598 *Organometallics* **1999,** *18,* 598−605

Monomeric Alkyne-Stabilized Complexes of Organo−Copper(I) and −Silver(I)

Heinrich Lang,* Katrin Köhler, and Gerd Rheinwald

Technische Universität Chemnitz, Institut für Chemie, Lehrstuhl Anorganische Chemie, Strasse der Nationen 62, D-09107 Chemnitz, Germany

Laszlo Zsolnai, Michael Büchner, Alexander Driess, and Gottfried Huttner

Ruprecht-Karls-Universität Heidelberg, Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Joachim Strähle

Universität Tübingen, Institut für Anorganische Chemie, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Received October 6, 1997

The synthesis of heterobimetallic $\{[Ti](C{\equiv}CR^1)_2\}MX$ $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; M = Cu, $R^1 = SiMe_3$: **4a**, X = SCF_3; **4b**, X = SEt; M = Ag, $R^1 = {}^tBu$: **5a,** X = OC(O)Me; **5e**, X = NO_3; M = Ag, $R^1 = SiMe_3$: **5b**, X = OC(O)Me; **5c**, X = OC(O)Ph; **5d**, X = $NO_3\}$ is described. These compounds together with $\{[Ti](C{\equiv}CR^1)_2\}CuX$ (**4c**, $R^1 = SiMe_3$, X = $SC_6H_4CH_2NMe_2$-2; **4d**, $R^1 = {}^tBu$, X = $SC_6H_4CH_2NMe_2$-2) can be used for the preparation of a large variety of different organo−copper(I) and −silver(I) species. The titanium−copper complexes $\{[Ti](C{\equiv}CR^1)_2\}CuR^2$ [$R^1 = SiMe_3$: **6a**, $R^2 = C_6F_5$; **6b**, $R^2 = C_6H_2(CF_3)_3$-2,4,6; **6c**, $R^2 = C_6H_2Ph_3$-2,4,6; $R^1 = {}^tBu$: **6d**, $R^2 = C_6H_2Ph_3$-2,4,6; **7**, R^2 = Me] are accessible by the reaction of **4c** or **4d** with suitable organic nucleophiles. Monomeric organo−silver(I) compounds can be prepared by using different starting materials: While the silver(I) aryls $\{[Ti](C{\equiv}CSiMe_3)_2\}AgR^2$ [**8a**, $R^2 = C_6H_2(CF_3)_3$-2,4,6; **8b**, $R^2 = C_6H_2Ph_3$-2,4,6] are only available by the reaction of **5b** with $LiC_6H_2(CF_3)_3$-2,4,6 or $BrMgC_6H_2Ph_3$-2,4,6, the silver(I) methyl species $\{[Ti](C{\equiv}CR^1)_2\}AgMe$ (**9a**, $R^1 = SiMe_3$; **9b**, $R^1 = {}^tBu$) can be synthesized by using **5a**, **5b**, **5d**, or **5e** as starting materials. While compounds **6**−**8** are stable under the reaction conditions applied, **9a** already starts to decompose at low temperature: The heterobimetallic titanium−silver acetylide $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CAg)\}_2$ (**10**) is formed by nucleophilic substitution of one of the alkynyl Me_3Si groups, whereby $SiMe_4$ is eliminated. Moreover, compounds **6**−**9** react with Br_2 to produce R^2−Br along with $\{[Ti](C{\equiv}CR^1)_2\}MBr$ (M = Cu; **11a**, $R^1 = {}^tBu$; **11b**, $R^1 = SiMe_3$; M = Ag, **11c**, $R^1 = SiMe_3$), which yield with equimolar amounts of LiR^2 or $BrMgR^2$ the starting materials **6**−**9** back.The solid-state structures of **4a**, **5c**, **6c**, and **8b** are reported. All complexes contain a monomeric $(\eta^2\text{-alkyne})_2M(\eta^1\text{-}X)$ (**4**, **5**) or $(\eta^2\text{-alkyne})_2M(\eta^1\text{-}R^2)$ (**6**−**9**) entity in which the group 11 metal atom M is trigonally coordinated by the two alkynyl ligands $C{\equiv}CR^1$ and the η^1-bonded groups X or R^2, respectively.

Introduction

Recently, we have reported that monomeric organo−copper(I) entities CuR (R = singly bonded organic ligand) can be synthesized in a general way by the reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuSC_6H_4CH_2NMe_2$-2 $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti\}$ with organic nucleophiles.[1−3] In the obtained compounds $\{[Ti](C{\equiv}CSiMe_3)_2\}CuR$ both alkynyl ligands $Me_3SiC{\equiv}C$ coordinate in a η^2-fashion to the copper(I) center. Additionally, the copper atom is η^1-bonded by the organic group R, resulting in a trigonal-planar environment. A further method for the preparation of monomeric alkyne-stabilized copper(I) compounds is given by the reaction of aggregated or polymeric organo−copper(I) species $[CuR]_n$ with the tweezer molecule $[Ti](C{\equiv}CSiMe_3)_2$, but is limited to stable $[CuR]_n$ species.[1,2,4−6] Furthermore, the latter method is confined to the preparation of monomeric $AgC_6H_2Me_3$-2,4,6, starting out from stable pentameric $[AgC_6H_2Me_3\text{-}2,4,6]_5$.[5] In this context, it would be also of interest to show if $[Ti](C{\equiv}CSiMe_3)_2$ can successfully be used for the stabilization of monomeric $M(C_6H_2Ph_3$-2,4,6) entities (M = Cu, Ag), which are obviously not

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10.1021/om9708687 CCC: $18.00
Publication on Web 01/20/1999

Table 1. Synthesis of Compounds 4−8

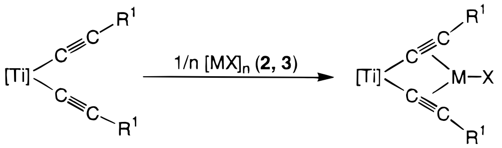
compd	R^1	MX	compd	MX	R^1	E	MR^2
4a	$SiMe_3$	$CuSCF_3$	**6a**	$CuSC_6H_4CH_2NMe_2$-2	$SiMe_3$	Li	CuC_6F_5
4b	$SiMe_3$	CuSEt	**6b**	$CuSC_6H_4CH_2NMe_2$-2	$SiMe_3$	Li	$CuC_6H_2(CF_3)_3$-2,4,6
4c[3]	$SiMe_3$	$CuSC_6H_4CH_2NMe_2$-2	**6c**	$CuSC_6H_4CH_2NMe_2$-2	$SiMe_3$	BrMg	$CuC_6H_2Ph_3$-2,4,6
4d[9]	^{t}Bu	$CuSC_6H_4CH_2NMe_2$-2	**6d**	$CuSC_6H_4CH_2NMe_2$-2	^{t}Bu	BrMg	$CuC_6H_2Ph_3$-2,4,6
			7	$CuSC_6H_4CH_2NMe_2$-2	^{t}Bu	Li	CuMe
5a	^{t}Bu	AgOC(O)Me					
5b	$SiMe_3$	AgOC(O)Me	**8a**	AgOC(O)Me	$SiMe_3$	Li	$AgC_6H_2(CF_3)_3$-2,4,6
5c	$SiMe_3$	AgOC(O)Ph	**8b**	AgOC(O)Me	$SiMe_3$	BrMg	$AgC_6H_2Ph_3$-2,4,6
5d	$SiMe_3$	$AgNO_3$	**9a**	$AgNO_3$	$SiMe_3$	Li	AgMe
5e	^{t}Bu	$AgNO_3$	**9b**	$AgNO_3$	^{t}Bu	Li	AgMe

accessible as isolated species unless they are stabilized by strong donor ligands as exemplified by $[(Me_2S)CuC_6H_3\text{-}2,4,6\text{-}Ph_3]_2$.[7] In general, the conversion of polynuclear organo−silver(I) compounds into neutral monomeric silver(I) units can be achieved by using fluorinated groups at the silver ion and suitable Lewis bases.[8] As a consequence, substantial interest exists in the nature of monomeric organo−silver(I) complexes as, for example, basic building blocks of higher aggregates. Moreover, monomeric η^1-bonded organo−silver(I) species should allow us to gain a better understanding of the structural features as well as the reactivity of the polynuclear counterparts.

