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C–C-bond formation in reactions of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CR^1)_2]CuR$ with acyl chlorides and anhydrides

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Abstract

The chemical behaviour of selected $\{[Ti](C{\equiv}CR^1)_2\}CuR$ complexes (**1a**: $R^1 = SiMe_3$, $R = CH_3$; **1b**: $R^1 = {}^tBu$, $R = CH_3$; **1c**: $R^1 = {}^tBu$, $R = C{\equiv}CSiMe_3$) towards a number of different acyl chlorides and anhydrides is described. The reaction of **1a** or **1b** with $R^2C(O)Cl$ (**2a**: $R^2 = CH_3$, **2b**: $R^2 = C_6H_5$) produces the ketones $R^2C(O)R$ (**4a**: $R = R^2 = CH_3$; **4b**: $R = CH_3$, $R^2 = C_6H_5$; **4c**: $R = C{\equiv}CSiMe_3$, $R^2 = CH_3$, **4d**: $R = C{\equiv}CSiMe_3$, $R^2 = C_6H_5$) along with $\{[Ti](C{\equiv}CR^1)_2\}CuCl$ (**3a**: $R^1 = SiMe_3$, **3b**: $R^1 = {}^tBu$). However, on treatment of **1b** or **1c** with $[CH_3C(O)]_2O$ (**5a**) the ketones **4a** or **4c** are formed along with the copper(I) acetate complex $\{[Ti](C{\equiv}C{}^tBu)_2\}CuOC(O)CH_3$ (**6**), while the reaction of **1b** or **1c** with CH_3CO_2H (**5b**) yields methane and **6**. In addition, when **1b** or **1c** are reacted with maleic (**7**), phthalic (**9a**) or tetrachlorophthalic anhydride (**9b**) the copper(I) carboxylates $\{[Ti](C{\equiv}C{}^tBu)_2\}CuOC(O)\text{-}cis\text{-}CH{=}CH{-}C(O)R$ (**8a**: $R = CH_3$, **8b**: $R = C{\equiv}CSiMe_3$) and $\{[Ti](C{\equiv}C{}^tBu)_2\}CuOC(O){-}C_6H_{4-n}Cl_n\text{-}2\text{-}C(O)R$ (**10a**: $n = 0$, $R = CH_3$; **10b**: $n = 0$, $R = C{\equiv}CSiMe_3$; **10c**: $n = 4$, $R = C{\equiv}CSiMe_3$) are produced, which upon addition of, e.g. HBr afford via cleavage of the copper–oxygen σ-bond $\{[Ti](C{\equiv}C{}^tBu)_2\}CuBr$ (**3c**) and the corresponding carboxylic acids $cis\text{-}HO_2C{-}CH{=}CH{-}C(O)CH_3$ (**11a**) or $HO_2C{-}C_6H_4\text{-}2\text{-}C(O)CH_3$ (**11b**), respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: C–C-bond formation; Acyl chlorides; Anhydrides; Copper; Titanium; Organometallic tweezer

1. Introduction

Organo-copper(I) compounds can be employed as organometallic reagents to prepare a high variety of different organic molecules, such as alkanes, alkenes, alkynes or functionalised derivatives thereof [1]. They also can be used to synthesise many novel and natural compounds [2]. These reactions are characterised by high chemo-, regio- and stereoselectivities. As specific reagents organo-copper(I) compounds, CuR [1], or cuprates, $[CuR_2]^-$ [3], are applied in these reactions [4].

However, there is only little known about the nature of the reactive species in copper-mediated reactions [1–3]. Thus, mononuclear and therefore well-defined organo-copper(I) compounds are of fundamental interest as model complexes for the study of such reactions. Recently, it has been demonstrated that the chelating effect of the organometallic π-tweezer molecule $R^1C{\equiv}C{-}[Ti]{-}C{\equiv}CR^1$ {e.g. $[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; $R^1 = SiMe_3$, ${}^tBu$, C_6H_5} enables the stabilisation of a high number of different monomeric organo-copper(I) entities [4,5]. Complexes of type $\{[Ti](C{\equiv}CR^1)_2\}CuR$ (R = singly bonded organic ligand), which contain an early (Ti) and a late transition metal (Cu) connected by alkynyl groups, are thereby formed in excellent yields. In these molecules the copper(I) center possesses a trigonal-planar environment, involving η^2-coordination of the alkynyl ligands of the bis(alkynyl) titanocene moiety and η^1-bonding of the corresponding organic groups R. The $(\eta^2\text{-alkyne})_2CuR$ building block represents a 16-valence-electron complex fragment [4,5].

In this respect, we here describe the reaction chemistry of selected $\{[Ti](C{\equiv}CR^1)_2\}CuR$ species towards different organic substrates, such as acyl chlorides and anhydrides.

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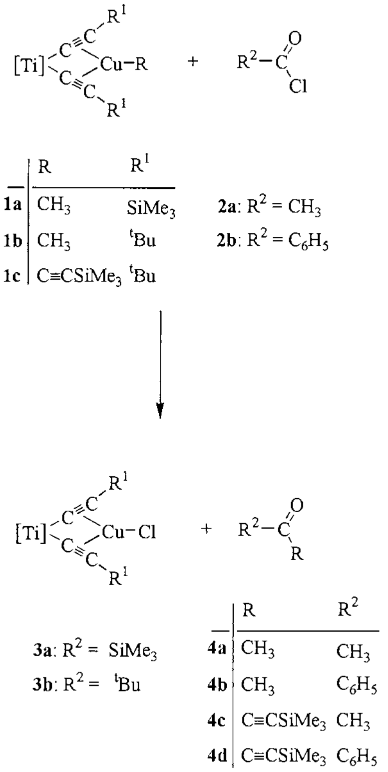
2. Results and discussion

