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(η^2-Alkyne)$_2$CuMe as a Synthetic Tool in the Preparation of Numerous Inorganic and Organic Copper(I) Species

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The application of the heterobimetallic tweezer molecule $\{[Ti](C{\equiv}CR^1)_2\}CuCH_3$ $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; **1a**, $R^1 = SiMe_3$; **1b**, $R^1 = {}^tBu\}$ as a synthetic tool in the synthesis of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuOR^2$ [**3a**, $R^2 = CH_3$; **3b**, $R^2 = CH_2CH_3$; **3c**, $R^2 = {}^tBu$; **3d**, $R^2 = C_6H_5$; **3e**, $R^2 = C_6H_4{}^tBu\text{-}2$; **3f**, $R^2 = C_6H_3({}^tBu)_2\text{-}2,6$], $\{[Ti](C{\equiv}CSiMe_3)_2\}Cu(acac)$ (**6**), $\{[Ti](C{\equiv}CSiMe_3)_2\}CuSR^2$ (**11a**, $R^2 = C_2H_5$; **11b**, $R^2 = C_6H_5$), $\{[Ti](C{\equiv}CSiMe_3)_2\}CuN(SiMe_3)_2$ (**16**), $\{[Ti](C{\equiv}C{}^tBu)_2\}CuP(C_6H_5)_2$ (**17**), $\{[Ti](C{\equiv}CR^1)_2\}CuC{\equiv}CR^3$ [$R^1 = {}^tBu$: **19a**, $R^3 = {}^tBu$; **19b**, $R^3 = SiMe_3$; **19c**, $R^3 = (CH_2)_2CH_3$; **19d**, $R^3 = H$; **19e**, $R^3 = Fc$; **19f**, $R^3 = C_6H_4NO_2\text{-}4$; $R^1 = SiMe_3$; **20a**, $R^3 = C_6H_5$, **20b**, $R^3 = CO_2Me$; **20c**, $R^3 = SiMe_3$; **20d**, $R^3 = Fc$; $Fc = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$], and complexes $\{[Ti](C{\equiv}C{}^tBu)_2\}CuO_2C{-}C{\equiv}CH$ (**8**) and $\{[Ti](C{\equiv}C{}^tBu)_2\}CuO_2C{-}C{\equiv}C{-}Cu\{({}^tBuC{\equiv}C)_2[Ti]\}$ (**9**) is described. In all of these reactions evolution of CH_4 is the driving force for the formation of the corresponding complexes **6**, **8**, **9**, **16**, **17**, **19**, and **20**. A characteristic feature of the copper(I) alcoholates **3a**−**f** and the copper(I) amide **16** is the elimination of Me_3SiOR^2 (for **3**) or $N(SiMe_3)_3$ (for **16**) to produce the tetranuclear titanium(IV)−copper(I) acetylide $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)\}_2$ (**4**). The result of the X-ray structure analysis of the copper acetylides **19a** and **19f** is reported. These complexes contain a trigonally planar coordinated 16-valence-electron copper(I) center, comprised of two η^2-coordinated ${}^tBuC{\equiv}C$ groups and a η^1-bonded $C{\equiv}C{}^tBu$ (**19a**) or $C{\equiv}C{-}C_6H_4NO_2\text{-}4$ (**19f**) entity.

Introduction

Recently, a powerful method for the synthesis and characterization of the alkyne-stabilized copper(I) methyl complex $\{[Ti](C{\equiv}CR^1)_2\}CuCH_3$ (**1a**, $R^1 = SiMe_3$; **1b**, $R^1 = {}^tBu$) was described.[1] These complexes exhibit a remarkably enhanced thermal stability when compared to the parent copper(I) methyl aggregate $[CuCH_3]_n$.[2,3] While solid $[CuCH_3]_n$ can explode above −15 °C, the corresponding (η^2-alkyne)$_2$CuCH$_3$ complexes **1a** or **1b** melt at approximately 100 °C with smooth decomposition.[1,3] The advantage of their thermal stability as well as their greater ease of manipulation, as compared with $[CuCH_3]_n$ makes $\{[Ti](C{\equiv}CR^1)_2\}CuCH_3$ complexes ideal starting materials for the preparation of numerous different inorganic and organic copper(I) species.[4]

In this respect, we here describe the reaction chemistry of $\{[Ti](C{\equiv}CR^1)_2\}CuCH_3$ toward various acidic substrates HX [$X = OR^2$, SR^2, $N(R^2)_2$, $P(R^2)_2$, $C{\equiv}CR^3$].

Results and Discussion

Reaction Behavior of $\{[Ti](C{\equiv}CR^1)_2\}CuCH_3$ ($R^1 = SiMe_3$, ${}^tBu$). Reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCH_3$ (**1a**) with an equimolar amount of an alcohol HOR^2 [**2a**, $R^2 = CH_3$; **2b**, $R^2 = CH_2CH_3$; **2c**, $R^2 = {}^tBu$; **2d**, $R^2 = C_6H_5$; **2e**, $R^2 = C_6H_4{}^tBu\text{-}2$; **2f**, $R^2 = C_6H_3({}^tBu)_2\text{-}2,6$] affords the titanium(IV)−copper(I) acetylide $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)\}_2$ (**4**) at 25 °C in tetrahydrofuran as solvent in excellent yields (Scheme 1).[5]

We found that tetrametallic **4** is instantaneously formed even at low temperature (−70 °C) irrespective of the R^2 groups present. As an intermediate, the coordination complex $\{[Ti](C{\equiv}CSiMe_3)_2\}CuOR^2$ [**3a**, $R^2 = CH_3$; **3b**, $R^2 = CH_2CH_3$; **3c**, $R^2 = {}^tBu$; **3d**, $R^2 = C_6H_5$; **3e**, $R^2 = C_6H_4{}^tBu\text{-}2$; **3f**, $R^2 = C_6H_3({}^tBu)_2\text{-}2,6$] is proposed. On elimination of Me_3SiOR^2, as detected by GC/MS, these species afford at first $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)\}$, which then dimerizes to yield **4**.[5]

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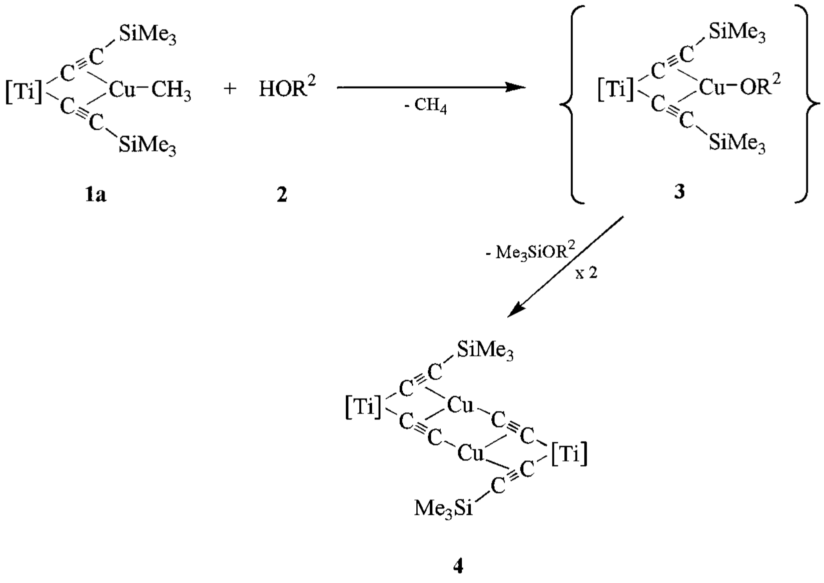
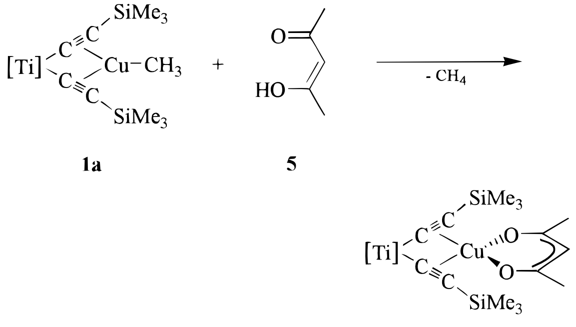
Scheme 1. Preparation of Tetrametallic 4 via Intermediate 3; Reaction of 1a with 2a−f



In this context it might be of interest to note that the reaction of the copper(I) methyl complexes $\{[Ti](C{\equiv}CR^1)_2\}CuCH_3$ (**1a**, $R^1 = SiMe_3$; **1b**, $R^1 = {}^tBu$) with H_2O produces an unstable copper(I) hydroxo species $\{[Ti](C{\equiv}CR^1)_2\}CuOH$ as an intermediate, which reacts further. In the case of $R^1 = SiMe_3$ the tetranuclear complex $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)\}_2$ along with $Me_3SiOSiMe_3$ is formed, and in the case of $R^1 = {}^tBu$, the formation of the heterodinuclear complex $\{[Ti](C{\equiv}C^tBu)_2\}CuC{\equiv}C^tBu$, $[CuC{\equiv}C^tBu]_n$, and oxo-titanium species is expected.

