Organometallics **2000,** *19,* 5769−5779

Mono-, Di-, and Tricarboxylic Acids: Central Building Blocks for the Formation of Multinuclear Transition Metal Complexes

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Received July 17, 2000

The synthesis and characterization of the di-, tetra-, and hexanuclear titanium(IV)−copper(I) carboxylates $\{[Ti](C\equiv CSiMe_3)_2\}CuO_2CR^2$ (**3**) {**3a**: $R^2 = Me$, **3b**: $R^2 = C_6H_5$, **3c**: $R^2 = CH_2C_6H_5$, **3d**: $R^2 = CH{=}CMe_2$; $[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$}, $\{[Ti](C\equiv C^tBu)_2\}CuOC(O){-}X{-}C(O)OH$ [**12a**: X = *trans*-CH=CH, **12b**: $X = CH_2C(=CH_2)$], $\{[Ti](C\equiv C^tBu)_2\}CuOC(O){-}X{-}C(O)OCu\{(R^1C\equiv C)_2[Ti]\}$ [$R^1 = {}^tBu$, **13a**: X = *trans*-CH=CH, **13b**: X = *cis*-CH=CH, **13c**: X = 1,4-C_6H_4, **13d**: X = C≡C, $R^1 = SiMe_3$, **14a**: X = *trans*-CH=CH, **14b**: $X = CH_2C(=CH_2)$], $[\{[Ti](C\equiv C^tBu)_2\}CuO(O)C]_2$ (**13e**) as well as $\{[Ti](C\equiv C^tBu)_2\}CuO(O)C\text{-}1\text{-}C_6H_3(CO_2H)_2\text{-}3,5$ (**16**), $[\{[Ti](C\equiv C^tBu)_2\}CuO(O)C]_2\text{-}1,3\text{-}C_6H_3(CO_2H)\text{-}5$ (**17**), and $[\{[Ti](C\equiv C^tBu)_2\}CuO(O)C]_3\text{-}C_6H_3\text{-}1,3,5$ (**18**) is described. All of these complexes are easily accessible by the reaction of $\{[Ti](C\equiv CR^1)_2\}CuMe$ (**1a**: $R^1 = SiMe_3$, **1b**: $R^1 = {}^tBu$) with the corresponding carboxylic acids in different stoichiometric ratios of the reactants. Furthermore, the preparation and reaction chemistry of the alkyne-stabilized copper(I) percarboxylate $\{[Ti](C\equiv CSiMe_3)_2\}CuO_2C(O)C_6H_4Cl\text{-}3$ (**10**) is discussed. As the central organic building block, all complexes contain mono-, di-, or tricarboxylic units. The latter two allow for the subsequent addition of further titanium(IV)−copper(I) assemblies onto these entities. The X-ray structure analyses of **3a** and **13a** are reported. Within the $\{[Ti](C\equiv CR^1)_2\}CuOC(O)R^2$ array the copper(I) center is η^2-coordinated by both $R^1C\equiv C$ groups of the organometallic tweezer $[Ti](C\equiv CR^1)_2$ and η^1-bonded by one oxygen atom of the O_2CR^2 unit. Cyclic voltammetric studies on representative examples are presented and discussed comparatively.

Introduction

Copper carboxylates play an important role as catalysts in homogeneous catalysis; for example, cuprous carboxylate compounds are considered to be the first complexes involved in homogeneously catalyzed hydrogenation reactions.[1] Another example that is of synthetical importance is the Hurtley reaction, involving the condensation of 2-halobenzoic units with β-dicarbonyls.[2] However, there are only limited structural information as well as detailed reactivity studies of copper carboxylates available.[3−10]

Previously, di- or tetranuclear copper(I) carboxylate species with alkenes or alkynes as additional donor components have been reported and were partly structurally identified.[4] In this low-nuclearity copper(I) species, the carboxylic units act as μ-bridging ligands between two copper centers, involving both oxygen atoms of the RCO_2 moiety.[4−10]

Recently, it was shown that η^1-bonded carboxylate ligands are present in monomeric η^2-alkyne-stabilized

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[§] To whom correspondence should be addressed pertaining to the X-ray study of complex **3a**.

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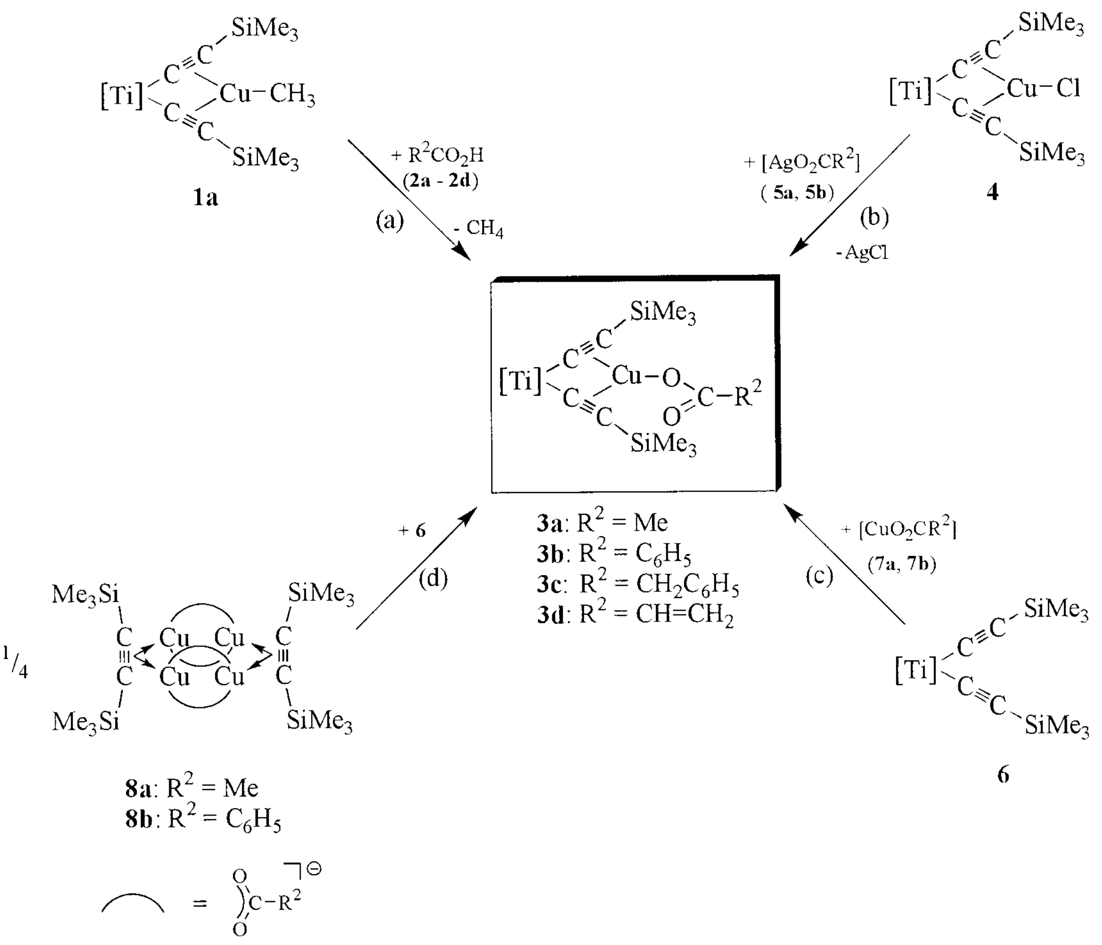
10.1021/om000617p CCC: $19.00
Publication on Web 11/30/2000

Scheme 1. Different Synthetical Methods for the Preparation of Complexes $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCOC(O)R^2$ (3a–3d)



copper(I) carboxylates of structural type $\{[Ti](C{\equiv}CR^1)_2\}CuO(O)CR^2$ $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; $R^1 = SiMe_3$, ${}^tBu$; R^2 = Me, $C_6H_5\}$.[4] In addition, monomeric copper(I) carboxylates are accessible by applying, for example, multidentate phosphanes as additional donors.[9,10]

In this study we describe the synthesis, structure, and bonding of numerous alkyne-stabilized copper(I) carboxylates using mono-, di-, or trifunctionalized carboxylic building blocks, such as R^2CO_2- (R^2 = singly bonded organic ligand), $-O_2C-CO_2-$, *cis*- or *trans*-$O_2C-CH{=}CH-CO_2-$, $-O_2C-C{\equiv}C-CO_2-$, $C_6H_4(CO_2)_2$-1,4, or $C_6H_3(CO_2)_3$-1,3,5. Preliminary cyclic voltammetric studies are discussed comparatively.

Results and Discussion

Preparation of Titanium(IV)–Copper(I) Carboxylates. The titanium(IV)–copper(I) carboxylate complexes **3**, **12**–**14**, and **16**–**18** as well as the copper(I) percarboxylate **11** are accessible in excellent to quantitative yield, by starting out from $\{[Ti](C{\equiv}CR^1)_2\}CuMe$ (**1a**: $R^1 = SiMe_3$, **1b**: $R^1 = {}^tBu$),[13] $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCl$ (**4**),[14,15] or $[Ti](C{\equiv}CSiMe_3)_2$ (**6**)[12] $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti\}$ and a suitable carboxylate source (Scheme 1).

Thus, the reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuMe$ (**1a**) with R^2CO_2H (**2a**: R^2 = Me, **2b**: $R^2 = C_6H_5$, **2c**: $R^2 = CH_2C_6H_5$, **2d**: $R^2 = CH{=}CMe_2$) in a 1:1 molar ratio in tetrahydrofuran at −20 °C produces the alkyne-stabilized monomeric copper(I) carboxylates $\{[Ti](C{\equiv}CSiMe_3)_2\}CuOC(O)R^2$ (**3a**: R^2 = Me, **3b**: $R^2 = C_6H_5$, **3c**: $R^2 = CH_2C_6H_5$, **3d**: $R^2 = CH{=}CMe_2$). Complexes **3a**–**3d** are formed in quantitative yields (Scheme 1, path a). This type of reaction is accompanied by the loss of CH_4.

A further possibility to synthesize, for example, complexes **3a** and **3b** is given by treatment of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCl$ (**4**) with 1 equiv of $[AgO_2CR^2]$ (**5a**: R^2 = Me, **5b**: $R^2 = C_6H_5$) in dichloromethane at 25 °C (Scheme 1, path b) or, as represented by path c in Scheme 1, by reacting the bis(alkynyl) titanocene $[Ti](C{\equiv}CSiMe_3)_2$ (**6**) with equimolar amounts of $[CuO_2CR^2]$ (**7a**: R^2 = Me, **7b**: $R^2 = C_6H_5$) in diethyl ether.

