

Monomeric Bis(η^2 -alkyne) Complexes of Copper(I) and Silver(I) with η^1 -Bonded Alkyl, Vinyl, and Aryl Ligands

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Abstract: Two synthetic routes to compounds $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{MR}$ (abbreviated as **[1•MR]**; M = Cu: R = Me (**5**), CH_2SiMe_3 (**6**), Et (**7**), ^iBu (**8**), $\text{C}(\text{H})=\text{CH}_2$ (**9**), $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ (**13**), $\text{C}_6\text{H}_4\text{Me-4}$ (**14**), $\text{C}_6\text{H}_4\text{OMe-4}$ (**15**), $\text{C}_6\text{H}_4\text{NMe}_2\text{-4}$ (**16**), C_6H_5 (**17**); M = Ag: R = $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ (**18**)) are described. These compounds contain monomeric MR entities, which are η^2 -bonded by both alkyne ligands of the organometallic 3-titanio-1,4-pentadiyne $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$ (**1**). The X-ray structures of **5**, **13**, and **18** have been solved. Crystals of **5** are monoclinic, space group $C2/c$, with $a = 19.477(1)$ Å, $b = 10.3622(6)$ Å, $c = 16.395(1)$ Å, $\beta = 95.287(5)^\circ$, $V = 3294.8(3)$ Å³, $Z = 4$, and final $R = 0.030$ for 3232 reflections with $F \geq 4\sigma(F)$ and 240 parameters. Crystals of **13** are orthorhombic, space group $Pbcn$, with $a = 12.4290(9)$ Å, $b = 19.8770(8)$ Å, $c = 15.532(1)$ Å, $V = 3837.2(4)$ Å³, $Z = 4$, and final $R = 0.026$ for 3082 reflections with $I \geq 2.5\sigma(I)$ and 217 parameters. The mesitylcopper compound **13** is isostructural with the mesitylsilver compound **18**, and crystals of **18** are orthorhombic, space group $Pbcn$, with $a = 12.47(3)$ Å, $b = 20.00(3)$ Å, $c = 15.53(3)$ Å, $V = 3873(13)$ Å³, $Z = 4$, and final $R = 0.055$ for 2068 reflections with $I \geq 2.5\sigma(I)$ and 188 parameters. All compounds contain a monomeric bis(η^2 -alkyne)M(η^1 -R) unit (M = Cu or Ag) in which the group 11 metal atom is trigonally coordinated by the bis(η^2 -alkyne) chelate **1** and an η^1 -bonded monoanionic organic ligand. A bonding description of the bis(η^2 -alkyne)M(η^1 -R) entity (M = Cu, Ag) is discussed. The alkylcopper compounds **5–8** decompose in solution either *via* nucleophilic substitution of one SiMe_3 group in **1** to eliminate RSiMe_3 or *via* β -hydride elimination (**7** and **8**) to eliminate the corresponding alkene, whereas arylcopper compounds **14–17**, which lack *ortho*-substituents rearrange in solution *via* addition of the monomeric arylcopper entity to one of the alkynes within **[1•CuR]** to yield unstable 1,1-bimetallaalkene complexes. When R is the monoanionic terdentate ligand $\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}$, the coordination complex **[1•CuR]** is not isolated, while the corresponding addition product is favored. The X-ray structure of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)\text{-}\{\mu\text{-C}=\text{C}(\text{SiMe}_3)(\text{R})\}\text{Cu}]$, **22**, which is a rare example of a 1,1-bimetallaalkene, has been solved. Crystals of **22** are pseudomerohedrally twinned and monoclinic, space group $P2_1/c$, with $a = 31.05(2)$ Å, $b = 14.323(3)$ Å, $c = 20.014(8)$ Å, $\beta = 108.53(5)^\circ$, $V = 8440(7)$ Å³, $Z = 8$, and final $R = 0.1233$ for 8564 reflections with $F > 4\sigma(F)$ and 462 parameters.

Introduction

Organocopper(I) and -silver(I) compounds CuR and AgR (R = alkyl,¹ alkenyl,² alkynyl,³ aryl⁴), as well as inorganic copper(I) and silver(I) salts CuX and AgX (X = alkoxide,⁵ phenoxide,⁶

thiolate,⁷ amide,⁸ etc.), are generally encountered as polynuclear species, which exist either as discrete aggregates or as polymers. Conversion of these aggregates and polymers into neutral structural units with a lower nuclearity can be achieved either by using R groups with steric constraints or by the application of suitable Lewis bases,^{9,10} while N, P, O, or S donors as well as alkynes have been reported to stabilize cationic copper(I) and silver(I) monomers.¹¹ Although a number of anionic mononuclear cuprate structures $[\text{CuR}_2]^-$ have been reported,¹²

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(1) Alkylcoppers. $[\text{CuCH}_2\text{SiMe}_3]_4$: (a) Jarvis, J. A. J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 999. (< -15 °C) $[\text{CuMe}]_\infty$ and (< -15 °C) CuEt : (b) Gilman, H.; Jones, R. G.; Woods, L. A. *J. Org. Chem.* **1952**, *17*, 1630–1634. (< -15 °C) CuEt : (c) Costa, G.; DeAlti, G.; Stefanie, L.; Boscarato, G. *Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis. Mat. Nat.* **1961**, *31* (8), 267. CuMe , Et, Pr (-78 to -50 °C) from R_2Zn : (d) Thiele, K. H.; Köhler, J. *J. Organomet. Chem.* **1968**, *12*, 225. (80 °C) $\text{CuC}(\text{CF}_3)_3$: (e) Cairncross, A.; Sheppard, W. A. *J. Am. Chem. Soc.* **1968**, *90*, 2186.

(2) Alkenylcoppers. (< -40 °C) $\text{CuC}(\text{H})=\text{CH}_2$: (a) Kaufman, T.; Sahm, W. *Angew. Chem.* **1967**, *79*, 101. (b) Whitesides, G. M.; Casey, C. P. *J. Am. Chem. Soc.* **1966**, *88*, 4541. (c) Nilsson, M.; Wahren, R. *J. Organomet. Chem.* **1969**, *16*, 515.

(3) Alkynylcoppers. (a) For a review on metal alkynyls, see: Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89–124. $[\text{Cu}(\text{C}\equiv\text{CPh})(\text{PMe}_3)]$: (c) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *20*, 502–508. $[\text{Cu}_3(\mu^3\text{-}\eta^1\text{-C}\equiv\text{CPh})_2(\text{dppm})_3]\text{BF}_4$ and $[\text{Cu}_3(\mu^3\text{-}\eta^1\text{-C}\equiv\text{CPh})(\text{dppm})_3](\text{BF}_4)_2$: (d) Diez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Aguirre, A.; García-Granda, S. *Organometallics* **1993**, *12*, 2213–2220. $[\text{Cu}_3(\mu^3\text{-}\eta^1\text{-C}\equiv\text{C}^i\text{Bu})(\mu^3\text{-Cl})(\text{dppm})_3]\text{PF}_6$: (e) Yam, V. W.-W.; Lee, W.-K.; Lai, T.-F. *Organometallics* **1993**, *12*, 2383–2387. $[\text{Cu}_3(\text{SAR})_2\text{C}\equiv\text{C}^i\text{Bu}]_2$: (f) Knotter, D. M.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1992**, *11*, 4083–4090. $[\text{CuC}\equiv\text{CPh}]_\infty$: (g) Corfield, P. W. R.; Shearer, H. M. M. In *Organometallic Compounds*; Coates, G. E., Green, M. L. H., Wade, K., Eds.; Chapman and Hall: London, 1977; Vol. 2. $[\text{CuC}\equiv\text{C}^i\text{Bu}]_n$ (M = Cu, Ag): (i) Haszeldine, R. N. *J. Chem. Soc.* **1951**, 588–591. (k) Royer, E. C.; Barral, M. C.; Moreno, V.; Santos, A. *J. Inorg. Nucl. Chem.* **1981**, *43*, 705–709.

there are very few reports dealing with the formation of neutral mononuclear organocopper(I) and organosilver(I) species, e.g., $(\text{Ph}_3\text{P})_3\text{CuMe}$,^{10a} $\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{CuPh}$,^{10b} and $[(\text{Me}_2\text{S})\text{Cu}(\text{C}_6\text{H}_2^1\text{Bu}_3-2,4,6)]$.^{10c} As a consequence considerable interest exists in the formation as well as the nature of monomeric, η^1 -bonded organocopper(I) and organosilver(I) complexes, as these are basic building blocks of higher aggregates. Information on these points may facilitate the understanding of the structural features and reactivity of the polynuclear counterparts.

Recently, we have found that the organometallic 1,4-diyne complex $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$ (**1**) can be successfully applied to stabilize monomeric inorganic MX entities (M = Cu, Ag; X = halide, pseudohalide, and arenethiolate).^{13a} Moreover, we have reported similar complexes of **1** in which X is an η^1 -bonded alkynyl ligand,^{13b} and have briefly communicated on species in which X is an η^1 -bonded aryl group (i.e., mesityl, $\text{C}_6\text{H}_2\text{Me}_3-2,4,6$).^{13c} In the resulting species $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{MX}$ (abbreviated as $[\mathbf{1}\cdot\text{MX}]$), both alkyne groups of the bis(alkynyl)titanocene fragment coordinate to the copper or silver atom in an η^2 -fashion. These compounds possess a high order of symmetry: i.e., a 2-fold rotation axis

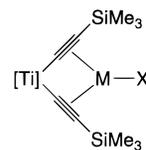


Figure 1. Schematic structure of $[\mathbf{1}\cdot\text{MX}]$. $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$ is abbreviated as [Ti].

runs through the titanium atom and the group 11 metal center as well as through the connecting atom of the ligand X as a result of the symmetric bis(η^2 -chelate) bonding of the two alkynes to the group 11 metal atom (Figure 1). The ligand X in these systems is η^1 -bonded to the copper or silver atom, resulting in a trigonally planar environment of these metal centers.¹³

In the present study we investigate the influence of the nature of an organic ligand R which is $\sigma\text{-C-M}$ bonded on the formation and stability of the complexes $[\mathbf{1}\cdot\text{MR}]$. The successful synthesis of such species provides materials which for the first time afford structural information concerning the binding of methyl, ethyl, butyl, vinyl, and substituted phenyl groups to a group 11 metal atom in a consistent series of three-coordinate, monomeric, organocopper species $[(\eta^2\text{-alkyne})_2\text{-CuR}]$, and this allows a more detailed bonding description of both the η^1 -copper-carbon bond and the η^2 -alkyne-to-copper bonding. Moreover, it has proved possible to follow not only the decomposition of monomeric $[\mathbf{1}\cdot\text{Cu}(\eta^1\text{-alkyl})]$ complexes via either nucleophilic substitution or β -hydride elimination, but also the decomposition of $[\mathbf{1}\cdot\text{Cu}(\eta^1\text{-aryl})]$ complexes via intramolecular addition that generates novel 1,1-bimetalloalkenyl species.

Results

Two routes have been applied for the synthesis of compounds $[\mathbf{1}\cdot\text{MR}]$ (R = η^1 -bonded organic ligand): (i) the reaction of the bis(alkynyl)titanocene $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$

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(5) Alkoxide. $[\text{CuO}^i\text{Bu}]_4$: (a) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142. $[\text{CuO}^i\text{Bu}(\text{PPh}_3)]_2$: (b) Lemmen, T. H.; Goeden, G. V.; Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3680–3685. $[\text{CuOSiPh}_3]_4$: (c) Cited in Coan, P. S.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 4207–4209. $[(\text{L})\text{Cu}(\text{OCH}_2\text{CH}_2\text{OMe})]_4$: (d) Bidell, W.; Shklover, V.; Berke, H. *Inorg. Chem.* **1992**, *31*, 5561.

(6) Phenoxide: (a) Knotter, D. M.; Wehman, E.; Spek, A. L.; Stam, C. H.; van Koten, G. To be published. (b) Wehman, E.; van Koten, G.; Knotter, D. M.; Erkamp, C. J. M.; Mali, A. N. S.; Stam, C. H. *Recl. Chim. Pays-Bas* **1987**, *106*, 370. (c) Paul, P. P.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 6331–6332.

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(10) Monomeric Lewis base species. $(\text{Ph}_3\text{P})_3\text{CuMe}$: (a) Coan, P. S.; Foltling, K.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1989**, *8*, 2724–2728. $\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{CuPh}$: (b) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1984**, *3*, 1444–1445. $(\text{Me}_2\text{S})\text{Cu}(\text{C}_6\text{H}_2^1\text{Bu}_3-2,4,6)$: (c) He, X.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 9668–9670. $(\text{Ph}_3\text{P}=\text{CH}_2)\text{Ag}(\text{C}_6\text{F}_5)$: (d) Uson, R.; Laguna, A.; Uson, A.; Jones, P. G.; Meyer-Base, K. *J. Chem. Soc., Dalton Trans.* **1988**, 341–345.

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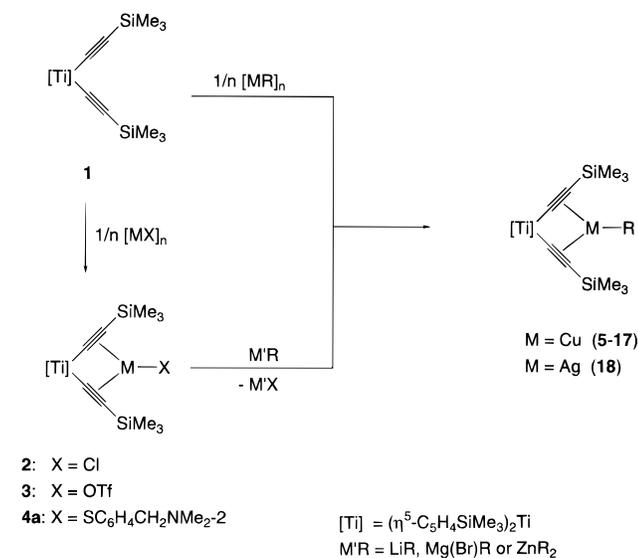
(12) $[\text{CuMes}_2]^-$: (a) Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240–241. $[\text{Cu}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$: (b) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1985**, *263*, C23–C25. $[\text{CuMe}_2]^-$, $[\text{CuPh}_2]^-$, and $[\text{Cu}(\text{Br})\{\text{CH}(\text{SiMe}_3)_2\}_2]^-$: (c) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337–4338.