Nevertheless, the application of oxygen-containing chelating molecules, such as Hacac (**5**) (acac = acetylacetonate), or carboxylic acids HO_2CR^2 (**7**) enables the formation of stable copper−oxygen bonds. Thus, treatment of the tweezer complex **1a** with stoichiometric amounts of **5** produces the complex $\{[Ti](C{\equiv}CSiMe_3)_2\}Cu(acac)$ (**6**) in 97% yield. This reaction is accompanied by the evolution of CH_4 (eq 1).



(1)

Complex **6** can also be prepared by reacting, for example, $\{[Ti](C{\equiv}CSiMe_3)_2\}CuX$ (X = Cl, Br) with Na(acac) or $[Ti](C{\equiv}CSiMe_3)_2$ with Cu(acac).[6] In **6** a pseudotetrahedrally coordinated copper atom, comprising two η^2-coordinated alkyne groups and a chelate-bonded diketonato unit, is present. Hereby, the $(\eta^2\text{-}C{\equiv}CSiMe_3)_2$-Cu(acac) moiety resembles an 18-valence-electron complex fragment. This is quite uncommon in titanium(IV)−copper(I) tweezer chemistry, where the copper(I) center normally prefers a trigonal-planar environment following a 16-valence-electron count.[7]

An alternative to create stable copper−oxygen bonds is given in the application of carboxylic acids, as it was demonstrated by treatment of $\{[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ (**1b**) with, for example, $HO_2C{-}C{\equiv}CH$ (**7**) in a 1:1 molar ratio in tetrahydrofuran at −70 °C. This reaction runs very selectively, since the hydrogen atom with the higher acidity ($-CO_2H$) is smoothly removed, and by evolution of CH_4 the complex $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)\text{-}C{\equiv}CH$ (**8**) is formed quantitatively as a red oil (Scheme 2).

Complex **8** possesses with the free acetylenic and thus acidic CH unit the potential to produce tetrametallic complexes in which an organic π-conjugated $O_2C{-}C{\equiv}C$ building block spans two organometallic titanium(IV)−copper(I) tweezer entities. Thus, **8** was reacted with additional **1b** in tetrahydrofuran at −20 °C. Upon evolution of CH_4, tetrametallic $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)\text{-}C{\equiv}CCu\{({}^tBuC{\equiv}C)_2[Ti]\}$ (**9**) was formed, again in quantitative yield.

As it was clearly demonstrated by IR spectroscopic studies, the CO_2 unit in **8** and **9** is η^1-bonded by only one oxygen atom to the copper(I) center. Two distinct ν_{CO} vibrations are found at 1706 and 1595 cm^{-1} for **8** as well as 1733 and 1588 cm^{-1} for **9**. The difference of the symmetrical and asymmetrical stretching frequencies is 111 cm^{-1} (**8**) or 145 cm^{-1} (**9**), and this resembles the criterion for σ-bonded $Cu{-}O{-}C(O){-}$ moieties.[8,9]

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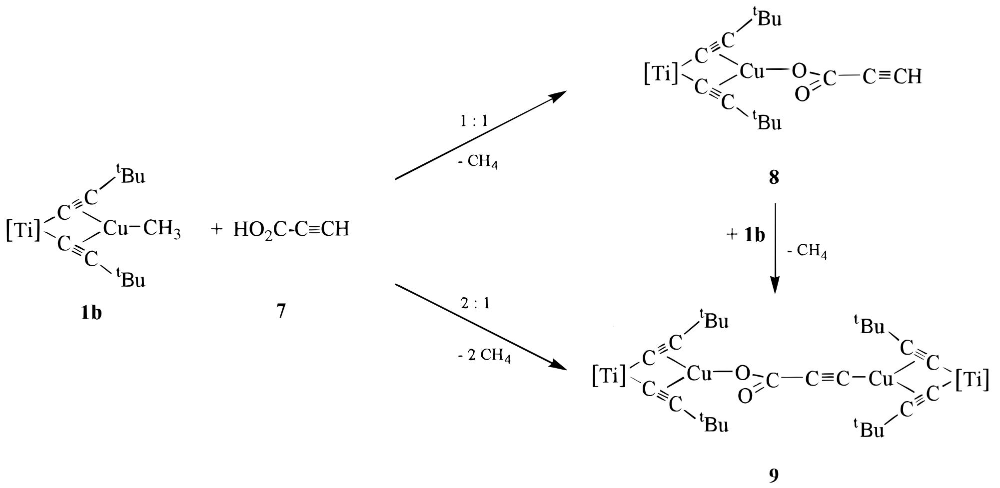
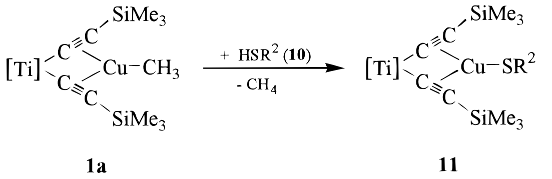
Scheme 2. Synthesis of Complex 8 by the Reaction of 1b with 7 and Complex 9 by Reacting 1b with 7 or 8, Alternatively



Similar observations were made for other copper carboxylate species in which the carboxylic group is O_2C-CH_3 or $O_2C-C_6H_5$, respectively.[9] The X-ray crystal structure analysis of, for example, the $Cu-OC(O)CH_3$ complex also fully corroborates the interpretation of an unsymmetrically bound carboxylic entity. [9b]

On changing from alcohols to thiols, stable $\{[Ti](C\equiv CSiMe_3)_2\}CuSR^2$ complexes are accessible. On addition of equimolar amounts of HSR^2 (**10a**, $R^2 = CH_2CH_3$; **10b**, $R^2 = C_6H_5$) to **1a** the bis(η^2-alkyne)-stabilized copper(I) thiolate species $\{[Ti](C\equiv CSiMe_3)_2\}CuSR^2$ (**11a**, $R^2 = CH_2CH_3$; **11b**, $R^2 = C_6H_5$) are readily formed via evolution of CH_4 (eq 2). After workup they were isolated as brown solids in quantitative yields (eq 2).



(2)

Upon using an excess of HSR^2 or reacting **11** with additional HSR^2, the $CuSR^2$ moiety is removed from the titanium(IV)–copper(I) tweezer complex **11a** or **11b** to afford $[Ti](C\equiv CSiMe_3)_2$ (**12**) together with the copper(I) thiolates $[CuSR^2]_n$ (**13**).[10,11] The bis(alkynyl) titanocene **12** can be separated easily from **13**, since the latter is unsoluble in the used solvents, while **12** remains dissolved. This reaction resembles an easy and quantitative way for replacing the copper entity in heterometallic titanium–copper tweezer molecules. A similar behavior is found when titanium–copper complexes are reacted with an excess of, for example, phosphites or phosphanes.[7,12]

Thiols as well as carboxylic acids and Hacac, can be used for the successful preparation of stable monomeric alkyne-stabilized $CuSR^2$ and Cu(acac) entities (vide supra). Thus the question arises if $\{[Ti](C\equiv CR^1)_2\}CuCH_3$ (**1a**, **1b**) can also be applied as starting material for the synthesis of copper(I) species in which Cu–E bonds are present (E = group 15 element of the periodic table). This is also of interest since there is only limited knowledge about copper–nitrogen as well as copper–phosphorus σ-bonds, compared to copper–oxygen or copper–sulfur bond containing entities.[13,14]

Therefore, $\{[Ti](C\equiv CR^1)_2\}CuCH_3$ (**1a**, $R^1 = SiMe_3$; **1b**, $R^1 = {}^tBu$) was reacted with 1 equiv of $HE(R^2)_2$ (**14**, E = N, $R^2 = SiMe_3$; **15**, E = P, $R^2 = C_6H_5$) under reaction conditions similar to those described above. The new complexes $\{[Ti](C\equiv CSiMe_3)_2\}CuN(SiMe_3)_2$ (**16**) and $\{[Ti](C\equiv C^tBu)_2\}CuP(C_6H_5)_2$ (**17**) were isolated as a deep red oil (**16**) or as orange crystalline material (**17**) in 97 or 98% yield, respectively (eq 3).

While **17** is stable at 25 °C in the solid state and in solution, it appeared that **16**, however, starts to eliminate $N(SiMe_3)_3$ at 0 °C by cleavage of the copper–nitrogen bond $[Cu-N(SiMe_3)_2]$ as well as a carbon–silicon bond ($\equiv C-SiMe_3$) to afford the heterobimetallic titanium(IV)–copper(I) acetylide $\{[Ti](C\equiv CSiMe_3)(C\equiv CCu)\}_2$ (**4**) in quantitative yield (vide supra). Nevertheless, complex **16** could fully be characterized by its IR and ^1H as well as $^{13}C\{^1H\}$ NMR spectra. Both complexes **16** and **17** are slightly sensitive to air and are somewhat hygroscopic.