Treatment of $\{[Ti](C\equiv CR^1)_2\}CuR$ $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; **1a**: $R^1 = SiMe_3$, $R = CH_3$; **1b**: $R^1 = {}^tBu$, $R = CH_3$; **1c**: $R^1 = {}^tBu$, $R = C\equiv CSiMe_3$) with the acyl chlorides $R^2C(O)Cl$ (**2a**: $R^2 = CH_3$, **2b**: $R^2 = C_6H_5$) in tetrahydrofuran or diethyl ether as solvent selectively produces at −30°C the heterodinuclear Ti(IV)–Cu(I) complexes $\{[Ti](C\equiv CR^1)_2\}CuCl$ (**3a**: $R^1 = SiMe_3$, **3b**: $R^1 = {}^tBu$) along with the ketones $R^2C(O)R$ (**4a**: $R = R^2 = CH_3$; **4b**: $R = CH_3$, $R^2 = C_6H_5$; **4c**: $R = C\equiv CSiMe_3$, $R^2 = CH_3$; **4d**: $R = C\equiv CSiMe_3$, $R^2 = C_6H_5$). The yield of **3** and **4** ranges between 90 and 100%, depending on the organic groups present (Eq. 1).



	R	R¹
1a	CH_3	$SiMe_3$
1b	CH_3	${}^tBu$
1c	$C\equiv CSiMe_3$	${}^tBu$

2a: $R^2 = CH_3$
2b: $R^2 = C_6H_5$

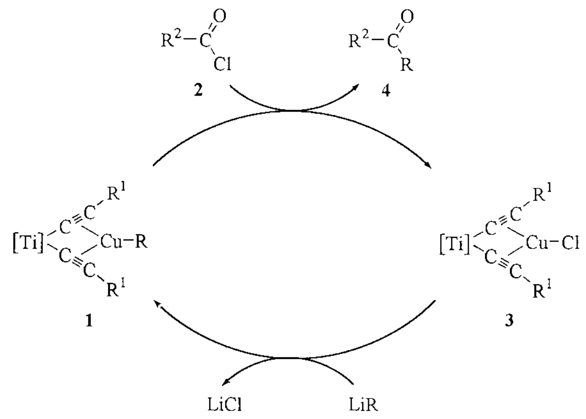
(1)

3a: $R^2 = SiMe_3$
3b: $R^2 = {}^tBu$

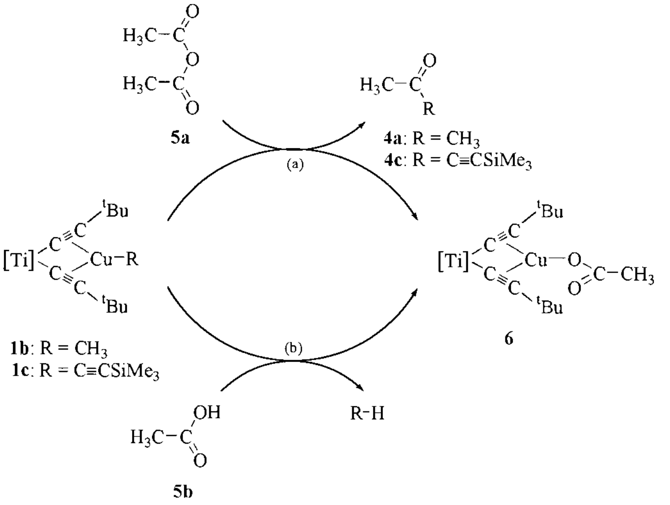
	R	R²
4a	CH_3	CH_3
4b	CH_3	C_6H_5
4c	$C\equiv CSiMe_3$	CH_3
4d	$C\equiv CSiMe_3$	C_6H_5

The driving force of this Gilman-type reaction [6] is the formation of the copper(I) chlorides **3a** and **3b**, respectively. In the reaction of **1** with **2** tetrahydrofuran as well as diethyl ether can be used as solvent. However, for a more convenient work-up diethyl ether is favourable, since in the latter solvent complexes **3a** and **3b** precipitate as orange solids. The corresponding ketones $R^2C(O)R$ (**4**) remain in solution and can be isolated simply by distillation. In contrast, the appropriate work-up in tetrahydrofuran is more lavish, since both reactants, **3** and **4**, are well-soluble in this solvent.

As outlined in Scheme 1, the organometallic starting materials **1a**–**1c** can be recovered by treatment of **3a** or **3b**, formed by the reaction of **1** with **2**, with equimolar amounts of, e.g. LiR or BrMgR.



Scheme 1. Copper(I)-mediated carbon–carbon bond formation; synthesis of the ketones $R^2C(O)R$ (**4**).

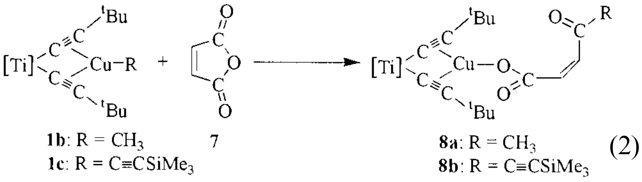


Scheme 2. Reaction of **1b** and **1c** with acetic anhydride (**5a**) or acetic acid (**5b**).

