\{1\}Cu]_2\{N\equiv CC\text{-}(H)=C(H)C\equiv N\}(OTf)_2$, in which each of the C≡N units of the bridge-bonded fumaronitrile ligand coordinates to a copper atom from a different Ti(C≡CSiMe$_3$)$_2$Cu moiety. Addition of excess nitrile to **10** and **11** neither increases the nitrile coordination to the copper atom nor does it lead to removal of the CuOTf entity from the organometallic bis(alkyne) ligand.

The two adducts **10** and **11** are only slightly soluble in pentane and toluene, while they are readily soluble in Et$_2$O and THF. In solution these species give NMR spectra with sharp signals, and the data are consistent with the formulation shown. The solid-state C≡C IR stretching vibrations of **10** and **11** appear at 1918 and 1930 cm^{-1}, respectively (1924 cm^{-1} for **2**), while for both **10** and **11** the coordinated C≡N moieties afford an absorption at 2230 cm^{-1}.

Reaction of **2** with weaker Lewis bases such as alkynes (RC≡CR; R = Ph, CO$_2$Me) and alkenes (R$_2$C=CR$_2$; R = H, Me) does not lead to the formation of the corresponding coordination complexes: in all cases **2** is recovered quantitatively.

However, reaction of **2** with a strong Lewis base, *i.e.* P(OMe)$_3$, leads to removal of CuOTf from this complex and the organometallic bis(alkyne) ligand **1** can be isolated from the resulting mixture. From this reaction mixture a yellow powder has also been obtained and this material contains P(OMe)$_3$ and CuOTf, but the exact composition has not been established.

Discussion

The complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]MX$ (M = Cu, Ag; X = OTf, SC$_6$H$_5$, SC$_6$H$_4$NMe$_2$-2, SC$_6$H$_4$CH$_2$NMe$_2$-2, S-1-C$_{10}$H$_6$NMe$_2$-8, Cl, (N≡CMe)PF$_6$) can be easily prepared and are the first examples of bis(η^2-alkyne)-stabilized monomeric inorganic copper(I) and silver(I) species. All these complexes are soluble in most polar and apolar organic solvents, and the organometallic bis(alkyne) ligand **1** can thus be used to dissolve monomeric units of salts such as [CuCl]$_\infty$, [AgCl]$_\infty$, and [CuSPh]$_\infty$ which are insoluble in common organic solvents.

The high thermal and kinetic stability of the complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]MX$ (M = Cu, Ag; **2**−**9**) is illustrated by their inertness toward known possible side reactions such as (a) transmetalation to form the alkynylcopper and the corresponding titanocene−X derivative as found when $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv C\text{-}t\text{-}Bu)_2]$ is reacted with [CuO-t-Bu]$_4$,[24] (b) nucleophilic substitution on the SiMe$_3$ group of the alkyne ligand, as occurs when $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]$ (**1**) is reacted with [CuO-t-Bu]$_4$,[9c] and (c) electrophilic addition of the MX moiety to the alkyne, as occurs when $[(\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}Ti(C\equiv CSiMe_3)_2]CuPh$ is heated at reflux in benzene.[24]

The group 11 metal in the complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti\text{-}(C\equiv CSiMe_3)_2]MX$ (M = Cu, Ag) is η^1-bonded by the inorganic ligand X and bis(η^2-alkyne)-chelated by the organometallic bis-(alkyne) ligand **1**. Therefore, these complexes allow a detailed examination of η^1 bonds in group 11 metal complexes and thereby provide information that is inaccessible from their polynuclear counterparts.[1−7]

The organometallic bis(alkyne) ligand **1** has a pronounced preference for binding to only one CuX or AgX entity,[25] and it is interesting to compare features of the new complexes with known examples of alkyne-coordinated copper and silver complexes. For example, in the copper triflate complex **2**, the OTf ligand is η^1(O)-bonded to the copper atom (Cu1−O1 = 1.969(2) Å), as in the structure of [cyclo-(C$_6$H$_4$C≡C)$_3$]Cu(OSO$_2$-CF$_3$) (Cu−O = 2.549(5) Å, C≡C = 1.222(10) Å, Cu−C(*mean*)

(24) Janssen, M. D.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Organomet. Chem.* **1995**, *505*, 123−126.

= 2.060(4) Å, Cu 0.18 Å above [(C≡C)₃] plane).[26a] The copper−oxygen distance in the latter complex is 0.5 Å longer than that in **2**; *i.e.*, there is a more covalent binding of the triflate ligand in **2**.[26a] Moreover, the [cyclo-(C₆H₄C≡C)₃] ligand is capable of binding more than one copper triflate moiety ([cyclo-(C₆H₄C≡C)₃]Cu₃(OSO₂CF₃)₃ is known[26b]).

The arenethiolate monoanionic ligand in **6** is η^1(S)-bonded to the metal center, and this is the first example of an η^1-bonded arenethiolate in copper thiolate chemistry. The Cu−S bond length in **6** is 2.237(3) Å and is comparable to the corresponding distance in the trimeric structure of the parent copper arenethiolate (2.231 and 2.198 Å).[4f] Apparently, the Cu−S bond length is not very sensitive to a change in aggregation state.