In general, monomeric $\{[Ti](C\equiv CR^1)_2\}CuCH_3$ (**1**) can also be applied as a synthetic tool for the preparation of a great variety of mononuclear alkyne-stabilized copper(I) acetylides. In these reactions the acidic acetylenic hydrogen atom in $H-C\equiv CR^3$ is replaced by the copper atom. On addition of the corresponding acetylides $HC\equiv CR^3$ [**18a**, $R^3 = {}^tBu$; **18b**, $R^3 = SiMe_3$; **18c**, $R^3 = (CH_2)_2CH_3$; **18d**, $R^3 = H$; **18e**, $R^3 = Fc$; **18f**, $R^3 = C_6H_4-NO_2-4$; **18g**, $R^3 = C_6H_5$; **18h**, $R^3 = CO_2CH_3$; Fc = (η^5-

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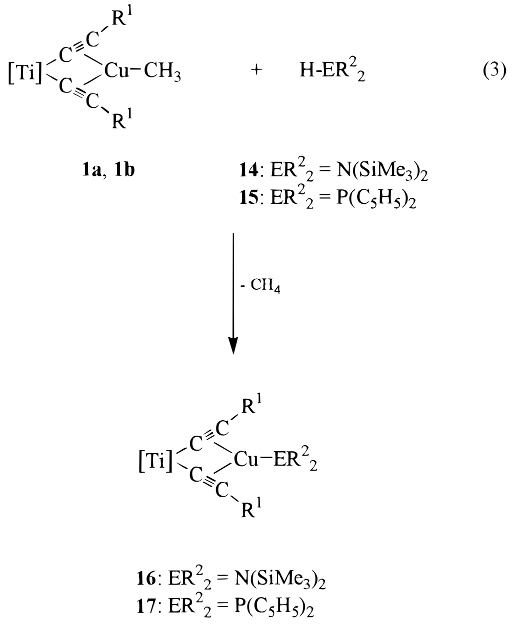
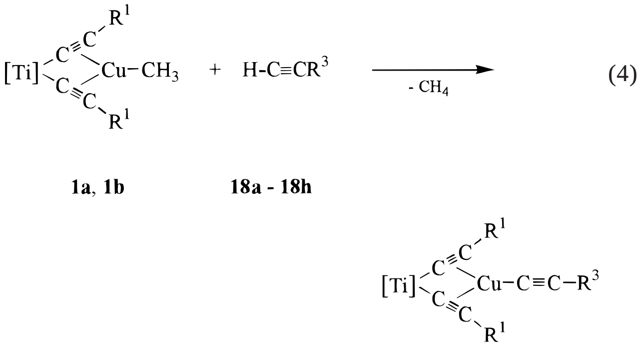


1a, **1b**

14: ER$^2_2$ = N(SiMe$_3$)$_2$
15: ER$^2_2$ = P(C$_5$H$_5$)$_2$

16: ER$^2_2$ = N(SiMe$_3$)$_2$
17: ER$^2_2$ = P(C$_5$H$_5$)$_2$

C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)] to a diethyl ether solution containing **1a** or **1b**, evolution of CH$_4$ takes place and the alkyne-stabilized copper(I) acetylides {[Ti](C≡CR^1)$_2$}CuC≡CR^3 (**19**, **20**) are produced (eq 4).



1a, **1b** **18a - 18h**

	R^1	R^2
19a	^{t}Bu	^{t}Bu
19b	^{t}Bu	SiMe$_3$
19c	^{t}Bu	(CH$_2$)$_2$CH$_3$
19d	^{t}Bu	H
19e	^{t}Bu	Fc$^{a)}$
19f	^{t}Bu	C$_6$H$_4$NO$_2$-4
20a	SiMe$_3$	C$_6$H$_5$
20b	SiMe$_3$	CO$_2$Me
20c	SiMe$_3$	SiMe$_3$
20d	SiMe$_3$	Fc$^{a)}$

a) Fc = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)

Orange- to red-colored **19a**−**f** and **20a**−**d** are formed in quantitative yields. Since the transformation of **1a** and **1b** to **19** or **20** is quantitative, the workup is very easy because volatile materials have only to be removed in vacuo; the remaining solids or oils are analytically pure.

Another high-yield method for the preparation of alkyne-stabilized copper(I) acetylides has been described previously and is based on the monomerically stabilized copper(I) thiolate {[Ti](C≡CR^1)$_2$}CuSC$_6$H$_4$CH$_2$NMe$_2$-2 as the starting material.[5] However, this reaction does not produce quantitative yields of the envisioned copper(I) acetylides, in contrast to the copper(I) methyl route described in this report. Also, it bears the disadvantage that only acetylenes HC≡CR^3 can be employed with metalation-tolerant substituents R^3.

Most interesting with respect to their chemical and physical properties are complexes **19d**, **19e**, and **20d**, since these species contain as reactive sites an acetylenic hydrogen atom or a η^1-bonded ferrocenyl moiety as end-grafted transition metal building block. Especially the latter two molecules are rare examples in organometallic chemistry in which early and late transition metal building blocks are bridged by π-conjugated organic units, such as C≡C and C$_5$H$_4$.[15,16]

Additionally, complex **19d** provides the potential to react with 1 equiv of, for example, **1a** or **1b** to form tetrametallic complexes containing a central Cu−C≡C−Cu entity. However, also numerous variations of the synthetic procedures described in this work (solvent, temperature, etc.) did not result in the formation of molecules of the type {[Ti](C≡CR^1)$_2$}CuC≡CCu{(R^{1}C≡C)$_2$[Ti]}. One reason is probably given in the steric congestion around the C≡C building block. Similar observations were made by the reaction of {[Ti](C≡CSiMe$_3$)$_2$}CuC≡N with other heterometallic π-tweezer molecules, e.g., {[Ti](C≡CSiMe$_3$)$_2$}AgBF$_4$.[15d]

All described reactions are straightforward, and the formation of the corresponding copper(I) carboxylates, thiolates, amides, phosphides, or even acetylides is generally achieved in quantitative yields. The driving force of these reactions is the formation and evolution of CH$_4$. However, the reactions described are limited to reagents that feature acidic hydrogen atoms. It was shown that no reaction takes place when nonacidic or only weakly acidic hydrogen atoms are present in the reactants applied, e.g., alkyls or aryls.

After evaporation of all volatiles the titanium(IV)−copper(I) tweezer complexes are obtained in an analytically pure form as orange to deep red crystalline solids (**4**, **6**, **11**, **17**, **19a**,**b**,**d**−**f**, **20a**,**c**−**f**) or as red oils (**8**, **9**, **16**, **19c**, **20b**).

It must be noted that all complexes, except **3a**−**f**, where a copper−oxygen bond is formed are very stable species, when compared with their noncoordinated copper(I) analogues. Furthermore, **1a** and **1b** are best suited as starting materials for the preparation of numerous different copper(I) complexes in which the copper(I) center is bound in a η^1-fashion to organic or inorganic groups or even chelating units, such as acac.

It is also found that the corresponding titanium(IV)−copper(I) species are better soluble than their noncoordinated counterparts; that is, the titanium(IV)−copper(I) tweezer complexes are already soluble in nonpolar organic solvents, such as toluene or n-pentane.

Solid-State Structures of {[Ti](C≡C^{t}Bu)$_2$}CuC≡C^{t}Bu (19a) and {[Ti](C≡C^{t}Bu)$_2$}CuC≡CC$_6$H$_4$NO$_2$-4

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Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] of 19a and 19f[a]

	19a	19f
Bond Lengths		
Ti(1)−C(1)	2.101(4)	2.0850(18)
Ti(1)−C(7)	2.082(3)	2.0963(18)
C(1)−C(2)	1.239(4)	1.232(2)
C(7)−C(8)	1.230(4)	1.233(2)
C(2)−C(3)	1.500(4)	1.497(3)
C(8)−C(9)	1.491(4)	1.496(2)
Cu(1)−C(13)	1.903(4)	1.9077(19)
C(13)−C(14)	1.199(4)	1.197(3)
C(14)−C(15)	1.479(5)	1.434(3)
Cu(1)−Ti(1)	2.909(4)	2.9209(4)
Cu(1)−C(1)	2.066(4)	2.0647(17)
Cu(1)−C(7)	2.067(4)	2.0691(17)
Cu(1)−C(2)	2.146(4)	2.1337(18)
Cu(1)−C(8)	2.157(4)	2.1406(18)
Ti(1)−D(1)[b]	2.0693(35)	2.0596(9)
Ti(1)−D(2)[b]	2.0675(35)	2.0631(11)
Bond Angles		
C(1)−Ti(1)−C(7)	90.50(2)	90.02(7)
Ti(1)−C(1)−C(2)	165.0(2)	165.15(15)
Ti(1)−C(7)−C(8)	165.3(3)	164.97(15)
C(1)−C(2)−C(3)	161.2(3)	160.89(18)
C(7)−C(8)−C(9)	160.0(3)	161.37(19)
Cu(1)−C(13)−C(14)	173.1(3))	174.08(18)
C(13)−C(14)−C(15)	178.5(3)	177.3(2)
Ti(1)−Cu(1)−C(13)	175.78(10)	175.54(6)
D(1)−Ti(1)-D(2)	133.83(11)	132.84(4)

[a] Standard deviation is given as the last significant figure in parentheses. [b] D(1), D(2): Centroids of the cyclopentadienyl ligands.