(13) (a) Janssen, M. D.; Herres, M.; Zsolnai, L.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *Inorg. Chem.*, in press. (b) Janssen, M. D.; Herres, M.; Zsolnai, L.; Grove, D. M.; Spek, A. L.; Lang, H.; van Koten, G. *Organometallics* **1995**, *14*, 1098–1100. (c) Janssen, M. D.; Herres, M.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1995**, 925–926.

Table 1. Complexes [1·MR] and Compounds [MR]_n

compd number	MR	[1·MR]	[MR] _n		ref
		<i>T</i> _{dec} (°C) ^a	<i>T</i> _{dec} (°C) ^a	<i>n</i>	
		Alkylcoppers			
5	CuMe ^b	143 [†]	< -15	∞	1b
6	CuCH ₂ SiMe ₃	115 [†]	78–79	4	1a
7	CuEt	±0 (soln)	<< -15	∞	1b,c
8	Cu ⁿ Bu	±0 (soln)	< -50 ^c	∞	1b–d
		Alkenylcoppers			
9	CuC(H)=CH ₂	±0 (soln)	-40 (soln)		2
		Alkynylcoppers			
10	CuC≡CSiMe ₃	121 [†]	> 200 ^d	8	3
11	CuC≡C ⁿ Bu	132 [†]	> 200 ^d	8	3h
12	CuC≡CPh	163 [†]	> 200 ^d	∞	3g
		Arylcoppers			
13	CuMes ^e	124 [†]	100	5	4d,e
14	CuC ₆ H ₄ CH ₃ -4	73 [†]	110–120	4	4h
15	CuC ₆ H ₄ OMe-4	98 [†]	<i>f</i>		
16	CuC ₆ H ₄ NMe ₂ -4	82 [†]	117–120	∞	4k
17	CuC ₆ H ₅	±0 (soln)	100	∞	4g,h
		Arylsilvers			
18	AgMes ^e	119 [†]	<i>f</i>	4	4d

^a When the decomposition temperature (*T*_{dec}) is known, its value is stated; in other cases the melting point is given and annotated with †. Compounds determined in solution are annotated (soln). ^b Solid CuMe is *explosive!* ^c Unknown, but below -50 °C as extrapolated from CuⁿPr (ref 1d). ^d Alkynylcopper compounds are thermally stable: e.g., CuC≡C-*cyclo*-C₆H₁₁ decomposes above 200 °C in ref 3k. ^e Mes = mesityl (C₆H₂Me₃-2,4,6). ^f Unknown.

Scheme 1. Synthesis of Compounds [1·MR]

(1)^{14a} with an equimolar amount of organocopper(I) or organosilver(I) compounds (CuR or AgR) and (ii) the reaction of complexed monomeric CuX and AgX entities, [1·MX] (X = Cl (2), OTf (= OSO₂CF₃) (3), or SC₆H₄CH₂NMe₂-2 (4a))^{13a} with suitable organometallic reagents (Scheme 1). The newly prepared compounds [1·MR] (5–18) as well as the related parent species [MR]_n are listed in Table 1 together with information on their stability.

The reaction of the bis(alkynyl)titanocene [(η⁵-C₅H₄SiMe₃)₂-Ti(C≡CSiMe₃)₂] (1)^{14a} with equimolar amounts (based on Cu or Ag) of organocopper(I) or organosilver(I) compounds (CuR or AgR) in THF, Et₂O, benzene, or toluene at 25 °C affords in moderate to high yields (30–84%) the corresponding monomeric complexes [1·MR] (M = Cu, 5, 6, 10–17). This direct preparative route (Scheme 1) is successful for the copper series not only with alkynyl groups (10–12) and aryl groups (13–17), but also with the (trimethylsilyl)methyl group (6) and when

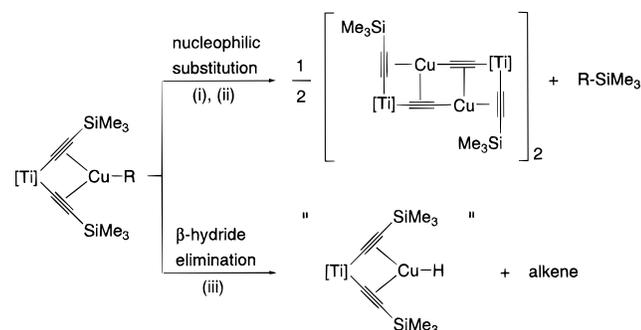
special precautions are taken also with a methyl group (5; **WARNING: CuMe is explosive!**). This direct pathway from 1 using an organosilver compound has also been successfully applied for the synthesis of 18 (MR = AgMes). This direct route to complexes [1·MR], although straightforward, relies on the availability of pure [MR]_n species, but since the arylcopper starting materials for the synthesis of 14–17 can contain copper bromide,^{4k} it is necessary to separate the product from the byproduct [1·CuBr] either by extraction or by recrystallization.

An alternative transmetalation route to organocopper complexes [1·CuR] is the reaction of the preformed complexes [1·CuX] (X = Cl (2), OTf (3), SC₆H₄CH₂NMe₂-2 (4a))^{13a} with an organometallic reagent M'R (M'R = LiR, Mg(Br)R, or ZnR₂), and with this route, one can obtain 5–17 in almost quantitative yield (Scheme 1). This transmetalation route avoids the problem due to traces of CuBr as encountered in the direct preparative route. An additional advantage of this transmetalation route is that compounds 5 (R = Me) and 7–9 (R = Et, ⁿBu, C(H)=CH₂) are now accessible; the organocopper compounds CuMe, CuEt, CuⁿBu, and CuC(H)=CH₂ are thermally unstable or very reactive and make the direct route difficult.

An important observation was the efficacy of the bis(η²-alkyne)copper(I) arenethiolate species 4a (X = SC₆H₄CH₂-NMe₂-2) as starting material for the preparation of 5–17 in this transmetalation route. While 4a as well as the products 5–17 are nicely soluble in polar and apolar solvents, the lithium, magnesium, or zinc arenethiolate species also formed in this route are insoluble in apolar solvents and can be easily separated. The presence of the *o*-[(dimethylamino)methyl] substituent is not important for the outcome of the reaction as similar results were obtained when other arenethiolate ligands were applied, i.e., X = SC₆H₄NMe₂-2 (4b), SC₆H₅ (4c), and S-1-C₁₀H₆NMe₂-8 (4d).^{13a}

In the new compounds 5–18 the bis(alkynyl)titanocene ligand 1 is chelate-bonded to the metal atom of a single organocopper or organosilver entity (CuR or AgR). Moreover, 5–18 are monomeric species in the solid state, and in solution we have found no evidence for the existence of equilibria between [1·MR] and aggregates [MR]_n. The copper complexes 5–17 have been isolated as orange to deep red crystalline solids, while

(14) (a) Lang, H.; Seyferth, D. Z. *Naturforsch.* **1990**, *45b*, 212–220. For the synthesis of related (η⁵-C₅H₅)₂Ti(C≡CSiMe₃)₂ see also: (b) Wood, G. L.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382–384.

Scheme 2. Decomposition of Alkyl- and Alkynylcopper Complexes [**1**·CuR] ($(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$ Abbreviated as [Ti])


- i: R = Me (25 °C), Et (-20 °C), Buⁿ (-20 °C), CH₂SiMe₃ (-20 °C); Bimolecular, slow
 ii: R = C≡CSiMe₃, C≡CBu^t, C≡CPh; Buⁿ, NF or NaOEt, 25 °C, Et₂O
 iii: R = Et, Buⁿ; 25 °C, Et₂O or benzene

mesitylsilver complex **18** is deep purple. These complexes are soluble in most common organic solvents.

The alkylcopper complexes **5–8** have a remarkably increased thermal stability when compared to their parent pure organocopper aggregates [CuR]_n. For example, whereas solid [CuMe]_∞ decomposes *explosively* above -15 °C, [**1**·CuMe] (**5**) melts at 143 °C with decomposition. Furthermore, the ethylcopper and butylcopper derivatives **7** and **8** can be safely isolated as solids at 25 °C, unlike the pure organocoppers which can only be handled below -50 °C.^{1b-d} In solution, however, the alkylcopper species **6–8** are less stable and at -20 °C, as described below, form the dimeric complex $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{CCu})]_2$.^{13b}

Similarly, although pure vinylcopper has so far not been isolated and can only be handled in solution at temperatures below -40 °C,² we find that vinylcopper species **9** is stable at 25 °C both in solution and in the solid state for several hours.

In itself, the good thermal stability of the alkynylcopper derivatives [**1**·CuC≡CR'] (**10–12**) might appear less remarkable, since aggregates [CuC≡CR']_n (R' = organic group) are also known to possess a high thermal stability. An interesting aspect of these complexes is that they react with nucleophiles in solution to form the dimeric titanium copper acetylide $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{CCu})]_2$ (*vide infra*, Scheme 2).^{13b}

Of the arylcopper species **13–17**, the mesitylcopper complex **13** has a remarkable stability (mp 124 °C), and it is also stable to air as a solid for several months. Its silver analogue **18** shows a similar solid state stability, but its solutions are slightly photosensitive even though the solid showed no visible change on exposure to light. However, the arylcopper complexes **14–17** which lack *ortho*-substituents are much less stable than **13** and when in solution they decompose within 2 h at 25 °C *via* addition of the monomeric CuR entity across one of the alkyne units within the complex [**1**·CuR] (*vide infra*, Scheme 3). At -20 °C, this reaction is effectively stopped, and solutions of **14–17** are then stable for several days.

Solid State Structures of the Methylcopper, Mesitylcopper, and Mesitylsilver Compounds 5, 13, and 18. The molecular structures in the solid state of **5**, **13**, and **18** have been established by X-ray diffraction analyses; selected geometrical details are listed in Tables 2 and 3.

The molecular structures of **5**, **13**, and **18** (Figures 2–4) show them to be isostructural monomeric species [**1**·MR], comprising the bis(η^2 -alkyne) chelate **1** and either a single organocopper or organosilver unit. The group 11 metal atom is η^1 -bonded to the organic methyl or mesityl entity and chelate bonded by the Ti(C≡CSiMe₃)₂ moiety. The Ti(C≡CSiMe₃)₂M (M = Cu, Ag)

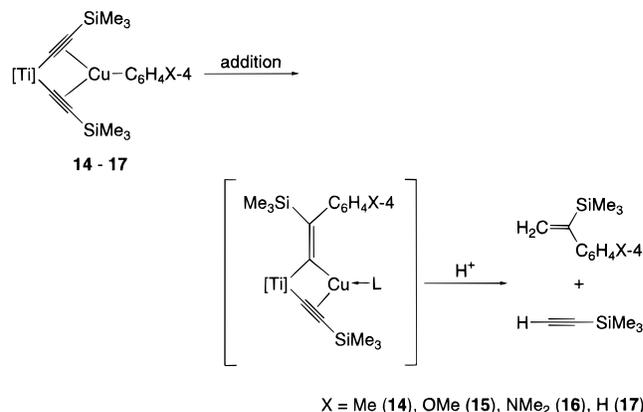
Scheme 3. Addition of Bis(η^2 -alkyne)copper(η^1 -C₆H₄X-4) Compounds **14–17**.


Table 2. Selected Geometrical Details of Compound **5**^a

Bond Distances (Å)			
Ti···Cu	2.9645(5)	Cu-C2	2.0802(18)
Cu-C14	1.966(2)	Ti-C1	2.0752(16)
Cu-C1	2.0763(16)	C1-C2	1.247(3)
Bond Angles (deg) ^d			
C1-Ti-C1 ^A	88.89(6)	Ti-Cu-C14	180 ^b
Ti-C1-C2	163.70(14)	mid-Cu-mid ^A	123.75(5) ^c
C1-C2-Si1	158.51(16)		

^a The estimated standard deviations of the last significant digits are shown in parentheses. ^b As defined by the space group *C2/c*. ^c mid is defined as the midpoint of C1-C2. ^d Note: from (x, y, z), A = (-x, y, 0.5 - z).

Table 3. Selected Geometrical Details of Compounds **13** and **18**^a

13		18	
Bond Distances (Å)			
Ti···Cu	2.9418(5)	Ti···Ag	3.104(7)
Cu-C14	1.947(2)	Ag-C14	2.099(5)
Cu-C1	2.064(2)	Ag-C1	2.270(9)
Cu-C2	2.082(2)	Ag-C2	2.305(9)
Ti-C1	2.078(2)	Ti-C1	2.090(8)
C1-C2	1.250(2)	C1-C2	1.24(1)
Bond Angles (deg) ^d			
C1-Ti-C1 ^A	89.11(6)	C1-Ti-C1 ^A	94.0(3)
Ti-C1-C2	163.7(1)	Ti-C1-C2	166.6(6)
C1-C2-Si1	155.5(2)	C1-C2-Si1	162.9(7)
Ti-Cu-C14	180 ^b	Ti-Ag-C14	180 ^b
mid-Cu-mid ^A	125.14(5) ^c	mid-Ag-mid ^A	116.2(2) ^c

^a The estimated standard deviations of the last significant digits are shown in parentheses. ^b As determined by the space group *Pbcn*. ^c mid is defined as the midpoint of C1-C2. ^d Note: from (x, y, z), A = (-x, y, 0.5 - z).

entity and the metal-bonded carbon atom of the η^1 -bonded organic ligand are in the same plane which results in a trigonally planar geometry of the group 11 metal. Consequently, the structures contain a crystallographic 2-fold rotation axis that runs through Ti1, the group 11 metal, and the η^1 -bonded organic ligand (C14 for **5** and the *ipso* (C14), *para* (C17), and *p*-Me (C19) carbon atoms for **13** and **18**). The plane of the η^1 -bonded mesityl ligand in both **13** and **18** is almost perpendicular to the Ti(C≡CSiMe₃)₂M (M = Cu, Ag) plane (the interplane angle is 84.0(1)° for **13** and 86.8(5)° for **18**).