However, the maximum isolated yields in the latter reactions amount only to 75% (reaction of **4** with **5**) or 83% (reaction of **6** with **7**), respectively. In contrast,

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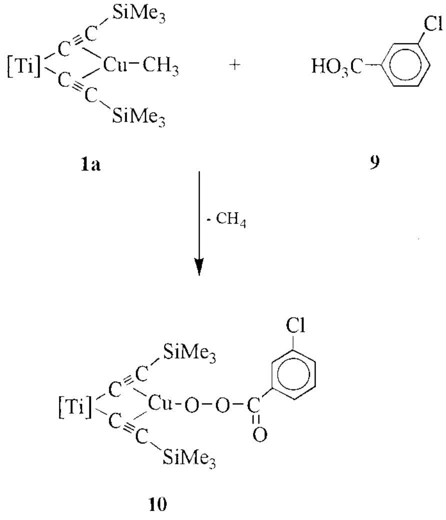
almost quantitative yields can be obtained, when the bis(alkynyl) titanocene **6** is treated with the tetranuclear complex $(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)_2(Cu\text{-}\mu\text{-}O_2CR^2)_4$ (**8a**: R = Me, **8b**: R = C_6H_5) in tetrahydrofuran (Scheme 1, path d).

In this respect it must be noted that the reaction of **1a** with **2a**−**2d** is straightforward, since the new species **3a**−**3d** are formed rapidly on mixing the corresponding reagents, even at low temperature. As compared with the other reactions outlined in Scheme 1, path a possesses the highest synthetic potential, since numerous easily prepared and/or commercially available carboxylic acids can successfully be applied. Another advantage of this procedure is the very simple workup: the loss of CH_4 as the only byproduct yields, after evaporation of all volatiles, the corresponding molecules analytically pure and in quantitative yields.

All complexes are soluble in polar organic solvents, such as diethyl ether and tetrahydrofuran, but are poorly soluble in *n*-pentane or toluene. In the solid state, **3a**−**3d** are stable to air for short periods of time, while in solution they slowly decompose to undefined products.

The approach decribed in Scheme 1, path a, also can successfully be applied to the preparation of the copper(I) percarboxylate $\{[Ti](C{\equiv}CSiMe_3)_2\}CuO_2C(O)C_6H_4Cl$-3 (**10**). Subsequently, treatment of **1a** with stoichiometric amounts of $HO_2C(O)C_6H_4Cl$-3 (**9**) at −70 °C in tetrahydrofuran affords quantitatively complex **10**, accompanied by the liberation of CH_4. The copper(I) percarboxylate **10** can be isolated as a brown oil (eq 1).



(1)

This new copper(I) percarboxylate moiety in complex **10** is stabilized by the η^2-coordination of both $Me_3SiC{\equiv}C$ ligands of the $[Ti](C{\equiv}CSiMe_3)_2$ fragment. This compound can safely be handled in the solid state as well as in solution and exhibits a high thermal stability. However, heating a toluene solution of **10** under reflux leads to its unselective decomposition within a few minutes.

On the basis of the aforementioned results, the synthetic potential of the titanium(IV)−copper(I) complex $\{[Ti](C{\equiv}CR^1)_2\}CuMe$ (**1a**: R^1 = $SiMe_3$, **1b**: R^1 = ^tBu) was expanded toward di- and tricarboxylic acids. This allows for an easy access to multinuclear organometallic complexes in which the corresponding di- or tricarboxylate units act as bridging moieties between early−late heterobimetallic titanium−copper building blocks of the form $\{[Ti]\ (C{\equiv}CR^1)_2\}Cu$ (Scheme 2, complexes **13** and **14**).

At low temperature, the reaction of $\{[Ti](C{\equiv}C^tBu)_2\}CuMe$ (**1b**) with an equimolar amount of a dicarboxylic acid $HO_2C{-}X{-}CO_2H$ [**11a**: X = *trans*-CH=CH, **11b**: X = $CH_2C({=}CH_2)$] affords $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O){-}X{-}C(O)OH$ [**12a**: X = *trans*-CH=CH, **12b**: X = $CH_2C({=}CH_2)$] by selective transformation of only one CO_2H group of the dicarboxylic acids **11a** or **11b**. Thus, the corresponding titanium−copper tweezer complexes **12a** and **12b** are formed quantitatively, and both possess, apart from the titanium−copper moiety $\{[Ti](C{\equiv}C^tBu)_2\}Cu$, a pendant CO_2H unit as a further reactive site.

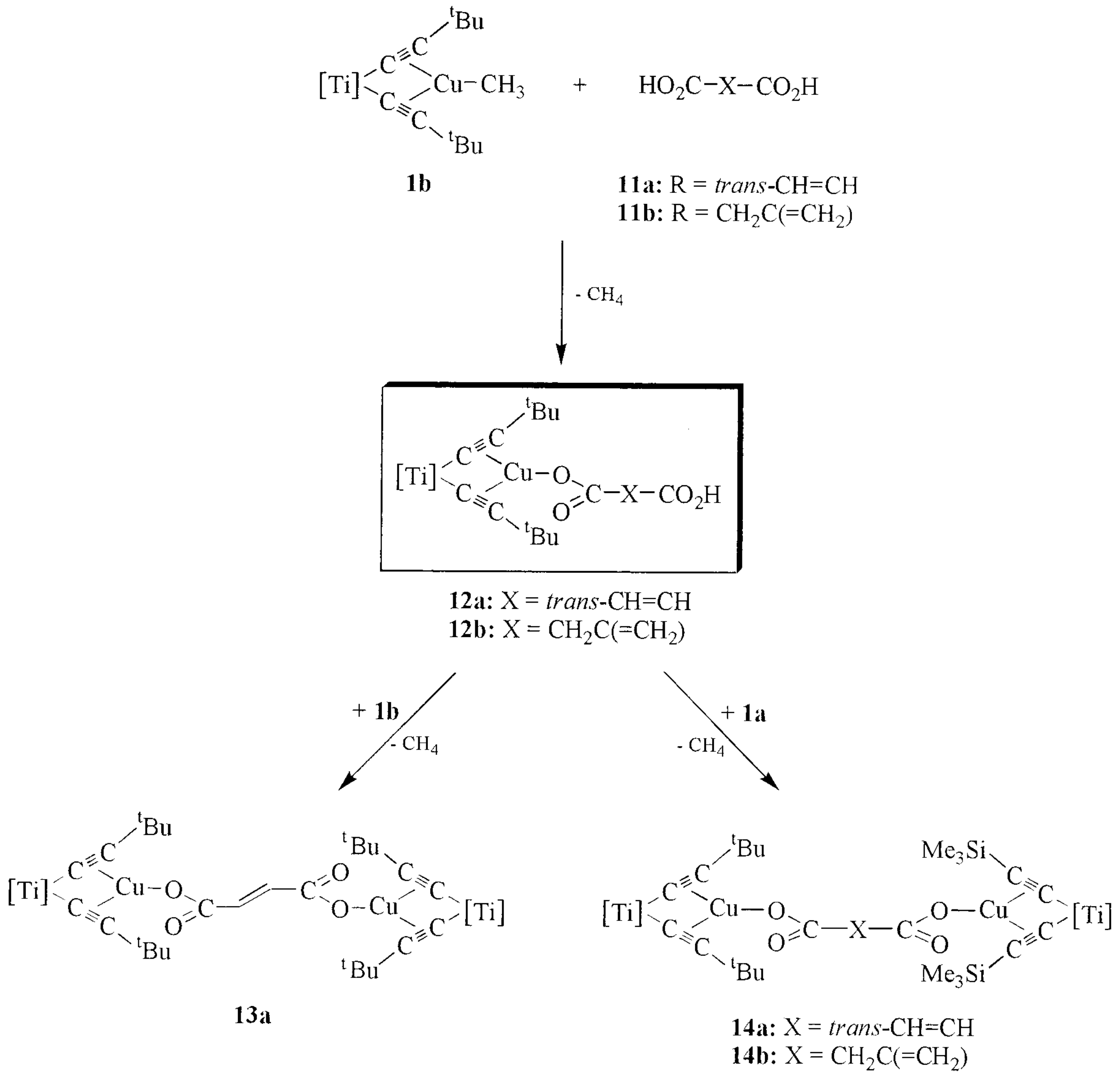
The prepartion of symmetric (**13a**) or mixed (**14a**, **14b**) organometallic coordinated copper(I) dicarboxylates of the type $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O){-}X{-}C(O)OCu\{(R^1C{\equiv}C)_2[Ti]\}$ [**13a**: R^1 = ^tBu, X = *trans*-CH=CH, **14a**: R^1 = $SiMe_3$, X = *trans*-CH=CH, **14b**: R^1 = $SiMe_3$, X = $CH_2C({=}CH_2)$] is made possible by the presence of this second, unreacted HO_2C functionality in **12a** or **12b**. Treatment of **12a** with **1b** gives symmetric **13a**, while the reaction of **12a** or **12b** with stoichiometric amounts of **1a** results in the asymmetric species **14a** or **14b**, respectively (Scheme 2). After appropriate workup, these tetrametallic complexes can be isolated as orange crystalline materials which are stable to air for short periods of time. In contrast with the titanium(IV)−copper(I) carboxylates **12a** and **12b**, complexes **13a**, **14a**, and **14b** are much more soluble in organic solvents; they possess almost the same solubility behavior as **3a**−**3d**.

In the synthesis of complex **13a** it is not necessary to isolate structural type **12** species (Scheme 2). When the dicarboxylic acids $HO_2C{-}X{-}CO_2H$ (**11a**: X = *trans*-CH=CH, **11c**: X = *cis*-CH=CH, **11d**: X = C_6H_4-1,4, **11e**: X = C≡C) or $HO_2C{-}CO_2H$ (**11f**) are combined with 2 equiv of **1b** in tetrahydrofuran at −20 °C, tetranuclear complexes of general composition $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O){-}X{-}C(O)OCu\{(^tBuC{\equiv}C)_2[Ti]\}$ [**13a**: X = *trans*-CH=CH, **13c**: X = *cis*-CH=CH, **13d**: X = C_6H_4-1,4, **13e**: X = C≡C] or $[\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)]_2$ (**13f**) are produced in one step, again in quantitative yields (Scheme 3).

Access to bi-, tetra-, or even hexametallic complexes, i.e., $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)\text{-}1\text{-}C_6H_3(CO_2H)_2\text{-}3,5$ (**16**), $[\{[Ti](C{\equiv}C^tBu)_2\}CuO_2C]_2\text{-}1,3\text{-}C_6H_3CO_2H\text{-}5$ (**17**), and $[\{[Ti](C{\equiv}C^tBu)_2\}CuO_2C]_3{-}C_6H_3\text{-}1,3,5$ (**18**), is given by applying $C_6H_3(CO_2H)_3\text{-}1,3,5$ (**15**) as starting material (Scheme 4).