Table 2. Crystal and Intensity Collection Data for Complexes 19a and 19f

	19a	19f
empirical formula	$C_{40}H_{59}CuSi_2Ti$	$C_{36}H_{48}CuNO_2Si_2Ti$
chemical formula	$C_{34}H_{53}CuSi_2Ti$, C_6H_6	$C_{36}H_{48}CuNO_2Si_2Ti$
molecular mass	707.49	694.37
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.514(11)	9.8549(2)
b (Å)	10.706(13)	11.6673(2)
c (Å)	19.17(2)	17.1104(3)
α (deg)	104.54(9)	90.900(1)
β (deg)	99.08(8)	102.240(1)
γ (deg)	97.46(9)	111.0118(1)
V (Å^3)	2030(4)	1785(62(6)
ρ_{calc} (g cm^{-3})	1.157	1.291
F(000)	756	732
Z	2	2
crystal dimens (mm)	0.7 × 0.6 × 0.2	0.5 × 0.4 × 0.2
diffractometer model	Siemens-Stoe AED2	Bruker SMART CCD
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
max., min. transmn	0.800, 0.614	0.782433, 0.651402
abs coeff (μ, mm^{-1})	0.804	0.917
temp (K)	218(2)	173(2)
scan mode	ω scans	ω scans
scan range (deg)	$1.99 \leq \theta \leq 25.01$	$1.22 \leq \theta \leq 30.40$
index ranges	$-12 \leq h \leq 10$ $-12 \leq k \leq 12$ $0 \leq l \leq 22$	$-12 \leq h \leq 13$ $-12 \leq k \leq 16$ $-23 \leq l \leq 21$
total no. of reflns	7021	13 278
no. of unique reflns	7021	9379
no. of obsd reflns [$I \geq 2\sigma(I)$]	5265	7066
completeness to θ max	98%	86.9%
no. of refined params	412	580
R1, wR2 [$I \geq 2\sigma(I)$]	0.0401, 0.0914[a]	0.0344, 0.0780
R1, wR2 (all data)	0.069, 0.1010[a]	0.0552, 0.0858
S	1.016[a]	0.972
max., min. peak in final Fourier map (e Å^{-3})	0.319, −2.87	0.329, −0.508

[a] $R1 = [\sum(||F_o| - |F_c|)/\sum|F_o|)]$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0450P)^2 + 0.6907P]$ with $P = [F_o^2 + 2F_c^2]/3$; $S = [\sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. [b] $R1 = [\sum(||F_o| - |F_c|)/\sum|F_o|)]$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.0000P]$ with $P = [F_o^2 + 2F_c^2]/3$; $S = [\sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. n = number of reflections, p = parameters used.

(19f). Crystals of **19a** and **19f** were obtained by cooling a concentrated *n*-pentane solution of **19a** or **19f** to −30 °C. Selected geometrical details are listed in Table 1 and crystallographic data are given in Table 2 (Experimental Section). The solid-state structures are depicted in Figure 1 (**19a**) and Figure 2 (**19f**).

Complexes **19a** and **19f** crystallize in the triclinic space group $P\bar{1}$. The molecular structures of **19a** (Figure 1) and **19f** (Figure 2) clearly show that the copper(I) center is trigonally planar coordinated, involving the bis(η^2-alkynyl) chelate [Ti](C≡C^{t}Bu)$_2$ and an η^1-bonded C≡C^{t}Bu (**19a**) or C≡C$C_6H_4NO_2$-4 unit (**19f**). The central [Ti](C≡C^{t}Bu)$_2$Cu entity as well as the copper(I) σ-bonded C≡CR^3 units are orientated in-plane [rms deviation from a best plane through the respective atoms: **19a**, Ti(1)−C(1)−C(2)−C(7)−C(8)−Cu(1)−C(13)−C(14) 0.0623 Å; **19f**, Ti(1)−C(1)−C(2)−C(7)−C(8)−Cu(1)−C(13)−C(14) 0.0810 Å]. The Cu−C≡C−^{t}Bu as well as the Cu−C≡C−$C_6H_4NO_2$-4 moiety are linear, which is typical for this type of bonding.[1b,3] In contrast, the alkynyl ligands Ti−C≡C-^{t}Bu, η^2-coordinated to copper(I), are *trans*-deformed, as is characteristic for heterobimetallic π-tweezers in which the C≡C triple bonds are likewise side-on bonded to low-valent transition metal fragments [**19a**: Ti(1)−C(1)−C(2) 165.0(2)°, C(1)−C(2)−C(3) 161.2(3)°, Ti(1)−C(7)−C(8) 165.3(2)°, C(7)−C(8)−C(9) 160.0(3)°; **19f**: Ti(1)−C(1)−C(2) 165.15(15)°, C(1)−C(2)−C(3) 160.89(18)°, Ti(1)−C(7)−C(8) 164.97(15)°, C(7)−C(8)−C(9) 161.37(19)°].[9−14]

In addition to η^2-coordinated alkynyl groups in **19a** and **19f** also σ-bonded acetylide units are present. While in **19a** the η^2-coordinated C≡C triple bonds are 1.239(4) Å [C(1)−C(2)] and 1.230(4) Å [C(7)−C(8)], the σ-bonded C≡C^{t}Bu moiety shows a distance of 1.199(4) Å [C(13)−C(14)]. The same is valid for complex **19f**: 1.232(2) Å [C(1)−C(2)], 1.233(2) Å [C(7)−C(8)], 1.197(3) Å [C(13)−C(14)]. It is noteworthy that in the solid-state structure of **19f** the plane of the C_6H_4 group is tilted 22.89(7)° with respect to the Ti(C≡C)$_2$CuC≡C-containing plane.

For both complexes a bite angle $C_{C≡C}$−Ti−$C_{C≡C}$ of 90.5(2)° (**19a**) or 90.02(7)° (**19f**) is observed. When compared with uncoordinated tweezer molecules, such as [Ti](C≡CSiMe$_3$)$_2$ [102.1(3)°] [7] or [Ti](C≡CFc)$_2$ [98.8(4)°],[15a] this angle is significantly reduced due to the η^2-coordination of the titanium-bonded alkynyl groups to the copper(I) acetylide fragment. However, the angle D1−Ti−D2 (D1, D2 = centroid of the cyclopentadienyl groups) is not influenced [**19a**: D(1)−Ti(1)−D(2), 133.83(11)°; **19f**: D(1)−Ti(1)−D(2), 132.84(4)°].

Spectroscopy. In the IR spectrum of **19a** two distinct $\nu_{C≡C}$ vibrations at 2099 (CuC≡C^{t}Bu) and 1941 cm^{-1} (TiC≡C^{t}Bu) are observed, which clearly indicate in addition to X-ray structure analysis that, apart from an η^1-bonded alkynyl copper unit, i.e., CuC≡C^{t}Bu, η^2-bonded TiC≡C^{t}Bu moieties are present. Similar obser-

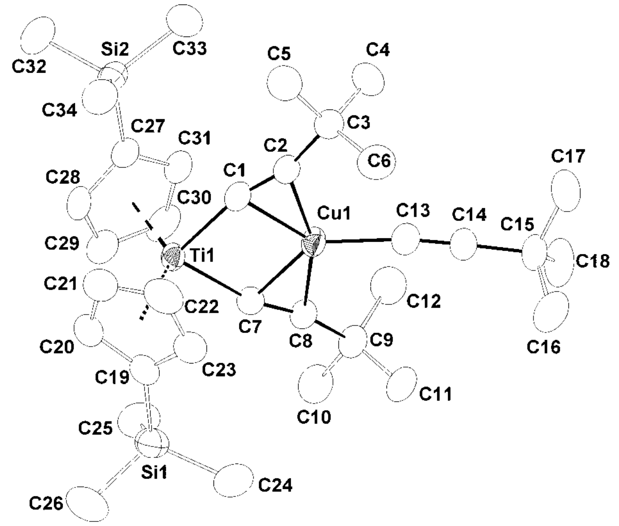

Figure 1. ZORTEP plot (50% probability level) of **19a** with the molecular geometry and atom-labeling scheme.