It is noticeable that the η^2 -alkyne coordination results in C≡C bond lengthening from 1.203(9) and 1.214(6) Å in the parent bis(alkynyl)titanocene **1**¹⁵ to 1.247(3) Å in **5**, 1.250(2) Å in **13**, and 1.24(1) Å in **18**. In addition, a significant change of the

(15) (a) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, 409, C7-C11. (b) Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1994**, 12, 5008-5011.

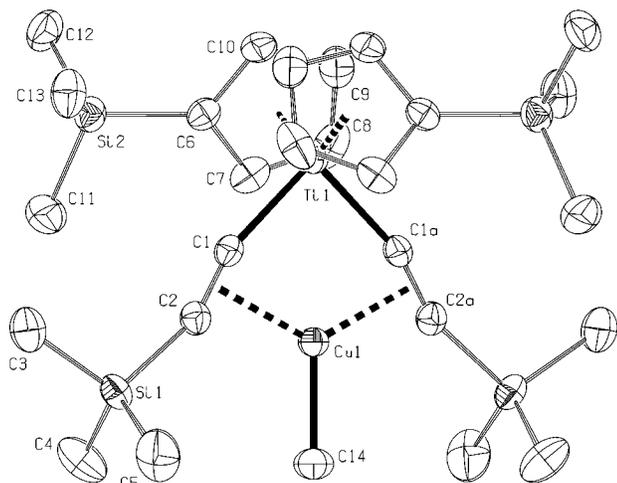


Figure 2. ORTEP drawing (drawn at 50% probability level) of [1·CuMe] (**5**) (with the exclusion of the hydrogen atoms) with the adopted atom-labeling scheme.

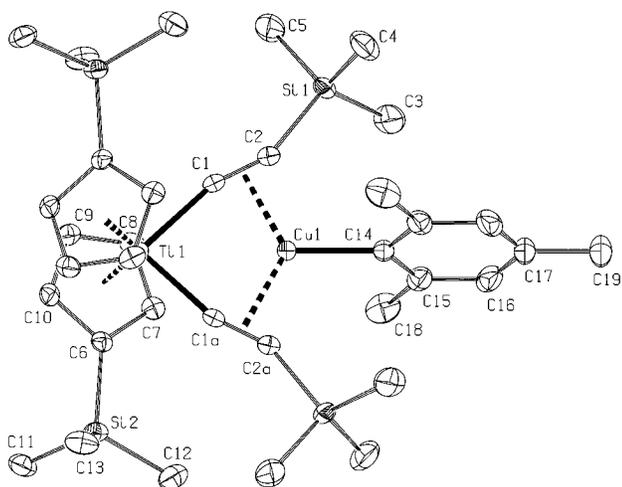


Figure 3. ORTEP drawing (drawn at 50% probability level) of [1·CuC₆H₂Me₃-2,4,6] (**13**) (with the exclusion of the hydrogen atoms) with the adopted atom-labeling scheme.

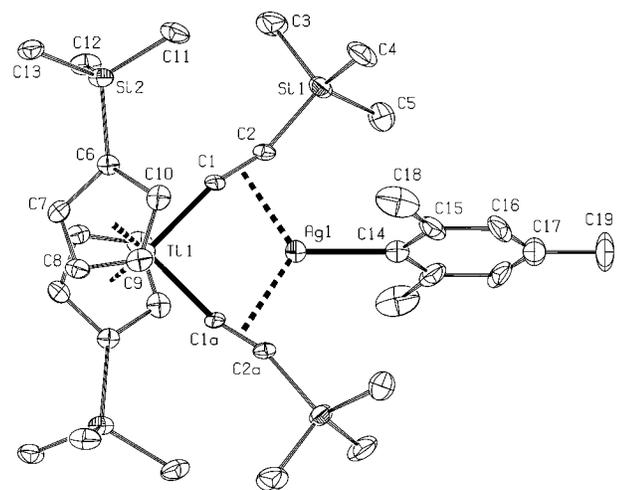


Figure 4. ORTEP drawing (drawn at 50% probability level) of [1·AgC₆H₂Me₃-2,4,6] (**18**) (with the exclusion of the hydrogen atoms) with the adopted atom-labeling scheme.

initially linear arrangement of the Ti—C≡C—Si units is observed. While the Ti—C—C and C—C—Si angles are 177 and 176.5°, respectively, in **1**,¹⁵ these angles become 163.7(1) and 158.5(2)°, respectively, in **5**, 163.7(1) and 155.5(2)°, respectively, in **13**, and 166.6(6) and 162.9(7)°, respectively,

in **18**. The Ti···Cu distances of 2.9645(5) Å in **5** and 2.9418(5) Å in **13** as well as the Ti···Ag distance of 3.104(7) Å in **18** are relatively short, but considered to be nonbonding (as detailed below).¹⁶

¹H and ¹³C NMR Studies. The ¹H NMR spectra of **5–18** in benzene-*d*₆ consist of sharp and well-resolved signals for each of the groupings present: *i.e.*, two singlets for the C≡CSiMe₃ and C₅H₄SiMe₃ trimethylsilyl protons, two pseudotriplets for the C₅H₄SiMe₃ cyclopentadienyl protons, and well-defined single proton patterns for the organic ligands R. The ¹³C{¹H} NMR spectra also show a single pattern consisting of sharp and well-resolved signals: two signals for the C≡CSiMe₃ and C₅H₄SiMe₃ methyl groups, three signals for the CH and C_{ipso} of the C₅H₄SiMe₃ entities, two signals for the alkyne carbon atoms of the Ti—C≡C—Si unit, and the expected signals for the organic ligand R. Noticeable features in the ¹H NMR spectrum of **9** are the vinyl signals, comprising three well-separated AB patterns at 5.96, 6.82 (CH₂), and 7.77 ppm (CuCH) with *J*_{trans} = 19.6 Hz, *J*_{cis} = 12.5 Hz, and *J*_{gem} = 3.4 Hz.

The ¹H and ¹³C NMR spectral patterns of **5–18** in toluene-*d*₈ are essentially temperature independent in the range of 200–317 K, and these data are consistent with a monomeric structure for these species in solution. This conclusion has been corroborated by cryoscopic molecular weight determination in benzene that showed **5** and **13** to be monomeric in this solvent; *i.e.*, the monomeric structures found in the solid state are retained in solution.

Upon the η^2 -coordination of the alkyne ligands to the copper or silver atoms in [1·MR], **5–18**, the signals of the C_α and C_β atoms in the Ti—C≡C entity (at 172.5 and 134.5 ppm in **1**) shift downfield for C_α and upfield for C_β (selected data of **5–18** are listed in Table 4).

In the case of the mesitylsilver complex **18**, direct information concerning the Ag—C interaction can be obtained from the ¹³C NMR spectra since on the C_{ipso}(mesityl) and the C_α and C_β alkyne resonances a Ag—C coupling is observed.¹⁷ This information directly corroborates that the mononuclear bis(η^2 -alkyne)(η^1 -mesityl)silver structure, as is observed in the solid state, is retained in solution and that the mesityl group is not involved in interaggregate exchange processes. The C_{ipso}(mesityl) resonance at 168.3 ppm appears as two doublets due to coupling with ¹⁰⁷Ag and ¹⁰⁹Ag: ¹*J*(¹⁰⁷Ag, ¹³C) = 142 Hz and ¹*J*(¹⁰⁹Ag, ¹³C) = 164 Hz,^{17b} while the C_α and C_β of the η^2 -bonded alkyne ligands at 184.5 and 125.8 ppm are doublets resulting from ¹*J*(^{107,109}Ag, ¹³C) values of 3 and 7 Hz, respectively. There is a ³*J*(^{107,109}Ag, ¹³C) of 7 Hz also present on the signal of the hydrogen-bearing aryl (mesityl) carbon atoms.

These data are the first ^{107,109}Ag coupling constant values for an η^1 -two-electron two-center silver—carbon bond. Examples of ¹*J*(¹⁰⁷Ag, ¹³C) and ¹*J*(¹⁰⁹Ag, ¹³C) values have been reported for two-electron three-center bonded arylsilver compounds, namely, 118.3 and 136.0 Hz, respectively, in [Ag₂Li₂(C₆H₄CH₂NMe₂-2)₄] and 115 and 132 Hz, respectively, in [Ag₂Li₂(C₆H₅)₄].¹⁸ The larger Ag—C coupling constant we find

(16) The alkyne ligands are each donating 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. (b) Villacorta, G. M.; Gibson, D.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6732. (c) Lang, H.; Köhler, K.; Zsolnai, L. To be published. (d) Aalten, H. L.; van Koten, G.; Riethorst, E.; Stam, C. H. *Inorg. Chem.* **1989**, *28*, 4140–4146.

(17) (a) Resonance frequencies of ¹⁰⁷Ag and ¹⁰⁹Ag at 4.6975 T are 8.093 and 9.304 MHz, respectively. (b) Natural abundance: ¹⁰⁷Ag (*I* = 1/2) 51.8%, ¹⁰⁹Ag (*I* = 1/2) 48.2%.

(18) (a) Leusink, A. J.; van Koten, G.; Marsman, J. W.; Noltes, J. G. *J. Organomet. Chem.* **1973**, *55*, 419–425. (b) Blenkins, J.; Hofstee, H. K.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1979**, *168*, 251–258.

Table 4. Selected Spectroscopic and Crystallographic Data of [1•MR] (5–18)^a

compd	MR	IR $\nu_{C\equiv C}$ (cm ⁻¹)	¹³ C NMR		X-ray	
			$\delta_{Ti-C\equiv}$ (ppm)	δ_{C-Si} (ppm)	Ti-C≡C (deg)	C≡C-Si (deg)
1	<i>b</i>	2012	172.5	135.4	175.8(4) 178.2(5)	174.8(4) 178.3(5)
			Alkylcoppers			
5	CuMe	1867	203.6	123.4	163.7(1)	158.5(2)
6	CuCH ₂ SiMe ₃	1930	202.9	125.3		
7	CuEt	1857	<i>c</i>	<i>c</i>		
8	Cu ⁿ Bu	1851	<i>c</i>	<i>c</i>		
			Alkenylcoppers			
9	CuC(H)=CH ₂	1868	199.3	125.3		
			Alkynylcoppers			
10	CuC≡CSiMe ₃	1896	183.7	129.0	165.0(3) 165.4(4)	162.8(3) 162.9(4)
11	CuC≡C ^t Bu	1902	183.1 ^d	128.6 ^d		
12	CuC≡CPh	1897	183.1	125.3		
			Arylcoppers			
13	CuMes ^e	1856	201.8	125.0	163.7(1)	155.5(2)
14	CuC ₆ H ₄ Me-4	1862	199.3	125.9		
15	CuC ₆ H ₄ OMe-4	1865	199.1	126.0		
16	CuC ₆ H ₄ NMe ₂ -4	1863	200.1	125.7		
17	CuC ₆ H ₅	1861	199.0	126.0		
			Arylsilvers			
18	AgMes ^e	1902	184.5 ^f	125.8 ^g	166.6(6)	162.9(7)

^a IR in KBr, NMR in C₆D₆. ^b (η^5 -C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)₂; see ref 14a. ^c Decomposes. ^d In CDCl₃. ^e Mes = C₆H₂Me₃-2,4,6. ^f Doublet, *J*(Ag, C) = 3 Hz. ^g Doublet, *J*(Ag, C) = 7 Hz.

Table 5. Selected Spectroscopic and Crystallographic Data of [1•MX] (2–4, 19–21)^a

compd	MX	IR $\nu_{C\equiv C}$ (cm ⁻¹)	¹³ C NMR		X-ray	
			$\delta_{Ti-C\equiv}$ (ppm)	δ_{C-Si} (ppm)	Ti-C≡C (deg)	C≡C-Si (deg)
			Copper Salts			
2	CuCl	1918	169.3 ^b	134.5 ^b		
3	CuOTf ^c	1923	162.2	140.2	166.7(3) 166.9(3)	156.8(4) 158.0(4)
4a	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)
4b	CuSC ₆ H ₄ NMe ₂ -2	1897	180.4	136.2		
4c	CuSC ₆ H ₅	1908	179.5	133.2		
4d	CuS-1-C ₁₀ H ₆ NMe ₂ -8	1893	182.8	133.1		
19	CuOC(O)Me	1901	170.9 ^b	132.4 ^b	163.6(9) 166(1)	164(1) 165(1)
20	Cu(acac) ^d	1919	171.2 ^b	132.1 ^b	165.8(3) 164.7(3)	163.8(3) 164.9(3)
			Silver Salts			
21	AgOTf ^c	1956	151.8 ^e	144.8 ^e	170.8(5) 172.7(5)	163.7(6) 170.2(5)

^a IR in KBr, NMR in C₆D₆. ^b In CDCl₃. ^c OTf = OSO₂CF₃. ^d acac = acetylacetonate. ^e In CD₂Cl₂.

in **18** reflects the anticipated higher degree of s-orbital participation in the silver-to-carbon bond.