When the tricarboxylic acid **15** is reacted with the appropriate stoichiometric amount of $\{[Ti](C{\equiv}C^tBu)_2\}CuMe$ (**1b**), the multimetallic complexes **16**−**18** are formed quantitatively by loss of CH_4 (Scheme 4). In this respect it must be noted that **18** can also be prepared by subsequent addition of **1b** to **15**, **16**, or **17**. Furthermore, tetra- or hexanuclear **17** and **18** are accessible by treatment of **1b** with 2 or 3 equiv of **1b** (Scheme 4). Noteworthy in the preparation of **16**−**18** is that with the increasing number of $\{[Ti](C{\equiv}C^tBu)_2Cu\}$ entities, the solubility of these complexes increases, too.

Scheme 2. Synthesis of Complexes 12−14 by the Reaction of 1b with 11a or 11b (preparation of 12a and 12b) and by Treatment of 12a or 12b with 1a or 1b (preparation of complexes 13a, 14a, and 14b)



Solid-State Structure of {[Ti](C≡CSiMe$_3$)$_2$}CuOAc (3a). Single crystals of **3a** were obtained by cooling a tetrahydrofuran/*n*-pentane solution of **3a** to −30 °C. **3a** crystallizes with two almost identical molecules and two molecules of tetrahydrofuran per asymmetric unit. The result of the X-ray diffraction study is shown in Figure 1; the second complex molecule and the tetrahydrofuran molecules are omitted for clarity. The most important interatomic distances and angles are given in Table 1; the experimental data for the X-ray structure analysis are presented in Table 3.

In **3a** a monomeric copper(I) acetate unit is bis-η^2-coordinated by two alkynyl ligands of the [Ti](C≡CSiMe$_3$)$_2$ entity (Figure 1). The acetate group is η^1-bonded to the central copper(I) center Cu(1) by O(1), whereas O(2) is noncoordinated. Apart from the IR data (vide infra), this can clearly be deduced from the different copper−oxygen distances found [Cu(1)−O(1) 1.934(7) Å, Cu(1)−O(2) 2.747(7) Å]. The copper(I) center possesses a trigonal-planar environment comprised of the alkynyl ligands C≡CSiMe$_3$ and the η^1-bonded OC(O)CH$_3$ entity. Due to the η^2-coordination of the alkynyl ligands to a mononuclear low-valent Cu(I) center, the C≡C triple bonds are lengthened from 1.214(4) or 1.203(9) Å in **6**[18] to 1.233(12) or 1.252(13) Å in **3a**. Furthermore, the bite angle C(1)−Ti(1)−C(6) is decreased from 102.8(2)° in **6** to 90.3(3)° in **3a**. A further typical observation for heterodinuclear tweezer complexes is a *trans*-deformation of the Ti−C≡C−SiMe$_3$ fragments [Ti(1)−C(1)−C(2) 163.9(7)°, C(1)−C(2)−Si(1) 163.9(8)°, Ti(1)−C(6)−C(7) 165.6(8)°, C(6)−C(7)−Si(2) 165.0(8)°], which are linear [Ti−C≡C 175.8(4)°, 178.2(5)°; C≡C−Si 174.8(4)°, 178.3-

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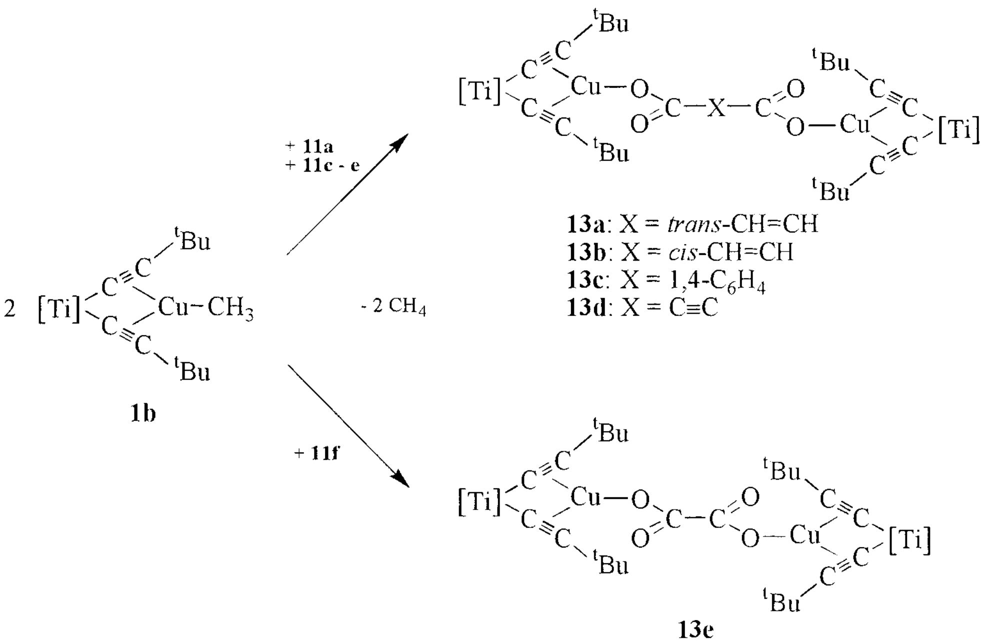
Scheme 3. Synthesis of Complexes 13a–13e by the Reaction of 1b with 11a and 11c–11f



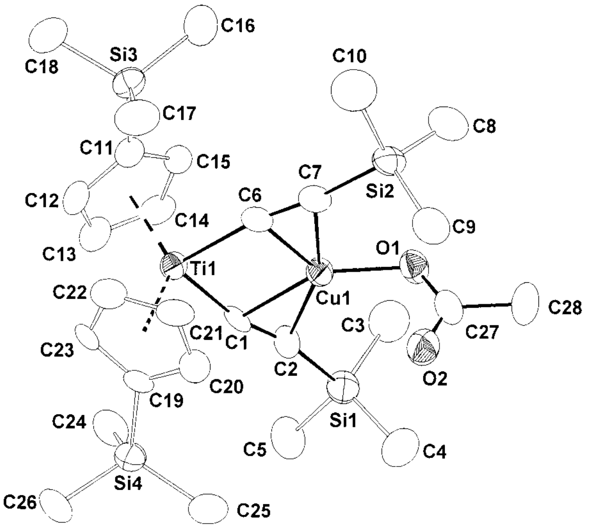


Figure 1. ORTEP drawing (50% probability level) of the titanium(IV)–copper(I) acetate complex **3a**, with molecular geometry and atom-numbering scheme.

(5)°] in the noncoordinated bis(alkynyl) titanocene species **6**.[18] This fragment is linear in the starting compound **6**.[18] The best plane through the atoms of the acetate group [C(28)–C(27)–O(1)–O(2)] is perpendicular (87.50(23)°) to a best plane through Ti(1)–C(1)–C(6)–Cu(1)–C(2)–C(7) [max. deviation from this plane: 0.0134(68) Å], which minimizes the steric repulsion between the acetate group and the $SiMe_3$ units.

Solid-State Structure of {[Ti](C≡Cᵗ Bu)$_2$}CuOC(O)-*trans*-CH═CH–C(O)OCu{(ᵗBuC≡C)$_2$[Ti]} (13a). The molecular structure of **13a** was determined by X-ray diffraction analysis (Figure 2) from single crystals obtained by cooling a tetrahydrofuran solution of **13a** to −30 °C. Selected geometrical details are listed in Table 2, and experimental data for the X-ray diffraction studies are given in Table 3.

The molecular structure of **13a** contains a center of inversion. All symmetry-generated atoms are marked with the suffix "a". Compound **13a** crystallizes in the monoclinic space group *C*2/*c* with two molecules of tetrahydrofuran per unit cell. The main characteristic of **13a** is that two early–late titanium(IV)–copper(I) moieties {Ti(C≡CᵗBu)$_2$}Cu are linked by a *trans*-configurated OC(O)–CH═CH–C(O)O unit of which only one oxygen atom per carboxylate group is σ-bonded to the copper(I) center (Figure 2). An identical feature was observed also for complex **3a** (for comparison see also IR studies).

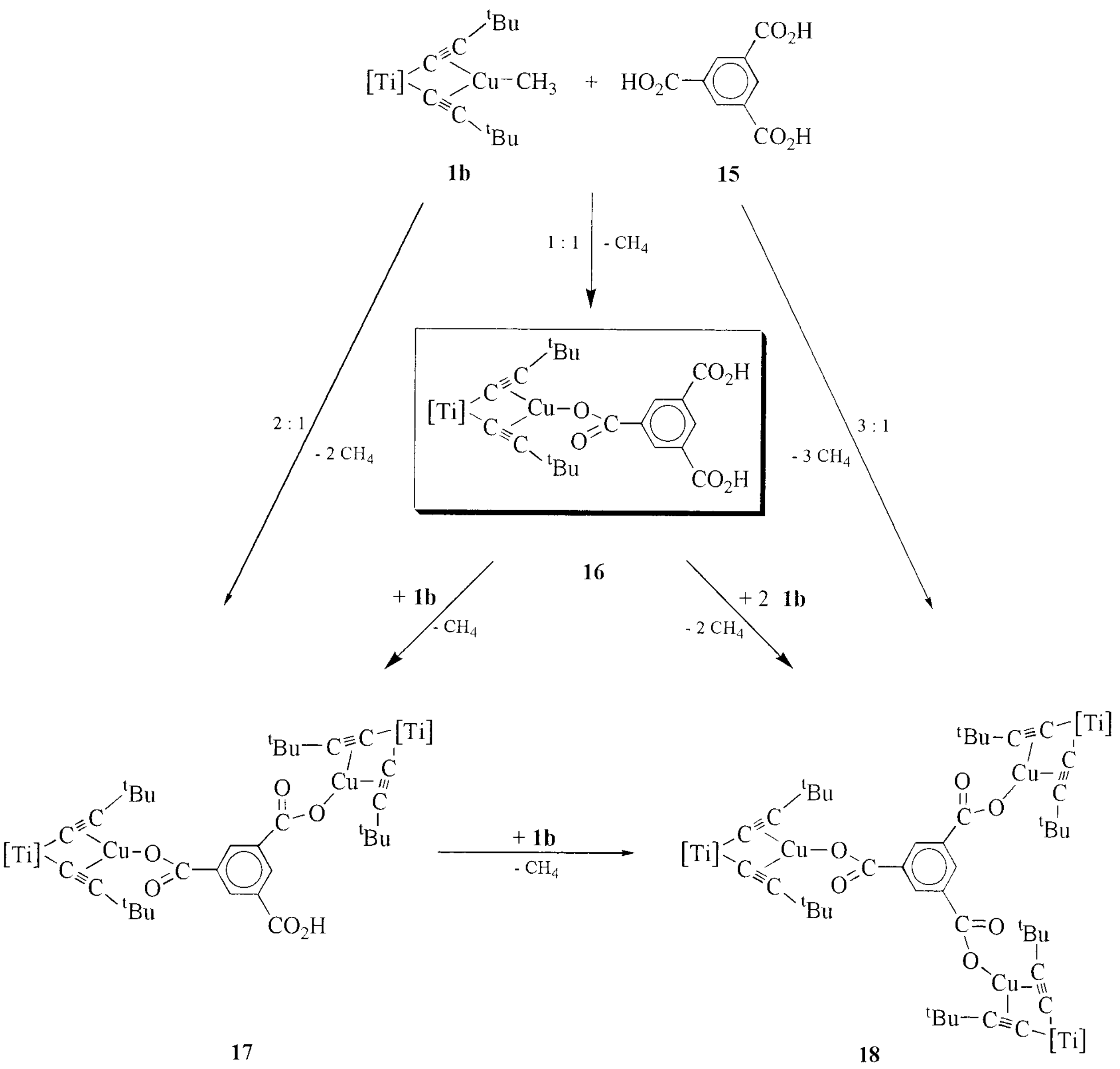
Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] for Complex 3a[a]