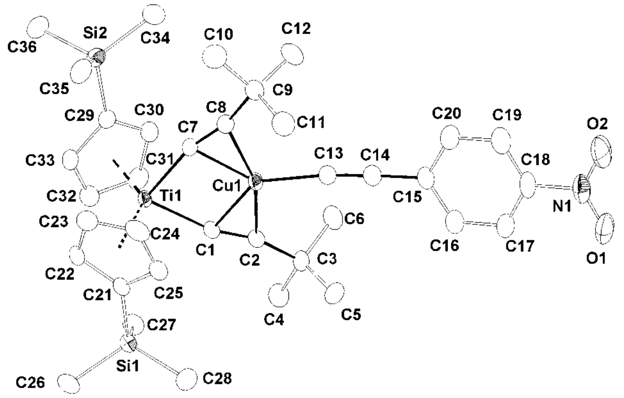

Figure 2. ZORTEP plot (50% probability level) of **19f** with the molecular geometry and atom-labeling scheme.

vations were made for all other copper acetylides **8**, **9**, **19**, and **20**. In **8** and **19d** two very characteristic absorption bands for the HC≡C fragment at 3263 cm^{-1} ($\nu_{\equiv C-H}$)/2067 cm^{-1} ($\nu_{C\equiv C}$) (**19d**) and 3276 cm^{-1} ($\nu_{\equiv C-H}$)/2085 cm^{-1} ($\nu_{C\equiv C}$) (**8**) are found. The ester functionality in **20b** and the carboxylate group in **8** and **9** appear as strong bands at 1671 cm^{-1} ($\nu_{C=O}$)/1295 cm^{-1} (ν_{C-O}) (**20b**), 1706 cm^{-1} ($\nu_{CO\ sym}$)/1595 cm^{-1} ($\nu_{CO\ as}$) (**8**), or 1733 cm^{-1} ($\nu_{CO\ sym}$)/1588 cm^{-1} ($\nu_{CO\ as}$) (**9**), respectively. In contrast, complexes **11**, **16**, and **17** show as the only distinguished stretching vibration the band of the C≡C triple bond between 1890 and 1980 cm^{-1}, a region that is typical for side-on bonded alkynyl groups in transition metal chemistry.[17]

The ^{1}H NMR spectra of all complexes in CDCl$_3$ consist of sharp and well-resolved signals for the organic groups present: for the protons of the cyclopentadienyl ligands a AA′BB′ spin system is observed with two pseudotriplets in the range 5.5−6.5 ppm with coupling constants J_{HH} between 2.0 and 2.5 Hz. However, for complexes **8** and **9** only broad singlets were observed around 6.1 ppm. Also, well-defined signal patterns for the σ-bonded organic ligands R^2 at the sulfur (**11a**,**b**), nitrogen (**16**), or phosphorus (**17**) atoms are found. While the SiMe$_3$ groups of the N(SiMe$_3$)$_2$ ligand in **16** exhibit two resonance signals at 0.06 and 0.12 ppm, the proton signals of the phenyl groups of the P(C$_6$H$_5$)$_2$ ligand appear in the region between 7 and 7.5 ppm, typical for this type of ligand.[18] The resonance signals of the alkynyl substituents R^3 in complexes **19** and **20** are also observed in typical regions; for example, for the ferrocenyl complex **20d** a singlet at 4.31 ppm and two pseudotriplets at 4.04 and 4.55 ppm with a coupling constant of J_{HH} = 1.8 Hz are found. In addition, for complex **8** the proton of the alkynyl unit is observed at 2.87 ppm, a typical value for alkynyl protons.[19]

The phosphorus resonance signal for **17** appears at −35.7 ppm in the ^{31}P{^{1}H} NMR spectrum. This chemical shift has been reported earlier for a copper-bound P(C$_6$H$_5$)$_2$ group, e.g., for (C$_6$H$_5$)$_3$PCuP(C$_6$H$_5$)$_2$ (−32.2 ppm).[18]

In the ^{13}C{^{1}H} NMR spectra of complexes **8**, **9**, **19**, and **20** two differently bonded alkynyl ligands, i.e., an η^2-coordinated TiC≡CR^1 and a σ-bonded C≡CR^3 ligand, is evidenced by the observation of a total of four carbon resonance signals for the C≡C building blocks in the region 148−158 ppm (C$_\alpha$, TiC$_\alpha$≡C^{t}Bu) and 131−145 ppm (C$_\beta$, TiC≡C$_\beta$tBu) or 180−185 ppm (C$_\alpha$, TiC$_\alpha$≡CSiMe$_3$) and 127−133 ppm (C$_\beta$, TiC≡C$_\beta$SiMe$_3$). In general it is found that the carbon resonance signals of the CuC≡CR^3 groups, when compared with the appropriate TiC≡CR^1 units, are observed at higher field. The carbon resonance signal of the terminal alkynyl group ≡C−H in **8** is found at 75.5 ppm, while the one for complex **19d** appears at 102.5 ppm. Comparing the shift of the terminal sp-hybridized carbon atom ≡C−H in **8** with the one in **9** (113.2 ppm) shows that upon replacement of the acetylenic proton in **8** by Cu(I), i.e., formation of **9**, the resonance is shifted to lower field.

In addition, complexes **19e** and **20d** possess four characteristic carbon signals for the cyclopentadienyl ligands of the ferrocenyl units between 67 and 75 ppm. Complex **20b** shows a specific resonance signal at 171.2 ppm for the sp^2-hybridized carbon atom of the CO$_2$Me group. The resonance signals of the other organic groups appear in regions characteristic for those moieties.

Experimental Section

General Methods. All reactions were carried out in an atmosphere of purified nitrogen (O$_2$ traces: CuO catalyst, BASF AG, Ludwigshafen; H$_2$O: molecular sieve 4 Å) using standard Schlenk techniques. Solvents were purified by distillation; *n*-pentane and dichloromethane, calciumhydride; diethyl ether and tetrahydrofuran, sodium/benzophenone ketyl; toluene, sodium. FT-IR spectra were obtained on a Perkin-Elmer FT-IR 1000 spectrometer as KBr pellets, as film between NaCl plates, or as solution between CaF$_2$ plates. NMR spectra were recorded on a Bruker Avance 250 spectrometer; ^{1}H NMR spectra were recorded at 250.130 MHz (internal standard relative to CDCl$_3$, δ = 7.27); ^{13}C{^{1}H} NMR spectra were recorded at 67.890 MHz (standard intern, relative to CDCl$_3$, δ 77.0); ^{31}P {^{1}H} NMR were recorded at 101.255 MHz

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in $CDCl_3$ with $P(OMe)_3$ as external standard (δ 139.0, rel to H_3PO_4 85%]. Chemical shifts are reported in δ units (ppm) downfield from $SiMe_4$ with the solvent signal as reference signal. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Organic Department at the Technical University of Chemnitz.

General Remarks. Compounds **1a**[1], **1b**[1], **11c**[19], **11d**,[20] and **15**[21] were prepared by published procedures. All other chemicals were purchased by commercial suppliers and were used as received.

1. Reaction of $\{[Ti](C\equiv CSiMe_3)_2\}CuCH_3$ (1a) with HOR^2 (2a−f). To $\{[Ti](C\equiv CSiMe_3)_2\}CuCH_3$ (**1a**) (180 mg, 0.320 mmol) in 50 mL of tetrahydrofuran were added dropwise the corresponding alcohols HOR^2 (0.320 mmol, **2a**, $R^2 = CH_3$, 10 mg; **2b**, $R^2 = CH_2CH_3$, 15 mg; **2c**, $R^2 = {}^tBu$, 25 mg; **2d**, $R^2 = C_6H_5$, 30 mg; **2e**, $R^2 = C_6H_4$-2-^tBu, 50 mg; **2f**, $R^2 = C_6H_4$-2,6-$^tBu_2$, 65 mg) dissolved in 10 mL of tetrahydrofuran at −70 °C. After stirring for 30 min at this temperature, the reaction mixture was gradually warmed to −10 °C and all volatiles were removed in vacuo. The obtained red-colored residues were washed with cold *n*-pentane (2 × 5 mL) to yield quantitatively the titanium(IV)−copper(I) acetylide $\{[Ti](C\equiv CSiMe_3)(C\equiv CCu)\}_2$ (**4**) (325 mg, 0.160 mmol). Complex **4** was fully spectroscopically characterized.

The obtained spectroscopic data are in agreement with the data reported in ref 5.

2. Synthesis of $\{[Ti](C\equiv CSiMe_3)_2\}Cu(acac)$ (6). A solution of Hacac (**5**) (50 mg, 0.492 mmol) in 10 mL of tetrahydrofuran was slowly added to $\{[Ti](C\equiv CSiMe_3)_2\}CuCH_3$ (**1a**) (293 mg, 0.492 mmol) in 50 mL of tetrahydrofuran at −20 °C. After stirring for 30 min at this temperature, the reaction mixture was gradually warmed to 25 °C and stirred for 1 h. All volatile materials were removed in vacuo. The dark red residue was crystallized from *n*-pentane by cooling to −30 °C. $\{[Ti](C\equiv CSiMe_3)_2\}Cu(acac)$ (**6**) was obtained analytically pure in 97% yield (325 mg, 0.477 mmol).

The spectroscopic data of **6** are listed in ref 6.

3. Synthesis of $\{[Ti](C\equiv C^tBu)_2\}CuOC(O)$-$C\equiv CH$ (8). A 15 mg sample of $HC\equiv C-CO_2H$ (0.231 mmol) was added in one portion to $[Ti](C\equiv C^tBu)_2\}CuCH_3$ (**1b**) (130 mg, 0.231 mmol) in 70 mL of tetrahydrofuran at −70 °C and stirred at this temperature for 30 min. After gradually warming the reaction mixture to 25 °C, it was stirred for 1 h at this temperature. All volatiles were removed in vacuo, and **8** remained as a red oil in quantitative yield (140 mg, 0.231 mmol).