We here report the synthesis of monomeric η^1-bonded organo−copper(I) and −silver(I) compounds, which results from the application of the bis(alkynyl) titanocene $[Ti](C{\equiv}CR^1)_2$ (R^1 = $SiMe_3$, ^{t}Bu) as an organometallic chelating ligand (organometallic π-tweezer). The structure and bonding, as well as the reaction chemistry, of the heterobimetallic compounds $\{[Ti](C{\equiv}CR^1)_2\}MR^2$ (M = Cu, Ag; R^2 = alkyl, aryl) will be discussed.

Results and Discussion

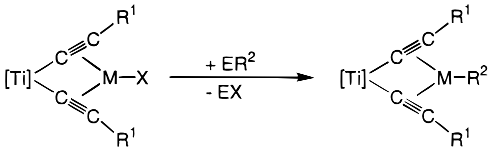
1. Synthesis of the Starting Materials $\{[Ti](C{\equiv}CR^1)_2\}MX$. The reaction of the bis(alkynyl) titanocene $[Ti](C{\equiv}CR^1)_2$ (**1a**, R^1 = $SiMe_3$; **1b**, R^1 = ^{t}Bu)[9] with equimolar amounts, based on copper or silver, of $[MX]_n$ (M = Cu, **2a**, X = SCF_3; **2b**, X = SEt; **2c**, X = $SC_6H_4CH_2NMe_2$-2;[3] M = Ag, **3a**, X = O_2CMe; **3b**, X = O_2CPh; **3c**, X = NO_3) in diethyl ether or tetrahydrofuran at 25 °C is straightforward and affords in high yields the corresponding heterobimetallic complexes $\{[Ti](C{\equiv}CR^1)_2\}MX$ (**4**, **5**) (eq 1, Table 1).



1 4, 5 (1)

Complexes **4** and **5** are the only isolated products obtained by extraction of the reaction residues with diethyl ether (**4a**−**4d**) or tetrahydrofuran (**5a**−**5e**), followed by filtration through a pad of Celite. **4** and **5** were isolated as red (**4a**), brown (**4b**−**4d**), or ochre (**5a**−**5e**) solids.

2. Synthesis of Monomeric Bis(η^2-alkyne) Organo−Copper(I) and −Silver(I) Compounds, $\{[Ti](C{\equiv}CR^1)_2\}MR^2$. Compounds **4c**, **4d**, and **5a**−**5e** (Table 1) are very efficient as starting materials for the preparation of monomeric organo−copper(I) as well as −silver(I) moieties. A metathesis route to the appropriate organo-group 11 metal complexes is the reaction of **4** and **5** with the organometallic reagents ER^2 (E = Li, BrMg; R^2 = singly bonded organic group) in diethyl ether at −80 to −20 °C. With this synthetic route molecules **6**−**9** (eq 2) can be obtained in moderate to high yields.



4, 5 6 - 9 (2)

The tweezer compounds **6**−**9** are rapidly formed on mixing the appropriate reagents at low temperature. **6a**−**6d** and **7** are isolated as red crystalline materials, whereas the silver compound **8a** is yellow, **8b** blue, and **9a** as well as **9b** deep purple. All compounds **6**−**9** have a remarkably increased thermostability when compared to their free organo−group 11 metal aggregates $[MR^2]_n$. However, it is found that **6**−**8** are stable at 25 °C in solution, whereas compounds **9a** and **9b** undergo further reactions (for a detailed discussion see below). Complexes **6**−**9** readily dissolve in nonpolar organic solvents, such as *n*-pentane, benzene, and toluene. **9a** and **9b** are sensitive to light.

An important observation in the preparation of the organo−copper(I) species **6** and **7** was the validity of molecules **4c** and **4d**, which contain an arenethiolate entity (X = $SC_6H_4CH_2NMe_2$-2).[2,3] While the products **6** and **7** are nicely soluble in nonpolar solvents, the starting materials **4c** and **4d** as well as the lithium or magnesium arenethiolate species also formed in the metathesis reaction are only soluble in polar solvents. On this basis complexes **6** and **7** can easily be separated from the other products formed.

In the preparation of the organo silver(I) complexes **8** and **9** two major aspects have to be considered: (i)

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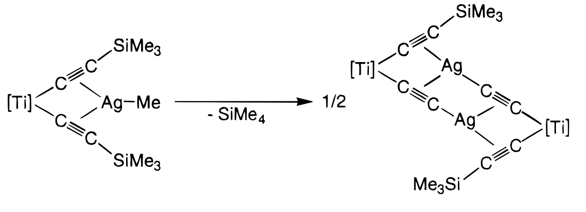
the character of the organometallic reagents ER^2 (Table 1) and (ii) the coordination mode of the groups X in the starting materials $\{[Ti](C{\equiv}CR^1)_2\}AgX$ [X = OC(O)Me, a η^1-bonded ligand; X = NO_3, a η^2-bonded ligand] (Table 1). There are two possibilities to account for the synthesis of the monomeric silver(I) methyl compounds **9a** and **9b**: the reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}AgOC(O)Me$ (**5b**) and $\{[Ti](C{\equiv}CR^1)_2\}AgNO_3$ (**5d**, $R^1 = SiMe_3$; **5e**, $R^1 = {}^tBu$) with an equimolar amount of LiMe (Table 1). In this case the organometallic reagent LiMe is strong enough to substitute the η^1-bonded OC(O)Me ligand, as well as the chelate bonded NO_3 group. However, changing to the organometallic reagents $ER^2 = LiC_6H_2(CF_3)_3$-2,4,6 and $BrMgC_6H_2Ph_3$-2,4,6, it is found that these reagents react only with the η^1-bonded carboxylate ligand in **5b** to produce the silver(I) aryls **8a** and **8b**, respectively. No reaction takes place when **5d** or **5e** is treated with $LiC_6H_2(CF_3)_3$-2,4,6 or $BrMgC_6H_2Ph_3$-2,4,6, which can be explained by the greatly reduced steric accessibility of the C_{ipso} anionic site as compared with CH_3^-.

3. Reaction Behavior. In earlier studies we were able to show that monomeric copper(I) alkyls can be stabilized by using the chelating effect of bis(alkynyl) titanocenes.[1,2,4] In this respect the copper methyl complexes $\{[Ti](C{\equiv}CR^1)_2\}CuMe$[8] [$R^1 = {}^tBu$; $R^1 = SiMe_3$[1,2]] show a high thermostability, when compared with noncoordinated polymeric $[CuMe]_n$. In contrast, the isostructural bis(η^2-alkyne)−silver methyl species $\{[Ti](C{\equiv}CR^1)_2\}AgMe$ (**9a**, $R^1 = SiMe_3$; **9b**, $R^1 = {}^tBu$) already start to decompose at low temperature. However, when compared to their parent polynuclear aggregates $[AgMe]_n$, they show a remarkable high thermostability, too; $[AgMe]_n$, decomposes at −80 to −50 °C.[8a,12] Consequently, **9a** and **9b** can be safely handled in solution up to −20 °C in the dark; no decomposition is observed. It turned out that ^1H NMR spectroscopical studies of **9a** showed that at −10 to 0 °C $SiMe_4$ is eliminated and the formation of the heterobimetallic titanium−silver acetylide $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CAg)\}_2$ (**10**) is instantaneous (eq 3). On warming **10** to 10 °C, it starts to decompose by forming silver films and other products, which could not unambiguously be characterized.

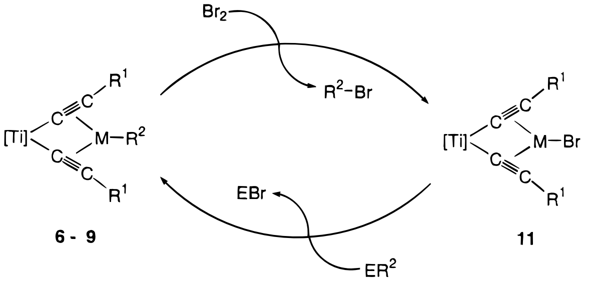


(3)

9a **10**

10 is isostructural with the titanium−copper acetylide $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)\}_2$, although the latter complex is much more thermally and kinetically stable.[6] **10** comprises a dimer of $[Ti](C{\equiv}CSiMe_3)(C{\equiv}CAg)$ fragments in which the C_2 unit in the $TiC{\equiv}CAg$ moiety is additionally η^2-coordinated to a second silver(I) center, thus forming an alkyne-brigded dimer. The $(\eta^2\text{-}C{\equiv}C)_2$-$Ag_2$ building block has a structural arrangement, which corresponds to that observed in $[AgC{\equiv}CR]_n$.[13]

Most common for all compounds listed in Table 1 is their reaction behavior toward Br_2. Addition of Br_2 to diethyl ether solutions of monomeric organo−copper(I) or organo−silver(I) compounds in an 1:1 molar ratio leads to the quantitative formation of R^2−Br and the corresponding complexes $\{[Ti](C{\equiv}CR^1)_2\}MBr$ (M = Cu; **11a**, $R^1 = {}^tBu$; **11b**, $R^1 = SiMe_3$;[14] M = Ag; **11c**, $R^1 = SiMe_3$).[15] The latter complexes can easily be converted into the starting materials **6**−**9** by treatment with equimolar amounts of the organometallic reagents ER^2 (Table 1) in diethyl ether solutions.