bond lengths [Å]		bond angles [deg]	
Ti(1)–C(1)	2.102(10)	C(1)–Ti(1)–C(6)	90.3(3)
Ti(1)–C(6)	2.085(10)	Ti(1)–C(1)–C(2)	163.9(7)
C(1)–C(2)	1.233(12)	Ti(1)–C(6)–C(7)	165.6(8)
C(6)–C(7)	1.252(13)	C(1)–C(2)–Si(1)	163.9(8)
C(2)–Si(1)	1.851(10)	C(6)–C(7)–Si(2)	165.0(8)
C(7)–Si(2)	1.851(10)	Cu(1)–O(1)–C(27)	110.7(6)
Cu(1)–O(1)	1.934(7)	O(1)–C(27)–O(2)	123.2(9)
Cu(1)–O(2)	2.747(7)	O(1)–C(27)–C(28)	116.2(10)
O(1)–C(27)	1.276(13)	O(1)–Cu(1)–Ti(1)	172.6(2)
O(2)–C(27)	1.224(12)	D(1)–Ti(1)–D(2)[b]	133.16(44)
Cu(1)–Ti(1)	2.929(2)		
Cu(1)–C(1)	2.080(8)		
Cu(1)–C(2)	2.125(9)		
Cu(1)–C(6)	2.072(9)		
Cu(1)–C(7)	2.149(9)		
Ti(1)–D(1)[b]	2.0459(44)		
Ti(1)–D(2)[b]	2.0416(44)		

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

As in the solid-state structure of **3a**, in **13a** the copper(I) center Cu(1) is trigonally coordinated by a η^1-O-bonded monoanionic carboxylate ligand and two η^2-bonded alkynyl groups of the organometallic π-tweezer [Ti](C≡CᵗBu)$_2$ (Figure 2). The latter bonding is forced by the chelating effect of the bis(alkynyl) titanium entity to occur almost in-plane, which means that the Cu(1) center is only by 0.1585(16) Å positioned out of the best plane through Ti(1)–C(1)–C(2)–C(7)–C(8)–Cu(1). The plane of the η^1-bonded organic carboxylate ligand *trans*-

Scheme 4. Synthesis of Complexes 16−18 by (i) the Reaction of 1b with 15 in the Ratios of 1:1, 2:1, or 3:1, (ii) the Reaction of 16 with 1b in the Ratios of 1:1 or 1:2, and (iii) Treatment of 17 with 1b



$O_2C{-}CH{=}CH{-}CO_2$ [O(1)−O(2)−C(29)−C(30)] is almost perpendicular to the Ti(1)−C(1)−C(2)−C(7)−C(8)−Cu(1) plane [interplane angle: 88.93(14)°] (Figure 2). A similar coordination motif around the Cu(I) center was observed for complex **3a** (vide supra).

Further characteristics of **13a** are comparable with those of other known heterodinuclear tweezer complexes of the general type $\{[Ti](C{\equiv}CR^1)_2\}CuX$ (X = singly bonded inorganic or organic ligand), including (i) a bond lengthening of the C≡C triple bond [C(1)−C(2): 1.240 (5) Å, C(7)−C(8): 1.233 (5) Å], (ii) a *trans*-distortion of the $Ti{-}C{\equiv}C{-}C{-}{}^tBu$ units [Ti(1)−C(1)−C(2): 165.7(3)°; Ti(1)−C(7)−C(8): 166.3(3)°; C(1)−C(2)−C(3): 163.4(4)°; C(7)−C(8)−C(9): 163.5(4)°], and (iii) the reduction of the bite angle C(1)−Ti−C(7) [91.3(1)°] compared with noncoordinated $[Ti](C{\equiv}CR^1)_2$ species (e.g., R^1 = $SiMe_3$: 102.8(2)°].[13−16] The copper−oxygen distance Cu(1)−O(1) is 1.933(2) Å, in accordance with other known Cu−O bonds.[4,9,17]

Structure of Complexes 3, 10, 12−14, and 16−18 in Solution. The IR spectra of all compounds show one characteristic C≡C stretching vibration for the alkynyl groups between 1900 and 1920 cm^{-1} for the $[Ti](C{\equiv}CSiMe_3)_2$ moiety[14] or 1975 to 1990 cm^{-1} for the $[Ti](C{\equiv}C^tBu)_2$ entity.[14] This shift of $\nu_{C\equiv C}$ to lower wavenumbers is typical for the change from noncoordinated bis(alkynyl) titanocenes to heterodinuclear organometallic tweezer complexes of the type $\{[Ti](C{\equiv}CR^1)_2\}MX$ or $\{[Ti](C{\equiv}CR^1)_2\}MX_2$ (MX, MX_2 = low-valent mononuclear transition metal complex fragment with 10−12 valence electrons).[9,13−17] As compared with the starting materials **1a** ($\nu_{C\equiv C}$ = 1867 cm^{-1})[13] and **1b** ($\nu_{C\equiv C}$ = 1909 cm^{-1}),[13] the $\nu_{C\equiv C}$ bands in the corresponding titanium(IV)−copper(I) carboxylates **3**, **12**−**14**, and **16**−**18** are generally shifted to higher frequencies. These data show that due to the alkyne−metal interaction, the C≡C triple bond is weaker in the case of **1a** and **1b** than in the corresponding carboxylate specimen. This clearly demonstrates that, in the case of the ligands η^1-bonded to copper(I), the substitution of a stronger σ-donating ligand (e.g., Me) by a weaker σ-donor ligand (e.g., O_2CR^2) results in a stronger C≡C triple bond.[13]

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] for Complex 13a[a,b]

bond lengths [Å]		bond angles [deg]	
Ti(1)−C(1)	2.112 (4)	C(1)−Ti(1)−C(7)	91.30 (4)
Ti(1)−C(7)	2.115 (4)	Ti(1)−C(1)−C(2)	165.7 (3)
C(1)−C(2)	1.240 (5)	Ti(1)−C(7)−C(8)	163.3 (3)
C(7)−C(8)	1.233 (5)	C(1)−C(2)−C(3)	163.4 (4)
C(2)−C(3)	1.496 (5)	C(7)−C(8)−C(9)	163.5 (4)
C(8)−C(9)	1.513 (5)	Cu(1)−O(1)−C(29)	110.6 (2)
Cu(1)−O(1)	1.933 (2)	O(1)−C(29)−O(2)	124.9 (3)
O(1)−C(29)	1.286 (4)	O(1)−C(29)−C(30)	116.1 (3)
O(2)−C(29)	1.240 (4)	C(29)−C(30)−C(30a)	123.7 (4)
C(29)−C(30)	1.518 (5	O(1)−Cu(1)−Ti(1)	171.32 (8)
C(30)−C(30a)	1.314 (7)	D(1)−Ti(1)−D(2)[c]	133.46(18)
Cu(1)−Ti(1)	2.8775 (7)		
Cu(1)−C(1)	2.075 (4)		
Cu(1)−C(7)	2.068 (3)		
Cu(1)−C(2)	2.219 (4)		
Cu(1)−C(8)	2.213 (4)		
Ti(1)−D(1)[c]	2.0597 (14)		
Ti(2)−D(2)[c]	2.0640 (17)		

[a] Standard deviations are given as the last significant figure in parentheses. [b] Transformations used to generate symmetry equivalent atoms: $-x + {}^1/_2$; $-y + {}^1/_2$; $-z + 1$. [c] D(1), D(2): centroids of the cyclopentadienyl ligands.

Table 3. Crystal and Collection Data for Complexes 3a and 13a

	3a	**13a**
empirical formula	$C_{64}H_{110}Cu_2O_6Si_8Ti_2$, C_4H_8O	$C_{60}H_{90}Cu_2O_4Si_4Ti_2$
mol mass	1423.12	1210.56
cryst syst	monoclinic	monoclinic
space group	$P2(1)/n$	$C2/c$
a (Å)	21.686(9)	28.4022(6)
b (Å)	16.678(6)	16.4644(4)
c (Å)	23.963(8)	19.7488(4)
V (Å^3)	7758(5)	7821.7(3)
β (deg)	116.48(3)	97.97(3)
ρ_{calc} (g cm^{-3})	1.218	1.028
F(000)	3024	2560
Z	4	4
cryst dimens (mm)	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.15
diffractometer model	Siemens R3m/V	Bruker SMART CCD
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
abs coeff (μ, mm^{-1})	0.905	0.828
temp (K)	193(2)	173(2)
scan mode	ω-scan	ω-scan
scan range (deg)	$1.61 \leq \theta \leq 21.06$	$1.50 \leq \theta \leq 30.16$
index ranges	$-7 \leq h \leq 21$ $-16 \leq k \leq 16$ $-24 \leq l \leq 21$	$-39 \leq h \leq 23$ $-6 \leq k \leq 22$ $-26 \leq l \leq 27$
total no. of reflns	8505	13 674
no. of unique reflns	8237	8510
no. of obsd reflns [$I \geq 2\sigma(I)$]	5329	4357
no. of refined params	765	337
R1, wR2 [$I \geq 2\sigma(I)$]	0.0755, 0.1819[a]	0.0568, 0.1180[b]
R1, wR2 (all data)	0.1240, 0.2170[a]	0.1090, 0.1319[b]
S	1.012[a]	0.827[b]
max., min. peak in final Fourier map (e Å^{-3})	0.757, −1.690	1.027, −1.155

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$, $w = 1/[s^2(F_o^2) + (0.1173P)^2 + 24.2255P]$ with $P = [F_o^2 + 2F_c^2]/3$; $S = [\sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$, $w = 1/[s^2(F_o^2) + (0.0440P)^2 + 0.0000P]$ 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.