IR (NaCl, ν, cm^{-1}): 3276 ($\equiv C-H$), 2085 ($C\equiv CH$), 1944 ($TiC\equiv C$), 1706 (CO_{sym}), 1595 (CO_{as}). ^1H NMR ($CDCl_3$): 0.24 (s, 18H, $SiMe_3$), 1.28 (s, 18H, ^tBu), 2.87 (s, 1H, $\equiv CH$), 6.09 (bs, 4H, C_5H_4), 6.12 (bs, 4H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.0 ($SiMe_3$), 31.0 (^tBu), 31.1 (^tBu, C_q), 75.0 ($\mathit{C}\equiv CH$), 75.5 ($C\equiv \mathit{C}H$), 114.8 (C_5H_4), 117.5 (C_5H_4), 121.3 (C_5H_4, C_{ipso}), 131.1 ($TiC\equiv \mathit{C}$), 149.9 ($Ti\mathit{C}\equiv C$), 156.1 ($CuCO_2$). Anal. Calcd for $C_{31}H_{45}CuO_2Si_2Ti$ (617.29): C, 60.32; H, 7.35. Found: C, 59.81; H, 7.29.

4. Synthesis of $\{[Ti](C\equiv C^tBu)_2\}CuOC(O)-C\equiv CCu$-$\{(^tBuC\equiv C)_2[Ti]\}$ (9). Method A. A 15 mg sample of $HC\equiv CCO_2H$ (0.231 mmol) was added in one portion to $[Ti](C\equiv C^tBu)_2\}CuCH_3$ (**1b**) (260 mg, 0.462 mmol) in 100 mL of tetrahydrofuran at −20 °C. After stirring for 15 min at this temperature, the reaction mixture was gradually warmed to 25 °C. After another 1 h stirring all volatiles were removed in vacuo. Complex **9** was obtained as an orange oil in quantitative yield (280 mg, 0.231 mmol).

Method B. To a solution of $[Ti](C\equiv C^tBu)_2\}CuCH_3$ (**1b**) (120 mg, 0.213 mmol) dissolved in 50 mL of tetrahydrofuran was added $\{[Ti](C\equiv C^tBu)_2\}CuO_2C-C\equiv CH$ (**8**) (130 mg, 0.213 mmol) dissolved in 30 mL of tetrahydrofuran at 25 °C. After 3 h stirring at this temperature all volatiles were removed in vacuo to afford **9** as an orange oil in quantitative yield (280 mg, 0.231 mmol).

IR (NaCl, ν, cm^{-1}): 2089 ($CuC\equiv C$), 1978 ($TiC\equiv C$), 1951 ($TiC\equiv C$), 1733 (CO_{sym}), 1588 (CO_{as}). ^1H NMR ($CDCl_3$): 0.27 (s, 18H, $SiMe_3$), 0.27 (s, 18H, $SiMe_3$), 1.31 (s, 18H, ^tBu), 1.50 (s, 18H, ^tBu), 6.01 (bs, 16H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): −0.1 ($SiMe_3$), 0.0 ($SiMe_3$), 30.9 (^tBu), 31.1 (^tBu, C_q), 31.2 (^tBu, C_q), 31.4 (^tBu), 112.2 (C_5H_4), 113.2 ($Cu\mathit{C}\equiv C$), 114.1 (C_5H_4), 115.3 (C_5H_4), 115.5 (C_5H_4, C_{ipso}), 116.7 (C_5H_4), 116.9 ($CuC\equiv \mathit{C}$), 117.7 (C_5H_4, C_{ipso}), 133.2 ($TiC\equiv \mathit{C}$), 145.1 ($TiC\equiv \mathit{C}$), 148.1 ($Ti\mathit{C}\equiv C$), 158.0 ($Ti\mathit{C}\equiv C$), 161.3 ($CuCO_2$). Anal. Calcd for $C_{59}H_{88}Cu_2O_2Si_4Ti_2$ (1164.54): C, 60.85; H, 7.62. Found: C, 60.42; H, 7.74.

5. Synthesis of $\{[Ti](C\equiv CSiMe_3)_2\}CuSR^2$ (11a, $R^2 = CH_2CH_3$; 11b, $R^2 = C_6H_5$). A 0.420 mmol sample of HSR^2 (**10a**, $R^2 = CH_3CH_2$, 26 mg; **10b**, $R^2 = C_6H_5$, 46 mg) in 10 mL of tetrahydrofuran was added dropwise to $\{[Ti](C\equiv CSiMe_3)_2\}$-$CuCH_3$ (**1a**) (250 mg, 0.420 mmol) in 50 mL of tetrahydrofuran at −40 °C. After stirring for 30 min at this temperature, the reaction mixture was gradually warmed to 25 °C. After stirring for an additional 1 h all volatiles were evaporated in vacuo. The brown residue was dissolved in 10 mL of diethyl ether. Crystallization at −30 °C yielded analytically pure $\{[Ti](C\equiv CSiMe_3)_2\}CuSR$ (**11a**, R = CH_2CH_3; **11b**, R = C_6H_5) in quantitative yield (0.412 mmol; **11a**, 265 mg; **11b**, 285 mg). Complexes **11a** and **11b** were fully spectroscopically characterized.

The obtained spectroscopic data are in agreement with the data reported in ref 19.

6. Synthesis of $\{[Ti](C\equiv CSiMe_3)_2\}CuN(SiMe_3)_2$ (16). $HN(SiMe_3)_2$ (**14**) (41 mg, 0.252 mmol) in 10 mL of tetrahydrofuran was slowly added to $\{[Ti](C\equiv CSiMe_3)_2\}CuCH_3$ (**1a**) (150 mg, 0.252 mmol) in 30 mL of tetrahydrofuran at −20 °C. After stirring for 1 h at this temperature, all volatiles were removed in vacuo to afford $\{[Ti](C\equiv CSiMe_3)_2\}CuN(SiMe_3)_2$ (**16**) quantitatively as a red oil (185 mg, 0.250 mmol).

IR (NaCl, ν, cm^{-1}): 1892 ($TiC\equiv C$). ^1H NMR ($CDCl_3$): 0.06 (s, 9H, $SiMe_3$), 0.12 (s, 9H, $SiMe_3$), 0.25 (s, 18H, $SiMe_3$), 0.40 (s, 18H, $SiMe_3$), 5.64 (pt, J_{HH} = 2.3 Hz, 4H, C_5H_4), 5.96 (pt, J_{HH} = 2.3 Hz, 4H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.3 ($SiMe_3$), 0.4 ($NSiMe_3$), 0.7 ($SiMe_3$), 112.7 (C_5H_4), 115.1 (C_5H_4), 119.7 (C_5H_4, C_{ipso}), 128.4 ($TiC\equiv \mathit{C}$), 182.5 ($Ti\mathit{C}\equiv C$). FAB-MS [*m/e* (rel int)]: M^+ 741 (20), $M^+ - N(SiMe_3)_2$ 578 (70), $(C_5H_4SiMe_3)_2Ti^+$ 322 (100). Anal. Calcd for $C_{32}H_{62}CuNSi_6Ti$ (740.81): C, 51.88; H, 8.44. Due to the thermal instability of **16**, no satisfactory elemental analysis could be obtained. Spectroscopic data of **4** are listed in ref 5.

7. Synthesis of $\{[Ti](C\equiv C^tBu)_2\}CuP(C_6H_5)_2$ (17). $HP(C_6H_5)_2$ (**15**) (40 mg, 0.213 mmol) in 10 mL of tetrahydrofuran was added dropwise to $\{[Ti](C\equiv C^tBu)_2\}CuCH_3$ (**1a**) (120 mg, 0.213 mmol) dissolved in 30 mL of tetrahydrofuran at −20 °C. After stirring for 30 min at this temperature, the reaction mixture was warmed to 25 °C and stirred there for 1 h. All volatiles were evaporated in vacuo. The residue was crystallized from *n*-pentane at −30 °C. $\{[Ti](C\equiv C^tBu)_2\}CuP(C_6H_5)_2$ (**17**) was isolated as an orange solid in 98% yield (155 mg, 0.209 mmol).

Mp: 158 °C (dec). IR (KBr, ν, cm^{-1}): 1979 ($TiC\equiv C$). ^1H NMR ($CDCl_3$): 0.27 (s, 18H, $SiMe_3$), 1.45 (s, 18H, ^tBu), 6.02 (pt, J_{HH} = 2.1 Hz, 4H, C_5H_4), 6.06 (pt, J_{HH} = 2.1 Hz, 4H, C_5H_4), 7.0−7.5 (m, 10H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.1 ($SiMe_3$), 30.9 (^tBu), 31.7 (^tBu, C_q), 114.3 (C_5H_4), 116.9 (C_5H_4), 120.6 (C_5H_4, C_{ipso}), 128−135 (C_6H_5), the signals of the alkynyl carbon atoms could not unequivocally be detected. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −35.7. EI-MS [*m/z* (rel int)]: M^+ 733 (25), $M^+ - P(C_6H_5)_2$ 547

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(20), $M^+ - CuP(C_6H_5)_2 - C_2tBu$ 404 (25), $(C_5H_4SiMe_3)_2Ti^+$ 322 (100). Anal. Calcd for $C_{40}H_{54}CuPSi_2Ti$ (733.43): C, 65.51; H, 7.42. Due to the thermal instability of **17**, no satisfactory elemental analysis could be obtained.