IR Studies. The IR spectra of **5–18** show only one C≡C stretching vibration, which is found in the region 1960–1850 cm⁻¹ (Table 4); cf. the $\nu_{C\equiv C}$ of 2012 cm⁻¹ in **1**.^{14a} This shifting of $\nu_{C\equiv C}$ to lower frequencies upon η^2 -coordination to the MR entity in [1•MR] is similar to that generally observed for π -bonding of alkynes to copper(I) moieties in which the alkyne is acting as a two-electron donor.¹⁶ Moreover, changing the monoanionic ligand R in [1•MR] from a poor σ -donor (e.g., OTf) to a stronger σ -donor (e.g., mesityl) shows a distinct shift of the C≡C stretching vibration to lower frequencies (Table 4); selected spectroscopic data of inorganic complexes [1•MX] (**2–4** and **19–21**) are listed in Table 5. Unfortunately, in the series [1•CuC₆H₄X-4] (**14–17**) the range of inductive and mesomeric effects is too narrow to make a Hammett correlation meaningful.

Relation between the Nonlinearity of Ti-C≡C-Si and the C≡C Stretching Frequency. From this study there are two important aspects with respect to η^2 -bonding of the Ti-

(C≡CSiMe₃)₂ entity to the group 11 metal atom that are worth mentioning. First, there is a C≡C bond lengthening in the series going from **1** to **5**, **13**, and **18** (*vide supra*), and secondly, the Ti-C≡C-Si moieties in **5**, **13**, and **18** are bent from their linear arrangement in **1** (*vide supra*; see also Table 4). With respect to the latter reduction in Ti-C-C and C-C-Si angles, the whole series [1•CuX] (where X is either an organic or an inorganic ligand) shows a trend: stronger σ -donating properties of the ligand X result in a consistently larger decrease of the Ti-C-C and C-C-Si angles (Tables 4 and 5).

Relation between ¹³C Chemical Shift and C≡C Stretching Frequency. Changing the σ -donating capacity of the ligand X in [1•MX] (M = Cu, Ag) is also nicely reflected in the ¹³C chemical shift of the alkyne carbon atoms: upon changing the monoanionic ligand X from a weak σ -donor (e.g., OTf) to a stronger σ -donor (e.g., Mes) the C_α (Ti-C≡C) signal moves downfield while the C_β (Ti-C≡C) signal moves upfield. Moreover, the ¹³C chemical shift and the C≡C stretching frequency of **2–21** do appear to show a correlation as depicted in Figure 5 (Tables 4 and 5).

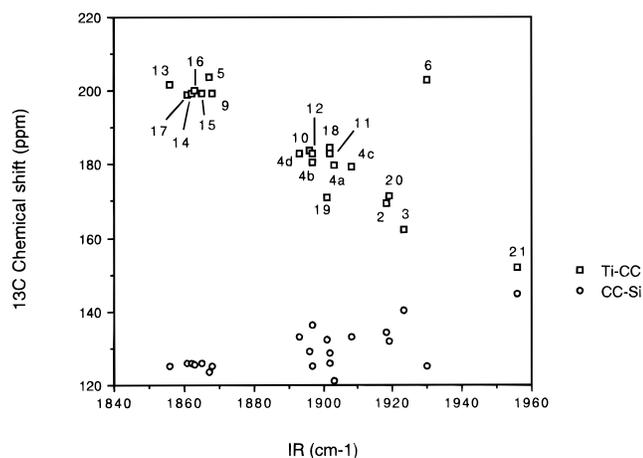


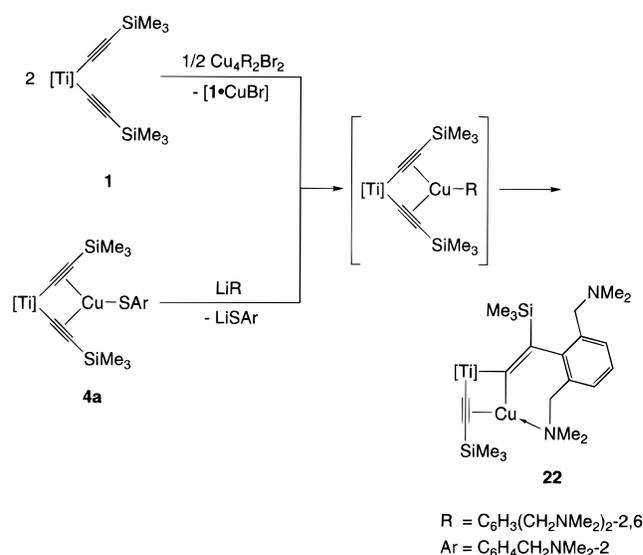
Figure 5. Correlation between the ^{13}C chemical shift data (C_α and C_β) and the $\text{C}\equiv\text{C}$ frequency for $[\mathbf{1}\cdot\text{CuR}]$ ($\text{R} = \text{Cl}$ (**2**), OTf (**3**), $\text{SC}_6\text{H}_4\text{-CH}_2\text{NMe}_2\text{-2}$ (**4a**), $\text{SC}_6\text{H}_4\text{NMe}_2\text{-2}$ (**4b**), SC_6H_5 (**4c**), $\text{S-1-C}_{10}\text{H}_6\text{NMe}_2\text{-8}$ (**4d**), Me (**5**), CH_2SiMe_3 (**6**), C(H)=CH_2 (**9**), $\text{C}\equiv\text{CSiMe}_3$ (**10**), $\text{C}\equiv\text{C}^t\text{Bu}$ (**11**), $\text{C}\equiv\text{CPh}$ (**12**), $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ (**13**), $\text{C}_6\text{H}_4\text{CH}_3\text{-4}$ (**14**), $\text{C}_6\text{H}_4\text{-OCH}_3\text{-4}$ (**15**), $\text{C}_6\text{H}_4\text{NMe}_2\text{-4}$ (**16**), C_6H_5 (**17**), OC(O)Me (**19**), acac (**20**); $\text{M} = \text{Ag}$: $\text{R} = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ (**18**), OTf (**21**).

Rearrangement Reactions in $[\mathbf{1}\cdot\text{CuR}]$ Complexes. As briefly mentioned above, the stability of complexes $[\mathbf{1}\cdot\text{CuR}]$ ($\text{R} = \text{alkyl, alkynyl, or aryl}$) is strongly dependent on the nature of the ligand R . Firstly, alkylcopper complexes **5–8** in solution very slowly convert to a stable bimetallic titanium copper acetylide $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{CCu})]_2^{13b}$ (i, Scheme 2) by nucleophilic substitution of one of the trimethylsilyl groups of the $\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2$ fragment. While the most stable of the alkylcopper complexes, *i.e.*, $[\mathbf{1}\cdot\text{CuMe}]$ (**5**), is only converted in pentane at 25°C after 4 days, the [(trimethylsilyl)methyl]-, ethyl-, and ⁿbutylcopper complexes **6**, **7**, and **8** react already at -20°C , as was found during crystallization attempts of these complexes. The alkynylcopper complexes **10–12** in solution can also rearrange to this bimetallic acetylide complex, but in this case external nucleophiles are necessary to promote the reaction (ii, Scheme 2). In a related substitution reaction, the bis(alkynyl)titanocene **1** reacts extremely fast with $[\text{Cu}(\text{O}^t\text{Bu})_4]$ to afford the same bimetallic acetylide complex.^{13b}

Additionally, the alkylcopper complexes **7** and **8** decompose in solution at 25°C *via* β -hydride elimination which leads to the formation of ethene in the case of **7** and to the formation of a mixture of (*E*)- and (*Z*)-2-butene in the case of **8**; these organic products were detected and identified with GC–MS (iii, Scheme 2). The formation of 2-butene was additionally confirmed by NMR techniques. The copper hydride species which is also formed in this reaction decomposes rapidly to give, among other products, $\text{Me}_3\text{SiC(H)=CH}_2$, which most likely is the result of the addition of the Cu-H bond across the $\text{C}\equiv\text{C}$ bond; *cf.* the reaction in Scheme 3 (*vide infra*). The β -hydride elimination of **7** and **8** can be suppressed by the addition of an extra ligand such as norbornene.

Since, as compared to their uncoordinated organocopper aggregates $[\text{CuR}]_n$, the alkylcopper complexes **5–8** possess a remarkable thermal and kinetic stability in the solid state, a similar increased stability was expected for the corresponding arylcopper series **13–17**. Indeed, $[\mathbf{1}\cdot\text{CuMes}]$ (**13**) is thermally stable, and the solid only decomposes above 124°C . However, the corresponding bis(η^2 -alkyne) $\text{Cu}(\eta^1\text{-aryl})$ complexes which lack *ortho*-substituents (**14–17**) are less stable and rearrange in solution *via* addition of the monomeric CuR entity across one of the alkyne ligands to result in complexes which we believe to have the formulation $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)\{\mu\text{-C}=\text{C}(\text{SiMe}_3)(\text{R})\}\text{Cu}]$. The identity of this species has been established by heating **14–17** at reflux in benzene to generate

Scheme 4. Synthesis of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)\{\mu\text{-C}=\text{C}(\text{SiMe}_3)(\text{R})\}\text{Cu}]$ (**22**) ($\text{R} = \text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}$)



the rearrangement product, followed by acidic hydrolysis and GC–MS analysis of the resulting volatile compounds. From these experiments the alkyne $\text{HC}\equiv\text{CSiMe}_3$ (resulting from the intact $\text{TiC}\equiv\text{CSiMe}_3$ moiety), the alkene $\text{H}_2\text{C}=\text{C}(\text{SiMe}_3)(\text{R})$ (from the $\text{Ti}\{\mu\text{-C}=\text{C}(\text{SiMe}_3)(\text{R})\}\text{Cu}$ entity), and (trimethylsilyl)cyclopentadiene could be identified as major products (Scheme 3).

Synthesis of a 1,1-Bimetallaalkene. Reaction of **1** with $[\text{Cu}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}_2\text{Br}_2]$ (abbreviated as $\text{Cu}_4\text{R}_2\text{Br}_2$)¹⁹ in a 4:1 molar ratio in Et_2O at 25°C results in the formation of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)\{\mu\text{-C}=\text{C}(\text{SiMe}_3)(\text{R})\}\text{Cu}]$, **22**, and $[\mathbf{1}\cdot\text{CuBr}]$ (Scheme 4). As **22** is soluble in most organic solvents (even in pentane), it is easily separated from $[\mathbf{1}\cdot\text{CuBr}]$ which is insoluble in alkanes. Compounds **22** and $[\mathbf{1}\cdot\text{CuBr}]$ have been isolated in 86 and 98% yield, respectively. Independent synthesis of **22** was achieved by reacting the monomeric copper arenethiolate complex $[\mathbf{1}\cdot\text{Cu}\{\text{SC}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2}\}]$, **4a**,^{13a} in a 2:1 molar ratio with $[\text{LiC}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]_2$,²⁰ and **22** has been isolated in 97% yield. Compound **22** is an orange to red crystalline solid which is stable in air for several hours. In solution **22** slowly decomposes upon exposure to air.

Solid State Structure of Addition Product 22. The molecular structure in the solid state of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)\{\mu\text{-C}=\text{C}(\text{SiMe}_3)(\text{R})\}\text{Cu}]$ ($\text{R} = \text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}$, **22**) has been established by an X-ray diffraction study; selected geometrical details are listed in Table 6.

The crystal structure of **22** contains two crystallographically independent, but chemically identical, molecules which each contain a $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$ unit, which is σ -bonded to both a $\text{C}\equiv\text{CSiMe}_3$ group and a $\text{C}=\text{C}(\text{SiMe}_3)(\text{R})$ group (Ti11-C11 2.044(14) Å). Further, C11 is also σ -bonded to a copper atom (Cu11-C11 2.031(14) Å). The C11-C21 bond length of 1.357(19) Å is compatible with a $\text{C}=\text{C}$ double bond and is significantly longer than the $\text{C}\equiv\text{C}$ bond C181-C191 , which is 1.24(2) Å. The copper atom Cu11 is trigonally planar coordinated by η^2 -bonding to a $\text{C}\equiv\text{CSiMe}_3$ fragment, σ -bonding to C11 of the $\text{C}=\text{C}(\text{SiMe}_3)(\text{R})$ entity, and finally N-donor (N11)

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Table 6. Selected Geometrical Details of Compound **22**^a

	residue 1	residue 2	residue 1	residue 2
Bond Distances (Å)				
Ti11...Cu11	2.639(4)	2.635(4)	C11—C21	1.357(19)
Cu11—C11	2.031(14)	2.042(16)	C181—C191	1.24(2)
Cu11—C181	1.972(16)	1.967(15)	Ti11—C11	2.044(14)
Cu11—C191	2.236(18)	2.209(16)	Ti11—C181	2.153(16)
Cu11—N11	2.027(12)	1.996(13)		2.149(16)
Bond Angles (deg)				
Cu11—C11—Ti11	80.7(5)	80.8(6)	mid1 ^b —Cu11—C11	119.9(6)
Ti11—C11—C21	160.6(11)	163.0(13)	Ti11—C181—C191	163.7(14)
Cu11—C11—C21	117.6(10)	115.8(12)	C181—C191—Si21	163.1(16)
				161.4(14)

^a The estimated standard deviations of the last significant digits are shown in parentheses. ^b mid1 is defined as the midpoint of C181—C191.

coordination from one of the (dimethylamino)methyl *ortho*-substituents of the R group. The other *o*-[(dimethylamino)methyl] group does not coordinate.

The trigonal planar geometry of the copper atom is slightly distorted as the angles C11—Cu11—N11 and N11—Cu11—mid1 are 109.0(5) and 127.7(6), respectively (mid1 is defined as the midpoint of C181—C191; mid1—Cu11—C11 is 119.9(6)°). This distortion most probably relates to the strain in the seven-membered chelate ring Cu11—C11—C21—C61—C71—C81—N11.