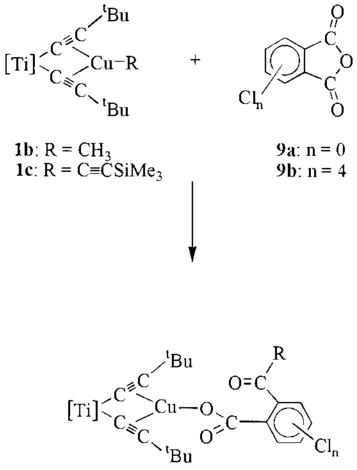
A further method to prepare symmetrical or unsymmetrical ketones is given by reacting, e.g. **1b** or **1c** with $[CH_3C(O)]_2O$ (**5a**) in a 1:1 molar ratio. In the temperature range of −30 to +25°C, the ketones $CH_3C(O)R$ (**4a**: $R = CH_3$, **4c**: $R = C\equiv CSiMe_3$) and $\{[Ti](C\equiv C^tBu)_2\}CuOC(O)CH_3$ (**6**) are formed in almost quantitative isolated yield when tetrahydrofuran is used as the solvent [Scheme 2, pathway (a)].

In contrast, the reaction of **1b** or **1c** with stoichiometric amounts of acetic acid (**5b**) produces under the same reaction conditions as described for the treatment of **1** with **5a** (vide supra) by evolution of R–H ($R = CH_3$, $C\equiv CSiMe_3$) complex **6** in quantitative yields [Scheme 2, pathway (b)].

The formation of $CH_3C(O)R$ (**4a**: $R = CH_3$, **4c**: $R = C\equiv CSiMe_3$) involves the cleavage of one carbon–oxygen-σ-bond in the applied anhydride, when **1b** or **1c** is reacted with **5a**. In contrast, cyclic anhydrides, such as maleic anhydride (**7**), phthalic anhydride (**9a**) or tetrachlorophthalic anhydride (**9b**), produce with **1b** or **1c** in a 1:1 molar ratio in polar organic solvents the keto-functionalised copper(I) carboxylates $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)$-*cis*-$CH{=}CH{-}C(O)R$ (**8a**: $R = CH_3$, **8b**: $R = C{\equiv}CSiMe_3$, Eq. 2) or $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O){-}C_6H_{4-n}Cl_n$-2-$C(O)R$ (**10a**: $n = 0$, $R = CH_3$; **10b**: $n = 0$, $R = C{\equiv}CSiMe_3$; **10c**: $n = 4$, $R = C{\equiv}CSiMe_3$; Eq. 3) in high yields. In the course of these reactions, a cleavage of a carbon-oxygen bond in **7** or **9** takes place, which means that for example **10** is formed by a formal insertion of the $O_2C{-}C_6H_{4-n}Cl_n$-2-$C(O)$ moiety into the copper-R bond in mononuclear **1b** or **1c**, respectively. Complexes **8** and **10** are produced without any side-products. They can be isolated in analytically pure form by simply evaporating the solvent.



(2)

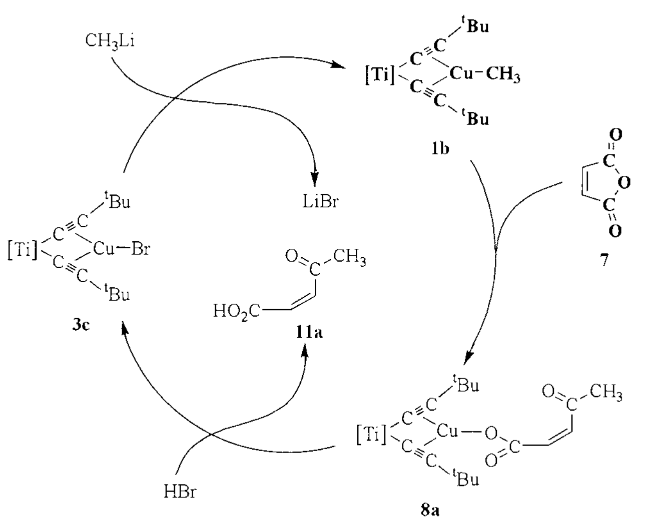


(3)

	n	R
10a	0	CH_3
10b	0	$C{\equiv}CSiMe_3$
10c	4	$C{\equiv}CSiMe_3$

The organic bifunctional subunits O_2C-*cis*-$CH{=}CH{-}C(O)R$ and $O_2C{-}C_6H_{4-n}Cl_n$-2-$C(O)R$ ($n = 0$, 4) in **8** and **10** can be transferred to the corresponding carboxylic acids by treatment of **8** and **10** with stoichiometric amounts of e.g. HBr in diethyl ether or dichloromethane at low temperatures (Scheme 3).

Nevertheless, it should be noted that the selectivity of the above mentioned reactions is strongly temperature dependent: In the temperature range of − 70 to − 40°C the copper–oxygen-σ-bond is upon addition of HBr selectively cleaved, as it could be demonstrated exemplary for **8a** and **10a**. Consequently, $\{[Ti](C{\equiv}C^tBu)_2\}CuBr$ (**3c**) and *cis*-$HO_2C{-}CH{=}CH{-}C(O)CH_3$ (**11a**) or $HO_2C{-}C_6H_{4-n}Cl_n$-2-$C(O)R$ (**12a**: $n = 0$, $R = CH_3$; **12b**: $n = 4$, $R = C{\equiv}CSiMe_3$) are formed in excellent yields. However, at higher temperature mixtures of products are obtained from which only **3c** could be isolated and characterised unequivocally.



Scheme 3. Copper(I)-mediated conversion of cyclic anhydrides to keto-functionalised carboxylic acids. Exemplary, the reaction of **1b** with **7** is outlined.

The copper bromide **3c** can be transferred to the starting material **1b** by its treatment with one equivalent of e.g. CH_3Li in diethyl ether at − 70°C (Scheme 3).