Next to the C≡C stretching vibrations, another two absorptions are observed that can be assigned to the unsymmetrically coordinated CO_2 group. The symmetric C−O stretching vibration appears in the region 1740−1650 cm^{-1} and the band for asymmetric C−O vibration between 1620 and 1550 cm^{-1}. These absorptions are found in an area that is typical for copper(I) carboxylate building blocks.[4,9,17,19] Furthermore, the individual differences of the symmetrical and asymmetrical vibrations strongly suggest that the carboxylic groups are only σ-bonded by one oxygen atom to the copper(I) center.[19] This was confirmed independently by the X-ray structure analyses (vide supra). For the percarboxylate complex **10** two distinct CO vibrations are found at 1595 cm^{-1} ($\nu_{CO,as}$) and 1771 cm^{-1}($\nu_{CO,sym}$). However, to the best of our knowledge, no comparable spectroscopic studies concerning copper(I) percarboxylates have been published so far.[20]

The $\nu_{C=C}$ stretching vibration of the $C{=}CH_2$ building block in **12b** appears at 1632 cm^{-1}, while characteristic absorptions for the ν_{CH} vibrations of the olefinic ═C−H units are found between 3080 and 3095 cm^{-1} for **12a**, **12b**, **14a**, and **14b**, respectively. In the region of the asymmetric C−O vibration (1620−1550 cm^{-1}) also the bands for the C═C stretching modes of the carbon−carbon double bonds for complexes **3d**, **12a**, **13a**, **13b**, **14a**, and **14b** are observed.

The ^{1}H NMR spectra of complexes **3**, **10**, **12**−**14**, and **16**−**18** are comprised of sharp and well-resolved resonance signals of the organic groups present. Noteworthy are two facts: while for complexes **3a**, **3d**, **13a**, and **13d** an AA′XX′ pattern is found for the cyclopentadienyl protons with coupling constants J_{HH} between 2.1 and 2.4 Hz, all other multimetallic species show broad signals, which for **12a**, **12b**, **14a**, **14b**, and **16** become magnetically almost equivalent. The olefinic protons appear in the expected region between 5.6 and 6.9 ppm as broad signals. The proton of the carboxylic acid functionalities in complexes **12a** and **16** appear as very broad singlets around 12 ppm.[26] However, corresponding signals for complexes **12b** and **17** could not be assigned unequivocally.

The $^{13}C\{^1H\}$ NMR spectra of all complexes are in agreement with their formulation as heterobimetallic titanium(IV)−copper(I) moieties, linked by di- or tricarboxylic ligands. The corresponding carbon resonance signals are found at the expected chemical shifts without peculiarities (Experimental Section). It is noteworthy to mention that the Cu(I) center in complexe **12b** appearently leads to an almost identical chemical shift of the carbon atom of the carboxylic unit, as does a proton.[26] In the case of the unsymmetrically bound dicarboxylic acid in complex **12a** or tricarboxylic acid in complexes **16** and **17**, the resonance signals of the CuOC(O) and the CO_2H units are not distinguishable and appear at the same chemical shift.

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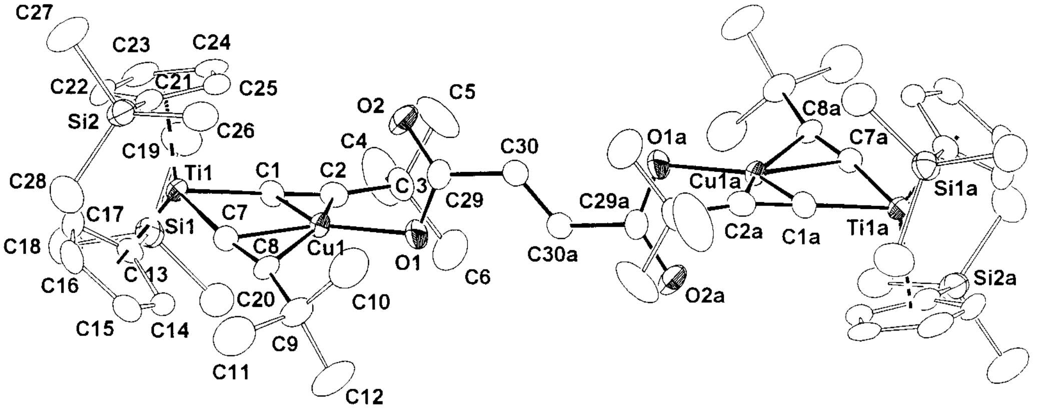

Figure 2. ORTEP drawing (50% probability level) of the titanium(IV)−copper(I) carboxylate complex **13a**, with molecular geometry and atom-numbering scheme.

With complex **13a** as a representative example, orientating cyclic voltammetric studies were conducted in a tetrahydrofuran solution at 25 °C; all potentials were referenced to the FcH/FcH$^+$ couple ($E_{1/2} = 0.00$ V). As already observed in the case of tri- or pentametallic 1,1′-ferrocenyl dicarboxylate bridged titanium(IV)−copper(I) species,[21] an irreversible Cu(I)/Cu(0) reduction was found at $E_{\mathrm{red}} = -1.83$ V. However, in contrast with these Ti(IV)−Cu(I)−Fe(II)-containing multimetallic complexes,[21] the one-electron Ti(IV)/Ti(III) reductive process observed for **13a** at $E_{\mathrm{red}} = -2.00$ V is irreversible.

In the oxidative region, a reversible one-electron process at $E_{1/2} = 0.12$ V ($\Delta E = 80$ mV) was observed. This could be assigned to the reversible Cu(I)/Cu(II) oxidation.[22]

In addition, these experiments reveal that a possible electronic communication between the heterobimetallic titanium(IV)−copper(I) building blocks via the linking carboxylic units and the π-conjugated system in **14a** is not detectable electrochemically. This can be interpreted as the carboxylic entity acting rather as an impedance than as a transmitter.

Experimental Section

General Methods. All reactions were carried out in an atmosphere of purified nitrogen (O_2 traces: CuO catalyst, BASF AG, Ludwigshafen; H_2O: molecular sieve 4 Å) using standard Schlenk techniques. Solvents were purified by distillation (*n*-pentane and dichloromethane: calcium hydride; diethyl ether and tetrahydrofuran: sodium/benzophenone ketyl; toluene: sodium). FT-IR spectra were recorded on a Perkin-Elmer FT-IR 1000 spectrometer (KBr pellets, as film between NaCl plates or as solution between CaF_2 plates). NMR spectra were recorded on a Bruker Avance 250 spectrometer, operating in the Fourier transform mode; ^{1}H NMR spectra were recorded at 250.130 MHz (internal standard relative to $CDCl_3$, $\delta = 7.27$; d_8-thf, $\delta = 1.73/3.58$); $^{13}C\{^1H\}$ NMR spectra were recorded at 67.890 MHz (internal standard, relative to $CDCl_3$, $\delta = 77.0$; d_8-thf, $\delta = 25.5/67.7$). Chemical shifts are reported in δ units [ppm] downfield from $SiMe_4$ with the solvent 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.

Cyclic voltammetric studies were carried out in a solution of [n-Bu_4N][PF_6] (0.1 mol dm^{-3}) in tetrahydrofuran at 25 °C on a Radiometer DEA 101 digital electrochemical analyzer, using a standard three-electrode cell arrangement (Pt, Pt, SCE) and were referenced to the ferrocene/ferrocenium couple FcH/FcH$^+$ ($E_{1/2}$= 0.00 V) as internal standard.

General Remarks. Compounds **1**,[13] **4**,[14,15] **5**,[23] **6**,[12] and **8**[4] were prepared by published procedures. All other chemicals were purchased by commercial suppliers and were used as received.

1. Synthesis of {[Ti](C≡CSiMe$_3$)$_2$}CuOAc (3a). Method A. $MeCO_2H$ (**2c**) (25 mg, 0.417 mmol) was added in one portion to {[Ti](C≡CSiMe$_3$)$_2$}CuMe (**1a**) (250 mg, 0.417 mmol) in 50 mL of tetrahydrofuran at −20 °C. After stirring for 30 min at this temperature, the reaction mixture was slowly warmed to 25 °C and stirred for an additional 1 h at this temperature. All volatile materials were removed in vacuo. The orange-colored residue was washed with cold *n*-pentane (2 × 5 mL) to yield **3a** as an orange solid in quantitative yield (265 mg, 0.417 mmol).

Method B. To {[Ti](C≡CSiMe$_3$)$_2$}CuCl (**4**) (300 mg, 0.490 mmol) in 40 mL of dichloromethane was added 1 equiv of [AgO_2CMe] (**5a**) (80 mg, 0.490 mmol) in one portion at 25 °C. After 4 h stirring at this temperature, the reaction mixture was filtered through a pad of Celite. All volatiles were removed in vacuo, and the residue was washed twice with *n*-pentane (2 × 5 mL). Crystallization from tetrahydrofuran/*n*-pentane (5:1) at −30 °C yielded **3a** as an orange solid (235 mg, 0.370 mmol, 75% based on **4**).

Method C. To [Ti](C≡CSiMe$_3$)$_2$ (**6**) (300 mg, 0.580 mmol) in 80 mL of diethyl ether was added in one portion 1 equiv of [CuO_2CMe] (**7a**) (70 mg, 0.580 mmol) at 25 °C. The color of the reaction mixture gradually changed from orange to red. After stirring for 30 min at this temperature, an orange solid started to precipitate. The reaction mixture was stirred for another 3 h, and all volatiles were removed in vacuo. Crystallization from tetrahydrofuran at −30 °C yielded **3a** as an orange solid (310 mg, 0.480 mmol, 83% based on **6**).

Method D. To [Ti](C≡CSiMe$_3$)$_2$ (**6**) (125 mg, 0.240 mmol) in 30 mL of diethyl ether was added 0.25 equiv of (η^2-Me$_3$SiC≡CSiMe$_3$)$_2$(CuOAc)$_4$ (**8a**) (50 mg, 0.060 mmol) in one portion at 25 °C. After stirring for 30 min at this temperature, an orange solid started to precipitate. The reaction mixture was stirred for another 4 h. Afterward all volatiles were removed in vacuo. Crystallization from tetrahydrofuran at −30 °C yielded **3a** in analytically pure form (150 mg, 0.230 mmol, 97% based on **6**). Mp (°C): 145 (dec). IR (NaCl, cm^{-1}): 1901 ($\nu_{C\equiv C}$), 1598 [ν_{CO}(sym)], 1380 [ν_{CO}(asym)]. ^{1}H NMR ($CDCl_3$, δ): 0.25 (s, 18 H, $SiMe_3$), 0.28 (s, 18 H, $SiMe_3$), 2.01 (s, 3 H, Me), 5.97 (pt, $J_{HH} = 2.3$ Hz, 4 H, C_5H_4), 6.10 (pt, $J_{HH} = 2.3$ Hz, 4 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 0.0 ($SiMe_3$), 1.2 ($SiMe_3$), 24.1 (Me), 113.2 (*CH*/C_5H_4), 116.1 (*CH*/C_5H_4), 121.5 (^{i}*C*/C_5H_4), 132.4 (TiC≡*C*), 170.9 (Ti*C*≡C), 177.0 (CO_2Cu). Anal. Calcd for $C_{28}H_{47}CuO_2Si_4Ti$ (639.46): C, 52.59; H, 7.41. Found: C, 52.93; H, 7.31.