(4)

6 - 9 **11**

4. Structure and Bonding. Solid-State Structures of Compounds 4a, 5c, 6c, and 8b. The molecular structures in the solid state of compounds **4a**, **5c**, **6c**, and **8b** have been verified by X-ray diffraction analysis and are shown in Figure 1 (**4a**, **5c**) and Figure 2 (**6c**, **8b**). Crystallographic parameters and selected geometrical details are listed in Table 3.

The molecular structures of **4a**, **5c** (Figure 1) as well as **6c** and **8b** (Figure 2) show that these compounds are monomeric species of general type $\{[Ti](C{\equiv}CSiMe_3)_2\}$-MX, which comprise a trigonally coordinated group 11 metal atom, which is η^1-bonded by the X [X = SCF_3, OC(O)Ph] or R^2 group ($R^2 = C_6H_2Ph_3$-2,4,6) as well as η^2-bonded by both alkynyl ligands of the organometallic chelate $[Ti](C{\equiv}CSiMe_3)_2$ (**1a**).[1−8,11,14−26]

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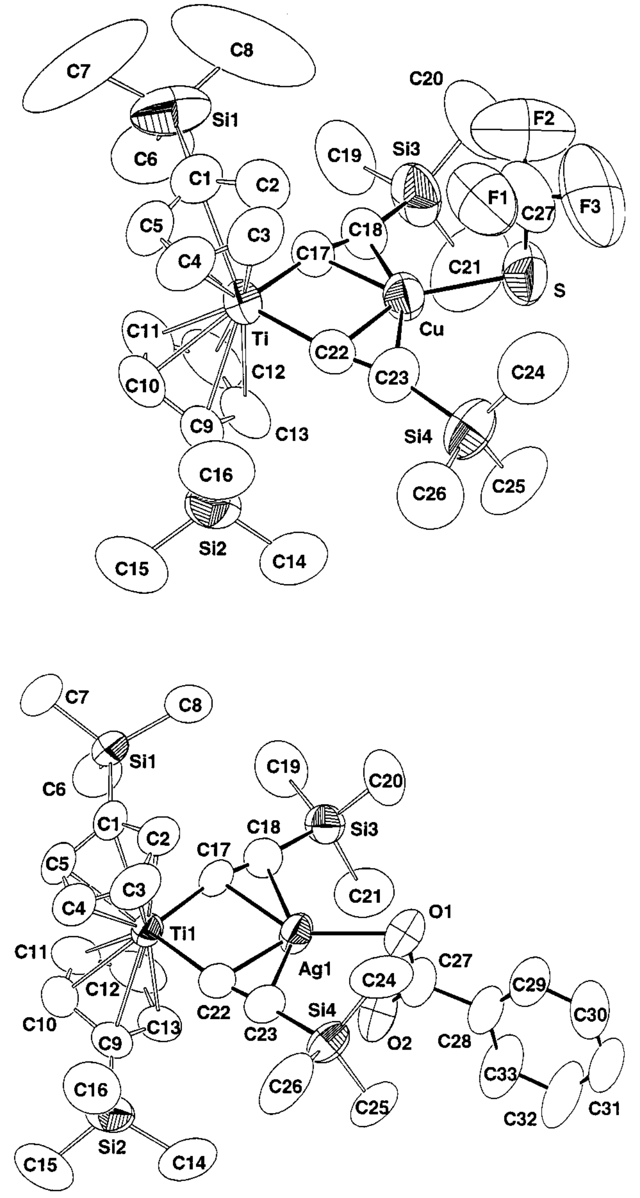

Figure 1. Molecular geometry and atom-numbering scheme for compound **4a** (top) and **5c** (bottom). Selected bond lengths [Å] and angles [deg] are given in Table 2.

In all four compounds the η^2-bonding of the Me$_3$SiC≡C units to the copper or silver atom is forced by the chelating effect of the [Ti](C≡CSiMe$_3$)$_2$ entity to occur in-plane. The group 11 metal atoms are only within 0.198 Å in **4a**, 0.087 Å in **5c**, 0.0013 Å in **6c**, or 0.012 Å in **8b** out of the least-squares plane through the Ti(C≡C)$_2$ML fragment (**4a**, M = Cu, L = S; **5c**, M = Ag, L = O1; **6c**, M = Cu, L = C27; **8b**, M = Ag, L = C27). With respect to the η^2-coordination of the alkynyl ligands a C≡C bond lengthening from 1.203(9) and 1.214(6) Å in the uncoordinated complex **1a**[15] to 1.236(8) and 1.251(9) Å in **4a**, 1.23(1) and 1.24(1) Å in **5c**, 1.25(2) and 1.28(2) Å in **6c**, and 1.252(5) Å in **8b** is found (Table 2). Additionally, the Ti−C≡C−Si units are deformed from linearity [Ti−C17−C18: **4a** 168.3(5)°, **5c** 168.2(6)°, **6c** 166(1)°, **8b** 167.5(3)°. Ti−C22−C23: **4a** 167.8(5)°, **5c** 168.9(6)°, **6c** 165(1)°, **8b** 168.1(3)°. C17−C18−Si3: **4a** 161.4(6)°, **5c** 170.7(6)°, **6c** 153(1)°, **8b** 161.1(3)°. C22−C23−Si4: **4a** 164.2(6)°, **5c** 170.3(7)°, **6c** 151(1)°, **8b**

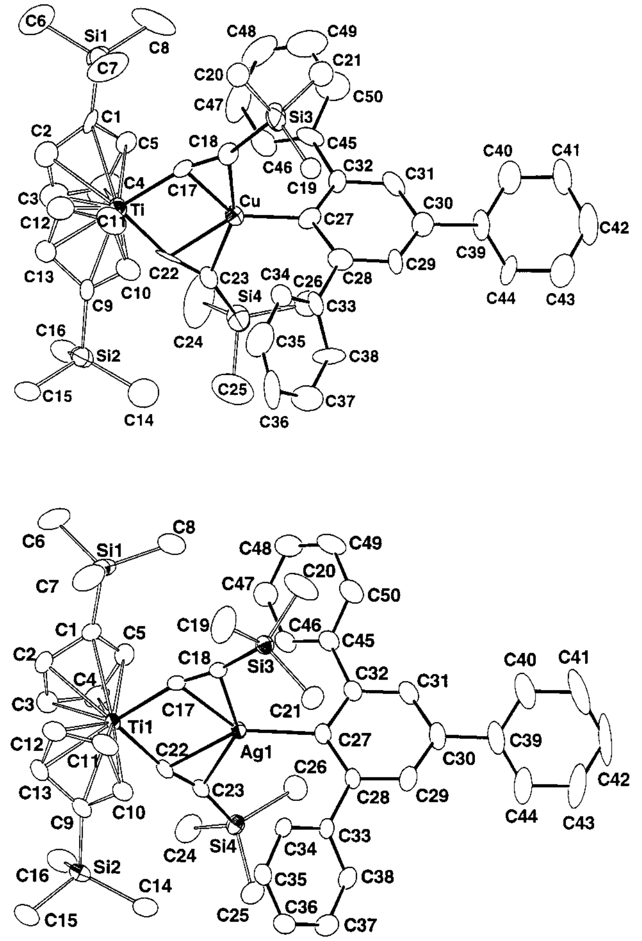

Figure 2. Molecular geometry and atom-numbering scheme for compounds **6c** (top) and **8b** (bottom). Selected bond lengths [Å] and angles [deg] are given in Table 2.