In general, the titanium-copper complexes **1a**–**1c** can be applied as reagents for organo-copper mediated carbon-carbon bond formations as presented by their reaction with diverse acyl chlorides and anhydrides (vide supra). The resulting symmetrical and unsymmetrical ketones or keto-functionalised carboxylates are the only organic products formed apart from the monomeric copper(I) chlorides **3a** and **3b**, when **1** is reacted with **2**.

Non-coordinated, free organo-copper reagents of type CuR react in a 1,2- or 1,4-addition with ketones or α,β-unsaturated ketones [7]. In contrast to this behaviour, we found that the CuR moiety in the organometallic titanium(IV)–copper(I) tweezer molecules **1a**–**1c** does not add to C=O or C=C double bond systems at all, which was clearly demonstrated by the reaction of **1** with **4** or **7**–**10**. Even when an excess of **1** is applied, no addition reactions at the sp^2-hybridised carbon atoms occur. However, at higher temperatures decomposition of the employed reaction components took place. One explanation is given by the fact that in these reactions as intermediate a thermally unstable mononuclear copper(I) alcoholate, $\{[Ti](C{\equiv}CR^1)_2\}CuOR^3$, is generated. The chemical behaviour of such an entity is well-known for example $\{[Ti](C{\equiv}CSiMe_3)_2\}CuOR^3$ (R^3 = e.g. CH_3, C_2H_5, $SiMe_3$, ^tBu) [4,8]. Under the conditions applied, these complexes eliminate Me_3SiOR^3 and the in-situ generated

$\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)$ building block affords the titanium(IV)–copper(I) acetylide $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)\}_2$ by dimerisation [4,8]. Similar observations were made when **1** was reacted with carboxylic esters instead of ketones or α,β-unsaturated ketones.

Another typical reagent for copper-mediated carbon-carbon bond formation are cuprates, $Li[CuR_2]$ (R = singly bonded organic ligand, e.g. CH_3) [3]. Therefore, we were interested to apply the bis(alkynyl) titanocene $[Ti](C{\equiv}C^tBu)_2$ (**12**) as organometallic chelating system for anionic $[CuR_2]^-$ entities. In principle, following procedures can be employed to synthesise compounds of type $\{[Ti](C{\equiv}C^tBu)_2\}CuR_2^-$: (i) reaction of $\{[Ti](C{\equiv}C^tBu)_2\}CuSC_6H_4CH_2NMe_2$-2 (**13**) [4,5a,c,9] with two equivalents of LiR; (ii) treatment of $\{[Ti](C{\equiv}C^tBu)_2\}CuR$ with equimolar amounts of LiR; or (iii) the reaction of $[Ti](C{\equiv}C^tBu)_2$ (**12**) with $Li[CuR_2]$. However, it appeared that in all of these reactions the only isolated product is $[Ti](CH_3)_2$ (**14**), when the corresponding CH_3-functionalised copper(I) species are used [5a]. Independently, this compound could be synthesised by the reaction of $[Ti]Cl_2$ (**15**) with two equivalents of CH_3Li in diethyl ether at low temperature [10]. Similar observations were made for other organic groups R, such as alkyls and aryls. In this respect, it must be noted that $\{[Ti](C{\equiv}C^tBu)_2\}CuR$ is formed at first, which yields by subsequent reaction with R^- the corresponding $[Ti]R_2$ species. A possible reaction mechanism was published earlier and includes as initial step the nucleophilic attack of R^- at the titanium(IV) centre [11].

All compounds were characterised by elemental analysis and spectroscopic studies [IR, ^1H-NMR, $^{13}C\{^1H\}$-NMR]. In agreement with the formulation of compounds **3**, **6**, **8** and **10** as heterobimetallic titanium(IV)–copper(I) tweezer molecules in which the alkynyl ligands of the $[Ti](C{\equiv}CR^1)_2$ building blocks are likewise η^2-coordinated to the copper(I) halide (compound **3**) or a copper(I) carboxylate moiety (compounds **6**, **8** and **10**) is the observation of the distinct $\nu_{C{\equiv}C}$ vibration in the IR spectra of these complexes between 1975 and 1990 cm^{-1} [4,5]. Compared to the starting materials **1a**–**1c** [$\nu_{C{\equiv}C}$ 1867 cm^{-1} (**1a**) [12], 1909 cm^{-1} (**1b**) [5a], 1939 cm^{-1} (**1c**)] [13] the C≡C stretching vibrations in **3**, **6**, **8** and **10** are shifted to higher wavenumbers. These data verify that a change of the copper η^1-bonded groups CH_3 or $C{\equiv}CSiMe_3$, as given by complexes **1a**–**1c**, from a stronger to a weaker σ-donor ligand (**3**, **6**, **8**, **10**) leads to a stronger $C{\equiv}CR^1$ triple bond [4,5,14]. Moreover, in the copper(I) carboxylates **6**, **8** and **10** two distinct ν_{CO} vibrations are found between 1700 and 1720 cm^{-1} (ν_{sym}) and 1540 and 1560 (ν_{as}), respectively, in a region, which is typical for η^2-alkyne-stabilised copper(I) carboxylates [15].

The difference of the symmetric and asymmetric stretching vibration $\Delta\nu$ is 160 cm^{-1}. This clearly demonstrates that the carboxylic ligands in **6**, **8** and **10** are η^1-bonded via one oxygen atom to the copper(I) ion [15]. Also the ν_{CO} vibrations of the keto-functionalities in **8** and **10** appear in this region. In contrast, the CO stretching vibration of ketones **4a**–**4c** is observed between 1690 and 1710 cm^{-1} as a very strong band [14].