X-ray Structure Determination of 3a. The solid-state structure of **3a** was determined from single-crystal X-ray diffraction. Data collection was performed on a Siemens-Nicolet Syntex R3m/V diffractometer using Mo Kα radiation. Crystallographic data of **3a** are given in Table 3. The structure was solved by direct methods (Sheldrick, G. M. *SHELX 97*; 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 placed in calculated positions.

2. Synthesis of $\{[Ti](C\equiv CSiMe_3)_2\}CuOC(O)C_6H_5$ (3b) and $\{[Ti](C\equiv CSiMe_3)_2\}CuOC(O)CH_2C_6H_5$ (3c). $C_6H_5CO_2H$ (**2b**) (55 mg, 0.450 mmol) or $C_6H_5CH_2CO_2H$ (**2c**) (60 mg, 0.450 mmol) was added in one portion to $\{[Ti](C\equiv CSiMe_3)_2\}CuMe$ (**1a**) (270 mg, 0.450 mmol) in 80 mL of tetrahydrofuran at −20 °C. After stirring for 30 min at this temperature, the reaction mixture was gradually warmed to 25 °C and additionally stirred for 2 h. All volatile materials were removed in vacuo. The resulting brown residues were washed with cold *n*-pentane (2 × 5 mL) to afford **3b** (orange solid) or **3c** (yellow-brown oil) in quantitative yields (0.450 mmol; **3b**, 315 mg; **3c**, 320 mg).

3b. The analytical as well as spectroscopic data are given in ref 17b.[17b]

3c. IR (NaCl, cm^{-1}): 1917 ($\nu_{C\equiv C}$), 1700 [ν_{CO}(sym)], 1558 [ν_{CO}(asym)]. ^1H NMR ($CDCl_3$, δ): 0.15 (s, 18 H, $SiMe_3$), 0.23 (s, 18 H, $SiMe_3$), 3.59 (s, 2 H, CH_2), 5.95 (bs, 4 H, C_5H_4), 6.07 (bs, 4 H, C_5H_4), 7.1−7.4 (m, 5H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 0.1 ($SiMe_3$), 0.2 ($SiMe_3$), 45.1 (CH_2), 113.3 (CH/C_5H_4), 116.1 (CH/C_5H_4), 121.5 ($^iC/C_5H_4$), 125.5 (CH/C_6H_5), 127.7 (CH/C_6H_5), 129.8 (CH/C_6H_5), 132.5 ($^iC/C_6H_5$), 137.6 ($TiC\equiv C$), 170.3 ($TiC\equiv C$), 175.9 (CO_2Cu). Anal. Calcd for $C_{34}H_{51}CuO_2Si_4Ti$ (715.55): C, 57.07; H, 7.18. Found: C, 56.72; H, 6.89.

3. Synthesis of $\{[Ti](C\equiv C^tBu)_2\}CuOC(O)CH{=}CMe_2$ (3d). $Me_2C{=}CH{-}CO_2H$ (**2d**) (50 mg, 0.520 mmol) was added in one portion to $\{[Ti](C\equiv CSiMe_3)_2\}CuMe$ (**1a**) (290 mg, 0.520 mmol), dissolved in 100 mL of tetrahydrofuran at −20 °C. After appropriate workup (see preparation of **3a**) $\{[Ti](C\equiv C^tBu)_2\}$-$CuOC(O)CH{=}CMe_2$ (**3d**) was isolated as an orange oil in 98% yield (330 mg, 0.510 mmol). IR (NaCl, cm^{-1}): 3073 ($\nu_{=C-H}$), 1985 ($\nu_{C\equiv C}$), 1651 [ν_{CO}(sym)], 1580 ($\nu_{C=C}$), 1558 [ν_{CO}(asym)]. ^1H NMR ($CDCl_3$, δ): 0.26 (s, 18 H, $SiMe_3$), 1.31 (s, 18 H, ^tBu), 1.32 (s, 6 H, $=CMe_2$), 6.02 (pt, J_{HH} = 2.1 Hz, 4H, C_5H_4Ti), 6.04 (pt, J_{HH} = 2.1 Hz, 4 H, C_5H_4), 6.05 (s, 1 H, $=CH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 0.1 ($SiMe_3$), 29.5 ($^qC/^tBu$), 30.8 ($Me/^tBu$), 31.0 ($=CMe_2$), 113.5 (CH/C_5H_4), 116.3 (CH/C_5H_4), 119.3 ($^iC/C_5H_4$), 121.4 ($=CMe_2$), 131.8 ($=CH$), 135.8 ($TiC\equiv C$), 146.5 ($TiC\equiv C$), 175.1 (CO_2Cu). Anal. Calcd for $C_{33}H_{51}CuO_2Si_2Ti$ (647.36): C, 61.22; H, 7.94. Found: C, 60.87; H, 7.79.

4. Synthesis of $\{[Ti](C\equiv CSiMe_3)_2\}CuOOC(O)C_6H_4Cl$-3 (10). $HO_3C{-}C_6H_4Cl$-3 (**9**) (100 mg, 0.570 mmol) was added in one portion to $\{[Ti](C\equiv CSiMe_3)_2\}CuMe$ (**1a**) (350 mg, 0.570 mmol) in 100 mL of tetrahydrofuran at −70 °C. After appropriate workup (see preparation of **3a**) complex **10** was obtained as a brown oil in 98% yield (420 mg, 0.559 mmol). IR (NaCl, cm^{-1}): 1917 ($\nu_{C\equiv C}$), 1771 [ν_{CO}(sym)], 1595 [ν_{CO}(asym)], 839 (ν_{C-Cl}). ^1H NMR ($CDCl_3$, δ): 0.13 (s, 18 H, $SiMe_3$), 0.24 (s, 18 H, $SiMe_3$), 6.00 (bs, 4 H, C_5H_4), 6.11 (bs, 4 H, C_5H_4), 7.2−8.1 (m, 4 H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 0.1 ($SiMe_3$), 0.2 ($SiMe_3$), 113.2 (CH/C_5H_4), 116.1 (CH/C_5H_4), 121.7 ($^iC/C_5H_4$), 127.7 (CH/C_6H_4), 128.7 (CH/C_6H_4), 129.7 (CH/C_6H_4), 129.8 (CH/C_6H_4), 132.2 ($^iC/C_6H_4$), 133.3 ($^iC/C_6H_4$), 138.4 ($TiC\equiv C$), 170.0 ($TiC\equiv C$), 170.1 (CO_3Cu). Anal. Calcd for $C_{33}H_{48}ClCuO_3Si_4Ti$ (752.01): C, 52.71; H, 6.43. Found: C, 52.89; H, 6.18.

5. Synthesis of $\{[Ti](C\equiv C^tBu)_2\}CuOC(O)$-*trans*-$CH{=}CH{-}CO_2H$ (12a) and $\{[Ti](C\equiv C^tBu)_2\}CuOC(O)CH_2C({=}CH_2)CO_2H$ (12b). HO_2C-*trans*-$CH{=}CH{-}CO_2H$ (**11a**) (20 mg, 0.178 mmol) or 25 mg (0.178 mmol) of $HO_2C{-}CH_2C({=}CH_2)CO_2H$ (**11b**) was added in one portion to $\{[Ti](C\equiv C^tBu)_2\}CuMe$ (**1b**) (100 mg, 0.178 mmol) in 60 mL of tetrahydrofuran at −70 °C. After stirring for 30 min at this temperature, the reaction mixture was slowly warmed to 25 °C and stirred additionally for 1 h. All volatile materials were removed in vacuo. The orange-colored residue was washed with cold *n*-pentane (3 × 5 mL) to yield quantitatively **12a** as an orange solid (120 mg, 0.178 mmol) or **12b** as a red oil (120 mg, 0.178 mmol).

12a. Mp (°C): 179 (dec). IR (NaCl, cm^{-1}): 2950 (ν_{OH}), 1983 ($\nu_{C\equiv C}$), 1705 [ν_{CO}(sym)], 1610 ($\nu_{C=C}$), 1568 [ν_{CO}(asym)]. ^1H NMR ($CDCl_3$, δ): 0.25 (s, 18 H, $SiMe_3$), 1.26 (s, 18 H, ^tBu), 6.05 (bs, 8 H, C_5H_4), 6.87 (s, 2 H, $=CH$).[a)] $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): −0.4 ($SiMe_3$), 30.8 ($Me/^tBu$), 31.1 ($^qC/^tBu$), 113.9 (CH/C_5H_4), 116.8 (CH/C_5H_4), 119.8 ($^iC/C_5H_4$), 134.4 ($TiC\equiv C$), 135.2 ($=C-H$), 147.7 ($TiC\equiv C$), 170.6 (CO_2Cu). Anal. Calcd for $C_{32}H_{47}CuO_4$-Si_2Ti (663.32): C, 57.94; H, 7.14. Found: C, 57.55; H, 6.94. A signal for the CO_2H group could not be assigned unequivocally.

12b. IR (NaCl, cm^{-1}): 2958 (ν_{OH}), 1986 ($\nu_{C\equiv C}$), 1700 [ν_{CO}(sym)], 1632 ($\nu_{C=C}$), 1558 [ν_{CO}(asym)]. ^1H NMR ($CDCl_3$, δ): 0.24 (s, 18 H, $SiMe_3$), 1.24 (s, 18 H, ^tBu), 3.34 (s, 2 H, $-CH_2-$), 5.57 (bs, 1 H, $=CH_2$), 6.05 (bs, 8 H, C_5H_4), 6.15 (bs, 1 H, $=CH_2$), 12.3 (bs, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 0.4 ($SiMe_3$), 30.8 ($Me/^tBu$), 31.1 ($qC/^tBu$), 41.7 ($-CH_2-$), 114.3 (CH/C_5H_4), 117.1 (CH/C_5H_4), 121.0 ($^iC/C_5H_4$), 126.5 ($=CH_2$), 132.9 ($TiC\equiv C$), 136.6 ($C{=}CH_2$), 148.1 ($TiC\equiv C$), 173.2 (CO_2Cu), 173.4 (CO_2H). Anal. Calcd for $C_{33}H_{49}CuO_4Si_2Ti$ (677.35): C, 58.52; H, 7.29. Found: C, 58.35; H, 7.63.