8. Synthesis of {[Ti](C≡C^{t}Bu)$_2$}CuC≡CR^3 (19a, R^3 = ^{t}Bu; 19b, R^3 = SiMe$_3$; 19c, R^3 = (CH$_2$)$_2$CH$_3$; 19e, R^3 = Fc; 19f, R^3 = C$_6$H$_4$NO$_2$-4). Method A. To [Ti](C≡C^{t}Bu)$_2$}CuSC$_6$H$_4$-CH$_2$NMe$_2$-2 (**11d**) (180 mg, 0.250 mmol) in 80 mL of diethyl ether was slowly added 1 equiv of LiC≡CR^3 (R^3 = ^{t}Bu, 20 mg; R^3 = SiMe$_3$, 25 mg; R^3 = (CH$_2$)$_2$CH$_3$, 20 mg; R^3 = Fc, 55 mg; R^3 = C$_6$H$_4$-4-NO$_2$, 40 mg) in 30 mL of diethyl ether at 0 °C. After stirring for 1 h at this temperature, the reaction mixture was gradually warmed to 25 °C and stirred additionally for 3 h at this temperature. All volatiles were removed in vacuo. The orange residue was dissolved in 10 mL of *n*-pentane and filtered through a pad of Celite. Removing the solvent in vacuo afforded complexes **19a** (145 mg, 0.228 mmol, 91% based on **11d**), **19b** (145 mg, 0.223 mmol, 89% based on **11d**), **19c** (135 mg, 0.220 mmol, 88% based on **11d**), **19e** (175 mg, 0.230 mmol, 92% based on **11d**), and **19f** (155 mg, 0.225 mmol, 90% based on **11d**) in analytically pure yield.

Method B. A 0.178 mmol sample of HC≡CR^3 (**18a**, R^3 = ^{t}Bu, 20 mg; **18b**, R^3 = SiMe$_3$, 20 mg; **18c**, R^3 = (CH$_2$)$_2$CH$_3$, 15 mg; **18e**, R^3 = Fc, 35 mg; **18f**, R^3 = C$_6$H$_4$-4-NO$_2$, 25 mg) was added in one portion to [Ti](C≡C^{t}Bu)$_2$}CuCH$_3$ (**1b**) (100 mg, 0.178 mmol) dissolved in 60 mL of tetrahydrofuran at 25 °C. After stirring for 2 h, all volatiles were removed in vacuo to afford orange- to red-colored **19a**−**f** in quantitative yield (0.178 mmol; **19a**, 110 mg; **19b**, 115 mg; **19c**, 115 mg; **19e**, 135 mg; **19f**, 125 mg).

19a: Mp: 71 °C (dec). IR (NaCl, ν, cm^{-1}): 2099 (CuC≡C), 1941 (TiC≡C). ^{1}H NMR (C$_6$D$_6$): 0.21 (s, 18H, SiMe$_3$), 1.50 (s, 9H, ^{t}Bu), 1.75 (s, 18H, ^{t}Bu), 5.41 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$), 5.72 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 0.4 (SiMe$_3$), 29.6 (^{t}Bu, C$_q$), 31.7 (^{t}Bu), 32.5 (^{t}Bu), 112.3 (C$_5$H$_4$), 115.1 (C$_5$H$_4$), 117.6 (C$_5$H$_4$, C$_{ipso}$), 123.4 (CuC≡*C*), 144.2 (TiC≡*C*), 151.7 (Ti*C*≡C), the signals for C$_q$ and the C$_\alpha$ atom of the CuC≡C^{t}Bu groups could not be detected unequivocally. EI-MS [*m*/*e* (rel int)]: M$^+$ 628 (30), M$^+$ − C$_2$tBu 546 (30), M$^+$ − 2 C$_2$tBu 466 (100), M$^+$ − CuC$_2$tBu − C$_2$tBu 402 (65). Anal. Calcd for $C_{34}H_{53}CuSi_2Ti$ (629.39): C, 64.88; H, 8.49. Found: C, 64.35; H, 7.94.

X-ray Structure Determination of 19a. The solid-state structure of **19a** was determined from single-crystal X-ray diffraction. Data collection was performed on a Siemens-Stoe AED2 diffractometer using Mo Kα radiation (graphite monochromator). Crystallographic data of **19a** are given in Table 2. The structure was solved by direct methods (SHELX 97; Sheldrick, G. M. University of Göttingen: Göttingen, Germany, 1997). A semiempirical absorption correction based on ψ-scans was applied. The structure was refined by the least-squares method based on F^2 with all reflections. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in calculated positions.

19b: IR (NaCl, ν, cm^{-1}): 2038 (CuC≡C), 1939 (TiC≡C). ^{1}H NMR (CDCl$_3$): 0.13 (9H, SiMe$_3$), 0.27 (s, 18H, SiMe$_3$), 1.52 (s, 18H, ^{t}Bu), 5.68 (pt, J_{HH} = 2.2 Hz, 4H, C$_5$H$_4$), 5.86 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$): 0.3 (SiMe$_3$), 0.9 (SiMe$_3$), 31.3 (^{t}Bu, C$_q$), 31.5 (^{t}Bu), 112.5 (CuC≡C), 112.6 (C$_5$H$_4$), 115.2 (C$_5$H$_4$), 117.6 (C$_5$H$_4$, C$_{ipso}$), 123.1 (CuC≡*C*), 145.4 (TiC≡*C*), 148.3 (Ti*C*≡C). Anal. Calcd for $C_{33}H_{53}CuSi_3Ti$ (645.47): C, 61.41; H, 8.28. Found: C, 61.74; H, 8.53.

19c: IR (NaCl, ν, cm^{-1}): 2102 (CuC≡C), 1952 (TiC≡C). ^{1}H NMR (CDCl$_3$): 0.28 (s, 18H, SiMe$_3$), 0.99 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH$_3$), 1.52 (s, 18H, ^{t}Bu), 1.55 (m, $^3J_{HH}$ = 7.2 Hz, 2H, *C*H$_2$CH$_3$), 2.32 (t, $^3J_{HH}$ = 7.2 Hz, 2H, ≡C-*C*H$_2$), 5.66 (pt, J_{HH} = 2.1 Hz, 4H, C$_5$H$_4$), 5.87 (pt, J_{HH} = 2.1 Hz, 4H, C$_5$H$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$): 0.3 (SiMe$_3$), 14.1 (CH$_3$), 23.5 (CH$_2$), 23.7 (CH$_2$), 31.3 (^{t}Bu, C$_q$), 31.4 (^{t}Bu), 112.5 (C$_5$H$_4$), 115.0 (C$_5$H$_4$), 116.8 (Cu*C*≡C), 117.5 (C$_5$H$_4$, C$_{ipso}$), 129.8 (CuC≡*C*), 145.0 (TiC≡*C*), 149.0 (Ti*C*≡C). Anal. Calcd for $C_{33}H_{51}CuSi_2Ti$ (615.36): C, 64.41; H, 8.35. Found: C, 64.75; H, 8.12.

19e: Mp: 122 °C (dec). IR (NaCl, ν, cm^{-1}): 2102 (CuC≡C), 1952 (TiC≡C). ^{1}H NMR (C$_6$D$_6$): 0.21 (s, 18H, SiMe$_3$), 1.77 (s, 18H, ^{t}Bu), 4.01 (pt, J_{HH} = 1.8 Hz, 2H, C$_5$H$_4$Fe), 4.29 (s, 5H, C$_5$H$_5$Fe), 4.56 (pt, J_{HH} = 1.8 Hz, 2H, C$_5$H$_4$Fe), 5.41 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$Ti), 5.74 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$Ti). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 0.4 (SiMe$_3$), 30.3 (^{t}Bu, C$_q$), 31.8 (^{t}Bu), 67.4 (C$_5$H$_4$Fe), 69.7 (C$_5$H$_5$Fe), 70.5 (C$_5$H$_4$Fe), 73.9 (C$_5$H$_4$Fe, C$_{ipso}$), 112.5 (C$_5$H$_4$Ti), 115.3 (C$_5$H$_4$Ti), 116.1 (CuC≡*C*), 118.2 (C$_5$H$_4$-Ti, C$_{ipso}$), 144.7 (TiC≡*C*), 150.3 (Ti*C*≡C), the signal for Cu*C*≡C could not be assigned unequivocally. Anal. Calcd for $C_{40}H_{53}CuFeSi_2Ti$ (757.30): C, 62.44; H, 7.05. Found: C, 62.33; H, 7.33.

19f: Mp: 156 °C (dec). IR (NaCl, ν, cm^{-1}): 2087 (CuC≡C), 1951 (TiC≡C), 1523/1337 (NO$_2$). ^{1}H NMR (CDCl$_3$): 0.29 (s, 18H, SiMe$_3$), 1.54 (s, 18H, ^{t}Bu), 5.78 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$), 5.95 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$), 7.4−8.2 (m, 4H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$): 0.0 (SiMe$_3$), 31.2 (^{t}Bu), 31.6 (^{t}Bu, C$_q$), 112.8 (C$_5$H$_4$), 114.8 (CuC≡*C*), 115.5 (C$_5$H$_4$), 116.8 (C$_5$H$_4$, C$_{ipso}$), 118.7 (C$_6$H$_4$, C$_{ipso}$), 123.3 (C$_6$H$_4$), 130.7 (C$_6$H$_4$), 132.8 (C$_6$H$_4$, C$_{ipso}$), 135.2 (TiC≡*C*), 146.1 (Ti*C*≡C). Anal. Calcd for $C_{36}H_{48}CuNO_2Si_2Ti$ (694.38): C, 62.27; H, 6.97. Found: C, 61.93; H, 7.13.