The ^1H-NMR spectra of all compounds consist of well-resolved resonance signals for the corresponding organic ligands with the expected resonance patterns and ratios. Noticeable is the observation that the cyclopentadienyl protons, which usually appear as well-structured AA′XX′ patterns, are broadened in **10c** (6.09, 6.19 ppm), while for complexes **8a**, **8b**, **10a** and **10b** only a broad resonance signal at 6.03 (**6**), 6.10 (**8a**), 6.07 (**8b**), 6.13 (**10a**) or 6.12 ppm (**10b**) is found.

In the $^{13}C\{^1H\}$-NMR spectra of complexes **8** and **10**, the region of 114–122 ppm shows a total of three resonance signals for the cyclopentadienyl carbon atoms. The resonance signals of the carbon atom of the corresponding keto groups are observed between 190 and 200 ppm, a region, which is characteristic for these groupings [16]. Additionally, it is found that the resonance signal of the sp-hybridised carbon atoms of the $C{\equiv}CR^1$ groups in complexes **6**, **8**, and **10** ($TiC{\equiv}\underline{C}^tBu$: 127–134 ppm, $Ti\underline{C}{\equiv}C^tBu$: 148–150 ppm) are shifted to higher field with respect to the starting material **1b** ($TiC{\equiv}\underline{C}^tBu$: 138.6 ppm, $Ti\underline{C}{\equiv}C^tBu$: 169.1 ppm) [4,5]. This finding is in agreement with the earlier mentioned shift of the $\nu_{C{\equiv}C}$ stretching vibration, where a very distinct influence is observed by changing from a stronger to a weaker σ-donor ligand or vice versa.

3. Experimental

3.1. 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: calciumhydride; diethyl ether and tetrahydrofuran: sodium/benzophenone ketyl; toluene: sodium. FT-IR spectra were recorded 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, operating in the Fourier transform mode; ^1H-NMR spectra: 250.130 MHz (internal standard relative to $CDCl_3$, $\delta = 7.27$); $^{13}C\{^1H\}$-NMR spectra: 67.890 MHz (standard intern, relative to $CDCl_3$, $\delta = 77.0$). 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.

3.2. General remarks

Compounds **1a** [12], **1b** [5a], **1c** [13], **13** [4,5a,c,9], **15** [20], and $Li[Cu(CH_3)_2]$ [3] were prepared by published procedures. All other chemicals were purchased by commercial suppliers and were used as received.

Caution: When repeating the experiments for the preparation of the methyl copper(I) compounds **1a** and **1b** [14,15], it must be noted that the uncomplexed species $[CuCH_3]$ is highly explosive when dry [18]. For this reason care has to be taken with all safety precautions required.

*3.3. Reaction of $\{[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ (**1b**) or $\{[Ti](C{\equiv}C^tBu)_2\}CuC{\equiv}CSiMe$ (**1c**) with CH_3COOH (**5b**). Synthesis of $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)CH_3$ (**6**) and CH_4 or $HC{\equiv}CSiMe_3$*

CH_3COOH (**5b**) (10 mg, 0.178 mmol) in 10 ml of tetrahydrofuran was added dropwise to $\{[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ (**1b**) (100 mg, 0.178 mmol) or $\{[Ti](C{\equiv}C^tBu)_2\}CuC{\equiv}CSiMe_3$ (**1c**) (115 mg, 0.178 mmol) in 40 ml of tetrahydrofuran at −40°C. After stirring at this temperature for 30 min, the reaction mixture was gradually warmed to 25°C. Thereby, the colour changed from red to orange. After stirring for 10 min at 25°C all volatiles were removed in vacuo to afford $\{[Ti](C{\equiv}C^tBu)_2\}CuOAc$ (**6**) as an orange solid in quantitative yield (110 mg, 0.178 mmol).

The exclusive formation of $HC{\equiv}CSiMe_3$ was proven by GC-MS techniques.

M.p. 163°C (dec.). IR (NaCl, ν, cm^{-1}) 1983 ($C{\equiv}C$), 1716 (CO_{sym}), 1556 (CO_{as}). ^{1}H-NMR ($CDCl_3$) 0.26 (s, 18H, $SiMe_3$), 1.32 (s, 18H, ^tBu), 2.13 (s, 3H, CH_3), 6.0 (bs, 8H, C_5H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$) 0.1 ($SiMe_3$), 21.5 (CH_3), 30.8 (^tBu), 31.1 (^tBu, C_q), 114.5 (CH/C_5H_4), 117.4 (CH/C_5H_4), 121.1 (iC/C_5H_4), 128.4 ($TiC{\equiv}\underline{C}$), 148.7 ($Ti\underline{C}{\equiv}C$), 171.4 (CO_2). Anal. Calc. for $C_{30}H_{47}CuO_2Si_2Ti$ (607.32): C, 59.33; H, 7.80. Found: C, 58.87; H, 7.65%.

*3.4. Reaction of $\{[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ (**1b**) and $\{[Ti](C{\equiv}C^tBu)_2\}CuC{\equiv}CSiMe_3$ (**1c**) with acetic anhydride (**5a**). Synthesis of $CH_3C(O)CH_3$ (**4a**), $CH_3C(O)C{\equiv}CSiMe_3$ (**4c**) and $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)CH_3$ (**6**)*

Acetic anhydride (**5a**) (35 mg, 0.355 mmol) in 10 ml of tetrahydrofuran was added dropwise to $\{[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ (**1b**) (200 mg, 0.355 mmol) or $\{[Ti](C{\equiv}C^tBu)_2\}CuC{\equiv}CSiMe_3$ (**1c**) (230 mg, 0.355 mmol) in 60 ml of tetrahydrofuran at −20°C. After stirring for 1 h at this temperature the reaction mixture was gradually warmed to 25°C and stirred for an additional 2 h. All volatile materials were removed in vacuo. By extraction with cold (−20°C) diethyl ether (3 × 5 ml) the compounds **4a** or **4c** were separated from $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)CH_3$ (**6**). The orange residue consisted of analytically pure **6**, which was isolated in 96% yield (205 mg, 0.341 mmol) after drying in vacuo. Evaporation of the solvent of the diethyl ether solution afforded **4a** or **4c** (0.330 mmol, 90–95% yield; **4a**: 20 mg; **4c**: 45 mg), which could be characterised by comparison of the spectroscopic data of authentic samples [17].