Table 2. Selected Bond Lengths [Å] and Angles [deg] of Compounds 4a, 5c, 6c, and 8b

	4a	**5c**[c]	**6c**	**8b**
	Bond Lengths			
Ti−M	2.998(2)	3.091(2)	2.994(3)	3.220(1)
M−X[a]	2.272(2)	2.248(6)	1.95(1)	2.166(3)
Ti−C17	2.109(5)	2.121(7)	2.06(1)	2.122(3)
Ti−C22	2.106(6)	2.118(7)	2.06(1)	2.116(4)
C17−C18	1.236(8)	1.24(1)	1.25(2)	1.252(5)
C22−C23	1.251(9)	1.23(1)	1.28(2)	1.252(5)
M−C17	2.099(5)	2.272(7)	2.07(1)	2.335(3)
M−C18	2.201(5)	2.381(7)	2.09(1)	2.403(3)
M−C22	2.105(5)	2.284(7)	2.09(1)	2.323(3)
M−C23	2.192(6)	2.396(8)	2.10(1)	2.392(3)
Ti−D1[b]	2.056	2.046	2.057	2.081
Ti−D2[b]	2.057	2.054	2.061	2.080
	Angles			
Ti−M−X	169.5(1)	173.3(2)	178.0(3)	178.41(9)
Ti−C17−C18	168.3(5)	168.2(6)	166(1)	167.5(3)
Ti−C22−C23	167.8(5)	168.9(6)	165(1)	168.1(3)
C17−C18−Si3	161.4(6)	170.7(6)	153(1)	161.1(3)
C22−C23−Si4	164.2(6)	170.3(7)	151(1)	161.2(3)
C17−Ti−C22	88.9(2)	94.9(3)	87.9(4)	92.5(1)
D1−Ti−D2[b]	134.1	134.1	132.8	134.0

[a] M = Cu, Ag; X = singly bonded organic or inorganic ligand. [b] D1, D2 = centroids of the cyclopentadienyl ligands formed by C1−C5 (D1) and C9−C13 (D2). [c] Ag−O2 2.623; C17−O1 1.24(1); C17−O2 1.25(1).

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Table 3. Crystallographic Parameters for Compounds 4a, 5c, 6c, and 8b

	4a	**5c**	**6c**	**8b**
empirical formula	$C_{27}H_{44}CuF_3SSi_4Ti$	$C_{33.5}H_{53}AgO_2Si_4Ti$	$C_{50}H_{61}CuSi_4Ti$	$C_{50}H_{61}AgSi_4Ti$
fw	681.49	791.92	885.79	930.12
cryst system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	10.754(4)	11.229(6)	12.281(4)	12.255(5)
b, Å	18.446(7)	13.745(9)	21.273(7)	18.749(7)
c, Å	18.32(1)	15.550(9)	19.350(6)	21.805(9)
α, deg		82.24(5)		
β, deg	99.22(4)	82.63(5)	107.34(2)	95.94(2)
γ, deg		66.06(4)		
V, Å^3	3587(3)	2166(2)	4825(3)	4983(3)
ρ_{calcd}, g cm^{-3}	1.262	1.214	1.219	1.240
Z	2	2	4	4
cryst size, mm	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.3	0.2 × 0.2 × 0.2	0.2 × 0.3 × 0.3
diff model	Siemens R3m/V	Siemens R3m/V	Siemens R3m/V	Siemens R3m/V
μ, mm^{-1}	1.04	0.77	0.74	0.68
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
(λ, Å)	(0.710 73)	(0.710 73)	(0.710 73)	(0.710 73)
temp, K	200	200	200	180
scan mode	ω-scan	ω-scan	ω-scan	ω-scan
scan range $\Delta\omega$, deg	0.60	0.60	0.60	0.55
scan speed, deg min^{-1}	6.0−29.3	5.0−29.3	5−60	8−60
2θ range, deg	3.8−46.0	2.7−50.1	2.9−45.0	3.8−48.0
index range	$-1 \le h \le 11$	$-4 \le h \le 13$	$0 \le h \le 13$	$-7 \le h \le 14$
	$-1 \le k \le 20$	$-14 \le k \le 16$	$0 \le k \le 22$	$-6 \le k \le 21$
	$-20 \le l \le 20$	$-18 \le l \le 18$	$-20 \le l \le 19$	$-24 \le l \le 24$
no. of unique reflns	4967	7685	6293	7824
no. of reflns obsd [$I \ge 2.0\sigma(I)$]	3203	5005	2915	6226
ref param	374	496	503	521
min/max resid el. density, e Å^{-3}	0.553/−0.538	3.047/−0.587	0.525/−0.594	0.364/−0.323
R1/wR2^a [$I > 2\sigma(I)$]	0.052/0.118	0.070/0.186	0.096/0.199	0.036/0.084
R1/wR2^a (all)	0.100/0.133	0.118/0.210	0.218/0.243	0.054/0.092
S (goodness-of-fit) on F^2 ^{b}	0.989	1.034	0.957	0.977

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|]$, $wR2 = \sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$. [b] $S = \sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}\}$ n = number of reflections, p = parameters used. Definition of w [where $P = (F_o^2 + 2F_c^2)/3$]: **4a:** $w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.0000P]$. **5c:** $w = 1/[\sigma^2(F_o^2) + (0.1241P)^2 + 0.0000P]$. **6c:** $w = 1/[\sigma^2(F_o^2) + (0.1053P)^2 + 0.0000P]$. **8b:** $w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.0000P]$.

161.2(3)°] (Table 2). The tweezer effect of the bis(alkynyl) titanocene induces a *trans*-deformation of the Ti−C≡C−Si units. Similar observations were made for other heterobimetallic tweezer molecules of general type $\{[Ti](C{\equiv}CR)_2\}M'L_n$.[1−8,11,14,15−26] As a consequence of the η^2-alkyne interaction with the metal centers of copper or silver, the bite angle C17−Ti−C22 is significantly reduced from 102.8(2)° in **1a**[15] to 88.8(2)° in **4a**, 95.2(3)° in **5c**, 87.9(4)° in **6c**, and 92.5(1)° in **8b**, which is typical for this type of molecule; the D1−Ti−D2 angle is thereby not influenced (Table 2). The larger bite angle in compounds **5c** and **8b**, as compared with **4a** and **6c**, reflects nicely the difference in the size of the metal ions of copper and silver.[4,5] Moreover, it is found that the copper-to-carbon distances within the bis(η^2-alkyne) copper segment of **4a** and **6c** are shorter than the corresponding bond lengths in the silver complexes **5c** and **8b** (Table 2), reflecting the difference in group 11 metal ion radii (Cu 0.96 Å, Ag 1.26 Å).[4,5] The two-electron two-center metal−C_{ipso}(aryl) bond distances [**6c**, Cu−C27 1.95(1) Å; **8b**, Ag1−C27 2.166(3) Å] fit perfectly in the ranges expected for this type of bonding with copper(I) and silver(I) centers (Table 2). A similar copper−carbon bond length was also experimentally observed in $CuC_6H_2Ph_3$-2,4,6 as its Me_2S adduct.[7c] When compounds **6c** and **8b** are compared with, for example, $\{[Ti](C{\equiv}CSiMe_3)_2\}MC_6H_2Me_3$-2,4,6,[5] one recognizes that in the newly synthesized compounds the silicon atoms of the Me_3Si alkynyl groups are bonded out of the $Ti(C{\equiv}C)_2MC_{ipso}$(aryl) plane (**6c**, Si3 0.35(1), Si4 0.30(1) Å; **8b**, Si3 0.478(3), Si4 0.266(4) Å), whereby one Me_3Si group is located below and the other one above the $Ti(C{\equiv}C)_2MC_{ipso}$ (M = Cu, Ag) segment. This phenomenon can best be explained by the bulkiness of the R^2 building blocks as compared with smaller R^2 fragments.[27] A further consequence of the η^2-alkyne interaction together with the geometric constraints of the organometallic chelating ligand **1a** is that in compounds **6c** and **8b** relatively short Ti···Cu and Ti···Ag distances [**6c**, 2.994(3) Å; **8b**, 3.220(1) Å] are found.[28]

Looking at the $C_6H_2Ph_3$-2,4,6 ligand in **6c** and **8b**, the three terminal bonded C_6H_5 groups of the C_6H_2 entity are located with respect to each other in a propeller-like conformation, forming atropisomers, due to the sterical constraints of the bulky Me_3Si group (Figure 2). This is reflected by the obstructed rotation around M−C27 (M = Cu, Ag), C28−C33, and C32−C45 in **6c** as well as **8b**.