A consequence of the η^2-alkyne interaction in combination with the geometric constraints of the organometallic bis(alkyne) ligand **1** is that in **2**, **3**, and **6** there are relatively short Ti⋯Cu and Ti⋯Ag distances (2.9880(8) Å in **2**, 3.157(2) Å in **3**, and 2.963(2) Å in **6**), but since the group 11 metal has a formal 16-electron count, these distances represent nonbonding situations.[22]

In a separate paper we discussed the bonding in the bis(η^2-alkyne)copper and -silver units in complexes of the type [(η^5-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)₂]MX, including **2**−**9**.[9a,b] The alkyne−metal interaction can arise from two components: (i) a σ donation of electron density from a filled π orbital on the alkyne to the empty sp hybrid on Cu (Ag) and (ii) a back-donating component involving the donation of electron density from filled d orbitals on the metal to empty π^* orbitals on the alkyne. The molecular orbitals responsible for the back-donating component in the alkyne−copper (silver) interaction are depicted in Figure 5. Preliminary extended Hückel calculations indicate that the back-donating component is more important and is to be found in the in-plane interaction, thus implying a dependence on the σ-dononating capacity of X. This is in particular the case for MO **a**, which seems to have a better overlap with C$_\alpha$ than with the C$_\beta$ atom.

This bonding description finds further support in the data we report now for complexes **2**−**9**. When X is an electron-donating ligand in [(η^5-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)₂]MX (M = Cu, Ag), the C≡C bond will be weakened by the enhanced back-donation of electron density from the metal to the alkynes, consequently resulting in lengthening of the C≡C bond (although the
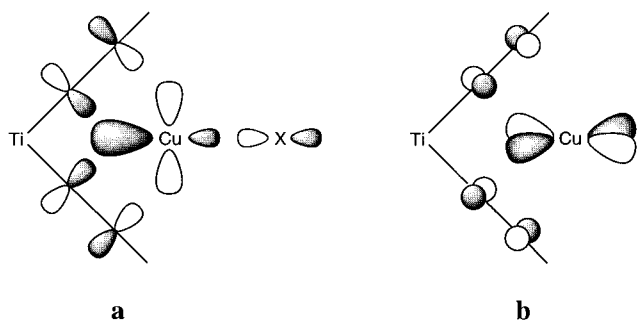

Figure 5. Metal-to-ligand (back-) donation.

differences can be small), bending of the Ti−C−C−Si entity, and lowering of the C≡C stretching frequency.

When X is a strongly electron withdrawing ligand (*i.e.* X = OTf (**2**), PF₆ (**9**)), it is possible to coordinate Lewis bases (nitriles) to the copper atom in these complexes. In contrast, when X is an electron-donating ligand, the corresponding Lewis base adducts are not formed and, furthermore, in complexes **4**−**7**, which possess an arenethiolate ligand, intramolecular coordination of the amine substituent has not been observed. Application of the strong Lewis base P(OMe)₃ to **2** leads to removal of the CuOTf unit from the chelating bis(η^2-alkyne) entity.

Complexes **2**−**8** show an interesting chemistry, and in a recent study we have shown that their reaction with a suitable organometallic reagent (*i.e.* LiR, Mg(X)R, or ZnR₂) leads to the formation of novel complexes of the type bis(η^2-alkyne)-copper(η^1-R) (R = alkyl, alkenyl, alkynyl, or aryl).[9b]

Conclusion

The organometallic bis(alkyne) ligand **1** is capable of breaking down polynuclear CuX and AgX assemblies, whereby soluble, air-stable, monomeric complexes [(η^5-C₅H₄SiMe₃)₂Ti(C≡C-SiMe₃)₂]MX (M = Cu, Ag) are formed. Since the organometallic bis(alkyne) ligand **1** functions as a bidentate chelate in these complexes, the one remaining coordination site on the trigonally coordinated group 11 metal is available for a systematic study of the properties of an isolated M−X bond at this position (*e.g.* electronegativity, dipole moment, etc.). The success of the use of species of this type based on **1** opens up the intriguing possibility of whether novel bis-chelating ligands based on heteronuclear or organometallic triple bonds could also be used as molecular pincers for other MX units in this area of chemistry.

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, and bond distances and bond angles for **2**, **3**, and **6** (25 pages). Ordering information is given on any current masthead page.

IC950710J

(25) [(η^5-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)₂] is also able to bind the metal-containing entities Co(CO) and Ni(CO): (a) Lang, H.; Imhof, W. *Chem. Ber.* **1992**, *125*, 1307−1311. (b) Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1991**, *406*, C5−C8. It can also function as a bis-(monodentate) ligand to two separate metal-containing entities such as Fe(CO)₄: (c) Lang, H.; Herres, M.; Zsolnai, L. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 429−431. (d) Lang, H.; Herres, M.; Imhof, W. *J. Organomet. Chem.* **1994**, *465*, 283−287. Moreover, complexes have been reported with a mononuclear FeCl₂ or CoCl₂ entity: (e) Lang, H.; Herres, M. *J. Organomet. Chem.* **1994**, *480*, 235−239. With Me₂-Si(C≡CSiMe₃)₂, generally [Me₂Si(C≡CSiMe₃)₂Cu₂X₂]ₙ species are isolated.

(26) (a) Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Organometallics* **1987**, *6*, 676−678. (b) Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Inorg. Chem.* **1988**, *27*, 2201−2202.

(27) Eyring equation: $\Delta G^\ddagger = -RT_c \ln[2\pi th(\Delta\nu)/kT_c\sqrt{3}]$ with $\Delta G^\ddagger$ = free energy of activation (J) T_c = coalescence temperature (K), and $\Delta\nu$ = chemical shift difference (Hz); the other symbols have their usual meaning.