The Ti11...Cu11 distance of 2.639(4) Å in **22** is approximately 0.27 Å shorter than that in **5** (2.9645(5) Å), **10** (2.9665(8) Å),^{13b} and **13** (2.9418(5) Å). But, as in the latter compounds, it is considered to represent a nonbonding situation (*vide infra*).

The copper to alkyne C_α distance (Cu11—C181) of 1.972(16) Å in **22** is somewhat shorter than that in **13**, which is 2.064(2) Å, while the copper to alkyne C_β distance (Cu11—C191) of 2.236(18) Å is slightly longer than that of 2.082(2) Å found in **13**. Moreover, as the angle Ti11—C181—C191 of 163.7(14)° in **22** is almost equal to the Ti—C_α—C_β angle of 163.7(1)° observed in **13**, the angle C181—C191—Si21 of 163.1(16)° is substantially more linear in **22** than the corresponding C_α—C_β—Si angle in **13**, where it is 155.5(2)°.

The Cu11—C11—Ti11 angle in **22** of 80.7(5)° is acute, and the alkene unit μ-C=C(SiMe₃)(R) is rotated 22.5(5)° from the Ti...Cu vector. Similar features are present in several 1,1-bimetalloalkene complexes, and reported M—C—M angles (M = transition metal) are in the range of 82.3–90.0°. ²¹ The twisting of the μ-C=C(SiMe₃)(R) entity around the Ti...Cu vector is likely to result from strain in the Ti11—C11—Cu11 bonding as well as from steric hindrance of the alkene SiMe₃ group with the η⁵-C₅H₄SiMe₃ ligand.

The geometry of the Cu atom and the alkene moiety in the structure of **22** suggests a σ-bond between Cu11 and C11 (Cu11—C11—C21 is 117.6(10)°), while the bond between Ti11 and C11 is highly distorted (Ti11—C11—C21 is 160.6(11)°) and can best be described as a bent bond in which the orbitals are positioned outside the Ti11—C11—Cu11 triangle. Similar features were concluded from extended Hückel calculations on μ-methylene transition metal compounds where the bonding is referred to as similar to the Walsh orbitals for cyclopropane.²²

Structure of 22 in Solution. The structure of **22** is retained in solution as can be concluded from variable temperature NMR measurements. In the ¹H NMR spectrum of **22** in toluene-d₈

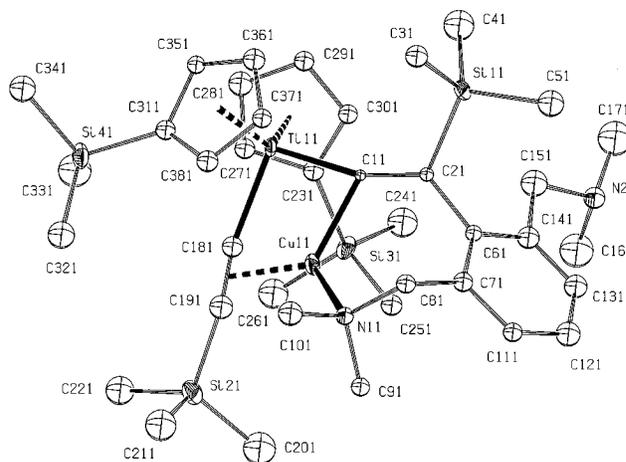


Figure 6. ORTEP drawing (drawn at 50% probability) of one of the independent molecules [(η⁵-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃){μ-C=C(SiMe₃)(C₆H₃(CH₂NMe₂)₂,6)}Cu] (**22**) (with the exclusion of the hydrogen atoms) with the adopted atom-labeling scheme.

at 298 K, all signals with the exception of the Me₃Si resonances are broad, and upon cooling to 287 K these signals become sharper. Finally, at 237 K the slow exchange limit spectrum is reached. This latter spectrum consists of three different aryl protons, seven broad singlets for the C₅H₄ protons (ratio 1:1:1:1:1:1:2), one AB pattern and one singlet for the benzylic protons, three singlets (ratio 2:1:1) for the dimethylamino protons, and four singlets for the SiMe₃ protons. This is consistent with an asymmetric molecule as found in the solid state structure (Figure 6).

Discussion

Stability. The bis(η²-alkyne)organocopper and -organosilver compounds [1•MR] (M = Cu, Ag) (**5–18**) are remarkably stable and include the first examples of room temperature stable methyl-, ethyl-, butyl-, and vinylcopper derivatives.

It is also found that the alkylcopper (**5–8**) and arylcopper (**14–17**) compounds slowly decompose in solution. The decomposition of the former complexes occurs *via* two pathways. Firstly, the low-temperature decomposition route is nucleophilic substitution, whereby elimination of RSiMe₃ yields [(η⁵-C₅H₄SiMe₃)₂Ti(C≡CSiMe₃)(C≡CCu)]₂.^{13b} Secondly, at higher temperatures, a β-hydride elimination prevails for the alkylcopper complexes **7** and **8**, and for these species the nucleophilic substitution process is only observed at low temperature. In the β-hydride elimination pathway an unstable copper hydride complex is formed as was concluded from the isolation of the alkene Me₃SiC(H)=CH₂, which probably results from addition of the Cu—H bond across the C≡C bond. In these reactions ethene (**7**) or *E*- and *Z*-isomers of 2-butene (**8**) were detected, and formation of the latter can be explained by the occurrence of a consecutive (reversible) β-hydride elimina-

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tion process, whereby insertion of initially formed 1-butene in the Cu—H bond results in a 2-butylcopper intermediate from which 2-butene can be eliminated. The fact that decomposition of **7** and **8** via β -hydride elimination can be suppressed by the addition of an extra ligand such as norbornene supports this proposal.

The arylcopper complexes **14**–**17** which lack *ortho*-substituents show decomposition in solution at temperatures above *ca.* 0 °C that proceeds neither *via* nucleophilic substitution nor *via* β -hydride elimination, but more interestingly *via* addition of the organocopper moiety across one of the alkynes. It seems likely that the synthesis of **22** (which is the result of an addition process), either by reacting **1** with [Cu₄R₂Br₂] or by reacting **4a** with [Li{C₆H₃(CH₂NMe₂)₂-2,6}]₂, proceeds *via* the bis(η^2 -alkyne) coordination complex [1·CuC₆H₃(CH₂NMe₂)₂-2,6] (**23**). Moreover, since arylcopper complexes **14**–**17** also rearrange to the addition products [(η^5 -C₅H₅SiMe₃)₂Ti(C≡CSiMe₃){(C=C(SiMe₃)(R)Cu)}], it is likely that this addition proceeds intramolecularly within the preformed species [1·CuR]. Finally, addition of *in situ* prepared organocopper reagents to alkynes is well known in organic chemistry,²³ but only a limited number of pure alkenylcopper compounds have been prepared and structurally characterized.²⁴ Unfortunately, complex **23** could not be identified during the course of this study.

Structural Features of Complexes [1·MR]. Compounds [1·MR] (M = Cu, Ag) (**5**–**18**) are the first examples of neutral monomeric organocopper (silver) units complexed by an organometallic bidentate bis(alkyne) ligand. In these complexes, the η^2 -bonded alkynes are donating two electrons each, due to the in-plane arrangement of both alkynes and the group 11 metal atom.¹⁶ Consequently, the copper and silver atoms have a formal 16-electron count, implying that the Ti···Cu and Ti···Ag distances represent nonbonding situations. In a series of compounds [1·MX], where X represents an organic or inorganic ligand, no correlation between the Ti···M distances and the σ -donating properties of X was found.

The two-electron two-center (2e–2c) Cu—C bond length found in complexes [1·MX] fits perfectly in the range expected for this bond. In other organocopper compounds, where two-electron two-center bonds have been reported, the Cu—C distances are 2.04(1) Å in [(Ph₃P)₃CuMe],^{10a} 2.020(4) Å in [MeC(CH₂PPh₂)₃CuPh],^{10b} 1.947(2) Å in [1·CuMes] (**13**), 1.916(3) Å in [(Me₂S)Cu(C₆H₂Bu₃-2,4,6)],^{10c} and 1.898(3) Å in [1·CuC≡CSiMe₃] (**10**).^{13b} Differences in these Cu—C bond lengths can be explained not only by the degree of carbon s-orbital participation in the Cu—C bond (sp³ > sp² > sp) but also by the different geometry around the metal center (Cu—C decreases in the order tetrahedral > trigonal planar > linear copper geometry). As an illustration one sees that the Cu—C14 bond length in **5** of 1.966(2) Å is somewhat longer than the corresponding distance of 1.947(2) Å in **13**. This is a reflection of the lower s-orbital participation in the copper to carbon (sp³-hybridized) bond in **5** as compared to that in **13** where copper is bonded to an sp²-hybridized carbon atom. The Cu—C bond length found in alkynylcopper complex [1·CuC≡CSiMe₃] (**10**; 1.898(3) Å) also supports this conclusion.^{13b}

The copper-to- η^2 -alkyne distances in the methylcopper complex **5** (Cu1—C1 2.076(2) Å; Cu1—C2 2.080(2) Å) and in the mesitylcopper complex **13** (Cu1—C1 2.064(2) Å; Cu1—C2 2.082(2) Å) are approximately 0.21 Å shorter than the corre-

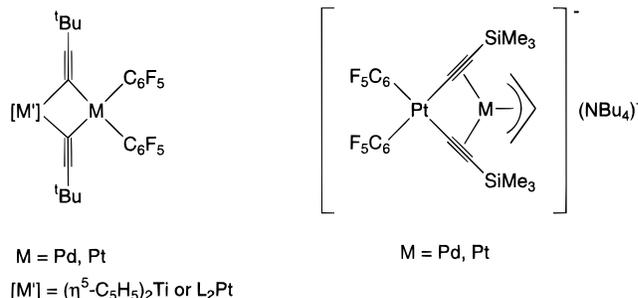


Figure 7. Interaction of bis(alkyne) chelates with electrophilic metal fragments: (left) bridging interaction, (right) η^2 -bonding in anionic species.

sponding distances in the mesitylsilver complex **18** (Ag1—C1 2.270(9) Å; Ag1—C2 2.305(9) Å) and reflect the smaller ionic radius of Cu⁺ (0.96 Å) as compared to that of Ag⁺ (1.26 Å).²⁵ Similarly, the Cu—C_{ipso} distance in **13** is 0.15 Å shorter (1.947(2) Å) than the corresponding Ag—C_{ipso} distance in **18** (2.099(5) Å).

Important observations with respect to the alkyne–copper interaction are (a) a C≡C bond lengthening from 1.203(9) and 1.214(6) Å (the uncoordinated C≡C bond lengths in **1**)¹⁵ to 1.247(3) Å in **5**, 1.250(2) Å in **13**, and 1.24(1) Å in **18** and (b) bending of the Ti—C—C and C—C—Si units from the linear arrangement in the free ligand **1** (Ti—C—C and C—C—Si 177 and 176.5°, respectively) to 166.6(6) and 162.9(7)° in **18**, 163.7(1) and 158.5(2)° in **5**, and 163.7(1) and 155.5(2)° in **13**.

Bonding Description. Compounds **5**–**18** are the first examples of neutral monomeric organocopper (silver) units complexed by an organometallic bidentate bis(alkyne) ligand. In this sense, the well-designed 3-titanio-1,4-pentadiyne **1** is capable of diminishing the aggregation number of organocopper and organosilver structures to monomeric bis(η^2 -alkyne)M(η^1 -R) entities (M = Cu, Ag), while other ligating molecules either do not interact with organocopper and organosilver aggregates or only result in adducts with a lower polynuclearity.^{9,10}

The experimental observation that reaction of **18** with mesitylcopper produces **13** and reaction of **21** with CuOTf produces **3**, whereas the reverse reactions do not occur, leads us to conclude that the η^2 -alkyne–copper bonding is stronger than the η^2 -alkyne–silver bonding.^{13,15}

Related reactions of organometallic bis(alkyne) chelates such as (η^5 -C₅H₅)₂Ti(C≡C^tBu)₂ and L₂Pt(C≡CR)₂ (L₂ = 2 PPh₃, dppe, COD; R = ^tBu, Ph) with *cis*-Pt(C₆F₅)₂(THF)₂ do not stop at the stage of bis(η^2 -alkyne) bonding as typified for [1·MR] (M = Cu, Ag; **5**–**21**). For example, the metal-containing unit Pt(C₆F₅)₂ interacts instead with the Ti—C≡C or Pt—C≡C σ -bond, which leads to a structure with an asymmetrically bridging C≡C fragment. In this case the electrophilic platinum atom interacts preferentially with the C _{α} atoms of the 3-titanio-penta-1,4-diyne (Figure 7).^{26a,b}

However, when (NBu₄)₂[*cis*-Pt(C₆F₅)₂(C≡CSiMe₃)₂] is reacted with [M(η^3 -C₃H₅)Cl]_n (M = Pt, n = 4; M = Pd, n = 2), complexes of the type [(C₆F₅)₂Pt(C≡CSiMe₃)₂M(η^3 -C₃H₅)]⁺(ⁿBu₄N)[−] are formed in which both alkynes are η^2 -bonded to the allylmethyl moiety (Figure 7). This η^2 -bonding is likely to result from the lower electrophilic character since the whole species is anionic.^{26c}

In complexes [1·MR] (M = Cu, Ag; **5**–**21**), the alkyne-to-MR interaction can be described as arising from two compo-