Spectroscopic data of **6** are given in **1**, those of **4a** in Ref. [17a] and of **4c** in Ref. [17b].

*3.5. Synthesis of $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)$-cis-$CH{=}CH{-}C(O)CH_3$ (**8a**)*

Maleic anhydride (**7**) (25 mg, 0.355 mmol) dissolved in 10 ml of tetrahydrofuran was added dropwise within 5 min to $\{[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ (**1b**) (200 mg, 0.355 mmol) in 60 ml of tetrahydrofuran at −40°C. After stirring at this temperature for 30 min, the reaction mixture was gradually warmed to 25 °C within 1 h. Then, all volatiles were evaporated in vacuo to yield **8a** (255 mg, 0.355 mmol) as orange–red oil in quantitative yield.

IR (NaCl, ν, cm^{-1}) 1983 ($C{\equiv}C$), 1707 (CO_{sym}), 1635 ($C{=}C$), 1550 (CO_{as}). ^{1}H-NMR ($CDCl_3$) 0.26 (s, 18H, $SiMe_3$), 1.26 (s, 18H, ^tBu), 2.26 (s, 3H, CH_3), 6.1 (bs, 8H, C_5H_4), 6.4 (bs, 2H, $=CH$). $^{13}C\{^1H\}$-NMR ($CDCl_3$) 0.1 ($SiMe_3$), 25.5 (CH_3), 30.9 (^tBu), 31.0 (^tBu, C_q), 114.3 (CH/C_5H_4), 117.1 (CH/C_5H_4), 121.5 (iC/C_5H_4), 127.3 ($TiC{\equiv}\underline{C}$), 131.8 ($=CH$), 134.7 ($=CH$), 148.2 ($Ti\underline{C}{\equiv}C$), 169.2 (CO_2), 189.7 ($C{=}O$). Anal. Calc. for $C_{33}H_{49}CuO_3Si_2Ti$ (661.35): C, 59.93; H, 7.47. Found: C, 60.34; H, 7.26%.

*3.6. Synthesis of $\{[Ti](C{\equiv}C^tBu)_2\}CuOC$-$(O)$-cis-$CH{=}CH{-}C(O)C{\equiv}CSiMe_3$ (**8b**)*

Maleic anhydride (**7**) (40 mg, 0.400 mmol) in 10 ml of tetrahydrofuran was slowly added to $\{[Ti](C{\equiv}C^tBu)_2\}$-$CuC{\equiv}CSiMe_3$ (**1c**) (260 mg, 0.400 mmol) in 50 ml of tetrahydrofuran at −20°C. After stirring for 1 h at this temperature the reaction mixture was gradually warmed to 25°C and stirred for another 3 h. All volatile materials were removed in vacuo and **8b** was obtained as red oil in quantitative yield (300 mg, 0.400 mmol).

IR (NaCl, ν, cm^{-1}) 2087 ($C{\equiv}CSiMe_3$), 1983 ($C{\equiv}C^tBu$), 1716 (CO_{sym}), 1632 ($C{=}C$), 1539 (CO_{as}). ^{1}H-NMR ($CDCl_3$) 0.06 (s, 9H, $SiMe_3$), 0.26 (s, 18H, $SiMe_3$), 1.26 (s, 18H, ^tBu), 6.1 (bs, 9H, C_5H_4, $=CH$), 6.4 (bs, 1H, $=CH$). $^{13}C\{^1H\}$-NMR ($CDCl_3$) 0.1 ($SiMe_3$), 30.7 (^{t}Bu), 31.2 (^{t}Bu, C_q), 67.6 ($C{\equiv}\underline{C}SiMe_3$), 68.9 ($\underline{C}{\equiv}CSiMe_3$), 114.1 ($CH/C_5H_4$), 117.4 ($CH/C_5H_4$), 121.8 ($iC/C_5H_4$), 127.7 ($TiC{\equiv}\underline{C}$), 131.2 (=CH), 135.2 (=CH), 148.6 ($Ti\underline{C}{\equiv}C$), 168.7 (CO_2), 188.6 (CO). Anal. Calc. for $C_{37}H_{55}CuO_3Si_3Ti$ (743.53): C, 59.77; H, 7.46. Found: C, 59.47; H, 7.19%.

3.7. Synthesis of $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O){-}C_6H_4{-}2{-}C(O)CH_3$ *(**10a**)*

Phthalic anhydride (**9a**) (45 mg, 0.290 mmol) in 30 ml of tetrahydrofuran was added dropwise to $\{[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ (**1b**) (165 mg, 0.290 mmol) in 50 ml of tetrahydrofuran at −20°C. After 45 min at −20°C, followed by stirring for 2 h at 25°C, all volatiles were removed in vacuo. Compound **10a** was obtained as orange–red oil in quantitative yield (205 mg, 0.290 mmol).