IR−Studies. The IR spectra of molecules **4**−**9** and **11** show for the $R^1C{\equiv}C$ ligands only one C≡C stretching vibration in the region of 2010−1860 cm^{-1}. As compared with the starting materials **1a** and **1b** the ν(C≡C) absorption is shifted to lower frequencies, as it is generally observed for η^2-coordination of alkynes to copper(I) or silver(I) moieties in which the alkynes act as two-electron donor ligands.[1,4] The obtained IR spectra verify that changing from weaker (e.g., compound **4a**) to stronger (e.g., compound **6a**) σ-donor ligands X and R^2 results in a weaker C≡C triple bond. These data show that in the alkyne-to-metal interaction the triple bond is more affected by copper than by silver.[1,2,5,28]

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In addition, **5a** and **5b** show two strong $\nu(CO_2)$ vibrations in the region of 1390−1570 cm^{-1} due to their asymmetric and symmetric stretching vibration. The difference of these two absorptions indicates that the carboxylate ligand is η^1-bonded to the silver(I) center,[29,30] which is also evidenced by X-ray structure analysis.[29,31−34] In contrast, the NO_3 entity in molecules **5d** and **5e** is chelate bonded, as evidenced by IR studies and X-ray structure analysis.[15,30]

^{1}H and ^{13}C{^{1}H} NMR Studies. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of all new synthesized compounds consist of sharp and well-resolved signals for each organic building block present.

In **6c**, **6d**, **8a**, and **8b** a sterical obstructed rotation around the copper−carbon σ-bond is $^{13}C\{^1H\}$ NMR spectroscopically observed, which gives additional information for the formation of atropisomers in solution (for comparison see X-ray structure analysis above).

Of interest are the ^{1}H NMR spectra of compounds **7**, **9a**, and **9b**. The copper-bonded methyl protons in compound **7** appear, as compared with the silver methyl species **9a** and **9b**, at higher field (**7**, $\delta = 0.78$; **9a**, $\delta = 1.03$; **9b**, $\delta = 0.93$), indicating a stronger shielding of the methyl protons in **7**. Additionally, it is found that the protons of the CH_3 group, σ-bonded to silver, as given in compounds **9a** and **9b** appear as doublets, due to coupling to silver [**9a**, $^2J(^{107,109}AgH) = 9.2$ Hz; **9b**, $^2J(^{107,109}AgH) = 8.9$ Hz].

In the $^{13}C\{^1H\}$ NMR spectra of all silver compounds (Table 1) there is a coupling to ^{107,109}Ag found on a number of resonance signals, such as the methyl group [**9b**, $^1J(^{107,109}Ag\ ^{13}C) = 120$ Hz], the aryl groups [**8b**, $^3J(^{107,109}Ag^{13}C) = 7.2$ Hz], and those of the C_α and C_β atoms of the alkynyl ligands $C{\equiv}CR^1$ [$R^1 = SiMe_3$, ^tBu; **8a**, $^1J_{AgC} = 5.6$ Hz (C_β), $^1J_{AgC} = 9.3$ Hz (C_α); **8b**, $^1J_{AgC} = 2.1$ Hz (C_β), $^1J_{AgC} = 5.5$ Hz (C_α)]. The latter data indicate that the alkynyl carbon atoms are directly bonded to the silver(I) ion. As expected, these values are larger than those reported for two-electron three-center silver-to-carbon bonds.[5,36] If one compares the Ag−C-coupling constant obtained for the alkyl species **9b** [$^1J(^{107,109}Ag^{13}C) = 120$ Hz] with the values typical for a silver−carbon(aryl) σ-bond [$^1J(^{107,109}Ag^{13}C) = 140−170$ Hz],[5] a higher value is found for the latter molecules, which can be explained by the higher degree of s-orbital participation in the two-electron two-center silver−carbon (sp^2) bond. In this series also fits the silver−carbon coupling constant of the alkyne-to-silver bonding: The lower coupling constant $^1J(^{107,109}Ag\ ^{13}C)$ with 2−10 Hz in compounds **8a** and **8b** is in agreement with the high p-character of the η^2-coordinated alkynyl ligands. Additionally, there is a $^3J(^{107,109}Ag\ ^{13}C)$ of 7.2 Hz also present in the $^{13}C\{^1H\}$ NMR spectra of compound **8b** on the signals of the phenyl bearing meta-carbon atoms. Additionally, in the isostructural molecules **6c** and **8a** (Table 1) coupling constants for ^{13}C and ^{19}F are observed: $^1J(^{19}F\ ^{13}C) = 266.2$ Hz as well as $^2J(^{19}F\ ^{13}C) = 28.3$ Hz in compound **6b** and $^2J(^{19}F\ ^{13}C) = 27.7$ Hz in **8a**.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Diethyl ether and *n*-pentane were purified by distillation from calcium hydride; tetrahydofuran was purified by distillation from sodium/benzophenone. 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, and the $^{13}C\{^1H\}$ 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. EI, FD, and FAB 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. *Caution: When repeating the experiments for the preparation of the methyl copper(I) and silver(I) compounds **7** and **9**, it must be noted that the uncomplexed species [MCH$_3$] (M = Cu, Ag) are highly explosive when dry, and for this reason care has to be taken with all safety precautions warranted. In addition, it must be noted that lithium aryl species with fluoro-substituents can be explosive when dry.*

(A) Synthesis of Compounds 4a, 4b, and 5b−5d. To [Ti]-$(C{\equiv}CSiMe_3)_2$ (**1a**)[9] {[Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2$ Ti} (250 mg, 0.48 mmol) were added in one portion the group 11 metal compounds $[MX]_n$ (**2a**, 80 mg, 0.48 mmol; **2b**, 70 mg, 0.48 mmol; **3a**, 80 mg, 0.48 mmol; **3b**, 110 mg, 0.48 mmol; **3c**, 90 mg, 0.48 mmol) in tetrahydrofuran (50 mL) at 25 °C. After stirring for 3 h at 25 °C the solution was filtered through a pad of Celite. The solvent was removed in a vacuum, and the residues were each washed with 20 mL of *n*-pentane. Crystallization at −30 °C in diethyl ether (**4a**, **4b**) or tetrahydrofuran (**5b**−**5d**) yielded **4a** (320 mg, 0.48 mmol, 98%) as a red solid, **4b** (290 mg, 0.45 mmol, 95%) as a brown solid, and **5b** (290 mg, 0.43 mmol, 89%), **5c** (3400 mg, 0.46 mmol, 95%), and **5d** (310 mg, 0.45 mmol, 93%) as ochre solids.

Data for 4a: mp 150 °C; IR (KBr) $\nu(C{\equiv}C)/cm^{-1}$ 1908; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 18 H, $SiMe_3$), 0.34 (s, 18 H, $SiMe_3$), 4.98 (pt, 4 H, C_5H_4, $J_{HH} = 2.3$ Hz), 6.12 (pt, 4 H, C_5H_4, $J_{HH} = 2.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 0.0 ($SiMe_3$), 0.7 ($SiMe_3$), 114.0 (C_5H_4), 116.7 (C_5H_4), 117.1 (q, CF_3, $^1J_{CF} = 168.1$ Hz), 123.3 ($^iC{-}C_5H_4$), 136.3 ($TiC{\equiv}\mathit{C}Si$), 172.2 ($Ti\mathit{C}{\equiv}C$); FD mass spectrum, *m/e* M^+, 681. Anal. Calcd for $C_{27}H_{44}CuF_3SSi_4Ti$ (681.49): C, 47.58; H, 6.51. Found: C, 47.33; H, 6.31.

Data for 4b: mp 140 °C (decomp); IR (KBr) $\nu(C{\equiv}C)/cm^{-1}$ 1886; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 18 H, $SiMe_3$), 0.38 (s, 18 H,

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SiMe$_3$), 1.24 (t, 3 H, CH$_2$C*H*$_3$, $^3J_{HH}$ = 7.2 Hz), 2.54 (q, 2 H, C*H*$_2$CH$_3$, $^3J_{HH}$ = 7.2 Hz), 5.78 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.2 Hz), 6.02 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.2 Hz); ^{13}C NMR (CDCl$_3$) δ 0.2 (SiMe$_3$), 0.7 (SiMe$_3$), 22.3 (CH$_3$), 24.2 (CH$_2$), 112.2 (C$_5$H$_4$), 115.1 (C$_5$H$_4$), 119.7 (^{i}C−C$_5$H$_4$), 129.3 (TiC≡CSi), 182.4 (Ti*C*≡C); FAB mass spectrum, *m/e* (relative intensity) M$^+$ − SC$_2$H$_5$, 579 (55); M$^+$ − SC$_2$H$_5$ − C$_2$SiMe$_3$, 418 (30); (C$_5$H$_4$SiMe$_3$)$_2$Ti$^+$, 322 (100). Anal. Calcd for C$_{28}$H$_{49}$CuSSi$_4$Ti (641.54): C, 52.42; H, 7.70. Found: C, 53.17; H, 7.63.