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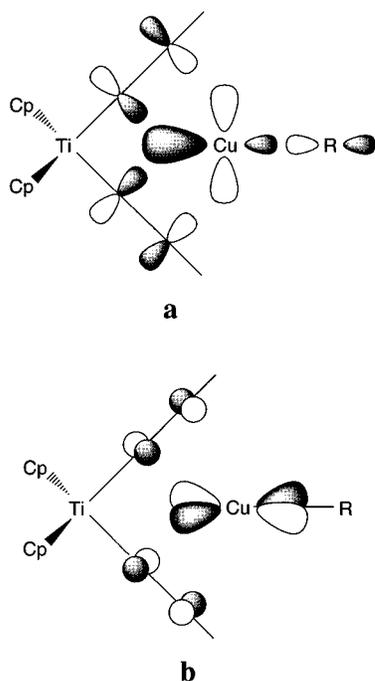


Figure 8. Molecular orbitals for the copper-to-alkyne back-donating interactions: (a) major in-plane contributing MO, (b) minor out-of-plane contributing MO. Note that the calculations were carried out for $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CH})_2\text{Cu}(\text{CH}_3)$ as a model system.

nents: a σ -donation of electron density from a filled π -orbital on the alkyne to a suitable empty orbital on Cu (Ag) and a back-donating component, involving the donation of electron density from a filled d-orbital on the metal to an empty π^* -orbital on the alkyne. A similar bonding description was already postulated on the basis of infrared spectra of alkynylcopper aggregates, but little evidence could be presented to substantiate this idea in more detail.^{3k}

EHT analysis of the molecular orbitals of the $\text{Cp}_2\text{Ti}(\text{C}\equiv\text{CH})_2\text{Cu}(\text{CH}_3)$ model system indicates that the back-bonding component in the alkyne-to-MR interaction is more important. Thus, the MR (M = Cu, Ag) unit can be described as a nucleophile in which M represents a metal with a low Lewis acidity (electrophilicity). In fact, two combinations of π^* alkyne orbitals were found to possess both suitable symmetry and energy to provide efficient interactions with a filled Cu^{I} (Ag^{I}) orbital (ds mixture). The first interaction (Figure 8a) takes place in the plane of the $\text{Ti}(\text{C}\equiv\text{CH})_2\text{Cu}$ entity while the second interaction (Figure 8b) occurs perpendicular to this plane. Note that in Figure 8a the overlap between the metal sd hybrid and the π^* alkyne orbitals is quite important, especially with the C_α atoms. In Figure 8b the overlap is of lesser extent, but again better with C_α than with C_β . The in-plane interaction shown in Figure 8a accounts for the dependence of the back-donation on the σ -donating capacity of the ligand R: more electron-donating R groups will destabilize more the sd Cu (Ag) hybrid which in turn will interact more with the π^* alkyne orbitals, thus transferring more electron density into these π^* alkyne orbitals.

The influence of the σ -donating capacity of the ligand R in compounds $[\mathbf{1}\cdot\text{MR}]$ (M = Cu, Ag) on the extent of back-donation is most obvious from the spectroscopic data for these compounds: more electron-donating ligands R result in a lower $\text{C}\equiv\text{C}$ stretching frequency, a higher C_α ($\text{Ti}-\text{C}\equiv\text{C}$), and a lower C_β ($\text{Ti}-\text{C}\equiv\text{C}$) ^{13}C chemical shift, as well as in a higher distortion of the $\text{Ti}-\text{C}\equiv\text{C}-\text{Si}$ entities from linearity. Moreover, $\nu(\text{C}\equiv\text{C})$ seems to correlate with the deviation of the $\text{Ti}-\text{C}-\text{C}$ and $\text{C}-\text{C}-\text{Si}$ angles and with the ^{13}C chemical shifts of both carbon atoms of the alkyne ligands. In addition, changing the

ligand R in $[\mathbf{1}\cdot\text{MR}]$ (M = Cu, Ag) from an electron-withdrawing to an electron-donating ligand or *vice versa* has a much larger influence on the ^{13}C chemical shift of C_α ($\text{Ti}-\text{C}\equiv\text{C}$) than on that of C_β ($\text{Ti}-\text{C}\equiv\text{C}$). The latter observation can be explained from Figure 8, since the Cu orbitals involved in back-donation have a better overlap with the orbitals from C_α than with those of C_β .

Conclusions

The striking property of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$ (**1**) to bind mononuclear metal fragments CuR or AgR gives access to a novel type of mononuclear bis(η^2 -alkyne)organo-copper and -silver species with an η^1 -bonded organic ligand R.

In this way organocopper compounds, *i.e.*, CuMe, CuEt, Cu^nBu , and $\text{CuCH}=\text{CH}_2$, which otherwise are unstable and decompose already at low temperatures, have been stabilized and isolated as their $[\mathbf{1}\cdot\text{CuR}]$ complexes. The alkylcopper compounds $[\mathbf{1}\cdot\text{CuR}]$, **5**–**8**, slowly decompose in solution, either *via* a nucleophilic substitution reaction pathway or *via* β -hydride elimination, depending on the temperature applied. At low temperature the bimetallic acetylide $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{CCu})_2]$ ^{13b} is formed as the main product as a result of nucleophilic substitution, whereas at high temperatures the β -hydride elimination affording a Cu–H intermediate is more favored.

These results have been discussed in terms of the alkyne–metal interaction, which is dominated by the (in-plane) back-donation of electron density from the group 11 metal atom to the π^* -orbital on the alkyne ligands. To our knowledge no other series in group 11 metal chemistry provides such a clear-cut demonstration of the influence of M-to- π^* -alkyne back-donation.

Experimental Section

All experiments were carried out using standard Schlenk techniques under an inert oxygen-free nitrogen atmosphere. THF, Et_2O , and C_6H_6 were distilled from sodium–benzophenone ketyl prior to use. CH_2Cl_2 was distilled from CaH_2 . ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 or Bruker AC-300 spectrometer. Melting (decomposition) points were determined by using a Büchi melting point apparatus or where indicated by using a Mettler TA-4000 differential scanning calorimeter. FT-IR spectra were recorded on a Mattson Galaxy 5000 series spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, and at the Organisch-Chemisches Institut der Universität Heidelberg, Germany. $[\text{CuMe}]_\infty$ ^{1b} (CAUTION: Dry methylcopper $[\text{CuMe}]_\infty$ is explosive. It can be handled as a suspension, but extreme care has to be taken with all safety precautions warranted. Work on a small scale (below 100 mg) is preferable.), $[\text{CuCH}_2\text{SiMe}_3]_4$,^{1a} $[\text{CuC}_6\text{H}_2\text{Me}_3-2,4,6]_5$, $[\text{AgC}_6\text{H}_2\text{Me}_3-2,4,6]_4$,^{4d} $[\text{CuC}_6\text{H}_4\text{Me}-4]_4$,^{4h} $[\text{CuC}_6\text{H}_4\text{NMe}_2-4]_\infty$,^{4k} $[\text{CuC}_6\text{H}_5]_\infty$,^{4e} $[\text{Cu}_4\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}_2\text{Br}_2]$,¹⁹ $[\text{Li}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}]_2$,²⁰ and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$ (**1**)^{14a} were prepared according to literature procedures. $[\text{CuC}_6\text{H}_4\text{OMe}-4]_n$ was prepared similar to 2-anisylcopper.^{4f,h} Compounds $[\mathbf{1}\cdot\text{CuX}]$ (X = Cl (**2**), OTf (**3**), $\text{SC}_6\text{H}_4\text{CH}_2\text{NMe}_2-2$ (**4a**), SC_6H_5 (**4c**), $\text{C}\equiv\text{CSiMe}_3$ (**10**), $\text{C}\equiv\text{C}^t\text{Bu}$ (**11**), $\text{C}\equiv\text{CPh}$ (**12**)) were synthesized as described elsewhere.^{13,15}

Alkylcopper Compounds. Synthesis of $[\mathbf{1}\cdot\text{CuMe}]$ (5**) from **1** and CuMe.** To a freshly prepared suspension of CuMe (4.44 mmol based on Cu) in Et_2O (30 mL) was added a solution of **1** (0.66 g, 1.28 mmol) in Et_2O (10 mL). Upon addition of **1** the reaction mixture turned deep red. After stirring for 1 h the red solution was separated from the remaining solid by centrifugation and subsequent decantation of most of the supernatant (CAUTION: The solid contains CuMe and can explode when dry. Immediately after the separation an aqueous NH_4Cl solution was added to the residue.). Finally, the red-colored solution was concentrated to a volume of approximately 5 mL, after which a small fraction of this solution was evaporated to dryness, leaving a red solid (for analytical and spectroscopic data *vide infra*).

Synthesis of [1·CuMe] (5) from 4a and ZnMe₂. To **4a** (0.30 g, 0.40 mmol) in Et₂O (20 mL) at 0 °C was added ZnMe₂ (2 mL of a 0.21 M solution in toluene, 0.42 mmol). Upon addition the initially orange solution immediately turned deep red. After stirring for 1 h at 0 °C, all volatiles were removed *in vacuo*. The product could be isolated by extraction with pentane (2 × 10 mL) and subsequent filtration of Zn(Me)SC₆H₄CH₂NMe₂-2^{7e} (yield 0.21 g (88%) of red powder). Crystals suitable for an X-ray structure determination were grown by cooling a saturated solution of **5** in Et₂O to -20 °C: mp = 143 °C dec; IR (C≡C) 1867 cm⁻¹; ¹H NMR (300.13 MHz, C₆D₆) δ (ppm) 0.25 (s, 18 H, SiMe₃), 0.46 (s, 18 H, SiMe₃), 0.74 (s, 3 H, Me), 5.18 (t, 4 H, Cp, *J* = 2 Hz), 5.69 (t, 4 H, Cp, *J* = 2 Hz); ¹³C NMR (75.47 MHz, C₆D₆) δ (ppm) -7.4 (Me), 0.6 (SiMe₃), 1.2 (SiMe₃), 110.1 (Cp), 113.6 (Cp), 116.1 (*ipso*-Cp), 123.4 (C≡C-Si), 203.6 (Ti-C≡C). Anal. Calcd for C₂₇H₄₇CuSi₄Ti: C, 54.46; H, 7.96; Cu, 10.67. Found: C, 54.55; H, 8.07; Cu 10.48.

Synthesis of [1·CuCH₂SiMe₃] (6) from 1 and CuCH₂SiMe₃. To CuCH₂SiMe₃ (0.11 g, 0.73 mmol) in Et₂O (20 mL) at 25 °C was added **1** (0.38 g, 0.74 mmol) in Et₂O (20 mL). After stirring the dark red reaction mixture for 3 h all volatiles were removed *in vacuo*, giving 0.44 g (90%, 0.66 mmol) of red-brown **6**: mp > 115 °C; IR (C≡C) 1930 cm⁻¹; FD-MS *m/z* (M⁺) = 668; ¹H NMR (200.13 MHz, C₆D₆) δ (ppm) 0.26 (s, 18 H, SiMe₃), 0.39 (s, 9 H, SiMe₃), 0.43 (s, 18 H, SiMe₃), 0.98 (s, 2 H, CH₂), 5.46 (t, 4 H, Cp, *J* = 2 Hz), 5.71 (t, 4 H, Cp, *J* = 2 Hz); ¹³C NMR (50.32 MHz, C₆D₆) δ (ppm) 0.5 (SiMe₃), 1.7 (SiMe₃), 9.4 (CuCH₂SiMe₃), 110.8 (Cp), 114.6 (Cp), 115.6 (*ipso*-Cp), 125.3 (C≡C-Si), 202.9 (Ti-C≡C). CuCH₂SiMe₃ is not observed.

Synthesis of [1·CuCH₂SiMe₃] (6) from 3 and LiCH₂SiMe₃. To **3** (0.50 g, 0.69 mmol) in THF (100 mL) at -70 °C was added dropwise an equimolar amount of LiCH₂SiMe₃ (0.07 g, 0.74 mmol) in THF (50 mL). Subsequently the reaction mixture was gradually allowed to warm to 25 °C over 2 h. After stirring for another 3 h, all volatiles were removed *in vacuo*. The residue was extracted with Et₂O (3 × 50 mL) and filtered through Celite. Evaporation of the volatiles *in vacuo* yields 0.41 g (89%) of **6** (for analytical and spectroscopic data *vide supra*).

Synthesis of [1·CuEt] (7) from 4a and ZnEt₂. The preparation of **7** is similar to that of **5** starting from **4a** (0.15 g, 0.20 mmol) in toluene (30 mL) and ZnEt₂ (0.20 mL of a 1 M solution in toluene, 0.20 mmol) (yield 0.12 g (71%) of red **7**): IR (C≡C) 1857 cm⁻¹; ¹H NMR (200.13 MHz, C₆D₆) δ (ppm) 0.26 (s, 18 H, SiMe₃), 0.45 (s, 18 H, SiMe₃), 1.76 (t, 3 H, CH₃, *J* = 7.5 Hz), 2.13 (q, 2 H, CH₂, *J* = 7.8 Hz), 5.17 (t, 4 H, Cp, *J* = 2 Hz), 5.68 (t, 4 H, Cp, *J* = 2 Hz). Since this product decomposes at temperatures above 0 °C, matching elemental analyses could not be obtained.

Synthesis of [1·CuⁿBu] (8) from 4c and LiⁿBu. The preparation of **8** is similar to that of **5** but starting from [1·CuSC₆H₅] (**4c**) (0.22 g, 0.32 mmol) in pentane (30 mL) and LiⁿBu (0.20 mL of a 1.6 M solution in hexane, 0.32 mmol) (yield 0.16 g (79%) of red **8**): IR (C≡C) 1851 cm⁻¹; ¹H NMR (200.13 MHz, C₆D₆) δ (ppm) 0.27 (s, 18 H, SiMe₃), 0.47 (s, 18 H, SiMe₃), 1.17 (t, 3 H, CH₃, *J* = 7.2 Hz), 1.6-1.8 (m, 2 H, CH₂), 1.9-2.2 (m, 4 H, CH₂CH₂), 5.19 (t, 4 H, Cp, *J* = 2 Hz), 5.69 (t, 4 H, Cp, *J* = 2 Hz). Since this product decomposes at temperatures above 0 °C, matching elemental analyses could not be obtained.