IR (NaCl, ν, cm^{-1}) 1983 ($C{\equiv}C$), 1707 (CO_{sym}), 1690 (CO, $C(O)CH_3$), 1553 (CO_{as}). ^{1}H-NMR ($CDCl_3$) 0.28 (s, 18H, $SiMe_3$), 1.25 (s, 18H, ^{t}Bu), 2.25 (s, 3H, CH_3), 6.13 (bs, 8H, C_5H_4), 7.9–8.1 (m, 4H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$) 0.3 ($SiMe_3$), 25.4 (CH_3), 30.9 (^{t}Bu), 31.1 (^{t}Bu, C_q), 114.4 (CH/C_5H_4), 117.1 (CH/C_5H_4), 121.5 (iC/C_5H_4), 125.6 (CH/C_6H_4), 131.1 (iC/C_6H_4), 131.2 (CH/C_6H_4), 132.2 ($TiC{\equiv}\underline{C}$), 133.2 (CH/C_6H_4), 133.5 (iC/C_6H_4), 136.1 (CH/C_6H_4), 148.0 ($Ti\underline{C}{\equiv}C$), 162.6 (CO_2), 191.3 (CO). Anal. Calc. for $C_{37}H_{51}CuO_3Si_2Ti$ (711.42): C, 62.47; H, 7.23. Found: C, 62.13; H, 6.89%.

3.8. Synthesis of $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O){-}C_6H_4{-}2{-}C(O)C{\equiv}CSiMe_3$ *(**10b**)*

Phthalic anhydride (**9a**) (40 mg, 0.270 mmol) in 20 ml of tetrahydrofuran was added to $\{[Ti](C{\equiv}C^tBu)_2\}CuC{\equiv}CSiMe_3$ (**1c**) (185 mg, 0.270 mmol) in 70 ml of tetrahydrofuran at −30°C. Appropriate work-up (see Section 3.7) affords **10b** as red oil in quantitative yields (215 mg, 0.270 mmol).

IR (NaCl, ν, cm^{-1}) 2083 ($C{\equiv}CSiMe_3$), 1987 ($C{\equiv}C^tBu$), 1705 ($CO_{sym,}$), 1695 (CO, $C(O)CH_3$), 1552 (CO_{as}). ^{1}H-NMR ($CDCl_3$) 0.06 (s, 9H, $SiMe_3$), 0.27 (s, 18H, $SiMe_3$), 1.27 (s, 18H, ^{t}Bu), 6.1 (bs, 8H, C_5H_4), 7.3–7.6 (m, 4H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$) 0.1 ($SiMe_3$), 0.9 ($SiMe_3$), 30.7 (^{t}Bu, C_q), 30.9 (^{t}Bu), 67.3 ($C{\equiv}\underline{C}SiMe_3$), 68.1 ($\underline{C}{\equiv}CSiMe_3$), 113.7 ($CH/C_5H_4$), 115.1 ($CH/C_5H_4$), 116.7 ($iC/C_5H_4$), 128.7 ($CH/C_6H_4$), 129.1 ($CH/C_6H_4$), 129.6 ($CH/C_6H_4$), 130.7 ($CH/C_6H_4$), 133.1 ($iC/C_6H_4$), 134.0 ($iC/C_6H_4$), 134.5 ($TiC{\equiv}\underline{C}$), 150.2 ($Ti\underline{C}{\equiv}C$), 179.1 ($CO_2$), 195.6 (CO). Anal. Calc. for $C_{41}H_{57}CuO_3Si_3Ti$ (793.58): C, 62.05; H, 7.24. Found: C, 61.64; H, 7.31%.

3.9. Synthesis of $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O){-}C_6Cl_4{-}2{-}C(O)C{\equiv}CSiMe_3$ *(**10c**)*

Tetrachlorophthalic anhydride (**9b**) (60 mg, 0.220 mmol) in 30 ml of tetrahydrofuran was added dropwise to $\{[Ti](C{\equiv}C^tBu)_2\}CuC{\equiv}CSiMe_3$ (**1c**) (150 mg, 0.220 mmol) in 50 ml of tetrahydrofuran at −50°C. Appropriate work-up (see Section 3.7) affords **10c** as red oil in quantitative yield (205 mg, 0.220 mmol).

IR (NaCl, ν, cm^{-1}) 2070 ($C{\equiv}CSiMe_3$), 1990 ($C{\equiv}C^tBu$), 1700 ($CO_{sym,}$), 1682 (CO, $C(O)CH_3$), 1557 (CO_{as}). ^{1}H-NMR ($CDCl_3$) 0.08 (s, 9H, $SiMe_3$), 0.26 (s, 18H, $SiMe_3$), 1.28 (s, 18H, ^{t}Bu), 6.1 (bs, 4H, C_5H_4), 6.2 (bs, 4H, C_5H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$) 0.2 ($SiMe_3$), 1.1 ($SiMe_3$), 31.1 (^{t}Bu, C_q), 31.2 (^{t}Bu), 67.9 ($C{\equiv}\underline{C}SiMe_3$), 68.5 ($\underline{C}{\equiv}CSiMe_3$), 114.6 ($CH/C_5H_4$), 118.0 ($CH/C_5H_4$), 120.3 ($iC/C_5H_4$), 130.0 ($C_6Cl_4$), 130.1 ($C_6Cl_4$), 130.8 ($C_6Cl_4$), 130.9 ($C_6Cl_4$), 132.0 ($C_6Cl_4$), 134.0 ($C_6Cl_4$), 134.1 ($TiC{\equiv}\underline{C}$), 147.7 ($Ti\underline{C}{\equiv}C$), 177.6 ($CO_2$), 198.6 (CO). Anal. Calc. for $C_{41}H_{53}CuCl_4O_3Si_3Ti$ (931.55): C, 52.86; H, 5.73. Found: C, 53.31; H, 5.93%.