6. Synthesis of $\{[Ti](C\equiv C^tBu)_2\}CuOC(O){-}X{-}C(O)OCu$-$\{(^tBuC\equiv C)_2[Ti]\}$ (13a: X = *trans*-CH=CH, 13b: X = *cis*-CH=CH, 13c: X = 1,4-C_6H_4, 13d: X = C≡C) and $[\{[Ti]$-$(C\equiv C^tBu)_2\}CuO_2C]_2$ (13e). To $[Ti](C\equiv C^tBu)_2\}CuMe$ (**1b**) (270 mg, 0.480 mmol) in 60 mL of tetrahydrofuran was added 0.5 equiv (0.240 mmol) of *trans*-$HO_2C{-}CH{=}CH{-}CO_2H$ (**11a**) (30 mg), *cis*-$HO_2C{-}CH{=}CH{-}CO_2H$ (**11c**) (30 mg), $C_6H_4(CO_2H)_2$-1,4 (**11d**) (40 mg), $HO_2C{-}C\equiv C{-}CO_2H$ (**11e**) (25 mg), or $HO_2C{-}CO_2H$ (**11f**) (20 mg) in one portion at −20 °C. After stirring for 30 min at this temperature, the appropriate reaction mixture was allowed to warm to 25 °C and stirred for another 2 h at this temperature. All volatiles were removed in vacuo. The orange-colored residue was washed with cold *n*-pentane (2 × 5 mL) to yield quantitatively (0.240 mmol) analytically pure **13a**−**13e** as orange solids (**13a**, 290 mg; **13c,** 300 mg; **13e**, 285 mg) or orange-red oils (**13b**, 290 mg; **13d**, 290 mg).

13a. Mp (°C): 189 (dec). IR (NaCl, cm^{-1}): 3071 ($\nu_{=C-H}$), 1980 ($\nu_{C\equiv C}$), 1713 [ν_{CO}(sym)], 1590 ($\nu_{C=C}$), 1566 [ν_{CO}(asym)]. ^1H NMR ($CDCl_3$, δ): 0.27 (s, 36 H, $SiMe_3$), 1.29 (s, 36 H, ^tBu), 6.02 (pt, J_{HH} = 2.1 Hz, 8 H, C_5H_4), 6.05 (pt, J_{HH} = 2.1 Hz, 8 H, C_5H_4), 6.86 (s, 2 H, $=CH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 0.0 ($SiMe_3$), 30.8 (^tBu), 31.1 ($C_q/^tBu$), 113.7 (CH/C_5H_4), 116.6 (CH/C_5H_4), 119.4 ($^iC/C_5H_4$), 135.3 ($TiC\equiv C$), 135.6 ($=CH$), 147.3 ($TiC\equiv C$), 172.3 (CO_2Cu). Anal. Calcd for $C_{60}H_{90}Cu_2O_4Si_4Ti_2$ (1210.57): C, 59.53; H, 7.49. Found: C, 59.74; H, 7.59.

X-ray Structure Determination of 13a. The solid-state structure of **13a** was determined from single-crystal X-ray diffraction. Data collection was performed on a Bruker SMART CCD diffractometer using Mo Kα radiation. Crystallographic data of **13a** are given in Table 3. The structure was solved by direct methods (Sheldrick, G. M. *SHELX 97*; 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 placed in calculated positions. Compound **13a** contains one disordered tetrahydrofuran molecule for which no satisfactory model could be refined. The SQUEEZE[24] procedure from PLATON[25] was used to take this electron density into account.

13b. IR (NaCl, cm^{-1}): 3077 ($\nu_{=C-H}$), 1983 ($\nu_{C\equiv C}$), 1699 [ν_{CO}(sym)], 1580 ($\nu_{C=C}$), 1558 [ν_{CO}(asym)]. ^1H NMR ($CDCl_3$, δ): 0.23 (s, 36 H, $SiMe_3$), 1.24 (s, 36 H, ^tBu), 6.08 (bs, 16 H, C_5H_4), 6.34 (bs, 2 H, $=CH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 0.1 ($SiMe_3$), 30.9

(^{t}Bu), 31.1 (*C*$_q$/^{t}Bu), 114.3 (*CH*/C_5H_4), 117.1 (*CH*/C_5H_4), 121.4 (^{i}*C*/C_5H_4), 131.8 (TiC≡*C*), 134.7 (═CH), 148.3 (Ti*C*≡C), 169.1 (CO_2Cu). Anal. Calcd for $C_{60}H_{90}Cu_2O_4Si_4Ti_2$ (1210.57): C, 59.53; H, 7.49. Found: C, 60.04; H, 7.71.

13c. Mp (°C): 164 (dec). IR (NaCl, cm^{-1}): 1983 ($\nu_{C\equiv C}$), 1700 [ν_{CO}(sym)], 1560 [ν_{CO}(sym)]. ^{1}H NMR ($CDCl_3$, δ): 0.28 (s, 36 H, $SiMe_3$), 1.29 (s, 36 H, ^{t}Bu), 6.07 (pt, J_{HH} = 2.4 Hz, 8 H, C_5H_4), 6.08 (pt, J_{HH} = 2.4 Hz, 8 H, C_5H_4), 8.08 (s, 4 H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 0.1 ($SiMe_3$), 31.2 (^{t}Bu), 31.5 (*C*$_q$/^{t}Bu), 114.1 (*CH*/C_5H_4), 117.3 (*CH*/C_5H_4), 120.7 (^{i}*C*/C_5H_4), 128.4 (*CH*/C_6H_4), 133.1 (^{i}*C*/C_6H_4), 137.4 (TiC≡*C*), 147.5 (Ti*C*≡C), 174.8 (CO_2Cu). Anal. Calcd for $C_{64}H_{92}Cu_2O_4Si_4Ti_2$ (1260.66): C, 60.98; H, 7.36. Found: C, 60.55; H, 7.06.

13d. IR (NaCl, cm^{-1}): 2085 ($\nu_{C\equiv C}$), 1977 ($\nu_{TiC\equiv C}$), 1701 [ν_{CO}(sym)], 1561 [ν_{CO}(asym)]. ^{1}H NMR ($CDCl_3$, δ): 0.20 (s, 36 H, $SiMe_3$), 1.28 (s, 36 H, ^{t}Bu), 6.01 (bs, 16 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 0.1 ($SiMe_3$), 30.6 (*C*$_q$/^{t}Bu), 30.9 (^{t}Bu), 71.6 (C≡C), 112.3 (*CH*/C_5H_4), 115.1 (*CH*/C_5H_4), 117.7 (^{i}*C*/C_5H_4), 133.2 (TiC≡*C*), 148.1 (Ti*C*≡C), 161.3 (CO_2Cu). Anal. Calcd for $C_{60}H_{88}Cu_2O_4Si_4Ti_2$ (1208.55): C, 59.63; H, 7.34. Found: C, 59.16; H, 7.27.

13e. Mp (°C): 134 (dec). IR (NaCl, cm^{-1}): 1982 ($\nu_{C\equiv C}$), 1680 [ν_{CO}(sym)], 1500 [ν_{CO}(asym)]. ^{1}H NMR ($CDCl_3$, δ): 0.25 (s, 36 H, $SiMe_3$), 1.29 (s, 36 H, ^{t}Bu), 6.07 (pt, J_{HH} = 2.1 Hz, 8 H, C_5H_4), 6.16 (pt, J_{HH} = 2.1 Hz, 8 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 0.3 ($SiMe_3$), 31.1 (*C*$_q$/^{t}Bu), 31.4 (^{t}Bu), 113.8 (*CH*/C_5H_4), 117.0 (*CH*/C_5H_4), 119.0 (^{i}*C*/C_5H_4), 133.2 ($Ti_{C\equiv C}$), 147.1 (Ti*C*≡C), 168.7 (CO_2Cu). Anal. Calcd for $C_{58}H_{88}Cu_2O_4Si_4Ti_2$ (1184.55): C, 58.81; H, 7.49. Found: C, 58.59; H, 7.81.

7. Synthesis of {[Ti](C≡C^{t}Bu)$_2$}CuOC(O)−X−C(O)OCu{(Me$_3$SiC≡C)$_2$[Ti]} [14a: X = *trans*-CH═CH, 14b: X = CH$_2$C(═CH$_2$)]. [Ti](C≡CSiMe$_3$)$_2$}CuMe (**1a**) (100 mg, 0.177 mmol) in 40 mL of tetrahydrofuran was added dropwise to {[Ti](C≡C^{t}Bu)$_2$}CuOC(O)-*trans*-CH═CH−CO_2H (**12a**) (120 mg, 0.177 mmol) or {[Ti](C≡C^{t}Bu)$_2$}CuOC(O)−CH$_2$C(═CH$_2$)CO_2H (**12b**) dissolved in 50 mL of tetrahydrofuran at −20 °C. After stirring for 30 min at this temperature the reaction mixture was warmed to 25 °C and stirred for 1 h. All volatiles were removed in vacuo. The orange-colored residue was washed twice with cold *n*-pentane (5 mL) to afford in 98% isolated yield of **14a** (orange oil, 215 mg, 0.173 mmol) or **14b** (red oil, 220 mg, 0.173 mmol).

14a. IR (NaCl, cm^{-1}): 3081 ($\nu_{=C-H}$), 1977 ($\nu_{C\equiv C-t-Bu}$), 1917 ($\nu_{C\equiv CSi}$), 1700 [ν_{CO}(sym)], 1595 ($\nu_{C=C}$), 1575 [ν_{CO}(asym)]. ^{1}H NMR ($CDCl_3$, δ): 0.18 (s, 18 H, $SiMe_3$), 0.22 (s, 18 H, $SiMe_3$), 0.24 (s, 18 H, $SiMe_3$), 1.26 (s, 18 H, ^{t}Bu), 5.94 (bs, 4 H, C_5H_4), 6.00 (bs, 8 H, C_5H_4), 6.06 (bs, 4 H, C_5H_4), 6.10 (bs, 4 H, C_5H_4), 6.81 (s, 2 H, ═CH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): −0.1 ($SiMe_3$), 30.8 (^{t}Bu), 31.1 (*C*$_q$/^{t}Bu), 113.0 (*CH*/C_5H_4), 113.7 (*CH*/C_5H_4), 116.0 (*CH*/C_5H_4), 116.5 (*CH*/C_5H_4), 119.4 (^{i}*C*/C_5H_4), 121.3 (^{i}*C*/C_5H_4), 130.1 (TiC≡*C*^{t}Bu), 132.4 (Ti*C*≡C^{t}Bu), 135.5 (TiC≡*C*SiMe$_3$), 135.8 (═CH), 147.2 (Ti*C*≡CSiMe$_3$), 172.7 (CO_2Cu). Anal. Calcd for $C_{58}H_{90}Cu_2O_4Si_6Ti_2$ (1242.72): C, 56.06; H, 7.30. Found: C, 56.24; H, 6.89.