X-ray Structure Determination of 19f. The solid-state structure of **19f** was determined from single-crystal X-ray diffraction. Data collection was performed on a Bruker SMART CCD diffractometer using Mo Kα radiation (graphite monochromator). Crystallographic data of **19f** are given in Table 2. The structure was solved by direct methods (SHELX 97; Sheldrick, G. M. University of Göttingen: Göttingen, Germany, 1997). An empirical absorption correction was applied. The structure was refined by the least-squares method based on F^2 with all reflections. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were located from the electron difference map and fully refined.

9. Synthesis of {[Ti](C≡C^{t}Bu)$_2$}CuC≡CH (19d). Method A. To [Ti](C≡C^{t}Bu)$_2$}CuSC$_6$H$_4$CH$_2$NMe$_2$-2 (**11d**) (250 mg, 0.350 mmol) in 50 mL of diethyl ether was added dropwise a solution of (Me$_2$NCH$_2$CH$_2$NMe$_2$)LiC≡CH (25 mg, 0.350 mmol) in 10 mL of diethyl ether at −20 °C. The color of the reaction mixture gradually changed from brown to red and (Me$_2$NCH$_2$CH$_2$-NMe$_2$)LiSC$_6$H$_4$CH$_2$NMe$_2$-2 precipitated. After stirring for 15 min at this temperature, all volatiles were removed in vacuo. The red-colored residue was dissolved in 15 mL of *n*-pentane and filtered through a pad of Celite. Removing the solvent in vacuo afforded **19d** in 98% yield (195 mg, 0.343 mmol).

Method B. [Ti](C≡C^{t}Bu)$_2$}CuCH$_3$ (**1b**) (250 mg, 0.444 mmol) was dissolved in 100 mL of tetrahydrofuran. Through this solution a stream of HC≡CH was bubbled at 0 °C within 30 min and afterward at 25 °C for another 10 min. The flask was then closed and the solution stirred for 1 h. All volatiles were removed in vacuo to afford red-colored **19d** in quantitative yield (255 mg, 0.444 mmol).

Mp: 100 °C (dec). IR (NaCl, ν, cm^{-1}): 3263 (≡C−H), 2067 (CuC≡C), 1944 (TiC≡C). ^{1}H NMR (CDCl$_3$): 0.27 (s, 18H, SiMe$_3$), 1.53 (s, 18H, ^{t}Bu), 2.39 (s, 1H, ≡CH), 5.73 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$), 5.90 (pt, J_{HH} = 2.3 Hz, 4H, C$_5$H$_4$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 0.4 (SiMe$_3$), 31.7 (^{t}Bu), 102.5 (C≡*C*H), 112.6 (C$_5$H$_4$), 115.5 (C$_5$H$_4$), 118.3 (C$_5$H$_4$, C$_{ipso}$), 145.3 (TiC≡*C*), 149.6 (Ti*C*≡C), the signals of C$_q$/^{t}Bu and the C$_\alpha$ atom of the CuC≡CH group were not detected unequivocally. EI-MS [*m*/*e* (rel int)]: M$^+$ 573 (45), M$^+$ − C$_2$H − C$_2$tBu 466 (10), M$^+$ − CuC$_2$H − C$_2$tBu 402 (100), $(C_5H_4SiMe_3)_2Ti^+$ 322 (90). Anal. Calcd for $C_{30}H_{45}CuSi_2Ti$ (573.29): C, 62.85; H, 7.91. Found: C, 63.14; H, 7.70.

10. Synthesis of {[Ti](C≡CSiMe$_3$)$_2$}CuC≡CR^3 (20a, R^3 = C$_6$H$_5$; 20b, R^3 = CO$_2$Me; 20c, R^3 = SiMe$_3$; 20d, R^3 = Fc). Method A. To [Ti](C≡CSiMe$_3$)$_2$}CuSC$_6$H$_4$CH$_2$NMe$_2$-2 (**11d**) (225 mg, 0.300 mmol) in 70 mL of diethyl ether was added dropwise 1 equiv of LiC≡CR^3 (R^3 = C$_6$H$_5$, 35 mg; R^3 =

CO_2Me, 25 mg; $R^3 = SiMe_3$, 30 mg; $R^3 = Fc$, 65 mg) in 40 mL of diethyl ether at 0 °C. After stirring for 30 min at this temperature, the reaction mixture was warmed to 25 °C and stirred additionally for 2 h. All volatiles were removed in vacuo. The corresponding orange-colored residue was dissolved in 20 mL of *n*-pentane and filtered through a pad of Celite. Removing the solvent in vacuo afforded **20a** (180 mg, 0.264 mmol, 88% based on **11d**), **20b** (180 mg, 0.273 mmol, 91% based on **11d**), **20c** (185 mg, 0.276 mmol, 92% based on **11d**), and **20d** (205 mg, 0.258 mmol, 86% based on **11d**) as orange solid (**15a**, **15c**, **15d**) or oil (**15b**).

Method B. 0.213 mmol of $HC{\equiv}CR^3$ (**8b**, $R^3 = SiMe_3$, 20 mg; **8e**, $R^3 = Fc$, 45 mg; **8g**, $R^3 = C_6H_5$, 20 mg; **8h**, $R^3 = CO_2Me$, 20 mg) was added in one portion to [Ti] $(C{\equiv}CSiMe_3)_2\}CuCH_3$ (**1a**) (120 mg, 0.213 mmol) in 50 mL of tetrahydrofuran at 25 °C and stirred at this temperature for 3 h. All volatiles were removed in vacuo to afford orange- to red-colored **20a**–**d** in quantitative yield (0.213 mmol; **20a**, 140 mg; **20b**, 165 mg; **20c**, 140 mg; **20d**, 140 mg).

20a, 20c: Spectroscopic data of these compounds are listed in ref 21.

20b: Mp: 115 °C. IR (NaCl, ν, cm^{-1}): 2109 ($CuC{\equiv}C$), 1892 ($TiC{\equiv}C$), 1671 ($C{=}O$), 1295 ($C{-}O$). ^1H NMR ($CDCl_3$): 0.25 (s, 18H, $SiMe_3$), 0.38 (s, 18H, $SiMe_3$), 3.69 (s, OCH_3), 5.72 (pt, $J_{HH} = 2.3$ Hz, 4H, C_5H_4), 6.02 (pt, $J_{HH} = 2.3$ Hz, 4H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.2 ($SiMe_3$), 0.5 ($SiMe_3$), 51.5 (OCH_3), 105.2 ($Cu\mathit{C}{\equiv}C$), 112.9 (C_5H_4), 115.8 (C_5H_4), 121.3 (C_5H_4, C_{ipso}), 124.2 ($CuC{\equiv}\mathit{C}$), 137.1 ($TiC{\equiv}\mathit{C}$), 171.2 (CO_2CH_3), 181.7 ($Ti\mathit{C}{\equiv}C$). EI-MS [*m*/*e* (rel int)]: M^+ 663 (10), $M^+ - C_2OMe$ 607 (9), $M^+ - CuC_2CO_2Me - 2\ CH_3$ 487 (12), $(C_5H_4SiMe_3)_2Ti^+$ 322 (100). Anal. Calcd for $C_{30}H_{47}CuO_2Si_4Ti$ (663.47): C, 54.31; H, 7.14. Found: C, 54.07; H, 7.11.

20d: Mp: 111 °C (dec). IR (NaCl, ν, cm^{-1}): 2039 ($CuC{\equiv}C$), 1892 ($TiC{\equiv}C$). ^1H NMR (C_6D_6): 0.20 (s, 18H, $SiMe_3$), 0.75 (s, 18H, $SiMe_3$), 4.04 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4Fe), 4.31 (s, 5H, C_5H_4Fe), 4.55 (pt, $J_{HH} = 1.8$ Hz, 2H, C_5H_4Fe), 5.29 (pt, $J_{HH} = 2.3$ Hz, 4H, C_5H_4Ti), 5.72 (pt, $J_{HH} = 2.3$ Hz, 4H, C_5H_4Ti). $^{13}C\{^1H\}$ NMR (C_6D_6): 0.4 ($SiMe_3$), 1.1 ($SiMe_3$), 67.4 (C_5H_4Fe), 69.9 (C_5H_5Fe), 70.7 (C_5H_4Fe), 74.2 (C_5H_4Fe, C_{ipso}), 112.0 (C_5H_4Ti), 115.3 (C_5H_4Ti), 118.2 ($CuC{\equiv}\mathit{C}$), 119.9 (C_5H_4Ti, C_{ipso}), 128.6 ($TiC{\equiv}\mathit{C}$), 183.8 ($Ti\mathit{C}{\equiv}C$), the signal of C_α atom of the $CuC{\equiv}CFc$ grouping could not be assigned unequivocally. FD-MS [*m*/*e* (rel int)]: M^+ 788 (100). Anal. Calcd for $C_{38}H_{53}CuFeSi_4Ti$ (789.46): C, 57.81; H, 7.28. Found: C, 57.47; H, 7.28.

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Supporting Information Available: Details about the X-ray crystal structures, including diagrams, and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **19a** and **19d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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