3.10. Reaction of $\{[Ti](C{\equiv}C^tBu)_2\}CuOC(O)$*-cis-*$CH{=}CH{-}C(O)CH_3$ *(**8a**) or* $\{[Ti](C{\equiv}C^tBu)_2\}{-}CuO_2C{-}C_6H_4{-}2{-}C(O)CH_3$ *(**10a**) with HBr*

To $[Ti](C{\equiv}C^tBu)_2\}CuOC(O)$-*cis*-$CH{=}CH{-}C(O)CH_3$ (**8a**) (190 mg, 0.290 mmol) or $\{[Ti](C{\equiv}C^tBu)_2\}{-}CuOC(O){-}C_6H_4{-}2{-}C(O)CH_3$ (**10a**) (205 mg, 0.290 mmol) in 60 ml of diethyl ether were slowly added equimolar amounts of HBr in 30 ml diethyl ether at −70°C. After stirring at this temperature for 20 min, the corresponding reaction mixture was warmed to −10°C within 1 h. All volatiles were removed in vacuo at this temperature. Fractional crystallisation from tetrahydrofuran yielded first $\{[Ti](C{\equiv}C^tBu)_2\}CuBr$ (**3c**) (160 mg, 0.252 mmol, 87%) and then HO_2C-*cis*-$CH{=}CH{-}C(O)CH_3$ (**11a**) (30 mg, 0.258 mmol, 89%) or (**11b**) $HO_2C{-}C_6H_4{-}2{-}C(O)CH_3$ (45 mg, 0.264 mmol, 91%). Compounds **3c**, **11a** and **11b** were characterised by comparison with the spectroscopic data of authentic **3c** [18], **11a** [19] and **11b** [17a].

Spectroscopic data of **3c** are listed in reference [19], those of **11a** in [19] and of **11b** in [17a].

3.11. Synthesis of $[Ti](CH_3)_2$ *(**14**) [10]*

3.11.1. Reaction of $\{[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ *(**1b**) with* CH_3Li

To $[Ti](C{\equiv}C^tBu)_2\}CuCH_3$ (**1b**) (180 mg, 0.320 mmol) in 40 ml of diethyl ether were added 0.320 mmol of CH_3Li (1.6 M in diethyl ether) at −70°C. After stirring at this temperature for 20 min the reaction mixture was warmed to 25°C within 1 h. All volatile materials were removed in vacuo. The residue was redissolved in 10 ml of diethyl ether and filtered through a pad of Celite (5 × 3 cm). After evaporation of all volatiles $[Ti](CH_3)_2$ (**14**) was obtained in 88% yield (100 mg, 0.282 mmol) [10].

M.p. 143°C (dec.). IR (NaCl, ν, cm^{-1}) 2961 (C–H), 1248 (C–Si); ^1H-NMR ($CDCl_3$) -0.12 (s, 6H, CH_3), 0.17 (s, 18H, $SiMe_3$), 6.19 (pt, $J_{HH} = 2.1$ Hz, 4H, C_5H_4Ti), 6.29 (pt, $J_{HH} = 2.1$ Hz, 4H, C_5H_4Ti); $^{13}C\{^1H\}$-NMR ($CDCl_3$) 0.3 ($SiMe_3$), 31.8 (CH_3), 116.3 (C_5H_4Ti), 120.3 (C_5H_4Ti), 121.2 (C_5H_4Ti, C_{ipso}); Anal. Calc. for $C_{18}H_{32}Si_2Ti$ (352.50): C, 61.33; H, 9.15. Found: C, 60.87; H, 9.23.

3.11.2. Reaction of $[Ti](C\equiv C^tBu)_2$ (12) with $Li[Cu(CH_3)_2]$ [3]

To $[Ti](C\equiv C^tBu)_2$ (**12**) (210 mg, 0.433 mmol) in 50 ml of diethyl ether was added one equivalent (0.433 mmol) of $Li[Cu(CH_3)_2]$ [3] in 40 ml diethyl ether at -70°C. After stirring at this temperature for 20 min the reaction mixture was slowly warmed to 25°C. The red solution was filtered through a pad of Celite (5 × 3 cm) to afford $[Ti](CH_3)_2$ (**14**) in 79% yield (120 mg, 0.342 mmol) after evaporation of all volatiles [10].

3.11.3. Reaction of $\{[Ti](C\equiv C^tBu)_2\}CuSC_6H_4$-$CH_2NMe_2$-2 (13) [4,5a,c,9] with CH_3Li

To $\{[Ti](C\equiv C^tBu)_2\}CuSC_6H_4CH_2NMe_2$-2 (**13**) [4,5a,c,9] (230 mg, 0.320 mmol) in 40 ml of diethyl ether were added two equivalents (0.640 mmol) of CH_3Li (1.6 M in diethyl ether) at -70°C. After appropriate workup (see Section 3.11.1) $[Ti](CH_3)_2$ (**14**) was obtained in 84% yield (95 mg, 0.269 mmol) [10].

3.11.4. Reaction of $[Ti]Cl_2$ (15) [20] with CH_3Li

To a suspension of $[Ti]Cl_2$ (**15**) [20] (150 mg, 0.381 mmol) in 70 ml of diethyl ether were added two equivalents (0.562 mmol) of CH_3Li (1.6 M in diethyl ether) at -70°C. After stirring at this temperature for 10 min the reaction mixture was warmed to 25°C. All volatiles were removed in vacuo. The residue was dissolved in 10 ml of diethyl ether and filtered through a pad of Celite (3 × 3 cm) to afford $[Ti](CH_3)_2$ (**14**) in 94% yield (125 mg, 0.358 mmol) [10].

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