Alkenylcopper Compounds. Synthesis of [1·CuC(H)=CH₂] (9) from 4a and BrMgC(H)=CH₂. To **4a** (0.30 g, 0.40 mmol) in Et₂O (15 mL) at 0 °C was added BrMgC(H)=CH₂ (1.22 mL of a freshly prepared 0.33 M solution in THF, 0.40 mmol). Upon addition, the initially orange solution immediately turned deep red. After stirring for 1 h at 0 °C, all volatiles were removed *in vacuo*. The product could be isolated by extraction with pentane (1 × 25 mL) and subsequent filtration of Mg(Br)SC₆H₄CH₂NMe₂-2 (yield 0.19 g (78%) of red **9**): IR (C≡C) 1868 cm⁻¹, (C=C) 1585 cm⁻¹; ¹H NMR (200.13 MHz, C₆D₆) δ (ppm) 0.24 (s, 18 H, SiMe₃), 0.48 (s, 18 H, SiMe₃), 5.19 (t, 4 H, Cp, *J* = 2 Hz), 5.67 (t, 4 H, Cp, *J* = 2 Hz), 5.96 (dd, 1 H, =CH₂, *J*_{trans} = 19.6 Hz, *J*_{gem} = 3.4 Hz), 6.82 (dd, 1 H, =CH₂, *J*_{cis} = 12.5 Hz, *J*_{gem} = 3.4 Hz), 7.77 (dd, 1 H, CuC(H)=, *J*_{trans} = 19.6 Hz, *J*_{cis} = 12.5 Hz); ¹³C NMR (50.32 MHz, C₆D₆) δ (ppm) 0.6 (SiMe₃), 1.3 (SiMe₃), 110.4, 113.6 (Cp), 112.1, 115.2, 116.7 (*ipso*-Cp and vinyl), 125.3 (C≡C-Si), 199.3 (Ti-C≡C). Since this product decomposes at temperatures above 0 °C, matching elemental analyses could not be obtained.

Arylcopper Compounds. Synthesis of [1·CuC₆H₂Me₃-2,4,6] (13) from 1 and CuC₆H₂Me₃-2,4,6. To CuC₆H₂Me₃-2,4,6 (0.19 g, 1.04

mmol) in THF (15 mL) was slowly added **1** (0.54 g, 1.04 mmol) in THF (25 mL). On addition of **1** the yellow solution immediately turned dark red. After stirring for 0.5 h the solvent was removed *in vacuo*. X-ray suitable crystals could be obtained by crystallization from a concentrated solution in Et₂O at -20 °C (yield 0.61 g (84%) of crystalline **13**): mp (DSC) = 113.9 °C; IR (C≡C) 1856 cm⁻¹; FD-MS *m/z* (M⁺) = 698; ¹H NMR (300.13 MHz, C₆D₆) δ (ppm) 0.11 (s, 18 H, SiMe₃), 0.30 (s, 18 H, SiMe₃), 2.36 (s, 3 H, *p*-Me), 2.37 (s, 6 H, *o*-Me), 5.17 (t, 4 H, Cp, *J* = 2 Hz), 5.82 (t, 4 H, Cp, *J* = 2 Hz), 6.99 (s, 2 H, ArH); ¹³C NMR (75.47 MHz, C₆D₆) δ (ppm) 0.2 (SiMe₃), 0.6 (SiMe₃), 21.4 (*p*-Me), 28.0 (*o*-Me), 110.7 (Cp), 113.0 (Cp), 116.7 (*ipso*-Cp), 125.0 (C≡C-Si), 126.3 (Ar-3), 133.6 (Ar-4), 145.2 (Ar-2), 201.8 (Ti-C≡C); mesityl C_{ipso} is not observed. Anal. Calcd for C₃₅H₅₅-CuSi₄Ti: C, 60.09; H, 7.92; Cu 9.08. Found: C, 59.96; H, 7.90; Cu, 8.94.

Synthesis of [1·CuC₆H₂Me₃-2,4,6] (13) from 2 and LiC₆H₂Me₃-2,4,6. To **2** (0.50 g, 0.81 mmol) in THF (100 mL) at -70 °C was added dropwise an equimolar amount of LiC₆H₂Me₃-2,4,6 (0.10 g, 0.79 mmol) in THF (50 mL). Subsequently the reaction mixture was gradually allowed to warm to 25 °C over 2 h and stirred for another 3 h. After removal of all volatiles *in vacuo*, the residue was extracted with Et₂O (3 × 50 mL) and filtered through Celite. Evaporation of the volatiles *in vacuo* yielded 0.43 g (78%) of **13** (for analytical and spectroscopic data *vide supra*).

Synthesis of [1·CuC₆H₂Me₃-2,4,6] (13) from 3 and LiC₆H₂Me₃-2,4,6. This preparation is similar to the one described from **2**, but starting from **3** (0.50 g, 0.69 mmol) and an equimolar amount of LiC₆H₂Me₃-2,4,6 (0.09 g, 0.71 mmol) (yield 0.40 g (83%) of **13**) (for analytical and spectroscopic data *vide supra*).

Synthesis of [1·CuC₆H₄Me-4] (14) from 1 and CuC₆H₄Me-4. To a suspension of CuC₆H₄Me-4 (0.27 g, 1.73 mmol) in THF (15 mL) was slowly added **1** (0.90 g, 1.74 mmol) in THF (15 mL). On addition of **1**, the slightly green suspension turned dark red, and finally resulted in a clear red solution. After stirring for 4 h, the solution was filtered, and all volatiles were removed *in vacuo*. Crystallization from Et₂O at -20 °C afforded an orange powder, which could be identified as [1·CuBr]. After a second filtration and concentration of the solution, **14** could be isolated as a red powder (yield 0.69 g (59%)) (for analytical and spectroscopic data *vide infra*).

Synthesis of [1·CuC₆H₄Me-4] (14) from 4a and LiC₆H₄Me-4. To freshly prepared LiC₆H₄Me-4 (0.04 g, 0.41 mmol) in Et₂O (25 mL) at 0 °C was slowly added **4a** (0.30 g, 0.40 mmol) in one portion. The reaction mixture turned deep red, and LiSC₆H₄CH₂NMe₂-2²⁷ precipitated. After stirring for 3 h at temperatures below 0 °C, all volatiles were removed *in vacuo*. **14** could be isolated by extraction with pentane and subsequent filtration of LiSC₆H₄CH₂NMe₂-2²⁷ (yield 0.25 g (93%) of red **14**): mp = 73 °C dec; IR (C≡C) 1862 cm⁻¹; ¹H NMR (300.13 MHz, C₇D₈, 253 K) δ (ppm) 0.16 (s, 18 H, SiMe₃), 0.27 (s, 18 H, SiMe₃), 2.30 (s, 3 H, Me), 5.15 (t, 4 H, Cp, *J* = 2 Hz), 5.72 (t, 4 H, Cp, *J* = 2 Hz), 7.16 (d, 2 H, ArH, *J* = 6.9 Hz), 7.67 (d, 2 H, ArH, *J* = 6.9 Hz); ¹³C NMR (75.47 MHz, C₇D₈, 253 K) δ (ppm) 0.5 (SiMe₃), 0.8 (SiMe₃), 22.9 (*p*-Me), 110.4 (Cp), 113.2 (Cp), 116.5 (*ipso*-Cp), 125.9 (C≡C-Si), 127.9, (Ar-3) 131.9 (Ar-4), 141.6 (Ar-2), 158.5 (Ar-*ipso*), 199.3 (Ti-C≡C); signals from Ar-2 and Ar-3 have been tentatively assigned. Since this product decomposes at temperatures above 0 °C, matching elemental analyses could not be obtained.

Synthesis of [1·CuC₆H₄OMe-4] (15) from 1 and CuC₆H₄OMe-4. This preparation is similar to that described for **14** but starting from CuC₆H₄OMe-4 (0.10 g, 0.59 mmol) in Et₂O (20 mL) and **1** (0.30 g, 0.58 mmol) in Et₂O (20 mL) (yield 0.24 g (60%)) (for analytical and spectroscopic data *vide infra*).

Synthesis of [1·CuC₆H₄OMe-4] (15) from 4a and LiC₆H₄OMe-4. To freshly prepared LiC₆H₄OMe-4·LiBr (0.10 g, 0.50 mmol) in Et₂O (30 mL) at 0 °C was added **4a** (0.38 g, 0.50 mmol) in one portion. The reaction mixture turned deep red, and LiSC₆H₄CH₂NMe₂-2²⁷ precipitated. After stirring for 2 h at temperatures below 0 °C, all volatiles were removed *in vacuo*. **15** could be isolated by extraction with pentane and subsequent filtration of LiSC₆H₄CH₂NMe₂-2²⁷ and LiBr (yield 0.26 g (75%) of red **15**): mp = 98 °C dec; IR (C≡C)

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1865 cm^{-1} ; ^1H NMR (300.13 MHz, C_7D_8 , 253 K) δ (ppm) 0.19 (s, 18 H, SiMe_3), 0.29 (s, 18 H, SiMe_3), 3.47 (s, 3 H, OMe), 5.16 (t, 4 H, Cp, $J = 2$ Hz), 5.74 (t, 4 H, Cp, $J = 2$ Hz), 7.02 (d, 2 H, ArH, $J = 7.6$ Hz), 7.64 (d, 2 H, ArH, $J = 7.6$ Hz); ^{13}C NMR (75.47 MHz, C_7D_8 , 253 K) δ (ppm) 0.3 (SiMe_3), 0.5 (SiMe_3), 54.0 (OMe), 110.5 (Cp), 113.3 (Cp), 116.6 (*ipso*-Cp), 126.0 ($\text{C}\equiv\text{C}-\text{Si}$), 132.3 (Ar-4), 141.8 (Ar-2), 157.5 (Ar-*ipso*), 199.1 (Ti-C \equiv C); the signal from Ar-3 could not be observed; signals from Ar-2 and Ar-3 have been tentatively assigned. Since this product decomposes at temperatures above 0 $^\circ\text{C}$, matching elemental analyses could not be obtained.

Synthesis of [1·CuC₆H₄NMe₂-4] (16) from 1 and CuC₆H₄NMe₂-4. This preparation is similar to that described for **14**, but starting from CuC₆H₄NMe₂-4 (0.15 g, 0.82 mmol) in Et₂O (50 mL) and **1** (0.50 g, 0.81 mmol) (yield 0.50 g (88%)) (for analytical and spectroscopic data *vide infra*).

Synthesis of [1·CuC₆H₄NMe₂-4] (16) from 4a and LiC₆H₄NMe₂-4. To freshly prepared LiC₆H₄NMe₂-4·LiBr (0.04 g, 0.19 mmol) in Et₂O (25 mL) at 0 $^\circ\text{C}$ was added **4a** (0.14 g, 0.19 mmol) in one portion. The reaction mixture turned deep red, and LiSC₆H₄CH₂NMe₂-2²⁷ precipitated. After stirring for 1 h at -20 $^\circ\text{C}$, all volatiles were removed *in vacuo*. **16** could be isolated by extraction with pentane and subsequent filtration of LiSC₆H₄CH₂NMe₂-2²⁷ and LiBr (yield 0.12 g (91%) of red **16**): mp = 82 $^\circ\text{C}$ dec; IR (C \equiv C) 1863 cm^{-1} ; ^1H NMR (300.13 MHz, C_7D_8 , 253 K) δ (ppm) 0.23 (s, 18 H, SiMe_3), 0.30 (s, 18 H, SiMe_3), 2.66 (s, 6 H, NMe₂), 5.16 (t, 4 H, Cp, $J = 2$ Hz), 5.74 (t, 4 H, Cp, $J = 2$ Hz), 6.89 (s, 2 H, ArH, $J = 8.0$ Hz), 7.65 (s, 2 H, ArH, $J = 8.0$ Hz). ^{13}C NMR (75.47 MHz, C_7D_8 , 253 K) δ (ppm) 0.5 (SiMe_3), 0.7 (SiMe_3), 40.8 (NMe₂), 110.3 (Cp), 113.2 (Cp), 116.3 (*ipso*-Cp), 125.7 ($\text{C}\equiv\text{C}-\text{Si}$), 141.8 (Ar-2), 148.2 (Ar-*ipso*), 200.1 (Ti-C \equiv C); the signals from Ar-3 and Ar-4 are not observed; signals from Ar-2 and Ar-3 have been tentatively assigned. Since this product decomposes at temperatures above 0 $^\circ\text{C}$, matching elemental analyses could not be obtained.

Synthesis of [1·CuC₆H₅] (17) from 1 and CuC₆H₅. This preparation is similar to that described for **14**, but starting from a suspension of CuC₆H₅ (0.34 g, 2.42 mmol) in THF (20 mL) and **1** (1.25 g, 2.42 mmol) in THF (20 mL) (yield 0.56 g (35%)) (for analytical and spectroscopic data *vide infra*).