Data for 5b: mp 120 °C (decomp); IR (KBr) ν(C≡C)/cm^{-1} 1944 (w), ν(CO$_2$)/cm^{-1} 1565 (s), 1398 (s); ^{1}H NMR (CDCl$_3$) δ 0.25 (s, 36 H, SiMe$_3$), 2.02 (s, 3 H, CH$_3$), 6.25 (s, 8 H, C$_5$H$_4$); ^{13}C NMR (CDCl$_3$) δ 0.1 (SiMe$_3$), 24.4 (CH$_3$), 115.6 (C$_5$H$_4$), 118.7 (C$_5$H$_4$), 124.3 (^{i}C−C$_5$H$_4$), 137.5 (TiC≡*C*Si), 155.8 (Ti*C*≡C), 177.0 (CO$_2$); FD mass spectrum, *m/e* M$^+$ − CO$_2$Me, 626. Anal. Calcd for C$_{28}$H$_{47}$AgO$_2$Si$_4$Ti (683.78): C, 49.18; H, 6.93. Found: C, 49.40; H, 6.94.

Data for 5c: mp 137 °C (decomp); IR (KBr) ν(C≡C)/cm^{-1} 1951; ^{1}H NMR (CD$_2$Cl$_2$) δ 0.22 (s, 18 H, SiMe$_3$), 0.30 (s, 18 H, SiMe$_3$), 6.33 (m, 8 H, C$_5$H$_4$), 7.37 (m, 5 H, C$_6$H$_5$); ^{13}C NMR (CD$_2$Cl$_2$) δ 0.2 (SiMe$_3$), 116.4 (C$_5$H$_4$), 119.0 (C$_5$H$_4$), 125.1 (^{i}C−C$_5$H$_4$), 128.0 (C$_6$H$_5$), 130.0 (C$_6$H$_5$), 130.2 (C$_6$H$_5$), 137.1 (^{i}C−C$_6$H$_5$), 137.4 (d, TiC≡*C*Si, $^1J_{AgC}$ = 15 Hz), 156.3 (d, Ti*C*≡C, $^1J_{AgC}$ = 15 Hz), 171.7 (CO$_2$); FD mass spectrum, *m/e* (relative intensity) M$^+$, 746 (71), M$^+$ − CO$_2$C$_6$H$_5$, 625 (18), M$^+$ − AgCO$_2$C$_6$H$_5$, 516 (100). Anal. Calcd for C$_{33}$H$_{49}$AgO$_2$Si$_4$Ti (745.85): C, 53.14; H, 6.62. Found: C, 52.85; H, 6.51.

Data for 5d: mp 143 °C (decomp); IR (KBr) ν(C≡C)/cm^{-1} 1950; ^{1}H NMR (acetone-*d*$_6$) δ 0.23 (s, 18 H, SiMe$_3$), 0.28 (s, 18 H, SiMe$_3$), 6.56 (m, 8 H, C$_5$H$_4$); FD mass spectrum, *m/e* M$^+$ − NO$_3$, 625. Anal. Calcd for C$_{26}$H$_{44}$AgNO$_3$Si$_4$Ti (687.75): C, 47.70; H, 6.77; N, 2.15. Found: C, 47.09; H, 6.84; N, 2.15.

(B) Synthesis of Compounds 5a and 5e. To [Ti](C≡C^{t}Bu)$_2$ (**1b**)[9] (250 mg, 0.52 mmol) were added the silver compounds [AgX]$_n$ (**3a**, 90 mg, 0.52 mmol; **3c**, 90 mg, 0.52 mmol) in one portion at 25 °C in tetrahydrofuran (50 mL). After stirring for 3 h at 25 °C the appropriate solutions were filtered through a pad of Celite. The solvent was removed in a vacuum, and the residues were washed with 20 mL of *n*-pentane. Crystallization at −30 °C in tetrahydrofuran yielded **5a** (310 mg, 0.47 mmol, 90%) and **5e** (330 mg, 0.50 mmol, 97%) as ochre solids.

Data for 5a: mp 125 °C (decomp); IR (KBr) ν(C≡C)/cm^{-1} 2014 (w), ν(CO$_2$)/cm^{-1} 1566 (vs), 1408 (s); ^{1}H NMR (CDCl$_3$) δ 0.27 (s, 18 H, SiMe$_3$), 1.32 (s, 18 H, ^{t}Bu), 2.02 (s, 3 H, CH$_3$), 6.18 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.3 Hz), 6.30 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.3 Hz); ^{13}C NMR (CDCl$_3$) δ 0.1 (SiMe$_3$), 23.5 (CH$_3$), 29.9 (C*Me*$_3$), 115.6 (C$_5$H$_4$), 119.5 (C$_5$H$_4$), 121.3 (^{i}C−C$_5$H$_4$), 177.2 (CO$_2$); FAB mass spectrum, *m/e* (relative intensity) M$^+$ − CO$_2$Me, 593 (65); M$^+$ − CO$_2$Me −Bu, 535 (5); M$^+$ − AgCO$_2$Me − C$_2$Bu, 402 (20); (C$_5$H$_4$SiMe$_3$)$_2$Ti$^+$, 322 (100). Anal. Calcd for C$_{30}$H$_{47}$AgO$_2$Si$_2$Ti (651.62): C, 55.29; H, 7.27. Found: C, 54.82; H, 7.08.

Data for 5e: IR (KBr) ν(C≡C)/cm^{-1} 2009 (vw), ν(NO$_3$)/cm^{-1} 1380 (vs); ^{1}H NMR (CDCl$_3$) δ 0.28 (s, 18 H, SiMe$_3$), 1.32 (s, 18 H, ^{t}Bu), 6.23 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.3 Hz), 6.36 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.3 Hz); ^{13}C NMR (CDCl$_3$) δ 0.0 (SiMe$_3$), 30.0 (*C*Me$_3$), 31.6 (C*Me*$_3$), 116.1 (C$_5$H$_4$), 120.0 (C$_5$H$_4$), 122.8 (^{i}C−C$_5$H$_4$), 153.4 (TiC≡*C*); FD mass spectrum, *m/e* M$^+$ − NO$_3$, 594. Anal. Calcd for C$_{28}$H$_{44}$AgNO$_3$Si$_2$Ti (654.59): C, 51.37; H, 6.78. Found: C, 51.14; H, 6.65.

(C) Synthesis of Compounds 6a−6c. To {[Ti](C≡CSiMe$_3$)$_2$}CuSC$_6$H$_4$CH$_2$NMe$_2$-2 (**4c**)[3] (300 mg, 0.40 mmol) were added equimolar amounts of ER^2 [ER^2 = LiC$_6$F$_5$, 70 mg, 0.40 mmol; ER^2 = LiC$_6$H$_2$(CF$_3$)$_3$-2,4,6, 120 mg, 0.40 mmol; ER^2 = BrMgC$_6$H$_2$Ph$_3$-2,4,6, 6.6 mL, 0.065 M tetrahydrofuran solution, 0.40 mmol] in one portion in diethyl ether (50 mL) at 25 °C. After stirring for 3 h at 0 °C all volatile materials were removed in a vacuum, and the residues obtained were each extracted with a total of 80 mL of *n*-pentane and filtered through a pad of Celite. Crystallization at −30 °C yielded **6a** (280 mg, 0.39 mmol, 97%), **6b** (290 mg, 0.39 mmol, 97%), **6c** (270 mg, 0.31 mmol, 95%), and **6d** (370 mg, 0.42 mmol, 97%) as red solids.

Data for 6a: mp 120 °C (decomp); IR (KBr) ν(C≡C)/cm^{-1} 1887; ^{1}H NMR (C$_6$D$_6$) δ 0.11 (s, 18 H, SiMe$_3$), 0.18 (s, 18 H, SiMe$_3$), 5.40 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.3 Hz), 5.79 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.3 Hz); ^{13}C NMR (C$_6$D$_6$) δ 0.0 (SiMe$_3$), 0.2 (SiMe$_3$), 112.8 (C$_5$H$_4$), 115.4 (C$_5$H$_4$), 120.8 (^{i}C−C$_5$H$_4$), 129.4 (TiC≡*C*Si), 184.2 (Ti*C*≡C); FD mass spectrum, *m/e* M$^+$, 746. Anal. Calcd for C$_{32}$H$_{44}$CuF$_5$Si$_4$Ti (747.47): C, 51.42; H, 5.93. Found: C, 51.47; H, 5.72.