14b. IR (NaCl, cm^{-1}): 3078 ($\nu_{=C-H}$), 1978 ($\nu_{C\equiv C-t-Bu}$), 1918 ($\nu_{C\equiv CSi}$), 1733 [ν_{CO}(sym)], 1590 ($\nu_{C=C}$), 1554 [ν_{CO}(sym)]. ^{1}H NMR ($CDCl_3$, δ): 0.18 (s, 18 H, $SiMe_3$), 0.21 (s, 18 H, $SiMe_3$), 0.23 (s, 18 H, $SiMe_3$), 1.27 (s, 18 H, ^{t}Bu), 3.38 (s, 2 H, −CH$_2$−), 5.71 (bs, 1 H, ═CH$_2$), 5.98 (bs, 4 H, C_5H_4), 6.01 (bs, 8 H, C_5H_4), 6.08 (bs, 4 H, C_5H_4), 6.11 (bs, 4 H, C_5H_4), 6.15 (bs, 1 H, ═CH$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 0.0 ($SiMe_3$), 0.1 ($SiMe_3$), 30.0 (^{t}Bu), 30.1 (*Cq*/^{t}Bu), 41.2 (CH$_2$), 113.3 (*CH*/C_5H_4), 113.8 (*CH*/C_5H_4), 116.2 (*CH*/C_5H_4), 116.6 (*CH*/C_5H_4), 119.6 (^{i}*C*/C_5H_4), 121.8 (^{i}*C*/C_5H_4), 123.9 (═CH$_2$), 132.7 (TiC≡*C*^{t}Bu), 134.8 (*C*═CH$_2$), 139.0 (TiC≡*C*SiMe$_3$), 147.5 (Ti*C*≡C^{t}Bu), 170.1 (CO_2Cu), 173.6 (Ti*C*≡CSiMe$_3$), 175.2 (CO_2Cu). Anal. Calcd for $C_{59}H_{92}Cu_2O_4Si_6Ti_2$ (1256.74): C, 56.38; H, 7.38. Found: C, 55.82; H, 7.12.

8. Synthesis of {[Ti](C≡C^{t}Bu)$_2$}CuOC(O)-1-C$_6$H$_3$(CO$_2$H)$_2$-3,5 (16). $C_6H_3(CO_2H)_3$-1,3,5 (**15**) (80 mg, 0.373 mmol) was added in one portion to {[Ti](C≡C^{t}Bu)$_2$}CuMe (**1b**) (210 mg, 0.373 mmol) in 150 mL of tetrahydrofuran at −70 °C. After stirring for 30 min at this temperature, the reaction mixture was slowly warmed to 25 °C. After stirring for 4 h at this temperature all volatiles were removed in vacuo. The orange-colored residue was washed with cold *n*-pentane (3 × 5 mL) to yield quantitatively complex **16** (280 mg, 0.373 mmol) as an orange solid. Mp (°C): 190 (dec). IR (NaCl, cm^{-1}): 3150 (ν_{OH}), 1978 ($\nu_{C\equiv C}$), 1700 [ν_{CO}(sym)], 1620 [ν_{COOH}(sym)], 1558 [ν_{CO}(asym)]. ^{1}H NMR ($CDCl_3$, δ): 0.27 (s, 18 H, $SiMe_3$), 1.26 (s, 18 H, ^{t}Bu), 6.08 (bs, 4 H, C_5H_4), 6.09 (bs, 4 H, C_5H_4), 9.01 (bs, 3 H, C_6H_3), 12.0 (bs, 2 H, OH). ^{13}C{^{1}H} NMR (d_8-thf, δ): 0.9 ($SiMe_3$), 30.8 (*Me*/^{t}Bu), 31.5 (^{q}*C*/^{t}Bu), 114.5 (*CH*/C_5H_4), 117.2 (*CH*/C_5H_4), 121.0 (^{i}*C*/C_5H_4), 133.8 (^{i}*C*/C_6H_3), 133.9 (^{i}*C*/C_6H_3), 134.3 (*CH*/C_6H_3), 134.4 (*CH*/C_6H_3), 136.6 (TiC≡*C*), 146.3 (Ti*C*≡C), 167.8 (CO_2Cu). Anal. Calcd for $C_{37}H_{49}CuO_6Si_2Ti$ (757.39): C, 58.68; H, 6.52. Found: C, 58.80; H, 6.54. A signal for the CO_2H group could not be assigned unequivocally.

9. Synthesis of [{[Ti](C≡C^{t}Bu)$_2$}CuOC(O)]$_2$-1,3-C$_6$H$_3$-5-CO$_2$H (17). Method A. {[Ti](C≡C^{t}Bu)$_2$}CuMe (**1b**) (110 mg, 0.198 mmol) in 50 mL of tetrahydrofuran was added in one portion to {[Ti](C≡C^{t}Bu)$_2$}CuO$_2$C-1-C$_6$H$_3$(CO$_2$H)$_2$-3,5 (**16**) (150 mg, 0.198 mmol) in 80 mL of tetrahydrofuran at −70 °C. After stirring for 30 min at this temperature the reaction mixture was slowly warmed to 25 °C and stirred additionally for 3 h. All volatiles were removed in vacuo. The orange-colored residue was washed with cold *n*-pentane (2 × 5 mL) to yield quantitatively analytically pure **17** (245 mg, 0.198 mmol) as a red solid.

Method B. {[Ti](C≡C^{t}Bu)$_2$}CuMe (**1b**) (180 mg, 0.320 mmol) in 70 mL of tetrahydrofuran was added in one portion to $C_6H_3(CO_2H)_3$-1,3,5 (**16**) (35 mg, 0.160 mmol) in 60 mL of tetrahydrofuran at −70 °C. After appropriate workup (see preparation of **16**) complex **17** was obtained in quantitative yield (200 mg, 0.160 mmol) as a red solid. Mp (°C): 163 (dec). IR (NaCl, cm^{-1}): 3050 (ν_{OH}), 1978 ($\nu_{C\equiv C}$), 1700 [ν_{CO}(sym)], 1620 [ν_{COOH}], 1558 [ν_{CO}(sym)], ^{1}H NMR ($CDCl_3$, δ): 0.26 (s, 36 H, $SiMe_3$), 1.28 (s, 36 H, ^{t}Bu), 6.02 (pt, J_{HH} = 1.8 Hz, 8 H, C_5H_4), 6.04 (pt, J_{HH} = 1.8 Hz, 8 H, C_5H_4), 8.95 (bs, 3 H, C_6H_3). ^{13}C{^{1}H} NMR (d_8-thf, δ): 0.7 ($SiMe_3$), 30.9 (*Me*/^{t}Bu), 31.2 (^{q}*C*/^{t}Bu), 114.3 (*CH*/C_5H_4), 117.4 (*CH*/C_5H_4), 120.8 (^{i}*C*/C_5H_4), 133.6 (^{i}*C*/C_6H_3), 134.1 (^{i}*C*/C_6H_3), 134.4 (*CH*/C_6H_3), 134.7 (*CH*/C_6H_3), 136.3 (TiC≡*C*), 146.7 (Ti*C*≡C), 168.2 (CO_2Cu). Anal. Calcd for $C_{65}H_{92}Cu_2O_6Si_4Ti_2$ (1241.10): C, 62.91; H, 7.47. Found: C, 62.56; H, 7.28. A signal for the CO_2H group could not be assigned unequivocally.

10. Synthesis of [{[Ti](C≡C^{t}Bu)$_2$}CuOC(O)]$_3$C$_6$H$_3$-1,3,5 (18). Method A. To 180 mg of {[Ti](C≡C^{t}Bu)$_2$}CuMe (**1b**) (0.315 mmol) in 80 mL of tetrahydrofuran was added 0.33 equiv of $C_6H_3(CO_2H)_3$-1,3,5 (**15**) (20 mg, 0.105 mmol) in one portion at −20 °C. After stirring for 15 min at this temperature, the reaction mixture was slowly warmed to 25 °C and stirred additionally for 2 h at this temperature. All volatile materials were removed in vacuo. The red-colored residue was washed with cold *n*-pentane (5 mL) to yield **18** (195 mg, 0.105 mmol) as a red solid in quantitative yield.

Method B. {[Ti](C≡C^{t}Bu)$_2$}CuMe (**1b**) (115 mg, 0.206 mmol) in 40 mL of tetrahydrofuran was added in one portion to {[Ti](C≡C^{t}Bu)$_2$}CuO$_2$C-1-C$_6$H$_3$(CO$_2$H)$_2$-3,5 (**16**) (75 mg, 0.103 mmol) in 80 mL of tetrahydrofuran at −20 °C. After appropriate workup **18** was obtained in quantitative yield (190 mg, 0.103 mmol) as a red solid.

Method C. {[Ti](C≡C^{t}Bu)$_2$}CuMe (**1b**) (60 mg, 0.103 mmol) in 40 mL of tetrahydrofuran was added in one portion to [{[Ti]-(C≡C^{t}Bu)$_2$}CuO$_2$C]$_2$-1,3-C$_6$H$_3$(CO$_2$H)-5 (**17**) (125 mg, 0.103 mmol) in 100 mL of tetrahydrofuran at −20 °C. After stirring for 10 min at this temperature, the reaction mixture was warmed to 25 °C and stirred additionally for 3 h. All volatiles were removed in vacuo. The red-colored residue was washed with cold *n*-pentane (5 mL) to yield quantitatively **18** (185 mg, 0.103 mmol). Mp (°C): 144 (dec). IR (NaCl, cm^{-1}): 1989 ($\nu_{C\equiv C}$), 1699 [ν_{CO}(sym)], 1558 [ν_{CO}(asym)]. ^{1}H NMR ($CDCl_3$, δ): 0.27 (s, 54 H, $SiMe_3$), 1.25 (s, 54 H, ^{t}Bu), 6.02 (bs, 12 H, C_5H_4), 6.04

(bs, 12 H, C_5H_4), 8.80 (s, 3 H, C_6H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 0.2 ($SiMe_3$), 30.9 (*Me*/^{t}Bu), 31.1 (^{q}*C*/^{t}Bu), 113.5 (*CH*/C_5H_4), 116.4 (*CH*/C_5H_4), 119.1 (*CH*/C_5H_4), 132.8 (*CH*/C_6H_3), 136.2 (^{i}*C*/C_6H_3), 136.3 (TiC≡*C*), 146.7 (Ti*C*≡C), 172.6 (CO_2Cu). Anal. Calcd for $C_{93}H_{135}Cu_3O_6Si_6Ti_3$ (1851.88): C, 60.32; H, 7.35. Found: C, 59.81; H, 7.25.

Acknowledgment. This work was supported by the Volkswagenstiftung, the Fonds der Chemischen Industrie, and the Konrad-Adenauer-Stiftung (W.F.). We are grateful to Mrs. S. Ahrens, Mrs. J. Ruder, and Mrs. U. Stöss for the preparation of the manuscript.

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 **3a** and **13a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000617P