Synthesis of [1·CuC₆H₅] (17) from 4a and LiC₆H₅. To freshly prepared LiC₆H₅ (0.04 g, 0.48 mmol) in Et₂O (25 mL) at 0 $^\circ\text{C}$ was added **4a** (0.35 g, 0.47 mmol) in one portion. The reaction mixture turned deep red, and LiSC₆H₄CH₂NMe₂-2²⁷ precipitated. After stirring for 1.5 h at -20 $^\circ\text{C}$, all volatiles were removed *in vacuo*. The product could be isolated by extraction with pentane and subsequent filtration of LiSC₆H₄CH₂NMe₂-2²⁷ (yield 0.30 g (97%) of red **17**): IR (C \equiv C) 1861 cm^{-1} ; ^1H NMR (300.13 MHz, C_7D_8 , 253 K) δ (ppm) 0.16 (s, 18 H, SiMe_3), 0.27 (s, 18 H, SiMe_3), 5.15 (t, 4 H, Cp, $J = 2$ Hz), 5.72 (t, 4 H, Cp, $J = 2$ Hz), 7.16 (t, 1 H, ArH, $J = 7.0$ Hz), 7.31 (t, 2 H, ArH, $J = 7.2$ Hz), 7.77 (d, 2 H, ArH, $J = 7.2$ Hz); ^{13}C NMR (75.47 MHz, C_7D_8 , 253 K) δ (ppm) 0.5 (SiMe_3), 0.7 (SiMe_3), 110.5 (Cp), 113.3 (Cp), 116.6 (*ipso*-Cp), 123.6 (Ar-4), 126.0 ($\text{C}\equiv\text{C}-\text{Si}$), 127.0 (Ar-3), 141.8 (Ar-2), 163.9 (Ar-*ipso*), 199.0 (Ti-C \equiv C). Since this product decomposes at temperatures above 0 $^\circ\text{C}$, matching elemental analyses could not be obtained.

Arylsilver Compounds. Synthesis of [1·AgC₆H₂Me₃-2,4,6] (18) from 1 and AgC₆H₂Me₃-2,4,6. To AgC₆H₂Me₃-2,4,6 (0.58 g, 2.55 mmol) in Et₂O (15 mL) was slowly added a solution of **1** (1.22 g, 2.36 mmol) in Et₂O (25 mL). On addition of **1**, the slightly yellow solution immediately turned deep purple. After stirring for 1 h, the clear violet solution was concentrated *in vacuo*. Crystalline **18** could be obtained by crystallization from a concentrated solution in Et₂O at -20 $^\circ\text{C}$: mp = 119 $^\circ\text{C}$ dec; IR (C \equiv C) 1902 cm^{-1} ; FD-MS m/z (M^+) = 744; ^1H NMR (300.13 MHz, C_6D_6) δ (ppm) 0.21 (s, 18 H, SiMe_3), 0.26 (s, 18 H, SiMe_3), 2.39 (s, 3 H, *p*-Me), 2.57 (s, 6 H, *o*-Me), 5.40 (t, 4 H, Cp, $J = 2$ Hz), 5.89 (t, 4 H, Cp, $J = 2$ Hz), 7.10 (s, 2 H, ArH); ^{13}C NMR (75.47 MHz, C_6D_6) δ (ppm) 0.4 (SiMe_3), 0.6 (SiMe_3), 21.5 (*p*-Me), 29.7 (*o*-Me), 112.9 (Cp), 115.1 (Cp), 119.6 (*ipso*-Cp), 125.6 (d, Ar-3,5, $^3J(\text{Ag}, \text{C}) = 7$ Hz), 125.8 (d, $\text{C}\equiv\text{C}-\text{Si}$, $J(\text{Ag}, \text{C}) = 7$ Hz), 133.4 (Ar-4), 144.6 (Ar-2,6), 168.3 (dd, Ar-1, $^1J(^{107}\text{Ag}, ^{13}\text{C}) = 142$, $^1J(^{109}\text{Ag}, ^{13}\text{C}) = 164$ Hz), 184.5 (d, Ti-C \equiv C, $J(\text{Ag}, \text{C}) = 3$ Hz). Anal. Calcd for C₃₅H₅₅AgSi₄Ti: C, 56.51; H, 7.45. Found: C, 56.28; H, 7.54.

Addition Product 22. Synthesis of [(η^5 -C₅H₄SiMe₃)₂Ti(C \equiv C-SiMe₃) μ -C=C(SiMe₃)(C₆H₃(CH₂NMe₂)₂-2,6)Cu] (22). To [Cu₄(C₆H₃(CH₂NMe₂)₂-2,6)₂Br₂] (0.38 g, 0.48 mmol of Cu₄ aggregate) in Et₂O (50 mL) was added in one portion **1** (0.99 g, 1.92 mmol) at 25 $^\circ\text{C}$. The reaction mixture gradually turned deep red, and after stirring for 3 h all volatiles were evaporated *in vacuo*. Extraction with pentane (3 \times 40 mL) and subsequent evaporation of the volatiles *in vacuo* yielded 0.64 g (86%, 0.83 mmol) of **22**. The residue is [1·CuBr] (0.63 g, 0.95 mmol, 100%), as was established by comparison of the analytical and spectroscopic data to an authentic sample.²⁸ Crystalline **22** can be obtained by cooling a saturated Et₂O solution to -20 $^\circ\text{C}$: mp = 138 $^\circ\text{C}$ dec; IR (C \equiv C) 1882 cm^{-1} , (C=C) 1591 cm^{-1} ; ^1H NMR (300.13 MHz, C_6D_6) δ (ppm) 0.21 (s, 18 H, SiMe_3), 0.28 (s, 18 H, SiMe_3), 2.35 (br s, 12 H, NMe₂), 4.05 (br s, 4 H, CH₂), 4.9 (br s, 4 H, Cp), 5.1 (br s, 4 H, Cp), 7.08 (m, 3 H, ArH); ^1H NMR (300.13 MHz, C_6D_6 , 237 K) δ (ppm) 0.15 (s, 9 H, SiMe_3), 0.27 (s, 9 H, SiMe_3), 0.34 (s, 9 H, SiMe_3), 0.48 (s, 9 H, SiMe_3), 2.10 (s, 3 H, NMe₂), 2.20 (s, 3 H, NMe₂), 2.44 (s, 6 H, NMe₂), 2.50 (d, 1 H, $^2J = 10$ Hz, CH₂), 3.91 (s, 2 H, CH₂), 4.11 (d, 1 H, $^2J = 10$ Hz, CH₂), 5.21 (s, 2 H, Cp), 5.27 (s, 1 H, Cp), 5.34 (s, 1 H, Cp), 5.45 (s, 1 H, Cp), 5.82 (s, 1 H, Cp), 6.05 (s, 1 H, Cp), 6.17 (s, 1 H, Cp), 6.79 (d, 1 H, $^3J = 7$ Hz, ArH), 7.13 (m, 1 H, ArH), 8.02 (d, 1 H, $^3J = 8$ Hz, ArH).

Synthesis of 22 from [Li{C₆H₃(CH₂NMe₂)₂-2,6}]₂ and 4a. To [Li{C₆H₃(CH₂NMe₂)₂-2,6}]₂ (0.17 g, 0.23 mmol) in Et₂O (20 mL) at 0 $^\circ\text{C}$ was added **4a** (0.05 g, 0.25 mmol) in Et₂O (20 mL). Cooling was stopped, and after stirring for 1 h at 25 $^\circ\text{C}$ all volatiles were removed *in vacuo*. Extraction with pentane (30 mL) and subsequent filtration of LiSC₆H₄CH₂NMe₂-2²⁷ gave 0.17 g (97%) of **22** (for spectroscopic data *vide supra*).

Structure Determination and Refinement of 5, 13, 18, and 22. Crystal data and numerical details of the structure determinations are given in Table 7. Crystals of the four complexes were glued on top of glass fibers and transferred to an Enraf-Nonius CAD4T rotating anode diffractometer for data collection at 150 K. Accurate unit cell parameters and orientation matrices were derived from the setting angles of 25 well-centered reflections (SET4)²⁹ in the range $11^\circ < \theta < 14^\circ$, and the unit cell parameters were checked for the presence of higher lattice symmetry.³⁰ All data were collected in the $\omega/2\theta$ scan mode, data were corrected for Lorentz polarization effects and for the observed linear decay of the intensity control reflections, and redundant data were merged into a unique data set. An empirical absorption correction was applied for **5**, **13**, and **18** using the DIFABS³¹ method as implemented in PLATON.³² The structures of **5**, **13**, and **18** were solved by automated Patterson methods using DIRDIF92³³ for **5** and **18** and SHELXS86³⁴ for **13** followed by subsequent difference Fourier techniques. The structure of complex **22** was solved by direct methods (SHELXS86)³⁴ and difference Fourier techniques. The crystal of **22** is pseudomerohedrally twinned by a 2-fold axis coinciding with *a**. The twinning (with twin index 1) was taken into account using the "TWIN" option of the SHELXL93³⁵ program, resulting in a twin ratio of 0.325(3):0.675(3). Hydrogen atoms in **5** with the exception of those on C(14) were located from difference Fourier maps and refined with individual isotropic atomic displacement parameters. Hydrogen atoms of **13**, **18**, of **22** and on the C(14) methyl in **5** were introduced at calculated positions and refined riding on their carrier atoms. All non-hydrogen atoms of **5**, **13**, and **18** were refined with anisotropic atomic displacement parameters. In view of the twinning and the related limited quality of the data of complex **22**, only the Cu, Ti, and Si atoms were refined with anisotropic atomic displacement parameters; all other

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Table 7. Experimental Data for the X-ray Diffraction Studies of **5**, **13**, **18**, and **22**

	5	13	18	22
formula	C ₂₇ H ₄₇ CuSi ₄ Ti	C ₃₅ H ₅₅ CuSi ₄ Ti	C ₃₅ H ₅₅ AgSi ₄ Ti	C ₃₈ H ₆₃ N ₂ CuSi ₄ Ti
formula weight	595.44	699.59	743.91	771.70
space group	C2/c	Pbcn	Pbcn	P2 ₁ /c
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Z	4	4	4	8
a (Å)	19.477(1)	12.4290(9)	12.47(3)	31.05(2)
b (Å)	10.3622(6)	19.8770(8)	20.00(3)	14.323(3)
c (Å)	16.395(1)	15.532(1)	15.53(3)	20.014(8)
β (deg)	95.287(5)			108.53(5)
volume (Å ³)	3294.8(3)	3837.2(4)	3873(13)	8440(7)
d_{calc} (g cm ⁻³)	1.200	1.211	1.276	1.215
temperature (K)	150	150	150	150
F(000)	1264	1488	1560	3296
μ (Mo K α) (cm ⁻¹)	10.5	9.0	8.5	8.3
crystal size (mm)	0.25 \times 0.55 \times 0.55	0.30 \times 0.50 \times 0.50	0.25 \times 0.25 \times 0.25	1.00 \times 0.10 \times 0.05
radiation (Å)	Mo K α (0.710 73)			
θ^{min} , θ^{max} (deg)	2.1, 27.5	1.90, 26.48	1.02, 25.00	0.69, 25.00
scan ($\omega/2\theta$ mode)	0.62 + 0.35 tan (θ)	0.50 + 0.35 tan(θ)	0.80 + 0.35 tan(θ)	0.89 + 0.35 tan(θ)
horiz aperture (mm)	3.00	3.00	3.00	3.91
vert aperture (mm)	4.00	4.00	4.00	4.00
decay, X-ray time	<1%, 23 h	<1%, 14 h	4%, 15 h	0.2%, 42 h
h ; k ; l (min, max)	-25, 25; 0, 13; -18, 21	-18, 18; -15, 0; 0, 23	0, 18; -14, 14; 0, 23	-36, 35; 0, 17; 0, 23
DIFABS ^a	0.762, 1.390	0.916, 1.106	0.776, 1.262	
no. of total, unique reflns (R_{av})	6355, 3784 (0.025)	7955, 3699 (0.022)	7273, 3393 (0.047)	15988, 14825
no. of observed reflns	3232 ($I > 4\sigma(I)$) ^b	3082 ($I > 2.5\sigma(I)$)	2068 ($I > 2.5\sigma(I)$)	12882 ($F_o^2 > 0$) ^b
N_{ref} , N_{par}	3784, 240	3082, 217	2068, 188	12882, 462
weight (w^{-1}) ^c	$\sigma^2(F_o^2) + (0.0439P)^2 + 0.51P$	$\sigma^2(F)$	$\sigma^2(F) + 0.00085F^2$	$\sigma^2(F_o^2) + (0.2281P)^2$
R^d	0.0304 ^f	0.026 ^e	0.055 ^e	0.1233 ^f
wR/wR_2	0.0766 ^f	0.031 ^e	0.063 ^e	0.3432 ^f
S	1.03	1.14	3.95	1.033
resd dens (e/Å ³)	-0.29, 0.36	-0.38, 0.27	-0.93, 0.88	-1.37, 3.31

^a Correction range. ^b All reflections used in the refinement. ^c $P = (\max(F_o^2, 0) + 2F_c^2)/3$. ^d $R = \sum||F_o| - F_c|/\sum|F_o|$. ^e Refinement on F : $wR = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. ^f Refinement on F^2 : $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]\}^{1/2}$.

non-hydrogen atoms in this complex were refined with individual isotropic atomic displacement parameters. Refinement of the structures with full-matrix least-squares techniques was carried out either on F (**13** and **18**) using reflections with $I > 2.5\sigma(I)$ (SHELX76)³⁶ or on F^2 (**5** and **22**) using all unique reflections (**5**) or unique reflections with $F_o^2 > 0$ (**22**) (SHELXL93).³⁵ Complex **22** contains some solvent accessible voids of about 35 Å³; no residual (integrated) electron density was found in these areas (PLATON).³² The final difference map of **22** shows residual densities in the range -1.37 to +3.31 e/Å³ probably due to residual twinning effects. Neutral atom scattering factors for **13** and **18** were taken from Cromer and Mann³⁷ and corrected for anomalous dispersion.³⁸ Neutral atom scattering factors and their anomalous dispersion corrections for **5** and **22** were taken from the *International Tables for Crystallography*.³⁹ Geometrical calculations and illustrations were performed with the PLATON package;³² all calculations were performed on a DEC-5000 cluster.

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Supporting Information Available: Tables of crystal data, details of the structure determination, 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 angles for **5**, **13**, **18**, and **22** (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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