Data for 6b: mp 140 °C (decomp); IR (KBr) ν(C≡C)/cm^{-1} 1877; ^{1}H NMR (C$_6$D$_6$) δ −0.08 (s, 18 H, SiMe$_3$), 0.22 (s, 18 H, SiMe$_3$), 5.52 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.2 Hz), 5.86 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.2 Hz), 8.07 (s, 2 H, C$_6$H$_2$); ^{13}C NMR (C$_6$D$_6$) δ 0.3 (SiMe$_3$), 112.9 (C$_5$H$_4$), 114.8 (C$_5$H$_4$), 119.4 (^{i}C−C$_5$H$_4$), 120.8 (q, CF$_3$, $^1J_{CF}$ = 266.2 Hz), 123.4 (C$_6$H$_2$), 130.2 (TiC≡*C*Si), 140.9 (q, C$_6$H$_2$, $^2J_{CF}$ = 28.3 Hz), 181.4 (CuC), 185.9 (Ti*C*≡C); FD mass spectrum, *m/e* M$^+$, 860. Anal. Calcd for C$_{35}$H$_{46}$CuF$_9$Si$_4$Ti (861.51): C, 48.79; H, 5.38. Found: C, 51.68; H, 6.08.

Data for 6c: mp 160 °C (decomp); IR (KBr) ν(C≡C)/cm^{-1} 1858; ^{1}H NMR (C$_6$D$_6$) δ 0.25 (s, 18 H, SiMe$_3$), 0.35 (s, 18 H, SiMe$_3$), 5.55 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.2 Hz), 5.89 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.2 Hz), 6.7−7.9 (m, 17 H, C$_6$H$_2$/C$_6$H$_5$); ^{13}C NMR (C$_6$D$_6$) δ 0.7 (SiMe$_3$), 1.4 (SiMe$_3$), 111.4 (C$_5$H$_4$), 114.9 (C$_5$H$_4$), 116.5 (^{i}C−C$_5$H$_4$), 123−152 (C$_6$H$_2$/C$_6$H$_5$), 126.3 (TiC≡*C*Si), 195.8 (Ti*C*≡C); FAB mass spectrum, *m/e* (relative intensity) M$^+$, 884 (5); M$^+$ − C$_6$H$_2$Ph$_3$, 578 (45); M$^+$ − C$_6$H$_2$Ph$_3$ − C$_2$SiMe$_3$, 482 (55); (C$_5$H$_4$SiMe$_3$)$_2$Ti$^+$, 322 (100). Anal. Calcd for C$_{50}$H$_{61}$CuSi$_4$Ti (885.80): C, 67.79; H, 6.94. Found: C, 68.03; H, 6.79.

(D) Synthesis of Compounds 6d and 7. To {[Ti](C≡C^{t}Bu)$_2$}CuSC$_6$H$_4$CH$_2$NMe$_2$-2 (**4d**)[3] (200 mg, 0.28 mmol) were added equimolar amounts of the organometallic reagents ER^2 (ER^2 = BrMgC$_6$H$_2$Ph$_3$-2,4,6, 4.3 mL, 0.065 M tetrahydrofuran solution, 0.28 mmol; ER^2 = LiMe, 0.24 mL, 1.6 M diethyl ether solution, 0.28 mmol) in one portion in diethyl ether (50 mL) at 0 °C. After stirring for 3 h at 0 °C all volatile materials were removed in a vacuum, and the residues formed were each extracted with 80 mL of *n*-pentane and filtered through a pad of Celite. Crystallization at −30 °C yielded compounds **6e** (180 mg, 0.21 mmol, 75%) and **7** (200 mg, 0.36 mmol, 93%) as red solids.

Data for 6d: mp 145 °C (decomp); IR (KBr) ν(C≡C)/cm^{-1} 1926; ^{1}H NMR (C$_6$D$_6$) δ 0.19 (s, 18 H, SiMe$_3$), 1.01 (s, 18 H, ^{t}Bu), 5.75 (s, 8 H, C$_5$H$_4$), 7.1−8.0 (m, 17 H, C$_6$H$_2$/C$_6$H$_5$); ^{13}C NMR (C$_6$D$_6$) δ 0.5 (SiMe$_3$), 31.9 (C*Me*$_3$), 32.6 (*C*Me$_3$), 112.0 (C$_5$H$_4$), 114.1 (^{i}C−C$_5$H$_4$), 115.9 (C$_5$H$_4$), 125−152 (C$_6$H$_2$/C$_6$H$_5$), 141.6 (TiC≡*C*), 159.4 (Ti*C*≡C); FAB mass spectrum, *m/e* (relative intensity) M$^+$, 852 (5); M$^+$ − Me, 837 (5), M$^+$ − C$_6$H$_2$Ph$_3$, 547 (100); M$^+$ − C$_6$H$_2$Ph$_3$ − C$_2$^{t}Bu, 466 (40); M$^+$ − CuC$_6$H$_2$Ph$_3$ − C$_2$^{t}Bu − Me, 388 (20); (C$_5$H$_4$SiMe$_3$)$_2$Ti$^+$, 322 (85). Anal. Calcd for C$_{52}$H$_{61}$CuSi$_2$Ti (853.64): C, 73.16; H, 7.02. Found: C, 71.17; H, 7.05.

Data for 7: mp 107 °C; IR (KBr) ν(C≡C)/cm^{-1} 1909; ^{1}H NMR (C$_6$D$_6$) δ 0.27 (s, 18 H, SiMe$_3$), 0.78 (s, 3 H, CuMe), 1.51 (s, 18 H, ^{t}Bu), 5.38 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.3 Hz), 5.68 (pt, 4 H, C$_5$H$_4$, J_{HH} = 2.3 Hz); ^{13}C NMR (C$_6$D$_6$) δ −9.2 (CuMe), 0.5 (SiMe$_3$), 31.9 (C*Me*$_3$), 32.8 (*C*Me$_3$), 110.6 (C$_5$H$_4$), 114.0 (C$_5$H$_4$), 114.5 (^{i}C−C$_5$H$_4$), 138.6 (TiC≡*C*), 169.1 (Ti*C*≡C); EI mass spectrum, *m/e* (relative intensity) M$^+$ − Me, 547 (20); M$^+$ − Me − C$_2$Bu, 466 (5); M$^+$ − CuMe − C$_2$Bu, 402 (60); (C$_5$H$_4$SiMe$_3$)$_2$Ti$^+$, 322 (100). Anal. Calcd for C$_{29}$H$_{47}$CuSi$_2$Ti (563.30): C, 61.83; H, 8.41. Found: C, 61.97; H, 8.25.

(E) Synthesis of Compounds 8a and 8b. {[Ti](C≡CSiMe$_3$)$_2$}AgOC(O)Me (**5b**) (200 mg, 0.29 mmol) was added in one portion to LiC$_6$H$_2$(CF$_3$)$_3$-2,4,6 (90 mg, 0.29 mmol) or BrMgC$_6$H$_2$Ph$_3$-2,4,6 (4.5 mL, 0.065 M tetrahydrofuran solution, 0.29 mmol) in tetrahydrofuran (50 mL) at 0 °C. After stirring for 3 h at 0 °C in the dark all volatile materials were removed in a vacuum, and the residues were extracted with 100 mL of *n*-pentane and filtered through a pad of Celite. Crystallization at −30 °C yielded **8a** (170 mg, 0.19 mmol, 66%) as a yellow solid and **8b** (250 mg, 0.27 mmol, 94%) as a blue solid.

Data for 8a: mp 122 °C (decomp); IR (KBr) ν(C$\equiv$C)/cm^{-1} 1930; ^{1}H NMR (C_6D_6) δ 0.03 (s, 18 H, SiMe$_3$), 0.19 (s, 18 H, SiMe$_3$), 5.78 (pt, 4 H, C_5H_4, J_{HH} = 2.3 Hz), 6.00 (pt, 4 H, C_5H_4, J_{HH} = 2.3 Hz), 8.12 (s, 2 H, C_6H_2); ^{13}C NMR (C_6D_6) δ 0.1 (SiMe$_3$), 0.5 (SiMe$_3$), 115.5 (C_5H_4), 117.0 (C_5H_4), 122.3 (^{i}C−C_5H_4), 122.5 (C_6H_2), 136.5 (d, TiC$\equiv$*C*Si, $^1J_{AgC}$ = 5.6 Hz), 141.7 (q, C_6H_2, $^2J_{CF}$ = 27.7 Hz), 154.0 (AgC), 166.7 (d, Ti*C*$\equiv$CSi, $^1J_{AgC}$ = 9.3 Hz); EI mass spectrum, *m*/*e* (relative intensity) M$^+$, 905 (10); M$^+$ − $C_6H_2(CF_3)_3$, 625 (30); M$^+$ − $AgC_6H_2(CF_3)_3$ − C_2-SiMe$_3$, 415 (100). Anal. Calcd for $C_{35}H_{46}AgF_9Si_4Ti$ (905.83): C, 46.40; H, 5.12. Found: C, 47.07; H, 5.50.

Data for 8b: mp 134 °C (decomp); IR (KBr) ν(C$\equiv$C)/cm^{-1} 1914; ^{1}H NMR (C_6D_6) δ 0.13 (s, 18 H, SiMe$_3$), 0.28 (s, 18 H, SiMe$_3$), 5.70 (pt, 4 H, C_5H_4, J_{HH} = 2.3 Hz), 6.00 (pt, 4 H, C_5H_4, J_{HH} = 2.3 Hz), 7.2−8.1 (m, 17 H, C_6H_2/C_6H_5); ^{13}C NMR (C_6D_6) δ 0.4 (SiMe$_3$), 0.7 (SiMe$_3$), 114.0 (C_5H_4), 116.0 (C_5H_4), 119.6 (^{i}C−C_5H_4), 124.9 (d, *meta*-C, AgC_6H_2, $^3J_{AgC}$ = 7.2 Hz), 123−150 (C_6H_2/C_6H_5), 131.1 (d, TiC$\equiv$*C*Si, $^1J_{AgC}$ = 2.1 Hz), 177.5 (d, Ti*C*$\equiv$CSi, $^1J_{AgC}$ = 5.5 Hz); FAB mass spectrum, *m*/*e* (relative intensity) M$^+$ − $C_6H_2Ph_3$, 625 (65); M$^+$ − $C_6H_2Ph_3$ − SiMe$_3$, 552 (5); M$^+$ − $AgC_6H_2Ph_3$ − C_2SiMe_3, 418 (20); $(C_5H_4SiMe_3)_2$-Ti$^+$, 322 (100). Anal. Calcd for $C_{50}H_{61}AgSi_4Ti$ (930.12): C, 64.56; H, 6.61. Found: C, 65.23; H, 6.30.

(F) Synthesis of Compounds 9a and 9b. To {[Ti](C$\equiv$CSiMe$_3$)$_2$}AgO(O)Me (**5b**) (200 mg, 0.29 mmol) and {[Ti](C$\equiv$C^{t}Bu)$_2$}AgO(O)Me (**5a**) (190 mg, 0.29 mmol) was added in one portion LiMe (0.16 mL, 1.6 M diethyl ether solution, 0.29 mmol) in diethyl ether (50 mL) at −60 °C. After stirring for 2 h at −50 °C all volatile materials were removed in a vacuum, and the residues were extracted with 50 mL of *n*-pentane at −50 °C and filtered through a pad of Celite. Crystallization at −80 °C yielded **9a** and **9b** as deep purple solids, very sensitive to temperature.

Data for 9a: IR (KBr) ν(C$\equiv$C)/cm^{-1} 1905; ^{1}H NMR (toluene-d_8, −50 °C) δ 0.17 (s, 18 H, SiMe$_3$), 0.57 (s, 18 H, SiMe$_3$), 1.03 (d, 3 H, AgMe, $^2J_{AgH}$ = 9.2 Hz), 4.94 (s, 4 H, C_5H_4), 5.74 (s, 4 H, C_5H_4); ^{13}C NMR (toluene-d_8, −50 °C) δ 0.3 (SiMe$_3$), 0.8 (SiMe$_3$), 112.2 (C_5H_4), 114.4 (C_5H_4), 118.6 (^{i}C−C_5H_4), 121.0 (TiC$\equiv$*C*Si), 185.7 (Ti*C*$\equiv$C); FD mass spectrum, *m*/*e* (relative intensity) M$^+$ − Me, 625 (40); M$^+$ − AgMe, 516 (100).

Data for 9b: ^{1}H NMR (toluene-d_8, −50 °C) δ 0.25 (s, 18 H, SiMe$_3$), 0.93 (d, 3 H, AgMe, $^2J_{AgH}$ = 8.9 Hz), 1.59 (s, 18 H, ^{t}Bu), 5.19 (s, 4 H, C_5H_4), 5.84 (s, 4 H, C_5H_4); ^{13}C NMR (toluene-d_8, −50 °C) δ −7.2 (d, AgMe, $^1J_{AgC}$ = 120 Hz), 0.6 (SiMe$_3$), 32.0 (C*Me$_3$*), 113.2 (C_5H_4), 114.8 (C_5H_4).

(G) Synthesis of Compound 10. {[Ti](C$\equiv$CSiMe$_3$)$_2$}AgMe (**9a**) was dissolved in toluene-d_8 and was warmed from −30 °C to 0 °C in a NMR tube, and the formation of **10** was spectroscopically followed.

Data for 10: ^{1}H NMR (toluene-d_8, 0 °C) δ 0.25 (s, 18 H, SiMe$_3$), 0.29 (s, 36 H, SiMe$_3$), 5.84 (m, 4 H, C_5H_4), 5.95 (m, 4 H, C_5H_4), 6.12 (m, 4 H, C_5H_4), 6.56 (m, 4 H, C_5H_4).[6]

(H) Synthesis of Compound 11a. Br_2 (70 mg, 0.40 mmol) in diethyl ether (50 mL) was added in one portion to {[Ti](C$\equiv$C^{t}Bu)$_2$}CuMe (**7**) (230 mg, 0.40 mmol) at 0 °C. After stirring for 2 h at 0 °C all volatile materials were removed in a vacuum, and the residue was washed with 30 mL of *n*-pentane. Crystallization at −30 °C in tetrahydrofuran yielded **11a** (240 mg, 0.38 mmol, 97%) as a red solid.

Data for 11a: mp 205 °C (decomp); IR (KBr) ν(C$\equiv$C)/cm^{-1} 1974; ^{1}H NMR (CDCl$_3$) δ 0.27 (s, 18 H, SiMe$_3$), 1.47 (s, 18 H, ^{t}Bu), 6.07 (s, 8 H, C_5H_4); ^{13}C NMR (CDCl$_3$) δ 0.2 (SiMe$_3$), 31.3 (C*Me$_3$*), 32.3 (*C*Me$_3$), 114.3 (C_5H_4), 117.2 (C_5H_4), 120.6 (^{i}C−C_5H_4), 136.9 (Ti*C*$\equiv$C), 150.7 (TiC$\equiv$*C*); FD mass spectrum, *m*/*e* M$^+$, 628. Anal. Calcd for $C_{28}H_{44}BrCuSi_2Ti$ (628.16): C, 53.53; H, 7.06. Found: C, 53.88; H, 6.75.

X-ray Structure Determination of Compounds 4a, 5c, 6c, and 8b. The structures of compounds **4a**, **5c**, **6c**, and **8b** were determined from single-crystal X-ray diffraction data, which were collected using a Siemens R3m/V (Nicolet Syntex) diffractometer. Crystallographic data for **4a**, **5c**, **6c**, and **8b** are given in Table 3. All structures were solved by direct methods (*SHELXTL PLUS*; Sheldrick, G. M. University of Göttingen: Göttingen, Germany, 1988). An empirical absorption correction was applied. The structures were refined by the least-squares method based on F^2 with all reflections (*SHELXL 97*; Sheldrick, G. M. University of Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms, except the disordered SiMe$_3$ group in **6c** and the toluene molecule in **5c**, were refined anisotropically; the hydrogens were placed in calculated positions. The toluene molecule in **5c** is heavily disordered, which causes a high residual electron density close to C6S, C1S, and C2S. Based on its position in the unit cell the toluene molecule has to be refined with a site occupancy factor of 0.5. The structure plots have been made using *ZORTEP* (Zsolnai,L.; Huttner, G. University of Heidelberg: Germany, 1994).

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Hermann-Schlosser Stiftung, Degussa AG Frankfurt (K.K.), for financial support. We are grateful to Prof. Dr. Dr. h. c. H. W. Roesky for a generous gift of $BrC_6H_2(CF_3)_3$-2,4,6. We thank Th. Jannack for carrying out the MS measurements, Miss S. Ahrens for many discussions, and Miss K. Dörr for assistance in drawing up the manuscript.

Supporting Information Available: Tables of crystal data and structure refinement, bond lengths and bond angles, and anisotropic displacement factors for compounds **4a**, **5c**, **6c**, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9708687